Effect of dielectric barrier discharge plasma hydrogenation on oxidation stability of
biodiesel derived from vegetable oils

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in Nuclear Engineering
Department of Nuclear Engineering
FACULTY OF ENGINEERING
Chulalongkorn University
Academic Year 2021
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ผลกระทบของไดอิเล็กทริคแบริเออร์ดิสชาร์จพลาสมาไฮโดรจีเนชันต่อเสถียรภาพการเกิดออกซิเดชัน
ของไบโอดีเซลที่ได้จากน้ำมันพืช

น.ส.กฤติมา คงประเวศ

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรดุษฎีบัณฑิต
สาขาวิชาวิศวกรรมนิวเคลียร์ ภาควิชาวิศวกรรมนิวเคลียร์
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2564
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

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                      hydrogenation on oxidation stability of biodiesel derived
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กฤติมา คงประเวศ : ผลกระทบของไดอิเล็กทริคแบริเออร์ดิสชาร์จพลาสมาไฮโดรจีเนชัน
ต่อเสถียรภาพการเกิดออกซิเดชันของไบโอดีเซลที่ได้จากน้ำมันพืช. (Effect of
dielectric barrier discharge plasma hydrogenation on oxidation stability of
biodiesel derived from vegetable oils) อ.ที่ปรึกษาหลัก : รศ. ดร.ดุลยพงศ์ วงศ์
แสวง

ไดอิเล็กทริคแบรริเออร์ดิสชาร์จหรือดีบีดีพลาสมาชนิดแผ่นอิเล็กโทรดแบบคู่ขนานถูก
นำมาใช้ในการเติมไฮโดรเจนในไบโอดีเซลเพื่อผลิตพีเอช-เฟมจากน้ำมันถั่วเหลืองและน้ำมันปาล์ม
พีเอช-เฟมที่ผลิตได้มีความต้านทานการเกิดออกซิเดชันได้สูงขึ้น ซึ่งจะช่วยให้สามารถเก็บรักษาได้
นานขึ้น อีกทั้งช่วยชะลอการเปลี่ยนแปลงคุณสมบัติความเป็นเชื้อเพลิงของไบโอดีเซล ปฏิกิริยาโดย
ดีบีดีพลาสมาจะเกิดขึ้นได้ที่ความดันบรรยากาศและอุณหภูมิสิ่งแวดล้อมโดยไม่ต้องใช้ตัวเร่ง
ปฏิกิริยา สำหรับการผลิตพีเอช-เฟมจากไบโอดีเซลน้ำมันถั่วเหลืองปริมาณ 35 มิลลิลิตร พบว่า
สภาวะที่ดีที่สุดคือ การใช้ก๊าซไฮโดรเจนเข้มข้น 25% ที่อุณหภูมิสิ่งแวดล้อมเป็นเวลา 5.5 ชั่วโมง
การเพิ่มขึ้นของกรดไขมันเมทิลเอสเทอร์ชนิดอิ่มตัวและชนิดไม่อิ่มตัวพันธะคู่ 1 ตำแหน่ง สอดคล้อง
กับการลดลงของค่าไอโอดีนจาก 128 เป็น 67.4 กระบวนการนี้ทำให้มีกรดไขมันทรานส์เกิดขึ้น
3.67% และทำให้ค่าเสถียรภาพต่อการเกิดออกซิเดชันเพิ่มขึ้นจาก 2.13 เป็น 10 ชั่วโมง ในขณะที่
จุดหมอกเพิ่มขึ้นจาก -1 เป็น 11°C สำหรับการผลิตพีเอช-เฟมจากปาล์มไบโอดีเซลปริมาณ 300
มิลลิลิตร พบว่าสภาวะที่ดีที่สุดคือ การใช้กำลังไฟฟ้า 100 W ระยะห่างระหว่างแผ่นอิเล็กโทรด
ด้านบนและพื้นผิวไบโอดีเซล 1 มิลลิเมตร และความเข้มข้นของก๊าซไฮโดรเจน 80% ที่อุณหภูมิ
สิ่งแวดล้อมเป็นเวลา 5 ชั่วโมง ทำให้ค่าไอโอดีนลดลงจาก 50.2 เป็น 43.5 โดยไม่มีกรดไขมันท
รานส์เกิดขึ้น ค่าเสถียรภาพต่อการเกิดออกซิเดชันเพิ่มขึ้นเป็น 20 จาก 12.8 ชั่วโมง ในขณะที่ค่าจุด
หมอกเพิ่มขึ้นจาก 13.5 เป็น 16°C ต้นทุนในการผลิตเอชเฟมจากไบโอดีเซลจากน้ำมันถั่วเหลือง
และน้ำมันปาล์มคือ 36.96 และ 8.39 บาทต่อลิตรตามลำดับ สำหรับดีบีดีพลาสมานี้เป็นอีกหนึ่ง
ทางเลือกที่สามารถนำมาใช้ในกระบวนการเติมไฮโดรเจน อย่างไรก็ตามยังคงต้องมีการปรับปรุงใน
ด้านต้นทุนการผลิตให้สามารถใช้งานได้จริง

สาขาวิชา	วิศวกรรมนิวเคลียร์	ลายมือชื่อนิสิต ....
ปีการศึกษา	2564	ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

6071404221 : MAJOR NUCLEAR ENGINEERING

KEYWORD: Oxidation stability; Biodiesel; Partial hydrogenation; Dielectric barrier discharge (DBD); Plasma.

Grittima Kongprawes : Effect of dielectric barrier discharge plasma hydrogenation on oxidation stability of biodiesel derived from vegetable oils. Advisor: Assoc. Prof. DOONYAPONG WONGSAWAENG, Ph.D.

A parallel-plate type dielectric barrier discharge (DBD) plasma was utilized to produce partially hydrogenated fatty acids methyl ester (PH-FAME) derived from soybean and palm FAME. PH-FAME exhibits improved oxidation resistance, resulting in a longer storage time and a delay in changing fuel properties. The DBD plasma reaction occurred at atmospheric pressure and ambient temperature without a catalyst. The best condition for 35 mL of soybean FAME hydrogenation was using 25% H_2 at ambient temperature for 5.5 h. An increase in saturated and monounsaturated FAMEs corresponded to a reduction of iodine value from 128 to 67.4. This condition created trans fatty acids of about 3.67%. The oxidation stability increased from 2.13 to 10 h and the cloud point increased from -1 to 11℃. As for 300 mL PH-palm FAME production, the optimal condition was 100 W input power, 1 mm gas gap size, and 80% H_2 at ambient temperature for 5 h. The iodine value decreased from 50.2 to 43.5 without trans fatty acid formation. The oxidation stability was enhanced to 20 from 12.8 h, while the cloud point rose from 13.5 to 16°C. The production costs of PH-FAME based on soybean and palm FAME were 36.96 and 8.39 baht per liter, respectively. The DBD plasma is one of the alternative methods that can be employed in the hydrogenation process, but it is necessary to be improved to obtain a reasonable production cost.

Field of Study: Nuclear Engineering   Student's Signature ....

Academic Year: 2021   Advisor's Signature ....

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

LIST OF TABLES

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LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Relation of the research articles

The first published article on "Improvement of oxidation stability of fatty acid methyl esters derived from soybean oil via partial hydrogenation using dielectric barrier discharge plasma" is about the enhancement of oxidation stability of biodiesel derived from soybean oil. In the reaction, the plasma gas: hydrogen (H_2) mixed with helium (He), was broken down by sufficient energy supplied from a high voltage, high-frequency power supply with the maximum output of 10 kV and 30 mA at a fixed frequency of 25 kHz. The studied parameters included the concentration of H_2/He at 5 - 25 vol% H_2 with 1 L/min of total flow rate, reaction temperature at 40 - 80°C, and the reaction time from 0.5 - 20 h. The biodiesel volume was initially 130 mL then it was reduced to 35 mL to improve the reaction kinetic. The optimal condition was found using 25% H_2 at ambient temperature. In the case of 130 mL at the reaction time of 20 h, the oxidation stability increased from 2.13 to 5.45 h with the average reaction rate of 0.72×10^{-3} mol/L-min. Using 35 mL appeared to have a faster average reaction rate of 4.44×10^{-3} mol/L-min at an optimal time of 5.5 h. The oxidation stability was 10 h whereas a cloud point rose from -1 to 11°C.

The second article was "Low-Temperature and Atmospheric Pressure Plasma for Palm Biodiesel Hydrogenation". Palm biodiesel was a raw material used to improve oxidation stability. This study was expanded from the previous investigation by using a more powerful high voltage power supply with a maximum output of 15 kV and 40 mA with a 20 kHz fixed frequency. The high voltage electrodes and dielectric material were larger to support the 300 mL biodiesel volume. The reaction parameters included H_2 concentration at 25 – 80 vol%, reaction temperatures at 20 – 60°C and reaction time from 0.5 - 6 h. The two more parameters which were different from the 1st study: consumed power at 50 – 100 W and gas-filled gap size of 1 – 5 mm were investigated. The best condition was 100 W, 1 mm gap size and

80% H_2 concentration at room temperature for 5 h. This resulted in an increase in the oxidation stability from 12.8 to 20 h with the change in the cloud point from 13.5 to 16℃.

The two published research articles are part of the dissertation for graduation. The articles achieved the objective of enhancing the oxidation stability of soybean and palm biodiesel using parallel-plate type dielectric barrier discharge plasma and covered all the scopes of the study as proposed.

1.2   Background and statement of the problem

The world's energy demand has constantly been increasing due to the increase in population, the growth of industries, the high level of car ownership, etc. Most energy is obtained from non-renewable resources and fossil fuels: coal, oil and natural gases because of their low cost, availability and transport convenience. This directly affects the environment, for they release polluting gases such as CO_2, SO_2 and NOx. Moreover, their residuals cause dust and ash, which significantly impacts human health. This kind of fuel cannot replenish itself readily, so it is limited in supply. Nowadays, renewable resources have been used more. This type of resource is much available such as solar, wind, geothermal energy, etc. Even though it is an eco-energy with unlimited supply, some type of energy needs a large or specific area to establish energy storage causing the high cost for building, transport system and maintenance [1]. As for the fuels we use in daily life (transportation, equipment in factories and agricultural machinery), fossil fuels are mostly used. They are the main part of the industrial revolution. The fuels have also been playing an important role in various economic developments. However, fossil fuels cannot be replenished and have many negative effects; alternative fuels are required to be used instead.

One of the important alternative fuels that can replace fossil fuels is biofuels derived from biomass or organic materials. Biodiesel is one of the biofuels that has been utilized to supersede conventional diesel. Biodiesel should be blended with petrodiesel in different ratios such as B5, B7 and B20 before use to avoid damaging engine parts. However, pure biodiesel or B100 is allowed to be used directly in some

heavy diesel engines [2]. In general, biodiesel can be produced from multiple methods including esterification, pyrolysis and transesterification processes [3]. On the commercial scale, the transesterification process is often applied. It is a reaction between triglycerides and alcohol (methanol or ethanol) catalyzed by a suitable catalyst which can be acid, base or enzymes in the form of either homogenous or heterogeneous catalyst [4]. In the case of using methanol in the process, biodiesel can be called fatty acid methyl esters or FAME. Biodiesel or FAME has many advantages over diesel fuel: safer and more benefits for the health and environment (high flash point, no sulfur and aromatics, biodegradability, low carbon residues, high lubricity), easier for ignition due to high cetane number, and stronger for burning because of oxygen content. However, its oxidation stability is lower than that of diesel because the fatty acid methyl ester is composed of double bonds (C=C) which readily react with oxygen in the air. This causes a short storage time and a change in fuel properties including acid number, flashpoint, density, color, cetane number, and viscosity which is harmful to some engine parts [5]. Normally, FAME can resist oxidation based on the Rancimat test of 0.2 – 9.4 h [6], while diesel fuel has greater oxidation stability of more than 35 h [7, 8].

The limitation of oxidation stability is one of the reasons that FAME should be blended with diesel to complement each other and to obtain better fuel properties. This is because diesel offers a good oxidation resistance and cold flow property, whereas FAME enhances cetane number assisting to avoid knocking in engines and decreases pollution. The factors that influence the oxidation stability of FAME are the storage conditions (air, light, moisture exposure), the existence of impurities (metals, fatty acids, over antioxidants), and the composition of FAME. There are several methods to delay oxidation: adding a suitable antioxidant, refining to remove impurities, and changing FAME compositions to transform unsaturated to saturated FAMEs. Polyunsaturated FAMEs containing C=C bonds have been reported to respond readily to the reaction, especially with oxygen radicals. This implies that FAME made from vegetable oils with a high unsaturated fatty acid composition has low oxidation stability.

When considering vegetable oil feedstocks of global biodiesel production as shown in Figure 1, palm oil and soybean oil are the most utilized oil types followed by rapeseed oil, used cooking oil, animal fats, and others [9]. Soybean and rapeseed oil comprise polyunsaturated fatty acid (PUFA) by about 51 - 58% and 10 - 36%, respectively [5], so the oxidation stability should be improved to achieve the standard value of about 6 h according to ASTM D6751 (United States) [10]. The interesting method to convert unsaturated FAMEs to saturated FAMEs is partial hydrogenated FAME (PH-FAME) production. After oxidation stability is enhanced, PH-FAME can be blended with diesel fuel at a higher ratio of about 20 - 30%. For example, PH-FAME produced from jatropha blended with diesel has oxidation stability of 46.25 h, while FAME and diesel blending provides resistance of 25 h [11, 12]. This presents that PH-FAME can resist oxidation by about two times.
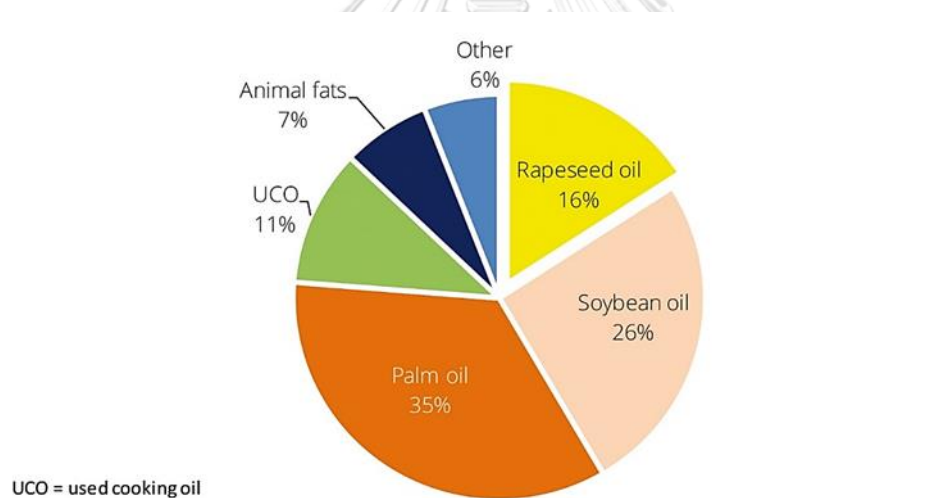
Figure 1 Vegetable oil feedstocks of global biodiesel production [9]
(source: https://www.ufop.de/?cID=1584)

Generally, the hydrogenation reaction occurs at high temperature and high-pressure conditions in the presence of a catalyst. For PH-FAME production, it has been recommended that polyunsaturated FAMEs, which contain the number of C=C bonds more than one position such as C18:2 and C18:3, should be converted into monounsaturated FAME that consists of one C=C bond: C18:1, C16:1. This is because

complete hydrogenation leads to poor cold flow properties causing FAME to become gel or solid at higher temperatures unsuitable for use in cold weather countries [13].

Many pieces of research have investigated PH-FAME production to improve the oxidation stability of vegetable FAME via the partial hydrogenation reaction. When focusing on PH-FAME-based on palm and soybean which are the main feedstocks for biodiesel production, in the study of Thunyaratchatanon et al. [14], they examined the partial hydrogenation of soybean FAME. A catalyst made from different metal types including Pd, Pt, and Ni supported SiO_2 with an Mg modifier was investigated. The reaction condition was 80°C and 0.4 MPa for 4 h. The best result was using Pd-Mg/SiO_2 which increased oxidation stability from 2 to 11 h, while the cloud point changed from 7 to 10 °C. This study evinces that Pd has the highest performance for partial hydrogenation compared to other metals.

As Pd can induce the reaction efficiently, Rungsi et al. [15] produced the PH-soybean FAME using Pd/MCM-41 with different catalyst supports: SiO_2 and silatrane. The suitable condition was using Pd/MCM-41-SiO_2 at 100°C and 0.4 MPa for 4 h. This increased the oxidation stability from 4.4 to 151 h and the cloud point rose from 1 to 21.5°C. This study showed that Pd/MCM-41-SiO_2 has a high potential for PH-FAME production via the hydrogenation reaction. As for palm FAME, S.Y. Chen et al. [16] reported that using Pd/SBA-15 provided an increase of 8.5 h in oxidation stability, whereas the cloud point changed from 12 to 13 °C. Besides the presented pieces of research, other catalysts were also practiced such as Ni/C, Ni/SiO_2, and so on. However, the reaction relying on a catalyst requires the catalyst preparation step which takes about 24 h. After the reaction is carried out, the catalyst must be completely removed. Furthermore, catalyst regeneration needs consideration, for this process demands much energy.

The hydrogenation reaction needs a catalyst to reduce the activation energy for breaking down the H_2 and C=C bonds to speed up the reaction rate. An interesting method to generate atomic hydrogen is by using plasma technology. Plasma, the fourth state of matter, comprises energetic electrons, positive ions, and neutral/ excited species. It has been used in many industries including microelectronics, packaging, and medical devices. Moreover, plasma has been

applied to the hydrogenation reaction to produce synthesis gas and methanol. There is one research that examined the plasma performance to produce hydrogenated oil by Yepez and Keener [17]. They used high-voltage atmospheric cold plasma (HVACP) to generate atomic hydrogen for hydrogenated soybean oil production. The reaction was operated at room temperature and 0.1 MPa in the absence of a catalyst. They presented that the atomic hydrogen successfully reacted with the C=C bond becoming a single bond to make oil more saturated. The results showed that the iodine value decreased from 133 to 92 at 12 h of reaction time and that there was no *trans* fatty acid formation due to the low-temperature operation.

According to the former study, plasma has the potential to be utilized in the hydrogenation process. This present work aimed to produce PH-FAME by using a parallel-plate dielectric barrier discharge (DBD) plasma without a catalyst. FAME derived from soybean and palm oil was investigated since they are the main feedstocks of global biodiesel production. This type of plasma can operate at atmospheric pressure and low temperature. Atoms and radicals of hydrogen are produced directly from the hydrogen gas in the plasma system. Then, they react with the double bonds of FAME molecules to convert polyunsaturated FAMEs into monounsaturated- and saturated FAMEs. This resulted in enhancing oxidation stability. Furthermore, the DBD plasma is a simple method that can be employed to initiate the hydrogenation reaction without using a catalyst, reducing the processes related to catalysts and saving energy for catalyst preparation and regeneration.

1.3   Objective

To enhance oxidation stability of fatty acid methyl esters derived from soybean oil and palm oil using Dielectric Barrier Discharge Plasma hydrogenation.

1.4   Scope of study

1) PH-FAME production using parallel-plate type DBD plasma reactor.

2) PH-FAME produced from FAME derived from soybean oil and palm oil.

3) Studied parameters are as follows:

<u>1st article</u>

- H_2 concentration: 5 – 25 vol.%

- Reaction temperature: 40 - 80 °C

- Reaction time: up to 20 h.

<u>2nd article</u>

- Consumed power: 50 – 100 W

- Gas-filled gap size: 1 – 5 mm

- H_2 concentration: 25 – 80 vol.%

- Reaction temperature: 20 – 60°C

- Reaction time: up to 6 h

1.5　Expectation

1) Obtain the new technology to enhance oxidation stability of FAME via PH-FAME production using the parallel-plate type DBD plasma reactor at low temperature and atmospheric pressure without any catalyst.

2) PH-FAME will be able to blend with diesel fuel at higher ratios.

3) The DBD plasma hydrogenation system will exhibit low cost, so the expenses for industrial-scale applications are expected to be low.

4) The DBD plasma hydrogenation system can be applied to other chemical reactions requiring low temperature and atmospheric pressure without a catalyst.

CHAPTER 2

IMPROVEMENT OF OXIDATION STABILITY OF FATTY ACID METHYL ESTERS DERIVED FROM SOYBEAN OIL VIA PARTIAL HYDROGENATION USING DIELECTRIC BARRIER DISCHARGE PLASMA

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Summary

Oxidation stability is an important biodiesel property. One of the methods to improve oxidation stability is partially hydrogenated fatty acid methyl esters (PH-FAME). The present research studied the novel production technique of PH-FAME derived from soybean FAME using non-thermal parallel-plate dielectric barrier discharge (DBD) plasma. This green hydrogenation method does not require a catalyst and can be performed under atmospheric pressure and at room temperature. The reaction using DBD plasma could effectively initiate the hydrogenation reaction, and the results showed similar performance to catalysis technique. The optimized process parameters for 35 mL of FAME were 25% H_2, 5.5 h of reaction time and ambient temperature. This condition exhibited the highest conversion of polyunsaturated FAMEs (C18:2 and C18:3) and the highest yield of C18:1. DBD plasma hydrogenation resulted in the reduction of iodine value from 128 to 67.4. The oxidation stability was enhanced from 2.13 to 10 h while the cloud point increased from -1 to 11 °C (still within the ASTM D6751 standard). This plasma process is a new alternative and eco-friendly method for PH-FAME production.

Keywords: Oxidation stability; Fatty acid methyl esters; Partial hydrogenation; Dielectric barrier discharge (DBD); Plasma.

2.1   Introduction

Biodiesel is a clean, locally available, sustainable, and renewable fuel which has received increasing attention for the current and future utilizations on transportation, power generation, heating system and so on. Biodiesel can be synthesized via transesterification by a reaction between vegetable oils or animal fats and alcohol (methanol or ethanol) with a suitable catalyst in mild conditions or without a catalyst in supercritical conditions [18-20]. In the case of using methanol as alcohol, biodiesel is called fatty acid methyl esters (FAME). Biodiesel offers considerable advantages over petroleum-based diesel such as higher cetane number, safer due to high flash point, less emission, higher lubricity, and better in combustion

[21, 22]. Biodiesel properties are similar to those of diesel fuel, but the oxidation stability is much lower. This is because it contains a number of C=C bonds that easily react with oxygen. Biodiesel with a high proportion of saturated fatty acids exhibits better oxidation stability than biodiesel rich in esters of unsaturated fatty acids [8, 23, 24]. The average induction time period of an oxidation reaction in biodiesel is around 0.2 – 9.4 h by Rancimat test [6]. The oxidation stability property influences the storage time resulting in the change of fuel property such as viscosity and acidity, or gums and sediment formation because of oxidation products [25, 26]. Due to the limitation of this property, pure biodiesel or B100 is not recommended for high-speed diesel engines and biodiesel should be blended with petroleum-based diesel before use. Moreover, the low heating value, high lubricity, high density and high viscosity of B100 decrease engine power and torque, resulting in higher fuel consumption. Oxygen present in biodiesel also causes NOx emission [27].

Partially hydrogenated fatty acid methyl esters (PH-FAME) offers FAME blended with diesel in higher ratio; for instance, in the case of B10 (jatropha FAME and diesel blend), PH-FAME/diesel has an oxidation stability of about 46.25 h, while it is about 25 h in FAME/diesel blended [11, 12].

When biodiesel is exposed to air, light, or stored at high temperature, these factors can activate biodiesel to form free radicals in the initiation phase as presented in Figure 2. In the propagation phase, the free radicals are very reactive toward oxygen causing more radicals and other product formation such as peroxide, hydroperoxide, fatty acid radical, hydroxyl radical, alcohol and water. Finally, in the terminal phase, the system comprises of many free radicals that can react with hydroperoxide and other radicals to generate soluble and insoluble polymers [28, 29]. The products from oxidation result in deterioration, clogging of engine parts and operation problems. In addition, when biodiesel is contaminated with a base catalyst from the production process, fatty acid, being one of the oxidation products (fatty acid radical), causes soap formation [25, 26]. Normally, oxidation of biodiesel can be delayed by adding an antioxidant (propyl gallate and lignin can be practiced, for example), using a suitable container and avoiding storage in pro-oxidizing condition, removing metals impurity especially Cu, Fe, Ni, Sn and brass by the refined FAME

method, or even using appropriate feedstocks with low percentages of polyunsaturated fatty acids [5, 30]. In case of a high proportion of polyunsaturated fatty acids in oils (soybean oil, canola oil, rapeseed oil, etc.) are used as raw materials [31], the hydrogenation reaction can be applied to convert into monounsaturated and saturated fatty acids known as PH-FAME production. The PH-FAME should contain monounsaturated fatty acid methyl ester as the main composition. This because the completed hydrogenation degrades cold flow properties, PH-FAME becomes solid at higher temperature and is unqualified to use in cold weather countries [13, 32].
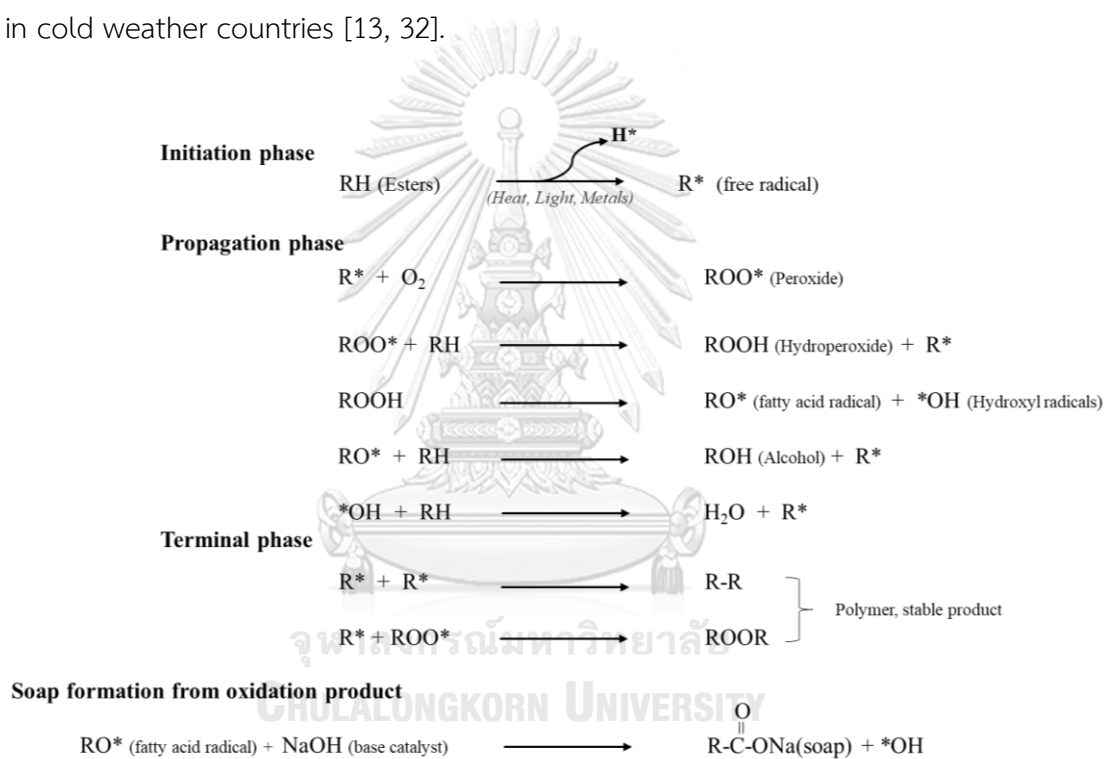
Figure 2 Oxidation process of biodiesel, oxidation products and soap formation modified from the study of Rashed et al. [28] and Bacha et al. [29]

Conventionally, the hydrogenation reaction of FAME is performed at high pressure (about 0.5 MPa) and elevated temperature (< 140℃) [12] with the use of a catalyst such as metals [(Pd, Pt, Ni)/SiO_2; Ni/C; Pd/ImS3-12@Al_2O_3; Pd/C; Pd/Al_2O_3/Al monolithic]. The catalysts are possibly added with modifier or promoter materials to enhance the performance in order to obtain high turnover frequency (TOF) of the

reaction. Although the main focus of the hydrogenation is to achieve the highest conversion of polyunsaturated FAMEs into monounsaturated ones, the *trans*-to-*cis* ratio should also be considered. Despite lubricity improvement by the *trans* isomer [33] which can be generated during the reaction with elevated temperature, it can result in poor cloud point because its melting point is higher than that of the *cis* counterpart. Also, the conventional catalyst-based FAME hydrogenation requires catalyst preparation and catalyst removal at the end of the reaction [15, 34, 35].

When focusing on partial hydrogenation of FAME made from feedstocks of high polyunsaturated fatty acids composition, Natthida et al. [36] evaluated the effect of pore size diameter of SiO_2 in a Pd/SiO_2 catalyst for the production of PH-FAME derived from rapeseed oil. The reaction was operated at 80°C and 0.3 MPa for 3 h. The findings were that after 1 h of the reaction using Pd/SiO_2 (SiO_2 with pores of ~30 nm), the oxidation stability of FAME and PH-FAME were 1.39 and 38.98 h, respectively, and the cloud point increased from -3 to 11°C. As for soybean FAME, Thunyaratchatanona et al. [37] studied a (Pd)/SBA-15 catalyst with Zr loading. The reaction conditions were 100°C and 0.4 MPa. It was found that the Zr loading ratio of 0.07 provided the high oxidation stability of 53 h, and that the pour point of 3°C. Rungsi et al. [15] used $Pd/MCM-41-SiO_2$ and Pd/MCM-41-silatrane catalysts. Even though the highest TOF was obtained from the Pd/MCM-41- silatrane catalyst, it exhibited a low *cis*-selectivity of C18:1. The desirable catalyst was $Pd/MCM-41-SiO_2$ with 2 wt% Pd, which increased the oxidation stability from 4.40 to 151 h with the change of the cloud point from 1 to 21.5°C. Thunyaratchatanon et al. [14] also considered different types of metals (Pd, Pt and Ni) on SiO_2 as a catalyst support and an Mg modifier over metal/SiO_2. The oxidation stability increased from 2 to 11 h with the change of the pour point from 7 to 11°C compared to the original FAME when $Pd-Mg/SiO_2$ was used.

Besides using a catalyst to reduce activation energy through the generation of free radical or intermediate species, plasma can also be utilized as a replacement or addition in the process. Routinely generated plasma contains positives ions, free electrons, neutral species, and excited species. It can assist to initiate a chemical reaction and/or can be used in a catalyst preparation process [38-40]. The plasma

source has been widely used in many hydrogenation processes: hydrogen and syngas production from glycerol, methanol production from CO_2, ammonia synthesis from N_2 and other products [41-43]. The gas-phase reaction is an effective method to obtain high yields of products. The reaction by plasma can proceed at low temperature without requiring a catalyst.

Plasma can also be applied directly in liquid and liquid/ gas phases. In biodiesel production, plasma was applied to initiate transesterification without using a catalyst. The reaction effectively occurred in a pulsed corona plasma reactor, and it provided a high biodiesel yield of 98% as presented in the study of Hyun et al. [44] Dielectric barrier discharge (DBD) plasma was also used. Abdul-Majeed et al. [45] produced biodiesel using a DBD plasma flying torch. About 72.3% yield was obtained after 100 min of the reaction time, while Istdi et al. [46] obtained 17% biodiesel yield within 11 min reaction time in a plasma reactor. In addition, the use of thermal plasma to convert bio-oil into H_2 and CO gases was presented in the study of Guénadou et al. [47] The plasma gases were Ar or a mixture of Ar and He. The reaction took place at atmospheric pressure and high temperature in the range of 2,227 – 2,727°C, resulting in the yield of H_2 and CO of above 93%mol.

Using hydrogen as feed in plasma, atomic hydrogen and excited-state molecular hydrogen in addition to negative ions can be generated. The energy required to dissociate a hydrogen gas molecule is about 15 eV [17, 38]. Atomic hydrogen is a highly-active free radical and when it comes into physical contact with a double carbon bond of FAME, it can incorporate into the bond. This reaction can occur at low temperature or room temperature, so trans-fatty acid should not be formed as mentioned in the study of Yepez and Keener [17]. They studied soybean oil hydrogenation using high-voltage atmospheric cold plasma (HVACP). The findings indicated that the iodine value of the hydrogenated soybean oil decreased from 133 to 92 after 12 h of reaction time. Nevertheless, there are limitations of using plasma in place of catalysts as it is challenging to control the reaction mechanism and the bond which is ionized or get excited [48]. Certain types of plasma such as microwave plasma and radio frequency (RF) plasma also require sophisticated vacuum and power supply systems.

During the analysis of the literature, no studies on DBD plasma technique for FAME hydrogenation were found. The purpose of the present research was to improve the oxidation stability of FAME derived from soybean oil using a novel application of DBD plasma hydrogenation to produce PH-FAME. The plasma-catalyzed reaction takes place at ambient temperature and atmospheric pressure without the use of a catalyst. The technique offers an alternative and eco-friendly method of PH-FAME production which is rich in monounsaturated fatty acid (C18:1, methyl oleate) and with increased oxidation stability. This method has the potential to provide new knowledge leading the path to the novel hydrogenation technique which could be applied to other hydrogenation processes.

2.2   Methodology

2.2.1   Materials

The following substances were used for FAME production: soybean oil of Morakot Industries PCL. brand obtained from a local department store, methanol (99.98%) and sodium hydroxide (97%) of analytical reagent grade obtained from Loba Chemie Pvt. Ltd. The following gases were used to generate plasma: H_2 and He gases of UHP (Ultra High Purity, >99.999%) grade. The following chemicals were used for iodine value determination: cyclohexane (99.5%) of analytical reagent grade obtained from Loba Chemie Pvt., Ltd., sodium thiosulfate 5-hydrate (>99.5%) purchased from KEMAUS, potassium iodide (99%) obtained from Ajax Finechem, starch solution made from corn starch of superfine brand obtained from a local department store, and Wijs solution prepared from iodine mono-chloride (98%) and glacial acetic acid (99.7%) purchased from Panreac Applichem and QRëC, respectively.

2.2.2   FAME production

FAME used for PH-FAME production in the present study was prepared by conventional transesterification. The base derivatization method presented in the study of Hewavitharana et al. [49] was applied to extract fatty acids from soybean oil. The average molar mass ($\overline{MW}$) of the soybean oil was determined from Eq. (2.1) to be about 925 g/mol.

$$\overline{MW} = \left[3 \times \left(\frac{1}{\sum_{i=1}^{n} \frac{x_i}{MW_i}} \right) \right] + MW_{glycerol} \qquad (2.1)$$

where n is the total number of fatty acids including C16:0, C18:0, C18:1, C18:2 and C18:3. MW_i and x_i are the molar mass and mass fraction of fatty acid i, respectively. $MW_{glycerol}$ is the molar mass of glycerol (92.09 g/mol).

The proportion of reactants and the reaction condition followed the study of Thanh et al. [50] by mixing 119.6 g (130 mL) soybean oil with a solution prepared by dissolving 0.96 g NaOH (0.8 wt%) in 25 g methanol (methanol: oil molar ratio of 6:1). The reaction temperature was 60°C with 2 h of reaction time in a batch reactor. After the reaction, FAME, by-product and other impurities were separated by letting the solution separate overnight. The purification method of the produced biodiesel was performed using warm water washing as indicated in the study of Demir and Soyhan [51] by adding 50°C of distilled water with stirring for a few minutes to remove excess methanol and the catalyst. To eliminate the remaining water and methanol, the liquid was heated at 120°C for 0.5 h. Other impurities were subsequently filtered out and the pure biodiesel was stored in a dry bottle covered with He gas and avoid exposure to the light to delay oxidation. The FAME storage time before use for PH-FAME production was no more than 2 weeks.

2.2.3 DBD plasma reactor system set-up

A non-thermal, parallel-plate type DBD plasma reactor for PH-FAME production was constructed as illustrated in Figure 3. The DBD plasma system consists of two aluminum electrodes connected to an adjustable neon sign transformer of cool neon brand model NG.B410ET1. The transformer provides a maximum open-circuit output of 10 kV and a closed-circuit current of 30 mA at a fixed frequency of 25 kHz. This transformer acts as a conventional high voltage, high-frequency power supply required to generate DBD plasma. Inside an 800 mL with a 5 mm thick borosilicate glass reaction chamber, an upper electrode plate was situated. A 1 mm thick glass dielectric plate was separating the electrode facing FAME to prevent contamination of the FAME during the reaction. The reaction chamber and

the lower electrode under it were placed on a hot-plate stirrer to allow stirring FAME and its temperature (80°C) when required. For a low-temperature study (40°C), a water bath was installed around the reaction chamber to provide active cooling. The gas-filled gap between the dielectric plate and the FAME surface was 5 mm. During the run, because of the stirring effect, the gap size changed continuously. The total distance between the upper electrode and the lower electrode was 35 mm. The H$_2$/He gas mixture was admitted into the chamber through a port at the top. A condenser was installed at the top of the chamber to condense any vapor leaving the system during gas exit from the chamber.
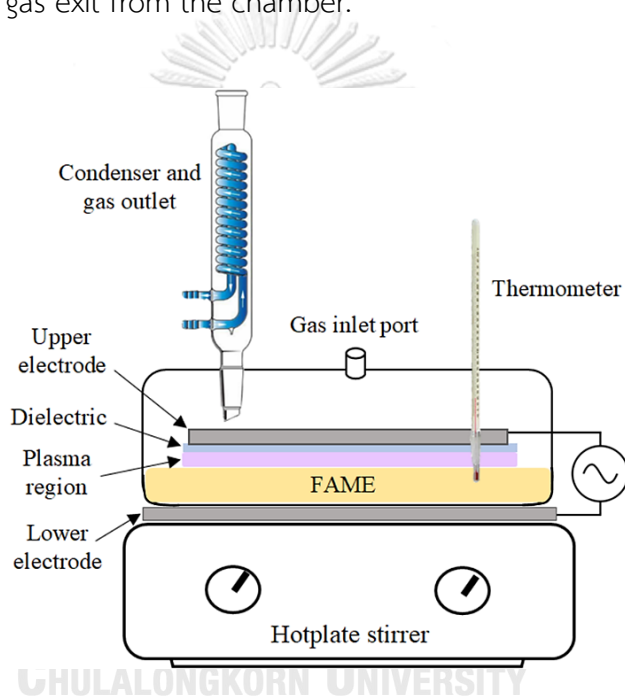
Figure 3 Constructed DBD plasma reactor

2.2.4   Partial hydrogenation of FAME

Produced FAME of 130 mL was added into the DBD plasma reaction chamber with 250 rpm of stirring rate. The stirring is essential as it promotes active mass transfer of FAME to the top surface to contact with generated atomic hydrogen. The studied parameters were: H$_2$/He concentration (5, 15 and 25 vol% H$_2$) with 1 L/min of total flow rate, temperature (ambient temperature, 40 and 80°C), and the reaction time (0.5-20 h). For every run, the output of the high voltage, high-frequency power supply was set at the same maximum value that can generate plasma. Also, at the

end of the study, a lower FAME volume of 35 mL for up to 10 h was studied in the same reaction chamber in an attempt to increase a reaction rate further.

2.2.5   Analysis of FAME and PH-FAME

Raw material FAME was examined for FAME yield based on EN14103 that presents the weight fraction in percent of fatty acid methyl esters content using methyl heptadecanoate (C17) as the internal standard [52]. After DBD plasma hydrogenation, fatty acid compositions of feed and product PH-FAME were analyzed by Gas Chromatography-flame ionization detector (GC-FID). FAME or PH-FAME of 1 μL was admitted into the oven of HP-88 fuse silica capillary column equipped in the GC-FID, a Hewlett Packard 5890 series II, with He carrier gas at 200°C injection temperature and 230°C detector temperature. Consequently, the temperature was raised at a rate of 1°C/min from 180 to 220°C with 5 min holding time. To indicate the FAME type in each composition, standard FAME was used as a benchmark.

The data on fatty acid composition changes from GC-FID was used to calculate the average reaction rate. When considering polyunsaturated FAMEs, C18:2 and C18:3, as reactants which were converted into C16:0, C18:0 and C18:1, the average reaction rate was calculated by using the following equation:

$$\text{Average reaction rate} = \frac{\Delta[\text{Polyunsaturated FAMEs] (M)}}{\Delta t \text{ (min)}} \qquad (2.2)$$

where Δ [Polyunsaturated FAMEs] (molar, M) represents the reduction in the number of moles of polyunsaturated FAMEs per liter of FAME solution and Δt (min) represents the reaction time in min.

Besides GC-FID analysis, iodine value was evaluated to determine the degree of saturation of PH-FAME by Wijs-cyclohexane method per ASTM D1959 [53]. Both FAME and product PH-FAME were analyzed by Perkin Elmer Spectrum One Fourier Transform Infrared (FTIR) Spectrometer to verify that PH-FAME exhibited the same characteristic functional groups as FAME and to observe the change of certain wavelengths related to the effect of hydrogenation, for instance, trans-fatty acid and C=C peaks. The FTIR conditions were: Universal Attenuated Total Reflectance (UATR)

sensor technique, resolution of 4.0 cm^{-1}, scan range of 4000 - 515 cm^{-1} and number of sample scan of 64.

The accelerated oxidation test technique was employed to measure the oxidation stability of FAME and PH-FAME by EC Meter, EC-450L, Istek inc., Korea. The test method follows WI-RES-EC Meter-001 and the in-house method based on the modified Rancimat test (EN 15751 :2009) [54]. For the cloud point and pour point, ASTM-D-2500 [55] and ASTM-D97 [56] methods were used with the equipment from Walter Herzog GmbH, Germany.

2.3 Results and discussion

2.3.1 FAME analysis

The produced FAME has 98% FAME yield. Examination of fatty acid compositions of the original FAME revealed that the FAME comprised of a high proportion of polyunsaturated fatty acid methyl esters including methyl linolenate (C18:3) of 5.10% and methyl linoleate (C18:2) of 53.97%. It also contained methyl oleate (C18:1) of 23.57%, methyl stearate (C18:0) of 4.20% and methyl palmitate (C16:0) of 12.12% shown in Table 1.

Table 1 Composition of original FAME

FAME	Structure	Content (%)
Methyl palmitate	C16:0	12.12
Methyl stearate	C18:0	4.20
Trans-methyl elaidate	*Trans*-C18:1	0.00
Cis-methyl oleate	*Cis*-C18:1	23.57
Trans- methyl linolelaidic	*Trans*-C18:2	0.00
Methyl linoleate	*Cis*-C18:2	53.97
Methyl linolenate	C18:3	5.10

The chemical functional groups were analyzed by FTIR. In Figure 4 (b), the characteristic peaks shown in the ATR-FTIR spectra has a peak at 3008 cm^{-1} corresponding to unsaturated fatty acid methyl esters, C=CH stretching. The next two peaks at wave numbers 2922 and 2853 cm^{-1} represent the alkane group, C-H, associated with the asymmetric and symmetric stretching vibration, respectively. The ester group, C=O stretching with mild vibration, represents the strongest peak at 1741 cm^{-1}. Besides these peaks, the peaks at 1435 and 1460 cm^{-1} represent the asymmetric stretching of CH_3 in FAME, and the peak at 1195 cm^{-1} corresponds to O–CH_3 stretching which confirms methyl esters formation. These three peaks were not found in soybean oil as shown in Figure 4 (a). However, the peak that could be merely detected in soybean oil was at 1377 cm^{-1} (between 1361 and 1435 cm^{-1}), which attributes to the glycerol group, O–CH_2. In addition, the peaks at 1361, 1016 and 1169 cm^{-1} correspond to CH_2, C-O anti-symmetric and C-O symmetric vibration, respectively. The peaks at 1244 and 1120 cm^{-1} correspond to C-O and C-O-C stretching of FAME. These characteristic peaks should be detected in FAME [32, 57, 58]. There are characteristic peaks of *cis*- and *trans*- configurations at 722 (*cis*) and 966 cm^{-1} (*trans*). *Trans* should not appear when soybean oil and most edible oils are used as feedstock [59]. The different functional groups of PH-FAME and FAME were the peak at 966 cm^{-1} due to *trans* fatty acid formation. Also, the 3008 cm^{-1} peak referring to =C-H stretching vibration of C=C was reduced, implying that the unsaturated FAMEs were partially converted into saturated FAMEs as presented in Figures 4 (c) and 4 (d) [37].
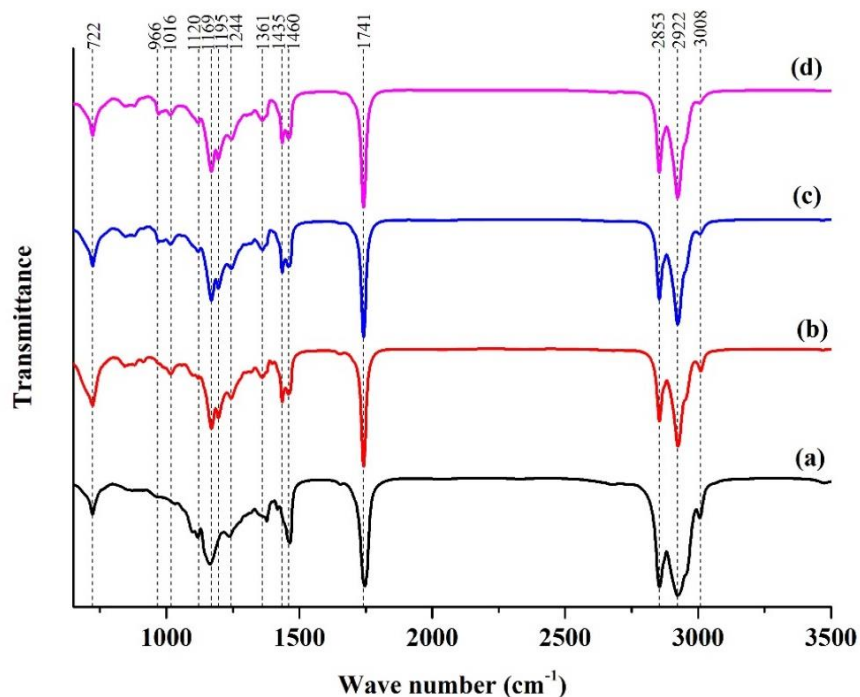
Figure 4 ATR-FTIR spectra of (a) soybean oil, (b) original FAME, (c) 130 mL PH-FAME and (d) 35 mL PH-FAME

2.3.2   Effect of H_2 concentration on PH-FAME production

The concentration of H_2 was studied at 5, 15 and 25 vol%. Over 25%, no plasma could be achieved in the present parallel-plate DBD reactor. The results showed that using 25% H_2, polyunsaturated fatty acid methyl esters (C18:2 and C18:3) decreased while monounsaturated fatty acid methyl ester (C18:1) increased with a higher percentage than that at 5 and 15% H_2 as presented in Figure 5. At 25% H_2 for 2 h of the reaction time, the increase of C16:0 from 12.12 to 12.46%, C18:0 from 4.20 to 4.83%, and C18:1 from 23.57 to 25.42% were observed, while C18:2 and C18:3 were reduced from 53.97 to 51.84% and from 5.10 to 4.42%, respectively. This is because higher H_2 percentage reactant gas generated higher hydrogen radicals concentration to react with the double-bonded carbon atoms. The experiment was performed in duplicate at ambient temperature and the averaged values are presented.

(a)   (b)
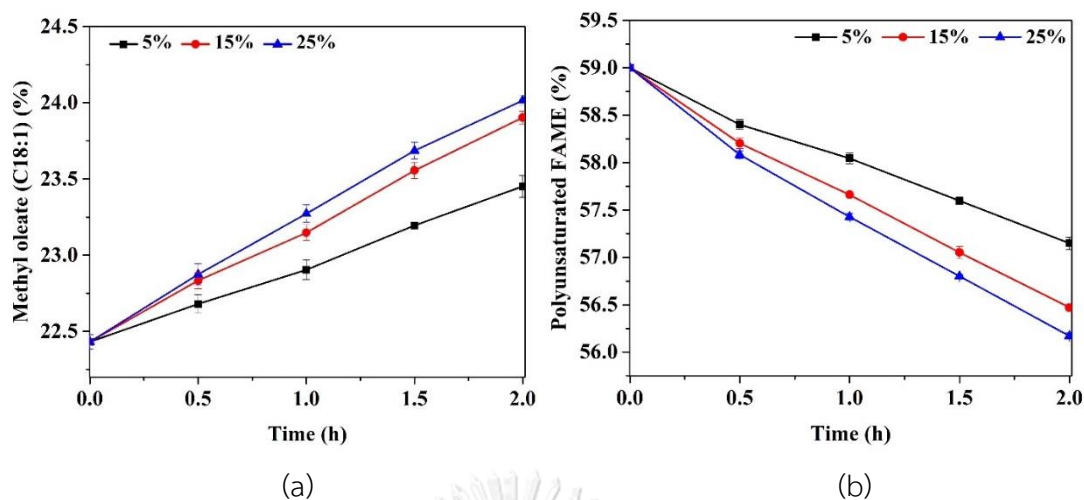
Figure 5 Composition of PH-FAME under different H_2 concentrations: (a) methyl oleate (C18:1) and (b) methyl linoleate (C18:2) and methyl linolenate (C18:3)

2.3.3   Effect of temperature on PH-FAME production

The effect of temperature was investigated because temperature generally affects the kinetics of chemical reactions. Studied values were ambient temperature (30.5 °C), 40 and 80°C with a fixed H_2 concentration at 25% for 2 h of the reaction time. For the ambient temperature, during the reaction, the temperature slowly rose to 58°C and stabilized due to plasma heating generated by power supplied into the system. For the 40°C case, the water bath surrounding the reaction chamber provided active cooling. For the 80°C case, a combination of plasma heating and controlled heating form the hot-plate stirrer maintained the temperature. The experiment was performed independently twice. The findings revealed no statistically significant differences in the effect of temperature as presented in Figure 6. Normally, a hydrogenation reaction can take place by receiving much enough energy to break triple or double bonds and H_2 molecules to atoms. The catalyst is utilized to reduce the activation energy so that to reach a reasonable rate of reaction. In the catalyst process, higher temperature exhibits considerable results: faster and higher conversion, higher product yield and selectivity because temperature affects the activity of a catalyst [14, 60, 61]. For the hydrogenation process in the DBD plasma reactor, atomic hydrogen was generated by applying the

high voltage, high-frequency source; thus, the reaction would depend on the power input to produce plasma. The changing of temperature would have no effect for the DBD plasma system. However, when considering C18:1 which is the desired composition of PH-FAME, the study found that the ambient temperature (rising to 58°C) showed the highest percentage of C18:1 as well as the highest conversion of polyunsaturated fatty acid methyl esters (C18:2 and C18:3). Room temperature with solely plasma heating appears to be the optimal condition for PH-FAME synthesis using the designed DBD plasma system.

(a)   (b)
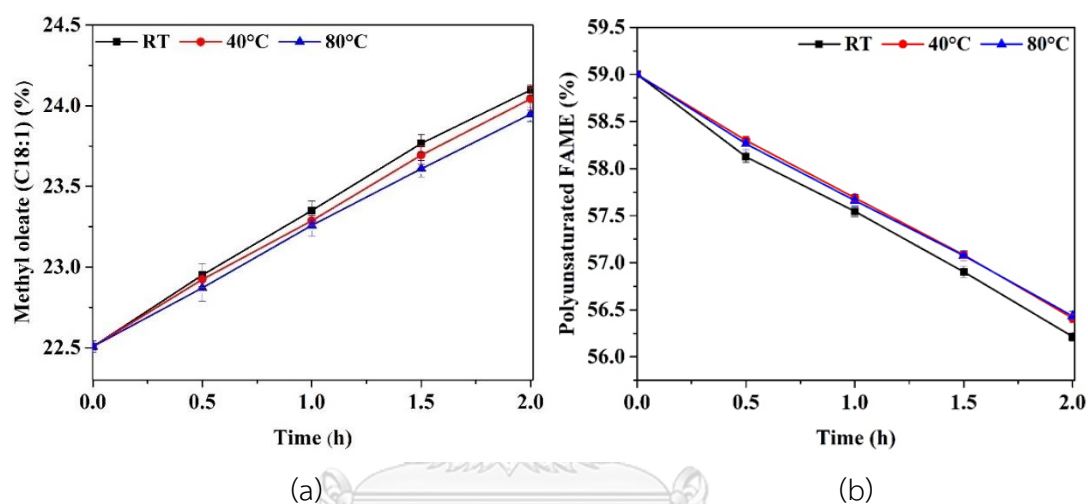
Figure 6 Composition of PH-FAME after hydrogenation under different reaction temperatures and 25% H_2: (a) methyl oleate (C18:1) and (b) methyl linoleate (C18:3), RT refers to ambient temperature.

2.3.4 Effect of reaction time on PH-FAME production

With 25% H_2 concentration and room temperature at the beginning, PH-FAME production was performed up to 20 h with product sampling every 2 h for analysis of the change in product compositions by GC-FID and the iodine value. Each product sample of 0.3 mL was rapidly sucked out of the reaction chamber via a small silicone tube while the plasma was still on, to least interrupt the process. Results demonstrated in Figure 7 showed that after 16 h, FAME consisted mainly of C18:1, which is required. During the reaction, hydrogen atoms reacted at the double bonds and caused the significant increase in saturated fatty acid methyl esters (C16:0 and

C18:0) and monounsaturated fatty acid methyl ester (C18:1), whereas polyunsaturated fatty acid methyl esters (C18:2 and C18:3) decreased significantly with reaction time. The increase in C16:0 was not expected as C16:1 and C16:2 were not presented in the feed FAME. Yepez and Keener [17] studied soybean oil hydrogenation using HVACP and also found the increase in C16:0 even though the starting soybean oil did not consist of any mono- and polyunsaturated fatty acid of hexadecanoic acid. This indicates that the hydrogenation process derived from both types of plasma can generate C16:0 carbon chains. Considering the hydrogenation process using a catalyst in soybean FAME, there was a change in C18:0, C18:1 (*cis-* and *trans-*), C18:2 and C18:3, while others were not [14, 37]. However, in the study of Grinevich et al. [62], a DBD plasma reactor was used for oil hydrocarbons destruction at atmospheric pressure using oxygen plasma. They found that the $-CH_2$, which closed to an alkyl radical, at the end of hydrocarbons chains was successfully decomposed, so C16:0 produced in the present study might come from the cracking process.
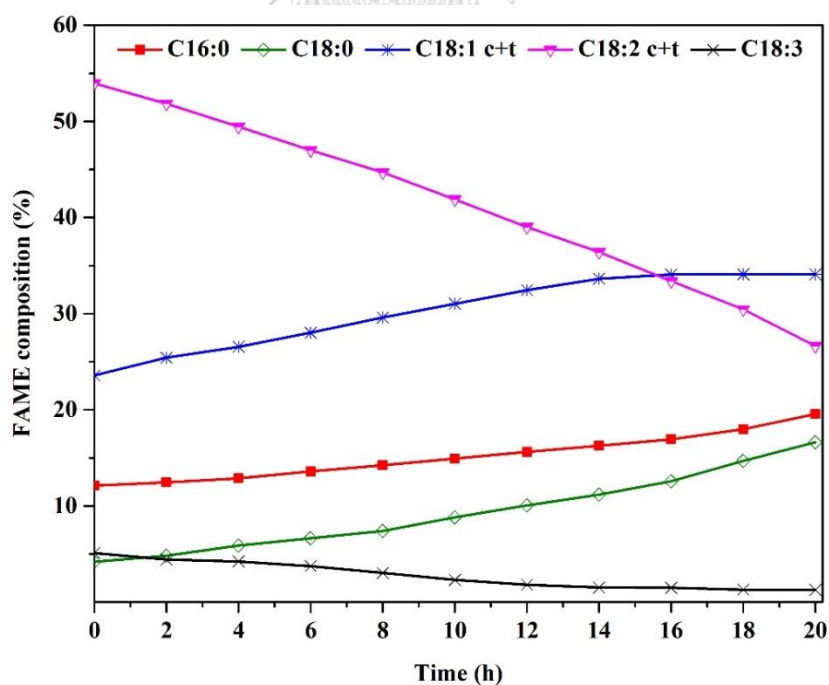
Figure 7 PH-FAME composition up to 20 h reaction time (130 mL FAME volume, ambient temperature, 25% H_2)

2.3.5 PH-FAME properties

The fatty acid compositions of FAME compared to PH-FAME at 20 h of reaction time are shown in Figure 8 and Table 2. The quantitative analysis was calculated from the area of methyl esters peak. In Figure 8, all peaks corresponding to those of FAME were detected. Two very weak and broad peaks were also found at the retention time around 35.5–36 and 38–39.5 min which represent the *trans* configuration that presented in only PH-FAME. The peak at 36.5 min, *cis* configuration [63], appeared in both original FAME and PH-FAME.
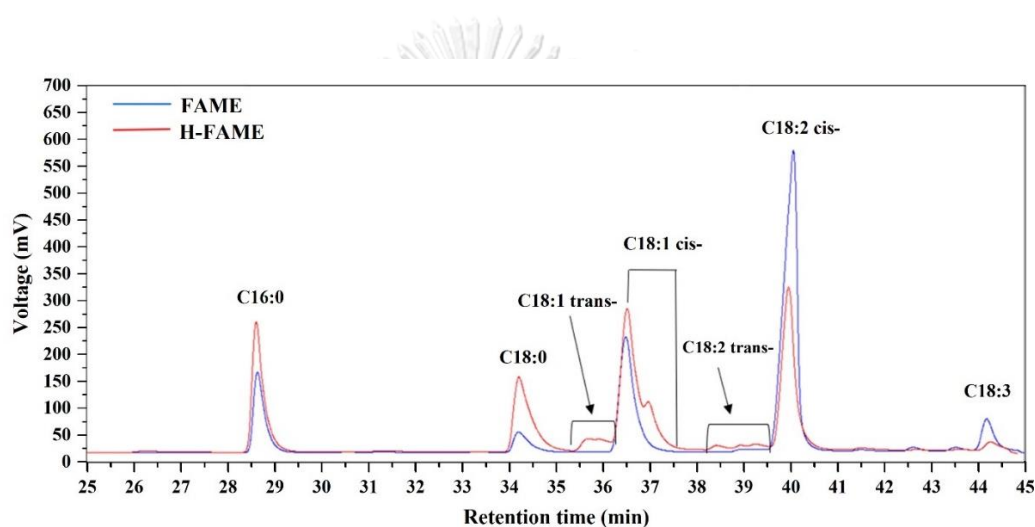
Figure 8 GC-FID chromatogram showing FAME and PH-FAME composition (20 h reaction time, 130 mL FAME volume, ambient temperature, 25% H_2)

Table 2 Composition of original FAME and PH-FAME obtained from the ambient temperature, 25% H_2

FAME composition (%)	FAME	PH-FAME[a]	PH-FAME[b]
Saturated fatty acid	16.32	36.17	52.79
C16:0	12.12	19.54	24.26
C18:0	4.20	16.62	28.53
Monosaturated fatty acid	23.57	34.08	37.03
trans-C18:1	-	2.03	3.67
cis-C18:1	23.57	32.05	33.36

FAME composition (%)	FAME	PH-FAME[a]	PH-FAME[b]
Polyunsaturated fatty acid	59.07	28.71	9.14
trans-C18:2	-	1.26	-
cis-C18:2	53.97	26.00	8.90
C18:3	5.10	1.45	0.24

[a]130 mL FAME and 20 h reaction time

[b]35 mL FAME and 5.5 h reaction time

As plasma dissipates thermal energy and generates hydrogen atoms in the reaction chamber, a small percentage of *trans*-fatty acid methyl ester in both C18:1 and C18:2 was observed. The *trans*-to-*cis* ratio in C18:2 and C18:1 was 0.048 (1.26% *trans*-) and 0.06 (2.03% *trans*-), respectively. On the aspect of *trans*-fatty acid formation, Souza et al. [64] investigated partial hydrogenation of soybean oil-based biodiesel using a catalytic system at 80°C and 7.6 MPa. In the case of using Pd/C, *trans*- C18:1 was produced with a ratio of 2 (16% *trans*-). In addition, in the study of Rungsi et al., [15] H-soybean FAME was produced using Pd/MCM-41-SiO$_2$ catalyst. When considering the *trans*-to-*cis* ratio at about 50% conversion of C18:2, the study obtained the ratio of 0.22. It can be concluded that the hydrogenation reaction by the DBD plasma generates a small amount of *trans* isomers compared to the conventional method operating at high pressure and high temperature using catalysts. In the DBD plasma system, the *trans* isomer was formed because the *cis* configuration is less stable than the *trans* counterpart. As a consequence, when FAME received activation energy from the DBD plasma, a small amount of the *cis* isomer was inevitably transformed into the *trans* one.

Table 3 displays the properties of FAME and PH-FAME compared to the biodiesel standard.

Table 3 Properties of FAME and PH-FAME (ambient temperature, 25% H_2) compared to biodiesel standard

Property	FAME	PH-FAME[c]	PH-FAME[d]	Standard
Cloud point (°C)	-1	9	11	-3 to 12[b]
Pour point (°C)	-3	5	9	-15 to 16[b]
Oxidation stability, 110 °C (h)	2.13	5.45	10	6[a], 3[b]
Iodine value	126.7[c] 128[d]	82.05	67.4	< 120[a]

[a]European biodiesel standard (EN 14214)

[b]ASTM D6751 (United States) [10, 65]

[c]130 mL FAME and 20 h reaction time

[d]35 mL FAME and 5.5 h reaction time

For the oxidation stability, as the original FAME comprised mainly of polyunsaturated fatty acid methyl esters, it exhibited undesirably low oxidation stability of only 2.13 h which is lower than the minimum value required in both EN 14214 and ASTM D6751 standard of 6 and 3 h, respectively. Partial DBD plasma hydrogenation could transform C18:3 and C18:2 into C18:1 and saturated FAME with the average reaction rate at 20 h of 0.72×10^{-3} mol/ L-min. After treatment, the oxidation stability was improved to 5.45 h. According to Table 2.2, the reaction offered completed hydrogenation -- instead of obtaining mostly monounsaturated FAME, saturated FAME was excessively produced. The completed hydrogenation and a minor amount of the *trans*-isomer of PH-FAME have a negative impact on the cold flow property as the cloud point of PH-FAME increased from -1 to 9°C, but it is still within the standard of 12°C.

Figure 9 shows bis-allylic methylene and allylic groups indicated by the circle solid line and the circle dash line, respectively. These groups are very reactive and the bis-allylic methylene group is more reactive than the allylic group [66]; therefore,

C18:3 is easy to incorporate with hydrogen atoms and other free radicals especially with oxygen in the oxidation process [67]. The 18-carbon unsaturated FAME which readily responses to radicals can be ordered from reactivity as C18:3 > C18:2 > C18:1 [66, 68]. When considering the PH-FAME composition, it still comprises of C18:2 of 27.26% and C18:3 of 1.45%. This explains why the oxidation stability increased by only 3.32 h due to the influence of the existing reactive allylic and bis-allylic methylene group.
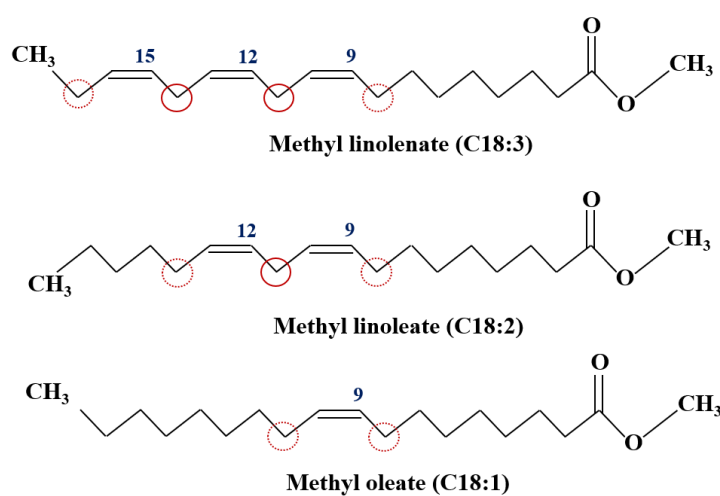
Figure 9 Allylic and bis-allylic methylene groups in molecules of unsaturated fatty acid methyl esters

2.3.6   Additional experiment to increase oxidation stability

Even though the hydrogenation experiment for 20 h yielded satisfactory results as the oxidation stability increased, an additional effort was made to increase the value further. In the same DBD plasma reactor, the FAME volume was reduced to 35 mL causing the increase in the contact area per volume of the hydrogenation. The separation distance between the upper and lower electrodes was also automatically decreased to 15 mm as the FAME layer thickness in the chamber reduced and as the gap between the dielectric plate and the upper surface of the FAME layer remained unchanged. With the electrode gap reduced, more plasma and

atomic hydrogen were also generated. Other process parameters were not altered, and the hydrogenation reaction was allowed to proceed for 10 h.

Figure 10 demonstrates the reduction of the iodine value with reaction time. It can be observed that the iodine value dramatically declined from 128 to 40.84. The decrease was rapid compared to the 130 mL case which was 100.4 at 10 h and 82.05 at 20 h from initially 126.7. Figure 11 shows the time-dependent of FAME composition. The C18:3 and C18:2 polyunsaturated chains were quickly eliminated during the first 5 h of hydrogenation, generating C18:1, C18:0 and C16:0 fatty acid chains. After that, C18:1 started to decrease rapidly as the C18:3 and C18:2 chain precursors were used up and as hydrogenation continued to consume the only double bond present. C18:0 and C16:0 increased all the time as the unsaturated chain precursors were hydrogenated to produce saturated fatty acid chains. Accordingly, the speed of iodine value reduction after 7.5 h appeared to be slower than that at earlier reaction time. This is because at 7.5 h, most of C18:3 and C18:2 chains were fully hydrogenated. The only available monounsaturated fatty acid chain was C18:1, which was significantly reduced in quantity as well. Thus, the results of the iodine value and the fatty acid composition correspond to each other very well.
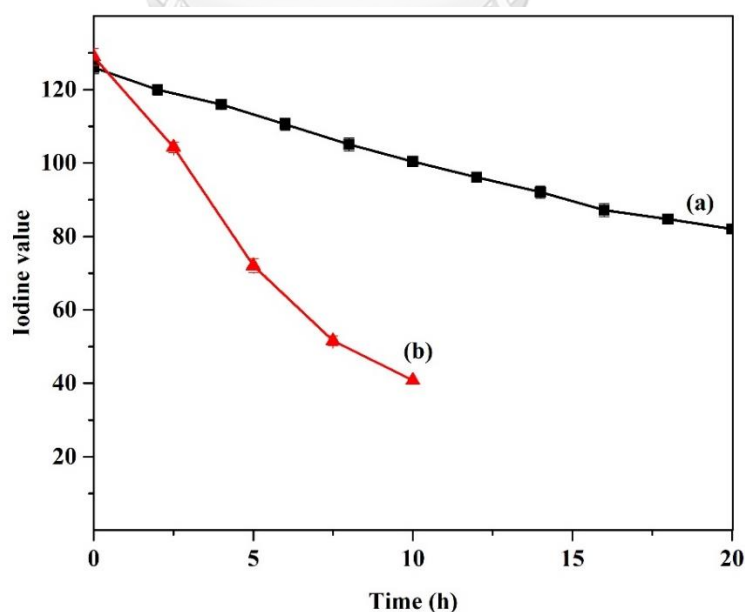
Figure 10 Iodine value of FAME using (a) 130 mL and (b) 35 mL (ambient temperature and 25% H_2)
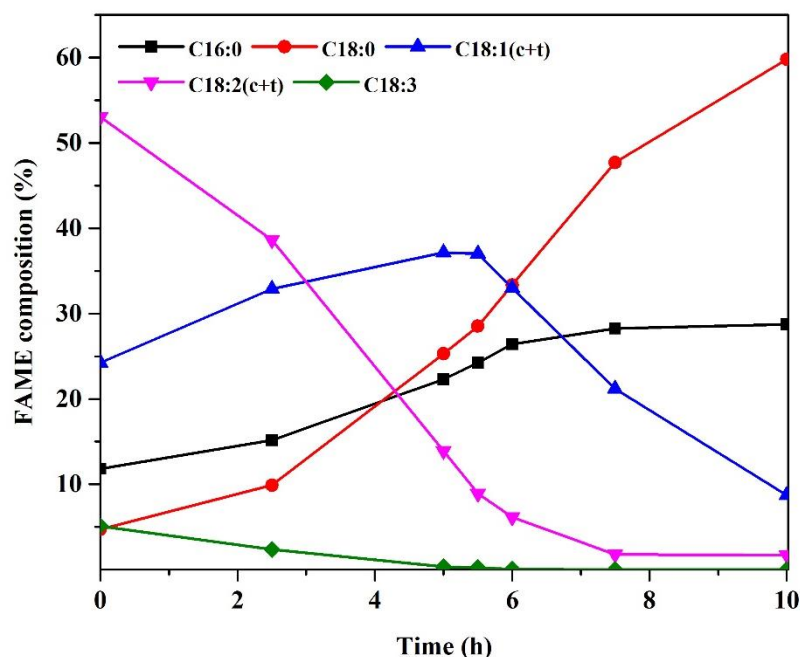
Figure 11 FAME composition (35 mL, ambient temperature and 25% H_2)

As it is preferred for PH-FAME to have a high composition of the monounsaturated fatty acid chain (C18:1) due to tradeoff between oxidation stability and cloud point, the optimized time for this plasma hydrogenation system was about 5.5 h. At this reaction time, the average reaction rate was 4.44 × 10^{-3} mol/ L-min, which was faster than that of the 135 mL system. The FAME composition at this reaction time is as follows: saturated chains (24.26% of C16:0 and 28.53% of C18:0), monounsaturated chain (37.02% of C18:1) and polyunsaturated chains (8.90% of C18:2 and 0.24% of C18:3). The product at this reaction time was selected and analyzed for other properties as presented in Table 3. However, there was a minor *trans*-C18:1 formation of 3.67%.

The iodine value decreased from 128 to 67.4 in 5.5 h, or a reduction rate of 8.61%/h. As a comparison, in the study of Yepez and Keener [17], 10 mL of soybean oil was hydrogenated using the HVACP system for 12 h, and the iodine value decreased from 131 to 92, or a reduction rate of 2.48%/h. As for the conversions of polyunsaturated compositions in the present study, they were 83.2% for C18:2 and 95.2% for C18:3.

The cloud point of the PH-FAME increased from -1 to 11℃. This was obviously because the PH-FAME contained more saturated fatty acid content. For tropical countries, the cloud point of 11 ℃ will present no problem as it will be very rare that this low temperature will be reached. The oxidation stability was significantly improved from 2.13 to 10 h due to lower polyunsaturated compositions. The heterogeneous metal-type catalysts (Pd, Pt and Ni catalyst supported on SiO_2 with Mg modifier) used for soybean PH-FAME production were studied by Thunyaratchatanon et al. [14]. The reaction was operated at 0.4 MPa and 80 ℃ for 4 h. The Pt-Mg/SiO_2 showed the oxidation stability of 5.4 h from the initial value of 2 h, while the cloud point increased from 7 to 12℃. As for Ni-Mg/ SiO_2, the oxidation stability and cloud point were 3.5 h and 12℃, respectively. The best performance catalyst was Pd-Mg/ SiO_2, which improved the oxidation stability to 11 h and the cloud point rose to 10℃ with 10.95% *trans*-C18:1 generated. Although it is apparent that the developed green plasma hydrogenation technique cannot selectively converse polyunsaturated FAMEs into the monounsaturated counterpart, the EN 14214 and ASTM D6751 standards focus on the oxidation stability and cloud point regardless of the synthesis pathway. The potential for PH-FAME production using the environmental-friendly DBD plasma technique is similar to the method using Pd-Mg/SiO_2 but with much less *trans*-isomer formation. Moreover, the eco-friendly DBD plasma technique obviously performed better than Pt-Mg/ SiO_2 and Ni-Mg/ SiO_2 catalysts.

2.3.7 Preliminary suggestion on large-scale and environmental-friendly production of PH-FAME

Although the production capacity of the present study is low, at the end of the 10 h run, the measured energy consumption by a plug-in power meter was only 0.256 kWh, presenting 25.6 W of average instantaneous power consumption. At 5.5 h, the optimal hydrogenation time in the designed DBD plasma reactor, the energy consumption was calculated to be only 0.14 kWh. It is understood that by using the plug-in power meter, the power consumed by the high voltage, high-frequency power supply, not the plasma discharge power, was measured. Nonetheless, this

represents a conservative power measurement as the power supply was by no means 100% energy efficient. A much larger batch production capacity can be realized by using a larger set of electrodes and a more powerful power supply specifically designed to generate higher intensity DBD plasma with maximized energy efficiency (e.g., with proper impedance matching of the source and the load to maximize the power delivered to the load). Although in the present study, He and H_2 gases exiting the reaction chamber were not recycled, in a large-scale batch production using a closed reaction chamber, they can easily be 100% recycled and only periodic replenishment of H_2 would be required to maintain the optimal H_2 partial pressure. Because the system operates under 1 atmosphere, no thick reactor wall would be required and only a very simple recirculating pump with a sufficient flow rate would be needed to perform simple gas recirculation. Essentially, the only major costs to produce PH-FAME using the studied DBD plasma hydrogenation technique are the electricity cost to power the DBD power supply and the cost of H_2 consumed by the double bonds of FAME.

A continuous green production process can also be envisioned. FAME can enter a shallow oil tank on one side and produced PH-FAME can leave the oil tank on the opposite side. Similar to the batch production discussed earlier, the top of the tank can be open to the high-intensity DBD plasma at 1 atmosphere and both He and H_2 gases can be completely recycled with only periodic replenishment of H_2. With the appropriate stirring speed of FAME in the tank, FAME injection rate and FAME volume in the tank, exiting PH-FAME can have the desired fatty acid composition.

Besides PH-FAME production, DBD plasma has the potential to be applied to other processes requiring hydrogenation of C=C, C≡C, or even C=X/ C≡X bonds. The reaction can occur in liquid-gas and solid-gas interface, as well as in the gas phase, in the absence of a catalyst. This technique has been successfully applied to produce margarine with low trans-fatty acid formation [69]. The technique can be applied to the pharmaceutical industry: hydrogenation of fructose and glucose into hexitols as well as vitamin production [70, 71]. The process is able to hydrogenate heavy oil in the cracking process for light product generation [72]. The technique can be utilized

to create other atomic species: oxygen and nitrogen atoms (air plasma) for wastewater treatment, nitrogen atoms for ammonia production and synthesis gas production [43, 73, 74].

2.4   Conclusions

Partially hydrogenated FAME was successfully produced in the parallel-plate DBD plasma reactor. The optimized condition was 25% H_2, 5.5 h of reaction time and ambient temperature. This condition showed the highest conversion of polyunsaturated FAMEs (C18:2 and C18:3) and the highest yield of C18:1. For 35 mL of FAME, the oxidation stability was enhanced from 2.13 to 10 h while the cloud point increased from -1 to 11°C. The green reaction using DBD plasma could effectively initiate the hydrogenation reaction without using a catalyst, and the results showed that the performance was similar to catalysis.

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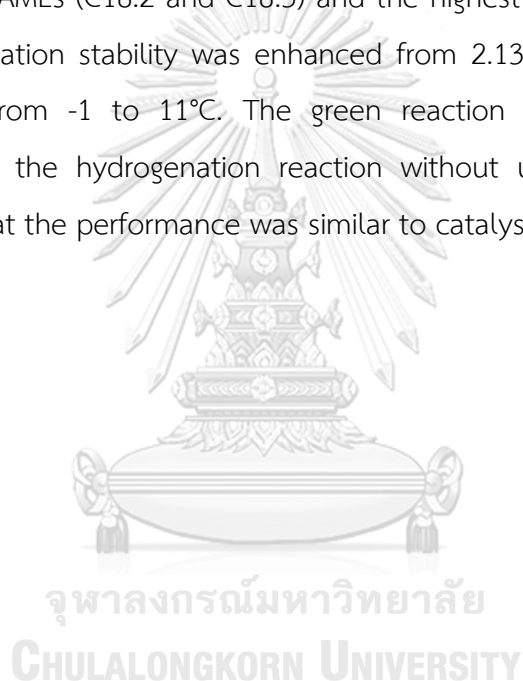
CHAPTER 3

LOW-TEMPERATURE AND ATMOSPHERIC PRESSURE PLASMA FOR PALM BIODIESEL HYDROGENATION

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Abstract

Partially hydrogenated fatty acid methyl ester (PH-FAME) is conventionally produced through partial hydrogenation under high pressure and elevated temperature in the presence of a catalyst. Herein, a novel green, catalyst-free, non-thermal and atmospheric pressure dielectric barrier discharge (DBD) plasma was employed instead of a conventional method to hydrogenate palm FAME. PH-FAME became more saturated with the conversion of C18:2 and C18:3 of 47.4 and 100%, respectively, at 100 W input power, 1 mm gas-filled gap size and 80% H_2 in the mixed gas at room temperature for 5 h, causing a reduction of the iodine value from 50.2 to 43.5. Oxidation stability increased from 12.8 to 20 h while a cloud point changed from 13.5 to 16°C. Interestingly, DBD plasma hydrogenation resulted in no *trans*-fatty acid formation which provided a positive effect on the cloud point. This green DBD plasma system showed a superior performance to a conventional catalytic reaction. It is an alternative method that is safe from explosion due to the mild operating condition, as well as being highly environmentally friendly by reducing waste and energy utilization from the regeneration process required for a catalytic process. This novel green plasma hydrogenation technique could also be applied to other liquid-based processes.

Keywords: Dielectric barrier discharge plasma; Partial hydrogenation; Oxidation stability; Fatty acid methyl esters; Palm oil

3.1   Introduction

The increase in population, as well as advances in several technological areas, result in higher energy demands. One of the important sources is fossil fuel that has been used in transportation, electric power generation, agricultural machines, shipping, etc. Nowadays, the utilized fuel is fossil-based diesel or petrodiesel that cannot be replenished and has many negative effects such as highly toxic pollutants and greenhouse gases [75]. To reduce the use of petrodiesel,

alternative fuels such as renewable energy: wind, solar and biofuel have been developed [76].

Biodiesel is one of the renewable energy types that can be used in place of petroleum-based diesel. Typically, it can be synthesized from crop oil, animal fats or even waste cooking oil via several methods such as microemulsion, pyrolysis, esterification and transesterification [77]. On the commercial scale, transesterification is often utilized by mixing triglycerides in oils with short-chain alcohol catalyzed by appropriate catalysts which can be acid, base or enzyme in the homogenous or heterogeneous form at mild conditions [4, 78]. Besides, the reaction can proceed in the absence of a catalyst, but a supercritical condition is required[79]. The final products are fatty acid methyl esters (FAMEs) and glycerol. Biodiesel can be mixed with petrodiesel in any proportion such as B5, B10 and B20, although neat biodiesel (B100) can be directly used in certain heavy diesel engines [2]. Biodiesel consists of very low carbon residue, no sulfur and about 10% oxygen which assists complete combustion. These advantages result in a significant reduction of emission and pollution: NO_x, SO_x and dust particles, which drastically affect both climate change and human health [76]. However, biodiesel composes of long-chain carbon atoms containing C=C bonds, resulting in low oxidation stability compared to petrodiesel [80].

The oxidation in biodiesel (FAME) can be initiated by light, heat or certain metals to generate free radicals. During the propagation process, the reaction between the free radical and oxygen in the air forms peroxide as an oxidation product. Additionally, the peroxide radical can react with a stable FAME to produce hydroperoxide which can continually generate hydroxyl radicals, water, as well as soluble and insoluble polymers. These oxidation products alter fuel properties: acid value, viscosity, cloud point and so on leading to degradation of engine parts[25, 26]. There are multiple ways to delay the oxidation, for example, avoiding conditions prone to oxidation, storing in a suitable container, adding proper additives and using feedstocks with a low unsaturated composition [5, 30]. For the last method, besides selecting an appropriate feedstock for biodiesel synthesis, a hydrogenation reaction can be performed on FAME to partially saturate the carbon chains.

Partial hydrogenation of fatty acid methyl ester (PH-FAME) has been utilized to improve the ability to withstand oxidation. This method is to produce the more saturated FAME, specifically, to decrease the polyunsaturated compositions (C18:2, C18:3), for this kind of FAME composes of bis-allylic and allylic methylene groups which are readily reactive with both O* and H* free radicals [66]. In general, the hydrogenation process requires high temperature, high pressure and a suitable catalyst, which normally is a Group VIII metal: Ni, Co, Pd, Pt and Rh with or without proper support materials [32]. The proposed mechanism is that this reaction forms atomic hydrogen and breaks down the double bond, and then the H atoms react at the bond to form a single bond [32, 81]. Hydrogenation not only greatly improves the oxidation stability of FAME, but also enhances other properties such as higher flash point, lower sulfur content and lower acid value [82]. However, one aspect that should be considered when biodiesel becomes more saturated is the degradation in the cold flow property: the cloud point and the pour point [80]. This property affects the phase of the fuel to become gum or gel at a higher temperature, which limits the use in cold-weather countries.

For catalytic hydrogenation of FAME, a Pd catalyst is widely used as it provides a high catalytic activity compared to other metals. As presented by Thunyaratchatanon et al. [35], Pd/SiO_2 was investigated at 120°C and 0.4 MPa for 4 h. It was found that the oxidation stability was enhanced from 1.4 to 30.5 h and that the cloud point changed from 1 to 6°C within the reaction time of 2 h. Besides, Thunyaratchatanon et al. [14] improved the catalyst performance by adding a Mg modifier to form $Pd-Mg/SiO_2$. This assisted the reaction to take place at a lower temperature of 80°C at 0.4 MPa for 4 h. The results showed that the oxidation stability rose from 2 to 11 h and that the cloud point changed from 7 to 10°C. Moreover, alkaline and alkaline earth metals such as Na, Ca or Ba can be used as modifiers to improve the conversion of polyunsaturated fatty acid [83]. In the case of PH-FAME produced from palm FAME, a Pd catalyst on SBA-15 support was also practiced as reported in the study of Chen et al. [16]. The reaction conditions were 100°C and 0.3 MPa for 2 h. The findings revealed that the oxidation stability was increased from 19.4 to 27.9 h and that the cloud point rose from 12 to 13°C. The

study of Ramayeni et al. [84] was on using a Ni/C catalyst at 120°C, 0.6 MPa and 2.5 h. The results revealed that Ni offered desirable results with the increase in oxidation stability of palm FAME from about 4.75 to 10.03 h while the cloud point was not reported.

According to the previous studies, the catalytic hydrogenation reaction must be performed at high pressure (0.3 – 0.6 MPa) and elevated temperature (80 – 120°C). It perhaps faces problems with high operating and maintenance costs from the high hydrogen pressure environment, as well as a slow deactivation of catalyst performance from the deposition of carbon or metals on the catalyst surface [85]. To avoid these issues, one of the alternative methods is to utilize plasma technology. Plasma is the fourth state of matter consisting of active species including energetic electrons, positive ions, excited and neutral atoms/molecules. It can be generated by appropriately supplying sufficient energy to gas to create partially/ fully ionized plasma [38]. Different types of plasma can be generated under various conditions such as at different pressures. When emphasizing atmospheric-pressure plasma, a dielectric barrier discharge (DBD) plasma is one of the many types of plasma that is easily generated and utilized. It can be produced by supplying the power from an AC or a pulsed high voltage with a frequency of 500 Hz to 500 kHz to two electrodes separated by a dielectric material which assists in preventing sparks and arcs causing local high temperature [86, 87]. The reactive species occur in the electrode gap of typically 0.1 - 10 mm [88]. The DBD plasma discharges can be divided into filamentary and diffuse structures, but in most cases, it is filamentary or microdischarge. It is a small light stream between the electrodes and then expands radially when hitting the dielectric, forming a "foot" structure. The parameters affecting the characteristics and number of microdischarge are applied voltage, discharge gap size, specific capacitance of the barrier material, type of gas and pressure. The filamentary DBD is crucial because there are intense free radicals and reactive species generated in the plasma stream. Furthermore, it produces local heat. Typically, some heat is released from the electrodes, indicating that heat generation can occur when using a DBD plasma [86]. The heat and light/ photon (UV-vis) produced in a DBD plasma influence the performance of a plasma-assisted reaction.

Therefore, it is widely used in several chemical production processes. and in many industries such as ozone generation, CO_2 laser, excimer lamps [38], as well as to assist a catalyst for syngas, ammonia or methanol production [89-91]. It is also practiced for liquid-phase hydrogenation of heavy oil and oil without a catalyst.

In the experiments of Hao et al. [72], a low-temperature DBD plasma was employed in the cracking process for the value-added of heavy oil. The plasma was generated from 3 gases: N_2, CH_4 and H_2. The findings were that the hydrogen plasma can enhance the yield of trap oil to approximately 19%, which was higher than those of the non-plasma processes by about 8 – 33%. Plasma was utilized to break down the H–H bond of hydrogen gas and to drive the hydrogenation reaction to form a light product. This low-temperature plasma can be produced at reduced or atmospheric pressure. Although the high temperature was still necessary for the decomposition of heavy oil, the required reaction temperature could be decreased, for example, from 420 to 380°C. High-Voltage Atmospheric Cold Plasma (HVACP) was also used in the study of Yepez and Keener [92]. Hydrogenation of soybean oil was studied at ambient conditions in the absence of a catalyst. The gas used to generate plasma was a mixture of 5% H_2 and 95% N_2. It was found that at the reaction time of 12 h, soybean oil became more saturated and that its properties were similar to margarine. The iodine value was decreased from 133 to 92. The composition of saturated and monounsaturated fatty acids increased by 12 and 4.6%, respectively, whereas polyunsaturated fatty acids decreased by 16.2%. More importantly, there was no detectable *trans* fatty acid formation.

Margarine production from palm oil using DBD plasma was likewise experimented with by Puprasit et al.[69]. The optimal conditions were 15% H_2 in a mixed gas (He and H_2) and room temperature for 8 h of reaction time. The DBD plasma reactor could be used to successfully produce margarine with a similar texture to that of commercial margarine. However, *trans* fat was created by a small amount of about 1.4%. In our previous work [93], PH-FAME derived from soybean oil was successfully synthesized in a DBD plasma reactor. The best results appeared when using 35 mL FAME, 25%H_2 in the He and H_2 gas mixture, and ambient temperature under atmospheric pressure. It was found that the produced PH-FAME

contained methyl oleate (C18:1) as the dominant composition at the reaction time of 5.5 h. The iodine value reduced from 128 to 67.4 while the oxidation stability was reasonably improved from 2.13 to 10 h, and the cloud point changed from -1 to 11°C.

From the above research findings, plasma reactors can effectively break down gas molecules into constituent atoms and successfully engendered the hydrogenation reaction. The present work aims to investigate PH-FAME production in a DBD plasma reactor at low temperature and atmospheric pressure without using a catalyst. FAME derived from palm oil, which is the main vegetable feedstock for global biodiesel production of about 35% [9], was studied. The utilized DBD plasma hydrogenation reactor was an improvement to the previous study [93] to have more production capacity via FAME recirculation, as well as higher plasma discharge power. The effects of parameters: power input, gas-filled gap size, H_2 concentration, reaction temperature and reaction time, were evaluated. This plasma treatment technique is highly environmentally friendly, for a catalyst is not required. This helps to reduce the processes of catalyst preparation and removal from the product. Also, since plasma hydrogenation occurs at low temperature and atmospheric pressure, the energy requirement, as well as the maintenance cost, can be reduced. This novel and green technology has a promising potential to be applied for hydrogenation of other high-value liquids, as well as for large-scale PH-FAME production.

3.2 Methodology

3.2.1 Materials

Palm FAME was obtained from an industrial plant in Thailand. The gases used for PH-FAME production, H_2 and He, were of Ultra High Purity (UHP) grade procured from Alternative Chemical Company Ltd., Thailand. FAME yield and composition were analyzed by Gas Chromatography (GC) using methyl heptadecanoate and n-heptane of analytical reagent grade purchased from Sigma-Aldrich. The following chemicals were used for the determination of iodine value, peroxide value and acid number: cyclohexane (99.5%) of analytical reagent grade purchased from Loba

Chemie Pvt., Ltd., sodium thiosulfate 5-hydrate (99.5 – 101%) obtained from KEMAUS, potassium iodide (99%) obtained from Ajax Finechem, a starch solution made from corn starch of Super-Fine brand purchased from a local department store, Wijs solution prepared from iodine mono-chloride (98%) and glacial acetic acid (99.7%) purchased from Panreac Applichem and QReC, respectively, chloroform (99.8%) and phenolphthalein indicator obtained from RCI Labscan, ethyl alcohol (95%) purchased from Samchai Chemical, Thailand, and sodium hydroxide (97%) of analytical reagent grade obtained from Loba Chemie Pvt., Ltd. All chemicals were used as received.

3.2.2   Experimental set-up

Figure 12 presents a drawing of the DBD plasma hydrogenation system used in the present research. The reaction chamber was made of borosilicate glass with a volume of 4 L and a thickness of 5 mm. The DBD plasma system comprised two electrodes made of aluminum plates with the upper one (20 × 16 cm) placed inside the reaction chamber and the lower one (24.5 × 17.5 cm) sealed to the bottom of the chamber using high-temperature silicone. A glass dielectric sheet (22 × 17 cm) was attached to the bottom of the upper electrode using a high-temperature silicone sealant to prevent any aluminum contamination in FAME. The two electrodes were electrically connected to a high-voltage, high-frequency neon sign transformer of NeonPro brand, model MXP-15000-40, which provided a maximum output of 15 kV and 40 mA at 20 kHz. Although the transformer was a commercial neon sign transformer, with its suitable electrical output characteristics, it was applied to effectively generate DBD plasma with a maximum power of 100 W. The transformer used in the study of Kongprawes et al. [93] had a maximum output of 10 kV, 30 mA, 25 kHz, thus, the present research presented an improvement to the previous work. Although the utilized transformer had no output adjustment knob, it was found that by connecting a variac directly to the transformer input, the output power can be easily regulated by adjusting the variac setting. The total power consumption of the neon sign transformer was measured by a plug-in power meter connected to the variac. The accumulated power consumption was recorded and presented in the unit

of kW-h. The waveform of the discharge voltage was measured by a high voltage probe connected to a digital oscilloscope (Tektronix TDS 2012). The gas mixture of H_2 and He was controlled by Unit Instruments mass flow controllers models UFC-1000 for H_2 and UFC-1260A for He. The mixed gas was supplied into the reaction chamber with the opening slightly below the glass dielectric plate (but not submerging into the FAME layer) to allow effective gas displacement in the gas-filled gap as shown in supplementary materials Figure A1 which is attached in the appendix. To allow a large FAME treatment volume while maintaining a thin FAME layer inside the chamber, as well as to allow sufficient mass circulation in the chamber, FAME was pumped into and out of the chamber via a peristaltic pump. The FAME line external to the chamber was connected to a stainless steel coil placed inside a water bath to allow reaction temperature control. A thermometer and a sampling port were installed to observe the temperature and to perform online sample collection. Reactive species produced in the plasma were observed using a spectrometer (Ocean Optics, USB4000 model, wavelength range approximately 200 – 1050 nm, XR1-500 line grating blazed at 250 nm and L4 lens) connected to a fiber optic cable to collect the plasma photons. The spectrometer was connected to a PC-based OceanView software version 1.6.7 (https://www.oceaninsight.com/support/software-downloads/oceanview-software-downloads/) for visualization.
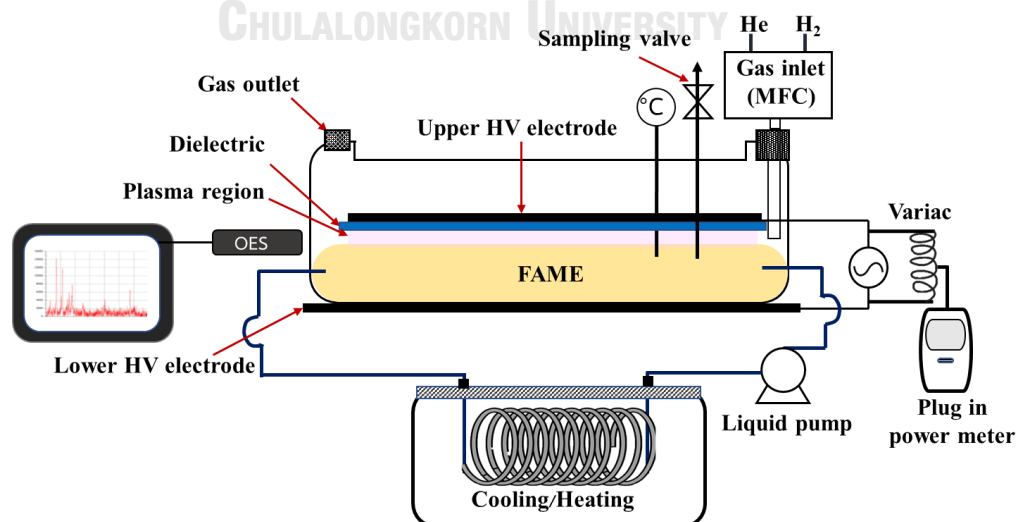

Figure 12 Drawing of constructed DBD plasma reactor

3.2.3   Hydrogenation of FAME

For each batch, 300 mL of FAME was plasma hydrogenated. The plasma was generated from a H_2/He gas mixture with an overall flow rate of 1 L/min. FAME was continuously circulated with a constant flow rate of 400 mL/min. He gas was selected as the inert gas for this study because plasma could be easily generated all over the electrode with few microfilament formations as explained in Appendix A section 1. The experimental investigation is shown in Figure A2. The system was initially purged with a He gas with a flow rate of 3 L/min for 2 min to completely remove air present in the reaction chamber. Before plasma generation, the correct H_2: He ratio was achieved by gradually increasing the H_2 flow rate while slowly reducing the He flow rate. When the gas was at the desired proportion, the neon power supply was energized to generate plasma. The studied parameters were the consumed power of the DBD power supply (50 – 100 W), gas-filled gap size (1 – 5 mm, which was the small clearance between the lower surface of the glass sheet and the surface of the FAME inside the chamber), concentration of H_2 (25 – 80 vol.%), FAME temperature (20 – 60°C) and reaction time. The thickness of the FAME layer inside the chamber was identical for every run, and the gas-filled gap size was manually adjusted by configuring the length of the small polyethylene supporting columns at the four corners of the glass plate. For the investigation on optimal parameters, the reaction took place for 1 h without water in the water bath except for the temperature study case. After the reaction, PH-FAME was stored in a plastic container at ambient temperature and covered with nitrogen gas to avoid oxidation. Plasma hydrogenation experiments were performed in duplicate and the reported values represented the average with the error bars showing the standard deviation.

3.2.4   FAME and PH-FAME analysis

FAME yield and fatty acid compositions were analyzed according to EN14103 standard [52] using gas chromatography (Shimadzu GC-2010 Plus with a DB-WAX capillary column equipped with a flame ionization detector using helium carrier gas). The introduced volume of the sample was 1 μL. The detector temperature was 250°C with a split ratio of 1/50. The temperature was increased from 150 to 220°C at

the rate of 3°C/min with a holding time of 5 min. FAME yield and composition were calculated from Eqs. (3.1) and (3.2), respectively.

$$\text{FAME yield (\%)} = \frac{\Sigma A - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m} \times 100\% \qquad (3.1)$$

where ΣA = total peak area, A_{IS} = internal standard (methyl heptadecanoate) peak area, C_{IS} = concentration of internal standard solution (mg/ mL), V_{IS} = volume of internal standard solution (mL) and m = mass of sample (mg).

$$X_{composition}(\%) = \frac{A_X}{\Sigma A - A_{IS}} \times 100\% \qquad (3.2)$$

where ΣA = total peak area, A_x = type of FAME composition peak area, e.g., methyl palmitate (C16:0), methyl stearate (C18:0) and methyl oleate (C18:1), A_{IS} = internal standard (methyl heptadecanoate) peak area.

Since the DB-WAX capillary column cannot detect the *trans*-configuration, to determine the *trans* quantity and functional groups of the feed compared to the final product, Perkin Elmer Spectrum One Fourier Transform Infrared (FTIR) was applied. The FTIR conditions were: Universal Attenuated Total Reflectance (UATR) sensor technique, resolution of 4.0 cm^{-1}, scan range of 4000 – 515 cm^{-1} and number of sample scans of 64. Feed FAME and PH-FAME obtained from the optimal condition were analyzed for the compositions from C8 to C20 by Gas Chromatograph- Mass Spectrometer (GC-MS) of 78908 GC -5977A MSD, Agilent, USA. The test technique was Gas Chromatography-Electron Ionization/ Mass Spectrometry (GC-EI/MS). The level of saturation indicated by iodine value was investigated by the Wijs-cyclohexane method, ASTM D1959 [53]. Acid number and peroxide value were measured according to the standards of AOAC, 1997 and AOCS, 1997, respectively. Oxidation stability of FAME and PH-FAME were analyzed by EC Meter, EC-450L, Istek Inc., Korea, following WI-RES-EC Meter-001 and the in-house method based on the modified Rancimat test (EN 15751:2009) [54]. In addition, Walter Herzog GmbH, Germany was utilized to determine the cloud point as in the standard of ASTM-D-2500 [55].

3.3 Results and discussion

3.3.1 FAME properties

As-received palm FAME showed a yield of 97.9%. It consisted of saturated and monounsaturated FAMEs as the main composition: 41.22% methyl palmitate (C16:0), 3.62% methyl stearate (C18:0) and 41.85% methyl oleate (18:1). The polyunsaturated FAMEs were composed of methyl linoleate (C18:2) and methyl linolenate (C18:3) of about 9.73 and 0.17%, respectively. This composition resulted in the oxidation stability of 12.8 h without adding any additive, while its cloud point was 13.5 °C. The iodine value and acid number were 0.5% g I_2/g and 0.2 mg KOH/g, respectively.

3.3.2 Effect of input power

The studied input power was 50, 75 and 100 W. The gas-filled gap of 1 mm was configured. The reaction was conducted using 25%H_2 in the gas mixture at room temperature (starting at 25°C and rising to about 38°C due to the heat from the DBD plasma [94]). The sine waveform of the discharge voltage is displayed in supplementary materials Figure A3. It indicated that more input power resulted in higher discharge voltage, while the frequency exhibited a minute fluctuation between 19.01 and 19.40 kHz. Supplying 50, 75 and 100 W of input power resulted in the peak-to-peak discharge voltage of 1.76, 1.84 and 2.10 kV, respectively. These closed-circuit voltages were much lower than the 15 kV open-circuit voltage rating of the utilized neon transformer, which was according to the expectation. Figure 13 presents the composition changes at the reaction time of 1 h. The consumption percentage referred to the conversion of the C=C bond into a single bond compared to the feed. The results revealed that applying 100 W of input power provided the highest conversion of polyunsaturated FAME followed by 75 and 50 W, respectively. The reduction of C18:2 and C18:3 from using 100 W was 9.35 (from 9.73 to 8.82%) and 27.59% (from 0.17 to 0.12%), respectively. In addition, saturated FAME increased as follows: 1.27% for C16:0 (from 41.21 to 41.74%) and 11.36% for C18:0 (from 3.62 to 4.03%). The response of FAME with input power was according to the expectation – high input power provided higher energy to produce more plasma density as well

as more intense filamentary discharges with a high concentration of electrons [95]. The generated energetic electrons could transfer the energy to activate the C=C bonds of FAME as well as to other gas atoms/molecules generating more reactive species. However, microfilaments caused local heating. In the present work, the temperature of FAME near the microfilaments was measured to be about 5℃ higher than that in other areas. In conclusion, high input power resulted in high plasma density generating a large amount of atomic hydrogen to readily react with the C=C bonds.
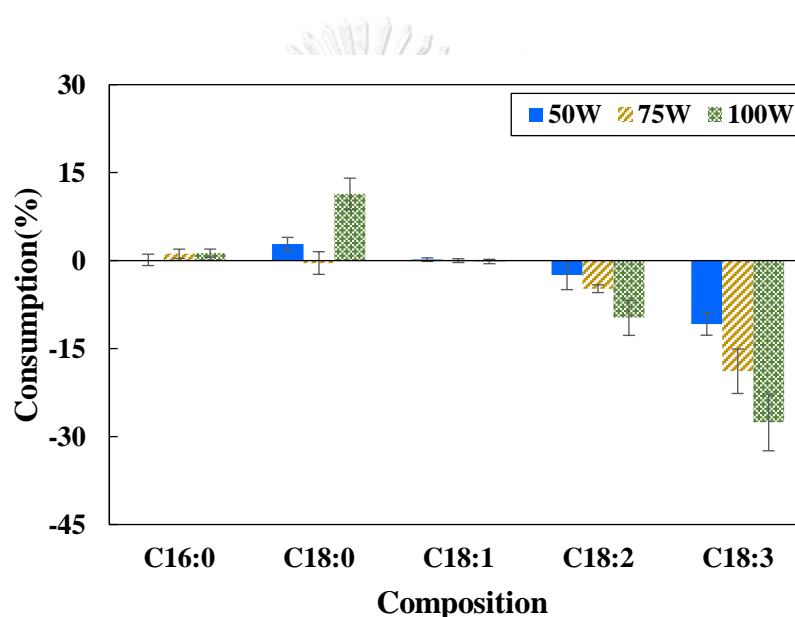
Figure 13 Effect of input power on FAME composition changes (1 mm gap and 25%H$_2$ at room temperature for 1 h)

3.3.3   Effect of gas-filled gap size

The gap size was configured at 1, 3 and 5 mm. The conditions were 100 W, 25% H$_2$ and room temperature. The reaction took place for 1 h. The discharge voltage for each gap size was measured for the power of 50 – 100 W. The different gap sizes resulted in dissimilar voltages under the same input power as presented in supplementary materials Figure A4. Using the larger gap size, the discharge voltage became higher. For the case of 100 W, the peak-to-peak voltage at 1, 3 and 5 mm gap size was 2.10, 2.46 and 2.96 kV, respectively. This behavior was expected as a

larger gap size resulted in the system becoming more open circuit electrically. For a very large electrode gap, the peak-to-peak voltage would become the neon transformer's open-circuit voltage rating of 15 kV. When considering the percent consumption of the C=C bonds including C18:2 and C18:3, it was found that the smallest gap of 1 mm offered the best overall result with a significant decrease in C18:2 and C18:3 followed by 3 and 5 mm, respectively as presented in Figure 14. The reduction of C18:2 and C18:3 obtained from the 3 mm gap was 6.24 (from 9.73 to 9.13%) and 28.51% (from 0.17 to 0.12%), respectively. For 5 mm, C18:2 and C18:3 decreased by 5.23 (from 9.73 to 9.51%) and 19.71% (from 0.17 to 0.14%), respectively. The gas-filled gap influenced the performance of the plasma catalyzed reaction. Being characteristic of the DBD plasma, the smaller the gap between the two electrodes, the denser the generated microfilament discharges and the resulting higher plasma intensity, and vice versa. On the contrary, a smaller gap might impede gas flow and might result in a diminished quantity of atomic hydrogen. For the plasma to be generated, the larger gas gap required a larger amount of supplied energy to exceed the breakdown voltage (V_b) of the gas within the gap. The breakdown voltage of a gas is the function of pressure (p) and gap distance (d). According to Paschen's curve for the He-H_2 gas mixture presented in the study of Das et al. [96], the value of pressure times gap distance of the present work should be 76, 228 and 380 Torr·cm for the gap size of 1, 3 and 5 mm, respectively. According to Paschen's curve in supplementary materials Figure A5, it showed that the bigger gap necessitated the higher breakdown voltage of gases. This implied that the applied voltage for the case of a small gap exceeded the voltage required to dissociate and ionize the gas molecules. Furthermore, a small gap resulted in a short distance for atomic hydrogen to travel and react with FAME, thus, more hydrogen atoms/ions could react with FAME before recombination to become hydrogen molecules ineffective for hydrogenation. With the result showing the smallest gap of 1 mm performing the best, the effect of higher plasma intensity and short travel distance for hydrogen radicals must have outweighed the effect of gas flow impediment if any.

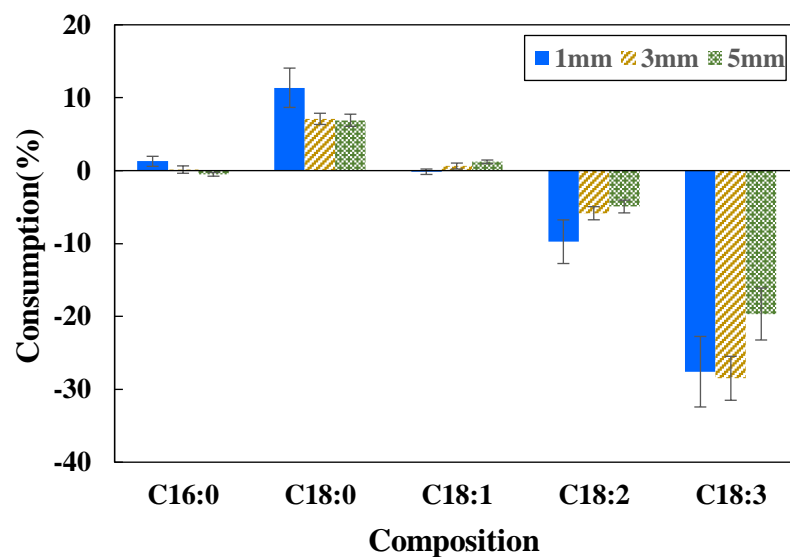*Figure 14 Effect of gas-filled gap on FAME composition changes (100 W and 25%H_2*
at room temperature for 1 h)

3.3.4 Effect of H_2 concentration

Firstly, the H_2 percentage was increased until plasma could not be sustained. The highest value was slightly over 80% when the plasma visually ceased to exist, confirmed by a sudden drop in the transformer power input (no plasma generation meant no power drawn by the transformer, a phenomenon similar to an AC transformer with an open circuit on the secondary winding which would draw no current on the primary side). The clearly audible high-frequency sound characteristic of a DBD plasma also went silent. Thus, the H_2 concentration was examined at 25, 52.5 and 80%. The most appropriate gas-filled gap of 1 mm and the input power of 100 W at room temperature were used. As the solubility of H_2 in biodiesel was very low, H_2 uptake by the biodiesel in the reaction chamber was negligible. As presented in the study of Tomoya et al. [97], H_2 can be fairly dissolved in bio-oil. For example, H_2 was dissolved in triolein (triglycerides with one unit of glycerol and three units of oleic acid) at a mole fraction of 0.1323 at about 80°C and 7.5 MPa. It was also reported that H_2 solubility increased with pressure. This demonstrates that there was a very small amount of H_2 incorporated into the liquid phase in this low-pressure and low-temperature treatment regime. Thus, the reaction was two-phase (gas/liquid)

that occurred at the plasma-FAME interface. Since the interfacial area remained unaffected with different H_2 concentrations, any observed effect on FAME composition changes reflected the effect of H_2 concentration.

As shown in Figure 15, the highest H_2 concentration of 80% appeared to show the highest conversion of polyunsaturated FAMEs, followed by 52.5 and 25%, respectively. For the case of 80%H_2, C18:2 and C18:3 were decreased by about 13.45 (from 9.73 to 8.42%) and 38.0% (from 0.17 to 0.11), respectively, whereas saturated FAME increased as follows: C16:0 by 1.46% (from 41.22 to 41.82%) and C18:0 by 20.42% (from 3.62 to 4.36%).
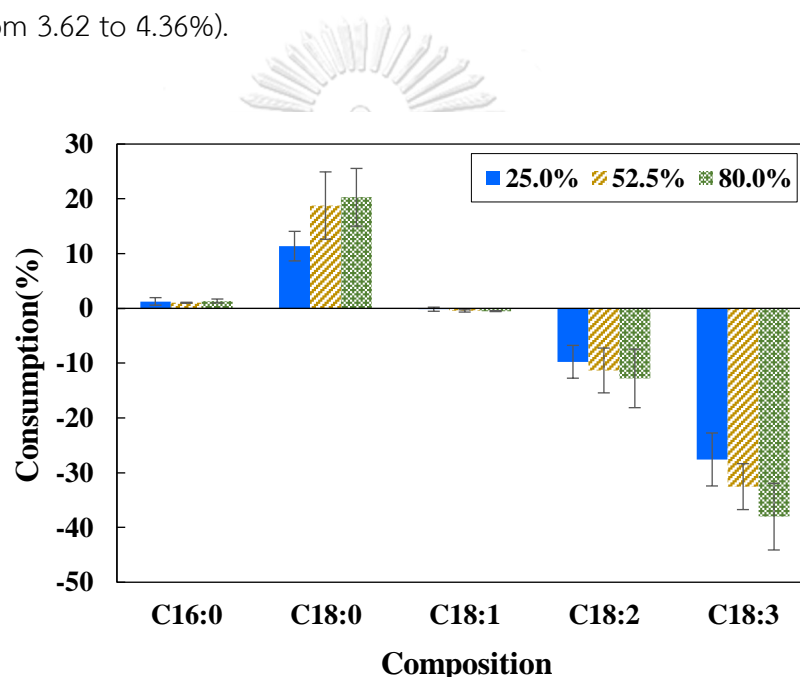
Figure 15 Effect of H_2 concentration on FAME composition changes (100 W and 1 mm gap at room temperature for 1 h)

3.3.5 Effect of reaction temperature

The temperatures of 20 ± 2℃, 38 ± 2℃ (due to plasma heating only), and 60 ± 2℃ were investigated. The reaction conditions were 100 W input power, 1 mm gas-filled gap and 80%H_2. Figure 16 demonstrates the effect of temperature on PH-FAME composition, which revealed that temperature played no significant role. High temperature could not enhance the reaction speed, while low temperature could not amplify the benefit of the exothermic hydrogenation. The gas outlet temperature

was also measured to be about 22.5 ± 0.7°C (initially at 18°C and became constant after plasma application for 15 min, for the case of the FAME temperature of 38 ± 2°C). This implied that reduced or elevated temperature was not required for plasma hydrogenation as also revealed in the previous work [93]. The energy required to ionize and split hydrogen molecules and to activate the double bonds of FAME relied on the applied voltage supplied from the neon sign transformer and not on thermal energy (for the studied DBD plasma system), unlike conventional chemical catalysis that the reaction normally required sufficient thermal energy to overcome the activation energy. Although the plasma channels where the plasma chemical reactions take place are usually at elevated temperatures [98], the elevated temperature was beyond the scope of the present study because performing the plasma treatment at ambient temperature is highly energy-efficient as well as cost-effective since no heating or cooling system is required.
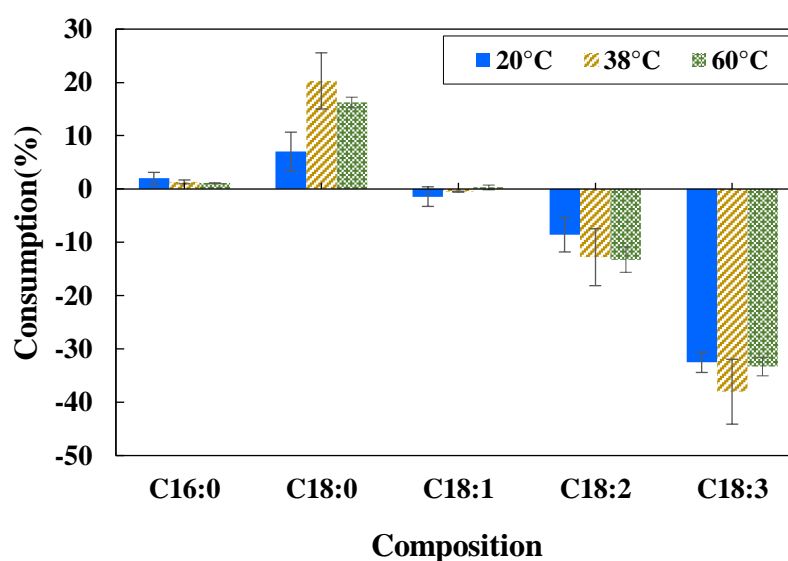

Figure 16 Effect of reaction temperature on FAME composition changes (100 W, 1 mm gap and 80%H_2 for 1 h)

3.3.6   Effect of reaction time

Catalyst-free hydrogenation was performed up to 6 h under the optimal parameters (100 W 1 mm gap and 80%H_2 at room temperature), with Figure 17 displaying the changes of FAME composition. The unsaturated FAMEs were hydrogenated resulting in the saturated ones accumulating over time. PH-FAME at 6 h of reaction time composed of 45.54% C16:0, 7.48% C18:0, 37.62% C18:1 and 4.60% C18:2, while C18:3 completely reacted with hydrogen atoms. When considering the bond dissociation energy (BDE) in a normal alkane, the $CH_3–nC_iH_{2i+1}$ bonds are the strongest with BDE of about 364.0 kJ/mol, while the $C_2H_5–nC_iH_{2i+1}$ bonds are the weakest of about 359.8 kJ/mol, with the bold letters referring to the dissociated atoms [99]. The ethyl group ($–C_2H_5$) in C18:0 could possibly cleavage, causing an increase in C16:0.

The oxidation stability increased with increasing hydrogenation duration due to FAME becoming more saturated. However, FAME at 6 h of plasma treatment was slightly over hydrogenated for its cloud point was 16.5℃, which was marginally above the biodiesel standard of Thailand (16℃ maximum). It was found that the optimal hydrogenation time to satisfy the Thai cloud point standard was 5 h and that the compositions of the final product measured by GC-MS contained saturated FAMEs as the largest component of about 54.08%. Besides, there were mono- and polyunsaturated FAMEs of 38.83 and 5.12%, respectively. Feed FAME and PH-FAME at 5 h of reaction time were analyzed by GC-MS. It was found that both consisted of carbon chains of fatty acid of methyl esters from C8 to C20. The main composition changes were C16 and C18. Table 4 shows the detected compositions. When considering the results obtained in catalytic hydrogenation of palm-based FAME using Pd/SBA-15 in the study of Chen et al. [16], the reported FAME composition was saturated FAME, mono-, di- and tri unsaturated FAMEs as presented in Table 4. The conversion of di-unsaturated FAME and tri-unsaturated FAME was 37.11 and 63.16%, respectively, after 2 h of reaction time. To achieve a similar level of conversion, the DBD plasma system needed to be conducted for 4 h. At this time, the conversion of C18:2 and C18:3 was 38.7 and 100%, respectively. However, a direct comparison of reaction efficacy between a physical catalyst and plasma catalysis cannot be readily

made because of different FAME volumes used, as well as different types and amounts of energy supplied into each system. Chen et al. [16] studied a continuous process of 0.37 g/min, so for 2 h, the treated volume was 53.49 mL (palm biodiesel density is 0.83 g/mL). The total volume used in the present study was 300 mL, which was about 5.6 times higher. The DBD plasma could also take place at ambient conditions and did not require a catalyst, which eliminated the problems of catalyst deactivation and material degradation due to high pressure and high-temperature operation.
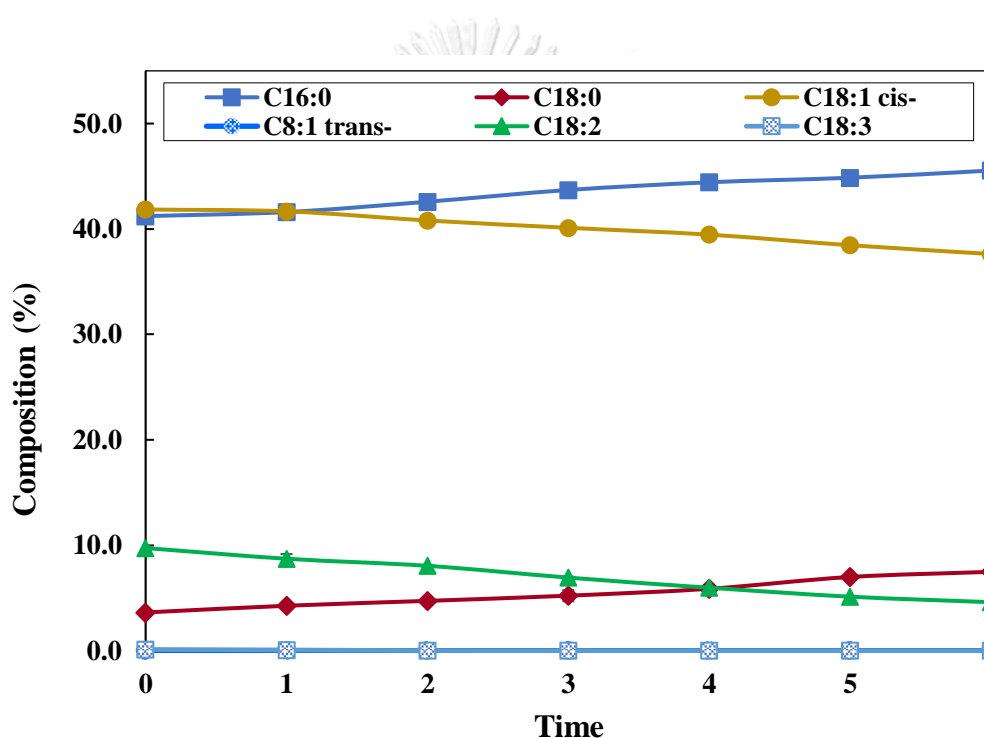

Figure 17 Effect of reaction time on FAME composition changes (100 W, 1 mm gap and 80%H$_2$ at room temperature)

Table 4 Compositions of FAME and PH-FAME determined by GC-MS (100 W, 1 mm gap, 80%H$_2$, room temperature and 5 h) compared to catalytic hydrogenation

Composition (%)	Present work		Ref. Chen et al.[16]	
	FAME	PH-FAME	FAME	PH-FAME
Saturated FAMEs	46.72	54.08	49.07	51.35
Methyl caprylate C8:0	0.01	0.03	-	-
Methyl caprate C10:0	0.02	0.01	-	-
Methyl laurate C12:0	0.22	0.28	-	-
Methyl myristate C14:0	1.08	1.40	-	-
Methyl pentadecanoate C15:0	0.04	0.03	-	-
Methyl palmitate C16:0	41.22	44.86	-	-
Methyl margarate C17:0	0.10	0.08	-	-
Methyl stearate C18:0	3.62	6.99	-	-
Methyl eicosanoate C20:0	0.41	0.40	-	-
Monounsaturated FAMEs	42.30	38.83	41.01	42.27
Total cis-	42.30	38.83	40.90	34.47
Total trans-	-	-	0.11	7.73
Methyl palmitoleate C16:1 (Cis-)	0.23	0.13	-	-
Methyl oleate C18:1 (Cis-)	41.85	38.46	-	-
Methyl oleate C18:1 (Trans-)	-	-	-	-
Methyl eicosenoate C20:1 (Cis-)	0.22	0.24	-	-
Polyunsaturated FAMEs	9.93	5.12	9.73	6.07
Methyl linoleate C18:2/di-	9.73	5.12	9.54	6.00
Methyl linolenate C18:3/tri-	0.20	0.00	0.19	0.07

3.3.7 Plasma hydrogenation of FAME mechanism and reactive species generated during reaction

When He and H_2 gases received sufficient energy from the applied high voltage, electrons can be stripped from molecules/atoms. This caused the formation of active species including energetic electrons, neutral and excited molecules/atoms, as well as positive ions. The He gas was also excited and ionized, but it was still inert and did not react with FAME. However, the reactive species of He still played an important role in the reaction because many possible reaction channels took place from this gas such as momentum transfer, dimer-induced dissociative ionization, ion-electron recombination and so on [100]. This assisted to produce more He species and free electrons that could transfer the energy to H_2 to maintain the plasma production. In addition, the FAME could be activated by these reactive species instigating methyl ester radical's formation. Then, the ions and energetic electrons collided with other atoms/molecules in a stable/excited state to generate more hydrogen ions (H^+)/ radicals ($H^•$) and other electrons which is called a Penning ionization. In a cold hydrogen plasma, it was reported that the generated reactive species were H^+, H^{3+} and $H^•$ of 0.0001%, 0.1%, and 1%, respectively. The system was rich in $H^•$, so they should most participate in the hydrogenation of FAME [101].

The chemical affinity of the C=C bonds or alkene is unstable, for they readily react with a substance or allow the addition of hydrogen atoms to become stable. Polyunsaturated FAMEs (C18:2, C18:3) are conjugated double bonds. They could be easily activated by the plasma light or plasma active species. This causes the hydrogen atom to be dislodged, especially at bis-allylic and allylic positions which are extremely weak, and the methyl ester radical to be generated results in double bonds shifting. Since the bonds were moving, polymerization or Diels-Alder condensation between FAME molecules was possible to be initiated. The carbon cracking initiated by photon/energetic electrons was able to occur in the plasma process [69, 92, 93], particularly at the $C_2H_5-nC_iH_{2i+1}$ bonds in alkene which are weakest as explained in section 3.3.6. This produced ethyl and methyl radicals [102] from eighteen carbon chains (C18) to form sixteen carbon chain (C16) radicals. After

that, the C16 radicals accepted the hydrogen radicals to form stable fatty acid methyl esters. In this work, the scission of C18 resulted in an increase in C16:0 by about 3.6%. Although the C16 radicals could incorporate with the methyl and hydrogen radicals to become seventeen carbon chains, C17 was not detected from the GC-MS results. As for the hydrogenation of FAME, the hydrogen radicals were added to the π-double bonds at the plasma-FAME surface. For one hydrogen radical to establish a bond with carbon resulting in -CH radical formation, 150 kJ/mol of energy was required [103]. Afterward, another H$^\bullet$ was combined, with the required energy of 414 kJ/mol [104], to create a stable single bond as depicted in Figure 18. Most of the reaction taking place in the DBD plasma system was hydrogenation to transform mono- and unsaturated compositions into saturated ones which were C18:0 (from 3.6 to 7.0%) and C16:0 (from 41.2 to 44.9%).
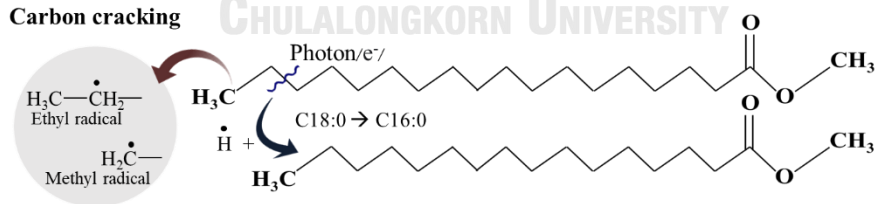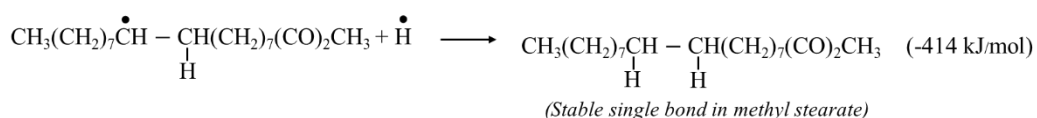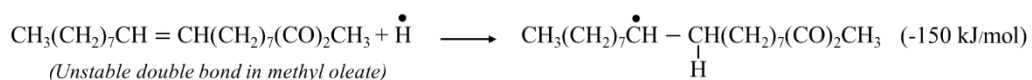

Figure 18 Plasma chemical mechanism for FAME hydrogenation

To observe the reactive species generated from the He-H$_2$ gas mixture and to detect the reactive species from other elements especially from carbon and hydrocarbon as some eighteen-carbon chains could be transformed into sixteen-carbon chains during plasma processing, reactive species were monitored by optical emission spectroscopy (OES) as presented in Figure 19 The reaction conditions were: input power of 100W and gas-filled gap of 1 mm at room temperature. The difference in H$_2$ percentage in the mixed carrier gas resulted in dissimilarly observed peaks. At 90%He and 10%H$_2$, all peaks of He species were clearly detected at 336, 356, 388, 501, 587, 667, 706 and 727.5 nm while only one peak of H$_2$ species appeared which was H$_\alpha$ at 656.3 nm representing hydrogen atom excitation. This was related to the characteristic of cold plasma presented in the study of El-Zeer et al. [105] and mentioned in Yepez et al. [101]'s work that cold plasma consisted mostly of hydrogen radicals responding in the reaction. For the case of 20%He and 80%H$_2$, the plasma color was visually observed to became brighter/lighter, having a more whitish tone as shown in supplementary materials Figure A6. The acquired plasma spectrum showed only the presence of H$_\alpha$ species. These results verified that He and H$_2$ reactive species were indeed generated in the system. Besides, there was no appearance in optical emission spectra of other strong peaks corresponding to a generation of other reactive species, carbon and hydrocarbon.
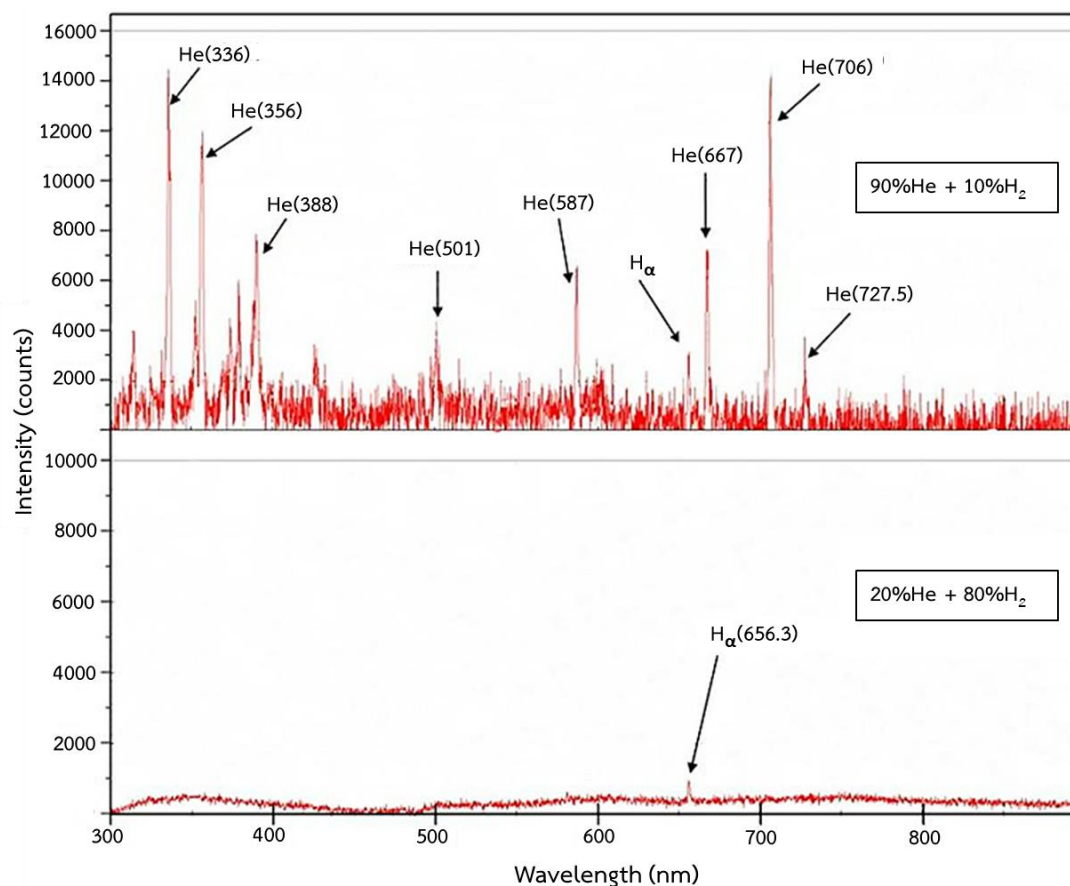
Figure 19 Optical emission spectra of He and H$_2$ plasma (100 W and 1 mm gap at room temperature)

3.3.8 FTIR analysis

The chemical functional groups were examined by FTIR as shown in Figure 20. Both FAME and PH-FAME consisted of a peak at 3008 cm^{-1} representing the unsaturated fatty acid methyl esters, C=CH stretching, and the peak decreased due to hydrogenation. The peaks at wave numbers 2922 and 2853 cm^{-1} were the asymmetric and symmetric stretching vibration of the alkane group, C-H, respectively. The strong peak at 1741 cm^{-1} corresponded to the ester group, C=O stretching. In addition, the asymmetric stretching of CH$_3$ was detected at wavenumbers 1435 and 1460 cm^{-1} while CH$_2$ was represented at 1361 cm^{-1}. The peak at 1195 cm^{-1} indicated O–CH$_3$ stretching which was methyl esters. Besides, C-O anti-symmetric and C-O symmetric vibrations were present at 1016 and 1169 cm^{-1}, respectively. The peaks at

1244 and 1120 cm^{-1} corresponded to C-O and C-O-C stretching. The characteristic peaks of *cis-* and *trans-* configurations appeared at 722 (*cis*) and 966 (*trans*) cm^{-1}. *Cis-* can be normally detected in FAME and PH-FAME, while *trans-* should not be present in FAME, for it was synthesized from edible oil [37]. Most importantly, no peak at 911 cm^{-1} was found — no *trans* fatty acid methyl ester formation from the hydrogenation reaction using low-temperature DBD plasma.
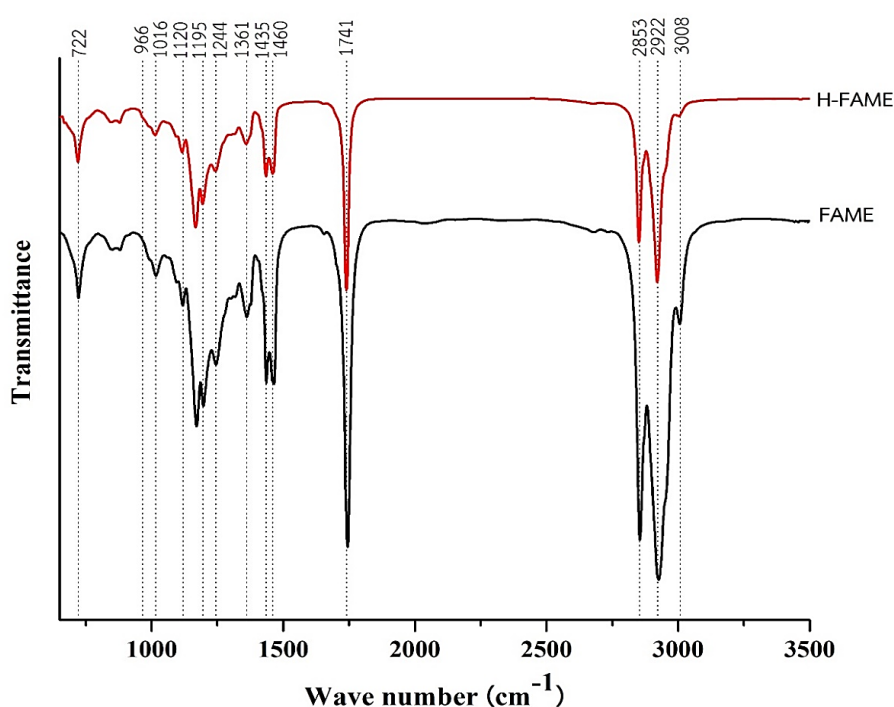
Figure 20 FTIR spectra of FAME and PH-FAME (100 W, 1 mm gap and 80%H$_2$ at room temperature)

3.3.9   PH-FAME properties

FAME and PH-FAME properties compared to biodiesel standards were demonstrated in Table 5. Feed FAME has high oxidation stability of 12.8 h with the cloud point somehow exceeding the ASTM D6751 requirement. After 5 h of plasma treatment (100 W, 1 mm gap, 80%H$_2$, room temperature), it achieved 20 h of oxidation resistance with an increase of the cloud point from 13.5 to 16°C. If 16.5°C of the cloud point was allowed following 6 h of hydrogenation, the oxidation

stability would be higher than 20 h. The more saturation level caused the reduction of iodine value from 50.2 to 43.5, verifying that the DBD plasma system could be practiced for effective PH-FAME production. It offered superior performances to a catalytic reaction as presented in the study of Chen et al. [16]. In the case of using 0.5 wt.% of the Pd/SBA-15 catalyst at 100°C, 0.3 MPa for palm PH-FAME production, the oxidation stability increased by 8.5 h (from 19.4 to 27.9 h) with a small change in the cloud point from 12 to 13°C after 2 h of hydrogenation. A conversion of C18:2 and C18:3 was about 37.11 and 63.16%, respectively, while the saturated- and monounsaturated compositions rose by 4.65 and 3.07%, respectively. There was also *trans*- formation of about 7.73% (per 100% PH-FAME content) after the reaction. The composition still consisted mostly of C18:1, and this was perhaps the reason why the cloud point increased by only 1°C. For the results obtained in the present study, every FAME composition with the C=C bond was hydrogenated into a single bond to a varying degree. The conversion of C18:1, C18:2 and C18:3 was 8.20, 47.39 and 100%, respectively, increasing the saturated FAME by 15.75%. The product could resist oxidation by an additional 7.2 h. However, due to the higher amount of saturated FAME, the increase in the cloud point was greater than that of the catalytic reaction.

The basic parameters directly related to oxidation products including an acid number and a peroxide value were measured. There were several parameters related to oxidation products, but the two were able to be determined with minimum effort by titration. The acid number remained unaffected whereas the peroxide value became lower, signifying that PH-FAME exhibited a lower oxidation rate corresponding to the increase in oxidation stability.

Table 5 Properties FAME and PH-FAME compared to biodiesel standards (100 W, 1 mm gap, 80%H_2, room temperature and 5 h)

Properties	FAME	PH-FAME	Standard
Oxidation stability (h)	12.8	20.0	> 6.0[a], 3.0[b], 10.0[c]
Cloud point (°C)	13.5	16.0	< 12.0[b],16.0[c]
Iodine value (gI_2/100)	50.2	43.5	< 120.0[a,b,c]
Acid number (mgKOH/g	0.3	0.3	< 0.5[a,b,c]
Peroxide value (mequi/kg oil)	11.7	10.0	–

[a] EN14214 (European biodiesel standard), [b] ASTM D6751 (United States), [c] Thailand [10, 13, 65]

3.3.10 Preliminary design for large-scale PH-FAME production

With 100 W of input power to the DBD power supply and with the production rate of 300 mL for 5 h, the energy efficiency in the present experiment was only 66.7 W/L-h. No power was required for FAME heating or catalyst preparation/removal/regeneration. There was no cost for initial catalyst procurement either. For a large-scale production using this novel green and non-thermal DBD plasma hydrogenation, one could employ a large set of electrodes to treat a large FAME surface with a powerful DBD power supply. He and H_2 gases could also be completely recycled using a simple recirculating pump operating at slightly above ambient conditions, with only occasional replenishment of H_2 gas to account for the consumed hydrogen by the C=C bonds. To continuously maintain the optimal gas concentration, a residual gas analyzer (RGA) through a gas sampling port could be installed for analysis of partial pressures of gases, assisting precise and real-time addition of H_2 into the system. Thus, the only major expenditures to produce PH-FAME using this novel green technique are electricity, hydrogen gas and FAME. Also, this technique is safe. Even though 80% hydrogen gas concentration was used and would, at first thought, be prone to explosion, in the closed system with no oxidizer present in the reaction chamber, e.g., O_2 gas or oxygen atoms in FAME or even in the electrode, the hydrogen gas cannot explode even with the presence of the

microfilament discharges. Operating at slightly above one atmosphere would ensure no atmospheric oxygen gas seeping into the system. The reaction chamber and the gas system must also be sealed properly to prevent gas leakage as the hydrogen gas is flammable. Its lower and upper explosive limits in the air at room temperature and atmospheric pressure are 4.3 and 76.5 mol%, respectively [106]. A similar safety infrastructure to that of conventional catalysis will ensure a safe operation of the DBD plasma hydrogenation system.

3.4   Conclusions

The constructed DBD plasma reactor was utilized to effectively hydrogenate palm FAME. The most suitable condition was 100 W input power, 1 mm gas-filled gap size, 80% H_2, room temperature and 5 h of reaction time for 300 mL FAME in the absence of a catalyst. This caused the reduction of C18:2 and C18:3 by 47.1 and 100%, respectively. The reduction of C=C bonds enhanced the oxidation stability from 12.8 to 20 h along with the change in the cloud point from 13.5 to 16°C. The low-temperature plasma treatment did not create *trans*-fatty acid methyl ester normally formed in catalytic hydrogenation. The green DBD plasma hydrogenation provided superior performances to catalysis and was much simpler, for it required no dedicated reactor and materials to withstand high pressure and high temperature. Moreover, this technique can eliminate the problems or processes associated with a physical catalyst such as catalyst deactivation, pellet breakup, filtration and regeneration requiring high energy in the process. This novel and green technology has a promising potential to be applied for the hydrogenation of other high-value liquids, as well as for large-scale PH-FAME production.

CHAPTER 4

4.1　Production costs estimation

For FAME-based palm oil, the reported cost of raw materials (production method not mentioned) was about 64% – 73% of the total manufacturing costs, with the average being 68.5%. The production price of hydrogenated FAME including variable and fixed costs was about $1,150 per ton (about $1.1 per liter) [107]. This is divided into the variable cost of $875 and the fixed cost of $275 per ton. Considering the PH-FAME production solely and ignoring the cost of FAME production, which is about $1,100 per ton, the capital cost of PH-FAME becomes $50 per ton or 1.56 baht per liter ($1 = 33.7 baht). If the variable cost is considered, the investment for one liter of PH-FAME production is about 0.78 baht per liter.

The production costs of PH-FAME produced from soybean and palm FAME using the plasma technology in a batch process are presented in Table 6. To compare with the conventional method, the cost of feed FAME production which is one of the variable costs was not calculated. In the plasma method, the reaction relied on energy supplied and hydrogen radicals. Therefore, the cost is related to the electricity consumed by the neon power supply and the hydrogen gas which are the variable cost excluding fixed costs: wage, reactor building, and facility construction costs. For large-scale production, a gas recirculation system is needed to be designed by using an atmospheric circulation pump. Therefore, unreacted hydrogen and helium gases can be refed into the system. The amount of hydrogen gas that participated in the reaction to transform the double bonds into single bonds 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 FAMEs molecules, the mole number was multiplied by Avogadro's number of 6.02×10^{23}. All changes in the unsaturated FAMEs were assumed to become saturated FAME, so C18:1, C18:2, and C18:3 needed 2, 4, and 6 hydrogen atoms to be added, respectively. The cost of hydrogen gas, ultra-high purity (UHP) grade, was about 0.43 baht per liter.

For the PH-soybean FAME, the number of hydrogen atoms required to generate single bonds was 3.66×10^{20} atoms or 32.19 mL for 35 mL of PH-FAME. This means that the hydrogen gas necessary for one liter of PH-soybean FAME production was 919.76 mL that costed 0.39 baht. This system consumed the power of 0.26 kWh for 35 mL of PH-FAME. The cost of electricity was 5 baht per unit, so it was about 36.57 baht per liter. Therefore, the total production cost was 36.96 baht per liter. The next calculation is for PH-palm FAME production. The number of hydrogen atoms that participated in the reaction was 4.4×10^{20} atoms or 38.68 mL for 300 mL of PH-FAME. At this condition, this results in hydrogen gas and the electricity costs (power consumption of 0.50 kWh) of about 0.06 and 8.33 baht per liter, respectively. The total cost was 8.39 baht per liter which was much cheaper than soybean FAME raw material.

The main expense of the DBD plasma technology was electricity, so finding a suitable and effective high voltage power supply would be an important point to save the cost. The DBD plasma reactor used for soybean FAME hydrogenation resulted in the final temperature of 58°C which was about 1.5 times higher than 38°C in the palm FAME system. This implied that a larger portion of the energy generated by the power supply was converted into heat instead of being used to produce plasma. In addition, the longer reaction time resulted in the higher electricity cost in the PH-soybean FAME system. The soybean FAME has a higher level of unsaturation, so it required more hydrogen gas in the reaction resulting in the higher cost of hydrogen gas by about 6.50 times. According to the cost of PH-palm FAME production using DBD plasma and the conventional method (there is no report on the production cost of soybean FAME hydrogenation), the DBD plasma is about 10.76 times higher than that of the conventional method. However, the DBD plasma is not complicated as the reaction can occur at atmospheric pressure and slightly above room temperature. This implies that the specific materials that resist high pressure and high-temperature conditions are not mandatory. This is desirable to reduce the price of the reactor. Nevertheless, installing the gas controlling and monitoring systems and using an inert gas shield to prevent explosion should be scrupulously considered. It can be concluded that PH-FAME production employing the DBD

plasma system is an attractive alternative method that is simple in terms of reactor construction, yet the production process needs to be improved for possible commercial utilization.

Table 6 Production cost of PH-FAME produced from soybean and palm FAME using plasma technology

Method	DBD plasma			
FAME type	Soybean		Palm	
%Composition	FAME	PH-FAME	FAME	PH-FAME
C16:0	12.12	24.26	43.62	47.48
C18:0	4.20	28.53	4.40	8.49
C18:1	23.57	37.03	41.18	37.85
C18:2	53.97	8.90	9.66	5.08
C18:3	5.10	0.24	0.17	0.00
Batch volume (mL)	35.00		300.00	
Reaction time (h)	5.50		5.00	
Power consumption (kWh)	0.26		0.50	
Electricity rate (Baht/kWh)	5.00		5.00	
Electricity per liter (Baht)	36.57		8.33	
Reacted H_2 per liter PH-FAME (mL)	919.76		128.94	
H_2 price per liter (Bath)	0.43		0.43	
H_2 needed to produce PH-FAME (Baht)	0.39		0.06	
Total production cost per liter PH-FAME (Baht)	36.96		8.39	
Chamber and equipment cost (Baht per reactor)	3000.00		5000.00	
Labor (Baht per day-person)	1000.00		1000.00	

CHAPTER 5

5.1   Conclusion

Partial hydrogenation of FAME produced from soybean and palm oil was successfully performed in the DBD plasma reactor. The reaction took place at atmospheric pressure and ambient temperature (with a slight increase in temperature during the reaction) in the absence of a catalyst. For 35 mL of PH-soybean FAME production, the best condition was 25% H_2 in the mixed gas at ambient temperature for 5.5 h. This caused the conversion of C18:2 of 83.2% and C18:3 of 95.2%, while monounsaturated and saturated FAMEs increased. With more content of a saturated composition, the iodine value reduced from 128 to 67.4. In addition, its oxidation stability rose from 2.13 to 10 h, whereas the cloud point changed from -1 to 11℃. The production cost of this process was about 36.96 baht/L.

The most suitable condition for 300 mL of PH-palm FAME production was 100 W, 1 mm gas gap size, 80% H_2 and ambient temperature for 5 h. This condition affected the abatement in C18:2 and C18:3 of 47.1 and 100%, respectively, leading to the decrease in iodine value from 50.2 to 43.5. The oxidation stability was enhanced from 12.8 to 20 h and the cloud point rose from 13.5 to 16˚C. The production cost for this process was 8.39 baht/L which was higher than that of a commercial method of 0.78 baht/L. The results from the two studies show that the DBD plasma system is one of the alternative methods. It can be employed for the hydrogenation reaction to produce PH-FAME providing greater oxidation stability; however, the process needs to be improved to achieve a reasonable production cost. Moreover, this method offered similar performance to the reaction using a catalyst but was simpler and more environmentally friendly.

5.2   Limitations of study

The DBD plasma system has the potential to hydrogenate FAME at ambient conditions without using any catalyst, yet its limitations are as follows.

5.2.1   The reaction is difficult to control. It depends on the concentration of plasma and the reactive species to collide with the double bonds to initiate unstable FAME molecules, allowing hydrogen radicals in the plasma to incorporate with FAME molecules.

5.2.2   The side reactions besides hydrogenation such as bond cracking and polymerization are possible because the reaction does not depend on a catalyst that has selectivity and controllability of the reaction route. Therefore, it needs to be carefully considered when using DBD plasma for other reactions and to produce other products.

5.2.3   The high voltage, high-frequency power supply is very important to supply sufficient energy to generate plasma. It should not dissipate a large amount of heat because a high temperature is not suitable for an exothermic reaction, and high temperatures can also damage the equipment.

5.2.4   A stirring system to allow FAME circulation, particularly in the 2nd study, might be developed to make FAME flow faster with turbulence to speed up the reaction because most reactions happened at the FAME surface.

5.3   Suggestion

5.3.1   The high voltage, high-frequency power supply needs to be improved to reduce the dissipated heat resulting in the high temperature in the reactor. Also, the power supply should consume less electric energy.

5.3.2   The systems related to controlling and monitoring the gas composition in the reactor are very important to prevent the oxygen contamination that is the cause of oxidation acceleration and significantly the risk of fire and explosion.

5.3.3   The use of lower-grade hydrogen gas, instead of the UHP grade, should be studied to reduce the production cost. This is crucial and significantly affects large-scale production.

5.3.4   A comparison of the DBD plasma to other types of plasma such as microwave plasma, corona plasma, and so on and the different configurations of DBD plasma that are not parallel-plate type needs to be investigated.

5.3.5   A DBD plasma reactor should be employed to produce other products similar to PH-FAME production such as margarine, xylitol in the food industry, hydrogenated castor oil in the cosmetic industry, and so on.

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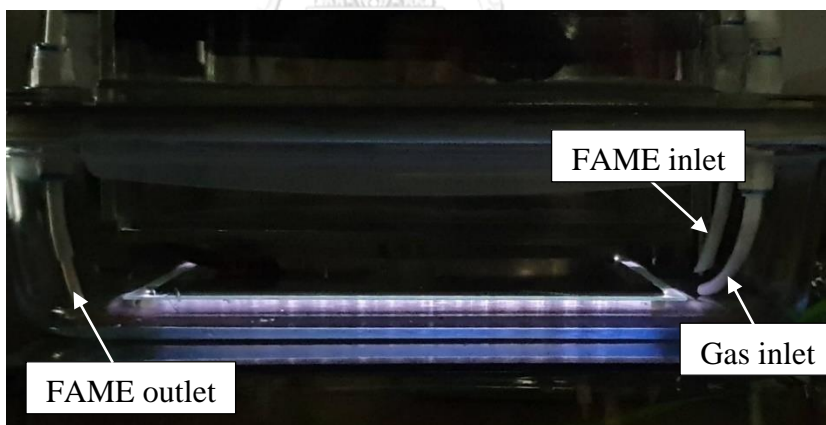
APPENDICES

APPENDIX A

Supplementary Materials for Low-Temperature and Atmospheric Pressure Plasma for Palm Biodiesel Hydrogenation


(a)

(b)

Figure A1. Plasma generated (a) with FAME and (b) without FAME in chamber

1) Experimental investigation of plasma gas

The constructed DBD plasma reactor could not generate plasma from pure H_2, so an appropriate inert gas mixture was needed. He gas was chosen because plasma could be easily generated all over the electrode with few microfilament formations. N_2 and Ar gases were also tested, but plasma could not be generated in the constructed reactor. We also tried to use N_2 gas in a different DBD configuration without the glass dielectric attached to the upper electrode. In this configuration, the bottom of the glass container acted as a dielectric material. Plasma could be generated, but N_2 plasma consisted of discrete large microfilament discharges at certain locations on the edges of the upper electrode compared to He gas, which was undesirable because of the very low plasma density and because microfilament discharges locally heated FAME in contact. With He gas, the diffuse plasma was observed all over the upper electrode, offering a much higher plasma density and much less intense microfilament discharges. As for using Ar gas, stable plasma could not be generated. Therefore, we decided to use the He/H_2 mixed gas as can be seen in Figure S2.

On an industrial scale, a simple gas recirculating system could be constructed and no He gas would be vented to the atmosphere. To maintain the optimal gas concentration, a residual gas analyzer (RGA) through a gas sampling port could be installed for analysis of partial pressures of gases, assisting precise and real-time addition of H_2 into the system.
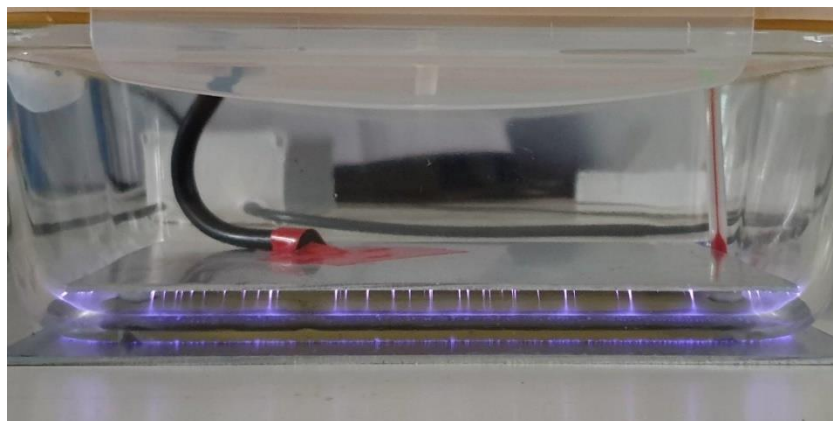
(a)
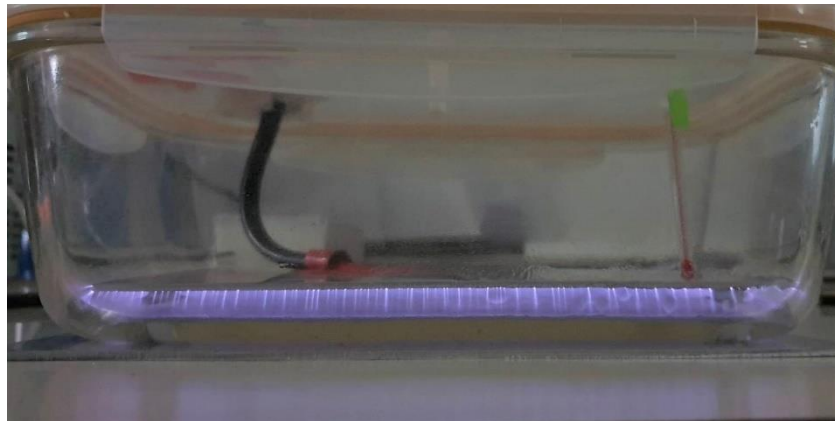
(b)

Figure A2. Generated plasma using different mixed gases (a) 25%H_2 and 75% N_2, (b) 25%H_2 and 75%He (ambient temperature, 100 W input power)
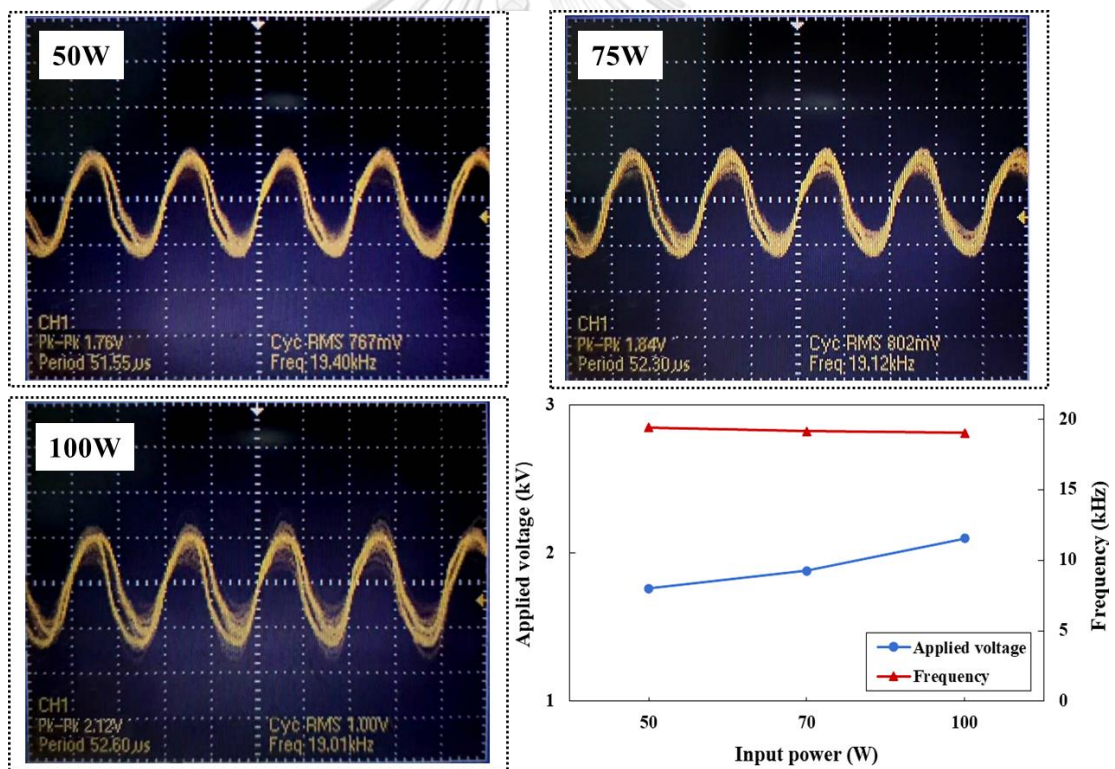

Figure A3. Discharge voltage characteristic of DBD plasma under different power levels (1 mm gap, 25%H_2, room temperature)
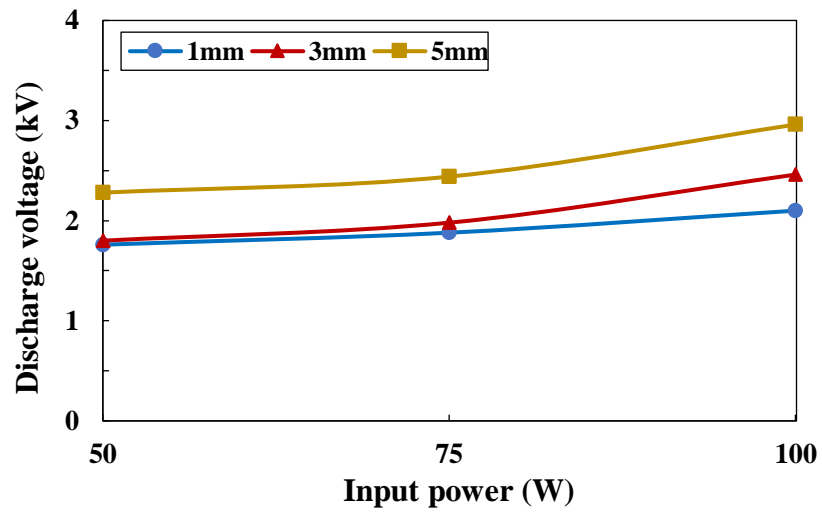
Figure A4. Discharge voltage under different gas-filled gap sizes
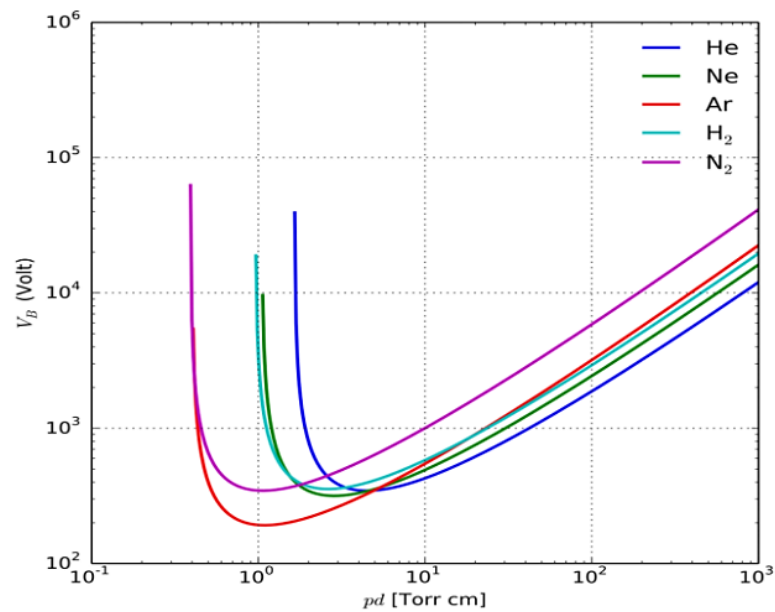

Figure A5. Paschen's curve obtained for helium, neon, argon, hydrogen and nitrogen gases using expression for breakdown voltage as function of parameters p and d presented in Das et al.'s study [96]
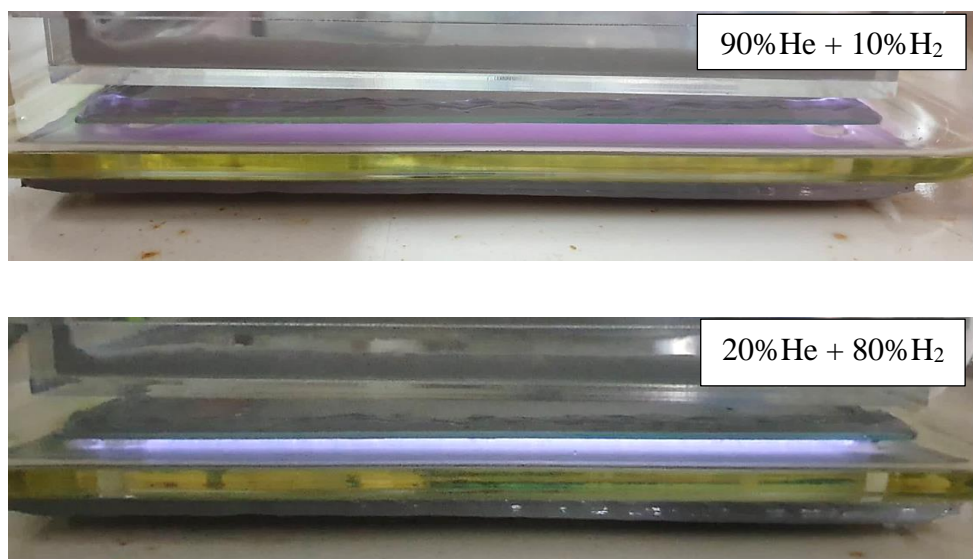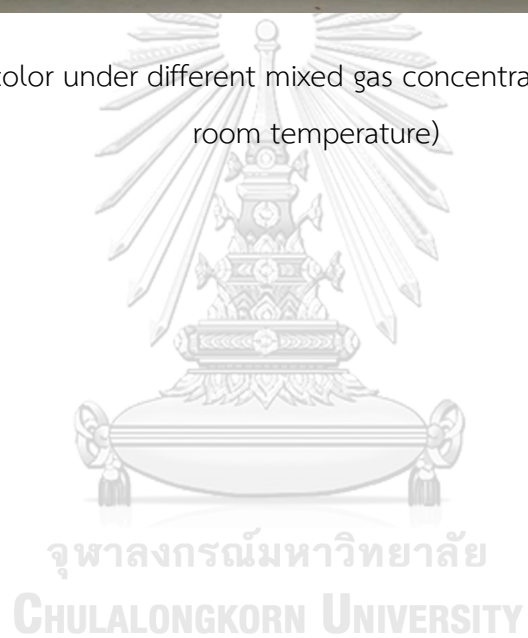
Fig. A6. Plasma color under different mixed gas concentrations (100 W, 1 mm gap, room temperature)

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