Low-Temperature and Atmospheric Pressure Plasma for Palm Biodiesel Hydrogenation

Grittima Kongprawes

Chulalongkorn University

Doonyapong Wongsawaeng (✉ doonyapong.w@chula.ac.th)

Chulalongkorn University

Kanokwan Ngaosuwan

Rajamangala University of Technology Krungthep

Worapon Kiatkittipong

Silpakorn University

Suttichai Assabumrungrat

Chulalongkorn University

Research Article

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

Posted Date: March 12th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-282528/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

Version of Record: A version of this preprint was published at Scientific Reports on July 9th, 2021. See the published version at <https://doi.org/10.1038/s41598-021-92714-x>.

Abstract

Partially hydrogenated fatty acid methyl ester (H-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. H-FAME became more saturated with the conversion of C18:2 and C18:3 of 47.1 and 100%, respectively, at 100 W input power, 1 mm gas-filled gap size and 80% H₂ 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.

Highlights

- Novel green catalyst-free partial hydrogenation of palm FAME using DBD plasma
- Reaction performed under atmospheric pressure and room temperature
- Superior performance to chemical catalytic reaction
- Oxidation stability increased by 7.2 h; iodine value reduced from 50.2 to 43.5
- No *trans*-FAME formation

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 a 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 gases¹. To reduce the use of petrodiesel, alternative fuels such as renewable energy: wind, solar and biofuel have been developed².

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 transesterification³. 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^{4,5}. Besides, the reaction can proceed in the absence of a catalyst, but a supercritical condition is required⁶. 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 engines⁷. 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 health². However, biodiesel composes of long-chain carbon atoms containing C=C bonds, resulting in low oxidation stability compared to petrodiesel⁸.

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^{9,10}. 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^{11,12}. 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 (H-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 radicals¹³. 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 materials¹⁴. 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^{14,15}. 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 value¹⁶. 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 point⁸. 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.¹⁷, Pd/SiO₂ 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.¹⁸ improved the catalyst performance by adding a Mg modifier to form Pd-Mg/SiO₂. 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 acid¹⁹. In the case of H-FAME produced from palm FAME, a Pd catalyst on SBA-

15 support was also practiced as reported in the study of Chen et al.²⁰. 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.²¹ 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 surface²². 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 plasma²³. 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 widely used in several chemical production processes, as well as in many industries such as ozone generation, CO₂ laser, excimer lamps²³, as well as to assist a catalyst for syngas, ammonia or methanol production²⁴⁻²⁶. It is also practiced for liquid-phase hydrogenation of heavy oil and oil without a catalyst.

In the experiments of Hao et al.²⁷, 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: N₂, CH₄ and H₂. 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 Yopez and Keener²⁸. 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% H₂ and 95% N₂. 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.²⁹. The optimal conditions were 15% H₂ in a mixed gas (He and H₂) 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 work³⁰, H-FAME derived from soybean oil was successfully synthesized in a DBD plasma reactor. The best results appeared when using 35 mL FAME, 25% H₂ in the He and H₂ gas mixture, and ambient temperature under atmospheric pressure. It was found that the produced H-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 a H-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%³¹, was studied. The utilized DBD plasma hydrogenation reactor was an improvement to the previous study³⁰ 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, H₂ 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 H-FAME production.

2. Methodology

2.1 Materials

Palm FAME was obtained from an industrial plant in Thailand. The gases used for H-FAME production, H₂ 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 QR&C, 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.

2.2 Experimental set-up

Fig. 1 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.³⁰ 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. Power consumption of the power supply was measured by a plug-in power meter. The gas mixture of H₂ and He was controlled by Unit Instruments mass flow controllers models UFC-1000 for H₂ and UFC-1260A for He. 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 for visualization.

2.3 Hydrogenation of FAME

For each batch, 300 mL of FAME was plasma hydrogenated. The plasma was generated from a H₂/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. 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 H₂ (25 – 80 vol.%), reaction 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, H-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.

2.4 FAME and H-FAME analysis

FAME yield and fatty acid compositions were analyzed according to EN14103 standard³² using gas chromatograph (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. (1) and (2), respectively.

$$\text{FAME yield (\%)} = \frac{\Sigma A - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m} \times 100\% \quad (1)$$

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).

$$X_{\text{composition}} (\%) = \frac{A_x}{\Sigma A - A_{IS}} \times 100\% \quad (2)$$

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. The level of saturation indicated by iodine value was investigated by the Wijs-cyclohexane method, ASTM D1959³³. Acid number and peroxide value were measured according to the standards of AOAC, 1997 and AOCS, 1997, respectively. Oxidation stability of FAME and H-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)³⁴. In addition, Walter Herzog GmbH, Germany was utilized to determine the cloud point as in the standard of ASTM-D-2500³⁵.

3. Results And Discussion

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: 43.6 ± 0.6% methyl palmitate (C16:0), 4.4 ± 0.2% methyl stearate (C18:0) and 41.2 ± 0.1% methyl oleate (18:1). The polyunsaturated FAMEs were composed of methyl linoleate

(C18:2) and methyl linolenate (C18:3) of about 9.7 ± 0.3 and $0.2 \pm 0.1\%$, 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 $0.5\% \text{ g I}_2/\text{g}$ and 0.2 mg KOH/g , respectively.

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 plasma³⁶). Fig. 2 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 9.3 (from 9.7 ± 0.3 to $8.8 \pm 0.2\%$) and 27.6% (from 0.2 ± 0.1 to $0.1 \pm 0.0\%$), respectively. In addition, saturated FAME increased as follows: 1.4% for C16:0 (from 43.6 ± 0.6 to $44.2 \pm 0.3\%$) and 11.4% for C18:0 (from 4.4 ± 0.2 to $4.9 \pm 0.1\%$). The response of FAME with input power was according to the expectation – high input power provided higher energy to produce more plasma density³⁷. High plasma density meant a large amount of atomic hydrogen was present to react with C=C bonds.

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. 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 Fig. 3. The reduction of C18:2 and C18:3 obtained from the 3 mm gap was 6.2 (from 9.7 ± 0.3 to $9.1 \pm 0.1\%$) and 28.5% (from 0.2 ± 0.1 to $0.1 \pm 0.0\%$), respectively. For 5 mm, C18:2 and C18:3 decreased by 5.2 (from 9.7 ± 0.3 to $9.2 \pm 0.1\%$) and 19.7% (from 0.2 ± 0.1 to $0.1 \pm 0.0\%$), 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. With the result showing the smallest gap of 1 mm performing the best, the effect of higher plasma intensity must have outweighed the effect of gas flow impediment if any.

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.³⁸, 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 Fig. 4, 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 13.4 (from 9.7 ± 0.3 to $8.4 \pm 0.4\%$) and 38.0% (from 0.2 ± 0.1 to $0.1 \pm 0.0\%$), respectively, whereas saturated FAME increased as follows: C16:0 by 1.4% (from 43.6 ± 0.1 to $44.2 \pm 0.2\%$) and C18:0 by 20.4% (from 4.4 ± 0.2 to $5.3 \pm 0.2\%$).

3.5 Effect of reaction temperature

The temperatures of $20 \pm 2^\circ\text{C}$, $38 \pm 2^\circ\text{C}$ (due to plasma heating only), and $60 \pm 2^\circ\text{C}$ were investigated. The reaction conditions were 100 W input power, 1 mm gas-filled gap and 80% H_2 . Fig. 5 demonstrates the effect of temperature on H-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. This implied that reduced or elevated temperature was not required for plasma hydrogenation as also revealed in the previous work³⁰. Performing the plasma treatment at ambient temperature is highly energy-efficient as well as cost-effective since no heating or cooling system is required.

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 Fig. 6 displaying the changes of FAME composition. The unsaturated FAMES were hydrogenated resulting in the saturated ones accumulating over time. H-FAME at 6 h of reaction time composed of $48.2 \pm 0.1\%$ C16:0, $9.1 \pm 0.1\%$ C18:0, $37.0 \pm 0.1\%$ C18:1 and $4.6 \pm 0.1\%$ C18:2, while C18:3 completely reacted with hydrogen atoms. When considering the bond dissociation energy (BDE) in a normal alkane, the $\text{CH}_3\text{--nC}_i\text{H}_{2i+1}$ bonds are the strongest with BDE of about 364.0 kJ/mol, while the $\text{C}_2\text{H}_5\text{--nC}_i\text{H}_{2i+1}$ bonds are the weakest of about 359.8 kJ/mol, with the bold letters referring to the dissociated atoms³⁹. The ethyl group ($\text{--C}_2\text{H}_5$) 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°C , which was marginally above the biodiesel standard of Thailand (16°C 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 contained saturated FAMES as the largest component of about $56.0 \pm 0.3\%$. Besides, there were mono- and polyunsaturated FAME of 37.8 ± 0.1 and $5.1 \pm 0.1\%$, respectively as shown in Table 1.

When considering the results obtained in catalytic hydrogenation of palm-based FAME using Pd/SBA-15 in the study of Chen et al.²⁰, the conversion of C18:2 and C18:3 was 37.1 and 63.2%, 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, 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 amount of energy supplied into each system. Chen et al.²⁰ studied a continuous process of 0.37 g/min, so for 2 h, the treated volume was 53.5 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.

Table 1 Compositions of FAME and H-FAME (100 W, 1 mm gap, 80% H_2 , room temperature and 5 h) compared to catalytic hydrogenation

Composition (%)	Present work		Ref. Chen et al. ²⁰	
	FAME	H-FAME	FAME	H-FAME
Saturated FAME	48.0 ± 0.2	56.0 ± 0.3	49.07	51.35
Methyl palmitate C16:0	43.6 ± 0.1	47.5 ± 0.2	-	-
Methyl stearate C18:0	4.4 ± 0.1	8.5 ± 0.1	-	-
Monounsaturated FAME	41.2 ± 0.1	37.8 ± 0.1	41.01	42.27
Methyl oleate C18:1				
<i>Cis</i> -	41.2 ± 0.1	37.8 ± 0.1	40.90	34.47
<i>Trans</i> -	0.0 ± 0.0	0.0 ± 0.0	0.11	7.73
Polyunsaturated FAME	9.8 ± 0.3	5.1 ± 0.1	9.73	6.07
Methyl linoleate C18:2	9.7 ± 0.2	5.1 ± 0.1	9.54	6.00
Methyl linolenate C18:3	0.2 ± 0.1	0.0 ± 0.0	0.19	0.07

3.7 Reactive species generated during reaction

Reactive species were monitored by optical emission spectroscopy (OES) as presented in Fig. 7. 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_α at 656.3 nm. For the case of 20%He and 80% H_2 , the plasma color was visually observed to become brighter/lighter, having a more whitish tone as shown in Fig. 8. The acquired plasma spectrum showed only the presence of H_α species. These results verified that He and H_2 reactive species were indeed generated in the system.

3.8 FTIR analysis

The chemical functional groups were examined by FTIR as shown in Fig. 9. Both FAME and H-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 wave numbers 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 vibration 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 H-FAME, while *trans*- should not be present in FAME, for it was synthesized from edible oil⁴⁰. 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.

3.9 H-FAME properties

FAME and H-FAME properties compared to biodiesel standards were demonstrated in Table 2. 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 H-FAME production. It offered superior performances to a catalytic reaction as presented in the study of Chen et al.²⁰. In the case of using 0.5 wt.% of the Pd/SBA-15 catalyst at 100°C , 0.3 MPa for palm H-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% H-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 8.1, 47.4 and 100%, respectively, increasing the saturated FAME by 16.6%. 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 H-FAME exhibited a lower oxidation rate corresponding to the increase in oxidation stability.

Table 2 Properties FAME and H-FAME compared to biodiesel standards (100 W, 1 mm gap, 80%H₂, room temperature and 5 h)

Properties	FAME	H-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 ⁴¹⁻⁴³

3.10 Preliminary design for large-scale H-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 H₂ gases could also be completely recycled using a simple recirculating pump operating at ambient conditions, with only occasional replenishment of hydrogen gas to account for the consumed hydrogen by the C=C bonds. Thus, the only major expenditures to produce H-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., O₂ 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. ⁴⁴ A similar safety infrastructure to that of conventional catalysis will ensure a safe operation of the DBD plasma hydrogenation system.

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% H₂, 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 hydrogenation of other high-value liquids, as well as for large-scale H-FAME production.

Declarations

Acknowledgments

The authors would like to sincerely acknowledge The Royal Golden Jubilee Ph.D. Scholarship (funding number PHD/0151/2559), Agricultural Research Development Agency (ARDA) and the “Research Chair Grant” of National Science and Technology Development Agency (NSTDA) for supporting the study.

Conflict of interest

The authors declare no conflict of interest.

References

1. Corro, G. *et al.* Biodiesel and fossil-fuel diesel soot oxidation activities of Ag/CeO₂ catalyst. *Fuel* **250**, 17-26, doi:<https://doi.org/10.1016/j.fuel.2019.03.043> (2019).
2. Veera Raghavulu, K. *et al.* Effect on performance and emission of canola oil and snake gourd oil biodiesel blended in fossil Diesel-Biodiesel blend. *Materials Today: Proceedings*, doi:<https://doi.org/10.1016/j.matpr.2020.06.338> (2020).
3. Rajalingam, A., S P, J., Kumar, A. & Khan, M. A. Production methods of biodiesel. **8**, 170-173 (2016).
4. Patel, N. K. & Shah, S. N. in *Food, Energy, and Water* (ed Satinder Ahuja) 277-307 (Elsevier, 2015).
5. Wongsawaeng, D. *et al.* Simple and effective technology for sustainable biodiesel production using high-power household fruit blender. *Journal of Cleaner Production* **237**, 117842, doi:<https://doi.org/10.1016/j.jclepro.2019.117842> (2019).
6. Karki, S., Sanjel, N., Poudel, J., Choi, J. & Oh, S. Supercritical Transesterification of Waste Vegetable Oil: Characteristic Comparison of Ethanol and Methanol as Solvents. *Applied Sciences* **7**, 632, doi:10.3390/app7060632 (2017).
7. Energy, U. S. D. o. *Biodiesel Blends*, <https://afdc.energy.gov/fuels/biodiesel_blends.html> (
8. Sia, C. B., Kansedo, J., Tan, Y. H. & Lee, K. T. Evaluation on biodiesel cold flow properties, oxidative stability and enhancement strategies: A review. *Biocatalysis and Agricultural Biotechnology* **24**, 101514, doi:<https://doi.org/10.1016/j.bcab.2020.101514> (2020).
9. Tomić, M., Đurišić-Mladenović, N., Mičić, R., Simikić, M. & Savin, L. Effects of accelerated oxidation on the selected fuel properties and composition of biodiesel. *Fuel* **235**, 269-276, doi:<https://doi.org/10.1016/j.fuel.2018.07.123> (2019).
10. Kumar, S., Yadav, K. & Dwivedi, G. Impact analysis of Oxidation Stability for Biodiesel & its Blends. *Materials Today: Proceedings* **5**, 19255-19261, doi:<https://doi.org/10.1016/j.matpr.2018.06.283> (2018).
11. Pullen, J. & Saeed, K. An overview of biodiesel oxidation stability. *Renewable and Sustainable Energy Reviews* **16**, 5924-5950, doi:<https://doi.org/10.1016/j.rser.2012.06.024> (2012).
12. Knothe, G. Some aspects of biodiesel oxidative stability. *Fuel Processing Technology* **88**, 669-677, doi:<https://doi.org/10.1016/j.fuproc.2007.01.005> (2007).
13. Yaakob, Z., Narayanan, B. N., Padikkaparambil, S., Unni K, S. & Akbar P, M. A review on the oxidation stability of biodiesel. *Renewable and Sustainable Energy Reviews* **35**, 136-153, doi:<https://doi.org/10.1016/j.rser.2014.03.055> (2014).
14. Adu-Mensah, D., Mei, D., Zuo, L., Zhang, Q. & Wang, J. A review on partial hydrogenation of biodiesel and its influence on fuel properties. *Fuel* **251**, 660-668, doi:<https://doi.org/10.1016/j.fuel.2019.04.036> (2019).
15. Höfker, U. & Fels, G. *Hydrogenation of Alkenes*, <http://www.chemgapedia.de/vsengine/vlu/vsc/en/ch/12/oc/vlu_organik/alkene/hydrierung.vlu/Page/vsc/en/ch/12/oc/alkene/hydrierungen/hydrierung> (
16. Oguma, S. M. & Chollacoop, N. *Biodiesel Fuel Quality*. 27-62 (2010).
17. Thunyaratchatanon, C., Luengnaruemitchai, A., Chollacoop, N. & Yoshimura, Y. Catalytic upgrading of soybean oil methyl esters by partial hydrogenation using Pd catalysts. *Fuel* **163**, 8-16, doi:<https://doi.org/10.1016/j.fuel.2015.09.026> (2016).
18. Thunyaratchatanon, C. *et al.* Influence of Mg modifier on cis-trans selectivity in partial hydrogenation of biodiesel using different metal types. *Applied Catalysis A: General* **520**, 170-177, doi:<https://doi.org/10.1016/j.apcata.2016.04.019> (2016).
19. Thunyaratchatanon, C. *et al.* Influence of Alkaline and Alkaline Earth Metal Promoters on the Catalytic Performance of Pd–M/SiO₂ (M = Na, Ca, or Ba) Catalysts in the Partial Hydrogenation of Soybean Oil-Derived Biodiesel for Oxidative Stability Improvement. *Energy & Fuels* **32**, 9744-9755, doi:10.1021/acs.energyfuels.8b01498 (2018).
20. Chen, S.-Y. *et al.* Upgrading of palm biodiesel fuel over supported palladium catalysts. *Comptes Rendus Chimie* **19**, 1166-1173, doi:<https://doi.org/10.1016/j.crci.2015.12.005> (2016).
21. Ramayeni, E., Susanto, B. & Pratama, D. Palm H-FAME Production through Partially Hydrogenation using Nickel/Carbon Catalyst to Increase Oxidation Stability. *MATEC Web of Conferences* **156**, 03004, doi:10.1051/mateconf/201815603004 (2018).
22. Hao, H., Lian, P., Gong, J. & Gao, R. Theoretical Study on the Hydrogenation Mechanisms of Model Compounds of Heavy Oil in a Plasma-Driven Catalytic System. *Catalysts* **8**, 381, doi:10.3390/catal8090381 (2018).
23. Li, J. *et al.* A Review of Recent Advances of Dielectric Barrier Discharge Plasma in Catalysis. *Nanomaterials (Basel)* **9**, 1428, doi:10.3390/nano9101428 (2019).
24. Xie, Q. *et al.* Hydrogenation of plasma-excited nitrogen over an alumina catalyst for ammonia synthesis. *international journal of hydrogen energy* **43**, 14885-14891 (2018).
25. Wang, L., Yi, Y., Guo, H. & Tu, X. Atmospheric Pressure and Room Temperature Synthesis of Methanol through Plasma-Catalytic Hydrogenation of CO₂. *ACS Catalysis* **8**, 90-100 (2018).
26. Jwa, E. J., Moka, Y. S. & Lee, S. B. Conversion of carbon oxides into methane in a nonthermal plasma-catalytic reactor *Eur. Phys. J. Appl. Phys.* **56** (2011).
27. Hao, H. *et al.* Non-thermal plasma enhanced heavy oil upgrading. *Fuel* **149**, 162-173, doi:<https://doi.org/10.1016/j.fuel.2014.08.043> (2015).
28. Yepez, X. V. & Keener, K. M. High-voltage Atmospheric Cold Plasma (HVACP) hydrogenation of soybean oil without trans-fatty acids. *Innovative Food Science and Emerging Technologies* **38**, 160-174 (2016).
29. Puprasita, K., Wongsawaeng, D., Ngaosuwanb, K., Kiatkittipongc, W. & Suttichai Assabumrungratd, e. Non-thermal dielectric barrier discharge plasma hydrogenation for production of margarine with low trans-fatty acid formation. *Innovative Food Science and Emerging Technologies* (2020).

30. Kongprawes, G. *et al.* Improvement of oxidation stability of fatty acid methyl esters derived from soybean oil via partial hydrogenation using dielectric barrier discharge plasma. *International Journal of Energy Research*, 1-15, doi:10.1002/er.6121 (2020).
31. V. U. z. F. v. O.-u. P. e. UFOP Report on Global Market Supply 2019/2020: European and world demand for biomass for the purpose of biofuel production in relation to supply in the food and feedstuff markets., 1-53 (Berlin, 2020).
32. EN14103, *Fat and oil derivatives - Fatty Acid Methyl Esters (FAME) - Determination of ester and linolenic acid methyl ester contents.* (2003).
33. D1959-97, A. Standard Test Method for Iodine Value of Drying Oils and Fatty Acids (Withdrawn 2006). *ASTM International, West Conshohocken, PA, 1997.*
34. Standard, N. Automotive fuels -Fattyacid methylester (FAME) fuelandblends withdiesel fuel - Determination of oxidationstability by acceleratedoxidation method. (2014).
35. D2500-17a, A. Standard Test Method for Cloud Point of Petroleum Products and Liquid Fuels. *ASTM International, West Conshohocken, PA, 2017.*
36. Rodrigues, F., Pascoa, J. & Trancossi, M. Heat generation mechanisms of DBD plasma actuators. *Experimental Thermal and Fluid Science* **90**, 55-65, doi:<https://doi.org/10.1016/j.expthermflusci.2017.09.005> (2018).
37. Zigon, J., Petrič, M. & Dahle, S. Dielectric barrier discharge (DBD) plasma pretreatment of lignocellulosic materials in air at atmospheric pressure for their improved wettability: A literature review. *Holzforschung* **72**, doi:10.1515/hf-2017-0207 (2018).
38. Tsuji, T. *et al.* Hydrogen solubility in triolein, and propane solubility in oleic acid for second generation BDF synthesis by use of hydrodeoxygenation reaction. *Fluid Phase Equilibria* **362**, 383-388, doi:<https://doi.org/10.1016/j.fluid.2013.11.006> (2014).
39. Wu, J., Ning, H., Ma, L. & Ren, W. Accurate prediction of bond dissociation energies of large n-alkanes using ONIOM-CCSD(T)/CBS methods. *Chemical Physics Letters* **699**, 139-145, doi:<https://doi.org/10.1016/j.cplett.2018.03.041> (2018).
40. Thunyaratchanon, C., Luengnaruemitchai, A., Chollacoop, N., Chen, S.-Y. & Yoshimura, Y. Catalytic hydrogenation of soybean oil-derived fatty acid methyl esters over Pd supported on Zr-SBA-15 with various Zr loading levels for enhanced oxidative stability. *Fuel Processing Technology* **179**, 422-435, doi:<https://doi.org/10.1016/j.fuproc.2018.07.014> (2018).
41. Barabás, I. & Todoru, I.-A. Biodiesel Quality, Standards and Properties. (Technical University of Cluj-Napoca, Romania 2011).
42. Ibrahim, M. L., Rashid, U., Yunus, R. & Taufiq-Yap, Y. H. ChemInform Abstract: Carbohydrate-Derived Solid Acid Catalysts for Biodiesel Production from Low-Cost Feedstocks: A Review. *Catalysis Reviews* **56**, doi:10.1080/01614940.2014.891842 (2014).
43. Yoshimura, Y. & Chollacoop, N. Introduction of H-FAME Technology for Thai B10 Program. (Advance Industrial Science and Technology(AIST), Japan; Japan International Cooperation Agency (JICA); National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency (NSTDA) ,Thailand, NSTDA, Thailand, 2017).
44. Schroeder, V. & Holtappels, K. in *International Conference on Hydrogen Safety* (Germany, 2005).

Figures

Figure 1

Figure 2

Effect of input power on FAME composition changes (1 mm gap and 25%H2 at room temperature for 1 h)

Figure 3

Effect of gas-filled gap on FAME composition changes (100 W and 25%H2 at room temperature for 1 h)

Figure 4

Effect of H₂ concentration on FAME composition changes (100 W and 1 mm gap at room temperature for 1 h)

Figure 5

Effect of reaction temperature on FAME composition changes (100 W, 1 mm gap and 80%H₂ for 1 h)

Figure 6

Effect of reaction time on FAME composition changes (100 W, 1 mm gap and 80%H₂ at room temperature)

Figure 7

Optical emission spectra of He and H₂ plasma (100 W and 1 mm gap at room temperature)

Figure 8

Plasma color under different mixed gas concentrations (100 W and 1 mm gap at room temperature)

Figure 9

FTIR spectra of FAME and H-FAME (100 W, 1 mm gap and 80%H₂ at room temperature)