DEVELOPMENT OF NICKEL-DOPED PYROLYSED METAL-ORGANIC FRAMEWORK (MIL-101) CATALYSTS FOR FATTY ACID DEOXYGENATION REACTION

By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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The deoxygenation (DO) reaction is the fundamental step in producing high-quality green diesel, wherein the catalyst plays a pivotal role in this process. However, several challenges are still associated with catalysts employed for DO to produce green diesel. Firstly, the issue of active metal leaching significantly hampers both catalytic activity and its efficiency. Secondly, coke formation on the catalyst during DO reactions leads to catalyst deactivation. MIL-101-Cr is one of the most well-studied chromium-based metal-organic frameworks (MOF) comprising metal chromium ion and terephthalic acid ligands. It has a high specific surface area and a well-ordered tunable porous system. Therefore, MIL-101-Cr catalysts can enhance interaction with an active metal dopant, thereby preventing metal from leaching in the DO process. Additionally, the abundant acid-base sites of MIL-101-Cr catalysts can effectively avoid unexpected coke formation and improve the stability of catalysts.

In this study, palmitic acid (PA) was employed as the model compound to produce

green diesel through hydrodeoxygenation (HDO) using nickel-doped pyrolyzed MIL-101-Cr (Ni/P-MIL-101) catalysts. The preparation was started with pristine MIL-101 synthesis (MIL-101) via the solvothermal method, followed by Ni doping via the wet impregnation method. Then, the obtained catalyst precursors were pyrolyzed to produce pyrolyzed MIL-101 (P-MIL-101) and 4-25 wt% Ni/P-MIL-101.The HDO reaction optimization was performed using P-MIL-101 catalysts with different Ni loading. The results demonstrated that 100% conversion of PA and hydrocarbon selectivity were achieved by Ni loading > 8 wt.% on P-MIL-101 catalysts. Furthermore, the Ni/P-MIL-101 catalyst exhibited excellent stability and reusability in the PA HDO reaction. Notably, 14 wt.% Ni-doped P-MIL-101 catalysts could recycle up to 15 times, respectively, without losing their catalytic activity, and nearly 100% alkane yield was achieved, contributing to its most acidic sites and minimal metal leaching. The respond surface method (RSM) analysis showed that the highest green diesel yield could reach up to 94.4% in palm fatty acid distillate (PFAD) HDO reaction under the optimized conditions of temperature of 385 °C, reaction time of 119 min, H_2 pressure of 3 MPa and 4.5 wt.% catalyst loading. The property testing of produced green diesel also confirmed that it fully complied with ASTM D6751 and European EN14214 international biodiesel standards.

In the second part of the research, the DO reaction of PFAD was investigated under an N_2 atmosphere using a P-MIL-101 catalyst with different Ni loading. The PFAD DO reaction was optimized in the range of reaction temperature (280~360 °C), reaction time (1~5 h), and catalyst loading (1~7 wt.%). The results demonstrated that 14 wt.% Ni/P-MIL-101 catalyst exhibited superior catalytic activity in converting PFAD into paraffin hydrocarbons. The highest hydrocarbon yield (93%) and selectivity of n-(C_{15}+C_{17}) (91%) were achieved at 320 °C, 4 h and 3 wt.% catalyst loading. High DO

activity was attributed to acidity, specific surface area, and pore size of the catalyst, and decarbonylation was the main pathway in the PFAD DO process. Furthermore, our findings also indicated that the 14 wt.% Ni/P-MIL-101 catalyst exhibited excellent reusability and regeneration ability due to its most acidic sites and minimal metal leaching, which makes it an ideal candidate for the production of green diesel.

Keywords: Deoxygenation, Nickel, Fatty acids, Green diesel, MIL-101

SDG: GOAL 7: Affordable and Clean Energy

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijaza Doktor Falsafah

PEMBANGUNAN MANGKIN NIKEL-DIDOPKAN KERANGKA ORGANOLOGAM LOGAM (MIL-101) YANG DIPIROLISIS UNTUK TINDAK BALAS PENYAHOKSIGENAN ASID LEMAK

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Tindak balas penyahoksigenan (DO) ialah langkah asas dalam penghasilan diesel hijau berkualiti tinggi, di mana mangkin memainkan peranan penting dalam proses ini. Walau bagaimanapun, masih terdapat beberapa cabaran yang berkaitan dengan mangkin yang digunakan dalam tindak balas DO untuk menghasilkan diesel hijau. Pertama, isu larut lesap logam aktif dengan ketara menghalang aktiviti mangkin dan kecekapannya. Kedua, pembentukan karbon pada mangkin semasa tindak balas DO membawa kepada penyahaktifan mangkin. MIL-101-Cr ialah salah satu rangka kerja logam-organik berasaskan kromium (MOF) yang paling dikaji dengan baik yang terdiri daripada ligan kromium logam dan asid tereftalat. Ia mempunyai luas permukaan spesifik yang tinggi dan sistem berliang yang boleh ditala dengan baik. Oleh itu, mangkin MIL-101 boleh digunakan untuk meningkatkan interaksi dengan dopan logam aktif, serta dengan itu menghalang larut lesap logam dalam proses DO. Selain itu, kewujudan tapak asid-bes yang banyak pada mangkin MIL-101 dengan berkesan boleh mengelakkan pembentukan karbon yang tidak dijangka dan

meningkatkan kestabilan mangkin.

Dalam kajian ini, asid palmitik (PA) digunakan sebagai sebatian model untuk menghasilkan diesel hijau melalui hidropenyahoksigenan (HDO) menggunakan mangkin MIL-101-Cr (Ni/P-MIL-101) yang didop deyu nikel. Penyediaan dimulakan dengan sintesis MIL-101 murni (MIL-101) melalui kaedah solvoterma seterusnya diikuti denga tambahan Ni melalui kaedah impregnasi basah. Kemudian, prekursor mangkin yang diperolehi dipirolisis untuk menghasilkan pirolisis MIL-101 (P-MIL-101) dan 4-25 wt% Ni/P-MIL-101. Pengoptimuman tindak balas HDO telah dilakukan menggunakan pemangkin P-MIL-101 dengan pemuatan Ni yang berbeza. Keputusan menunjukkan bahawa 100% penukaran PA dan selektiviti hidrokarbon dicapai dengan kuantiti Ni > 8 wt.% pada mangkin P-MIL-101. Tambahan pula, mangkin Ni/P-MIL-101 mempamerkan kestabilan dan kebolehgunaan semula yang sangat baik dalam tindak balas PA HDO. Terutamanya, mangkin 14 wt.% Ni/ P-MIL-101 mampu kitaran semula sehingga 15 kali, tanpa kehilangan aktiviti mangkin dan hampir 100% hasil alkana telah dicapai, menyumbang kepada tapak yang paling berasid dan larut lesap logam yang minimum. Analisis kaedah permukaan tindak balas (RSM) menunjukkan bahawa hasil diesel hijau tertinggi boleh mencapai sehingga 94.4% dalam tindak balas HDO sulingan asid lemak kelapa sawit (PFAD) di bawah keadaan optimum suhu 385 °C, masa tindak balas 119 min, tekanan H_2 (3 MPa) dan muatan mangkin sebanyak 4.5 wt.%. Selain itu, ujian sifat bagi diesel hijau yang dihasilkan mengesahkan bahawa ia mematuhi sepenuhnya piawaian biodiesel antarabangsa ASTM D6751 dan EN14214 Eropah.

Dalam bahagian kedua penyelidikan ini, tindak balas DO PFAD telah diselidik di bawah atmosfera N_2 menggunakan mangkin P-MIL-101 dengan pemuatan Ni yang

berbeza. Tindak balas PFAD DO telah dioptimumkan dalam julat suhu (280~360 °C), masa tindak balas (1~5 jam) dan muatan mangkin (1~7 wt%). Keputusan menunjukkan bahawa mangkin 14 wt.% Ni/P-MIL-101 mempamerkan aktiviti pemangkin yang unggul dalam menukar PFAD kepada hidrokarbon parafin. Hasil hidrokarbon tertinggi (93%) dan selektiviti n-(C_{15}+C_{17}) (91%) dicapai pada 320 °C, 4 jam dan 3 wt.% pemuatan mangkin. Aktiviti penyahoksigenan yang tinggi dikaitkan dengan keasidan, luas permukaan tertentu, saiz liang mangkin, dan penyahkarbonilasi adalah laluan utama dalam proses PFAD DO. Tambahan pula, penemuan kami juga menunjukkan bahawa mangkin 14 wt.% Ni/P-MIL-101 mempamerkan kebolehgunaan semula dan penjanaan semula yang sangat baik kerana tapak yang paling berasid dan larut lesap logam yang minimum, yang menjadikannya calon yang sesuai untuk pengeluaran diesel hijau.

Kata Kunci: Penyahoksigenan, Nikel, Asid lemak, Diesel hijau, MIL-101

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Date: 7 November 2024

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LIST OF ABBREVIATIONS

AAS	Absorption spectroscopy
AC	Activated carbon
ANOVA	Analysis of variance
AOAC	Association of Official Agricultural Chemists
BET	Brunauer -Emmet-Teller
C_{15}	Pentadecane
C_{16}	Hexadecane
C_{8-14}	Cracking hydrocarbons
C-Cr_2O_3	Commercial Cr_2O_3
C.V.	Coefficient of variation
DCN	Decarbonylation
DCX	Decarboxylation
DO	Deoxygenation
FAME	Fatty acid methyl ester
FE-SEM	Field emission scanning electron microscope
FFA	Free fatty acids
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
HDO	Hydrodeoxygenation
HPA	Heteropoly acid
HR-TEM	High-resolution transmission electron microscopy
ICP-OES	Inductively coupled plasma atomic emission spectroscopy
MOFs	Metal-organic frameworks

Mtoe	Million tons of oil equivalent
Ni_3C	Nickel carbide
PA	Palmitic acid
PFAD	Palm fatty acid distillate
PKO	Palm kernel oil
RSM-CCD	Central composite design response surface methodology
SUB	Secondary building units
TGA	Thermogravimetric analysis
TPD	Temperature programmed desorption
WCO	Waste cooking oil
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
2FI	Two-factor interaction

CHAPTER 1

INTRODUCTION

1.1 Research Background

Energy is the most important material basis for human survival and social development (United Nations Development Programme, 2000). With the rapid development of the economy and the continuous growth of population from 2017 to 2020, global energy consumption continued to grow at an average rate of 2.3% per year, and the total world energy consumption in 2020 reached 9234.0 Mtoe (Sueyoshi et al., 2022). With the development of new energy technology and the enhancement of human awareness of environmental protection, the way energy is utilized and energy structures are constantly updated. Since the modern industrial society, the global energy consumption structure has undergone three major changes (Smil, 2019). The first one was the transition from traditional lignocellulosic biomass to coal-dominated energy structure after the British Industrial Revolution in the middle and late 18th century; The second was the addition of oil and gas to the energy mix at the beginning of the 20th century, and by the 1970s, the share of oil in global energy had reached 50%.

Fossil fuel is a non-renewable resource; it is difficult to regenerate in a short time; the rapid growth of the global population and the rapid economic development of the demand for energy put forward unprecedented challenges. It is predicted that the world's oil resources are likely to be exhausted by 2050 (Jagger, 2011). At the same time, due to the relatively high content of S and N in fossil fuels, the combustion process will produce a large amount of CO_2 greenhouse gases, bringing a series of environmental problems, such as atmospheric pollution, the formation of acid rain, the

destruction of the ozone layer and global warming (Goyal et al., 2008). Therefore, the development of green, renewable new energy is imminent.

So far, much renewable energy has been developed, including solar energy, wind energy, geothermal energy, ocean energy, fuel cells, and biomass energy, among which solar energy, wind energy, and geothermal energy utilization technology have been very mature and industrialized applications. However, in addition to biomass energy, other renewable energy sources are based on electrical energy as the main form of storage. Biomass energy is the only renewable energy source that can be converted to liquid fuel and stored as chemical energy. In the current proportion of global energy consumption, the transportation sector consumes the highest proportion of energy (Demirbas, 2007). Although some countries are actively promoting the replacement of liquid fuel vehicles with electric vehicles, the current slow charging speed of electric vehicles, low penetration rate of charging piles, and battery safety issues have been limiting the development of electric vehicles. Therefore, the use of biomass to prepare liquid fuel has a very broad development space.

Biodiesel, as one of the main components of bio-liquid fuel, has been developed for 86 years since its concept was first proposed in 1937. At present, its concept is well-known and widely accepted by the public. At the same time, its annual world production has increased from 4025 kg in 1937 to about 6 billion tons at present, thus becoming one of the important choices to replace traditional fossil fuels (Akram et al., 2022). With the continuous improvement of environmental awareness in various countries and the strengthening of restrictions on fossil fuels, the biodiesel market will usher in a broader space for development. At present, the various raw oil materials that can be used for biodiesel production have been explored, including plant oil, animal

oil, microbial oil, algal oil, and waste oil. The manufacturing of biofuels starts with obtaining a renewable feedstock (like animal fats, vegetable oils, and lignocellulose) produced from ecosphere carbon stocks (Pattanaik and Misra, 2017a). This sets them apart from fossil fuels, which are confined to the lithosphere.

Biodiesel includes fatty acid methyl ester (FAMEs), the first-generation biodiesel synthesized by transesterification reaction, and advanced aliphatic hydrocarbon (green diesel), the second-generation biodiesel synthesized by deoxygenation reaction, which has the advantages of renewable raw materials, can be used in existing compression combustion engines, easy transportation and storage, superior combustion performance, and no sulfur or aromatic emissions (Sarno and Iuliano, 2019). The first generation of biodiesel is the transesterification product of glycerol and methanol. Studies in the past 20 years have shown that FAME biodiesel has also been associated with some problems, such as the engine power being slightly lower than petrochemical diesel, the oxidation stability of high-unsaturated biodiesel being poor, the cetane number being low, meanwhile, the high saturation biodiesel has a high freezing point, which is easy to block oil pipelines, thus limiting the use of saturated biodiesel at low temperatures. The second-generation biodiesel uses a deep hydrogenation process to convert the oil and its derivatives into advanced aliphatic hydrocarbon liquid fuel, also known as green diesel, by removing the oxygen-containing part of the oil molecules. Its main component is liquid aliphatic hydrocarbon, whose molecular composition, structure, and performance are closer to that of petrochemical diesel, which can be directly applied to existing diesel engines, with high cetane number and greatly improved power, and has become a hot spot in the current international biomass resource conversion research.

The deoxygenation reaction is the most important reaction in the synthesis of green diesel, and it is generally divided into hydrodeoxygenation reaction, decarboxylation reaction, and decarbonylation reaction. In general, the deoxygenation reaction can be carried out without a catalyst or in the presence of a catalyst. Under the condition of no catalyst, relying only on high temperature and pressure, the deoxygenation rate of grease is very slow and accompanied by many thermal cracking reactions. To solve these problems, catalysts such as homogeneous, heterogeneous, or enzyme are added to the reaction system to improve the deoxygenation reaction rate and the yield of green diesel. Compared with homogeneous catalysts, heterogeneous catalysts have many advantages, such as being easy to carry and store, having a long life, and having low production costs. Therefore, it would be beneficial to develop an efficient heterogeneous catalyst to produce green diesel.

Traditional supported metal sulfide catalysts are usually W or Mo as the main component, Ni or Co as the auxiliary agent, and Al_2O_3, SiO_2, or Al_2O_3-SiO_2 as the supports (Hongloi et al., 2022). Previous studies have shown that these catalysts could produce better alkane yield. However, these heterogeneous catalysts also face some shortcomings. On the one hand, their pore sizes are too small, which reduces the mass transfer efficiency of the catalyst. On the other hand, the formation of macromolecular substances during the reaction process could block the pores of the catalyst easily, and result in deactivation of the catalyst. These problems affect the catalytic activity and selectivity of the entire HDO process. Therefore, developing novel catalyst systems using advanced materials such as metal-organic frameworks (MOFs) will be an interesting feature of enabling highly reliable and efficient catalysts for biofuel production through the HDO process.

MOF is a two-dimensional or three-dimensional porous crystal material composed of metal clusters or metal ions and organic ligands (Jamil et al., 2020). Compared with traditional porous materials, MOF has the following advantages including their rich topology, very high specific surface area, and adjustable porosity. The preparation of raw materials is easy, and it is also convenient to modify their physical and chemical properties by varying the parameters of synthetic materials, solvents, pH, reaction temperature, and so on (He et al., 2021). The fusion of rigidity and flexibility of MOFs derived from secondary building units (SBU) and organic linkers has led to many applications for the material, including gas storage, gas adsorption-separation, luminescent materials, sensors, and, most notably, as heterogeneous catalysts. Because of its uniform structure and adjustable pore system, MOFs are considered to be suitable materials for catalyst development for highly selective biofuel production (Ma et al., 2021). In addition, MOF can also be used as a promising catalyst carrier due to its high surface area and ability to promote good dispersion with strong doping surfaces. In addition, its own inherent Lewis acidity and the portion from the connectome allow for the insertion of acidic or alkaline groups into the MOF structure for ideal modification. Therefore, MOF-derived catalysts have great potential in improving the catalytic activity and selectivity of HDO reactions.

As a chromium-based MOF material, MIL-101 is a potential precursor for high-temperature treatment. It is known for its high surface area and large pore volume. It consists of chromium-based clusters linked by terephthalic acid, forming a porous crystalline octahedral structure (Fig.1) (Ertas et al., 2016). Thermal treatment leads to in situ conversion of the ordered metal center in MOF to metal oxide particles, while a significant number of ligands are thermally decomposed to form porous carbon. The porous structure facilitates high metal particle dispersion through charge transfer and

mechanical interaction, thereby preventing the aggregation of metal oxide particles (Chang et al., 2024). Researchers have reported that the strong interaction between metal nickel nanoparticles (NPs) and MIL-101 enables effective DO with higher thermal stability compared with traditional Ni-supported catalysts(Chen et al., 2019; Chen et al., 2018).

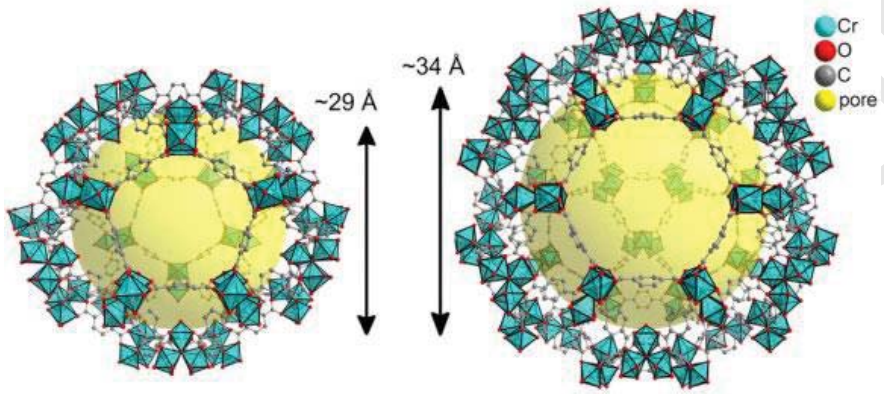

Figure 1.1: The composition and structure of MIL-101-Cr catalyst
(Source: Ertas et al., 2016)

1.2 Problem Statement/Hypothesis

The choice of catalyst plays an important role in the hydrodeoxygenation reaction. In biofuel synthesis, platinum, and palladium metal-based catalysts are found to be effective, particularly for green diesel production, via hydrodeoxygenation reactions of various bio-feedstocks. However, the potential for large-scale applications of these catalysts is limited by their rarity and expensive cost. Meanwhile, sulfide-based catalysts can have environmental impacts, while phosphates and nitrates require extensive and complex preparation methods, which are time-consuming and expensive. Therefore, exploring transition metal-based catalysts, known for their affordability and sulfur-free composition, emerges as the preferable option for efficient catalyst development. Furthermore, due to the inadequate support of the traditional

catalyst, severe active metal dopant leaching occurs during the catalytic reaction process; this not only reduces the catalyst activity but also increases the metal concentration in the fuel, affecting its overall performance. Simultaneously, the metal dopant on traditional catalysts tends to aggregate and lacks uniform dispersion, resulting in increased coking side reactions that negatively impact catalytic activity and reusability.

The development of a novel catalyst system using advanced materials such as Metal-Organic Frameworks (MOFs) could be a feasible method for achieving a highly reliable and efficient catalyst for biofuel production via the HDO process. With its adjustable porous structure, excellent hydrothermal stability, and unique Lewis acid unsaturated metal ions, MIL-101 is considered one of the most promising MOF materials for biomass catalytic upgrading. MIL-101-Cr has a very high surface area (~4000 m^2/g) and a large pore volume (2.3 cm^3/g), which provides a large amount of active sites for catalytic reactions and shows remarkable catalytic properties in various reactions. In the oxidative dehydrogenation of propane, the TOF of MIL-101 is 0.2 s^{-1}, which is better than the traditional zeolite catalyst. In the hydrogenation process of nitrobenzene, the reaction rate of MIL-101 is similar to that of Pd/C catalyst, and the selectivity to aniline can reach 98%. The addition of active dopants that include Ni into the porous structure of MIL-101 reduces the mobility of particles during the reaction and inhibits aggregation to a certain extent. In addition, the idea of applying pyrolyzed MIL-101 as a support further strengthens the thermal and chemical stability of the synthetic catalyst, thus expanding the possibility of biofuel synthesis using various feedstocks and reaction parameters. In addition, pyrolyzed MIL-101 can also be used as an excellent catalyst carrier for active metal dopants. During the pyrolysis process, MIL-101 nanocrystalline exhibits a strong metal-carrier interaction, thereby

effectively immobilizing metal nanoparticles and impeding their migration, sintering, and aggregation.

1.3 Scope of Research

In this study, palmitic acid was utilized as the model compound along with real biomass feedstock Palm Fatty Acid Distillates (PFAD), a byproduct produced from the palm oil processing mill used as the raw material. Ni-doped pyrolyzed MIL-101-Cr (Ni/P-MIL-101) heterogeneous catalysts were employed to produce green diesel through a deoxygenation reaction. The physical properties of the catalysts were characterized by XRD, TGA, FTIR, surface and porosity analysis, HR-TEM, FE-SEM, and TPD, respectively. The surface properties of the supported catalyst were analyzed using the N_2 adsorption/desorption isotherm. The quantity and strength of catalyst base sites were analyzed using the CO_2-temperature program reduction technique. The number and strength of acidic sites of the catalyst were analyzed by the NH_3-temperature programmed reduction technique. In addition, the structure of the synthesized catalyst was characterized by XRD. The deoxygenation reaction of palmitic acid and PFAD was studied using the prepared catalyst with various Ni loading and optimized reaction parameters such as catalyst/feedstock molar ratio, reaction time, reaction temperature, and hydrogen pressure on green diesel production. The composition of the catalyst was analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) and absorption spectroscopy (AAS), along with the metal leaching detection in the products during reusability studies. The relationship between the number of acid-base sites of the catalyst and the catalytic activity in the deoxygenation reaction was discussed. Furthermore, the optimal amount of Ni loading on P-MIL-101 support for the efficient catalytic activity was investigated while the

reaction parameters were optimized using the response surface analysis (RSM) method. The performance of the developed catalysts in the deoxygenation reaction of both palmitic acid and PFAD was evaluated from the aspects of green diesel yield and catalyst reusability. The composition of green diesel was analyzed by gas chromatography, and the fuel properties of the produced green diesel were characterized according to ASTM D-6751 and European 14214 standards.

1.4 Objectives

The aim of this investigation is to develop an efficient deoxygenation catalyst by integrating active metal Ni into a highly porous MOF material, specifically pyrolyzed MIL-101(P-MIL-101), for the conversion of palm-derived fatty acids into green diesel. The physical and chemical properties of the catalyst and the feasibility of producing green diesel through deoxygenation of (model compound) palmitic acid and (real feedstock) PFAD were also discussed. Various characterization techniques have been performed. To achieve the main objectives, a total of 5 research objectives were targeted as follows:

1. To synthesize Ni/P-MIL-101 catalysts and characterize their physicochemical properties.
2. To investigate the preliminary catalytic HDO activity of Ni/P-MIL-101 catalyst via palmitic acid as the model compound.
3. To optimize the condition of the HDO reaction of palmitic acid to maximize green diesel yield using response surface methodology (RSM) and determine the catalyst reusability and stability.

4. To optimize the condition of the HDO reaction of PFAD to maximize green diesel yield using response surface methodology (RSM) and determine the catalyst reusability and stability.
5. To investigate the feasibility of preparing green diesel by deoxygenation of PFAD in the atmospheric N_2 atmosphere.

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