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Optimization of the Biodiesel Production via Transesterification Reaction of Palm Oil using Response Surface Methodology (RSM): A Review

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Abstract— **The optimization method is vital in chemical synthesis and has been applied in many fields nowadays. Response surface methodology (RSM) is an example of an optimization method that is useful in examining the effects of multiple independent variables. RSM was applied in many studies to optimize the transesterification of biodiesel production from palm oil in the presence of a catalyst. This paper aims to provide an overview of recent catalyzed transesterification trends, as well as the benefits and drawbacks of heterogeneous, homogeneous, and enzyme catalysts in biodiesel production. RSM was used to design the process and statistically analyze the interaction effects of the independent reaction variables. The reaction variables, such as reaction time, reaction temperature, catalyst amount, and the molar ratio of the substrate, were optimized during the process. A statistical model and response surface plots were visualized graphically in the contour plots and three-dimensional figures to explain the interactive effects of variables on a response. In sum, this paper discussed the relationships between the reaction parameters and the production of biodiesel and the optimum conditions for biodiesel production using RSM.**

Keywords— **response surface methodology, transesterification, biodiesel production, homogeneous catalysts, heterogeneous catalysts, and enzyme catalysts.**

I. INTRODUCTION

Biodiesel has drawn a lot of attention and has been a widely used energy source in the world. It has become increasingly important as it can be used as an alternative to fossil fuels like petroleum and coal. The usage of these fossil fuels is threatening the entire globe with environmental consequences such as global warming and ozone depletion. The burning of fossil fuels can contribute to the high level of carbon dioxide, which is the main cause of the greenhouse effect [1]. Fossil fuels are classified as non-renewable energy, which means it is not easily replenished by the environment. In this current world situation, the supply of fossil fuels has become limited and is expected to run out because it takes millions of years to form. Fossil fuels are made from the decomposition of plants and

animals that can be found in the earth's crust, taking millennia to become carbon-rich deposits [2].

Facing this issue, the best way to deal with the problem is to introduce renewable energy sources in the form of biodiesel to replace the use of non-renewable fossil fuels. Biodiesel offers a lot of advantages over fossil fuels, and it has great potential to fulfill the requirements of an alternative energy source. The main advantage of biodiesel is it is produced from renewable sources like waste cooking oils, vegetable oils, and animal fats, which are environmentally friendly and non-toxicity. Biodiesel has high flash points, which makes it less combustible when burning [3]. According to Mat Yasin et al. [4], biodiesel has a great potential to lower CO_2 emissions by up to 78% on a life cycle basis and minimize smoke emissions while producing minimal soot. Due to this matter, it can reduce the environmental impacts by emitting fewer particle emissions that contribute to the greenhouse effect, such as carbon monoxide, hydrocarbons, and carbon dioxide [1].

For biodiesel production, palm oil appears to be the most suitable oil as a feedstock in the synthesis of biodiesel. Generally, the scientific name of palm oil, as stated by Parsons et al. [5], is known as Elaeis guineensis, which is cultivated across Malaysia as its leading agriculture in the world. Since oil palm is a tropical oil palm tree, the cultivation of oil palm is very extensive. The oil palm plantations have been rapidly increasing because of high profitability and productivity, as they can yield up to ten times more oil per hectare compared to other crops [6]. The continuous supply of palm oil makes it less expensive and leads to a low cost of biodiesel production. In addition, palm oil has great properties to offer in biodiesel production, including biodegradability, high heating value, and low content of aromatic and sulphur in its composition [2].

In the industrial sector nowadays, biodiesel is commonly synthesized via a transesterification reaction where the hydroxyl group of the alcohol reacts with the carboxylic group of triglycerides to form esters. The reaction between triglycerides from palm oil and short chains of alcohol such as methanol and ethanol will produce biodiesel and glycerol. Transesterification reaction requires a catalyst to speed up the reaction of biodiesel production. The type of catalysts that are commonly used in the transesterification reaction consists of homogeneous, heterogeneous, and enzymatic catalysts. Homogeneous and heterogeneous catalysts are classified into base and acid catalysts, while enzymatic catalysts are divided into extracellular and intracellular enzymes [7,8].

The optimization method is crucial in the synthesis of biodiesel to produce a high yield of biodiesel under optimum conditions. Response surface methodology (RSM) is an example of an optimization method used nowadays. RSM can be defined as a set of mathematical and statistical techniques that are useful in examining the effects of multiple independent variables [9]. RSM can help to design experiments, construct optimization models, and discover the optimum conditions to achieve desired results. By visualizing a three-dimensional, the overall behavior of the reaction system and the interactions between reaction variables can be explained clearly. Generally, the reaction variables that are usually used in the optimization of the biodiesel yield consist of reaction time, temperature, catalyst amount, and methanol to oil molar ratio [10].

Thus, this paper aims to discuss the application of optimization methods in the transesterification reaction of palm oil in the presence of various types of catalysts to achieve high biodiesel yield. The wide use of an effective optimization method which is RSM, in designing the process and optimizing the reaction condition is explained. This paper also highlighted the method, the type of catalysts and the reaction variables used in biodiesel production based on different studies. The main aim of this review paper is to develop an approach for a better understanding of the relationship between the independent variables and the transesterification reaction of palm oil to the biodiesel yield, as well as analyze the optimum conditions for the high yield of biodiesel production.
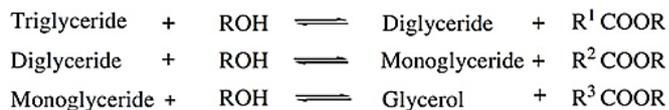
II. FEEDSTOCK FOR BIODIESEL PRODUCTION

Many types of feedstocks can be used for biodiesel production, such as Jatropha curcas, sunflower, rapeseed, soybean, and palm oil [4]. Feedstock selection is a crucial step in biodiesel production as it can affect many factors, including production cost, biodiesel yield, biodiesel composition, and purity of the biodiesel yield. Palm oil has greater potential as a feedstock for the synthesis of biodiesel as it provides a lot of advantages compared to other vegetable oil. According to Basili and Rossi [11], Malaysia is focusing on producing palm oil as a feedstock for biodiesel production since Malaysia is one of the world's leading industries in producing and exporting palm oil. Oil palm plantations produce the largest oil yield per hectare of the plantation, which is up to ten times higher than oil yields from other vegetable oils. The oil palm tree produces the most oil per unit area of farmed land, with an annual yield of 58.431 million metric tonnes (MT). According to the Malaysian Palm Oil Council (2020), palm oil production accounted for 25.8%, and palm oil exportation accounted for 34.3% in 2020. Palm oil is a perennial crop in Malaysia, which means that palm oil production is continuous and uninterrupted even though there are seasonal peaks and down cycles in the annual production. Palm oil is also a profitable oil for biodiesel production due to its compositional characteristics, high productivity at a low cost, whole-year well-distributed production, and lack of competition for feeding purposes with other crops [12].
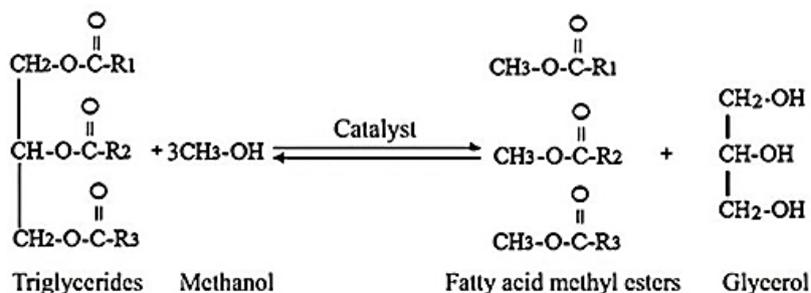
III. TRANSESTERIFICATION REACTION FOR BIODIESEL PRODUCTION

Biodiesel can be produced through several methods, such as pyrolysis, micro emulsification, direct blending, and transesterification. Transesterification is the most widely used method in producing biodiesel compared to the other methods. This is due to its advantages, such as being a cost-effective method and providing high conversion efficiency. The transesterification method also can reduce the oil viscosity, making it capable of replacing petroleum diesel [3]. This method is known as alcoholysis, where an alcohol group of an ester compound is exchanged with another alcohol. The process involves the reaction of fats or oils with low molecular weight alcohol such as methanol and ethanol under the presence of a catalyst. It is a reversible reaction that requires one mol of triglyceride and three moles of alcohol. As shown

in Scheme 1, the transesterification reaction starts with the conversion of triglycerides to diglycerides, then the conversion of diglycerides to monoglycerides, and lastly, the conversion of monoglycerides to glycerol. Each step of the reaction produces one alkyl ester molecule per mole of glyceride [13].

Triglyceride	+	ROH	⇌	Diglyceride	+	R^1COOR
Diglyceride	+	ROH	⇌	Monoglyceride	+	R^2COOR
Monoglyceride	+	ROH	⇌	Glycerol	+	R^3COOR

Scheme 1. Transesterification of triglycerides for the biodiesel production

Scheme 2. Transesterification of triglycerides with methanol for fatty acid methyl esters production.

As shown in Scheme 2, the transesterification reaction involves the reaction of a carboxylic group of triglycerides with the hydroxyl group of alcohol to produce fatty acid methyl esters and glycerol in the presence of a catalyst [14].

IV. CATALYSIS IN TRANSESTERIFICATION

A catalyst is required to speed up the transesterification reaction of biodiesel production, where it might be homogeneous, heterogeneous, or enzyme catalysts. Homogeneous and heterogeneous are divided into basic and acidic catalysts. The most used basic catalysts include sodium hydroxide and potassium hydroxide; acidic catalysts include sulfuric acid, hydrochloric acid, and phosphoric acid; and enzyme catalysts include lipases [12]. The selection of catalyst is an important parameter in the synthesis of biodiesel because

it can lower the production cost, where the extra process of purifying the end products can be avoided. Homogeneous catalysts can complete transesterification reactions with higher conversion compared to heterogeneous catalysts, but there is a high risk of soap formation, which is called saponification during the transesterification process. Saponification can affect the difficulty of separating the end products after the completion of biodiesel production. Due to this, enzyme catalysts are preferred to be used as the product purification is easier with low soap formation [13]. Besides, enzyme catalysts also provide an environmental advantage over other catalysts by reducing waste during biodiesel production. However, enzyme catalysts are not extensively used in industrial and large-scale production due to the expensive cost and long reaction time [15]. Figure 1 shows the classification of the type of catalysts used in the transesterification of biodiesel production.
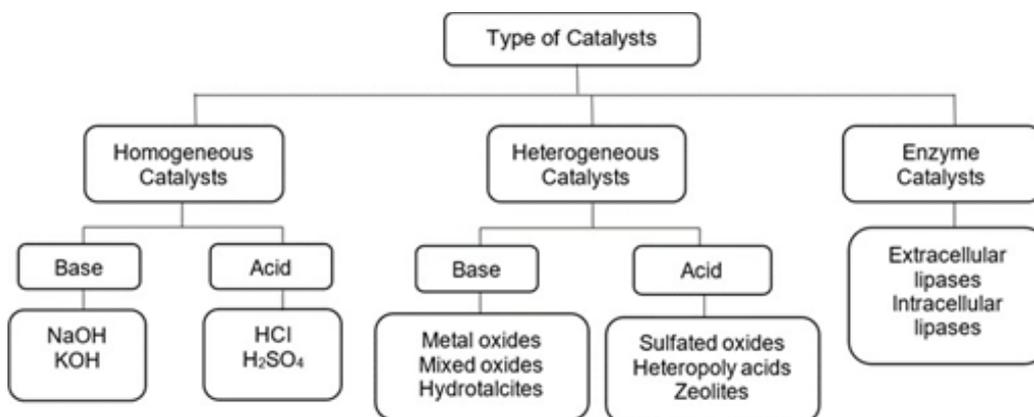

Figure 1. Classification of catalysts used for biodiesel production.

A. Homogeneous catalysts

Homogeneous catalysts are the first conventional method that has been used for transesterification reactions of biodiesel production. Homogeneous catalysts are those that are in the same phase as the reactants and are commonly dissolved in a solvent that is in the same phase as all of the reactants [16]. The catalysts exhibit high catalytic activity in transesterification reactions, where the reaction can occur at low pressure and temperature. The reaction using homogeneous catalysts is simple since it takes less time to complete the reaction [17]. However, the catalysts are difficult to recycle as the catalysts will dissolve in the intermediate reagent during the transesterification reaction. Besides, biodiesel produced from the use of the catalysts needs to be neutralized after the reaction, and the waste from the neutralization process can cause environmental problems [14].

1) Homogeneous base catalysts

Homogeneous base catalysts refer to alkaline liquids that are categorized into alkali metal-based hydroxides such as potassium hydroxide (KOH) and sodium hydroxide (NaOH), and alkali metal-based oxides such as sodium methoxide (CH3Ona) and potassium methoxide (CH3OK). Alkali metal-based hydroxides are commonly used as catalysts in biodiesel production because they are less expensive than alkali metal-based alkoxides [18]. When methanol is used as a solvent, NaOH catalysts are better than KOH catalysts due to their high solubility in methanol and large production yield. According to De Lima et al. [19], the reaction rate using base catalysts is 4,000 times faster than the reaction rate using acid catalysts. Besides, homogeneous base catalysts are commonly employed in the industrial scale of biodiesel production due to the advantages such as being inexpensive, producing high-quality products in a short time and being economically accessible [20].

However, homogeneous base catalysts have some drawbacks, such as the formation of unwanted side reactions like soap formation when FFA in the feedstock oil cannot be converted into biodiesel completely. According to Mandari & Devarai [20], soap formation will occur when FFA content is higher than 0.5 wt% and water content is higher than 0.06 wt%. The soap formation reduces the selectivity of biodiesel yield, prevents the separation of glycerol and fatty acid alkyl esters, and produces an emulsion during the cleaning process of the product. FFA is formed when a hydrolysis reaction occurs in the presence of a high amount of water content in the feedstock oil at a high temperature, where triglycerides convert to diglycerides and form FFA [13,14]. Another significant disadvantage of this method is the catalyst cannot be recovered and cannot be reused. This method also can cause environmental problems due to the high amount of wastewater produced in the biodiesel purification process [21]. In a recent study by Silva et al. [22], NaOH was used to catalyze the transesterification reaction of palm oil with methanol, producing 93% of biodiesel yield. In the study of Aworanti et al. [23], a biodiesel yield of 90% was produced in the transesterification of waste frying palm oil with methanol using a KOH catalyst.

2) Homogeneous acid catalysts

Homogeneous acid catalysts can be used to overcome the issue of the soap formation caused by homogeneous base catalysts due to the high FFA content in the feedstock oil. Homogeneous acid catalysts are insensitive to FFA content; hence, the catalysts can be effectively used in biodiesel production using any raw materials that contain high FFA, like waste cooking oils, non-edible oils, and animal fats. Examples of catalysts that are less sensitive to FFA content are bronsted acids such as sulfuric acid (H2SO4), sulfonic acid (H2SO3), hydrochloric acid (HCl), and ferric sulfate (Fe2(SO4)3). Among the catalysts, H2SO4 is the most used catalyst because of its favorable reaction conditions at moderate temperatures and atmospheric pressure [20].

Despite its benefits, homogeneous acid catalysts face the same separation difficulties as homogeneous base catalysts. Homogeneous acid catalysts present challenges in the catalyst recovery from the biodiesel and glycerol layers that cause product contamination and the difficulty of the separation process. Furthermore, the cost of biodiesel production using the catalysts is expensive because of the accumulation of extra energy while purifying the products [24]. Homogeneous acid catalysts can produce a high biodiesel yield, but the reaction is slow and requires high energy. Due to this, the application of the catalysts in biodiesel production at an industrial scale is not recommended. In the study of Bhuana et al. [25], H2SO4 was utilized in biodiesel production through in-situ microwave-assisted acid-catalyzed transesterification. In the reaction, microalgae oil was reacted with methanol, producing a 63.36% biodiesel yield. Likewise, in the study of Kim et al. [26], microalgae oil was reacted with methanol through in situ transesterification using HCl as a catalyst, producing 90% of biodiesel yield.

B. Heterogeneous catalysts

Heterogeneous catalysts have been widely used in the synthesis of biodiesel due to their advantages, which have excellent tolerance to the high content of FFA and water in the feedstock oil. It is possible to remove the catalyst at different stages since they are usually in the solid form and exist in a distinct phase from the reaction mixture. Due to this, the recovery of catalysts from the reaction mixture is easier, and it allows the catalysts to be used for multiple cycles [20]. The catalysts' reusability helps to minimize the total cost of biodiesel production and reduce pollution, making the production process cost-effective [27].

1) Heterogeneous base catalysts

Example of heterogeneous base catalysts includes alkaline oxides, alkaline earth metal oxides, transition metal-based, mixed metal-based, and hydrotalcite. Alkaline earth metal oxides are commonly utilized as solid base catalysts due to their inexpensive cost and strong basic strength [8]. Heterogeneous base catalysts can overcome the saponification problem that causes difficulty in separating glycerol from the methyl ester layer when using homogeneous base catalysts.

Heterogeneous base catalysts provide a high yield of products with a faster reaction rate. The ease of recovery and reusability of these catalysts after the reaction reduces the processing cost. Furthermore, these catalysts show some advantages to the environment where they are less corrosive and ease of disposal, making them environmentally friendly [16].

Meanwhile, heterogeneous base catalysts present some drawbacks, including the requirement of high methanol to oil molar ratio and catalyst poisoning when it is exposed to the air. Heterogeneous base catalysts are also sensitive to FFA content which leads to soap formation when FFA content is higher than 2 wt%. There is also a high probability of leaching at the active site, which may cause the contamination of the product [20]. Latchubugata et al. [28] studied that CaO, a metal-based catalyst is a suitable catalyst for biodiesel synthesis due to its long catalyst life, high basic strength, low solubility in methanol, and mild reaction conditions. In the recent study conducted by Qu et al. [14], a calcium-modified Zn-Ce/Al2O3 catalyst was used in biodiesel production through a transesterification reaction of palm oil with methanol. The reusability of the catalyst was analyzed, and the result showed that 87.37% of biodiesel yield is produced during the fifth reused cycle. Besides, Akhabue et al. [29] successfully produced a 96.395% biodiesel yield using a CaO catalyst derived from hen eggshell wastes in the transesterification of palm kernel oil with methanol.

2) Heterogeneous acid catalysts

The most used heterogeneous acid catalysts in biodiesel production consist of mixed oxides, metal oxides, sulfated metal oxides, sulfonated carbon materials, heteropoly acids, cation exchange resins, and zeolites [20]. According to Liu et al. [30], the ideal properties of heterogeneous acid catalysts are having a large pore size, hydrophobic properties, and a high concentration of strong acid sites. Heterogeneous acid catalysts are preferred to be used in biodiesel production compared to homogeneous acid catalysts due to their low corrosive and low toxic effects on the environment. Heterogeneous acid catalysts are insensitive to a high content of FFA and water in the feedstock oils, promoting biodiesel production from low-quality and low-cost feedstocks without the need for an acid pretreatment process [16].

Besides, heterogeneous acid catalysts are considered significant catalysts over homogeneous acid catalysts because of the existence of Bronsted and Lewis acid active sites that can provide necessary catalytic sites for transesterification processes [20]. Hanif et al. [31] reported that heteropoly acids (HPAs) and their salts are effectively used in biodiesel production as solid heterogeneous acid catalysts due to their ease of synthesis and high thermal stability. In the recent study conducted by Mohamed et al. [32], a sulphonated solid acid catalyst (RS-SO3H) was used to catalyze the transesterification reaction of waste cooking oil with methanol, producing a 92.5% biodiesel yield. Besides, Feng et al. [33] have successfully produced 98.4% of biodiesel yield in the transesterification of palm oil and methanol using Brønsted acidic ionic liquids. The reusability of the catalyst was analyzed, and the result indicated that the catalyst was thermally stable and recyclable. Despite all the advantages, heterogeneous acid catalysts show disadvantages in the reaction rate, where the reaction is slower than heterogeneous base catalysts. According to Mansir et al. [34], high temperature, large catalyst amount, and long reaction time are necessary when using heterogeneous acid catalysts.

3) Enzyme catalysts

Enzyme catalysts, also known as biocatalysts, are derived from living creatures that catalyze chemical reactions without causing any chemical changes to themselves [35]. The enzyme catalysts overcome the issue that develops during biodiesel synthesis with the use of basic or acid catalysts. The use of enzyme catalysts in biodiesel synthesis provides a lot of advantages, such as a simple production process, high tolerance of water content, and low energy consumption. In addition, the enzymatic biodiesel synthesis also presents advantages in the production of high yield and purity of biodiesel and glycerol by-products, as well as ease of immobilized enzyme recycling, product separation, and purification. Besides, enzymatic biodiesel synthesis meets the requirements of green chemistry by limiting waste generated during biodiesel production, lowering environmental problems [20,21].

The most used enzyme catalysts in biodiesel production consist of extracellular lipases and intracellular lipases. Extracellular lipases refer to the enzymes that have been purified after being recovered from the microorganism broth, while intracellular lipases are present either in the cell-producing walls or inside the cell. The most common extracellular lipase producers consist of Rhizopus oryzae, Mucor miehei, Candida antarctica, and Pseudomonas cepacia [13]. Most microbial lipases are categorized under extracellular lipase, and they are commonly used due to the easy extraction from the fermentation medium. Enzymatic catalysts such as lipases (triacylglycerol acylhydrolases, EC 3.1.1.3) have been recognized as a viable alternative for transesterification of biodiesel production because of their reusability, non-toxicity, insensitive to FFA, and tolerance to organic solvents [36]. However, the use of lipase in biodiesel production has some drawbacks, such as expensive cost of production, difficulties in downstream recovery and poor alcohol resistance. Hence, the application of immobilized lipases on matrix support can overcome these problems. In the study of Shahedi et al. [15], transesterification of palm oil with methanol was investigated using co-immobilized lipases. Lipase from Rhizomucor miehei and Candida antarctica in co-immobilized form was used to improve biodiesel production, resulting in 78.3% of FAME yield.

V. OPTIMIZATION USING RESPONSE SURFACE METHODOLOGY (RSM)

Optimization can be defined as the process of improving a system's performance to achieve the best possible outcomes. Several variables have an impact on the system's quality and experimental responses. The optimization method has been widely used in analytical chemistry to describe the process of determining the ideal conditions of experiments [37]. Optimization methods have been applied in various fields of study to identify many solutions that can maximize or minimize specific study parameters [38]. Response surface methodology (RSM) is an example of an optimization

technique that has been used nowadays. RSM refers to a set of statistical and mathematical techniques for designing, enhancing, and optimizing experimental processes. It is also useful in the development, formulation, design of new products and enhancement of existing product designs [9]. RSM is a powerful statistical technique for determining the optimum conditions for various complicated processes. It allows the optimization of several variables with a small number of experiments, making it less time-consuming and faster than other optimization techniques. RSM has been discovered to be a better method for determining the effect of multiple variables with less experimental data required, and it can provide the optimal operating conditions for different system responses [22].

A. Steps in RSM

RSM can be implemented in the following four steps:

Step 1: Identification of response variables

The first step in the optimization approach is to select a variable that will provide sufficient information for evaluating the method's analytical performance. This variable is also known as a response. In the optimization process, it is necessary to analyze more than one response at a time. Many variables can be selected as responses in particular studies, and it varies depending on the field of study [39]. In the study of Qu et al. [14], reaction temperature, catalyst amount, and methanol-to-oil molar ratio have been used as variables in the transesterification of palm oil for biodiesel production. Silva et al. [22] and Latchubugata et al. [28] used reaction time, reaction temperature, and methanol to oil molar ratio as variables in biodiesel production through the transesterification of palm oil.

Step 2: Selection of factors and their levels

All potential factors in the process must be properly identified and analyzed. For each factor, the experimental domain must be determined, as well as a method of control and measurement. The factors can be divided into quantitative, qualitative, and mixture-related. Performing screening experiments is required to determine the experimental variables that have significant effects on the responses. The factors are mostly analyzed at two levels (−1,

+1) in screening designs. The range between levels is the widest range where the factor may be varied for the system under investigation, and it is chosen based on literature or previous studies [39].

Step 3: Determination of experimental design

The main step in the optimization method is to select the best experimental design. According to Sahu & Andhare [40], response surface designs are referred to the experimental designs that are used to fit response surfaces and usually have three levels of factors. The example of experimental design for optimization in RSM includes three-level factorial design, Box–Behnken design, (BBD), central composite design, (CCD) and Doehlert design. The selection of experimental points, the number of levels, and the number of runs and blocks vary between these designs. The experimental designs commonly used in RSM are BBD and central composite designs (CCD)

[41]. According to recent studies, CCD has been applied more than BBD in the transesterification of palm oil for biodiesel production. In some studies by Qu et al. [14], Shahedi et al. [15], Akhabue et al. [29], and Mohamad et al. [42], CCD was applied to optimized reaction conditions in the biodiesel production through transesterification reaction of palm oil.

Step 4: Statistical analysis

The data obtained after conducting experiments will be analyzed using optimization software such as Design Expert and Statistica. The main analytical steps that are usually used are analysis of regression, analysis of variance (ANOVA), and response surfaces plotting. The regression model typically predicts the relationship between the dependent and independent variables. The Regression model clearly demonstrates the feasibility of testing the effect of parameters supported by experimental data [28]. The relationships between the independent variables of transesterification reaction and the experimental biodiesel yield are evaluated by the second-order polynomial in Eq. (1). Y refer to the percentage yield of biodiesel, n refers to the number of the independent variables, $\beta 0$ refers to the intercept, βj refer to the linear order coefficient of the model, βjj refer to the quadratic coefficient of the j factor, βij refer to the linear model coefficient for the interaction between the factors, and lastly, i and j, and Xi and Xj refer to the independent variables [14].

$$Y = \beta_0 + \sum_{j=1}^{n} \beta_j X_j + \sum \sum_{i < j} \beta_{ij} X_i X_j + \sum_{j=1}^{n} \beta_{jj} X_j^2 \quad (1)$$

ANOVA is defined as a set of statistical models for analyzing variations in means and associated procedures, such as "variation" within and between groups [39]. According to Aydar [43], ANOVA is used to test the fitness of the model using the experimental data. ANOVA and regression analysis are employed to assess the adequacy of the regression model and optimize the independent parameters of the transesterification reaction. The F-value, p-value, and significance of the "lack of fit" could be used to establish the significance and fitness of the designed model in ANOVA. For a term to be significant, the p-value must be lower than 0.05, and F-value must be higher than 0.05. Besides, the coefficient of determination (R2) is used as the sole confirming value for the model in the regression step. The excellence of the model established by the optimization software is estimated by R2. The model is stated to be better when the R2 value approaches 1 (unity) and predicts values that are closer to the actual [44]. Meanwhile, response surface plots can explain the interaction effects between independent transesterification variables on biodiesel yield by visualizing graphically in the contour plots and three-dimensional figures [40]. The graphical representations aid the researcher in visualizing the correlations between the process variables and product quality characteristics. Response surface plots can provide precise geometrical representation and important information about the system's behavior within the experimental design [9].

B. Uses of RSM

According to Myers et al. [9], there are several uses of RSM, including mapping a response surface over a specific area of interest to study the relationship between the process variables. Besides, RSM can be used to optimize the responses to

determine the optimal conditions in the experimental reaction. An optimum condition for a specific variable can be identified by statistical analysis of RSM. In addition, RSM can also be used to choose operating conditions to meet specifications or specific requirements. Other than that, RSM can identify the factor level that will satisfy the desired specification and illustrates the mutual interactions between factors. According to recent studies, RSM has been widely employed in many research on biodiesel production to optimize the operating parameters in the transesterification reaction. Some studies by Qu et al. [14], Latchubugata et al. [28], Akhabue et al. [29], and Mohamad et al. [42] studied the optimization of the transesterification reaction of palm oil with methanol for the production of biodiesel yield using RSM as an optimization method. From the studies, it is proven that the effectiveness of RSM in the optimization of the transesterification reactions as the biodiesel yield obtained is higher than 90% in the optimum conditions. Table 1 below shows the summary of the applications of RSM in many studies.

Table 1. Summary of the Applications of RSM

No.	Authors	Reaction	Operating parameters	Optimized conditions
1	Qu et al. [14]	Transesterification of palm oil with methanol using Ca-Ce-Zn/Al$_2$O$_3$ catalyst	Temperature, reaction time, catalyst amount, and methanol to oil molar ratio	99.44% of biodiesel yield is achieved at a temperature 66.12–°C, 3 hours of reaction time, 8.19 wt.% of catalyst amount and methanol to oil molar ratio of 18.53
2	Latchubugata et al. [28]	Transesterification of palm oil with methanol using CaO catalyst	Temperature, reaction time, catalyst amount, and methanol to oil molar ratio	93.5% of biodiesel yield has achieved at a temperatureof of 65°C, 4 h of reaction time, 6 wt.% of catalyst and methanol to oil molar ratio of 15:1
3	Akhabue et al. [29]	Transesterification of palm kernel oil with methanol using CaO catalyst	Temperature, reaction time, catalyst amount, and methanol to oil molar ratio	96.395% of biodiesel yield has been achieved at a temperature of 51.4–°C, 135.94 min of reaction time, 3.106 wt.% ofcatalyst and methanol to oil molar ratio of 9.02:1
4	Mohamad et al. [42]	Transesterification of palm oil with methanol using CaO-TiO$_2$ catalyst	Reaction time, catalyst amount,and methanol to oil molar ratio	96.67% of biodiesel yield has been achieved at a temperature 65°C, 145.51 min of reaction time, 2.52 wt.% ofcatalyst and methanol to oil molar ratio of 3:4

C. Interactive effects between independent variables using response surface plots

Response surface methodology was used to investigate the individual and interactive effects of three independent variables, which are reaction temperature, methanol to oil molar ratio, and catalyst amounts on the biodiesel yield. Response surface plots from the study of Qu et al. [14] were used to analyze the interactive effects between the variables.

1) Interactive effects between reaction temperature and methanol to oil molar ratio on the biodiesel yield

In Qu et al. the results showed that the three-dimensional response plot of the interactive effects between reaction temperature and methanol to oil molar ratio on the biodiesel yield at 7.5 wt.% of the catalyst amount [14]. It indicates that the production of biodiesel increases when the reaction temperature rises to around 65°C. The biodiesel yield gradually falls when the reaction temperature rises above the optimum value, as methanol immediately evaporates from the oil phase when the transesterification reaction takes place above the methanol boiling point at around 65°C. The three-dimensional response plots also indicate that the biodiesel yield increase with the increasing methanol to oil molar ratio at around 18.

The reason for the increment of biodiesel yield is due to the excess methanol driving the chemical reaction towards the product, which results in an increase in biodiesel production. When the molar ratio exceeds the optimal value, the biodiesel yield will rapidly decrease, resulting from the dilution of excess methanol to the catalyst concentration per unit volume of the transesterification system. Glycerol solubility is also enhanced by the excess methanol, causing difficulty in the separation process and resulting in low biodiesel production [45].

2) Interactive effects of the reaction temperature and catalyst amount on the biodiesel yield

Qu et al. [14] presented the interactive effects between the reaction temperature and catalyst amount on the biodiesel yield at the methanol to oil molar ratio of 18. The three-dimensional surface plot illustrates that the biodiesel yield initially increases with the increasing reaction temperature but then gradually decreases. This is due to the high temperature causing methanol to evaporate from the oil phase. Conversely, increasing the catalyst amount increases biodiesel production [14]. The trend will be reversed when the catalyst amount is above the optimum value where the undesired saponification occurs,

resulting in the low production of biodiesel. The soap formation that dissolves in glycerol will enhance the solubility of methyl ester, causing the loss of methyl ester during the separation process and lowering the biodiesel yield [46].

3) Interactive effects of the reaction temperature and catalyst amount on the biodiesel yield

In Qu et al. [14] also showed the interactive effects of the methanol to oil molar ratio and catalyst amount on the biodiesel yield at the reaction temperature of 65°C. The three-dimensional surface plot illustrates that the biodiesel yield increases with the increasing methanol to oil molar ratio and catalyst amount [14]. This effect is also observed by Mohamad et al. [42], where the combined effect of the high catalyst amount and high ratio of vegetable palm oil to methanol results in a high biodiesel yield. According to Cai et al. [47], high methanol to oil molar ratio is needed for the reversible transesterification of biodiesel production. Thus, increasing the catalyst amount is not effective in producing a high biodiesel yield when using low methanol to oil molar ratio. However, the use of excess methanol will reduce biodiesel production because it will dilute the catalyst concentration, causing the concentration of active sites per unit volume to decrease. Besides, the excess catalyst amount also decreases biodiesel production due to the saponification reactions.

VI. CONCLUSION

Biodiesel is a renewable and environmentally friendly energy source that appears to be an alternative to fossil fuels. Biodiesel can be produced via the transesterification process of vegetable oil in the presence of a catalyst. Palm oil appears to be the suitable feedstock oil in producing biodiesel due to its versatility and productivity compared to other crops. Various types of catalysts can catalyze the transesterification of biodiesel production, consisting of heterogeneous acid/base, homogeneous acid/base, and enzyme catalysts. The transesterification process can be optimized using RSM as an optimization method. RSM can analyze the interactive effects between operating parameters on the biodiesel yield and determine the optimum conditions for the production of high biodiesel yield. In the present review, the application of RSM in the optimization of biodiesel production from various studies has been discussed. The biodiesel yield obtained under optimum reaction conditions determined by RSM has led to a high yield which is higher than 90%. The interactive effects of the reaction variables, such as reaction temperature, reaction time, catalyst amount, and methanol to oil molar ratio, on the production of biodiesel have been discussed based on the response surface plots. The increasing of methanol to oil molar ratio and catalyst amount leads to a high biodiesel yield. However, the trend will be reversed when the methanol to oil molar ratio and catalyst amount exceed the optimal value and cause the low production of biodiesel. In summary, this review gives an overview of the various types of catalysts that can catalyze the transesterification process, as well as insights into the applications of RSM in recent biodiesel production research.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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