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Study of the Utilization of Spent Bleaching Earth as a Raw Material for the Production of Biodiesel Using the In-Situ Transesterification Process

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Abstract

Spent bleaching earth (SBE) is the primary by-product generated during crude palm oil (CPO) refining. The majority of the SBE is typically discarded in landfills, despite the fact that it still contains approximately 20-40 percent crude oil. The oil present in SBE can be converted into biodiesel using an in-situ transesterification procedure. In the in-situ esterification-transesterification process, the extraction of oil and the reactions of esterification and transesterification take place concurrently on the surface of the SBE in the reactor. The objective of the research was to investigate the impact of reaction temperature and time, NaOH concentration, methanol and hexane to SBE ratio on the generation of biodiesel from SBE through in-situ transesterification. The research findings indicated that the in-situ transesterification process at 65°C for 120 minutes, using a methanol/SBE ratio of 9.0 (v/w) and a NaOH concentration of four percent (w/w), resulted in the greatest biodiesel production of 85.6 percent. The biodiesel consisted of 97.47 percent methyl ester. The findings also indicated that SBE might be utilized as a resource for the manufacturing of biodiesel. By employing SBE as a feedstock for biodiesel, it not only minimizes waste but also enhances biodiesel production without compromising the availability of oil for food consumption.

Keywords: biodiesel, crude palm oil, in-situ, spent bleaching earth, transesterification
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1. Introduction

Before being consumed or processed further, crude palm oil (CPO) undergoes a purification process to remove impurity components. The CPO purification process includes degumming, neutralization, bleaching and deodorization. One of the stages in the CPO refining process is the bleaching process, which aims to absorb colour components, thereby producing vegetable oil that is lighter in colour. At the bleaching stage, bleaching earth was added as much as 0.5-2.0 percent of the weight of CPO which functions as an adsorbent for colour components and other minor components contained in CPO (Haas *et al*., 2004).

After being utilized in the bleaching of CPO, the bleaching earth undergoes a saturation process within its surface pores, rendering it unsuitable for further use. Consequently, it is classified as waste and referred to as spent bleaching earth (SBE). SBE is the primary by-product generated by the plant-based oil refining industry. Annually, over 120 million tons of crude oil undergo processing with bleaching earth, resulting in the production of around 2.5 million tons of SBE (Delgado-Plana *et al*., 2021). Typically, the vegetable oil refining sector disposes of SBE waste on land as landfill without any prior treatment, leading to contamination of soil, water, and air. Multiple researches had been conducted on the utilization of SBE, including its applications in brick production, paving block manufacturing, charcoal briquette production, and as a fertilizer. However, these utilization attempts had determined that SBE contained substantial quantities of unrefined oil, ranging from 20 to 40 percent (Aziz *et al*., 2001; Kheang *et al*., 2006), which was comparable to 0.5 - 1.0 million tons of crude oil. The quantity of residual crude oil is large, and it can be extracted and transformed into products with greater economic value. The crude oil obtained from SBE does not meet the criteria for edible oil due to its high quantities of free fatty acids. However, it can be utilized as a viable feedstock for the production of biodiesel.

Biodiesel is a compound known as a fatty acid methyl ester, which is produced by a chemical process involving the reaction of vegetable oil or animal fat with alcohol. Due to the rising demand for edible oil for human use and its high price, the production of biodiesel from edible oils like coconut oil, palm oil, or other food oils faces challenges. Approximately 60-80 percent of the overall expenses in biodiesel production were allocated to the acquisition of raw materials (Yucel & Terzioglu, 2013). The selection of feedstocks for biodiesel production significantly influences the cost of biodiesel manufacturing. Hence, it is imperative to seek out feedstocks with minimal economic value, such as oil derived from SBE.

Typically, the manufacturing of biodiesel from SBE involves three stages: oil extraction, oil refining, and esterification-transesterification. These steps result in elevated biodiesel production expenses. It is imperative to develop a biodiesel manufacturing procedure using SBE that is highly efficient, conserves energy and resources, and yields biodiesel of superior quality. The processes in question are referred to as in-situ esterification and transesterification processes. The in-situ esterification-transesterification process is a more efficient and economical method for producing biodiesel as it eliminates the need for oil extracting and processing. In-situ esterification-transesterification is a method of producing biodiesel, in which the extraction of oil and the processes of esterification and transesterification take place concurrently on the surface of the SBE in the reactor.

Numerous factors, such as the solvent type and ratio, catalyst type and concentration, reaction temperature and duration, stirring technique and speed, all have an impact on the in-situ esterification-transesterification procedure. The reaction temperature is directly proportional to the amount of heat needed to achieve the activation energy. As the temperature increases, the reactants have a greater amount of energy available to collide with each other and overcome the activation energy. As the temperature increases, the molecules travel faster and have greater kinetic energy. Consequently, the collisions between the reactant molecules also increase (Petrucci *et al.*, 2021). The Arrhenius equation predicted a direct relationship between the operating temperature and the level of conversion. With an increase in temperature, the value of k rose, leading to a faster reaction rate and higher conversion outcomes (Lower, 2021). During the transesterification process, raising the reaction temperature leads to enhanced molecular mobility, resulting in increased collisions between reactant molecules. Additionally, the higher energy levels of the molecules enable them to surpass the activation energy barrier (Kartika & Widyaningsih, 2012; Nawaz *et al.*, 2023). The esterification/transesterification process can be conducted at a temperature range of 30-65°C, which is below the boiling point of the reactant employed (Berrios *et al.*, 2010).

The biodiesel yield can be significantly affected by reaction time. The biodiesel yield reached its maximum value by varying the reaction period, typically ranging from 1 to 24 hours (Samuel & Dairo, 2012). It was observed that a longer reaction time resulted in a higher biodiesel production. Exceeding the optimal reaction time led to a decline in biodiesel output. This was because the reverse reaction and the synthesis of soap during the process could inhibit the biodiesel formation process, resulting in a lower biodiesel yield (Leung & Guo, 2006; Abdulkadir *et al.*, 2014).

Increasing the duration of the reaction leads to a higher yield of biodiesel, since it allows for a greater number of collisions between the reactant molecules. Once equilibrium is established, prolonging the reaction period does not impact the conversion reaction. The in-situ transesterification procedure takes a lengthier duration for the reaction in comparison to the regular process. The in-situ transesterification procedure requires a period of time for the extraction of oil from the material, in addition to the duration required for the conversion reaction that takes place in the conventional transesterification reaction. However, if the reaction has already reached equilibrium, prolonging the reaction time will not be advantageous as it will not enhance the yield. Additionally, a reverse reaction in which methyl ester turns back into triglyceride could result in a reduced yield (Eevera *et al.*, 2009).

Stoichiometry states that three moles of alcohol and one mole of oil are needed for the transesterification reaction to happen. This creates three moles of biodiesel or methyl ester and one mole of glycerol. To optimize biodiesel production in the in-situ transesterification process, it was necessary to use an appropriate excess of alcohol. This excess alcohol served as both a solvent and a reagent, ensuring that the reaction was focused on producing the desired product (Haas *et al.*, 2004)

The alcohol types commonly employed for in-situ esterification and transesterification reactions are methanol, ethanol, propanol, isopropanol, and butanol. Methanol is an unsuitable solvent for oil. However, it is a more economical option and possesses the shortest molecular chain, making it highly reactive for the reactions. Utilizing methanol as a solvent yielded biodiesel of superior purity in comparison to other forms of alcohol (Verma *et al.*, 2016). Vegetable oils exhibit a limited capacity to dissolve methanol when used as a solvent. According to the findings of Qian *et al.* (2008), the inclusion of 0.1M NaOH in the in-situ transesterification procedure for cotton seeds resulted in a significant increase in the oil extraction rate, reaching 99.7 percent. Additionally, the conversion of oil to methyl ester exhibited a yield of 98 percent. In contrast, the absence of NaOH led to a much lower oil extraction rate of only 22 percent, with an amount of oil converted to methyl ester of merely 33 percent.

The in-situ transesterification process faces issues, such as the occurrence of a two-phase reaction due to the limited solubility of oil in methanol. Hence, in order to initiate a reaction between methanol and oil, a significant amount of methanol is required. However, in the in-situ transesterification procedure, the separation of biodiesel and glycerol components will not occur if the amount of methanol in the mixture remains high. To address this issue, it is necessary to add a co-solvent that can enhance the solubility of both oil and methanol, thereby minimizing the quantity of methanol required during the transesterification procedure.

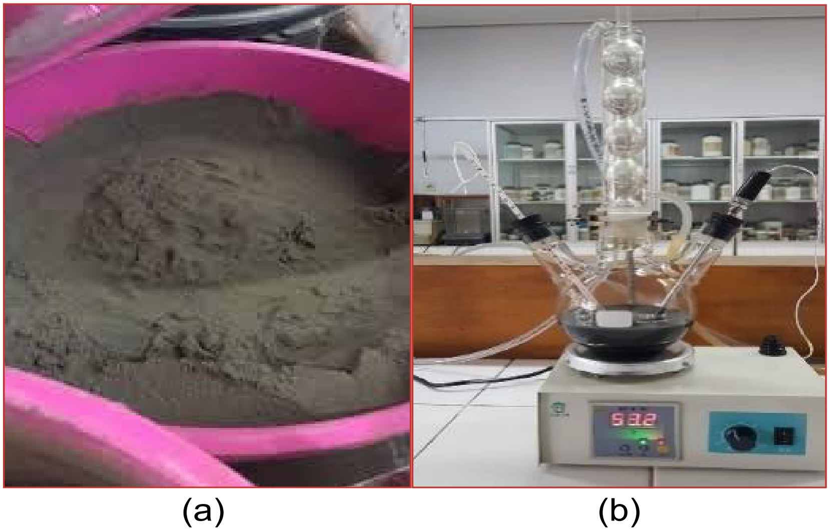
Methanol serves as both a solvent and a reagent for fatty acids in the in-situ transesterification process. Methanol's utilization as a solvent and reagent leads to the insufficient extraction of fatty acids. According to Dwita *et al.* (2019), to get the best results from the extraction and in-situ transesterification processes, extra solvents with polarity properties similar to fatty acids had to be used. A study by Daryono *et al.* (2020) found that using a co-solvent improved the efficiency of extraction and speeded up the rate of the in-situ transesterification processes. Nevertheless, the precise co-solvent ratio required to achieve both maximum biodiesel yield and high quality remains unknown.

The findings from prior research indicated that the yield of biodiesel produced in the in-situ transesterification process was affected by factors such as reaction temperature, reaction time, and the inclusion of methanol and base catalyst (NaOH). Thus far, the best conditions for achieving the highest yield of biodiesel, including temperature, reaction time, methanol to SBE ratio, and concentration of NaOH as the base catalyst, have not been determined. Hence, the objective of this study was to investigate the impact of temperature and reaction time during the in-situ transesterification process, concentration of the base catalyst, and the ratio of methanol and hexane to SBE on the synthesis of biodiesel from spent bleaching earth (SBE).

2. Materials and Methods

2.1 Materials

The primary substance utilized in this study was spent bleaching earth (SBE), supplied from a nearby crude palm oil (CPO) refining facility in Lampung Province, Indonesia. From preliminary research it was found that the CPO content in SBE was 27.5 percent. The primary research apparatus utilized was a reactor of a 1000mL boiling flask, which was equipped with a heater, magnetic stirrer, and condenser (Figure 1). Crude biodiesel was obtained using vacuum filtering and distillation instruments. The Thermo Scientific ISQ-7000 Gas Chromatography-Mass Spectrometry (GC-MS) apparatus was utilized to evaluate the methyl ester profiles. The process of separating components in GC-MS involved the utilization of a TraceGOLD™ TG-5MS column with specific dimensions: a film thickness of 0.25 μm, a particle size of 0.25 μm, an internal diameter of 0.32 mm, and a length of 30 m.



(a) (b)

Figure 1. (a) Spent Bleaching Earth (SBE); (b) The reactor utilized for the production of biodiesel from SBE through in-situ transesterification

2.2 Design of Experiment

The experiments were conducted in multiple phases, each corresponding to a specific research topic. The initial phase of the study was to investigate the impact of the temperature as well as the time of the in-situ transesterification process on the conversion of CPO in SBE to produce biodiesel. The reaction time was divided into four levels: 60, 90, 120, and 150 minutes. Similarly, the reaction temperature was divided into four levels: 50°C, 55°C, 60°C, and 65°C. The second phase of the study aimed to investigate the impact of the methanol-to-SBE ratio and NaOH concentration on the transformation of CPO in SBE into biodiesel. The v/w ratio of methanol-to-SBE consisted of four levels: 6.0, 7.0, 8.0, and 9.0. The w/w percentage of NaOH catalyst to SBE consisted of four levels: 2.0 percent, 3.0 percent, 4.0 percent, and 5.0 percent. The third phase of the research was investigating the impact of the methanol ratio and hexane ratio on the conversion of CPO in SBE to biodiesel. The v/w ratio of the methanol-to-the SBE was divided into three levels: 6.0, 7.0, and 8.0. Similarly, the v/w ratio for the hexane-to-the SBE was divided into three levels: 0.5, 1.0, and 1.5.

The research was conducted using a Complete Randomized Block Design (CRBD) structured factorially, with each experiment replicated three times. The research data were examined using analysis of variance (ANOVA) to calculate an estimate of error variance and conduct a significance test to assess the impact of different treatments. The data underwent additional analysis using Orthogonal Polynomial to ascertain the impact of treatment (independent variables) on the outcomes (dependent variables) and to forecast or approximate the value of the dependent variable in accordance with the value of the independent variable beyond the range of the sample.

2.3 Biodiesel Production

The production method of methyl ester (biodiesel) was conducted in two steps, namely in-situ esterification and in-situ transesterification. In the in-situ esterification process, a quantity of 100 grams of SBE was utilized and subjected to a reaction with methanol (the specific amount of methanol varies depending on the treatment), along with one gram of H_2SO_4 or one percent (w/w) of the weight of the SBE. The esterification process was conducted in-situ at 50°C with a stirring speed of 625 rpm for 90 minutes. Following the completion of the in-situ esterification process, the in-situ transesterification procedure was then carried out. The in-situ transesterification reaction initiated by introducing the NaOH catalyst, previously dissolved in 50 mL of methanol, into the reactor. The quantity of NaOH injected varies depending on the treatment. The in-situ transesterification process in this study was conducted at a temperature and duration that corresponded to the treatment requirements. After the in-situ transesterification process was finished, vacuum filtration was used to separate the solid part from the liquid part, which contained methyl ester, methanol, and glycerol. The distillation process was used to separate methanol from the liquid fraction. The liquid portion was subsequently washed with distilled water at a temperature of 60°C until the pH of the wash water reached neutral. Subsequently, the biodiesel was subjected to a drying process in an oven set at 105 °C for a duration of 4 hours. This procedure aimed to remove any residual water and solvent present in the biodiesel. The solid fraction obtained by the process of vacuum filtration still contained biodiesel, which was then recovered using hexane. The extracted and washed biodiesel was subsequently combined and analysed to determine the biodiesel yield, methyl ester composition, acid number, saponification number, iodine number, and cetane index.

2.4 Observation and Measurement

The biodiesel produced from the research was subjected to additional analysis to determine its properties. These included the biodiesel yield, which was calculated on the basis of the weight of the oil in SBE. The biodiesel methyl ester profile was determined using GC-MS. The acid number of the biodiesel was measured using the titration method. The iodine number and saponification number were determined using the Knothe method (2002). Additionally, the cetane index was calculated using the Krisnangkura method (1986).

3. Results and Discussion

3.1 Effect of Temperature and Reaction Time

The analysis of variance revealed that the time and temperature of the in-situ transesterification reaction had a substantial impact on the yield, cetane index, and acid number of the biodiesel produced. Subsequent data analysis using Orthogonal Polynomials revealed that elevating both reaction time and temperature resulted in an increase in biodiesel production while concurrently diminishing the cetane index and acid number. Figure 2 illustrates the impact of increasing the time and temperature of the in-situ transesterification reaction on the yield, cetane index, and acid number of biodiesel.

It is clear from Figure 2 that the amount of biodiesel made through the in-situ transesterification process goes up linearly as the reaction time is increased at all temperatures. Reaction time is one of many factors that affects the success of the in-situ transesterification reaction. Reaction time plays a crucial role in determining the time of contact between methanol and triglycerides in SBE. Increasing the time of contact between alcohol molecules and triglycerides leads to a higher conversion rate for each reactant, resulting in an anticipated rise in the yield of biodiesel produced.

The research findings indicate that the production of biodiesel increases steadily for a duration of up to 150 minutes during the in-situ transesterification reaction. This suggests that the formation of biodiesel is ongoing and that there are no inhibitory reverse reactions affecting biodiesel production. The yield continued to increase as equilibrium had not yet been achieved. As stated by Krisnangkura (1986), the in-situ transesterification reaction decreased in its reaction rate and eventually reached a steady state after 180 minutes. Prolonging the duration of the transesterification reaction beyond the point of equilibrium might result in a decrease in the yield of biodiesel (Zakaria & Harvey, 2012).

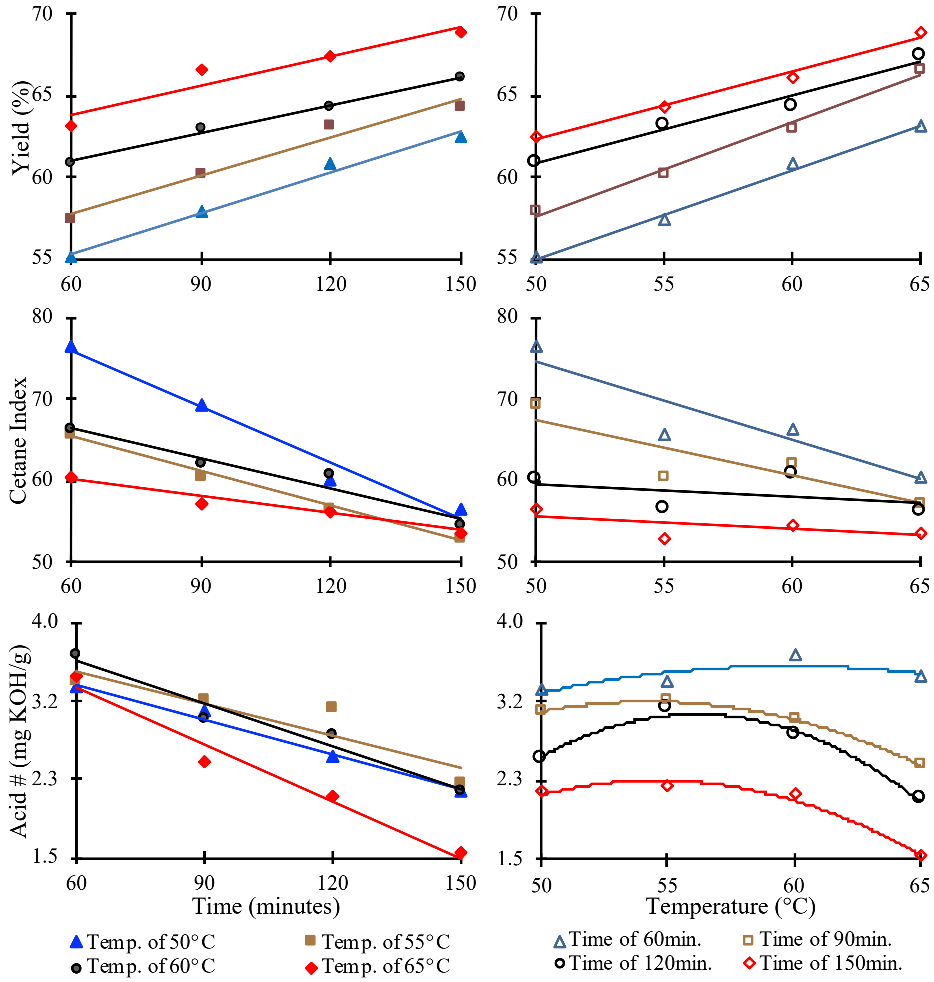


Figure 2. Pattern of changes in yield, cetane index, and acid number of biodiesel affected by increasing the time and temperature of the in-situ transesterification reaction of SBE

The reaction temperature has a big impact on the outcome of chemical processes like transesterification, which produces biodiesel. The transesterification reaction was an endothermic process that required elevated temperatures in order to achieve greater conversion. Raising the reaction temperature accelerated molecular motion, leading to an increase in collisions between reactant molecules or enabling the molecules to surpass the activation energy (Kartika & Wiydaningsih, 2012). The research findings indicated that raising the temperature of the in-situ transesterification reaction to 65°C led to a higher production of biodiesel (Figure 2). The transesterification reaction between triglycerides and methanol exhibits enhanced reactivity with an elevation in reaction temperature. However, applying an excessively elevated reaction temperature would result in the evaporation of methanol and a decrease in the interaction between methanol and triglycerides, consequently restricting the optimal production of biodiesel (Segdhamiz *et al*., 2019). Methanol has a boiling point of 64.7°C. In addition, Kiran & Hebbar (2021) discovered that increasing the reaction temperature over 65°C resulted in a reduction in biodiesel production.

Cetane index is a quantitative measure of the rate at which biodiesel fuel ignites. The biodiesel cetane index resulting from research was between 62.02 and 85.47, with an average of 70.69. The value fulfils the criteria established by the Indonesian Standard for Biodiesel, which mandates a minimum cetane index of 51.0 (BSN, 2015). The cetane index in this study was calculated using the equation proposed by Krisnangkura (1986), which utilizes the saponification number and iodine number as the basic parameters for the computations. This equation was derived from the research findings by Klopfenstein (1985), which established a correlation between the cetane index and the mix of fatty acids in biodiesel, specifically the number of carbon atoms and double bonds. In addition, a study conducted by Ramos *et al*. (2009) discovered that the cetane index was affected by the composition of the methyl ester, which was in turn linked to the level of unsaturation and the length of the carbon chain. The cetane index in Europe's biodiesel quality criteria can be forecasted by analysing the composition of saturated and unsaturated fatty acids in methyl esters. The methyl esters' fatty acid composition might be utilized to accurately determine the cetane index, with a precision of up to 98% (Tong *et al*., 2011). According to Krisnangkura (1986) equation, there was a negative correlation between the cetane index and the saponification number and iodine number. In other words, as the saponification number and iodine number increased, the cetane index declined.

Figure 2 demonstrates that elevating the time and temperature of the in-situ transesterification process resulted in a reduction in the cetane index of the produced biodiesel. The transesterification reaction is influenced by temperature, as higher temperatures can decrease the viscosity of the oil and hence accelerate the reaction rate. However, over the optimal threshold of temperature amplifies the saponification process of triglycerides. The acceleration of the saponification rate led to a drop in the cetane index (Leung & Guo, 2006). Similarly, an increase in response time beyond the optimal duration resulted in an elevated triglyceride saponification reaction (Eevera *et al*., 2009).

The acid number of biodiesel goes down as the temperature and length of time of the in-situ transesterification reaction are raised (Figure 2). The reduction in acid number is a result of the prolonged reaction time, which enhances the possibility that the oil in SBE will undergo a reaction with methanol. The process resulted in a decrease in the production of free fatty acids as they were transformed into methyl esters (Tubino & Aricetti, 2011). Hence, increasing the duration of the reaction can diminish the acid number. The reduction in acid number also took place at elevated reaction temperatures due to the increased possibility of oil in SBE colliding with methanol, resulting in a decrease in the production of free fatty acids since they were transformed into methyl esters (Kartika & Widyaningsih, 2012).

The acid number of biodiesel was influenced by various parameters, including the moisture level of the raw material and the process used to dry the biodiesel (Yasar, 2020). The moisture content of raw materials played a crucial role in transesterification reactions, regardless of whether they were catalysed by acids or bases. The catalyst's efficacy can be diminished in SBE due to the binding effect of water (Komers *et al*., 2001). Furthermore, the negative impact of water on the transesterification reaction is more severe than that of free fatty acids. The presence of water in the oil initiated a hydrolysis reaction, which transformed triglycerides into fatty acids and glycerol. As a result, the concentration of free fatty acids in biodiesel increased (Ma *et al*., 1998; Tomasevic & Marinkovic, 2003).

3.2 Effect of Methanol/SBE Ratio and NaOH Catalyst Concentration

Analysis of variance demonstrated that the methanol-to-SBE ratio and the concentration of NaOH had a substantial impact on the yield, cetane index, and acid number of the biodiesel produced from SBE by the in-situ transesterification reaction. Subsequent data analysis utilizing Orthogonal Polynomials revealed that increasing the methanol/SBE ratio and NaOH catalyst concentration increased the output of biodiesel generated while concurrently reducing the cetane index and acid number. Figure 3 shows how the higher methanol/SBE ratio and the concentration of NaOH catalyst in the in-situ transesterification process affect the increasing yield, decreasing cetane index, and acid number of biodiesel.

It can be seen in Figure 3 that increasing the methanol/SBE ratio in the in-situ transesterification process makes more biodiesel. The results of this investigation were consistent with research by Oluleye *et al.* (2019), which demonstrated that increasing the methanol/oil mole ratio increased biodiesel yield. The increase in the methanol/SBE ratio leads to a higher use of methanol, causing the reaction equilibrium to favour the production of biodiesel and thus enhancing the yield. More than that, methanol is needed for biodiesel production because it can be used as both an extractant and a reactant in the in-situ esterification and transesterification processes. Due to the limited solubility of oil in methanol, a significant quantity of methanol addition was necessary (Muslich *et al*., 2020).

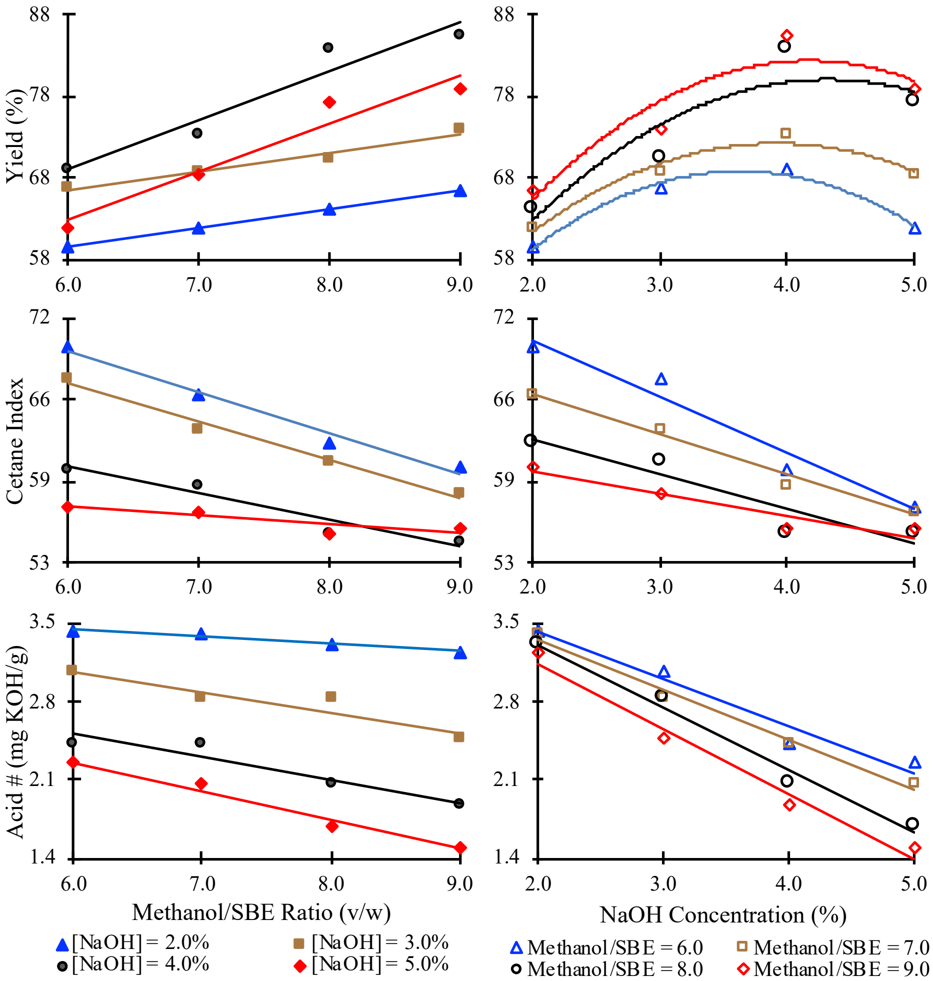


Figure 3. Pattern of changes in biodiesel yield, cetane index, and acid number caused by increasing the methanol/SBE ratio and NaOH catalyst concentration in the in-situ transesterification reaction of SBE

According to the research, more biodiesel could be made when the concentration of the catalyst in the in-situ transesterification reaction of SBE was raised. However, above a specific threshold of NaOH catalyst concentration, increasing the catalyst concentration may result in a decline in the yield of the biodiesel generated. This occurred as a result of the saponification reaction between the NaOH catalyst and triglycerides. The saponification reaction reduced both the catalyst and the number of triglycerides available for the transesterification reaction. Additionally, it complicated the process of separating biodiesel (Eevera *et al*., 2009; Leung & Guo, 2006).

The research findings indicated a linear decline in the biodiesel cetane index when the methanol/SBE ratio was increased in all experiments with varying NaOH catalyst concentrations. In the same way, the biodiesel cetane index went down in a straight line as the concentration of the NaOH catalyst went up in all the treatments, even those with different amounts of methanol and SBE. Pali *et al.* (2020) found that raising the catalyst concentration resulted in an elevation of the cetane index of biodiesel. Nevertheless, an excessive catalyst concentration led to an acceleration of the saponification reaction, which in turn caused a reduction in the cetane index.

As the methanol/SBE ratio goes from 6.0 to 9.0 (v/w), Figure 3 shows that the acid number goes down in a straight line for all NaOH catalyst concentrations. The reduction in acid number resulted from the increased use of methanol, which enhanced the completeness of the ester formation reaction. Consequently, a greater quantity of methyl ester (biodiesel) was generated, while the presence of free fatty acids was diminished. Similarly, elevating the concentration of the NaOH catalyst resulted in a linear drop in the acid number. Raising the concentration of the NaOH catalyst facilitated the interaction between triglycerides and methanol while inhibiting the hydrolysis reaction between triglycerides and water, thereby preventing the generation of free fatty acids. According to Faizal & Maftuchah (2013), increasing the amount of base catalyst in the transesterification process tended to lower the acid number of biodiesel. This study's results supported these findings.

3.3 Effect of Methanol/SBE Ratio and Hexane/SBE Ratio

An analysis of variance revealed that the change in the methanol/SBE ratio and the hexane/SBE ratio had significant effects on the biodiesel production, cetane index, and acid number generated during the in-situ transesterification reaction of SBE. Additional data analysis utilizing Orthogonal Polynomials revealed a direct linear relationship between the increase in the methanol/SBE ratio and the hexane/SBE ratio and the increase in biodiesel yield. Conversely, there was a linear decrease in both the cetane index and acid number. Figure 4 illustrates the impact of increasing the methanol/SBE ratio and the hexane/SBE ratio on the biodiesel yield, cetane index, and acid number.

The research findings showed that increasing the methanol/SBE ratio in the in-situ transesterification process resulted in a higher output of biodiesel. The increase in the methanol/SBE ratio resulted in a higher consumption of methanol, causing a shift in the reaction equilibrium towards the product. As a consequence, the yield of biodiesel produced increased. During the in-situ esterification and transesterification processes, methanol served as both an extractant and a reactant. Because of this, a large amount of methanol was needed to make biodiesel. An excess volume of methanol was required to enhance the possibility of a reaction between triglycerides and methanol (Tomasevic & Marinkovic, 2003).

The research findings also indicated that the incorporation of hexane solvent can enhance the production output of biodiesel. The biodiesel yield increased in a linear way as the hexane/SBE ratio increased. The biodiesel yield increased due to the use of hexane, a non-polar solvent, which enhanced the solubility of triglycerides in methanol. Hexane was used as a co-solvent in the transesterification reaction, which was a new way to improve the mixing and mass transfer between alcohol and triglycerides. The inclusion of a co-solvent not only enhanced the extraction of oil from SBE, but also increased the reaction (Daryono & Sinaga, 2017). The inclusion of hexane in the reaction medium increased the reaction rate by promoting collisions among the molecules of the reactants, leading to enhanced mass transfer and reduced reaction times (Encimar *et al*., 2010; Mohammed-Dabo, 2012). Moreover, the inclusion of hexane facilitated a more efficient separation of the biodiesel and glycerol phases, as compared to the absence of any supplementary solvent (Pena *et al*., 2009). However, a study conducted by researchers (Dianursanti *et al*., 2015; Fadhil & Mohammed, 2018) revealed that the introduction of an excessive amount of hexane resulted in a decrease in the production yield of biodiesel. This could be due to excessive hexane, which resulted in the dilution of the reactant and hence decreased the interaction between triglyceride molecules and methanol.

The study showed that the cetane index of biodiesel went down in a straight line as the methanol/SBE ratio went up in all of the treatments where the hexane/SBE ratio was changed. In the same way, the biodiesel cetane index went down straight away when the hexane/SBE ratio went up in all of the treatments where the methanol/SBE ratio went up. Pali *et al.* (2020) found that elevating the methanol/SBE ratio resulted in a higher cetane index for biodiesel. However, an excessive amount of methanol would lead to an increase in the saponification reaction, thus reducing the cetane index. In the process of making biodiesel, hexane effectively dissolved triglycerides and other lipid components, such as diglycerides, monoglycerides, and phospholipids. The lipids' presence enhanced the saponification rate, thus decreasing the cetane index of the biodiesel generated.

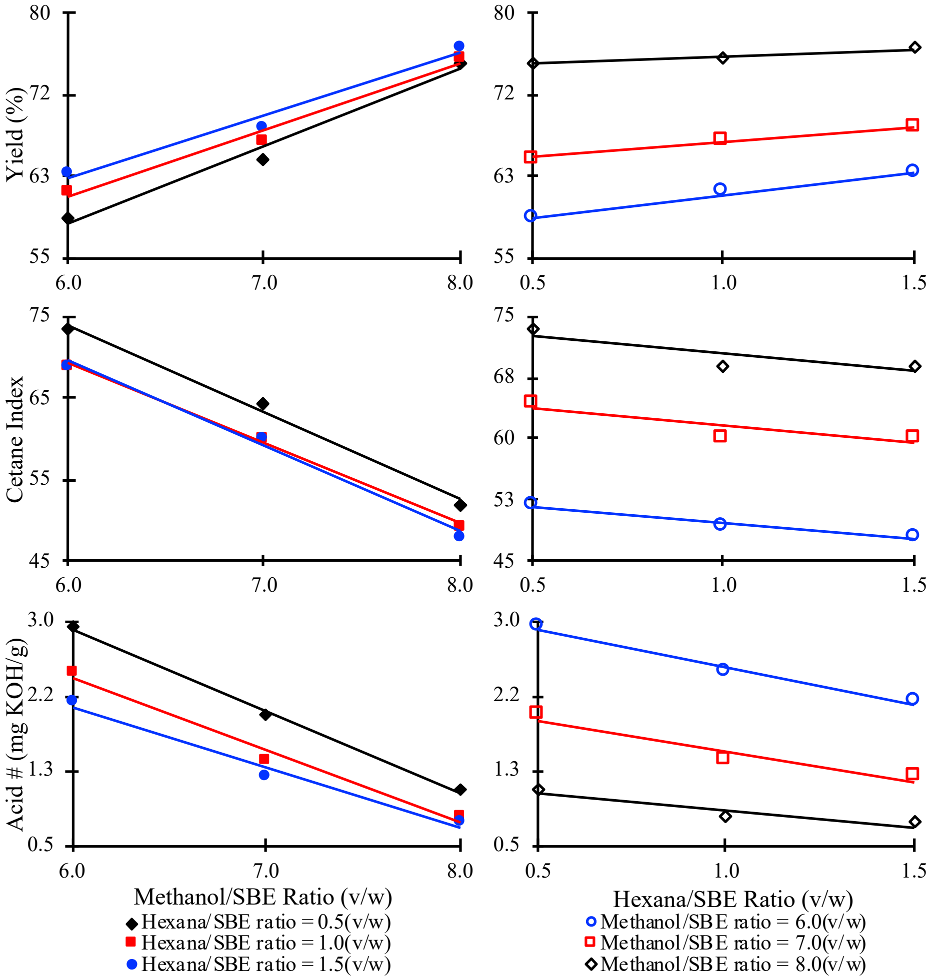


Figure 4. Pattern of changes in yield, cetane index, and acid number of biodiesel caused by an increase in the methanol/SBE ratio and hexane/SBE ratio in the in-situ transesterification reaction of SBE

The research findings demonstrated a linear decrease in acid number when the methanol/SBE ratio was increased from 6.0 to 9.0, across all hexane/SBE ratio treatments. It was possible that the lower acid number is because more methanol is being used, which makes the ester formation reaction more complete. Consequently, a greater quantity of methyl ester (biodiesel) is generated, while the amount of free fatty acids is diminished. Similarly, a rise in the hexane/SBE ratio resulted in a decrease in the acid number of biodiesel. Hexane was added as a co-solvent to the in-situ transesterification process, which made it easier to get non-polar components, like free fatty acids, out of SBE. Consequently, a greater quantity of free fatty acids interacted with methanol and underwent conversion into methyl esters. An investigation of biodiesel yield also revealed that increasing the ratios of methanol to SBE and hexane to SBE resulted in higher yields of biodiesel.

3.4 Methyl Ester Profile

The primary constituent of biodiesel is methyl ester. By using Gas Chromatography-Mass Spectrometry (GSMS), it was found that biodiesel had a methyl ester content of between 97.34 to 97.63 percent, with an average of 97.47 ± 0.15 percent, and the dominant types of methyl esters found in biodiesel from CPO were methyl oleate, methyl palmitate, methyl stearate, methyl linoleate, and methyl myristate (Figure 5 and Table 1). According to the Indonesian Standard (SNI 7182-2015), the biodiesel must have a minimum methyl ester content of 96.5 percent (BSN, 2015), therefore, biodiesel resulting from SBE processing by in situ esterification and transesterification meets Indonesian standards for biodiesel.

Fatty acids play a crucial role in determining the characteristics of oil triglycerides, which in turn influence the properties of fatty acid methyl ester (FAME) derived from oil processing. The properties of biodiesel, such as its combustion efficiency, are determined by the composition of fatty acids present in FAME (biodiesel). The presence of hydrocarbons and nitrogen-containing components in exhaust gases is directly affected by the makeup of the fatty acids found in biodiesel. Conversely, the quality of biodiesel is contingent upon the composition of the fatty acid esters and the fatty acids present in the raw material. The primary structural attributes that impact fuel qualities include the length of the carbon chain, the level of unsaturation, and the degree of branching in fatty acids (Martinez *et al*., 2014; Yang *et al*., 2018). According to the research findings, the primary varieties of fatty acid methyl ester (FAME) found in biodiesel include methyl oleate, methyl palmitate, and methyl stearate (Table 1). The fatty acids present in FAME are the same as the predominant fatty acids found in CPO, which include oleic acid, palmitic acid, stearic acid, linoleic acid, and myristate acid (Chowdhuri, 2007; Koushki, 2015).

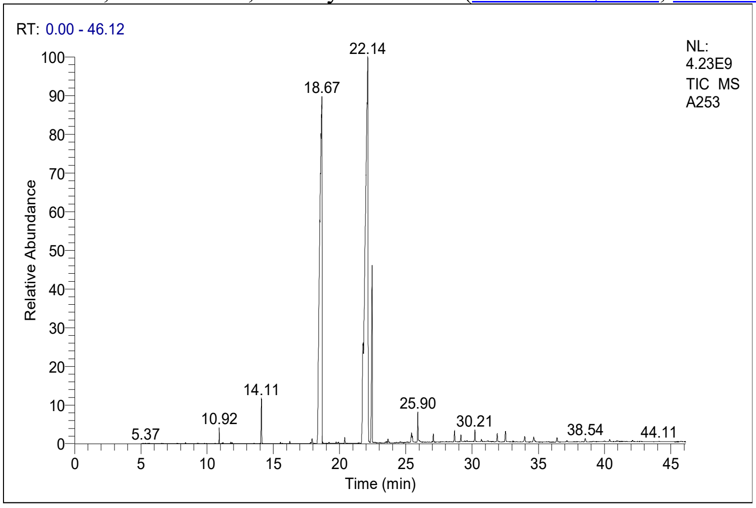


Figure 5. Profile of biodiesel methyl esters derived from the in-situ transesterification reaction of spent bleaching earth (SBE) analysed by GC-MS

The research findings indicate that the biodiesel has a free fatty acid content of 1.27 ± 0.17 percent. The free fatty acid concentrations in the biodiesel exceeded those specified by the Indonesian biodiesel standard (BSN, 2015), primarily as a result of the purification method applied to the crude biodiesel. The unrefined biodiesel underwent a water-washing process to remove the polar component, followed by a drying phase to eliminate any remaining water in the biodiesel. The drying process was carried out in an oven at a temperature of 105°C for a period of 4 hours, under standard atmospheric pressure. The material underwent a hydrolysis process when exposed to extended high-temperature heating, resulting in the production of extra free fatty acids (Kartika & Widyaningsih, 2012).

Additional constituents discovered through studies in biodiesel included trace levels of straight-chain hydrocarbon, hydrocarbons with hydroxyl (OH) groups, and the terpene group (specifically squalene). The minor components account for 1.28 ± 0.22 percent of the total (Table 1). The biodiesel produced from the research was unrefined, containing contaminants that had not been removed through a purifying process. During refining crude biodiesel using vacuum distillation, the impurities are removed and collected to produce a by-product known as palm phytonutrients concentrate. This concentrate comprised free fatty acids and other minor components (Chandrasekaram *et al*., 2009). The minor constituents present in crude biodiesel were believed to originate from CPO. Goh *et al*. (1985) observed that CPO contained approximately one percent of minor constituents, including carotenoids, tocopherols, phospholipids, glycolipids, sterols, triterpene alcohols, and other hydrocarbon components.

Table 1. Percentage of biodiesel methyl esters derived from the in-situ transesterification reaction of spent bleaching earth (SBE) analysed by GC-MS

No.	Chemical Name	Retention Time (minutes)	Percentage
1.	Fatty acid methyl ester	--	97,47 ± 0,15
	a. Methyl myristate	14.11	1,00 ± 0.09
	b. Methyl palmitate	18.67	39,49 ± 0,97
	c. Methyl linoleate	21.78	1,46 ± 0,10
	d. Methyl oleate	22.14	44,88 ± 0,59
	e. Methyl stearate	22.46	7,19 ± 0,63
	f. Other methyl esters	--	3,46 ± 0,23
2.	Free fatty acids	--	1,24 ± 0,17
3.	Other components	--	1,28 ± 0,22

4. Conclusion

The biodiesel yield exhibited a linear rise when the reaction temperature was raised to 65°C and the reaction duration was extended to 150 minutes. Additionally, increasing the hexane/SBE ratio and the methanol/SBE ratio also resulted in a linear increase in biodiesel yield. Increasing the concentration of the NaOH catalyst to 4.0 percent resulted in a rise in the biodiesel output. However, further addition of NaOH beyond 4.0 percent led to a decrease in the biodiesel yield. Simultaneously, elevating the temperature and reaction duration, reducing the concentration of NaOH catalyst, as well as increasing the ratios of methanol/SBE and hexane/SBE, resulted in a linear decrease in both the cetane index and acid number. The in-situ transesterification process in SBE achieved the highest biodiesel yield of 85.6 percent. This was achieved by conducting the process at a temperature of 65°C for 120 minutes, using a methanol/SBE ratio of 9.0 (v/w), and a NaOH catalyst concentration of 4.0 percent. The Gas Chromatography-Mass Spectrometry (GS-MS) study revealed that the biodiesel obtained from the research consisted of 97.47 ± 0.15 percent methyl ester.

The research findings indicated that spent bleaching earth (SBE), the primary waste generated by the CPO refinery industry, can be utilized as a viable feedstock for biodiesel production. By employing SBE as a primary substance for biodiesel, it not only minimizes waste but also enhances biodiesel production without compromising the accessibility of oil for food consumption.

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