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EFFECT OF ACIDITY, BASICITY, HETEROGENEOUS CaO/SILICA GEL CATALYST FROM BIOMASS WASTE ON BIODIESEL YIELD FROM CRUDE PALM OIL

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Abstract

The global energy sector has been dominated by non-renewable fossil fuels, prompting many countries to invest in renewable energy sources such as biodiesel. Crude palm oil (CPO), as a biodiesel feedstock, has a high FFA content, which can cause saponification reactions. This can reduce the quality of biodiesel if only CaO catalyst is used. Therefore, acid catalysts such as silica gel are needed to overcome this problem. Silica gel can also improve the stability, reactivity, and effectiveness of CaO catalyst in biodiesel production. This study aims to synthesize and characterize the heterogeneous CaO/silica gel catalyst obtained from biomass waste, and evaluate its activity in the conversion of CPO into biodiesel. The CaO/silica gel hybrid catalyst was prepared by wet impregnation method with varying percentage of silica gel (5%, 10%, and 15%), which was synthesized from coconut husk using sol-gel method, and mixed with CaO from calcination of blood clam shells at 900°C for 5 hours. The basicity characterized using the acid-base titration method, while the acidity was analyzed using pyridine adsorption method with FTIR, and the surface area was analyzed by BET method. The results showed that the synthesis of CaO/silica gel was successful, with confirmation of FTIR data at specific wavelengths. The addition of silica gel increased the acidity and surface area and decreased the basicity of CaO catalyst, with 10% CaO/silica gel showing optimal acidity and surface area. Testing the catalyst activity in the reaction of biodiesel formation from CPO produced the highest biodiesel yield of 96.71% using CaO/silica gel 10%. The conclusion of this study is that biomass waste-based heterogeneous catalysts have high potential for biodiesel production, which is influenced by their acidity and surface basicity, and offer a low-cost and environmentally friendly solution.

INTRODUCTION

The dependence of the global energy sector on non-renewable fossil fuels is still very high [1]. This condition encourages various countries to develop renewable energy sources as a more sustainable alternative [2]. Indonesia is among the countries that are proactive in this effort, considering that in 2021, the use of fossil fuels in the transportation sector reached 93.8% [3]. One promising solution is biodiesel, which offers several advantages, such as cleaner combustion, high biodegradability, low carbon emissions [4], and flexibility of use, both as a pure fuel (B100) and in blends with diesel [5]. As a global pioneer, Indonesia has implemented the B35 standard, which is a blend of 35% biodiesel with 65% diesel [3].

Biodiesel is generally produced through transesterification, which is the reaction of triglycerides with short-chain alcohols using a base catalyst [6]. Crude palm oil (CPO), as a biodiesel feedstock, has great potential in Indonesia which is the world's largest CPO producer [3]. However, the high Free Fatty Acid (FFA) content in CPO (>5%) often triggers saponification reactions, reducing biodiesel yield and complicating purification, especially with homogeneous catalysts [7]. This problem can be solved with heterogeneous catalysts such as CaO, which is cheap, durable, has high catalytic properties, and is abundant in nature [8]. As an environmentally friendly approach, biomass waste has been utilized to produce catalysts, including CaO, can be obtained directly from natural waste shells, which are reported to have characteristics comparable to conventional CaO [5]. Blood clam shell waste, which is rich in calcium carbonate ($CaCO_3$) can produce CaO by calcination at 900°C for 5 hours with purity up to 97.83% [7]. The use of CaO in the synthesis of biodiesel from CPO produced a yield of 77.89%, but the purity of biodiesel produced remains low

[9]. This is due to a decrease in catalyst activity, due to the low surface area of CaO from clam shell waste and its sensitivity to air contamination [10].

Various modifications have been made to improve the activity of CaO catalysts, such as with KOH [9], H_2SO_4 [11], and NaOH [12]. Although these methods improve catalyst performance, the biodiesel yield obtained is still not optimal in terms of both yield and quality. The wet impregnation method has been used in previous studies to synthesize CaO/silica catalysts from biomass waste. This modification successfully improved catalyst stability, prevented Ca^{2+} formation, and increased biodiesel yield to 81-98.3% [13], [10], [14], [15]. These advantages are mainly obtained through the addition of silica, especially in the form of silica gel, which is known for its large surface area, high pore volume, and good thermal stability [16]. As reported by Lani et al. (2020) that the use of silica gel from rice husk ash can increase the surface area of CaO from blood clam shells to 9.47 m^2/g [10]. This not only increases the stability of the catalyst by preventing Ca^{2+} formation but also improves its reactivity [17]. In addition, silica as an acid catalyst is also effective for increasing biodiesel yield from oils with high FFA content [16].

The success in improving the performance of CaO catalysts influenced by the characteristics and source of silica. Most previous studies utilized rice husk ash or palm kernel shell ash as silica sources [10], [14]. On the other hand, coconut husk ash, which contains up to 91.76% silica in the form of silica gel [18], also has great potential as a silica source. However, until now, the use of silica gel from coconut husk ash to modify CaO catalysts has not been reported in previous studies. Modification of CaO aims to improve its activity, surface basicity and acidity, stability, and specific surface area [19]. This research aims to synthesize heterogeneous catalysts by utilizing blood clam shells as a source of CaO, which is then combined with silica gel from coconut coir waste. Furthermore, the activity test of CaO/silica gel catalyst was conducted on the reaction of biodiesel formation from CPO, by studying the effect of acidity and basicity of the catalyst surface on biodiesel yield.

EXPERIMENT

Material

The materials used in this study include crude palm oil taken from PT Kuala Lumpur Kepong Berhad in Dumai City, as well as blood clam shells obtained from various seafood restaurants in Pekanbaru, and coconut husk from Kuantan Singingi Regency, CH_3OH (Merck), phenolphthalein indicator (Merck), hydrochloric acid (HCl) (Smart Lab), NaOH (Merck), CH_3COOH (Merck), Pyridine (Smart Lab) Whatman 42 filter paper, aqua DM.

Instrumentation

The instrumentation used to characterize the adsorption of pyridine vapor was a Shimadzu FTIR Type IRprestige-21 instrument and BET (Brunauer, Emmett, and Teller) method using a St 2 on NOVA touch 4LX instrument [s/n: 17018063001]. To characterize the surface area of the catalyst.

Procedure

Synthesis of CaO from Blood Clam Shells

The synthesis of CaO starts by grinding the blood clam shell waste using a mortar, then sieved through a 200 mesh sieve, and then calcined at 900°C for 5 hours [7].

Synthesis of Silica Gel from Coconut Husk

The synthesis of silica gel was carried out in two stages: first, SiO_2 extraction using acid [19] and followed by a modified sol-gel method [21]. The first stage involved calcination of coconut husk at 700°C for 2 hours. The ash obtained (10 g) was dissolved in 3N HCl, and heated to 110°C for 5 minutes, then the heater was turned off and the temperature was allowed to drop to 80°C. Next, the mixture was stirred at 600 rpm for 1 hour. After that, the mixture was filtered using Whatman 42 filter paper and washed with hot aqua DM (80°C) until the pH of the filtrate became neutral. The residue obtained was dried in an oven at 105°C until dry, then calcined at 700°C for 2 hours.

The second stage involved mixing 5 g of the obtained SiO_2 with 50 mL of 3,5 N NaOH in a triple neck flask equipped with a thermometer and reflux system. The mixture was heated to 100°C and stirred at 600 rpm for 1 hour. After that, the mixture was filtered, and the filtrate was added with 1N HCl drop by drop until a gel with pH 7 was formed. The formed gel was left for 18 hours for the aging process. Then, the gel was washed and dried at 70°C until it reached a constant weight. The solid formed was crushed and sieved using a 200 mesh sieve. The silica powder obtained from this process is known as silica gel.

CaO/Silica Gel Impregnation

The CaO and silica gel hybrid catalyst was prepared using a modified wet impregnation method. CaO as much as 10 g was suspended into 100 mL of aqua DM. The CaO suspension was added to a three-neck flask containing silica gel powder (variations of 5%, 10%, and 15% w/w). The mixture was refluxed with a stirring speed of 600 rpm at 80°C for 4 hours. After that, the mixture was dried in an oven for about 24 hours. The resulting catalyst was then calcined at 800°C for 3 hours [15].

Compound Characterisation

Catalyst basicity test

The basicity of the catalyst was measured using an acid-base titration method [22]. In this procedure, 100 mg of the catalyst was dissolved in 10 mL of a 0.1 mol/L aqueous NaOH solution. The mixture was stirred at room temperature for 45 minutes, and phenolphthalein was used as the color indicator. The suspension was then titrated with 0.1 mol/L aqueous acetic acid until the pink color disappeared and the solution turned colorless. The basicity of the catalyst was calculated using the equation:

$$\text{Basicity} = CAA\ X\,\frac{\Delta VAA}{mCat} \qquad (1)$$

Where:
CAA is the concentration of the acetic acid standard solution, ΔVAA is the difference in the volume of acetic acid solution consumed at equivalence for the solution containing solids, and mCat is the mass of the catalyst used in the test.

Catalyst acidity test

Pyridine adsorption method was used for catalyst acidity analysis [23]. A total of 20 mL of pyridine was placed in a desiccator to saturate and left for 24 hours in a fume hood. Meanwhile, several beaker glasses of the same size were cleaned and dried. All the beaker glass was weighed and stored in a desiccator. A total of 0.1 g of catalyst sample (free of moisture) was put into the beaker glass. The beaker containing the sample was allowed to interact for 24 hours. After 24 hours, the desiccator was opened for 1 hour, then the beaker was taken out and weighed again. The catalyst that had absorbed pyridine was analyzed using FTIR. Each sample was measured three times quantitatively using the gravimetric method. The total acidity in the sample was calculated using equation 2:

$$\text{Total Acidity} : \frac{w3-w2}{(w2-w1)\,BM}\ X\ 1000\ mmol/g \qquad (2)$$

Where:
w1 = empty beaker glass
w2 = beaker glass + sample
w3 = beaker glass + sample after pyridine adsorption
BM = Molecular weight of pyridine (79.10 g/mol)

CaO/silica gel catalyst activity test

The catalyst as much as 1.5% (w/b) was dried at 105°C for 10 minutes, then mixed with methanol in a ratio of 1:12 to oil in a three neck flask, and refluxed for 60 minutes. To separate the catalyst, the mixture was filtered using Whatman 42 filter paper. After the CPO was heated at 105°C for 30 minutes and had reached room temperature. The CPO was refluxed with methanol, at 60°C, at 500 rpm, for 90 minutes. The reaction results were allowed to stand overnight in a separatory funnel. This reaction condition was modified by considering the research reported [2]. The biodiesel was washed using aqua DM, then heated. The percentage of biodiesel formed was calculated using the equation:

$$Yield\ (\%) = \frac{\text{weight of biodiesel (g)}}{\text{weight of oil (g)}}\,\text{x}\ 100\% \qquad (3)$$

RESULT AND DISCUSSION

Identification of Catalyst Function Groups with FTIRS

The FTIR spectra of the catalyst samples CaO, Silica Gel, and the combination of both can be seen in the region of 400-4000 cm^{-1} presented in **Figure 1. Figure 1(a)**, is the spectra of CaO showing wave numbers at 1413, 1078, and 2518 cm^{-1} which correspond to the stretching vibration of CO_3^{2-} due to the chemisorption of CO_2 gas on the catalyst surface [10]. The strong absorption around 3643 cm^{-1} is the O-H bending vibration of calcium hydroxide, consistent with that reported by Khazaai et al. (2021) and this confirms that CaO can hydrolyze to $Ca(OH)_2$ when exposed to air [24]. In addition, the peaks at 872 and 710 cm^{-1} indicate the presence of Ca-O bonds. The same thing has been reported by Putra et al. (2017), that absorption in the range of 700 to 900 cm^{-1} can be associated with

Ca-O vibrations and the peak of 524 cm^{-1} indicates stretching vibrations of Ca-O bonds [25]. This proves the successful formation of CaO from blood clam shell waste after the calcination process.

The broad bands in the range of 2390 to 3360 cm^{-1}, in **Figure 1.(b)**, can be attributed to O-H bond stretching vibrations of silanol (Si-OH) groups [26]. The band at 1628 cm^{-1} corresponds to the O-H stretching and bending modes of water molecules adsorbed on the surface of silica gel [20]. The strong band at 1089 cm^{-1} is the dominant peak of silica gel, indicating asymmetric stretching of siloxane bonds (Si-O-Si), with the absorption range of this functional group being between 1075-1095 cm^{-1} [27]. While the wave number range at 935-980 cm^{-1} is the bond of Si-OH [28]. The peak in the 798 cm^{-1} region shows the symmetrical stretching of the siloxane bond [14]. The wave numbers in the range of 465-475 cm^{-1} are from the Si-O bending of the Si-O-Si group [29]. These results indicate the successful extraction of silica gel from coconut fiber.

The FTIR spectra of the CaO/silica gel catalysts (5%, 10%, and 15%) are shown in **Figure 1c**. The three IR spectra of these catalysts have a similar shape, there is only a difference in the transmittance intensity. These spectra display some functional groups similar to the CaO catalyst, with similar patterns at 3642 and 882 cm^{-1} identified as stretching vibrations of O-H groups and Ca-O bonds, respectively. The absorption band at 1408 cm^{-1} indicates the C-O-C asymmetric stretching of CO_3^{-2} groups. At 1089 cm^{-1}, there are asymmetric stretching vibrations of siloxane groups (Si-O-Si) that appear due to the addition of silica gel to the CaO catalyst.

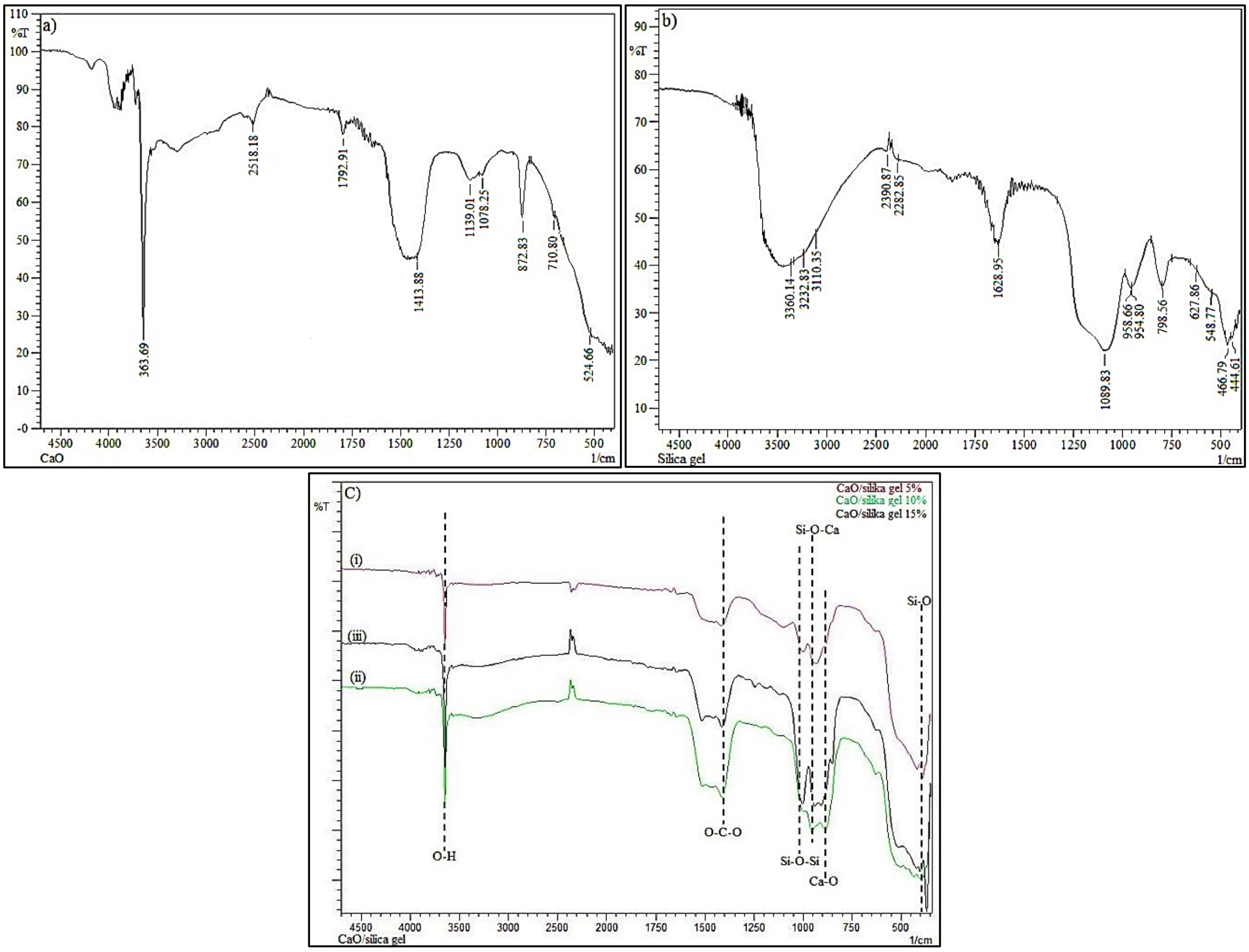

Figure 1. FTIR results of catalysts: a) CaO, b) Silica Gel, c) CaO/Silica Gel (i) 5%, (ii) 10%, (iii) 15%.

Waves 995 and 999 cm^{-1} are Si-O-Ca groups, from the formation of the Ca_2SiO_4 compound confirming that silica gel was successfully impregnated on CaO, in accordance with data reported [14] [15].

Catalyst Acidity Characterisation Results by Pyridine Adsorption Method

In addition to identifying the functional groups of the catalyst, FTIR can also be used for qualitative acidity analysis, on the catalyst surface using the pyridine adsorption method. Determination of acid sites on the catalyst surface is important to know its adsorption potential before it is used in certain applications. The acidic properties (Brønsted or Lewis) on the catalyst surface were determined after pyridine adsorption in the gas phase and analyzed using FTIR [30]. Lewis acid sites are acid sites formed through the coordination bonding of pyridine with the free electron pair of the N atom interacting with the center of the Lewis acid site on the sample. While Bronsted acid sites are formed through the transfer of H^+ ions from the Bronsted acidity $-OH^{2+}$ on the sample structure to pyridine, producing pyridinium ions [31].

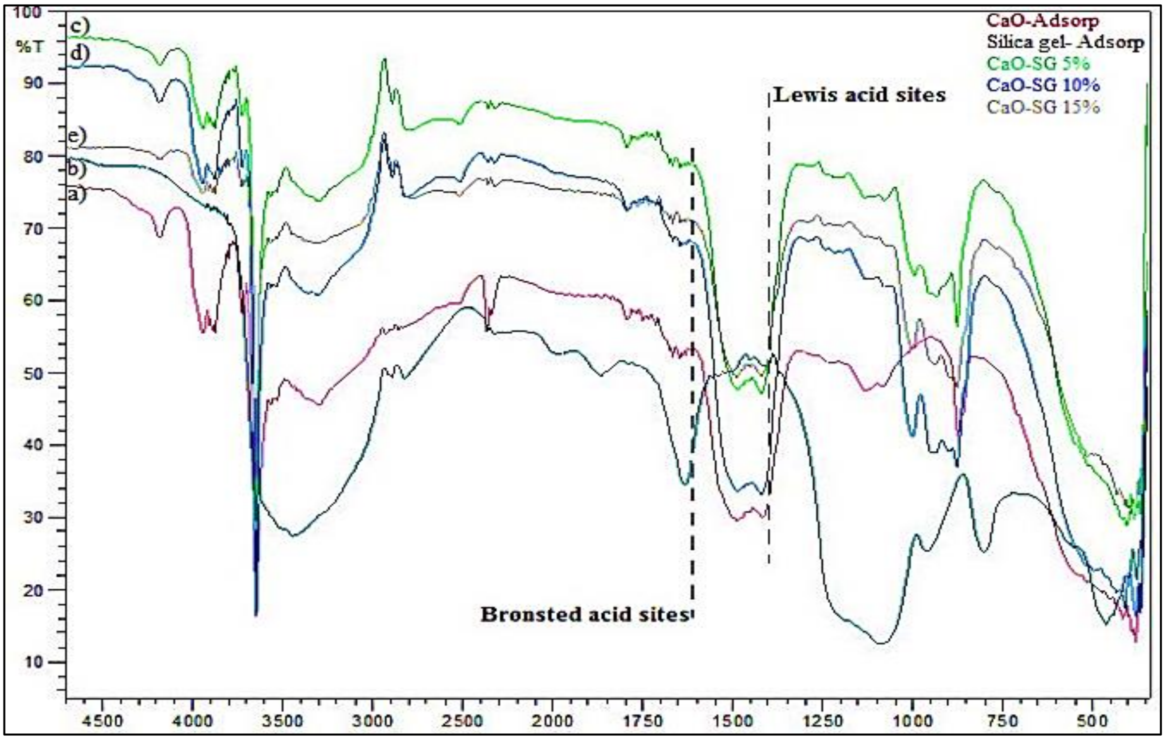

Figure 2. FTIR spectra of (a) CaO, (b) silica gel and CaO/Silica Gel (c) 5%, (d) 10%, (e) 15% which has absorbed pyridine.

Tabel 1. Result data of acidity determination by pyridine adsorption method

Sample	Weight of pyridine adsorbed (g)	Average acidity (mmol/g)
CaO	0	0
Silica gel	0.004	0.506
CaO/silica gel 5%	0.0023	0.291
CaO/silica gel 10%	0.003	0.367
CaO/silica gel 15%	0.0026	0.328

The absorption intensity of pyridine adsorption on Brønsted acid sites is around 1540 cm^{-1} and Lewis acid sites is 1450 cm^{-1} [32]. **Figure 2** shows that Lewis acid sites were detected on the CaO catalyst at a wave number of 1497 cm^{-1} but no peak was detected indicating the presence of bronsted acid sites. While in the silica gel sample, Lewis acid and bronsted acid sites were detected at wave numbers 1411 and 1631 cm^{-1}. **Figure 2. (c-d)** shows that Lewis acid sites for 5% and 10% CaO/silica gel catalysts are detected in the same region, namely 1418 and 1488 and at 1647 cm^{-1} absorption is a Brønsted acid site for CaO/silica gel 10%. The presence of pyridine absorption at 1425, 1495 cm^{-1} is Lewis acid sites and Brønsted acid sites at 1674 cm^{-1} for CaO/silica gel 15% the same results found by previous researchers [23], [33], [30]. In addition to pyridine vapor adsorption analysis, the FTIR technique can also be used to obtain information about hydroxyl groups at around 3600-3750 cm^{-1}, which is for Brønsted H^+ or basic OH^- sites [32]. The presence of strong Brønsted acid sites is indicated by the FTIR spectra at wave number 3641 cm^{-1} (-OH stretching vibrations).

Determining the number of acid sites using pyridine as the adsorbate base is based on the assumption that relatively large pyridine molecules can only be bound to the surface, so this measurement represents the number of acid sites on the surface [34]. **Table 1** shows the results of the acidity analysis of silica gel-impregnated CaO (5%, 10%, and 15%) by gravimetric adsorption of pyridine. From the data in **Table 1**, it can be seen that the acidity of the CaO catalyst which was initially 0 increased as the percentage of silica gel added increased from 0.291 to 0.367 mmol/g at 5% and 10% silica gel addition. Research reveals that increasing the amount of acid added will increase its acidity, which can increase catalytic activity [35]. However, the acidity decreased at 15% silica gel addition. As there is a possibility of aggregation or clumping of silica which reduces the effective surface area (**see Table 3**) and decreases the number of accessible acid sites. This can lead to an overall decrease in acidity even though the total amount of silica increases.

Results of Catalyst Basicity Characterization by Acidimetric Titration Method

The number of basic sites on a solid catalyst is referred to as the basicity of the catalyst, which is usually expressed in the number of moles of basic sites per unit weight of the solid. The basic strength of a solid catalyst surface refers to the ability of that surface to convert electrically adsorbed neutral acids into their conjugates [36]. The basicity value of the catalyst was determined using the acid-base titration method. **Table 2** displays the basicity values of the catalyst materials synthesized in this study.

Table 2. Result data of basicity determination by acid-base titration method.

Sample	basicity (mmol/g)
CaO	23.5
Silica gel	0
CaO/silica gel 5%	21.7
CaO/silica gel 10%	20.8
CaO/silica gel 15%	19.5

The basicity of CaO decreases as the amount of silica on the surface of CaO increases. Where the CaO basicity value is quite high at 23.5 mmol/g, research conducted by [19] is in accordance with these results. The basicity of the CaO catalyst decreased to 19.5 after the addition of 15% silica gel. The decrease in total basicity is due to the layer of Si compounds covering the active surface of CaO. Increasing the concentration of silica gel can reduce the alkalinity of the catalyst. Catalyst alkalinity is closely related to catalytic activity, because catalysts with low basic strength will reduce their catalytic effectiveness [14]. The addition of silica gel is quite beneficial because it can increase the surface area of CaO catalyst (**Table 3**), but the basicity value is still quite good.

Catalyst Surface Area Characterization Results

The Brunauer-Emmett-Teller (BET) method is used to measure the specific surface area of porous materials, such as solids and powders, based on the principle of gas adsorption. Adsorption isotherm measurements with a Surface Area Analyzer (SAA) instrument are required to determine the specific surface area. The surface area data, of CaO, silica gel as well as CaO/silica gel (5%, 10%, and 15%) are listed in **Table 3**. CaO catalyst from blood clam shell waste has a surface area of 1.032 m²/g, lower than commercial CaO of 3 m²/g [25] and close to the value of CaO from blood clam shells reported by Lani et al. (2020) of 1.36 m²/g [10]. This small surface area suggests the need for modification through impregnation of CaO on silica gel to increase catalyst activity by expanding the accessibility of active sites [15].

Tabel 3. Catalyst surface area result data.

Sample	Surface Area (m^2/g)
CaO	1.03
Silica gel	186.57
CaO/silica gel 5%	6.09
CaO/silica gel 10%	7.69
CaO/ silica gel 15%	5.86

After impregnation with silica gel from coconut coir ash (186.570 m²/g), the surface area of CaO increased to 6.097 m²/g (5% silica gel) and 7.695 m²/g (10% silica gel). This increase is due to the strong interaction between CaO and silica, which prevents sintering and stabilizes the CaO surface [37]. However, the addition of 15% silica gel caused a decrease in surface area, possibly due to non-optimal silica distribution or partial blockade of active sites [10]. A large specific surface area increases the chances of interaction between reactant molecules and catalyst active sites in the transesterification reaction [19]. The 10% CaO/silica gel catalyst has the highest surface area, indicating the best potential catalytic performance in the transesterification reaction.

Catalyst Activity Test Results on Biodiesel Formation

The amount of silica gel has a significant effect on the biodiesel yield produced using the modified CaO catalyst. In **Figure 3**, it can be seen that pure CaO catalyst and silica gel as the control produced biodiesel yields of 89.68% and 85.32%. The combination of CaO and silica gel yielded up to 96.71% at 10% silica gel addition. This is the highest yield when compared to the other variations. This condition is supported by the characteristics of the 10% CaO/silica gel catalyst. The acidity of the catalyst with 10% silica gel reached 0.367 mmol/g, while its basicity remained high at 20.8 mmol/g. This combination of acidity and basicity allows simultaneous activation of CPO and methanol, making the reaction faster and more efficient [10], [14]. The silanol groups (Si-OH) on silica gel contribute as acidity centers to overcome the FFA content in crude palm oil through esterification reactions, while the basic sites optimize triglyceride transesterification reactions [37].

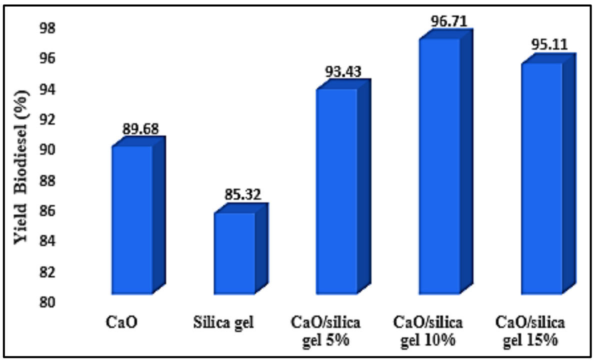

Figure 3. Biodiesel yield using catalysts, CaO, silica gel and CaO/silica gel (5%, 10% and 15%).

This study shows that the modification of CaO with silica gel effectively increases biodiesel yield compared to the use of pure CaO or silica gel alone. This occurs because the interaction between silica and the CaO surface during the activation process results in the formation of new compounds, such as Ca_2SiO_4, as shown by FTIR results confirming the presence of chemical interactions through bands associated with Si-O-Ca groups. The formation of these compounds indicates the filling of empty sites in the CaO structure, which increases the stability of the structure and improves its catalytic properties [2]. In addition, 10% CaO/silica gel catalyst, showed the highest surface area thus providing more active sites for reaction [20].

The addition of silica gel up to 15% caused a decrease in biodiesel yield to 95.11%. This decrease occurred because the excess silica covered the active sites on the CaO surface, reducing the catalyst activity [38]. The acidity, basicity, and surface area characteristics of 15% CaO/silica gel decreased, which can be caused by clumping on the catalyst surface [14]. These results indicate the importance of considering the right amount of silica gel to maximize biodiesel formation.

CONCLUSION

In this study, FTIR results confirmed the successful impregnation of silica gel from coconut coir waste with CaO from blood clam shell waste. The 10% CaO/silica gel catalyst showed high catalytic activity for the biodiesel formation reaction. With biodiesel yield reaching 96.71%, this result is influenced by different silica content, which can affect the surface condition of the catalyst. So it can be concluded that, the acidity and basicity of the catalyst affect the formation of biodiesel, and the biomass waste used can be a source of low-cost catalysts that are abundant in nature.

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