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# Biogasoline Production from Shallot Skin Waste with KOH-Clay Catalyst to Create Clean Energy

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A B S T R A C T

*Finding alternative fuels to replace fossil fuels has been made easier by the rise in the consumption of fuels like petrol and the fall in the production of national petroleum exploration activities. This research has been prompted using biomass as an alternative fuel. The primary raw material is shallot skin waste because it has enough lignocellulosic content to be used, one of which is to manufacture biogasoline by using the characteristics of petrol E10. A KOH-Clay catalyst is employed in a thermal and catalytic reaction to influence the reaction's pace. Starting with raw material preparation, conversion procedure, purification, and investigation of the physical properties of biogasoline at specific temperature fluctuations for an hour, the KOH-Clay catalyst is pretreated and characterised. It was discovered through this research that the montmorillonite KOH-Clay content was 5.73, indicating that the catalyst is hygroscopic and absorbs non-polar molecules, making it suitable for use as a catalyst with a pH of 6. As a result, at 60°C temperature circumstances, the best%yield results were attained of 35.025%. While the density value (0.950 gr/cm3) and colour (specific gravity, brownish yellow, and clear/bright) of the experimental results do not meet predetermined standards, they do when viewed from the viewpoint of physical parameters such as specific gravity (0.8358), oAPI biogasoline (37.794), and calorific value (18807.65 Btu/Ib). However, leftover shallot peels generally have the potential to be utilised as clean renewable energy.*

## INTRODUCTION

Increasing energy diversification activities through the development of the utilisation of new and renewable energy is one of the national energy development strategies. Though it is intended for the renewable energy mix to account for 23% of all national energy by 2025, as of the end of 2021 it only made up 11.5% [13]. Petroleum derived from fossil fuels is depleting, thus if new sources are not discovered soon, petroleum will run out. Fuel oil output peaked in 2015 at 825 barrels per day, but demand for fuel oil reached 1.628 barrels per day, causing Indonesia to import 350–500 barrels of oil per day [16]. Finding alternative fuels to replace petroleum-based energy sources has been made easier by the rise in the consumption of fuels like petrol and the fall in the production of national petroleum exploration activities.

Researchers have started to utilise biomass as an alternative fuel in recent years. The usage of biomass is meant to be a different strategy to cut back on the consumption of fossil fuels. The alternative fuel biogasoline is one such example. Because it is created from natural resources, biogasoline is a renewable energy source, thus there is no need to be concerned about finite resources. Shallot skin (Allium ascalonicum L.) is one of the materials that can be utilised as a raw material for biogasoline. According to the Central Statistics Agency (BPS), Indonesia will generate up to 2 million tonnes of shallots in 2021. The amount of shallot skin waste produced is directly correlated with the rate of shallot production. Shallot skin waste is typically simply discarded at this time or used as animal feed. Due to the relatively high lignocellulosic content of this waste, it can be used in a variety of ways, one of which is to create biogasoline by using the same principles as petrol E10. Thus, shallot skin waste *(Allium ascalonicum L)* will be used in this study to create biogasoline, which will then be known as BIO-ALASCA (Biogasoline) using natural clay (KOH-clay) as a catalyst.

**Table 1.** Contents of Shallot Skin Waste

| | |
|---|---|
| Cellulose | 41.10% |
| Hemicellulose | 16.20% |
| Lignin | 38.90% |

Source: Retnaningsih [19]

The thermal and catalytic reaction method involves heating biomass to a specific temperature and accelerating the reaction with a catalyst. Natural clay was chosen as a catalyst because of its substantial specific surface area and good thermal stability. The clay structure also has larger pores than zeolite, great thermal stability, a larger surface area, and good catalytic activity [7].

Natural clay is a crucial mineral since it serves as the primary component of many different products, including adsorbents, catalysts, photocatalysts, and ion exchange resins [11]. It is also utilised in the manufacture of ceramics.

Cristobalite (C), montmorillonite (M), anortite (A), and quartz (Q) are the four primary clay minerals. In contrast, the original clay's chemical make-up included Al2O3 (16.21%), SiO2 (55.04%), Fe2O3 (4%), Na2O (0.37%), CaO (1.39%), and MgO (1.11%). SiO2/Al2O3's mole ratio (mole ratio value) is 5.46, and the pH is 7. Due to the clay's mole ratio, montmorillonite can be seen chemically [3]. Additionally, Kagonbé et al. (2021) [10] studied natural clay minerals that contained metal oxides such as SiO2 (46–55%), Al2O3 (19–21%), and Fe2O3 (6.58–10.82%) based on prior findings.

The objective of this study is to produce biogasoline from shallot peels using a natural clay catalyst (KOH-clay) and compare the findings with the features of petrol that meet quality standards.

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## METHODS

The research was conducted in the Process Unit Laboratory. Department of Chemical Engineering, Bandung State Polytechnic.

### Pre-Treatment of Natural Clay Catalysts and Raw Materials

*Activation of Natural Clay into KOH- Clay*

In this activation approach, 50 g of clay are heated to 105 °C for 24 hours, after which 5% KOH/Clay (w/w) is added using the impregnation method to fill the pores with a metal salt solution at a concentration high enough to perform the loading. right [19]. At room temperature, KOH was dropped onto the clay, which was then agitated for three hours at 60$^{o}$C. The mixture's outcome is dried in an oven set at 105°C and dried outside. Stage The following procedure involves calcination at 300 °C for three hours, followed by cooling in a desiccator. KOH-Clay, the final activation sample, is now ready for characterisation.

### Characterization of montmorillonite on KOH-Clay

1. *Determination of Silica Yield*

Determination of Silica Yield refers on the gravimetric method (SNI 13-6668-2002)

$$\%SiO = \frac{m1-m2}{0{,}5\ gram} \times 100\% \qquad (1)$$

2. *Determination of Alumina Yield*

Determination of Alumina Yield refers to the gravimetric method (SNI 13-6668-2002).

$$\%Al_2O_3 = \frac{BM\ Al_2O_3}{BM\ 2AlPO_4} \times 100\% \qquad (2)$$

3. *Raw material preparation*

The skin of shallots is obtained from industrial waste. The first treatment is done with onion waste.

It is first cleaned with water to remove any debris that can stick and obstruct the subsequent conversion process. It is then diced into smaller pieces to facilitate processing. After that, mash till it turns into flour using a blender so as not to interfere with the subsequent conversion process. Next, slice it into smaller pieces so as to facilitate processing. Then use grinding to mash till it turns into flour.

### Biogasoline Production

Using catalytic reactions and a heat process, up to 10 g of already produced raw materials, 50 mL of methanol solvent, and a comparison catalyst that was mixed with raw materials one to one were then added to the reactor. Operating circumstances provide for the conversion to take place for an hour at temperatures of 60 °C, 100 °C, 140 °C, and 180 °C. To separate residues and products, filtering is the next step.

### Characterization of the Physical Properties of Biogasoline

1. *Density determination*

The pycnometer bottle (60 mL) is weighed at the beginning (m1). Place the sample in the pycnometer until it is full, then weigh it again (m2).

$$\rho = \frac{m2 - m1(gr)}{Vol.piknometer\ (mL)} \qquad (3)$$

2. *Determination of specific gravity*

The density of water is measured as density measurement. Calculate the specific gravity with formula

$$Spesific\ gravity = \frac{\rho sampel}{\rho air} \qquad (4)$$

Determination of $°\boldsymbol{API}$

$$°\mathrm{API} = \frac{141.5}{Sg} - 131.5 \qquad (5)$$

## RESULTS AND DISCUSSION

### KOH-Clay catalyst

Based on the results of the KOH-Clay catalyst characterisation test, which looked at the amount of montmorillonite and pH, the results are displayed in **Table 2.**

**Table 2.** Montmorillonite Content

| A1 (gr) | A2 (gr) | B1 (gr) | B2 (gr) |
|---|---|---|---|
| 0.3909 | 0.1324 | 5.3544 | 0.4749 |
| $\%\boldsymbol{SiO_2}$ | $\%Al_2O_3$ | $SiO_2/Al_2O_3$ | Mol $SiO_2/Al_2O_3$ (theoritical) |
| 51.7 | 15.337 | 5.73 | 4-6 |

Clay's degree of crystallinity can be determined by analysing its silica and alumina levels. The gravimetric approach was used to calculate the concentrations of Si and Al [15]. The level of stability of the catalyst is determined by this Si/Al ratio, thus note that. According to [17], where, for the parameters stated below. The catalyst in this study has a ratio of Si/Al of 5.73, indicating that it is hygroscopic and capable of absorbing nonpolar molecules, making it suitable for use as a catalyst. pH on the catalyst yields a value of 6. Whereas this illustration suggests that acid is a catalyst's characteristic. This is a substance that correlates to the esterification reaction used in the manufacture of biogasoline, which results in the formation of salicylic acid from the esterification reaction necessary for the breakdown of cellulose on shallot skin.

The level of clay's crystallinity can be determined by analysing its silica and alumina concentration. The results of the characterisation show an Al/Si value of 5.73, which falls within the excellent range. This value suggests a higher amount of acidity than research [3], which is larger than this value. An increase in the total cracking conversion rate can be achieved by increasing the Si/Al ratio of the catalyst (high Si concentration but low Al and acidity).

One of the standards for distinguishing montmorillonite minerals is this value. Montmorillonite, a clay mineral, has the benefit of a number of characteristics, including a large specific surface area and good thermal stability, which make it useful as an absorbent and catalytic support. These characteristics make the clay mineral montmorillonite suitable for use as a solid catalyst [6].

The montmorillonite crystal structure is directly related to the characteristic value. It is known that the crystal structure of montmorillonite is composed of sheets made up of 2:1 tetrahedral and octahedral layers. Silica makes up the tetrahedral layer, whereas aluminium oxide fills the octahedral layer. The conversion of biogasoline can be increased by increasing the montmorillonite content [3]. [14] added to this by stating that if the Si/Al ratio fell, the acidity would rise. This figure is less when compared to research from [6] than the study's Si/Al ratio of 12.13. This is possible because, in accordance with [6], high-temperature calcination will result in the release of protons from the -OH condensation between cations and clay, increasing the number of acid sites.

### Yield of biogasoline

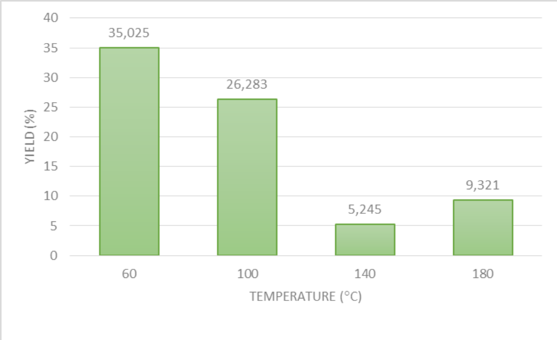


**Figure 1.** Effect of temperature on % produce biogasoline

Based on Figure 1, which shows the relationship between reaction temperature and the percentage yield achieved, it can be determined whether biogasoline production was minimal or dropped and then increased at temperatures of 60°C, 100°C, and 140°C. This is pertinent to the study done by Arifin (2018) because when the temperature rises throughout the conversion process, the trend for liquid carbon products decreases. Due to the greater process temperature and decline in conversion to liquid products, the final gas product will increase while the liquid product will drop. According to the findings of the experiment, the best conditions were attained at a temperature of 60 oC for 60 minutes, with a yield of 35.025%. The cellulose found in bagasse is broken down as a whole and catalysed will help bond the H-O fragments to make fuel. This occurs when the methanol will evaporate to the top until it wets the entire set of raw materials. As explained in the reaction below, this is done by doing the following in accordance with the principle of completion reactions:

$$R - COOH + CH3OH \rightarrow R - COOCH3 + H2O$$

However, in contrast to Herawati's (2018) research findings, which found that at 100 C for 1 hour, the yield of biogasoline from sugar cane dregs was 48.74%, this study found that the temperature and time at which biogasoline was created were lower, at 26.283%. This shows that bagasse has a higher lignocellulosic content than onion peel waste, which is why the yield was lower. Meanwhile, Netty Herawati (2018) displays the percentage of the results attained by 65.85% at a temperature of 180 C and 60 minutes of study duration. When compared to the experiment's findings under the identical circumstances, the output of biogasoline is 9.321%. This is due to deactivation brought on by undesired carbon build up on the catalyst's surface. The polymerization of aromatic molecules during the cracking event also contributes to the deactivation of this catalyst. Coke formation is a process that results from the complicated event-related reactions that take place during the uplift. Because of the carbon compound deposits inside the catalyst pores of KOH-Clay, the diffusion of reactants and products is therefore made more challenging. In addition, a sizable amount of alcohol helps the reaction move towards the proper product. The time component of this experiment has an impact on the outcomes since the interchange reaction between methanol molecules and biomass is a very sluggish procedure that determines the perfection of the whole reaction process. Because the tool employed at the time of the research was less efficient, raw materials produced by this research do not yet yield goods that are at their best.

## Biogasoline physical parameters

Based on the outcomes of the experiments, the liquid biogasoline products that were produced can be characterised as follows:

## Density

The density is seen in **Figure 2.** According to principle, density tends to fluctuate in relation to temperature; the greater the temperature, the lower the density will rise [8]. This holds true for both run 1 (60 ºC) and run 2, which decreases (100 ºC). The temperature has risen to 140 °C in the interim. Due to the fluctuating temperature factor and the excess solvent pressure, this is a rather serious situation. This is due to the theory behind it, which states that the density will increase as the pressure increases [1]. When compared to the density of premium petrol, the experimental density does not meet value because it is greater than the premium's cutoff point of 0.800–0.825 gr/mL [2]. The ratio of too little solvent (methanol) to dissolve dissolved compounds is another determining factor. This fits with Wilhelm Ostwald's molality theory because the final element is the existence of incoming water content.

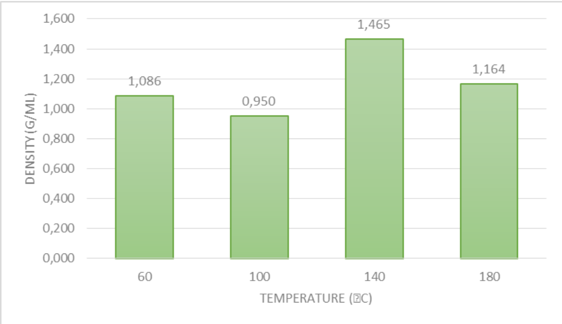


**Figure 2.** The effect of reaction temperature on the density value of biogasoline

## Specific gravity

Based on **Figure 3,** value the specific gravity parameter in the order of Run 3 (140°C), Run 4 (180°C), Run 1 (60°C), and Run 2 (100°C). This value will be inversely proportional to the acquired density. If compared to premium petrol with a specific gravity (60°F/60°F) value of 0.820–0.870 [2] sg, specifically in the 2nd Run (100ºC) of 0.8358. The result is determined by comparing the masses of numerous quantities of a substance at a particular temperature to the masses of pure volumes of water at the same temperature. In other words, a liquid product created falls within the category of lighter oil that resembles petrol. The value of sg increases between runs 1 (60°C) and 4 (180°C), with the largest increases occurring between runs 3 (140°C) and 4. Reaction temperature's impact on biogasoline density values [1] heavier than mass petrol, which results in less successfully obtained petrol quality because there is more contain residue.

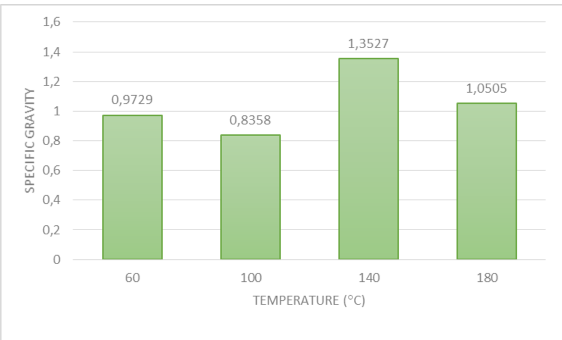


**Figure 3.** Effect of reaction temperature on value specific gravity of biogasoline

According to the idea, the °API value the lighter the proportion in the crude oils, the more gravity reveals [4]. According to Figure 4, the value of ºAPI in samples 1 and 4 belongs to the kind of oil with a very high proportion of aromatics, which has a negative impact on fuel quality and does not fit the characteristics of petrol [4]. Sample 3's value ºAPI is negative; the item indicated in the sample includes tar. This tar can break down into lighter hydrocarbons, methane, and other molecules. While in sample 2, the value was reached with a ºAPI value of 37.794 and an SG of 0.836, which is included in the oil criteria for medium light (medium light oil). This criterion can also be approached using the oil-light characteristic of petrol. Additionally, this product is produced already meeting the requirements for fuel oil with an SG value of 0.836.

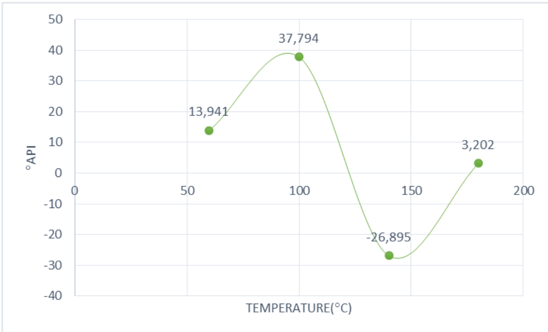


**Figure 4.** The effect of reaction temperature on the ºAPI value of biogasoline

## Calorific value

Figure 5 shows that the best calorific value is getting close to the petrol calorific value found in samples 1 and 2. This is due to the calorific value of fuel oil, which according to theory typically varies from 18,300 to 19,800 Btu/lb or 10,160 to 11,000 kcal/kg [10].

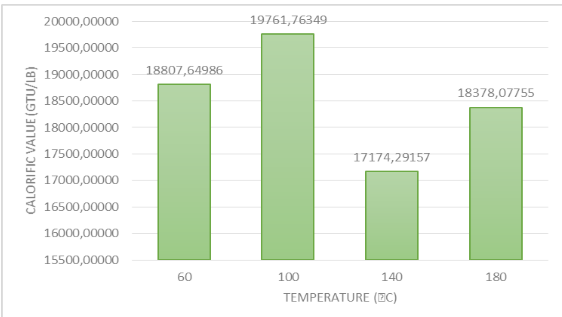


**Figure 5.** The effect of reaction temperature on the calorific value of biogasoline

## Color

The findings of the experimental

colour test are tawny, as shown in Figure 6. According to the Letter Decree of the Director General of Oil and Gas No. 3674 K/72/DJM/ 2006 dated 17 March 2006, the colour of this petrol more closely complies with the petrol colour standards on the type of the specifications 91 petrol. The skin's natural yellow colour is to blame. Flavonoids, which give shallots their characteristic yellow colour, have excellent antioxidant properties thanks to their hydroxyl groups. In addition, cyanidin-type anthocyanins found in red onion skin contribute to the vegetable's red or purple colour, and flavonols like quercetin give it a brown hue [18]. However, the quality of the petrol is not determined by its colour.

**Figure 6.** Visual appearance of biogasoline products

According to SNI 3506:2017, the physical properties of biogasoline in trials are close to the value at standard petrol grade. According to the table below, the trial's best outcomes (60°C, 1 hour) are as follows:

**Table 3.** Physical parameters of biogasoline

| Parameters | Value | |
|---|---|---|
| Density (gr/mL) | 0.950 | Approach |
| *Spesific gravity* (60°F) | 0.8358 | Fulfil |
| °*API* | 37.794 | Fulfil |
| Color | brownish yellow | Approach |
| Visual | clear and bright | Approach |

## CONCLUSION

Thermal technique and catalytic reaction yielded a 35.025% yield of biogasoline from leather waste material in an optimum condition (60°C, 1 hour) with a montmorillonite content of 5.73. According to SNI 3506:2017, the physical properties of biogasoline that condition are close to the value at standard petrol grade.


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