

# DESULFURIZATION OF WASTE ENGINE OIL ASSISTED BY LOW-RANK COAL AS ACTIVATED CARBON USING PYROLYSIS DISTILLATION METHOD

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## ABSTRACT

Waste engine oil is a component that is harmful to the environment. One of the dangerous components of waste engine oil is sulfur content. One way to recycle waste engine oil is to convert waste engine oil into alternative liquid fuels such as diesel. The pyrolysis distillation process assisted by activated carbon from low-rank coal as an adsorbent is expected to provide a solution for recycling waste engine oil into a base fuel like diesel. Low-rank coal has less economic value, therefore it needs to be utilized to produce a more economically valuable product, namely activated carbon. In this study, activated carbon can act as a sulfur-absorbing medium and increase pyrolysis conversion. Based on the research conducted, the adsorption capacity based on the iodine number parameter before activation was 103.145 mg/g and increased after activation to 1163.513 mg/g. The pyrolysis distillation process was carried out at various temperatures of 300°C – 500°C by adding 10% coal-activated carbon from engine oil waste. The best pyrolysis conditions were obtained at 350°C with a yield content of 75% and a percent sulfur removal of 73%. The use of activated carbon from low-rank coal has a very significant impact on increasing the amount of yield and maximum sulfur removal compared to without the assisted by coal activated carbon.

**Keywords:** Activated Carbon, Adsorption, Desulfurization, Low-Rank Coal, Pyrolysis, Waste Engine Oil.

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## INTRODUCTION

Energy needs are increasing every year, especially in the transportation industry. This is certainly directly proportional to the amount of engine oil used. Engine oil has a lifetime when used as a lubricant in motor vehicle engines. Engine oil will eventually damage its lubricating quality and eventually become useless and only become waste that damages the environment. Waste engine oil (WEO) is a hazardous and toxic material, containing several carcinogenic combustion residues, deposits, and heavy metals that are acidic and corrosive.<sup>1</sup> One of the bad factors of engine oil that has been used is the high value of sulfur contained in waste engine oil so one form of processing is to reduce sulfur content.<sup>2,3</sup> The sulfur contained in waste engine oil is not refrigerated because it can cause several problems such as corrosion of pipes, purification equipment, pumps, and catalytic poisoning converters used in automotive engines.<sup>4</sup> During the combustion period, sulfur compounds are converted mainly to sulfur dioxide (SO<sub>2</sub>), which is a major cause of air pollution and acid rain.<sup>5</sup> By using adsorbents such as activated carbon, clay minerals are known to be able to remove nitrogen compounds, sulfur, and several other metals. The manufacture of activated carbon can be done by chemical and physical activation techniques, or a combination of both, but the best conditions for activation are in the temperature range of (600-800)<sup>0</sup>C, the results show that under these conditions the activated surface of the carbon will increase significantly so that the carbon will have large porosity.<sup>6</sup> The distillation pyrolysis method will produce residue and condensation. Condensate is extracted as a result which can be used as an alternative to basic fuels such as diesel.<sup>7</sup> The amount of carbon in the adsorbent not only affects the sulfur adsorption process but can also increase the yield of pyrolysis. Pyrolysis is

conversion technology that breaks the carbon chain which becomes shorter and simpler with the help of thermals or catalysts with a very limited amount of air.<sup>8</sup> The pyrolysis process can take place at moderate temperature levels for example 300°C and 450°C or more than that.<sup>9</sup> This study aims to reduce the sulfur content contained in waste engine oil with the help of activated carbon from low-rank coal using the pyrolysis distillation method.

## EXPERIMENTAL

### Material and Methods

The raw material in the form of engine oil waste (WEO) is obtained from PT. Astra Honda Samarinda which comes from the engine oil waste collection. The engine oil waste is then allowed to stand and filtered to obtain cleaner engine oil waste. The raw material in the form of low-rank coal is obtained from PT. Tribakti Inspektama Samarinda comes from feedstock with low-grade specifications, the calorific value of its low-rank coal is 3800 Cal. The chemical as a coal activator is a mixture of phosphoric acid and sodium phosphate with a ratio of 1:1, with a concentration of 2.5 Molar for each chemical.

### Activation Low-Rank Coal

Initially, low-rank coal is crushed into smaller sizes and then carbonized to make low-rank coal converted into the carbon-rich residue. The carbonization process was carried out at 600°C for 3 hours. after the carbonization stage is complete, the coal is filtered to obtain a size of +100-120 mesh, then 1 kg of coal is immersed in a mixture of chemical solutions, namely H<sub>3</sub>PO<sub>4</sub> - NaHCO<sub>3</sub>, with a total volume of the solution of 2 liters, the soaking process lasts for 8 hours. Then, the coal is physically activated for 1.5 hours at 800°C using furnaces. After the activation is complete, the next step is to test the iodine number to determine the adsorption ability. The formula used to determine the iodine number is as follows.

$$\text{Adsorption of iodine number} = \frac{10 - \left( \frac{V \text{ Na}_2\text{S}_2\text{O}_3 \times N \text{ Na}_2\text{S}_2\text{O}_3}{N \text{ iod}} \right)}{\text{Coal activated carbon}} \times BM \text{ iod} \times fp \times N \text{ iod}$$

Where,

BM = Molecular weight (g/mol)

N = Normality Concentration (greek/L)

fp = Dilution factor

### Pyrolysis Waste Engine Oil

The pyrolysis process is carried out in 2 ways, the first is pyrolysis without using coal-activated carbon, and the second is mixing 10% coal-activated carbon in waste engine oil in the pyrolysis distillation unit. Both methods were carried out to determine whether or not there was a significant effect after the addition of coal-activated carbon. Coal-activated carbon will act as an absorbent medium during the pyrolysis period of waste engine oil. The pyrolysis temperature was varied to obtain the optimum temperature based on the parameters of high distillate volume and low amount of sulfur expressed in % Yield and % Sulfur removal. The yield calculation follows the equation:

$$\text{Yield (\%)} = \frac{V_d \text{ (ml)}}{V_o \text{ (ml)}} \times 100\%$$

And the removal of sulfur followed by calculation as follows:

$$(\%) \text{Removal Sulfur} = \frac{([S]_o - [S]) \text{ (ppm)}}{[S]_o \text{ (ppm)}} \times 100\%$$

Where,

V<sub>o</sub> = Initial Volume

V<sub>d</sub> = Distillate Volume (mL)

[S]<sub>o</sub> = Initial sulfur concentration (ppm)

[S] = Final Sulfur concentration (ppm)

### Sulfur Detection

To detect sulfur we can use the ICP analysis tool. The ICP stands for Inductively Coupled Plasma is a laboratory tool that serves to analyze metals in solution. ICP belongs to the atomic spectrum, which is a technique used to detect traces of metals in samples and to obtain the characteristics of elements that emit

certain waves. This tool uses the emission spectrophotometer method for testing the sulfur content using the ICP tool, starting with the nebulization process, which is the process of converting liquid into aerosol then followed by atomization where gas bonds are broken into atoms.

## RESULTS AND DISCUSSION

It is known that engine oil waste contains hazardous components, one of which is the presence of sulfur. By means of pyrolysis distillation, the waste engine oil can be converted into base fuel, resembling diesel, but it is important to remove sulfur because it can pollute the environment. Therefore, this research intends to reduce the sulfur content using pyrolysis assisted with activated carbon made from low-rank coal. Low-rank coal is used because it has no economic value, but by activating low-rank coal it can be converted into activated carbon which can play a role in helping sulfur adsorption and increasing the conversion of engine oil waste into base fuel through pyrolysis distillation. The study started with the trial of the adsorption of low-rank coal that had been previously activated. The next stage is the pyrolysis stage of waste engine oil using a pyrolysis distillation tool, waste engine oil is pyrolysis with a temperature variation of (300-500)<sup>0</sup>C and then inserted into the pyrolysis distillation apparatus. The low-rank coal is also added to the distillation apparatus with a ratio of 10% to waste engine oil. To make low-rank coal into activated carbon, one of the important parameters is iodine number or iodine adsorption, iodine number is a typical method to detect carbon adsorption, and its capacity and value are directly related to the surface area. The amount of iodine is 500-1200 mg I<sub>2</sub>/g, which is equivalent to a surface area of 900-1100 m<sup>2</sup>/g. Since adsorption is a surface phenomenon, the larger the specific surface area, the greater the adsorption capacity. The activation mechanism, particle size, and pore structure also affect the adsorption capacity of activated carbon.<sup>10</sup> Figure -1(a) is low-rank coal that was not activated, and Fig.-1(b) is the result obtained after low-rank coal is activated. There is a change in color from brown in Fig.-1(a) to solid black in Fig.-1(b), and the adsorption of iodine number before activation is 103.145 mg/g to be increased after activation is 1163.513 mg/g. Then Fig.-2 is the result of the pyrolysis process of waste engine oil using a pyrolysis distillation tool. Figure-2(a) is the result of the pyrolysis process without the addition of low-rank coal as activated carbon, in Fig.-2(b) is the result of pyrolysis with the addition of low-rank coal as activated carbon, the composition of the feed in the pyrolysis distillation apparatus is 350 mL of waste engine oil, and activated low-rank coal is 10% of waste engine oil.

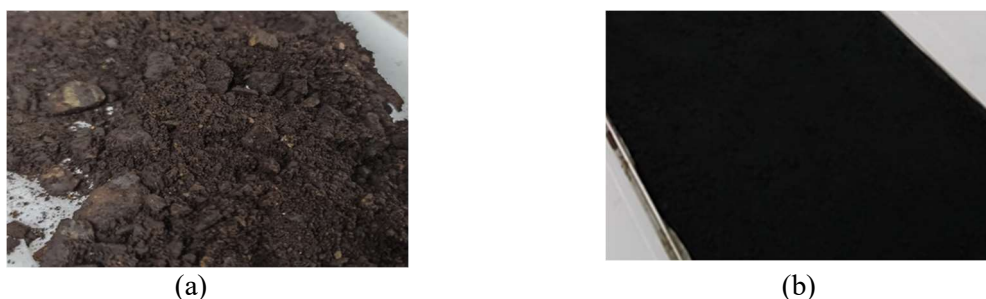
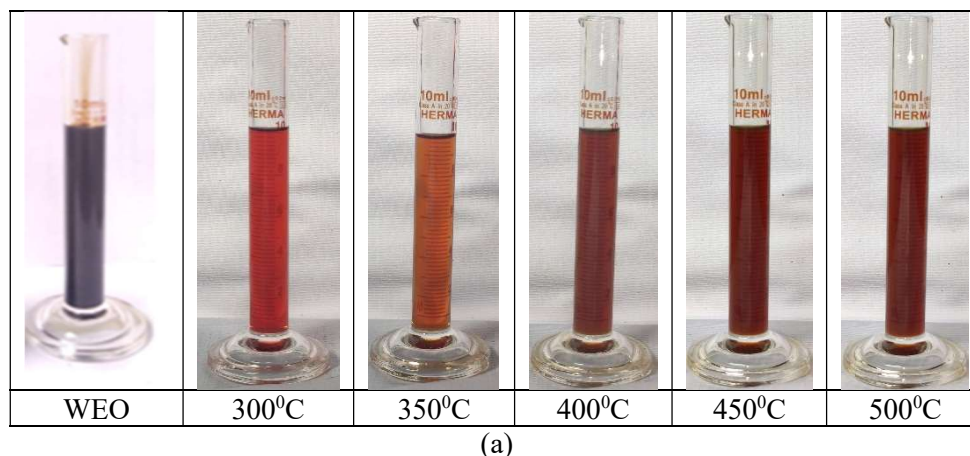


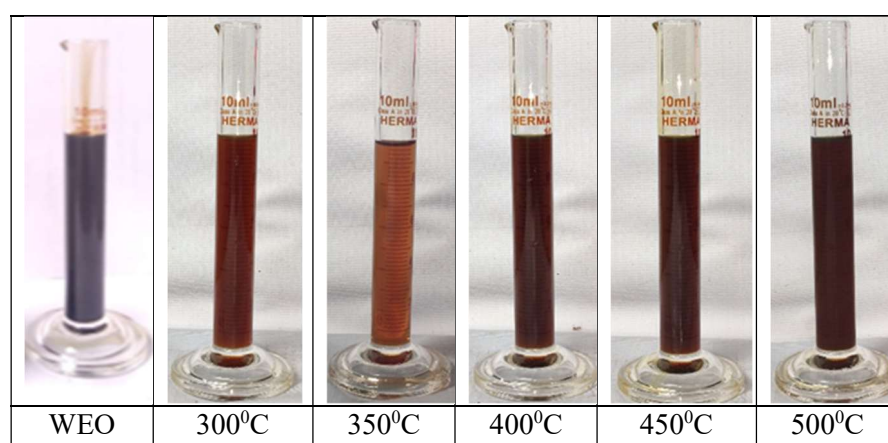
Fig.-1: Comparison Coal of Low-Rank Coal Initial (a); Low-Rank Coal of Activated (b)

The pyrolysis distillation process has an effect on the distillate results obtained. It was found that the use of low-rank coal activated as an adsorbent medium, visually shows that the results obtained are clearer in color than without the addition of low-rank coal activated, as shown in Fig.-2 below.

The best pyrolysis results were found at a temperature of 350<sup>0</sup>C either using an adsorbent or not using an adsorbent as shown in Fig.-2 above, but the best results between the two found in Fig.-2 are in Fig.-2(a). This is based on the measurement data of sulfur concentration and rate condensation gain shown in the table below (Table-1). The sulfur content contained in used engine oil will become an aggressive gas during combustion or processing. In general, sulfur is difficult to remove, this can also be proven in this study, where the sulfur content, although reduced during the pyrolysis process, is not significant, but after the addition of activated carbon, the data shows that the reduction in sulfur content is better than without active carbon. Desulfurization of waste engine oil with the help of activated carbon shows that during the pyrolysis period, the amount of sulfur is significantly reduced and the yield increases from the previous state. Pyrolysis will produce gas that condenses into light fraction hydrocarbons.<sup>11</sup>



(a)



(b)

Fig.-2: Comparison of WEO with Distillation Pyrolysis Results at Various Temperature Variations of Pyrolysis Distillate using Coal (a); Pyrolysis Distillate without using Coal-Activated Carbon (b)

The data shows that the condensation rate obtained the higher the pyrolysis temperature, the condensation rate will also increase, but decreases after the temperature exceeds 400°C, at the same time the sulfur concentration will also increase. The lowest sulfur concentration with a high condensation rate was found at 350°C using coal-activated carbon as an adsorbent. however, when compared to the absence of activated carbon, the condensation rate obtained is smaller, this indicates that the presence of the adsorbent affects the optimum temperature of the reaction, which causes the time required for pyrolysis to reach a constant state slower, but the yield obtained is higher, as shown in (Table-1).

Table-1: The Effect of Pyrolysis without and using Coal Activated Carbon to Rate Condensation and the Sulfur Concentration

| The initial volume of WEO (mL) | Activated carbon of coal (g) | Temp (°C) | The volume of distillat, Vd (mL) | Time, t (minute) | Condensation rate (Vd/t = L/min) | Initial Sulfur (ppm) | Final Sulfur (ppm) |
|--------------------------------|------------------------------|-----------|----------------------------------|------------------|----------------------------------|----------------------|--------------------|
| 350                            | 3.5                          | 300       | 197                              | 643              | 0.306                            | 3244                 | 659                |
|                                |                              | 350       | 263                              | 273              | 0.963                            |                      | 875                |
|                                |                              | 400       | 290                              | 64               | 4.531                            |                      | 897                |
|                                |                              | 450       | 283                              | 67               | 4.228                            |                      | 896                |
|                                |                              | 500       | 277                              | 70               | 3.957                            |                      | 895                |
|                                |                              | 300       | 105                              | 200              | 0.525                            |                      | 1569               |
|                                |                              | 350       | 152                              | 96               | 1.583                            |                      | 1311               |

|     |   |     |     |    |       |      |     |
|-----|---|-----|-----|----|-------|------|-----|
| 350 | 0 | 400 | 205 | 31 | 6.613 | 3244 | 939 |
|     |   | 450 | 229 | 37 | 6.189 |      | 969 |
|     |   | 500 | 260 | 44 | 5.909 |      | 998 |

In the pyrolysis distillation process using an adsorbent, it has a great influence on the distillate results obtained from both yield and sulfur concentration than without an adsorbent shows that the optimum % sulfur removal was found at a temperature of 300°C with the addition of an adsorbent and the yield was found at a temperature of 400°C using an adsorbent, this is certainly very reasonable because the presence of coal-activated carbon as an adsorbent is capable of not only adsorbing sulfur but also can help cracking events resulting in easier adsorbent binding sulfur and breaking down carbon bonds into simpler ones so that the amount of yield obtained increases, in this case, the presence of coal activated carbon in addition to functioning as an adsorbent can also act as a heterogeneous catalyst. The reaction temperature used plays a role in obtaining a higher yield conversion amount, this activity is of course supported by the presence of activated carbon. Activated carbon which was previously used as an adsorbent can act as a catalyst in the pyrolysis process with a dual function, namely cracking heavy hydrocarbons and hydrogenating unsaturated waste engine oil.<sup>12</sup> An indication found in the acquisition of a high yield higher if using activated carbon as shown below (Fig.-3 and Fig.-4).

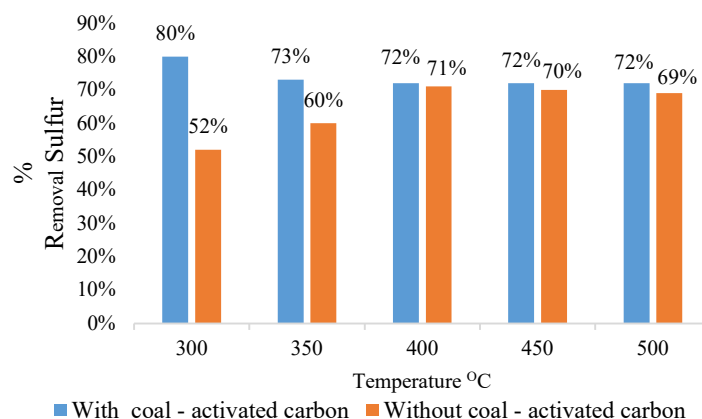


Fig.-3: Removal of Sulfur from Pyrolysis Distillation using Adsorbent and Without Adsorbent

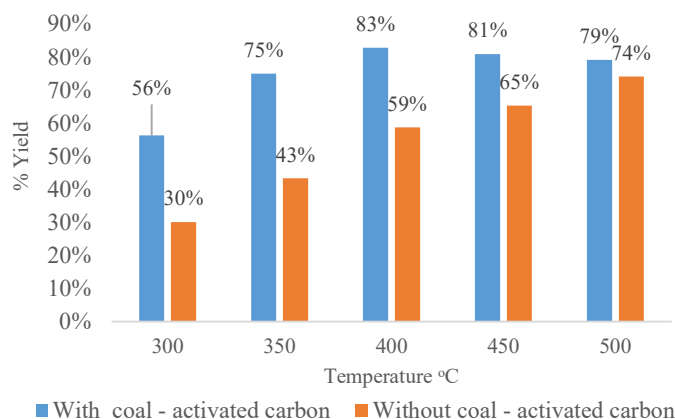


Fig.-4: The Yield of Distillation Results of Pyrolysis Using and Without of Coal-Activated Carbon

## CONCLUSION

The results showed that there was a significant effect on the desulfurization process with the addition of coal-activated carbon. It was found that a temperature of 350°C can represent the optimum conditions of the parameters of color, sulfur removal, and yield.

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### CONFLICT OF INTERESTS

We as the authors hereby declare that there is no conflict of interest in writing and publishing this article.

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All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the faculty authors can be verified from their ORCID ids, given below:

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