



## **Potential Crude glycerol from Transesterification WCO (Waste Cooking Oil) as an anti-fungisida Spray**

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**Abstract :** Waste cooking oil (WCO) can be used as an alternative raw material of biodiesel production with glycerol as a byproduct. Crude glycerol generated should be purified first. Glycerol purification process is done in two stages, namely saponification and acidification process. In the process of saponification strong alkali KOH is added to form the soap and then continued the acidification process with variation of pH 9.7; 9.6; 8.5; 4.7; 4.4 and the concentration of H<sub>3</sub>PO<sub>4</sub> 65%, 75%, 85%. This purification process produces byproducts that K<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> salt. Both the salt is being used as an anti-fungi spray (fungicide), particularly for powdery mildew on plants mango. In this study, the optimum concentration of phosphoric acid in the purification process of glycerol is 85% phosphoric acid concentration and pH optimum in the process of acidification on the purification of glycerol is pH 9.7 with K<sub>2</sub>HPO<sub>4</sub> salts results and pH 4.7 with salt results KH<sub>2</sub>PO<sub>4</sub>. The melting point of each of the salt is 464 ° C and 252 ° C. As for the anti-fungi spray, K<sub>2</sub>HPO<sub>4</sub> most effective in reducing the powdery mildew of mango plant with an efficiency of 13%.

**Keywords :** waste cooking oil, crude glycerol, saponification, acidification, anti-fungi spray.

### **Introduction**

Waste cooking oil is the oil derived from oil frying foodstuff from several restaurants<sup>1,2</sup>. Waste cooking oil has always been considered a waste by some communities. The number of exploration conducted to find alternative energy, making the used cooking oil starts to peep utilization. One is as a feedstock for biodiesel production<sup>3,4,5,6</sup>. In the manufacture of biodiesel or waste cooking oil transesterification reaction byproducts generated in the form of glycerol with a low level of purity, which is commonly referred to as crude glycerol. The amount of glycerol produced as much as 10-15% of its production capacity with a purity level of glycerol ranges between 40-50% because they contain components of water and other impurities. In Indonesia, currently has a production capacity of biodiesel industry reached 4 million KL/year, it will produce crude glycerol around 400000-600000 tons/year. Increased production capacity biodiesel industry will lead to increased production of crude glycerol, so if it is not accompanied by advances in technology utilization and expansion of the market, the availability of excess glycerol will certainly make the price of glycerol in the world market into fall. Glycerol conversion into other products should be made to avoid any environmental concerns due to the waste glycerol, as well as improve the efficiency of the biodiesel industry<sup>2</sup>. Anti-fungi spray them is one useful product obtained from the purification of crude glycerol.

Javani, A. (2012) conducted a study by varying the molar ratio of KOH to esters are 0.25, 0.5, 0.75, 1, 1.2, 1.4 and 1.6 as well as free fatty acid concentrations at 65% , 80%, 87%, 95.3%, 99.4% 99.51% and 99.58% in the production of high quality potassium phosphate through the purification step of glycerol, obtained purity potassium phosphate namely  $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$  with 98% purity and 98 , 05%. In his research using the acidification process with the addition of 85% phosphoric acid and pH in the acidification process 4.67 and 9.67.

Research Yildirm, Onogur E. & Irshad M. (2002) investigate about the efficacy of some of the natural chemicals against powdery mildew (*Uncinula Necator*) on vines that  $\text{KH}_2\text{PO}_4$  has the effect of undermining the hyphae of fungi pathogens and depreciation conidia and conidiophores mold, mildew and penetrate cells disrupt the balance of potassium and cause rupture of walls of conidia. Additionally  $\text{KH}_2\text{PO}_4$  could provide systemic resistance to fungi by forming insoluble compounds crystallize with  $\text{Ca}^{2+}$  in the cell healthy plants.

Research Azza M. Azmy K. (2014) regarding the control of powdery mildew on mango with some salt, biofungicide AQ10 growth regulator and fungicide compared with an exterminator in Egypt showed that  $\text{K}_2\text{HPO}_4$  a salt more effective. This proves there is a reduction mango powdery mildew on plants by inhibiting the development of further damage to the mango and active in addressing the effects of the fungus. The results obtained are  $\text{K}_2\text{HPO}_4$  efficiency of 82% and produced 82.1 kg of fruits/tree. Rapid absorption of phosphate by plant tissue and extreme mobility of phosphate in the network, as well as low cost, low toxicity to animals, the impact on the environment is safe and the nutritional value of phosphate, making phosphate as spraying the leaves are ideal for the control of plant diseases.

Based on the above, this study was developed to use crude glycerol from the transesterification WCO (Waste Cooking Oil) that will serve as an anti-fungi spray on plants of mango with variations in the concentration of phosphoric acid and pH in the acidification process.

Variations in the concentration of phosphoric acid in this study were taken from the concentration of phosphoric acid used in the main study Javani A. is 85%. Where in concentration 85%, Javani secured  $\text{K}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$  salt crystals with high purity. From it, we want to find the optimum concentration of phosphoric acid with variation phosphoric acid concentration of 65%, 75% and 85% in the manufacture of anti-fungi spray material is the same as Javani of  $\text{K}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$  salt crystals.

Variations in pH in the acidification process in this study were taken from the formation of salt crystals pH conditions  $\text{K}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$  in major journals Javani A. and based on the data of each MSDS salt  $\text{K}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$ . The main journal Javani A. using pH 9.67 and pH 4.67. While the data MSDS,  $\text{K}_2\text{HPO}_4$  salt crystals formed in the pH range from 8.5 to 9.6 and  $\text{KH}_2\text{PO}_4$  salt crystals formed in the range from 4.1 to 4.5. From it, we want to find the pH at optimum acidification process with the variation of pH 9.7, 9.6, 8.7, 4.7 and 4.4 in the manufacture of anti-fungi spray where the pH determines the best condition of the formation of salt crystals  $\text{K}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$  using the acidification process.

Acidification processes (pickling) aims to outline the soap into acid glycerol fatty acid that will easily separate itself so it's easier to be purified. Parameters were made include the determination of the melting point and test% efficiency effectiveness of anti-fungai spray.

## Experimental

### Making Biodiesel and Crude Glycerol

- Filtering waste cooking oil with a filter paper and heated to over 110°C temperature to remove the water content of the waste cooking oil then cooled to a temperature of 60°C.
- Mixing methanol and 1% KOH catalyst of the mass of oil, then heated to 60 ° C, with a mole ratio of methanol and oil is 6: 1
- Mixing of waste cooking oil and a mixture of methanol-KOH in a three-neck flask, and refluxed with stirring speed of 500 rpm for 60 minutes to produce a crude methyl ester and glycerol (main product).

**Saponification Process**

- Considering crude glyserol as much as 50 ounces and was added to the glass batch reactor
- Adding KOH with a molar ratio of 1.6: 1 and mixed with stirring 500 rpm
- Keep mixing temperature at 25°C temperature and atmospheric pressure for 60 minutes and then obtained crude glyserol saponification results that will be used for the acidification process.

**Acidification Process**

- Preparing crude saponification glyserol results
- Adding a phosphoric acid with a certain concentration during mixing until the pH has been ditentukan
- Continue stirring for 15 minutes and then left until a precipitate is formed and then filtered with filter paper to obtain a powder potassium phosphate

**Manufacture of crystalline potassium phosphate Anti Fungi**

- Prepare a potassium phosphate deposition process results acidification and washed with IPA (Isoprophyl alcohol)
- Heating the mixture at a temperature 90°C for 60 minutes to remove the IPA and sediment will be crystallized
- Obtained crystals of potassium phosphate which is used as an anti-fungi spray..

**Making anti-fungi spray**

- Crystal K<sub>2</sub>HPO<sub>4</sub> at pH acidification process and optimum concentration of phosphoric acid obtained was made in a concentration of 25 mM (435 g/100 liters of water)
- Crystal KH<sub>2</sub>PO<sub>4</sub> at pH asdifikasi process and optimum concentration of phosphoric acid obtained was made in a concentration of 40 mM (544 g / 100 liters of water)
- Add Triton (B 1956) in each of K<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> mixture of 25 mL / 100 liters of water
- Spray anti-fungi analyzed and tested

**Testing Melting Point Crystals**

1 g sample is inserted within the capillary, then compacting it by means menjatuh-drop the capillary. Putting a capillary tube at the heating part in deciding the melting point apparatus. Further decisive tool turned on the heater melting point. Then set the heating to set the temperature control knob coarse and fine temperature control. Then observe samples diselediki, then press the button display when the sample melts. Read the temperature or the melting point indicated on the tool. (Suleman, Nita, 2012)

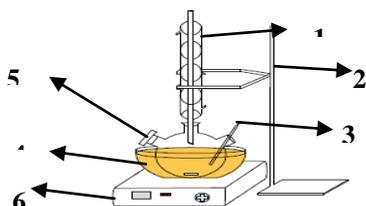
**Test% Effectiveness Efficiency Spray Anti-Fungi <sup>7</sup>**

Used a mixture of K<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> mixture and spraying only water on a controlled variable. Spraying is applied at intervals of 2 days from watering plants

$$\% \text{ Efficiency} = \frac{\% \text{ infection control} - \% \text{ experimental infection}}{\% \text{ infection control}}$$

**Equipment description**

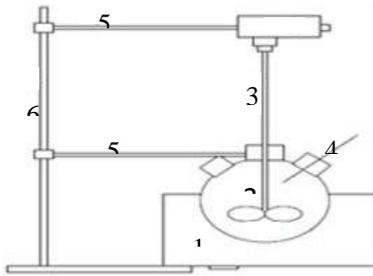
Making Biodiesel and Results Side *Crude Gliserol*



Explanation :	
1. Condenser	4. Container and heating medium
2. Support	5. Three neck flask
3. Termometer	6. Hot plate magnetic stirrer

**Figure 1. Transesterification reactor**

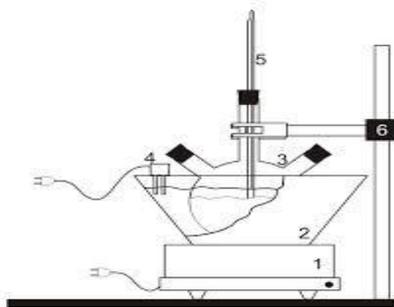
**Proses Saponifikasi**



Explanation :	
1. Water bath	4. Termometer
2. Batch glass reactor	5. Clamp
3. Mixer	6. Support

**Figure 2. Batch glass reactor**

**Asidification Process and production of crystalline potassium phosphate**



Explanation :	
1. Hotplate magnetic stirrer	4. Heater
2. Container and heating medium	5. Termometer
3. Three neck flask	6. Support

**Figure 3. Acidification reactor**

**Result and Discussion**

Results of analysis of crude glycerol in the manufacture of biodiesel from waste cooking oil

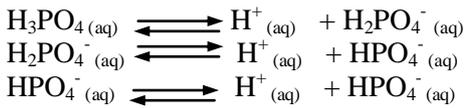
**Table 1. Analysis results Crude Glicerol**

Property	Value
pH	13,82
KOH	8,42 %
Soap (in K-linoleat)	19,23 %
Ash	17 %

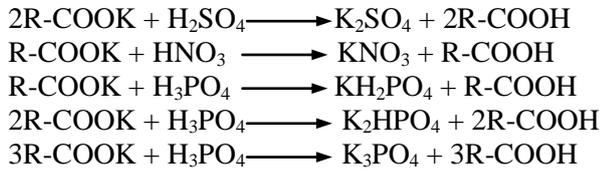
pH tests show that glycerol byproduct of biodiesel used cooking oil having a pH of 13.82. The degree of acidity (pH) glycerol showed alkaline nature. This is due to the content of KOH and potassium soap. The content of KOH in glycerol derived from potassium base catalyst used in transesterikasi. The remaining catalyst along with other byproducts are glycerol. The content of potassium soaps derived from the saponification reaction of the ester and KOH.

**Salt  $K_2HPO_4$  and Salt  $KH_2PO_4$**

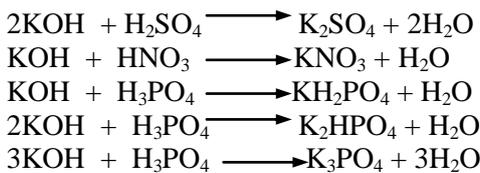
Phosphoric acid is a weak acid polyprotic (having three hydrogen atoms can be ionized). Ionization of hydrogen atoms in the phosphoric acid is shown in Figure 4. The salt of phosphoric acid and alkaline K can be formed by replacing one, two, or three  $H^+$  ions with one, two, or three of  $K^+$  ions to produce a salt  $KH_2PO_4$ ,  $K_2HPO_4$ , or  $K_3PO_4$  (image 5 ). In alkaline neutralization and soap solution K, a potassium salt formed from the neutralization reaction of alkaline and soap K with mineral acids as shown in Figure 5 and Figure 6.



**Figure 4. Ionization phosphoric acid**



**Figure 5. Reaksi Pemecahan Sabun**



**Figure 6. Alkaline neutralization reaction of potassium**

Neutralization of alkaline and soap solution produces salt, water, and free fatty acids. Salt solubility in glycerol and methanol is very low. Many salt settles in a layer of glycerol. Water and residual methanol is more soluble in glycerol layer. Free fatty acids are not soluble in glycerol and form a separate layer on top of a layer of glycerol. Soap can cause the emulsion of glycerol and free fatty acids that are difficult to separate. The separation between the layers of glycerol and free fatty acids is complete after all the soap and the salt is broken down into free fatty acids. The use of KOH as base catalyst in the transesterification of triglycerides and methanol leaving the majority of bases potassium in glycerol. Residual base catalyst potassium contained in the glycerol byproduct of biodiesel transesterification of vegetable oil with potassium base catalyst is neutralized with a mineral acid into a potassium salt. This process is part of the purification of glycerol

### Melting Point Test

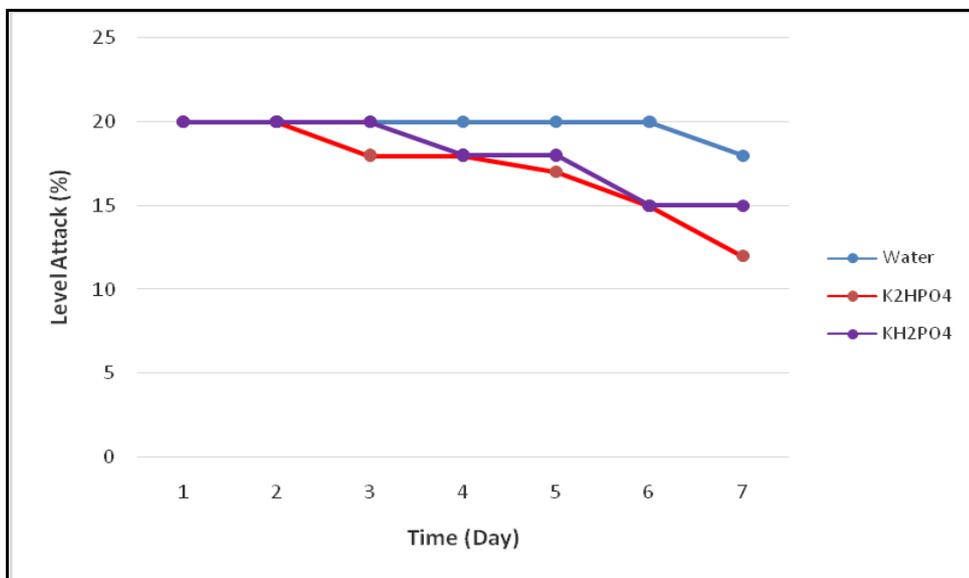
The melting point of the test results in various concentrations of phosphoric acid and various pH acidification process obtained the following results.

**Table 2. Test result of the melting point of Potassium Phosphate salts**

No	Sample	Test Result
1	65% H <sub>3</sub> PO <sub>4</sub> pH 4,4	205°C
2	65% H <sub>3</sub> PO <sub>4</sub> pH 4,7	215°C
3	65% H <sub>3</sub> PO <sub>4</sub> pH 8,5	241°C
4	65% H <sub>3</sub> PO <sub>4</sub> pH 9,6	262°C
5	65% H <sub>3</sub> PO <sub>4</sub> pH 9,7	280°C
6	75% H <sub>3</sub> PO <sub>4</sub> pH 4,4	220°C
7	75% H <sub>3</sub> PO <sub>4</sub> pH 4,7	232°C
8	75% H <sub>3</sub> PO <sub>4</sub> pH 8,5	321°C
9	75% H <sub>3</sub> PO <sub>4</sub> pH 9,6	330°C
10	75% H <sub>3</sub> PO <sub>4</sub> pH 9,7	343°C
11	85% H <sub>3</sub> PO <sub>4</sub> pH 4,4	241°C
12	85% H <sub>3</sub> PO <sub>4</sub> pH 4,7	252°C
13	85% H <sub>3</sub> PO <sub>4</sub> pH 8,5	440°C
14	85% H <sub>3</sub> PO <sub>4</sub> pH 9,6	458°C
15	85% H <sub>3</sub> PO <sub>4</sub> pH 9,7	464°C

In Table 2 above shows that at different concentrations of phosphoric acid and pH changes in the acidification process affects the level of purity crystalline potassium phosphate salts. Potassium phosphate salts to be achieved in this research is the potassium salt monohydrogen phosphate ( $K_2HPO_4$ ) and potassium dihydrogen phosphate ( $KH_2PO_4$ ) purity salt approached with salt  $K_2HPO_4$  and  $KH_2PO_4$  truth. at  $465^\circ C$  and  $252,6^\circ C$ . In the sample of 85%  $H_3PO_4$ , approaching the melting point of the salt  $K_2HPO_4$  and  $KH_2PO_4$  ie on the sample 85%  $H_3PO_4$  pH 9.7 and the sample 85%  $H_3PO_4$  pH 4.7, respectively  $464^\circ C$  and  $252^\circ C$ . Thus, the samples at concentration of 85%  $H_3PO_4$  salt formed  $K_2HPO_4$  pH 9.7 and at 85%  $H_3PO_4$  pH 4.7  $KH_2PO_4$  salt formed. While the overall sample concentration of 65%  $H_3PO_4$  and 75%  $H_3PO_4$  only salt formed  $KH_2PO_4$ . This is because the melting point of the whole sample is closer to the melting point of salt  $KH_2PO_4$  than the melting point of salt  $K_2HPO_4$ . Of the three types of the concentration of phosphoric acid obtained optimum concentration of phosphoric acid at a concentration of 85%. This is due to the high acid levels will be better because the acidification process emulsion soap into fatty acids and salts getting bigger. So that the purity of the salt obtained even greater. Based on table 4.2, that the salt  $K_2HPO_4$  pH more alkaline than  $KH_2PO_4$  salt is above 7. In a sample concentration of 85%  $H_3PO_4$  salt formed  $K_2HPO_4$  pH 9.7 and the sample 85%  $H_3PO_4$  pH 4.7  $KH_2PO_4$  salt formed. In each of the pH with  $H_3PO_4$  concentration of 85% obtained second level of purity salt is very high, almost the same / approaching the melting point of the actual salt.

**Test% Effectiveness Efficiency Spray anti-fungi**



**Figure 7. The relationship between the spraying time and the attack level**

Based on Figure 7, the level of fungi attack on the leaves of mango tested with three materials sprayers are spraying only water as the controlled variable (without material fungicide), sprayers  $K_2HPO_4$  (plus triton B-1956) as well as spraying  $KH_2PO_4$  (plus triton B-1956). The leaves were tested amounted to 9 leaves of mango plant. On the first day until the seventh day obtained fungi attack rate decreases with each increment difference in the materials used. On the use of materials such as water (controlled variable without fungicide mixture) obtained degree of fungi attack first day to the sixth is still the same, there is no reduction in the level of attack, on the seventh day began to decrease 18% rate of fungi attack.

In the use of materials such  $K_2HPO_4$  fungi attack level obtained third day began to decrease by 18%, the next level is reduced fungi attack added a lot on the fifth, sixth and seventh, respectively 17%, 15% and 12% levels of fungi attack. In the use of materials such fungi attack level obtained  $KH_2PO_4$  fourth day began to decrease by 18%, the next level is reduced fungi attack added a lot on the sixth day and remained constant until the seventh day, respectively by 15% the level of fungi attack. Thus, the results of which are shown during the 7 days of spraying the material tested third level obtained fungi attack the mango crop is reduced more rapidly by spraying material  $K_2HPO_4$  compared with that of  $KH_2PO_4$  and water.

## Conclusion

- The optimum concentration of phosphoric acid in the purification process of glycerol is 85% phosphoric acid concentration and pH optimum in the process of acidification on the purification of glycerol is pH 9.7 with  $K_2HPO_4$  salts results and pH 4.7 with salt results  $KH_2PO_4$ .
- The melting point of each of the salt is 464 ° C and 252 ° C, approaching the melting point of salt  $K_2HPO_4$  and  $KH_2PO_4$  actual
- Spray antifungi  $K_2HPO_4$  more effectively reduce powdery mildew on the leaves of mango by 13%

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