Solvent Characterization of Lycopene Extraction in Tomato Fruits as Sensitizer Candidates in Dye-Sensitized Solar Cell (DSSC)

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Abstract: This study is an experimental study aimed at clarifying the characteristics of the solvent in the extraction of lycopene in tomato (Solanum lycopersicum) as a candidate photosensitizer for dye-sensitized solar cells (DSSC). The performance of DSSC depends on the type of dye commonly used as a sensitizer. Tomatoes contain lycopene. Yields of lycopene extract in tomatoes were characterized by FTIR and UV-Vis spectrophotometers. The extraction methods used in this study are the maceration method and liquid-liquid extraction. The procedure of this study was carried out in two main stages, the extraction stage and the characterization stage. The first step was the extraction of lycopene from tomatoes using the maceration and liquid-liquid extraction methods. The maceration process compared the use of acetone and ethyl acetate as solvents. This extraction step produced 6.514 g (acetone) and 5.6702 g (ethyl acetate) lycopene extracts. The second step is to identify the functional groups of the compound formed using an FTIR spectrophotometer and use a UV-Vis spectrophotometer to determine the absorbance and maximum wavelength value of the lycopene and M-lycopene complex. The results of the FTIR spectrophotometer test showed that using acetone as the solvent produced wavenumbers similar to lycopene compared to ethyl acetate. UV-Vis spectrophotometer test results show the maximum wavelengths of the lycopene extract using acetone as the solvent were 447 nm, and 294 nm when ethyl acetate was used as the solvent. The Eg results revealed that the Eg values for the acetone and ethyl acetate extracts were 4.52 eV and 2.68 eV. Based on the results of property analysis of the two solvents used, acetone was more suitable than ethyl acetate for the extraction of tomato lycopene used as a DSSC sensitizer.

Keywords: Lycopene; Tomato Fruit; Sensitizer; Dye-Sensitized Solar Cells.

Introduction

Since the development of solar energy is in demand to meet the current energy demands associated with the decline in energy supply, cheap and environmentally friendly energy-producing materials are needed. As for solar energy, Indonesia has considerable potential as a tropical country (Harahap, 2019; Rimbawati, et al, 2019), so the development of renewable energy sources such as solar energy is the most as follows: It could be one of the potential alternative energy sources. It is abundant and eco-friendly. Hayat et al., 2019; Gong et al., 2012). The use of solar energy can be used to generate electrical energy in solar cell applications (Bagher et al., 2015; Gaur & Tiwari, 2013). One type of widely studied solar cell is the Dye-Sensitized Solar Cell (DSSC), a third generation composed of dyes that can convert solar energy into electrical energy using photoelectrochemical principles.
The DSSC consists of a working electrode, a semiconductor, a dye-sensitized solar cell, an electrolyte, and a reference electrode (Yum et al., 2010). The principle of operation of DSSC is that light absorption is performed by the dye and charge separation is performed by the inorganic nanocrystal wide bandgap semiconductor. Wide bandgap semiconductors increase the flow of electrons from LUMO to HOMO (Nur, 2013). In addition, the performance of DSSC depends on the type of dye commonly used as a sensitizer. Sensitizers can be obtained from natural or synthetic dyes (Richhariya, 2017). Sensitizers can extend the photoresponse of TiO$_2$ to the visible range (Longo et al., 2003). Many researchers have developed various types of natural sensitizers from plant extracts of DSSC (Amogne et al., 2020; Purwoko et al., 2019; Syafinar et al., 2015; Supriyanto et al., 2018; Zhou et al., 2011).

One of the natural sensitizers developed in this study is a lycopene extract from tomato (Solanum lycopersicum). This is due to its abundant availability and low cost. Tomato fruit is a tropical plant commonly found in Indonesia and contains the main compound lycopene (pigment of tomato fruit) (Tarigan et al., 2016). Lycopene is found in some fruits and plants. In addition to tomatoes and tomato products, which are the main sources of lycopene (Rao et al., 2006), watermelon, pink grapefruit, pink guava, and ar Ngbay also contain lycopene, but to a lesser extent (Mourvaki et al., 2005). The highest levels of lycopene were found in tomatoes (40.59 mg/kg) compared to watermelon (34.98 mg/kg). Research results of Tristiyanity et al. (2013) shows that the lycopene content of watermelon is 33 mg/100 g, guava 7.5 mg/100 g, and ar Ngbay 9 mg/100 g. In addition, a study by Alfa and Mustofa (2019) reported lycopene levels in a variety of plants: raw tomatoes (8.8 mg/100 g), watermelons (4.0 mg/100 g), and pink grapefruits (4.0 mg/100 g). Based on multiple lycopene sources and their levels, this study selected lycopene in tomato fruit extracts with high lycopene content.

In general, tomatoes contain vitamins, minerals, pigments, and organic acids (Maulida & Zulkarnaen, 2010). The red pigment in tomatoes is the carotenoid lycopene (Dewi et al., 2019). Carotenoids are pigments that give foods a yellow, orange to red color (Maleta et al., 2018). There are several types of carotenoids, including carotene, -carotene, astaxanthin, lycopene, lutein, zeaxanthin, -cryptoxanthin, and fucoxanthin (Takaichi et al., 2013; Wrolstad & Culver, 2012). Carotenoids have a carboxylic acid group at the end of the connecting chain, so they can bind to the TiO$_2$ surface of DSSC components (Ortiz et al., 2009).

Lycopene with the molecular formula C$_{40}$H$_{56}$ is an aliphatic hydrocarbon with 13 double bonds. Eleven conjugated double bonds are arranged in a straight line, and lycopene is longer than other carotenoids. Lycopene’s acyclic structure causes planar symmetry (Preedy et al., 2008). According to George et al. (2004), the lycopene content of tomatoes depends on the ripening of the fruit at harvest (generally due to genetic effects) and the effects of agriculture and environmental conditions during planting. An increase in the amount of carotenoids can be seen in the change in pigment. Similarly, an increase in lycopene concentration causes an increase in red pigment.

The choice of lycopene dye is of DSSC efficiency due to its chemical properties, is easily degradable, having a conjugated 11 double bond, a wavelength range of 400-510 nm, and commonly found in Indonesia. It has excellent potential as a pigment sensitizer. Environmentally friendly, the dye extraction process is simple (Sing et al., 2021; Moradiya et al., 2019). However, the production of a good lycopene extract suitable for use as a sensitizer can be affected by several factors, including the extraction method, the solvent used, and the type of tomato used. A simple and easy-to-execute method is the softening method (immersion).

The focus of this research is to characterize the use of the solvent in the maceration (immersion) process by comparing
the solvents acetone and ethyl acetate. Therefore, in this study, we performed a solvent characterization to extract lycopene in tomato as an excellent alternative sensitizer used in DSSC.

**Material and Method**

**Research Tool and Materials**

The equipment used in this study included beakers, measuring cups, analytical scales, oven, hot plate, Erlenmeyer, dropper, measuring flask, extraction flask, Buchner funnel, spatula, stirring rod, and knife. Meanwhile, the characterization process used a set of Shimadzu brand UV-1601PC spectrophotometer tools and PerkEimer brand FTIR spectrophotometers.

The materials used in this study were fresh red tomatoes, acetone (CH₃COCH₃), ethyl acetate (C₆H₄O₂), n-hexane (C₆H₁₄), aquadest, ethanol AR (C₂H₅OH), filter paper, tissue, clear plastic, aluminum foil.

**Procedure**

1. Extraction Stage of Lycopene from Tomato Fruit (Solanum lycopersicum)

Extraction of lycopene from tomatoes consists of four stages, namely; the sample preparation stage, the maceration stage, the liquid-liquid extraction stage and the concentration stage. In the sample preparation stage, 5 kg of fresh tomatoes were cleaned, the flesh and seeds were separated, then cut into small pieces and dried in an oven at 60°C for 3 hours. Furthermore, the maceration stage was soaked by adding each dried tomato with acetone and ethyl acetate solvent, a ratio of 1:4 (material: solvent), and soaked for 5 x 24 hours. After that, filtering is carried out. Then the filtered filtrate is extracted liquid-liquid with a non-polar solvent. Macerate with acetone was extracted with n-hexane (1:1), while for ethyl acetate magerate was extracted with aquadest (1:1). After each magerate was added the solvent was then shaken for 5-10 minutes until 2 fractions were formed. Furthermore, the upper fraction (organic) and the lower fraction (water) were separated. The last stage of the upper fraction (organic) was concentrated with a hot plate at a temperature of 60°C-70°C to obtain a thick extraction of lycopene. The obtained lycopene viscous extraction is called dye.

2. Characterization Stages

The dye samples obtained were then analyzed using UV-Vis spectrophotometer and FTIR spectrophotometer. Prior to the test, each 0.5 ml of thick extract was prepared and dissolved in p.a ethanol in a 100 ml volumetric flask. Furthermore, the lycopene solution was analyzed on each spectrophotometer.

**Results and Discussion**

1. Lycopene Extraction from Tomato Fruit

In this study, lycopene was extracted from tomato (Solanum lycopersicum) with two types of solvents, namely ethyl acetate and acetone. The extraction process is carried out in four stages, namely; sample preparation stage, maceration stage, liquid-liquid extraction stage, and concentration stage. Before maceration with these two solvents, preparations were made by cutting and drying. Each sample used was fresh red tomatoes. Fresh tomatoes were cleaned, separated from the flesh and seeds, then cut into small pieces and dried in an oven at 60°C-70°C for 3 hours. The purpose of cutting tomatoes into small pieces is to expand the surface and speed up drying (Supriyanto et al., 2018; Ramadhani, et al., 2020). Drying at a temperature of 60°C-70°C aims to reduce the water content in tomatoes so that the extraction process of lycopene compounds can be optimal (Dewi et al., 2019). Next is the maceration stage by adding each solvent acetone and ethyl acetate to the dried tomato flesh in a ratio of 1:4 (material: solvent) and soaking for 120 hours. After 120 hours filtered. The filter results for each solvent obtained in ethyl acetate are more orange in color, while for acetone the color is yellow. Furthermore, the results of filtering (macerate) are carried out by liquid-liquid extraction to reduce the impurities contained in the extract. Liquid-liquid extraction used solvents of different polarities (Dewi, et al., 2018). Ethyl acetate macerate was extracted with aquadest as solvent (Tarigan, 2016), while acetone was extracted with n-hexane as solvent. In the liquid-liquid extraction stage, two fractions are formed, namely the upper fraction (organic phase) and the
lower fraction (aqueous phase). Then the two fractions were separated and the upper fraction (organic phase) was taken for concentration to remove the solvent. To obtain a thick extract of lycopene from each solvent. The viscous extract of lycopene obtained is called dye. The extract obtained was 5.6702 g using ethyl acetate solvent, and 6.514 g using acetone as a solvent. The following is a picture of the extraction results from each solvent (figure 2).

2. Characterization of Lycopene Extraction Results from Tomato Fruit

The extracted dyes were characterized by FTIR and UV-Vis spectrophotometers. FTIR spectrophotometer was used to determine the functional groups and bonds of the thick extract of lycopene from tomato fruit. The results of the FTIR analysis showed that the wavenumber absorption peak for acetone solvent had similar functional groups and the same bonds with lycopene compounds based on the results of research by Aghel et al. (2011), while the lycopene extract with ethyl acetate solvent has different wave numbers where the absorption wave numbers for bond markers \( R_2C=CR \) and \( R-CH=CH \) were not identified in the lycopene extract with ethyl acetate solvent.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Lycopene (Aghel, et al., 2011)</th>
<th>Lycopene Extract with Ethyl Acetate</th>
<th>Lycopene Extract with Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_2C=CR )</td>
<td>612.84</td>
<td>-</td>
<td>664.1</td>
</tr>
<tr>
<td>( R-CH=CH-R )</td>
<td>957.33</td>
<td>-</td>
<td>952.67</td>
</tr>
<tr>
<td>C-C and C-C-H</td>
<td>1100 – 1400 (Bunghez, et al., 2011)</td>
<td>1165.98 ; 1260.05 ; 1377.89</td>
<td>1274.7 ; 1329.69 ; 1381.15</td>
</tr>
<tr>
<td>(stretching)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H alkene</td>
<td>1400 ; 1446.92</td>
<td>1462.41</td>
<td>1420.22 ; 1454.81</td>
</tr>
<tr>
<td>(bending)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=C ( \text{str} ) (Trans)</td>
<td>1640 ; 1670</td>
<td>1639.37</td>
<td>1655.03</td>
</tr>
<tr>
<td>( \text{C-H}_{sp} ) (SP)</td>
<td>2851.05 ; 2918.92</td>
<td>2851.37 ; 2923.21</td>
<td>2889.23 ; 2928.07</td>
</tr>
</tbody>
</table>

The results of the FTIR characterization analysis of the results of the preliminary study can be seen in table 1. Based on table 1 it is shown that the absorption peaks in the wave number region for lycopene compounds based on the theory are 612.84 cm\(^{-1}\), 957.33 cm\(^{-1}\), 1400 cm\(^{-1}\), 1446.92 cm\(^{-1}\), 1670 cm\(^{-1}\), 2851.05 cm\(^{-1}\), and 2918.92 cm\(^{-1}\) (Aghel et al., 2011). To characterize the results of lycopene extract with ethyl acetate solvent (figure 2), the results of the analysis of the detected functional groups were C-H alkenes (bending) at a wave number of 1462.41 cm\(^{-1}\). In the C-C and C-C-H (stretching) strain groups, the wave numbers are 1165.98 cm\(^{-1}\), 1260.05 cm\(^{-1}\), and 1377.89 cm\(^{-1}\), respectively. For the bonding group C=C
aliphatic alkenes at wave numbers 1639.37 cm\(^{-1}\), and C-H groups (stretching) aliphatic detected at wave numbers 2851.37 cm\(^{-1}\) and 2923.21 cm\(^{-1}\). Meanwhile, the R\(_2\)CH=CR and R-CH=CH-R bonds in lycopene extract with ethyl acetate were not detected.

Figure 3. Graph of FTIR Characterization of Lycopene Extracted Results from Tomato Fruit (Aghel, et al., 2011)

While the results of FTIR characterization for lycopene extract with acetone solvent (figure 3), obtained an analysis of fungal groups detected at wave numbers of 664.1 cm\(^{-1}\) and 952.67 cm\(^{-1}\) which are R=C=CR bonds at the end of the lycopene chain and R-linkages, CH=CH-R in the lycopene chain. For the C-C and C-C-H (stretching) strain groups, respectively, the wave numbers are 1274.7 cm\(^{-1}\), 1329.69 cm\(^{-1}\), and 1381.15 cm\(^{-1}\). For the bonding group C=C aliphatic alkene at wave number 1655.03 cm\(^{-1}\), and C-H group (stretching) aliphatic detected at wave number 2889.23 cm\(^{-1}\) and 2928.21 cm\(^{-1}\). The absorption area of lycopene compounds based on the results of the FTIR spectrophotometer test (figure 1) research by Aghel et al., (2018) is not much different from the results of lycopene extraction with acetone solvent that the researchers did (Figure 3).

Figure 4. Graph of FTIR Characterization of Lycopene Extracted from Tomato Fruit with Ethyl Acetate Solvent
The results of characterization using UV-Vis spectrophotometer showed that the maximum wavelength absorption for lycopene extract with ethyl acetate solvent was 294 nm with an absorbance of 0.993 (figure 4), while for lycopene extract with acetone the maximum wavelength was 447 nm with an absorbance of 0.545 (figure 5). The maximum wavelength is used to identify the viscous extract produced. Lycopene compounds have characteristics in the absorption region, namely at wavelengths of 447 nm, 367 nm, 284 nm and 224 nm (Wahab, 2016). So what shows wave crests with the same characteristics as theoretical lycopene compounds is to use of acetone as a solvent instead of ethyl acetate.

The energy value of the band gap is the energy required for electrons to break covalent bonds so that they can move from the HOMO band to the LUMO band. The energy gap (Eg) value can be calculated using the tauc plot method based on the wavelength and absorbance data from UV-Vis measurements. The results of the Eg calculation show that the Eg value of lycopene extract in ethyl acetate solvent is 2.68 eV (figure 6), while the Eg value of lycopene extract in acetone solvent is 4.52 eV (figure 7). The energy band gap is small, so it is easier for electrons from the HOMO energy level to jump to the LUMO energy level (Curcuma and Setiarso, 2021; Wu and Zhu, 2013).
The smallest band gap energy will result in high efficiency performance (Imelda, 2020), so that when compared to the energy gap with acetone solvent extraction it is better, but for the character of the functional group on the absorption wavenumber and the maximum wavelength absorption character are appropriate and similar to lycopene compounds. So to use acetone solvent. So with ethyl acetate solvent, it is possible that the extracted compound is not lycopene.

**Conclusion**

Based on the results and discussion, it was found that acetone solvent was better used to extract lycopene from tomatoes than ethyl acetate as solvent. This is based on the weight of the viscous extract obtained and the results of its characterization with FTIR and UV-Vis spectrophotometers. The weight of the thick extract of lycopene from tomato fruit obtained using acetone solvent was more, namely 6.514 g compared to the use of ethyl acetate solvent which was 5.6702 g. In addition, the dye extract with acetone solvent has the characteristics of absorption of wavelength and maximum wavelength that are similar to the literature. The results of the absorption of wave numbers with acetone solvent were 664.1 cm\(^{-1}\), 952.67 cm\(^{-1}\), 1274.7 cm\(^{-1}\), 1329.69 cm\(^{-1}\), 1381.15 cm\(^{-1}\), 1655.03 cm\(^{-1}\), 2889.23 cm\(^{-1}\) and 2928.21 cm\(^{-1}\), and the maximum absorption wavelengths are 663 nm, 447 nm and 331 nm.

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**References**


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**Figure 8.** Plot Of The Lycopene Energy Gap With Ethyl Acetate Solvent

**Figure 9.** Plot Of The Lycopene Energy Gap With Acetone Solvent
and Photonics, 3(5), 94-113. https://doi.org/10.11648/j.aiop.20150305.17


