



SYNTHESIS OF AZELAIC ACID FROM OLEIC ACID WITH GREEN OXIDANT H_2O_2 / H_2WO_4

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ABSTRACT

Azelaic acid or nonanedioic acid is an organic compound that has important applications in the textile and pharmaceutical industries. The synthesis of azelaic acid was carried out by oxidizing oleic acid (OA) with hydrogen peroxide (H_2O_2) as an oxidizer and tungstic acid (H_2WO_4) as a catalyst. This study was conducted to determine the correlation and significance of the effect of variable comparison to the resulting percent conversion of Iodine Number as well as to develop a more effective, selective and environmentally friendly process with H_2O_2/H_2WO_4 as oxidizer. The interactions effect of substrate mole ratio, percent catalyst, and temperature were observed to obtain maximum yield of azelaic acid by utilizing the Central Composite Design (CCD) and Response Surface Methodology (RSM). The results showed that all variables influenced the percent conversion of Iodine Number expressed by the value of coefficient of determination (R^2) of 92.08% and the results of variance analysis showed that all models contribute significantly to the percent conversion resulted. The oxidative cleavage reaction was evidenced by the decrease of iodine number and the product of the reaction was analyzed by Fourier transform-infrared spectroscopy (FT-IR). The largest decrement of iodine number was recorded 99.12% and it was obtained on variation of substrate mole ratio of 1: 8 (OA/ H_2O_2), 3% ($wH_2WO_4/wt. OA$) catalyst at temperature of 70 °C. From the results of biocompatibility analysis, the process of synthesis of azelaic acid is eco-friendly because the waste generated is environmentally friendly and the catalyst used can be recycled.

Keywords: azelaic acid, oleic acid, oxidative cleavage, hydrogen peroxide.

INTRODUCTION

The azelaic acid is one of the products produced on oxidative solutions of oleic acid and has many uses that can be applied into three areas: as an intermediate compound of the polymerization process in the manufacture of polyamides, polyesters, polyurethane layers, fibers, adhesives and resins; as an anti-inflammatory and acne medicine in the pharmaceutical world; and the diester compound produced from this acid can be used as a lubricant in an industrial machine [1]. Not only the azelaic acid, pelargonic acid is also produced in this oxidation-breakdown reaction. No less functional with azelaic acid, pelargonic acid is also in demand in the Bio-Lubricant industry as a plasticizer, perfume, fungicide, and resin [2].

Industrially this acid is produced by oxidizing oleic acid by the ozonolysis method to break the double bond of the carbon chain and takes place at a sufficiently high temperature and pressure [3]. This method has been used since 1953 [4]. The use of ozone and oxygen as an oxidant at high temperatures and pressures has a considerable risk of burning and explosion and this method is considered uneconomical because it requires enormous energy and cost in the process.

Oxidants such as chromic acid, nitric acid, potassium permanganate, periodate, potassium peroximonosulfate (oxone), formic acid and sodium hypochlorite have been extensively studied to improve this oxidation-breakdown process, but this oxidant also has not solved the problem in this reaction Waste that is not environmentally friendly as well as low conversion rate [2]. It is therefore important to find a new, safer, environmentally friendly and economical process that is

the use of hydrogen peroxide (H_2O_2) compounds as oxidants whose atoms can oxidizing specifically, are environmentally friendly and more economical when compared to other reactants [1].

Hydrogen peroxide is an ideal oxidant because it contains high levels of active oxygen, safe in storage and use, and is easy to obtain. This oxidant also includes an environmentally friendly where water is the only by-product in heterolytic oxidation. The reasons for this oxidant are more commonly used, but this compound reacts slower without an activator [5]. Transition metals such as osmium, cobalt, copper, gold, magnesium, iron; ruthenium and tungsten are commonly used as active catalysts, where ruthenium and tungsten are highly recommended [6].

Wolfram or so-called tungsten is a compound naturally present in the soil and rocks as a mineral. This compound cannot be synthesized from other compounds, but can be converted into other forms [7]. Tungstic acid as a catalyst in this oxidation reaction is a strong acid, which can be prepared by reacting pure tungsten with hydrogen peroxide [8]. This compound is selected because tungsten is considered to be highly reactive and specific, environmentally friendly and has a conversion rate of over 90% in oxidation of oleic acid with hydrogen peroxide, which forms azelaic acid [6].

Oleic acid (cis-9-octadecenoic acid) is a monounsaturated fatty acid having 18 carbon atoms with symmetric double bonds between C-9 and C-10 atoms [9, 10]. This fatty acid is naturally contained in the *Elaeis guineensis jacq* plant known as palm oil, which is about 39% in its flesh [11]. The main raw material of oleic acid used is derived from fractionation of oil palm fruits. This



is chosen because palm oil is considered more economical, renewable resources and environmentally friendly [12].

Today, azelaic acid is one of the most commonly studied of oleo chemical derivatives due to its widespread application in polymer [10]. For the above reason, the writer wants to do research about synthesis of azelaic acid with raw material of oleic acid using environmentally friendly H_2O_2/H_2WO_4 to get important information about determine the correlation and significance of the effect of variable comparison to the resulting conversion as well as to develop a more effective, selective and environmentally friendly synthetic azelaic acid process so that this method can later be developed for a larger scale.

EXPERIMENTAL PROCEDURES

Materials and reagents

The main raw materials in synthesis of azelaic acid are oleic acid ($C_{18}H_{34}O_2$), tungstic acid (H_2WO_4), ethyl acetate ($C_4H_8O_2$), hydrogen peroxide (H_2O_2) and sodium sulfate (Na_2SO_4). They are purchased from Merck, Darmstadt. The product amount was titrated with an iodometry method with the raw material is chloroform ($CHCl_3$), reagent, potassium iodide (KI 15%), sodium tiosulfate ($Na_2S_2O_3$), and starch indicator.

Procedures of the synthesis

The procedure of synthesis azelaic acid was described as in [1] with the following procedure: A total of x grams of tungstic acid and x gram of hydrogen peroxide (30%) were introduced into a 300 ml round-bottom flask at 70 ° C. Added 5 grams of oleic acid to the solution mixture on the three neck flask and stirred with a magnetic

stirrer at 200 rpm for 8 hours. After 8 h, the mixture was cooled to room temperature and added as much as 50 ml of cold water. The solution mixture was in the extraction with hot ethyl acetate 4 x 100 ml. The organic layer mixture is dried by adding anhydrous sodium sulfate and evaporated under vacuum pressure. Products obtained were analyzed with iodometry titration method, and Fourier transform-infrared Spectroscopy (FT-IR).

RESULTS AND DISCUSSIONS

Optimized oxidation solution results

To obtain the azelaic acid, a direct oleic acid oxidative breaking method with an environmentally friendly oxidizer H_2O_2 and H_2WO_4 as a catalyst is used. There are three independent variables selected in this research are substrate mole ratio (OA/H_2O_2), percent catalyst (wH_2WO_4/wOA) and reaction temperature ($^{\circ}C$).

The experimental was carried out using Central Composite Design (CCD) method which consisting of 2 factorial design with the addition of central run and axial run [13]. The research data obtained from the 20 treatments were then analyzed using Response Surface Methodology (RSM) using MINITAB 17[®] (Trial Version) software to form the relationship between the variables that can be determined by regression analysis [14]. The obtained equation is then tested with ANOVA (Analysis Of Variance). ANOVA is used to test individual parameter freedom and compare between the components of total deviation [15]. The variables and coded levels are listed in Table-1.

Table-1. Variables and levels developed for synthesis of azelaic acid.

Variables	The variable coded level				
	-1,682	-1	0	1	1,682
Substrate mole ratio (OA/H_2O_2)	1:6.3	1:7	1:8	1:9	1:9.7
Percent catalyst (wH_2WO_4/wOA)	1:100	2:100	3:100	4:100	5:100
Temperature ($^{\circ}C$)	53	60	70	80	87

Levels on the above variables are obtained by taking into account the limits of operating tools and materials as well as the properties of the reactants used. The observed response to be measured is the conversion of oxidative breakdown of unsaturated fatty acids into saturated fatty acids in terms of the decrease in iodine number that occurs after the reaction takes place. The oxidative breakdown conversions obtained at each run were analyzed using iodine analysis. This experiment consisted of 20 combinations in various percent catalysts, substrate mole ratio and reaction temperature. This study chose CCD as a form of experimental design because it is considered to provide a systematic design to obtain interaction between variables [16]. From this design will be obtained interaction of three variables namely substrate

mole ratio (X_1), percent catalyst (X_2) and reaction temperature (X_3).

The optimization result of synthesis of azelaic acid in percent conversion of iodine number is shown in Table-2. Percent conversion of iodine number expresses conversion value of unsaturated fatty acid to saturated fatty acid in the form of azelaic acid on oxidative splitting that has been done.

Model development

To minimize the deviation of the equation model generated in RSM, the first step can be done is to predict the regression model and proceed with the analysis of variance (ANOVA) as well as to verify the model [17]. This regression model was made to determine the relationship between the percent conversion of oxidation



represented by the determination of the iodine number (Y) with the substrate mole ratio (X_1), percent catalyst (X_2) and reaction temperature (X_3) as well as optimizing the response. The value of P test conducted through ANOVA testing aims to determine the significance of variables to product conversion.

The significance factor used is $\alpha = 0.05$. The variable is significant if the value of $P \leq \alpha$. based on prediction results for preparing response surface models, the equation model that can represent the relationship of the reaction variable and its interaction to percent conversion that is evaluated through the decrease of iodine number in the synthesis of azelaic acid is as follows:

Table-2. Experimental results.

No	Substrate ratio (X_1)		Percent catalyst (X_2)		Temperature (X_3)		Conversion (%)
	Actual	Code	Actual	Code	Actual	Code	
1	1:7	-1	2:100	-1	60	-1	89,63
2	1:9	1	2:100	-1	60	-1	95,11
3	1:7	-1	4:100	1	60	-1	91,13
4	1:9	1	4:100	1	60	-1	98,11
5	1:7	-1	2:100	-1	80	1	77,56
6	1:9	1	2:100	-1	80	1	84,76
7	1:7	-1	4:100	1	80	1	83,76
8	1:9	1	4:100	1	80	1	94,05
9	1:6,3	-1.682	3:100	0	70	0	84,76
10	1:9,6	1.682	3:100	0	70	0	98,68
11	1:8	0	1,3:100	-1.682	70	0	74,83
12	1:8	0	4,6:100	1.682	70	0	92,59
13	1:8	0	3:100	0	53	-1.682	91,71
14	1:8	0	3:100	0	87	1.682	74,84
15	1:8	0	3:100	0	70	0	94,09
16	1:8	0	3:100	0	70	0	99,12
17	1:8	0	3:100	0	70	0	98,16
18	1:8	0	3:100	0	70	0	99,05
19	1:8	0	3:100	0	70	0	99,10
20	1:8	0	3:100	0	70	0	99,12

$$Y = 97,99 + 3,907 X_1 + 3,651 X_2 - 4,556 X_3 - 1,467 X_1^2 - 4,299 X_2^2 - 4,453 X_3^2 + 0,57 X_1 X_2 + 0,63 X_1 X_3 + 1,37 X_2 X_3 \quad (1)$$

where, Y = % Conversion, X_1 = Substrate Mole Ratio, X_2 = Percent Catalyst, and X_3 = Temperature.

The value of determination coefficient ($R^2=92,80\%$) indicated that the independent variable in the experiment affected the dependent variable. Therefore, it can be concluded that the interaction between the substrate mole ratio, catalyst percentage and reaction temperature is said to affect the synthesis of azelaic acid from oleic acid with environmentally friendly oxidizing agent H_2O_2/H_2WO_4 .

The interaction effect of substrate mole ratio and percent catalyst against conversion

The catalysts and oxidizers used in this study are tungstic acid (H_2WO_4) and hydrogen peroxide (H_2O_2), which are considered to be specific, efficient and environmentally friendly in this oxidative-breaking reaction. The catalyst concentration and the substrate ratios determined are based on the results of a study conducted as in [1] with 1% catalyst concentration and a 1: 8 substrate to produce azelaic acid. Synthesis of azelaic acid was carried out for 8 hours with a speed of 300 rpm stirring.

The effect of percent catalyst interactions and substrate ratios is shown in the contour plots and surface responses in Figure-1.

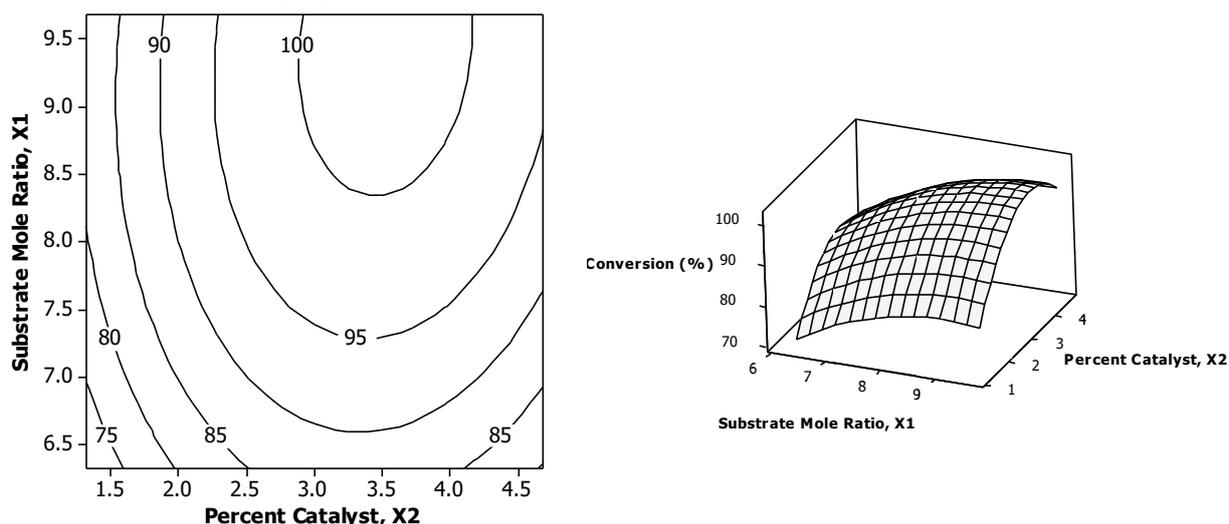


Figure-1. Contour and surface plot of percent conversion of iodine number as function of substrate mole ratio, X_1 (OA/H₂O₂) and percent catalyst, X_2 (wH₂WO₄/wOA) at temperature of 70 °C.

Figure-1 shows that the % conversion has a significant effect on the substrate mol ratio and percent catalyst change with the fixed reaction temperature variable 70 °C. The contour plot shows that if the percent of the H₂WO₄ catalyst is maintained at a certain amount and the H₂O₂ substrate ratio is increased, then the percent conversion increases. When the percent of the H₂WO₄ catalyst is raised and the H₂O₂ substrate ratios are maintained constant, it is seen that the obtained conversion also increased in the synthesis of the azelaic acid.

This happens because the H₂O₂ added to the substrate works specifically and efficiently in the oxidative-solvoling reaction of oleic acid in the synthesis of azelaic acid. Hydrogen peroxide is a powerful oxidizer with an active oxygen amount of 47% [18]. Active oxygen is able to oxidize unsaturated fatty acids well. In its use this oxidizer requires a catalyst to speed up the course of the oxidative breakdown reaction. The oxidative breakdown reaction is carried out to produce the azelaic acid, the catalyst transfer method chosen because it is considered more effective and selective. The catalyst will assist the donor transfer process donated from donors [2]. Tungstic acid as a transfer catalyst is selected because it is considered to be safer, environmentally friendly and works specifically on the reaction [1]. This is evident from the increased acquisition of product conversion along with the increased percentage of catalyst added. However, the excess amount of catalyst can also cause this oxidizer to undergo a decomposition reaction along with the oxidation reaction so that the efficiency of the oxidative breakdown reaction decreases [6].

The results of the research on the contour surface of Figure-1 above show that when the reaction temperature remains 70 °C, the maximum conversion is obtained when the number of H₂WO₄ catalysts is 3% and the ratio of oleic acid and H₂O₂ substrate of 1: 9, 6 with the acquisition % of oxidation-breaking conversion of 98.68 % In terms of decreased oleic acid iodine values before reaction and after reaction.

The interaction effect of substrate mole ratio and temperature against conversion

The reaction temperature specified in the synthesis of this azelaic acid has 5 levels of variation. The interaction effect of substrate mole ratio and temperature against the catalyst percentage is shown in the contour and surface plot of Figure-2.

It is seen that the increase in temperature has a significant influence in the acquisition of % conversion at a fixed percent catalyst condition of 3% (wH₂WO₄/wOA). It appears that if the reaction temperature is maintained at a certain amount and the H₂O₂ substrate ratio is increased, the percent conversion increases significantly. When the reaction temperature is raised and the substrate ratio of H₂O₂ is maintained constant, it is seen that the conversion obtained also changes, where the high reaction temperature causes a decrease to the percent conversion produced.

Increased conversions can occur because high temperatures can increase the reaction rate and can increase transfers between substrates [12]. The heating process is also one of the factors that can accelerate the occurrence of oxidation reactions.

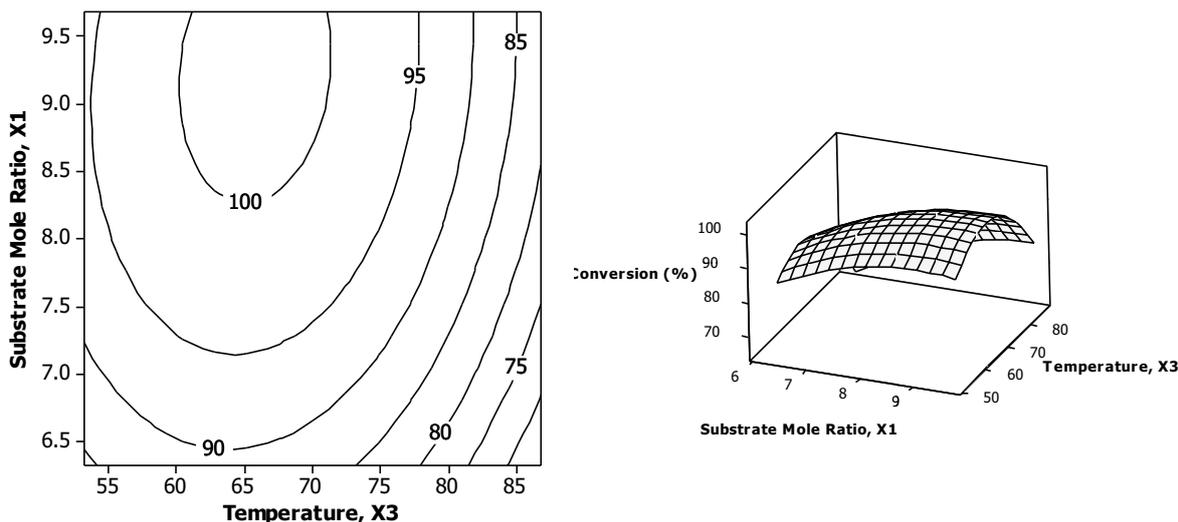


Figure-2. Contour and surface plot of percent conversion of iodine number as function of substrate mole ratio, X_1 (OA/H₂O₂) and temperature, X_3 (°C) at percent catalyst of 3% (wH₂WO₄/wOA).

In general, fatty acids are increasingly reactive to oxygen by increasing the number of double bonds in the molecular chain. Oxidative decomposition in saturated fatty acids during the heating process at high temperatures is easier to occur, because double bonds are easily attacked by oxygen. Fatty acid molecules containing unsaturated fatty acid radicals are oxidized. Then, this radical with oxygen forms an active peroxide which when reacted with one molecule of fatty acid will form hydro peroxide and unsaturated fatty acid radical. This hydro peroxide is very unstable [18]. If the reaction temperature is too high then the percentage of conversion will be decreased. Figure-2 shows that in the fixed variable percent catalyst 3%, maximum conversion is obtained when the number of substrate ratio 1: 8 with reaction temperature 70 °C is 99.12%.

The interaction effect of temperature and percent catalyst against conversion

The effect of variable substrate-ratio interaction with reaction temperature is shown in the contour response plot and surface response on Figure-3.

It show that both variables greatly affect of the resulting % conversions. If the reaction temperature is maintained at a certain amount and the percent of the

H₂WO₄ catalyst is raised, the percent conversion increases significantly. As the reaction temperature is raised and the percent of the H₂WO₄ catalyst is maintained constant, it is seen that the conversion obtained also changes, where the high reaction temperature causes a decrease in the percent of conversion produced.

Increased conversions can occur because high temperatures can increase the reaction rate and can increase transfers between substrates [13]. At temperature more than 75 °C the catalyst is less actively working. This condition indicates that temperature can also trigger the catalyst activity on the substrate in the synthesis of azelaic acid. The use of high temperatures can cause the catalyst to undergo a denaturation process. If this process occurs, the catalyst will decrease and the reaction rate will decrease. This condition greatly affects the resulting % conversion, in which the catalyst is no longer able to transfer oxygen in oxidative breakdowns in the synthesis of azelaic acid.

The result of the research on the contour surface of Figure-3 shows that in the fixed variable, the substrate mole ratio of 1: 8 maximum conversions is obtained when percent catalyst 3% with reaction temperature 70 °C is 94, 09%.

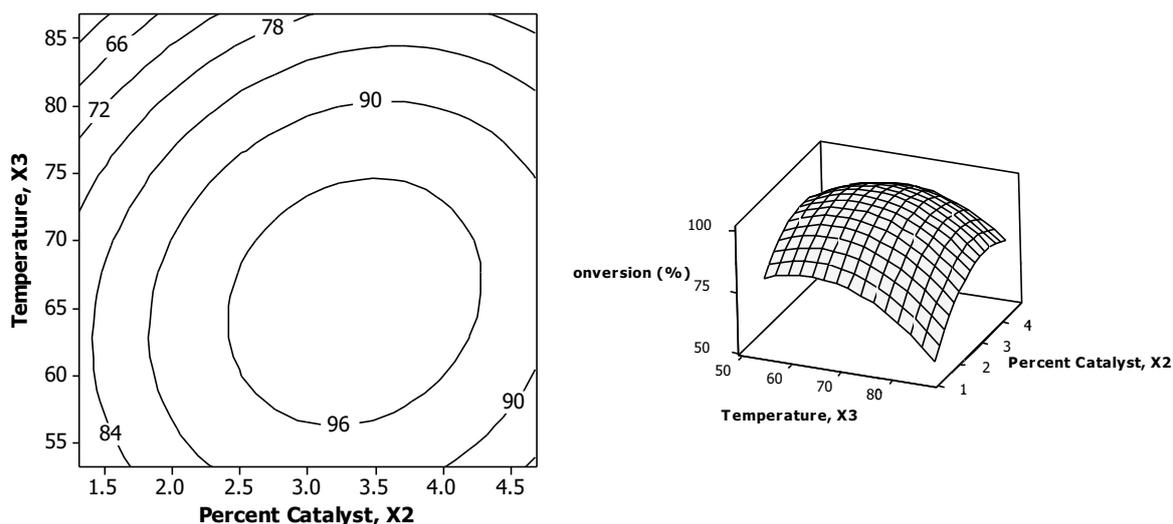


Figure-3. Contour and surface plot of percent conversion of iodine number as function of percent catalyst, X_2 (wH_2WO_4/wOA) and temperature, X_3 ($^{\circ}C$) at substrate mole ratio 8:1 (OA/H_2O_2).

Identification of Azelaic acid with FT-IR spectroscopy

Infrared spectrophotometry is one tool that can be used to analyze chemical compounds. This instrument can provide a description and structure of a molecule about a chemical compound [19]. The infrared radiation energy will be absorbed by organic compound so that the

molecule will experience rotation or vibration. Each type of bond has different frequency properties such as C-C, C-H, C = O, O-H and so on [20]. To obtain a clearer interpretation, a correlation table of infrared is required. The result of the obtained azelaic acid spectrum is shown in Figure-4.

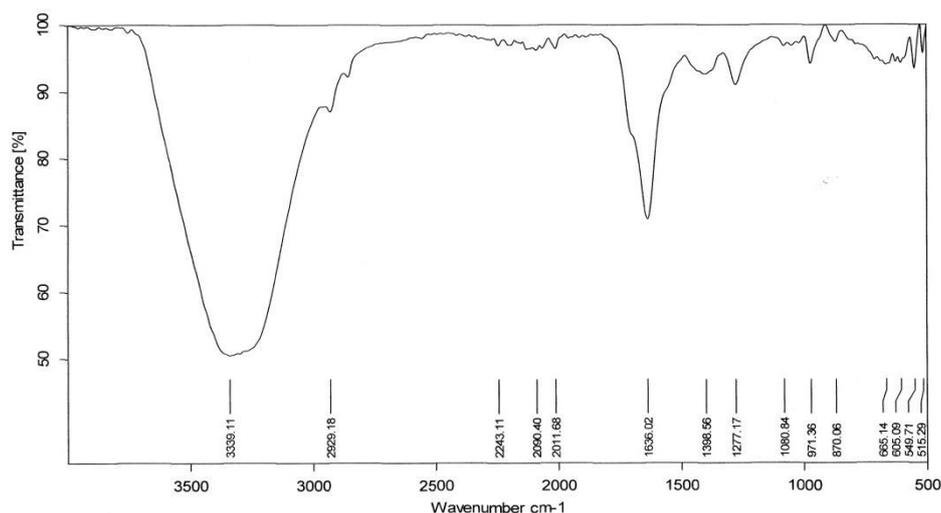


Figure-4. Result of identification of Azelaic acid with FT-IR spectroscopy.

Figure-4 shows the results of FTIR spectrum analysis at run XVI with the lowest iodine value of 0.79 with the conversion of iodine degradation is 99.12%. In the figure above shows that the product of azelaic acid has a spectrum 3339.11 cm^{-1} (OH bond). The methylene strain vibration ($-CH_2-$) appears at the wave number 2929.18 cm^{-1} , the oxygen double bond in the azelaic acid compound appearing at 1636.02 cm^{-1} (C = O) and 1277.17 cm^{-1} for the carboxyl ($-C-OH$). The presence of the C = O and C-OH groups shows the sample containing azelaic acid compounds or groups of carboxylic acids.

Biocompatibility analysis of synthesis process of Azelaic acid

Chemical compound synthesis often only evaluates the efficiency of the process based on the amount of product acquisition without considering the by product and waste generated from the process. In the early 1990s, Anastas began to evaluate the environmental impact of the synthesis of these chemicals. Therefore developed a method to reduce and even eliminate the use of compounds considered harmful to the environment. Green indicators are one method created to measure the environmental impact of chemical processes [2].



A process can be categorized as a safe, environmentally friendly and sustainable process when it meets the following principles: the economic value of atoms is close to 100%, chemically designed products and processes are used to reduce or eliminate the use of

hazardous materials, and the by-products and waste generated are environmentally friendly [21].

In this study, the synthesis of azelaic acid from oleic acid is carried out using H_2O_2 / H_2WO_4 as oxidizing agent. By that, the reaction and calculation of Atomic Economy (AE) are as follows:



$$\text{As in [21]: } AE = \frac{M_{\text{Azelaic Acid}} + M_{\text{Pelargonic Acid}} + M_{\text{Water}}}{M_{\text{Oleic Acid}} + 4M_{\text{Hydrogen Peroxide}}} \cdot 100\% \quad (2)$$

From the equation, AE value is obtained 82.7% for the synthesis process of this azelaic acid. It means that 82.7% of atomic reactant is converted into product while 17.3% is converted as by product. In this case, by product is water and it is no harm to environment. Due to this result, the reaction is considered as one kind of environmentally friendly.

In the synthesis of azelaic acid, there is an oxidation process which requires an oxidizing agent as an oxygen contributor in the breaking of the C = C oleic acid double bond [2]. H_2O_2 / H_2WO_4 are selected as oxidizer and catalyst because it is considered to be very environmentally friendly, working specifically and safely. When decomposed H_2O_2 will form water and oxygen that is not harmful to the environment. The oxidative breakdown of the synthesis of azelaic acid by using H_2O_2 as its oxidant also produces only safe and non-toxic waste. H_2WO_4 tungstate acid is a metal salt, which can be used as a catalyst for oxidation reaction with H_2O_2 as its oxidant. This catalyst is chosen because it can work specifically and efficiently. In solvent-free conditions, tungstate acid is easily separated from the product mixture. This catalyst also can still be used more than 6 times so it is considered very economical and can minimize the use of chemicals [5].

CONCLUSIONS

Based on the results of research of synthesis of azelaic acid from oleic acid with oxidizing agent H_2O_2 / H_2WO_4 , it can be taken some conclusion. The actual model by RSM represents the relationship of each reaction variable (the ratio of substrate mole (X_1), percent of catalyst (X_2) and reaction temperature (X_3)) and its interaction with percent conversion based on the decrease of iodine number in the synthesis of azelaic acid is as follows:

$$\begin{aligned} \% \text{ conversion} &= 97,99 + 3,907 X_1 + 3,651 X_2 - 4,556 X_3 - 1,467 X_1^2 - 4,299 X_2^2 - 4,453 X_3^2 + 0,57 X_1 X_2 + 0,63 X_1 X_3 + 1,37 X_2 X_3 \end{aligned}$$

The result of variance analysis shows that each variable has significant influence to percent conversion resulted. Based on the analysis of the biocompatibility of the process, the synthesis of azelaic acid from oleic acid

with an environmentally friendly H_2O_2 / H_2WO_4 oxidizer can be expressed as a safe, efficient, economical and sustainable process.

ACKNOWLEDGEMENTS

This work was supported by Universitas Sumatera Utara for providing research funds.

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