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Synthesis of fructone from ethyl acetoacetate and ethylene glycol using phosphotungstic acid catalyst

Asep Kadarohman[(a)]*, K. H. Gustiawan[(a)], Ratna Eko Sardjono[(a)], A. Pratiwi[(a)], L. L. Khumaisah[(b)]

[(a)] Departemen Pendidikan Kimia, Fakultas Pendidikan Matematika dan Ilmu Pengetahuan Alam, Universitas Pendidikan Indonesia, Jl. Dr. Setiabudhi No. 229 Bandung 40154, Indonesia

[(b)] Departemen Kimia, Fakultas Sains dan Teknologi, Universitas Muhammadiyah Sukabumi, Jl. R. Syamsudin, S.H. No. 50 Sukabumi 43113, Indonesia

** Corresponding author:*
kadar@upi.edu
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Abstract

Fructone is a perfume compound with the aroma of apples. Fructone can be synthesized through the acetalization reaction of ethyl acetoacetate and ethylene glycol using an acid catalyst. This study aims to determine the effect of the cyclohexane-water azeotropic method and to determine the optimum conditions for the synthesis of fructone using phosphotungstic acid as a catalyst. Fructone synthesis using reflux equipped with Dean-Stark apparatus. Determination of the optimum conditions includes temperature variations of 75, 78, and 81°C; mol ratio of ethyl acetoacetate and ethylene glycol 1:1.5; 1:2; and 1:3; the number of mol of catalyst 2; 1; 0.5; 0.25; and 0.125 mmol. The reaction time is 30, 60, 90, 120, 150, 180, 210, and 240 min. The synthesis products were analyzed by GC and GCMS. The optimum conditions for the synthesis of fructone were found at a temperature of 78□C, the ratio of mol of ethyl acetoacetate and ethylene glycol 1: 3, the amount of catalyst was 1 mmol and the reaction time was 3 hours. Fructone produced is 93.42%.

Keywords: *Acetalization, Ethyl Acetoacetate, Ethylene Glycol, Fructone, Phosphotungstic Acid.*

1. Introduction

The number of food flavoring, cosmetic, and fragrance industries in Indonesia continues to increase. The Indonesian Central Bureau of Statistics shows that export and import data for essential oils, resinoids, fragrances, and cosmetics are increasing every year, as presented in Table 1. Table 1 shows that Indonesia's total exports are greater than imports. However, the value of imports is almost 2 times greater than the value of exports. Therefore, efforts need to be made to reduce the total value of Indonesia's imports. Fructone is one of the perfume ingredients imported by Indonesia. Fructone (Ethyl 2-methyl-1,3-dioxolane-2-acetate) is a perfume ingredient with an apple scent. Fructone can be synthesized from the acetalization reaction between ethyl acetoacetate and ethylene glycol using an acid catalyst [1]. Figure 1 shows the synthesis of fructone from ethyl acetoacetate and ethylene glycol with an acid catalyst. The acid catalyst used can be in the form of homogeneous and heterogeneous catalysts [2, 3] [A, G]. Sulfuric acid and p-toluensulphonic acid are commonly used homogeneous acid catalysts [2, 4]. However, these catalysts are toxic, corrosive, and difficult to separate from the reaction mixture [3, 5]. Therefore, it is necessary to investigate the use of other acid catalysts that are easily separated from the reaction mixture and are environmentally friendly. Heteropoly acid is a strong Bronsted acid catalyst, solid, easy to separate, and environmentally friendly. Phosphotungstic acid ($H_3PW_{12}O_{40}.xH_2O$) with a relative molecular mass (Mr) of 2880 g/mol (anhydrous) is a heteropoly acid with strong acidity and can be used as a homogeneous or heterogeneous acid catalyst [5, 6]. Phongphotungstic acid (PTA) is a complex compound with a Keggin structure which has a P (phosphorus) and W metal (tungsten) heteroatom as the central atom shown in Figure 2. In the PTA structure, there are three types of oxygen atoms bonded in the complex. The complexation of all oxygen atoms around this heteroatom causes heteropoly acids to have very strong acidic properties, so they are considered super acids with pKa -13. The high acidity of phosphotungstic acid and good solubility in water and other polar solvents allows its use as a homogeneous catalyst [6, 7]. The acetalization reaction between carbonyl and alcohol with an acid catalyst is a reversible reaction with water as a by-product [7, 8]. To increase the fructone produced, water in the reaction system must be removed so that the equilibrium shifts towards the reaction products [8, 9]. One way to remove water in the reaction system can be the azeotropic reflux method [9, 10]. Synthesis of fructone using toluene as an azeotrope with phosphotungstic acid as a catalyst produced 86.7% of fructone. The use of the toluene-water azeotrope will produce a boiling point of 85°C. Cyclohexane is a compound that can also form an azeotrope with water. Cyclohexane-water azeotrope contains 5.6 w% in water with a boiling point of 69.5°C [10, 11]. The low temperature of the cyclohexane-water azeotrope is expected to accelerate the release of water from the reaction system so that it will be more effective in removing water. In addition, the use of lower temperatures will reduce the reaction by-products. In this article, we discussed the effect of using the cyclohexane-water azeotrope system on the reaction of fructone synthesis from ethyl acetoacetate and ethylene glycol with a phosphotungstic acid catalyst, as well as determined the optimum conditions for the reaction.

Table 1. ***Indonesia's import-export data of essential oils, resinoids, fragrances, and cosmetics. Data was obtained from https://www.bps.go.id/exim/***

Year	Export		Import	
	Value (USD)	Weight (kg)	Value (USD)	Weight (kg)
2017	50,184,2 95.81	6,687,325.29	89,695,965.00	6,436,838.00
2018	50,583,443.82	6,939,025.40	94,399,771.00	6,747,136.00
2019	58,050,357.59	7,491,704.71	97,094,296.00	7,154,479.00
2020	68,672,795.64	8,364,030.87	102,547,270.00	8,156,428.00

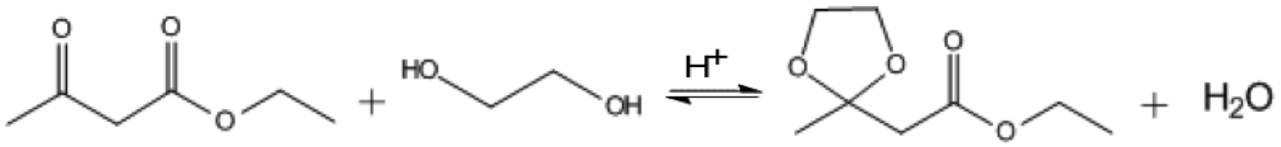

Figure 1. Fructone synthesis reaction from ethyl acetoacetate and ethylene glycol with an acid catalyst

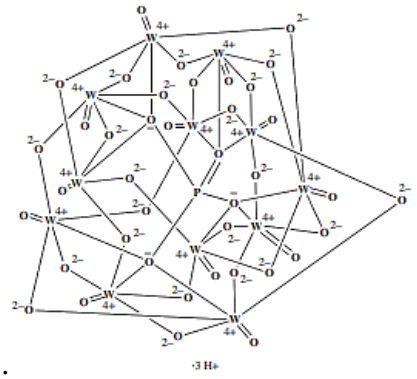

Figure 2. Phosphotungstic Acid Structure

2. Materials and methods

2.1. Materials

Ethyl acetoacetate, ethylene glycol, cyclohexane, diethyl ether, chloroform, NaOH, Na_2CO_3, NaCl, anhydrous Na_2SO_4 from Merck, phosphotungstic acid ($H_3PW_{12}O_{40}.xH_2O$) from Shandong Horel Co., distilled water, universal indicator, filter paper, and vaseline.

2.2. Apparatus

The equipment used consists of glassware, reflux set equipped with dean-stark, distillation apparatus set, Buchi rotary evaporator, hot plate with stirrer, micropipette (100-1000 L), oven, hot plate, an analytical balance, GC Shimadzu QP 2010 (FID detector, column DB5, 30 m long and 0.25 mm in diameter), GC-MS Shimadzu QP 2010 SE (5 MS RT-X column, 30 meters long, and 0.25 mm in diameter).

2.3. Gas chromatography (GC) and gas chromatography-mass spectrometry (GCMS) condition

The GC analysis conditions used an injector temperature of 260°C, a detector temperature of 300 °C, and an initial column temperature of 60°C followed by an increase in temperature of 10 °C/min to a temperature of 280°C. GCMS analysis conditions used injector temperature of 250°C, detector temperature of 260 °C, and initial column temperature of 60°C followed by an increase in temperature of 8 °C/min to 260 °C and held for 2 min. Detailed information regarding GC-MS is presented in elsewhere [12]

2.4. Experimental procedure

Ethyl acetoacetate (0.1 mol), 0.3 mol of ethylene glycol, $2x10^{-3}$ mol of phosphotungstic acid, and 20 mL of cyclohexane were put into a three-neck flask equipped with a reflux device and dean stark. The reaction mixture was heated at 78°C for 2 hours. The reaction mixture was neutralized with 10% of NaOH in a separatory funnel to pH 8 and then 10 mL of NaCl (10%) was added. The bottom layer (aqueous phase) in the separatory funnel is discarded. The top layer (organic phase) was washed with 10 mL of NaCl (10%) solution twice. The top layer was dried with anhydrous Na_2SO_4. The cyclohexane solvent was removed by a rotary evaporator. The reaction products were

analyzed by GC and GCMS. The reaction was repeated without using the azeotropic method. Determination of the optimum conditions was carried out by varying the temperatures (75, 78, and 81°C). Variations in the amount of ethylene glycol are 0.15, 0.2, and 0.3 mol. Variations of phosphotungstic acid catalyst concentrations are 2; 1; 0.5; 0.25; and 0.125 mmol. Variation of reaction time 30; 60; 90; 120; 150; 180; 210; and 240 min.

3. Results and Discussion

There are several parameters involving the changing of reaction. Specifically, some parameters involved are amount of reactants, temperature, and existence of catalyst [13].

3.1. Acetalization reaction of ethyl acetoacetate and ethylene glycol

Fructone synthesis reaction products were analyzed using GC and GCMS. The GCMS chromatogram is presented in Figure 3. There are 4 peaks on the GCMS chromatogram of the fructone synthesis reaction products. Fructone as a reaction product has a retention time of 5.298 min, ethyl acetoacetate as the rest of the reagent at 2,469 min, cyclohexane as an azeotrope at 1,392, and chloroform as an impurity at 1,307 min. The mass spectra of fructone are presented in Figure 4. Figure 4 shows that the fourth peak had a 96% similarity with fructone with the base peak m/z 87.

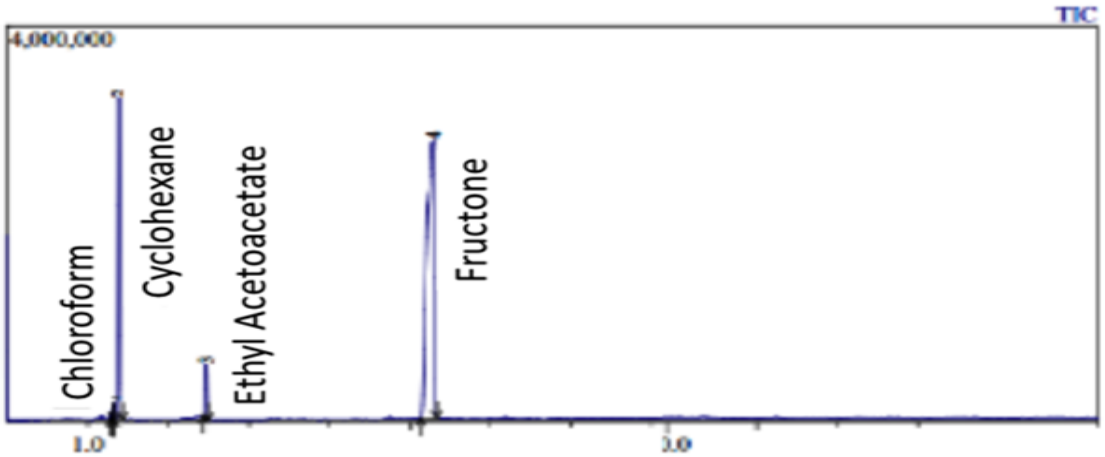

Figure 3. Chromatogram of GCMS reaction product of fructone synthesis from 0.1 mol of ethyl acetoaceate, 0.3 mol of ethylene glycol, 1 mmol of phosphotungstic acid at 78°C for 2 hours with a cyclohexane-water azeotropic system

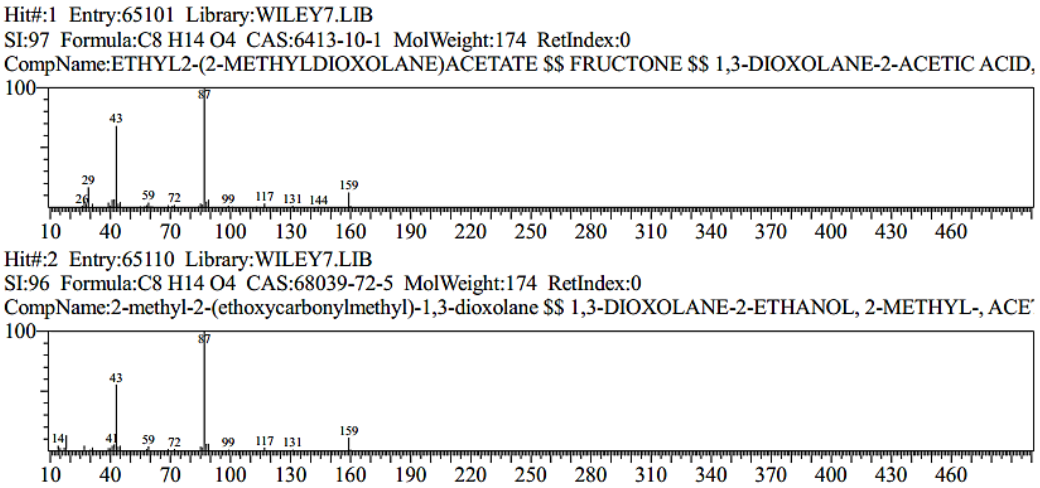

Figure 4. Mass spectra of fructone

3.2. The effect of the azeotropic system on the amount of fructone produced

A fructone synthesis reaction is an equilibrium reaction with water as a by-product. The cyclohexane-water azeotropic system is used to remove water in the reaction system. The reduction of water in the system will shift the reaction towards the formation of fructones. The data on the synthesis of fructones in the reaction of 0.1 mol of ethyl acetoacetate, 0.3 mol of ethylene glycol, and 1 mmol of phosphotungstic acid at 78°C for 2 hours without and using the cyclohexane-water azeotrope system are presented in Figure 5. Figure 5 shows the amount of fructone produced using the azeotropic system of 90.97%, higher than the amount of fructone produced without using the azeotropic system of 73.62%. This shows the reduction of water from the reaction system shifts the equilibrium toward the formation of products. Thus, the amount of fructone produced is more. The next step is to determine the optimal conditions for the fructone synthesis reaction using an azeotropic system.

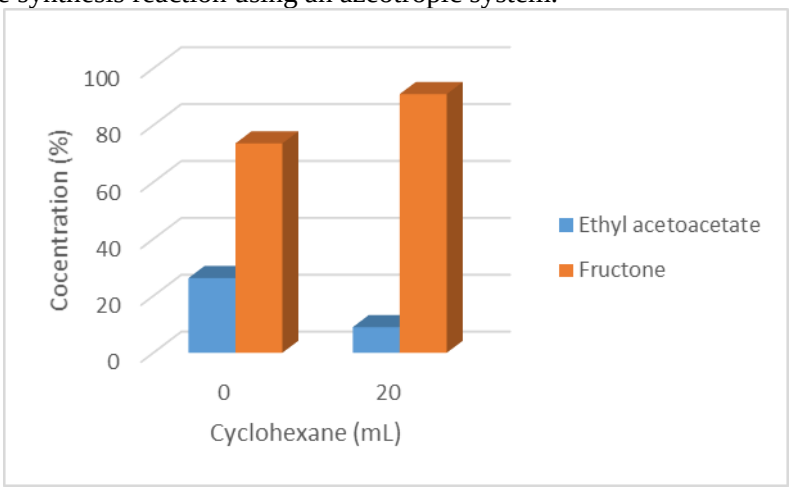

Figure 5. The product of the fructone synthesis reaction without and with the cyclohexane-water azeotropic system

3.3. Effect of acetalization reaction temperature

The temperature has a role in increasing the frequency and effectiveness of collisions between molecules so that they can produce energy to achieve the required activation energy [14-16]. Determination of the optimum reaction temperature was carried out at 75, 78, and 81°C. The reaction products of fructone synthesis at various temperatures, the amount of ethyl acetoacetate 0.1 mol, ethylene glycol 0.3 mol, and phosphotungstic acid 1 mmol for 2 hours are presented in Figure 6.

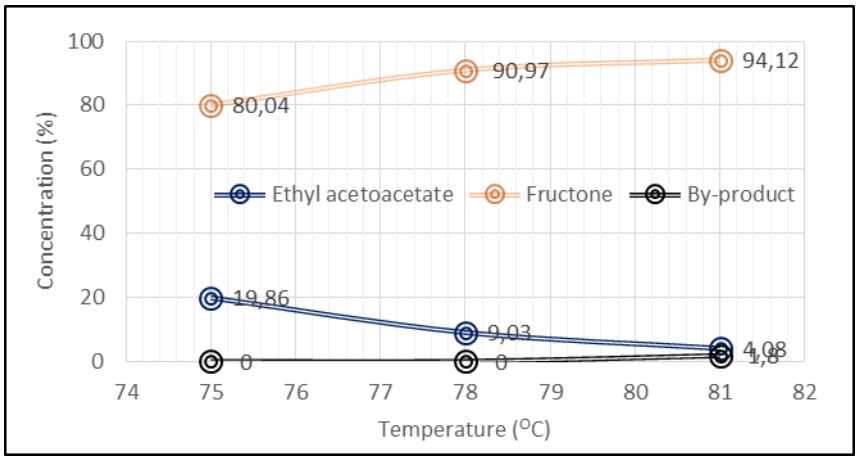

Figure 6. The effect of temperature on fructone synthesis products

Figure 6 shows the fructone conversion increased from 80.04, 90.97, and 94.12%, which are due to the increase in reaction temperature. An increase in temperature will increase the kinetic energy of the molecules [14, 16]. An increase in temperature causes molecules to move faster and collisions occur more frequently. Several collisions that occur can produce enough energy to reach the activation energy of the reaction. At higher reaction temperatures, the possibility of molecular collisions to produce energy exceeds the activation energy of the reaction, resulting in reaction by-products [2]. This is shown at the reaction temperature of 81°C the highest amount of fructone produced is 94.12%. However, at the reaction temperature of 81°C, 1.8% of by-products were also produced. Therefore, the optimum condition for the synthesis of fructone from ethyl acetoacetate and ethylene glycol with phosphotungstic acid catalyst is 78°C.

3.4. Effect of acetalization reaction temperature

Determination of the mol ratio of the reagent is carried out after the optimum reaction temperature is found. Theoretically, the ratio of the number of mol of ethyl acetoacetate and ethylene glycol in the acetalization reaction is 1:1. However, because the acetalization reaction is reversible, an excess amount of ethylene glycol is used to shift the equilibrium towards product formation. The use of the number of mol of ethylene glycol reacted in excess, because ethylene glycol is easily soluble in water, so it is easy to separate from the reaction mixture. Variations in the amount of ethylene glycol reacted were 0.15; 0.2; and 0.3 mol. The reaction product for the synthesis of fructone at various mol of ethylene glycol with 0.1 mol of ethyl acetoacetate and 1 mmol of catalyst at 78°C for 2 hours is presented in Figure 7. Figure 7 shows that increasing the amount of ethylene glycol can reduce the number of by-products. With the addition of 0.2 mol of ethylene glycol, the amount of fructone produced was 93.8% and the by-product was 2.54%. The presence of by-products will interfere with the fructone separation process. Therefore, the optimum condition for fructone synthesis was 0.3 mol of ethylene glycol with a total fructone product of 90.98%, because no by-products were produced.

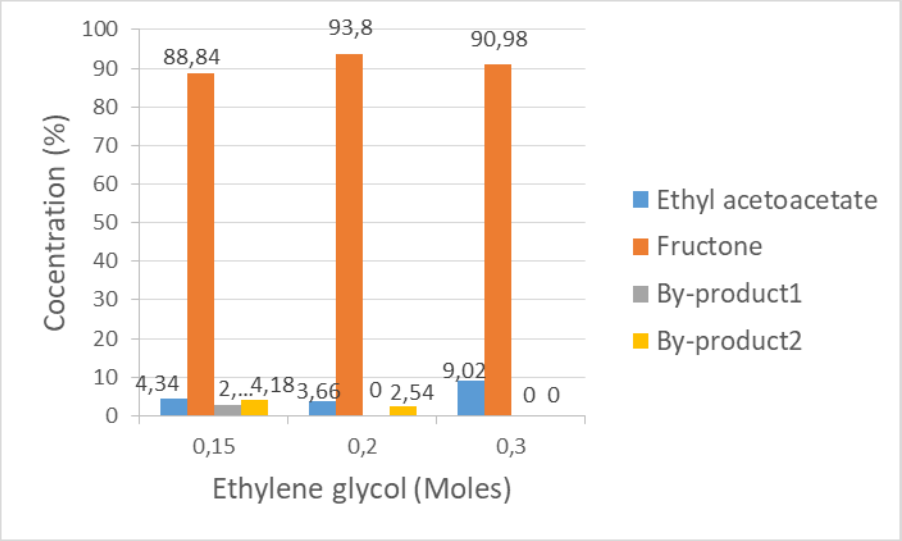

Figure 7. The effect of variations in ethylene glycol on the synthesis product of fructone

3.5. Effect of amount of catalyst

Chemical reactions require a minimum of energy to reach the activation energy [17]. The addition of a catalyst will change the reaction pathway with lower activation energy so that the reaction becomes easier to take place. The reaction product for the synthesis of fructone with varying amounts of the catalyst with 0.1 mol of ethyl acetoacetate

and 0.3 mol of ethylene glycol at a temperature of 78 °C for 2 hours is presented in Figure 8. Figure 8 shows that increasing the amount of catalyst can increase the amount of fructone produced, ranging from 73.12% (with the addition of 0.125 mmol of catalyst) to 95.45% (with the addition of 2 mmol of catalyst). Increasing the amount of catalyst from 0.5 to 1 mmol can increase the amount of fructone by 4.51% and increasing the amount of catalyst from 1 to 2 mmol can increase the number of fructones by 4.48 %. The addition of a 2-fold catalyst from 1 to 2 mmol is not proportional to the increase in the amount of fructone produced. Therefore, the optimum number of additions of catalyst is 1 mmol.

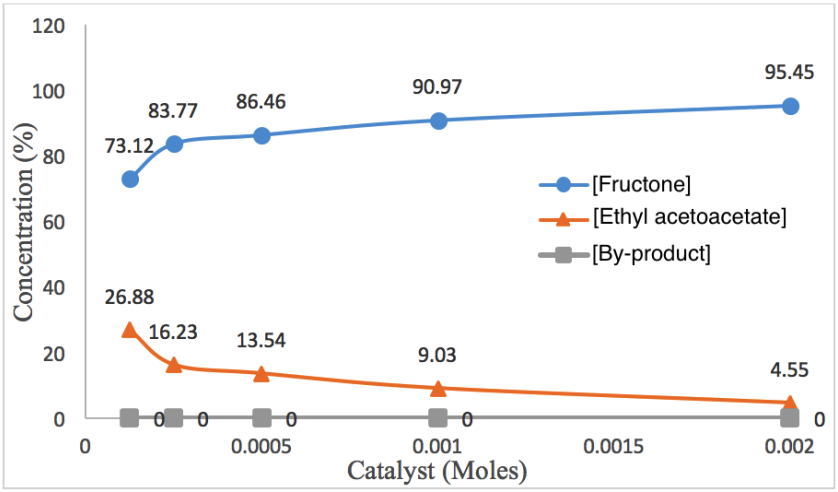

Figure 8. The effect of the number of mol of catalyst on the product of the fructone synthesis reaction

3.6. Effect of reaction time

Determination of the reaction time of the fructone synthesis reaction is the final step in determining the optimum reaction conditions. To determine the optimum reaction time, the fructone synthesis reaction was carried out for 4 hours with the reaction products analyzed every 30 min. The effect of time on the reaction product of fructone synthesis at a temperature of 78°C, with the amount of ethyl acetoacetate 0.1 mol and ethylene glycol 0.3 mol, as well as 1 mmol as a phosphotungstic acid catalyst is presented in Figure 9. Figure 9 shows that increasing the reaction time can increase the amount of fructone produced. However, starting from the 210th minute, besides producing fructone, by-products are also produced. Therefore, the optimum reaction time for the fructone synthesis reaction is 180 min (3 hours).

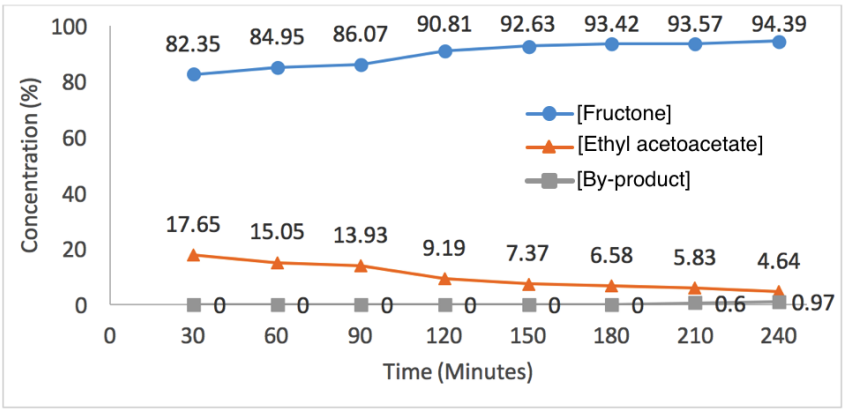

Figure 9. The effect of reaction time on the product of the Fructone synthesis reaction

Conclusion

The reaction product of fructone synthesis using the cyclohexane-water azeotrope system produced a higher amount of fructone than the amount of fructone produced without the use of the cyclohexane-water azeotrope system. Optimum conditions for the reaction of fructone synthesis with the cyclohexane-water azeotrope system, the amount of reagent 0.1 mol of ethyl acetoacetate, and 0.3 mol of ethylene glycol with 1 mmol of phosphotungstic acid as a catalyst at 78°C for 3 hours and obtained a fructone conversion of 93.42%.

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