Makara J. Sci. 19/2 (2015), 85-90
doi: 10.7454/mss.v19i2.4778

Production of Adipic Acid from Mixtures of Cyclohexanol-Cyclohexanone using Polyoxometalate Catalysts

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Abstract

Adipic acid production through catalytic conversion of cyclohexanol-cyclohexanone using polyoxometalate $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$ as catalysts was carried out systematically. Polyoxometalates $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$ were synthesized using an inorganic synthesis method and were characterized using Fourier transform infrared spectroscopy (FTIR). Adipic acid was formed from conversion of cyclohexanol-cyclohexanone and was characterized by using melting point measurement, identification of functional group using FTIR spectrophotometer, analysis of gas chromatography-mass spectrometry (GC-MS), and ^1H and ^{13}C NMR (nuclear magnetic resonance) spectrophotometer. This research investigated the influence of reaction time and temperature on conversion. The results showed that adipic acid was formed successfully with a yield of 68% by using $H_5[\alpha\text{-}BW_{12}O_{40}]$ as catalyst at the melting point of 150-152 °C after optimization. In contrast, using $H_4[\alpha\text{-}SiW_{12}O_{40}]$ as catalyst, formation of adipic acid was only 3.7%. Investigation of time and temperature showed 9 h as the optimum reaction time and 90 °C as the optimum temperature for conversion of up to 68% adipic acid. Identification using FTIR, ^1H, and ^{13}C NMR showed that the adipic acid from conversion of cyclohexanol-cyclohexanone was in agreement with the standard adipic acid data in the literatures. GC-MS analysis indicated that several by-products were formed in conversion of cyclohexanol-cyclohexanone using $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$ as catalysts.

Abstrak

Produksi Asam Adipat dari Campuran Sikloheksanol-Sikloheksanon menggunakan Katalis Senyawa Polioksometalat. Produksi asam adipat melalui reaksi konversi katalitik sikloheksanol-sikloheksanon menggunakan senyawa polioksometalat $H_5[\alpha\text{-}BW_{12}O_{40}]$ dan $H_4[\alpha\text{-}SiW_{12}O_{40}]$ sebagai katalis telah dilakukan secara sistematis. Polioksometalat $H_5[\alpha\text{-}BW_{12}O_{40}]$ dan $H_4[\alpha\text{-}SiW_{12}O_{40}]$ disintesis menggunakan metoda sintesis anorganik dan dikarakterisasi menggunakan spektroskopi FTIR. Asam adipat yang terbentuk dari hasil konversi sikloheksanol-sikloheksanon dikarakterisasi melalui penentuan titik leleh, analisis gugus fungsional menggunakan spektrofotometer FTIR, analisis GC-MS dan analisis menggunakan spektrometer ^1H dan ^{13}C NMR. Pengaruh waktu reaksi dan temperatur reaksi pada proses konversi dipelajari pada penelitian ini. Hasil penelitian menunjukkan bahwa asam adipat berhasil terbentuk dengan rendemen sebesar 68% menggunakan $H_5[\alpha\text{-}BW_{12}O_{40}]$ sebagai katalis dengan titik leleh sebesar 150-152 °C hasil optimasi. Pada sisi lain, pembentukan asam adipat hanya menghasilkan rendemen 3,7% menggunakan katalis $H_4[\alpha\text{-}SiW_{12}O_{40}]$. Pengamatan lebih lanjut melalui optimasi terhadap proses konversi sikloheksanol-sikloheksanon menjadi asam adipat menghasilkan waktu optimum reaksi 9 jam dan temperatur reaksi 90 °C menghasilkan asam adipat dengan rendemen sebesar 68%. Identifikasi menggunakan FTIR, ^1H dan ^{13}C NMR menunjukkan bahwa asam adipat hasil konversi dari sikloheksanol-sikloheksanon sesuai dengan asam adipat standar dari kepustakaan. Analisis menggunakan GC-MS mengindikasikan pembentukan beberapa produk samping hasil konversi sikloheksanol-sikloheksanon menggunakan katalis $H_5[\alpha\text{-}BW_{12}O_{40}]$ dan $H_4[\alpha\text{-}SiW_{12}O_{40}]$.

Keywords: adipic acid, cyclohexanol-cyclohexanone, polyoxometalate

Introduction

Green synthesis of adipic acid is extremely urgent for environmental reasons. Adipic acid is a precursor for nylon 6,6 and polyurethane plastic synthesis. The main method of synthesizing adipic acid through catalytic methods using nitric acid releases toxic nitrous oxide into the environment [1]. Thus, a catalytic conversion that

forms adipic acid using an eco-friendly catalyst is needed. An approach to synthesizing adipic acid by oxidation of cyclohexanone, cyclohexanol, cyclohexane, or mixtures of these has been developed, using H_2O_2 as a green oxidant and appropriate catalyst, as shown in Figure 1.

Various catalysts have been tested for adipic acid synthesis, including ionic liquid by two catalytic functions [2], hybrid porous tin (IV) phosphonate [3], manganese catalyst [4], and tungstate-based catalyst [5]. Recently, development of tungstate-based catalyst for adipic acid synthesis has been explored deeply using H_2WO_4 [6], silica functionalized ammonium tungstate [7], sodium tungstate with stearyl dimethyl benzyl ammonium chloride as surfactant [8], and polyoxometalate compounds. Polyoxometalates are oxygen-metal clusters with various structures and oxidation states and can be used as potential catalyst due to very high acidity and non-toxic solid materials. Polyoxometalates are used intensively as catalyst for adipic acid synthesis. Keggin-type polyoxometalate $H_{3+x}PMo_{12-x}V_xO_{40}$ (x=1 and 2) has catalyzed conversion of cyclohexanone to adipic acid [9]. Effect of addenda and heteroatoms in polyoxometalate has been studied by Zhu *et al.* using peroxotungstate and peroxomolobdates as catalyst [10]. Common Keggin-type $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ with different addenda atoms have been converted into glycine phosphotungstate, and glicine phosphomolybdate acted as catalyst for conversion of cyclohexanone to adipic acid with high yield and selectivity [11]. In addition, structure effect has been investigated in the polyoxometalate, which was Anderson type $[(C_{18}H_{37})_2N(CH_3)_2]_6Mo_7O_{24}$, as catalyst for the conversion of cyclohexane to adipic acid [12].

Herein, we demonstrate the basic structure with different heteroatoms of polyoxometalate $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$ and with similar addenda atoms (tungsten) but different heteroatoms (boron and silica) used as catalyst for converting a 1:1 mixture of cyclohexanol-cyclohexanone to adipic acid. Based on our knowledge, this is the first report to investigate these polyoxometalate catalysts in conversion of cyclohexanol-cyclohexanone. In addition, several factors affecting formation of adipic acid, such as time and temperature reactions, were investigated in cyclohexanol-cyclohexanone conversion.

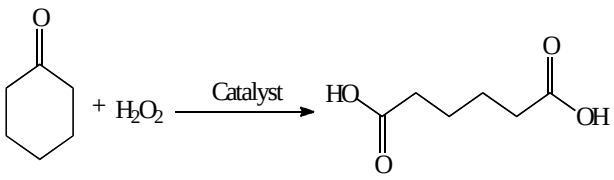

Figure 1. Synthesis of Adipic Acid Via Oxidation of Cyclohexanone

Materials and Methods

Materials and instrumentation. Chemicals were supplied from Merck and Sigma Aldrich, including sodium tungstate (Merck), potassium hydrogen carbonate (Merck), potassium carbonate (Merck), sodium meta silicate (Aldrich), ammonium chloride (Merck), potassium chloride (Merck), and disodium hydrogen phosphate dihydrate (Merck). Cyclohexanol and cylohexanone were obtained from Sigma-Aldrich and used without further purification. FTIR spectrum was recorded using the Shimadzu FTIR 8201PC. Gas Chromatography-Mass Spectrometer Shimadzu 2010QP was used to identify product. ^1H and ^{13}C NMR were performed by Jeol 500 MHz and 125 MHz using DMSO and acetone as solvents, respectively.

Synthesis of polyoxometalate $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$. Synthesis of polyoxometalate $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$ was adopted from Lesbani [13] and was characterized using an FTIR spectrophotometer using a KBr disk at room temperature at the range of 400-4000 cm^{-1}. Synthesis of $H_5[\alpha\text{-}BW_{12}O_{40}]$ was as follows: boric acid (150 g) and sodium tungsten (100 g) were dissolved in 450 mL warm water, and the solution was stirred for 3 h. The solution was cooled and filtered. Boric acid (70 g) was added to the solution with slow stirring for 1 h. The solution was added to 10 mL of hydrochloric acid and stirred for 30 min. The solution was extracted with diethyl ether-hydrochloric acid and the etherate layer was collected and dried by a rotary evaporator to form a white solid of $H_5[\alpha\text{-}BW_{12}O_{40}]$. Synthesis of $H_4[\alpha\text{-}SiW_{12}O_{40}]$ was as follows: In a 1 L Beaker glass equipped with magnetic stirring, 11 g of sodium metasilicate was dissolved in 100 mL of water (A). Then, 182 g of sodium tungsten was dissolved in 300 mL of hot water (B). Solution B was added to 165 mL of 4 M hydrochloric acid with vigorous stirring, followed by addition of solution A. The pH of the solution was adjusted to 5–6, and the solution was stirred for 1 h at 100 °C. The solution was cooled at room temperature, and 50 g of potassium chloride was added to obtain solid material. The solid material was dissolved in water, and 100 mL of diethyl ether and 10 mL of hydrochloric acid were added. The solution was extracted, and the bottom layer was collected to obtain a white solid of $H_4[\alpha\text{-}SiW_{12}O_{40}]$ after vacuum process using a rotary evaporator.

Catalytic conversion of cyclohexanol-cyclohenanone to adipic acid. Conversion of the mixture of cyclohexanol-cyclohexanone was performed in a 100 mL flask according to the procedure of Zhang *et al.*, with slight modifications, as follows: 10 mL of the cyclohexanol-cyclohexanone mixture (1:1) and 0.1 g of catalyst were added to a flask equipped with a magnetic bar. The mixture was stirred for 15 min, followed by addition of 44 ml of 30% H_2O_2 with stirring for 10 min. Reaction

mixtures were refluxed for 8 h at 90 °C. After completed reaction, the mixture was cooled in a refrigerator for 12 h at 5 °C. White crystals of adipic acid were formed in the solution, and then the crystal was filtered, washed with cool water, and dried at room temperature [14]. Adipic acid was characterized using an FTIR spectrophotometer and ^{1}H and ^{13}C NMR analysis.

Results and Discussion

Polyoxometalates $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$ with different heteroatoms were characterized using FTIR spectroscopy, as shown in Figure 2.

Polyoxometalates $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$ are Keggin-type with $MX_{12}O_{40}^{n-}$ where M is the heteroatom and X is the addenda atom. In this research, M is B and Si, and X is tungsten. Table 1 shows specific vibrations of these polyoxometalates.

The vibrations in Table 1 are specific to $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$. Vibrations of W-Oc-W and W-Oe-W are similar in wavenumber, from 780–930 cm^{-1}, depending on their heteroatom. Vibrations of B-O are 914 cm^{-1} and those of Si-O are 1020 cm^{-1}, indicating that the heteroatom oxygen stretches the vibrations. According to these data, polyoxometalates $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$ were synthesized successfully, and their FTIR spectra are in agreement with those in the literature [15].

Polyoxometalates $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$ were used as catalyst for converting the cyclohexanol-cyclohexanol mixture to adipic acid using H_2O_2 as an oxidant. Catalysts $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$ activated the H_2O_2 to be an active oxidant in this reaction. The first trial of conversion using $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$ as catalysts yielded isolated adipic acid, as shown in Table 2.

The data in Table 2 show that $H_5[\alpha\text{-}BW_{12}O_{40}]$ is more effective for conversion than $H_4[\alpha\text{-}SiW_{12}O_{40}]$. Probably, a Keggin-type heteroatom is key to conversion of cyclohexanol-cyclohexanone into adipic acid. Boron is more acidic than silicon, according to the Lewis acid concept; therefore, activation of H_2O_2 needs a more acidic heteroatom [16]. Adipic acid was isolated and characterized using FTIR spectroscopy and then compared with the adipic acid standard, as shown in Figure 3.

Table 1. Vibration of $H_5[\alpha\text{-}BW_{12}O_{40}]$ and $H_4[\alpha\text{-}SiW_{12}O_{40}]$

Vibration	$H_5[\alpha\text{-}BW_{12}O_{40}]$	$H_4[\alpha\text{-}SiW_{12}O_{40}]$
B-O	914 cm^{-1}	-
W-Oc-W	810 cm^{-1}	786 cm^{-1}
W-Oe-W	902 cm^{-1}	925 cm^{-1}
W=O	960 cm^{-1}	979 cm^{-1}
Si-O	-	1020 cm^{-1}

Figure 3 shows that isolated adipic acid (B) is similar to standard adipic acid (A). Vibrations of isolated adipic acid appear at wave number of 2954 cm^{-1} for O-H, 2877 cm^{-1} for aliphatic methylene (CH_2), 1697 cm^{-1} for C = O, 1280 cm^{-1} for C-O, and 1195 cm^{-1} for aliphatic C-C. All these vibrations are in agreement with those of standard adipic acid reported in the literature [17]. Characterization of isolated white crystals of adipic acid was conducted using ^{1}H, ^{13}C NMR, and mass spectroscopy. Figure 4 shows the ^{1}H NMR spectrum.

Table 2. The Yield of Adipic Acid from Conversion of Cyclohexanol-cyclohexanone

Adipic acid	$H_5[\alpha\text{-}BW_{12}O_{40}]$	$H_4[\alpha\text{-}SiW_{12}O_{40}]$
Yield (Isolated)	60.7%	< 10%

Condition: 0.1 g catalyst, 44 mL H_2O_2 30%, 10 mL cyclohexanol-cyclohexanone (1:1), 8 h reaction time, temperature 90 °C.

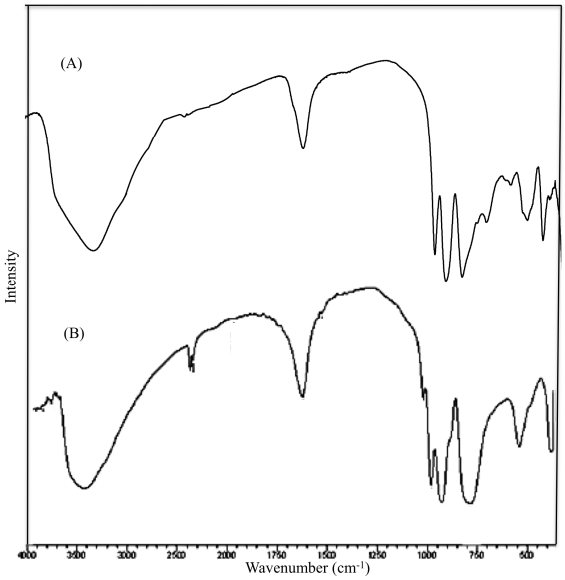

Figure 2. FTIR Spectrum of $H_5[\alpha\text{-}BW_{12}O_{40}]$ (A) and $H_4[\alpha\text{-}SiW_{12}O_{40}]$ (B)

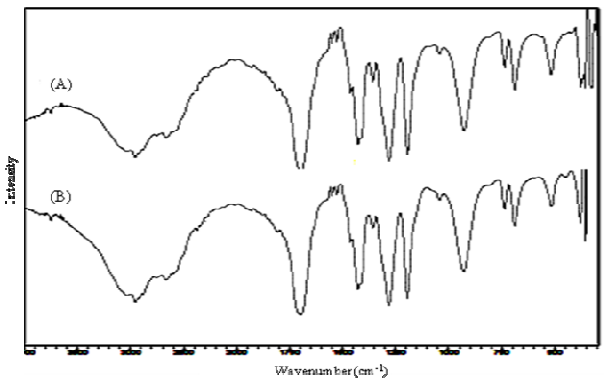

Figure 3. FTIR Spectra of (A) Standard Adipic Acid and (B) Isolated Adipic Acid

The structure of adipic acid having a symmetric molecule can be identified using ^{1}H NMR and various deuterated solvents. A peak of DMSO-D6 used as solvent appears at 2.50 ppm. Other peaks related to adipic acid appear at 1.49 ppm (CH_2), δ 2.20 ppm (CH_2), and δ 12.02 ppm (COOH). The isolated adipic acid from this research has high purity compound indicated by no other peaks besides deuterated DMSO and adipic acid peaks were observed. The ^{1}H NMR result is supported by the ^{13}C NMR result, as shown in Figure 5.

Similar to the ^{1}H NMR spectrum, the ^{13}C NMR spectrum for adipic acid detects only three peaks. Acetone D6 was used to measure ^{13}C NMR of isolated adipic acid. As mentioned earlier, adipic acid can be measured using various solvents, and acetone appeared at 206.4 ppm. Peaks of adipic acid can be observed at 25.2 ppm, 33.9 ppm, and 17 4.7 ppm. Further characterization was conducted using a mass spectrometer (Figure 6).

Adipic acid has a molecular weight of 146 g/mol and a molecular peak of *m/z* 146. The molecular peak at *m/z* 146 is cannot be observed clearly in Figure 6. However, other peaks related to molecular fragments at *m/z* 128, 112, and 100 are obvious, with the highest intensity appearing at *m/z* 100 (100%) [18]. Figure 7 shows the fragmentation pattern of adipic acid.

Although all characterizations of isolated adipic acid show high purity of the compound, moderately isolated adipic acid obtained from cyclohexanol-cyclohexanone using $H_5[\alpha\text{-}BW_{12}O_{40}]$ indicated formation of several by-products and remaining cyclohexanol-cyclohexanone. Figure 8 shows three by-products identified using GC-MS.

On the basis of these results and from comparison with the literature [3,19-20], we propose a plausible mechanism for converting cyclohexanol-cyclohexanone into adipic acid, as shown in Figure 9. Oxygen from peroxide was activated with boric tungsten from polyoxometalate to attack cyclo species from cyclohexanol-cyclohexanone. Intermediate derivative lactone was formed, followed by re-arrangement of lactone to adipic acid and oxygen as a green by-product. This study also investigated reaction time and temperature of conversion. Data are presented in Figures 10 and 11.

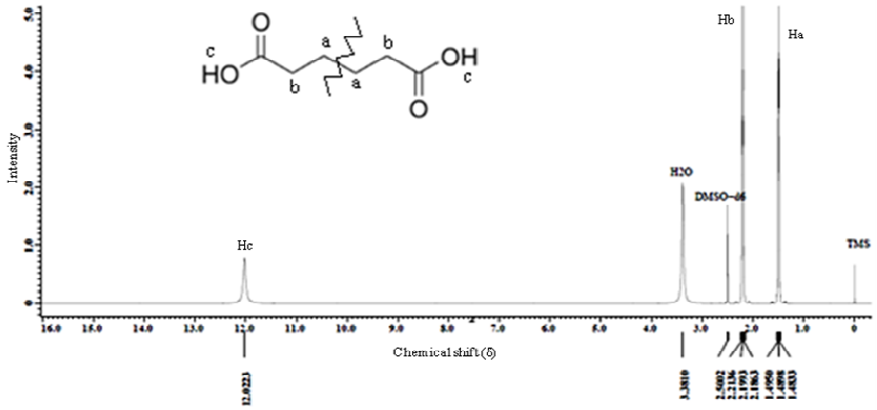

Figure 4. ^{1}H NMR Spectra of Adipic Acid from Synthesis

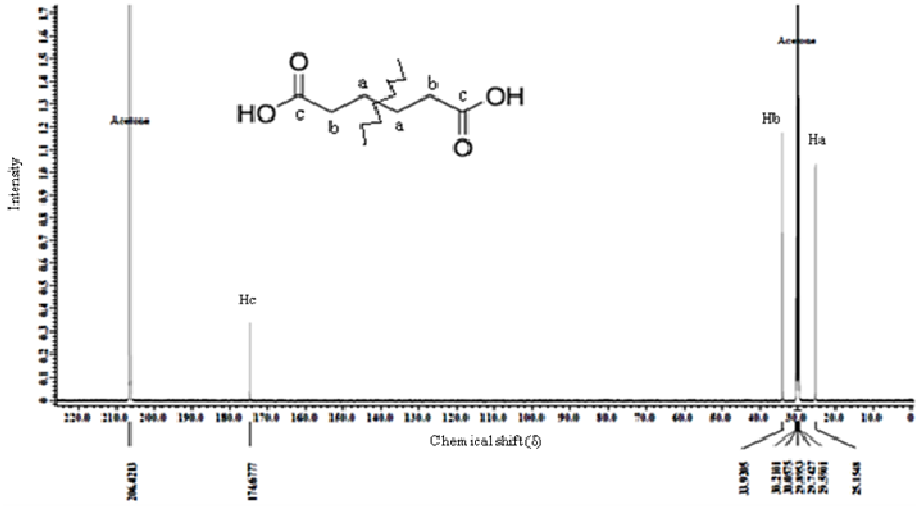

Figure 5. ^{13}C NMR Spectrum of Synthesized Adipic Acid

According to Alcañiz-Monge *et al.*, conversion of cyclohexene to adipic acid was achieved at 3 h [21]. In this study, the reaction time needed to convert the mixture of cyclohexanone-cyclohexanol was 7-10 h. As shown in Figure 10, at 9 h, up to 61% of cyclohexanol-cyclohexanone can be converted to adipic acid. The yield of adipic acid obtained at 7 h is not significantly different from that obtained at 8 h, 59.5%. By increasing

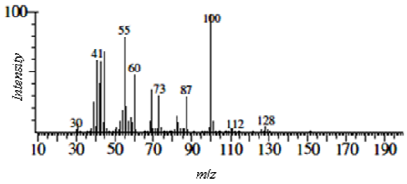

Figure 6. Mass Spectrum of Adipic Acid from Synthesis

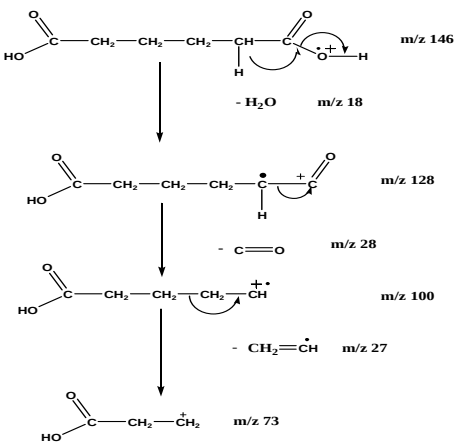

Figure 7. Fragmentation of Adipic Acid

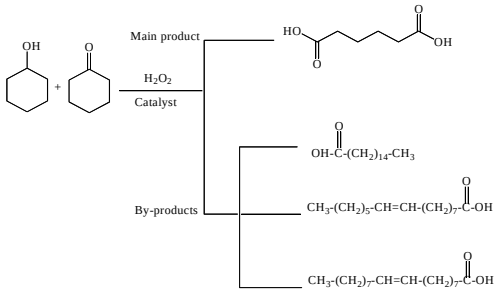

Figure 8. By-Products of Synthesis of Adipic Acid from Mixture of Cyclohexanol-cyclohexanone

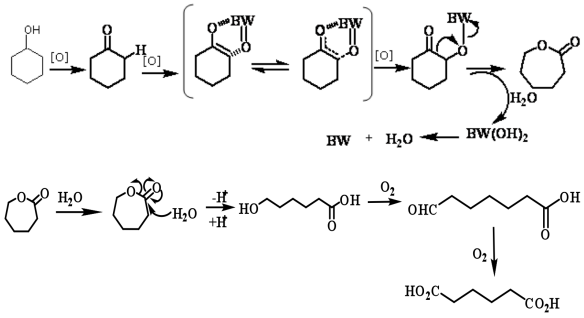

Figure 9. Plausible Reaction Mechanism

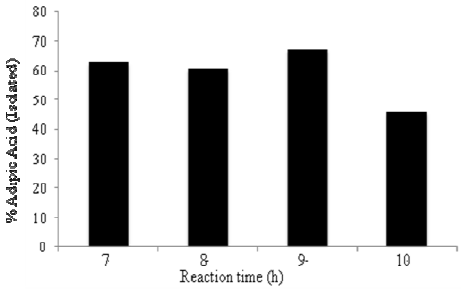

Figure 10. Effect of Reaction Time on Conversion of Cyclohexanol-cyclohexanone to Adipic Acid

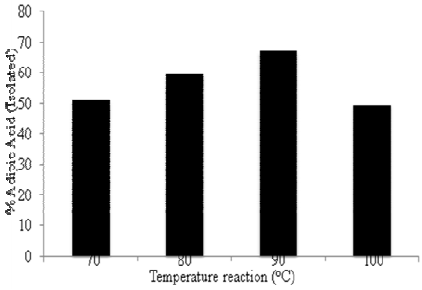

Figure 11. Effect of Temperature on the Conversion of Cyclohexanol-cyclohexanone to Adipic Acid

reaction time into 10 h, the yield of adipic acid decreases to 46%. Therefore, the experiment was terminated at the reaction time of 10 h.

Temperature is an important factor in the catalytic conversion of cyclohexanol, cyclohexanone, and cyclohexanol-cyclohexanone mixtures into adipic acid [22]. In this study, temperature was adjusted to 100 °C due to stability of hydrogen peroxide. Figure 11 shows that a temperature of 90 °C yields isolated adipic acid of up to 68%. At lower temperatures, adipic acid formation is about 50-60%. At 100 °C, formation of adipic acid falls to 49%. All results indicated that the 1:1 mixture of cyclohexanol-cyclohexanone could form adipic acid with moderate isolated yield.

Conclusions

After optimization of the cyclohexanol-cyclohexanone mixture, adipic acid was synthesized successfully at the yield of 68% at a reaction time of 9 h and a temperature of 90 °C, using $H_5[\alpha\text{-}BW_{12}O_{40}]$ as the catalyst and with the melting point of 150-152 °C. Characterization using FTIR spectrophotometer, ^{1}H, and ^{13}C NMR showed that highly pure white crystalline adipic acid was obtained from synthesis.

Acknowledgments

The authors thank the Department of Chemistry and the Faculty of Mathematic and Natural Sciences, Universitas

Sriwijaya, for the use of laboratory facilities for this research.

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