Kinetics of Complex Reaction of Eugenol Hydrogenation to 2-Methoxy-4-Propylphenol in Pd/Y Catalyst

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ABSTRACT

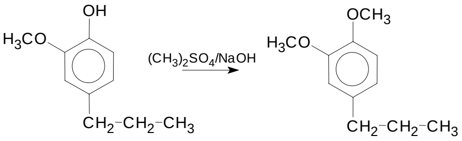
Eugenol and isoeugenol hydrogenations using Pt, Pd, Ni as a single or combined metal, that was supported on X and Y zeolite have been carried out. The experiment result showed that in hydrogenation reaction using metal that was supported on zeolite, eugenol is more easily hydrogenated than isoeugenol. Pd metal that was supported on Y zeolite as a catalyst in eugenol hydrogenation is more effective than Ni, Pt or combined metal (Pt,Pd,Ni/X). The highest conversion selectivity of eugenol hydrogenation is in 6% catalyst of Pd (10%)/Y that produced 98.24% of 2-methoxy-4- propylphenol. Kinetic of reaction is very important data that is needed in processing for industry scale, because kinetic can show how fast the starting material is converted into products. In this research, kinetic of the reaction was done by eugenol hydrogenation at 245°C with variation of time using Pd/Y catalyst. The result shows that eugenol hydrogenation is a complex reaction, because the reaction yields not only 2-methoxy-4-propylphenol as a main product, but also cis-isoeugenol and trans-isoeugenol as the side products. The reaction pathway of eugenol hydrogenation in Pd/Y catalyst is a combination of parallel and consecutive pathway and pseudo first order reaction with k = 0.5509.

Keywords: Kinetic, eugenol, hydrogenation, 2-methoxy-4-propylphenol

INTRODUCTION

Kadarohman (1994) reported that eugenol isomerization yields not only isoeugenol as a main product, but also a new compound (X compound), and analysis showed that the X compound is 2-methoxy-4-propylphenol. 2-Methoxy-4-propylphenol is a compound that can be used as a raw material of 1.2-dimethoxy-4-propylbenzena, male fruit fly pheromone (*Dacus dorsalis* Hendel) 50% more effective than methyl eugenol that was already used by people (Demilo *et al.* 1994).

1.2-Dimethoxy-4-propylbenzena can be synthesized from 2-methoxy-4-propylphenol by hydroxyl groups methylation in the benzene ring. The reaction can be seen in Figure 1.



2-Methoxy-4-propylphenol 1,2-Dimethoxy-4-propylbenzena

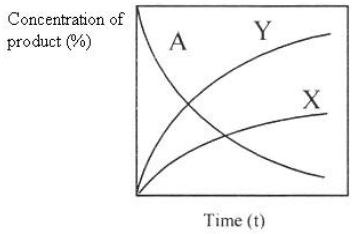
Figure1. Synthesis of 1,2-dimethoxy-4-propylbenzena.

Alkene hydrogenation to alkane using Pt or Pd metal that was supported on zeolite or silica as a catalyst has been done (Dominguez-Quintero *et al.* 2003; Oliviera 2007; Pawelec *et al.* 2002; Tadepalli *et. al.* 2007), while Ni metal as a hydrogenation catalyst was used by Fernández *et al.* (2007).

Synthesis of 2-methoxy-4-propylphenol by eugenol or isoeugenol hydrogenation has been carried out using Pt, Pd, and Ni metals that were supported on X or Y zeolite (Kadarohman 2003). The experiment result showed that in hydrogenation reaction using metal that was supported on zeolite, eugenol is more easily hydrogenated than isoeugenol. Pd metal that was supported on Y zeolite as a catalyst in eugenol hydrogenation is more effective than Ni, Pt or combined metal (Pt, Pd, Ni/X). The highest conversion selectivity of eugenol hydrogenation is in 6% catalyst of Pd(10%)/Y that produced 98.24% of 2-methoxy-4-propylphenol.

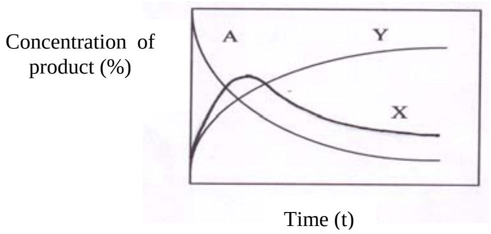
Frost & Pearson (1961) stated that there were two possibilities of the first order complex reaction, i.e. parallel and consecutive reactions. In parallel pathway, a reaction can proceed in more than one way to give different products, whereas in consecutive reaction, the product formed in one step becomes the reactant in the following step (Bansal 1978). The graph models that describe parallel and consecutive reaction pathways are shown in Figure 2 and Figure 3 respectively (Kadarohman 2003).

Chemical kinetic includes investigations of how different experimental conditions can influence the speed of a chemical reaction. One of the main factors that influence the reaction rate is whether or not any catalysts that are present in the reaction. A catalyst is a substance that accelerates the rate of a chemical reaction but remains chemically unchanged afterwards. The catalyst increases rate reaction by providing a different reaction mechanism to occur with a lower activation energy without being consumed in the process.



A: Raw Material; X: Product 1; Y: Product 2

Figure 2. Model of parallel reaction pathway graph.



A: Raw Material; X: Product 1; Y: Product 2

Figure 3. Model of consecutive reaction pathway graph.

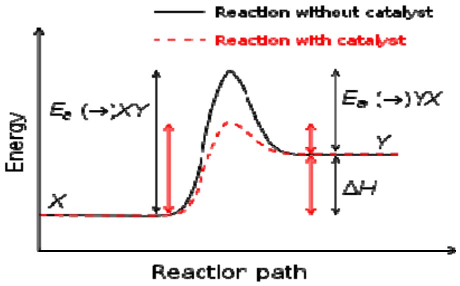


Figure 4. The influence of catalyst to decrease activation energy of reaction.

Study of eugenol hydrogenation kinetics is the most important step in the investigation of reaction mechanisms, because it gives about the nature and course of the reaction, assists in the determination of the yields of the products, the relative reactivity of molecules, and the possibility of weather or not a reaction will take place under certain experimental conditions.

METHODS

Material

Eugenol was procured from PT. Indesso Aroma, $PdCl_2$, $(NH_4)_2SO_4$, Y zeolite, methanol, diethylether, acetone, vacuum Vaseline (from Merck), Whattman filter paper, O_2 gas, H_2 gas, and aquadest.

Research equipment and instrument analysis

Horizontal shaker with water batch, twist shaker, vacuum filter, furnace (1200^{o}C), oven, glassware for hydrogenation reaction, IR spectrophotometer (Shimazu FTIR-8201PC), GC (Hewlett Packard 5890 series II), GC-MS (Shimazu QP-5000).

Preparation of H-zeolite

20 g of zeolite was submerged in the 50 mL of 1 M aqueous solution of $(NH_4)_2SO_4$ with shaking at 80^{o}C for 5 hours (using water steam bath). Aqueous solution of $(NH_4)_2SO_4$ was changed thrice repeatedly. Zeolite was filtered, and washed with water, and then air dried. Dried zeolite was heated at 500^{o}C for 5 hours.

Preparation of catalyst

5 g of zeolite was added to 50 mL of methanol that contains of 5 g of ion metal that will be impregnated. Solution was shaking at room temperature for 24 hours. Impregnated zeolite was dried in an oven at 70^{o}C, and then calcinated at 500^{o}C for 5 hours. Impregnated zeolite of ion metal was made to a solid phase. Activating of zeolite was prepared by oxidation reaction at 350^{o}C for 3 hours with the followed by hydrogenation reaction at 350^{o}C for 3 hours.

Synthesis of 2-methoxy-4-propylphenol by hydrogenation reaction

0,3 g of catalyst was added into reactor, and heated at 350^{o}C by flowing through of hydrogen gas into batch system from the bottom for an hour to change back a formed oxide to be a metal. In flowing through of H_2, the temperature of the reactor was decreased until 100^{o}C, and then 5 g of eugenol was added. Temperature of the reactor was increased until 250^{o}C for 3 hours. The products were analyzed by GC, GC-MS and FTIR respectively. The experiment was repeated with the variation of kind and catalyst concentration, and the variation of metal concentration.

RESULTS AND DISCUSSION

Eugenol hydrogenation using Pd/Y catalyst at 245°C has been done. GC chromatogram and MS spectra of the reaction products are shown in Fig 5. There are three products in the eugenol hydrogenation, i.e 2-methoxy-4-propylphenol as a main product, *cis*-isoeugenol and *trans*-isoeugenol as the side products. It indicates that eugenol hydrogenation is a complex reaction.

The change of eugenol to 2-methoxy-4-propylphenol can observe on infrared spectra (Figure 6 and Figure 7). There were no 3074.3 cm^{-1} (C-H sp^2 of alkene), 1639.4 cm^{-1} (double bond of alkene (C=C)), and 914.2 cm^{-1} (double bond of propenyl group) absorptions in infrared spectra of 2-methoxy-4-propylphenol (Figure 7) show that double bond of propenyl group (C=C) has changed to single bond of propyl group (C-C).

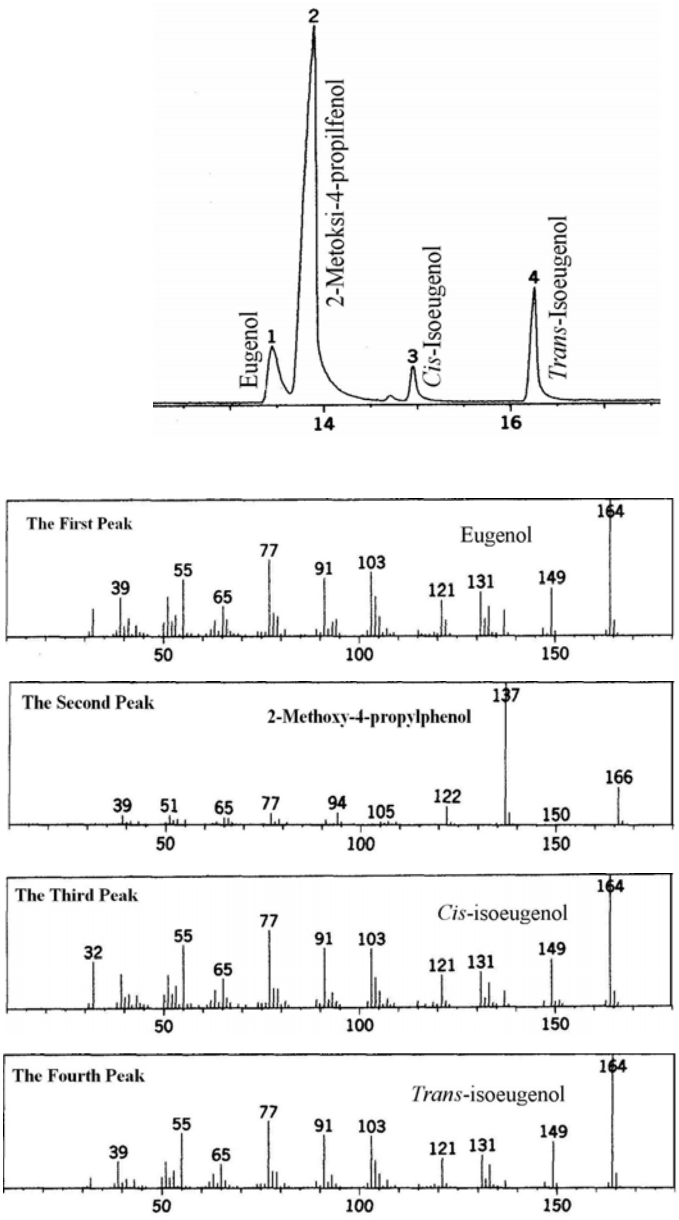


Figure 5. GC chromatogram and MS spectra of reaction products of eugenol hydrogenation using Pd/Y catalyst at 245°C.

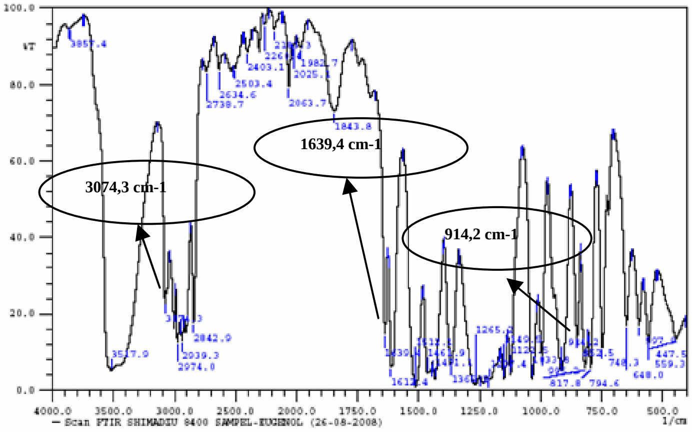


Figure 6. IR Spectra of eugenol.

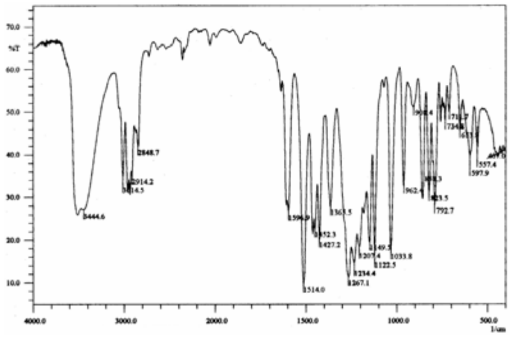


Figure 7. IR Spectra of 2-methoxy-4-propylphenol.

Table 1. The products of eugenol hydrogenation using Pd/Y catalyst at 245^{o}C with variation of time.

Time	Product of Eugenol Hydrogenation (%)			
(hour)	Eugenol	2-methoxy-4-propylphenol	*Cis*-Isoeugenol	*Trans*-isoeugenol
0.00	99.89	0.00	0.00	0.00
0.50	58.62	23.18	3.01	15.19
0.75	50.09	29.64	3.29	16.98
1.00	42.81	33.50	3.75	19.93
1.50	31.33	45.51	3.58	19.58
2.00	23.22	53.35	3.39	20.04
2.50	18.19	59.30	3.19	19.36
3.00	14.48	64.10	3.04	18.37
3.50	11.26	67.66	3.03	18.01

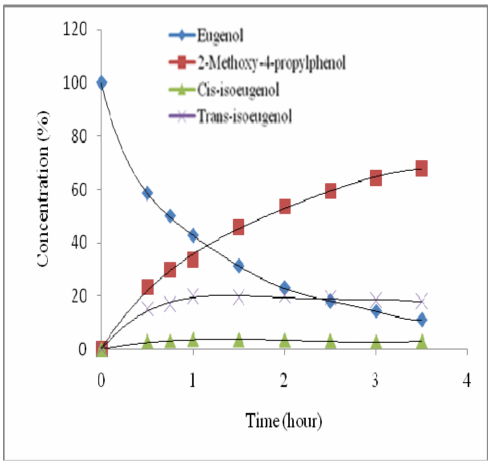


Figure 8. Graph plot between products of eugenol hydrogenation using Pd/Y catalyst at 245°C and time (t).

The effect of different processing conditions viz. variation of time using Pd/Y catalyst at 245°C were studied to determine the kind of complex reactions. Data of the experiment are shown in Table 1 and Figure 8 respectively.

During the kinetic study, it was observed (Figure 8) that in the begining, the amount of eugenol decreased, while the amount of 2-methoxy-4-propylphenol, *cis*-isoeugenol and *trans*-isoeugenol were increasing in different way. But after 1,5 hours of reaction, *cis*-isoegenol and *trans*-isoeugenol were decreasing that followed by increasing of 2-methoxy-4-propylphenol. It indicates that the reaction pathway of eugenol hydrogenation is a combination of parallel and consecutive reaction pathway (Figure 9).

Chemical kinetics can describe the characteristics of a chemical reaction. Kinetic deals with the study of change of concentration of the components of a system with the passage of time and results are summarized in the form of a rate expression. The rate of eugenol hydrogenation reaction is measured by following the change in the concentration of the components of the reaction mixture at suitable intervals of time. The order of the reaction determining was undertaken by curve of –ln(C/Co) against time (t) for the first order reaction (Figure 10), curve of 1/[C] against time (t) for the second order reaction (Figure 11), and curve of [C] against time (t) for the zero order reaction (Figure 12), where the values of C is the concentrations of the eugenol at different time intervals.Based on those graphs (Figure 8, 9 and 10), it has been found that the most linear relationship is obtained in plot between –ln (C/Co) and time (t). It is shown from the highest value of R squared of the line, i.e. 0.9961. Then, it indicates that the eugenol hydogenation is the first order. However, in the reaction system was used excessive hydrogen gas, so concentration of the hydrogen gas was constant. Therefore, the true order of eugenol hydrogenation reaction using Pd/Y catalyst is pseudo first order with the rate constant (k) in the amount of 0.5509.

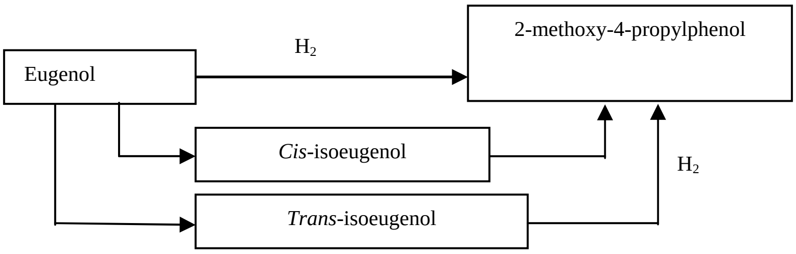


Figure 9. Combination of parallel and consecutive reaction pathway chart of eugenol hydrogenation

Table 2. Concentrations of the eugenol at different time intervals.

Time (hour)	Eugenol [C]	1/[C]	-ln (C/Co)
0.00	99.89	1.0100	0.0000
0.50	58.62	0.0171	0.5330
0.75	50.09	0.0200	0.6902
1.00	42.81	0.0234	0.8473
1.50	31.33	0.0319	1.1595
2.00	23.22	0.0431	1.4591
2.50	18.19	0.0550	1.7032
3.00	14.48	0.0691	1.9313
3.50	11.26	0.0888	2.1828

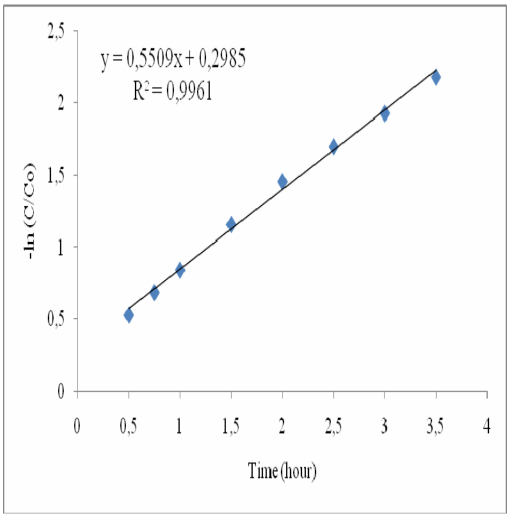


Figure 10. First order plot between –ln (C/Co) and time (t).

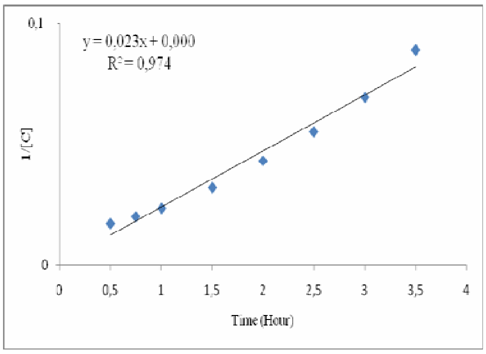


Figure 11. Second order plot between 1/[C] and time (t).

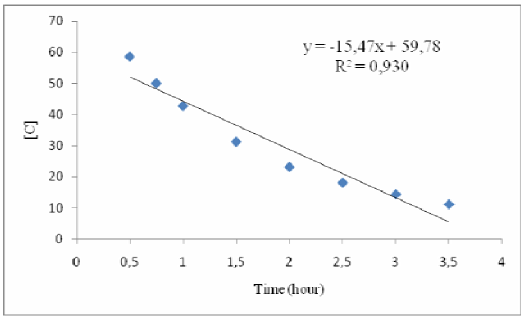


Figure 12. Zero order plot between [C] and time (t).

CONCLUSION

The reaction of eugenol hydrogenation with Pd/Y catalyst is a complex reaction in a combination of parallel and consecutive pathway. Eugenol hydrogenation reaction using Pd/Y catalyst is pseudo first order. The value of rate constant (k) of eugenol hydrogenation in Pd/Y catalyst is in the amount of 0.5509.

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