Kinetic Study of Ethyl Lactate Synthesis from Magnesium Lactate

Boonpradab Daengpradab and **Panarat Rattanaphanee***

School of Chemical Engineering, Institute of Engineering,
Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand
*E-mail: panarat@sut.ac.th

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ABSTRACT

Ethyl lactate is widely used as solvent for several industries and usually produced from lactic acid esterification with ethanol. In order to lower the production cost, attempt to synthesis ethyl lactate directly from fermentation-derived magnesium lactate was made. In this research, kinetics of magnesium lactate esterification with ethanol catalyzed by sulfuric acid was studied. Effect of reaction temperature, initial feed molar ratio, and catalyst loading on the production yield were investigated. Specific rate and equilibrium constant were determined and found that both parameters were influenced by reaction temperature, initial feed molar ratio, and catalyst loading. Relationship between the rate constant and process variables was elucidated. The result was compared with commercial lactic acid esterification under the same process condition. It was found that the values of kinetic parameters obtained from magnesium lactate esterification were lower, which could be due to the presence of impurities in fermentation-derived magnesium lactate.

***Keyword**: Ethyl lactate, lactic acid, magnesium lactate, esterification, kinetic study.*

1 INTRODUCTION

Ethyl lactate ($CH_3CHOHCOOCH_2CH_3$) is an acid ester that can be considered as a green chemical due to its nontoxic, biodegradable and excellent solvent properties [1]. It was used in many industries with general application as solvent for production of nitrocellulose, food additive, perfumery, flavor chemicals as well as drug industries [2].

Normally, ethyl lactate is produced from esterification of lactic acid with ethanol. Sulfuric acid and cation exchange resins can be used as homogeneous and heterogeneous catalyst, respectively. However, this process is expensive due to the high cost of lactic acid separation and purification [3]. Using lactate salt such as magnesium lactate or calcium lactate, which can be obtained directly from fermentation to produce lactic acid, might be an approach that help decreasing the production cost of this chemical.

Several studies concerned kinetics of esterification reaction between commercial lactic acid and ethanol had been conducted and reported [4] – [5]. The important variables which are affecting to the kinetics of reaction is temperature, initial feed molar ratio of the reactant, as well as percent catalyst loading.

The purpose of this research is therefore to study the kinetics of magnesium lactate esterification with ethanol by study effect of reaction temperature, initial feed molar ratio, and catalyst loading on the reaction. The yield of ethyl lactate production is also evaluated. The relationship between reaction rate constant and involved parameters was determined.

2 RESEARCH METHODOLOGY

2.1 Materials and Equipments

Lactic acid (88 %w/w), absolute ethanol (99+ %w/w), and sulfuric acid (96 %w/w) were obtained from CARLO ERBA. Magnesium lactate is produced from lactic acid fermentation using magnesium oxide as neutralizing agent. Deionized water was produced from an Aquinity P LifeScience TI water purifier. Compositions of the reaction solution were analyzed by gas chromatography analyzer (GC) and high performance liquid chromatography (HPLC) from Shimadzu and Agilent Technologies, respectively. Rotary vacuum evaporator used for evaporation from BUCHI Thailand.

2.2 Experimental Procedure

Magnesium lactate was dissolved in 1 M sulfuric acid solution. The solution was stirred for 10 min, before it was left for precipitation for 90 min. Solid residue was separated by vacuum filtration. About 60% of water was removed from the solution by rotary vacuum evaporator in order to reduce its interference in esterification reaction. Lactic acid concentration in the magnesium lactate solution was analyzed by HPLC. Esterification reaction of magnesium lactate solution and commercial lactic acid with ethanol were performed in a 500-ml glass vessel using sulfuric acid as homogeneous catalyst. Total volume of the reaction solution was constant at 250 ml. The solution was stirred by magnetic stirrer and the reaction temperature was maintained by thermally-controlled oil bath. Kinetics of the reaction was studied by analyzing the reaction solution contents by GC. The effect of temperature, initial feed molar ratio, and catalyst loading were studied. The catalyst loading was expressed as volume percent of concentrated sulfuric acid in the reaction solution.

3 RESULTS AND DISCUSSION

In this study, kinetics experiment were performed in reaction temperature, initial feed molar ratio, and catalyst loading ranges of 65°C to 85°C, 3:1 to 30:1 and 1 to 3 %v/v, respectively. The esterification of lactic acid (LA), also lactic acid in magnesium lactate solution, with ethanol (EtOH) to produce ethyl lactate (EtLA) and water (W) can be written as

$$LA + EtOH \xleftrightarrow{k} EtLA + W \tag{1}$$

The rate expression of esterification reaction of lactic acid and the equilibrium constant of the reaction can be described in equation (2) and (3)

$$-r_{LA} = -\frac{dC_{LA}}{dt} = k\left(C_{LA}C_{EtOH} - \frac{C_{EtLA}C_W}{K_e}\right) \tag{2}$$

$$K_e = \frac{C_{EtLA,e}C_{W,e}}{C_{LA,e}C_{EtOH,e}} \tag{3}$$

where $-r_{LA}$ is rate of esterification (mol $L^{-1}min^{-1}$), C_i and $C_{i,e}$ are concentration of reaction species i at time t and at equilibrium (mol L^{-1}), respectively, t is reaction time (min), k is the reaction rate constant ($Lmol^{-1}min^{-1}$), and K_e is equilibrium constant.

Reaction rate constant (k) and equilibrium constant (K_e) of the reaction were determined by minimization the sum of squared of the errors (SSE) [6] between the experimental conversion (x_{exp}) and the calculated conversion (x_{cal}) as shown in equation (4). The calculated conversion was evaluated by 4^{th}-order Runge-Kutta method.

$$SSE = \sum_{1}^{n}\left(x_{\exp} - x_{cal}\right)^2 \tag{4}$$

The reaction rate constant can be expressed using Arrhenius equation:

$$k = A\exp\left(-\frac{E_A}{RT}\right) \tag{5}$$

where A is pre-exponential factor, E_A is activation energy of the reaction (J mol^{-1}), R is universal gas constant (J $mol^{-1}K^{-1}$), and T is absolute temperature (K), respectively.

3.1 Effect of Reaction Temperature

In order to study effect of reaction temperature, both esterification of magnesium lactate solution and commercial lactic acid were carried out in the reaction temperature range of 65-85 °C with constant initial feed molar ratio of ethanol to lactic acid and catalyst loading at 3:1 and 2 %v/v, respectively. The results are shown in Fig. 1. As expected, conversion of lactic acid in both processes was increased with reaction temperature. However, the conversion of magnesium lactate esterification was lower than that obtained from esterification of commercial lactic acid. This could be due to the presence of impurities in magnesium lactate solution, one of which is magnesium sulfate formed during the acidification of magnesium lactate with sulfuric acid. The reaction rate and equilibrium constants were determined and found that both parameters were increased with reaction temperature. The Arrhenius plots are shown in Fig. 2. The activation energy of magnesium lactate and commercial lactic acid esterification were approximately 26.7 and 53.5 kJ/mol, respectively. Activation energy for esterification of 88%w/w lactic acid evaluated in this study is in the region of the values reported by Troupe and Dimilla, whose obtained the activation energies of 62.4 and 50.6 kJ/mol for esterification of H_2SO_4-catalyzed esterification of 85%w/w and 44%w/w commercial lactic acid, respectively[7].

3.2 Effect of Initial Feed Molar Ratio

In this part, effect of initial feed molar ratio was investigated by varying the initial feed molar ratio of ethanol to lactic acid from 3:1 to 30:1 which constant reaction temperature at 75°C and catalyst loading at 2 %v/v. The results are shown in Fig.3. It was found that the conversion of lactic acid in both processes was increased with initial feed molar ratio. According to Le Chatelier's principle, increasing of initial feed molar ratio will increase the forward reaction rate. In this situation, ethyl lactate is produced more, and the conversion of lactic acid is increased.

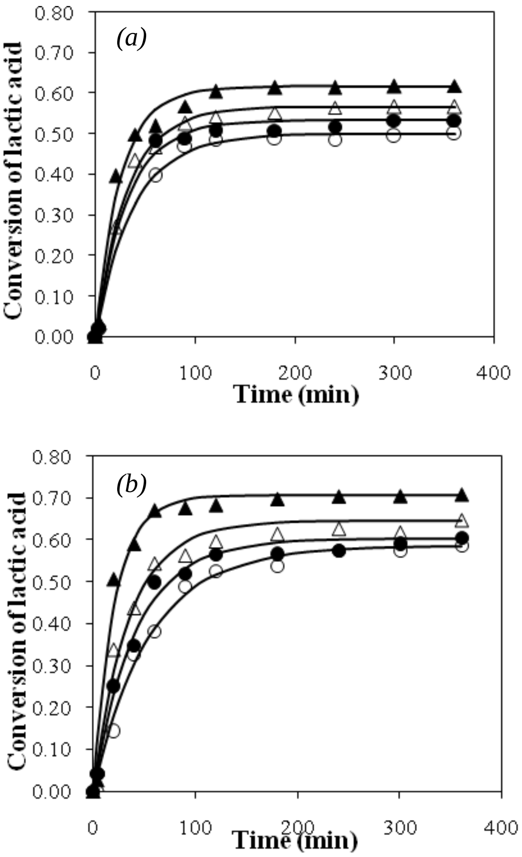

Fig. 1*Effect of Reaction Temperature on Conversion of Lactic Acid in Esterification of (a) Magnesium Lactate and (b) Commercial Lactic Acid. Reaction Temperature (▲) 85°C; (Δ) 80°C; (●) 75°C; (○) 65°C; Lines Indicated the Value from Calculation.*

3.3 Effect of Catalyst Loading

The effect of catalyst loading was investigated by varying the concentration of sulfuric acid in the reaction solution from 1 to 3 %v/v with constant reaction temperature and initial feed molar ratio of ethanol to lactic acid at 75°C and 30:1, respectively. The results are shown in Fig. 4. Esterification flavors the acidic environment, therefore, the conversion of lactic acid in both processes was increased with concentration of sulfuric acid in the process.

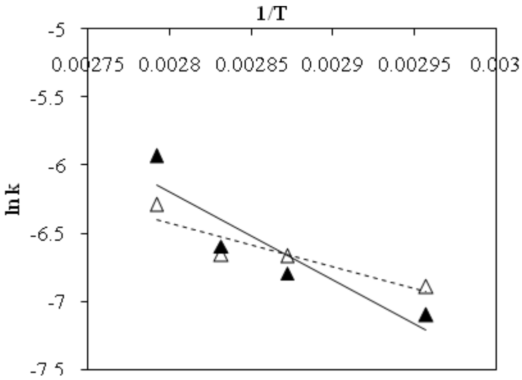

Fig. 2 *The Arrhenius Plots between ln k and 1/T (K^{-1}) for Esterification Reaction; (Δ---) Magnesium Lactate; (▲—) Commercial Lactic Acid.*

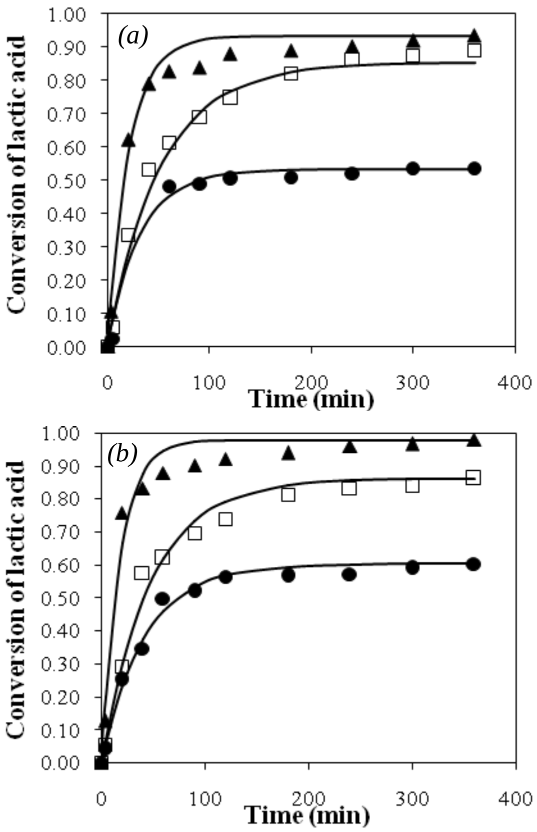

Fig. 3 *Effect of Initial Feed Molar Ratio on Conversion of Lactic Acid in Esterification of (a) Magnesium Lactate and (b) Commercial Lactic Acid. Initial Feed Molar Ratio of Ethanol to Lactic Acid (▲) 30:1; (□) 10:1; (●) 3:1; Lines Indicated the Value from Calculation.*

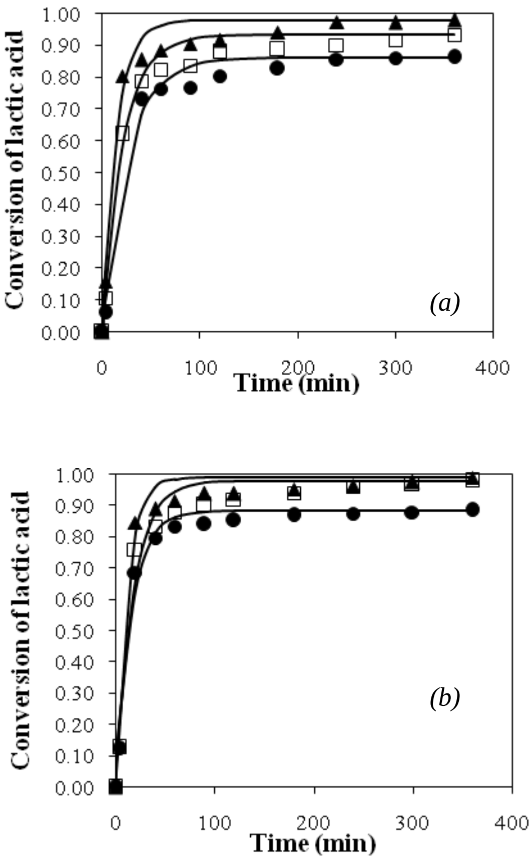

***Fig. 4** Effect of Catalyst Loading on Conversion of Lactic Acid in Esterification of (a) Magnesium Lactate and (b) Commercial Lactic Acid. Reaction Conditions: Constant Reaction Temperature at 75°C and Initial Feed Molar Ratio at 30:1, Catalyst Loading (▲) 3 %v/v; (□) 2 %v/v; (●) 1 %v/v; Lines Indicated the Value from Calculation.*

3.4 Kinetic Parameters

The reaction rate and equilibrium constant were calculated and shown in Table 1. Both kinetic parameters were found to increase with reaction temperature, initial feed molar ratio as well as catalyst loading. The parameters obtained from magnesium lactate esterification were less than that obtained from esterification of commercial lactic acid. Increasing of equilibrium constant is due to high equilibrium concentration of products in the reaction solution. The range of reaction rate constant of magnesium lactate and commercial lactic acid esterification are 0.0010-0.0098 and 0.0008-0.0123 $Lmol^{-1}min^{-1}$, respectively, as well as the range of equilibrium constant of magnesium lactate and commercial lactic acid esterification are 2.1778-17.4077 and 2.4653-31.9546, respectively. The coefficient of determination (R^2) in every experiment is close to unity, which indicates good agreement betweenthe experimental and the calculated conversion.Variation of the rate constant with the initial feed molar ratio clearly indicates the non-ideal nature of the solution mixture.

3.5 Correlation for Reaction Rate Constant

Relationships between reaction rate constant and reaction temperature, initial feed molar ratio, and catalyst loading have been reported for esterification of commercial lactic acid with concentration of 85%w/w and 44%w/w by Troupe and Dimilla [7]. In this research, these relationships were determined by plotting the rate constant against each corresponding variable. The plot of rate constant against catalyst loading is shown in Fig. 5. Correlations that obtained from Fig. 5 are as following equation (6)-(9).

For esterification of magnesium lactate:

For catalyst loading in %v/v:

$$k = 0.0027C_1 + 0.0016 \quad (6)$$

For catalyst loading in %w/w

$$k = 0.1286C_2 + 0.0015 \quad (7)$$

For esterification of commercial 88%w/w lactic acid:

For catalyst loading in %v/v:

$$k = 0.0024C_1 + 0.0044 \quad (8)$$

For catalyst loading in %w/w:

$$k = 0.1145C_2 + 0.0043 \quad (9)$$

C_1 and C_2 are catalyst loading in %v/v and %w/w, respectively. Intercepts of equation (6) to (9) are not at origin, which signifies the autocatalytic nature of the reaction. Equation (9) agrees quite well with the one reported by Troupe and Dimilla who studied H_2SO_4-catalyzed esterification of 85%w/w lactic acid and obtained k=0.117C+0.001895 for the correlation between the reaction rate constant and %w/w of H_2SO_4 in the reaction solution. The difference in coefficients of the correlation for esterification of magnesium lactate and commercial lactic acid shown in this study is likely due to the process impurities as previously explained.

Effect of initial feed molar ratio of ethanol to lactic acid (E/L) on the reaction rate constant of magnesium lactate esterification was established by plotting the parameter $(k-a)/C$ against the initial feed molar ratio

***Table 1** Kinetic Parameters for Esterification of Magnesium Lactate and Commercial Lactic Acid with Ethanol*

Process condition			Magnesium lactate				Commercial lactic acid			
Temperature (°C)	Initial feed molar ratio	Catalyst loading (%v/v)	Ke	k	SSE	R^2	Ke	k	SSE	R^2
85	3	2	7.8574	0.00185	0.0092	0.9823	12.9684	0.00266	0.0161	0.9753
80	3	2	5.7343	0.00128	0.0024	0.9948	9.0088	0.00136	0.0098	0.9854
65	3	2	4.7720	0.00102	0.0017	0.9947	7.3199	0.00082	0.0030	0.9937
75	3	2	5.4337	0.00127	0.0039	0.9899	7.8570	0.00112	0.0047	0.9918
75	10	2	9.5951	0.00141	0.0107	0.9905	10.1015	0.00158	0.0128	0.9891
75	30	2	6.0220	0.00641	0.0183	0.9906	18.7719	0.00809	0.0311	0.9797
75	30	1	2.1778	0.00451	0.0121	0.9899	2.4652	0.00741	0.0130	0.9884
75	30	3	17.4077	0.00987	0.0263	0.9856	31.9546	0.01230	0.0178	0.9896

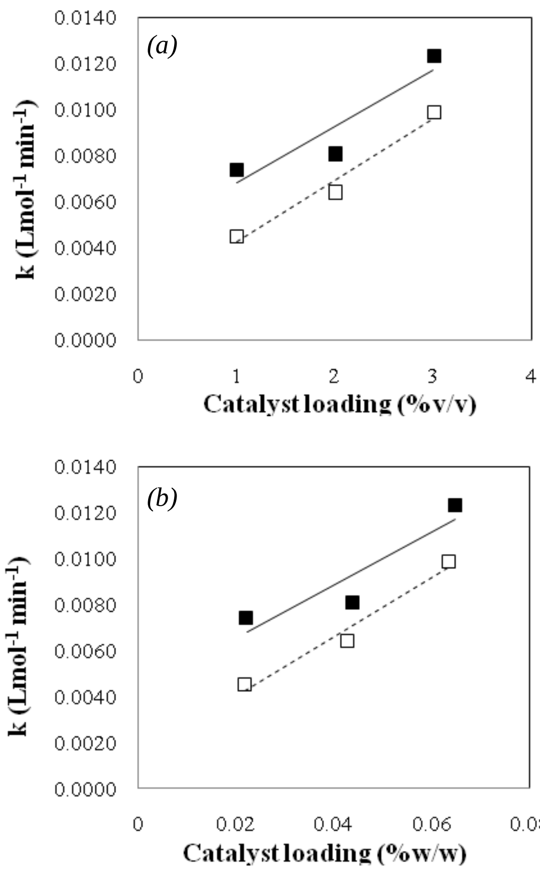

***Fig. 5**Relationship between Reaction Rate Constant and Catalyst Loading; (a) Catalyst Loading in %v/v; (b) Catalyst Loading in %w/w; (□---) Magnesium Lactate Solution; (■—) Commercial Lactic Acid.*

as shown in Fig. 6.Here, C is the catalyst loading in %w/w, and *a*is the rate constant of the autocatalytic esterification when no H_2SO_4 was added. This parameter can be evaluated from the intercept of equation (7). The correlation involved effect of initial feed molar ration and catalyst loading is written as:

$$k = 0.0048(E/L)C - 0.0325C + 0.0015 \quad (10)$$

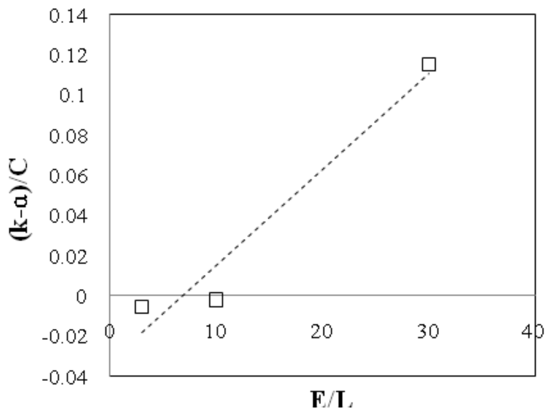

***Fig. 6**Relationship between (k-a)/C and E/L from Magnesium Lactate Esterification*

Effect of reaction temperature to reaction rate constant was acquired by plotting log k against the reciprocal of the absolute temperature (K) at constant initial feed molar ratio and catalyst loading as shown in Fig.7.

The relationship obtained from the plot was:

$$\log k = 1.1151 - 1394.6/T \quad (11)$$

Equation (11) may also be able to express in form:

$$k = 10^{(1.1151 - 1394.6/T)} \tag{12}$$

where k is the reaction rate constant in $\text{Lmol}^{-1}\text{min}^{-1}$ and T is the absolute temperature in K. In this research, effect of catalyst loading and initial feed molar ratio was studied at the reaction temperature of 75°C or 348.15 K. The reaction rate constant at this temperature is

$$k_{348.15K} = 0.001286 \tag{13}$$

The ratio of reaction rate constant at any temperature to that at 348.15 K can be written as:

$$\frac{k_T}{k_{348.15K}} = \left(\frac{10^{(1.1151-13946/T)}}{0.001286}\right) \tag{14}$$

Equation (10) and (14) were then combined to obtain the relationship between reaction rate constant and all the process variables, equation (15).

$$k = (0.0048(E/L)C - 0.0325C + 0.0015)\left(\frac{10^{(1.1151-13946/T)}}{0.001286}\right) \tag{15}$$

Equation (15) was used to re-calculate the reaction rate constant of each experiment. The experimental and calculated reaction rate constants were compared and shown in Table 2. Good agreement between the calculated and experimental reaction rate constant was achieved only in the experiments with high initial feed molar ratio. The large deviation between the two values in experiments with low initial feed molar ratio is likely caused by high concentration of magnesium sulfate in the reaction solution, which was resulted from large amount of magnesium lactate used in order to increase the number of moles of lactic acid, in other words, to lower the molar ratio between ethanol and lactic acid in the experiment. To have a clear point of view on this observation, effect of magnesium sulfate on kinetics of lactic acid esterification should be extensively investigated in the future study.

***Table 2** Comparison between Experimental and Calculated Rate Constant of Magnesium Lactate Esterification*

Temperature (°C)	Molar ratio E/L	Catalyst loading (%v/v)	Catalyst loading (%w/w)	k ($\text{Lmol}^{-1}\text{min}^{-1}$)	
				Calculation	Experiment
85	3	2	0.0426	0.00094	0.00185
80	3	2	0.0426	0.00083	0.00128
65	3	2	0.0426	0.00056	0.00102
75	3	2	0.0426	0.00073	0.00127
75	10	2	0.0426	0.00216	0.00141
75	30	2	0.0426	0.00625	0.00641
75	30	1	0.0217	0.00392	0.00451
75	30	3	0.0633	0.00856	0.00987

4 CONCLUSION

Kinetics of magnesium lactate esterification was studied. The activation energy of magnesium lactate esterification was found to be 26.7 kJ/mol. The reaction rate and equilibrium constants, were influenced by reaction temperature, initial feed molar ratio as well as catalyst loading. Both of parameters were increased with temperature, initial feed molar ratio and catalyst loading. The relationship between the reaction rate constant of magnesium lactate esterification and the process variables was established. Good agreement between the calculated and the experimental rate constant was achieved in experiments with high initial feed molar ratio. The deviation observed may be a result of high amount of magnesium sulfate in the reaction mixture when small initial feed molar ratio was used. Effect of magnesium sulfate quantity on the reaction kinetics should be further studied in order to gain accurate relationship between the reaction rate constant and the process variables.

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