

Research Article

Ultrasound-Assisted, Base-Catalyzed, Homogeneous Reaction for Ferulic Acid Production from γ -Oryzanol

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A method for producing ferulic acid by ultrasound-assisted, homogeneous, base-catalyzed hydrolysis of γ -oryzanol was developed. Experiments were conducted using various reaction temperatures and ratios of γ -oryzanol to base catalyst in both homogeneous and heterogeneous systems. The reaction performed without ultrasound under the homogeneous conditions of potassium hydroxide/ γ -oryzanol ratio (wt/wt) 20:1 and 75°C gave a ferulic acid yield of 83.3% in 3 h. Acceleration of the homogeneous reaction using ultrasound irradiation at 20 (horn type) and 200 kHz (planar type) was explored by evaluating the kinetic parameters. At 30°C, the ratios of ultrasonic irradiation at low (20 kHz, 50 W) and high (200 kHz, 50 W) frequencies versus those of the heating method increased by 2.0- and 1.4-fold in comparison with those at 60°C, respectively. The contribution of ultrasonic irradiation (50 W) to the hydrolysis reaction decreased with increase of temperature. However, irradiation at 20 kHz and a power of 180 W gave a 94% ferulic acid yield at 60°C in 3 h. These results indicate that the use of low frequency (horn type and high-power irradiation) enabled yields higher than 90% to be obtained.

1. Introduction

Ferulic acid (FA) is one of the most promising biomass of phenolic acid derivatives with its antioxidant properties such as UV protectant in cosmetics, food additive, and being used in various medical applications. FA also helps to prevent cardiovascular disease, diabetes, Alzheimer's disease, and colon cancer [1–8]. Nitrites, usually sodium nitrite, are used in the food industry as preservatives to maintain color and prevent pathogen growth. In acidic conditions in the stomach, nitrites can react with many other compounds to produce nitrosamines, which are known carcinogens. The

use of FA to block nitrosamine formation from nitrites has been investigated in the literature [9].

FA can be synthesized by the condensation of vanillin with malonic acid. The reaction gives a high yield of a mixture of *trans*- and *cis*-FA [10]; *trans*-FA, which can be crystallized, is commercially important because of its biological activities. Alkaline hydrolysis has been used to produce FA from natural sources, and various procedures for extraction of FA have been applied depending on the properties of the raw material [1, 11–13]. FA cannot be extracted directly from their matrix in the rice bran [14] because of existence of conjugated forms and/or its ester

form of γ -oryzanol. However, FA can be produced from γ -oryzanol-containing by-products by hydrolysis reaction, for example, soapstock from rice bran oil processing [15, 16].

Ultrasound irradiation has recently been evaluated as an effective method for accelerating hydrolysis reactions [17–27]. However, a few experiments on the hydrolysis of the hydrophobic compounds of γ -oryzanol consisting of bulky steroid groups and *para*-orientated hydroxyl group have been conducted. In our previous study, the ultrasound irradiation (78 kHz, 130 kHz, 50 W, and planar type) was explored, and the reaction was accelerated by around 10% [16] at the temperature of 60 and 75°C in comparison with the conventional heating method.

In this study, we examined the ferulic acid production from γ -oryzanol by various kinds of binary solvent systems: two kinds of homogeneous and one kind of heterogeneous systems. The experiments were performed using various ratios of γ -oryzanol/base catalyst and reaction temperatures. For accelerating the reaction, ultrasound irradiations of two kinds of frequency, for example, 20 kHz (horn type) and 200 kHz (planar type) with power of 50 W and 180 W were applied. The kinetic parameters of ultrasound-assisted homogeneous reaction systems were also estimated.

2. Materials and Methods

2.1. Chemicals and Equipment. The purities of *trans*-FA, γ -oryzanol, and ethyl ferulate (EF) standards (Sigma-Aldrich, USA) were over 99%. Inorganic compounds (potassium hydroxide (KOH), sulfuric acid, and phosphoric acid) and organic reagents and solvents (acetic acid, ethanol, and ethyl acetate) were of analytical grade and purchased from Merck (Germany). Acetonitrile, methanol, and water used as mobile phases were of HPLC grade and were also purchased from Merck.

A solution of γ -oryzanol (48 mg/mL) was prepared by dissolving γ -oryzanol (4.8 g) in ethyl acetate (100 mL). KOH solutions of concentrations 192, 240, 384, and 480 mg/mL were prepared by dissolving 48, 60, 96, or 120 g of KOH in water (250 mL). For comparison, KOH solutions of concentrations 96, 120, 192, and 240 mg/mL, that is, half the concentrations of the aqueous solutions, were prepared in methanol. The mass ratio of KOH/ γ -oryzanol, denoted by KO, was varied from 8:1 to 20:1.

A low-frequency (20 kHz) horn-type ultrasonicator (Sonifier 450, Ti horn of diameter 1.1 cm, maximum power 400 W, Branson Co., Tokyo, Japan) and a high-frequency (200 kHz) planar-type ultrasonicator (Kaijo Corporation, Tokyo, Japan) were used to accelerate the hydrolysis reaction. The dissipation powers were 50 and 180 W.

2.2. Hydrolysis of γ -Oryzanol. In our previous study, the experiment of γ -oryzanol hydrolysis was evaluated with the initial concentration of 12 mg/mL of γ -oryzanol under the reaction temperature of 60–75°C to prevent the precipitates in the homogeneous systems [16]. In this study, the initial concentration of γ -oryzanol was adjusted by 6 mg/mL, and

the reaction temperature was varied in the range of 30–75°C to avoid precipitation during the reaction.

2.2.1. Composition of Homogeneous Type A Solvent (Ethyl Acetate/Water/Ethanol). The homogeneous reaction system designated as Type A was prepared as follows. A γ -oryzanol solution (48 mg/mL, 4 mL) was added to ethanol (20 mL) in a 100 mL glass flask with a screw cap. The flask was placed in a water bath controlled at temperatures from 30 to 75°C using a temperature controller (Thermal Robo TR-2A, As One, Osaka, Japan). KOH solutions of various concentrations (192, 240, 384, and 480 mg/mL, 8 mL) were added to the mixture to prepare solutions with KO ratios of 8, 10, 16, and 20. The initial concentration of γ -oryzanol was 6 mg/mL. After closing the flask with the cap, the mixture was shaken by hand to form a uniform dispersion and then held in the water bath, without stirring or acceleration by ultrasound irradiation (hereinafter called the heating method). The reaction temperature was varied from 30 to 75°C. An aliquot (100 μ L) was removed every 30 min, and the reaction products and amount of γ -oryzanol were determined using HPLC. The reaction was monitored for 4 h.

2.2.2. Composition of Homogeneous Type B Solvent (Ethyl Acetate/Methanol/Ethanol). The procedure for preparation of the homogeneous reaction system designated as Type B was as follows. A γ -oryzanol solution (48 mg/mL, 4 mL) was added to ethanol (12 mL) in a 100 mL glass flask with a screw cap. Methanolic KOH solutions of concentrations 96, 120, 192, and 240 mg/mL (16 mL), corresponding to KO ratios of 8, 10, 16, and 20, were added. The subsequent process was the same as that described in Section 2.2.1.

2.2.3. Composition of Heterogeneous Type C Solvent (Ethyl Acetate/Water). The heterogeneous system designated as Type C consisted of a γ -oryzanol in ethyl acetate solution and aqueous KOH solution. The preparation procedure was the same as that described in Section 2.2.1, except for the addition of ethanol as a cosolvent and the volume of ethyl acetate (20 mL).

2.3. Hydrolysis Using Ultrasound Irradiation. The effects of ultrasound irradiation on the reaction were examined using a homogeneous aqueous organic phase (Type A) at 30 to 60°C. The procedure was as follows. A solution of γ -oryzanol (48 mg/mL, 16 mL) in ethyl acetate was added to ethanol (80 mL) in a 250 mL glass flask with a screw cap. This flask was placed in a water bath at a specified temperature, controlled by a Robo TR-2A thermal controller (As One Co., Osaka, Japan), and then KOH solution (32 mL) was quickly added. The flask was shaken by hand. For low-frequency (20 kHz) irradiation with a horn-type sonicator, the horn tip was immersed in the middle of the mixed solution. The flask was covered with paraffin film, and the dissipation power was 50 or 180 W. The reaction products were monitored for 4 h. For high-frequency (200 kHz) irradiation with a planar-type sonicator, the flask containing the reaction mixture was

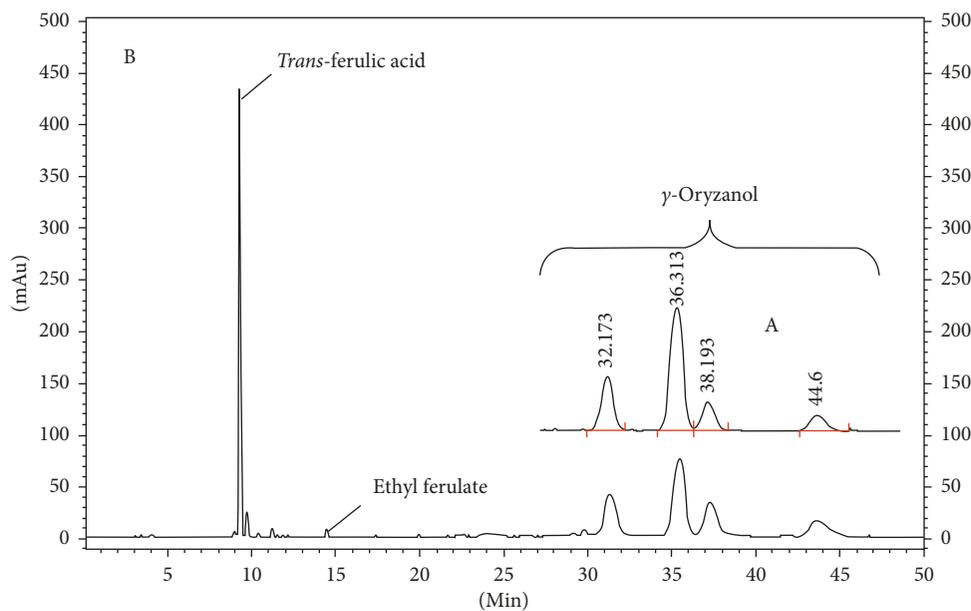


FIGURE 1: HPLC chromatogram (UV_{235 nm}) of γ -oryzanol standards (A) and hydrolysis products (B).

closed with the screw cap and placed on the transducer, and then irradiation was started.

2.4. HPLC Determination of γ -Oryzanol, FA, and EF. FA, γ -oryzanol, and EF were determined as follows: Concentrated acetic acid (100 μ L) was added to the reaction mixture (100 μ L) to terminate the reaction. The mixed solution was diluted to 1.5 mL with ethanol, and an aliquot (10 μ L) was subjected to high-performance liquid chromatograph (HPLC) analysis. The GL-7480 HPLC system (GL Science Inc., Tokyo, Japan) was equipped with a photodiode array detector (GL-7452, GL Science Inc., Tokyo, Japan) and an autosampler (GL-7420, GL Science Inc., Tokyo, Japan). A reverse-phase Inertsil ODS-3 C₁₈ (4.6 mm \times 250 mm, film thickness 5 μ m; GL Science, Tokyo, Japan) column was used. The analytical parameters were described in our previous study [16]. The FA, EF, and γ -oryzanol contents were determined using a direct calibration method with a coefficient of determination (R^2) greater than 0.9990 in the concentration ranges of 10–250, 10–100, and 100–1200 μ g/mL, respectively. Because γ -oryzanol is a mixture of four main components, the calibration curve for γ -oryzanol was based on the sum of the areas of the four peaks versus the concentration of FA. The yield of FA (%) and that of EF (%) were calculated as

$$\text{yield of FA (EF)} = \frac{\text{FAc (EFc)}}{\text{FAc} + \text{EFc} + \text{Orc}} \times 100\%, \quad (1)$$

where FAc is the molar concentration of FA, EFc is the molar concentration of EF, and Orc is the molar concentration of γ -oryzanol. The obtained values were the averages of triplicate measurements.

2.5. Kinetic Calculation. The base-catalyzed hydrolysis of ester is expressed as the second-order reaction as the reaction

rate depends on both concentrations of ester and hydroxide ion as follows:

$$\text{rate} = k[\text{OH}^-][\text{ester}]. \quad (2)$$

Usually, large amount of reagent $[\text{OH}^-]$ versus ester is added to the reaction system, and then the rate can be abbreviated and converted to pseudo-first-order reaction by dependency of ester concentration [28] as follows:

$$kt = -\ln\left(\frac{C_t}{C_0}\right), \quad (3)$$

where C_0 is the initial concentration (mg/mL) of γ -oryzanol and C_t is the concentration of γ -oryzanol (mg/mL) at reaction time t (min). The activation energy (E_a , J/mol) for γ -oryzanol hydrolysis was estimated using the following equations:

$$k = A \exp\left(\frac{-E_a}{RT}\right), \quad (4)$$

$$\ln k = \frac{-E_a}{RT} + \ln A, \quad (5)$$

where k is the rate constant, T is the Kelvin temperature, R is the molar gas constant (8.3415×10^{-3} kJ/(mol/K)), and A is the pre-exponential factor.

3. Results and Discussion

3.1. HPLC Analysis of γ -Oryzanol, FA, and EF. The HPLC chromatogram (photodiode array detection at 325 nm) of γ -oryzanol and its hydrolysis products of homogeneous system of Type A is shown in Figure 1. The peaks eluted in the range of 32–45 min were assigned to γ -oryzanol by comparing with authentic standards (Figure 1(a)). As hydrolysis proceeded, peaks for *trans*-FA and the intermediates ethyl ferulate (EF) appeared at retention times of 9.3 and 14.4 min, respectively (Figure 1(b)).

TABLE 1: The yields of ferulic acid from hydrolysis of γ -oryzanol by heterogeneous and homogeneous systems with assistance of ultrasonic irradiation.

Type of reaction	γ -oryzanol* (mg/mL)	KO ¹ ratio	Temp. ² (°C)	Heating method	Yield of ferulic acid (%)			
					US (20 kHz) ³		US (200 kHz) ⁴	
					50 W	180 W	50 W	180 W
Homogeneous condition (ethyl acetate/H ₂ O/cosolvent: ethanol)								
Type A	6	8	75	37.3	—	—	—	—
	6	10	75	56.5	—	—	—	—
	6	16	75	81.4	—	—	—	—
	6	20	75	83.3	—	—	—	—
	6	20	60	62.3	65.8	94.0	63.1	63.8
	6	20	50	45.8	52.2	—	52.0	—
	6	20	40	25.2	42.1	—	33.7	—
	6	20	30	18.8	34.2	—	26.1	—
Homogeneous condition (ethyl acetate/methanol/cosolvent: ethanol)								
Type B	6	8	75	0.7	—	—	—	—
	6	10	75	0.9	—	—	—	—
	6	16	75	1.1	—	—	—	—
	6	20	75	1.8	—	—	—	—
Heterogeneous condition (ethyl acetate/H ₂ O)								
Type C	6	10	75	8.9	—	—	—	—
	6	20	75	12.3	—	—	—	—

*Initial concentration of γ -oryzanol in ethyl acetate. ¹Mass ratio of KOH/ γ -oryzanol (wt/wt). ²Reaction temperature. ³Ultrasound-assisted method with 20 kHz. ⁴Ultrasound-assisted method with 200 kHz. Reaction time: 180 min.

3.2. Hydrolyses Using Homogeneous and Heterogeneous Systems. Two homogeneous solvent systems, that is, binary solvents consisting of ethanol/ethyl acetate combined with water (Type A) or methanol (Type B), and heterogeneous one (Type C, KOH/water) were investigated. The yields of FA were evaluated using various KO ratios and reaction temperatures as shown in Table 1. Under aqueous heterogeneous conditions (Type C), the maximum yield of FA was 12.3% even at 75°C. As in the case of esters containing acidic protons, such as methyl *p*-hydroxybenzoate and methyl salicylate, hydrolysis was sluggish because of the formation of stable anions [29]. γ -oryzanol contains an acidic proton on the *para*-substituted hydroxyl group of an aromatic skeleton. Furthermore, the alcoholic portions of γ -oryzanol consist of bulky steroidal groups, which could prevent reactant molecules attacking γ -oryzanol. Hydrolysis, therefore, hardly occurred in the Type C solvent system.

The yields of FA obtained using the Type A system contained with solvent of water were in the range of 37.3–83.3%, but the yields obtained using the Type B system contained with solvent of methanol were only 0.7–1.8%, and none of peaks corresponding to ferulic acid esters were observed. Hydrolysis and/or transesterification proceed rapidly under homogeneous conditions [30]. However, these results indicate that the presence of water as a solvent in the reaction system is important in the hydrolysis reaction. Hydrolysis is an equilibrium reaction; therefore, the FA produced dissolved in water as the potassium salt, and then the forward reaction proceeded to form FA.

The yields of FA using Type A were investigated by varying the reaction temperature from 30 to 75°C and the KO ratio from 8 to 20 at 75°C. The FA yield increased with

increasing reaction temperature and KO ratios. When the KO ratio was greater than 16, the FA yield reached greater than 80% at 75°C in 3 h (Table 1). Experimentally, a KO ratio of 20 (A20) was the maximum value for maintaining homogeneous conditions of system, and then, the FA yield of 83.3% was obtained with the initial γ -oryzanol concentration of 6 mg/mL and the KO ratio of 20:1 by the heating method. The reaction temperature was lower, and the reaction time was half in comparison with those using the heterogeneous conventional method reported by Taniguchi et al. [15].

3.3. EF Formation. The time dependences of the EF yields from hydrolysis of γ -oryzanol in a homogeneous aqueous system (A20) at 50°C are shown in Figure 2. The yield of EF, which is an intermediate in γ -oryzanol transesterification, increased rapidly, reached a maximum in less than 60 min, and then decreased. These results indicate simultaneous transesterification and hydrolysis when both water and ethanol solvent are present. Ultrasound irradiation of 20 and 200 kHz (50 W) accelerated the reactions compared with the heating method. The intermediate of EF was hydrolyzed to FA, and its content was less than 3% in 3 h.

3.4. Effect of Ultrasound Irradiation. The effect of ultrasound irradiation on the hydrolysis of γ -oryzanol was investigated using low-frequency (horn type, 20 kHz) and high-frequency (planar type, 200 kHz) ultrasonicators. The experiments were conducted by ultrasonic power of 50 W at temperature from 30 to 60°C. The results for 20 kHz irradiation and those for 200 kHz in comparison with the

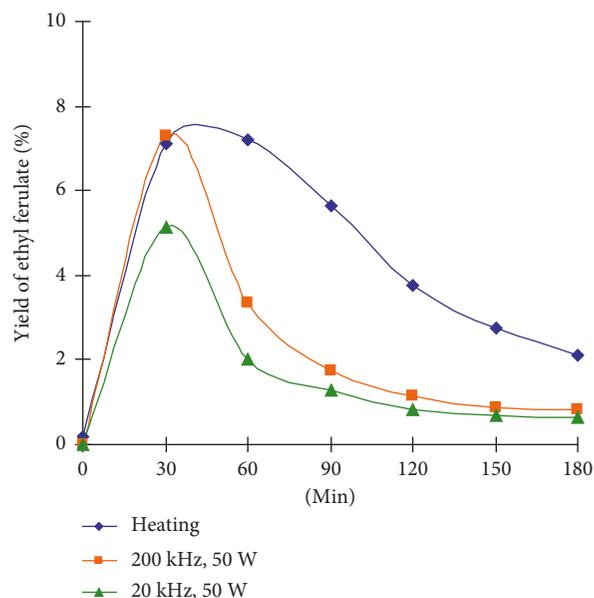


FIGURE 2: Behavior of ethyl ferulate produced as an intermediate under hydrolysis of γ -oryzanol by the heating method and ultrasonic irradiation of 20 kHz and 200 kHz with power of 50 W at 50°C. Reaction conditions: initial concentration of γ -oryzanol of 6 mg/mL, KO ratio of 20:1 (wt/wt), and homogeneous system of Type A (ethyl acetate/ H_2O /ethanol) (A20).

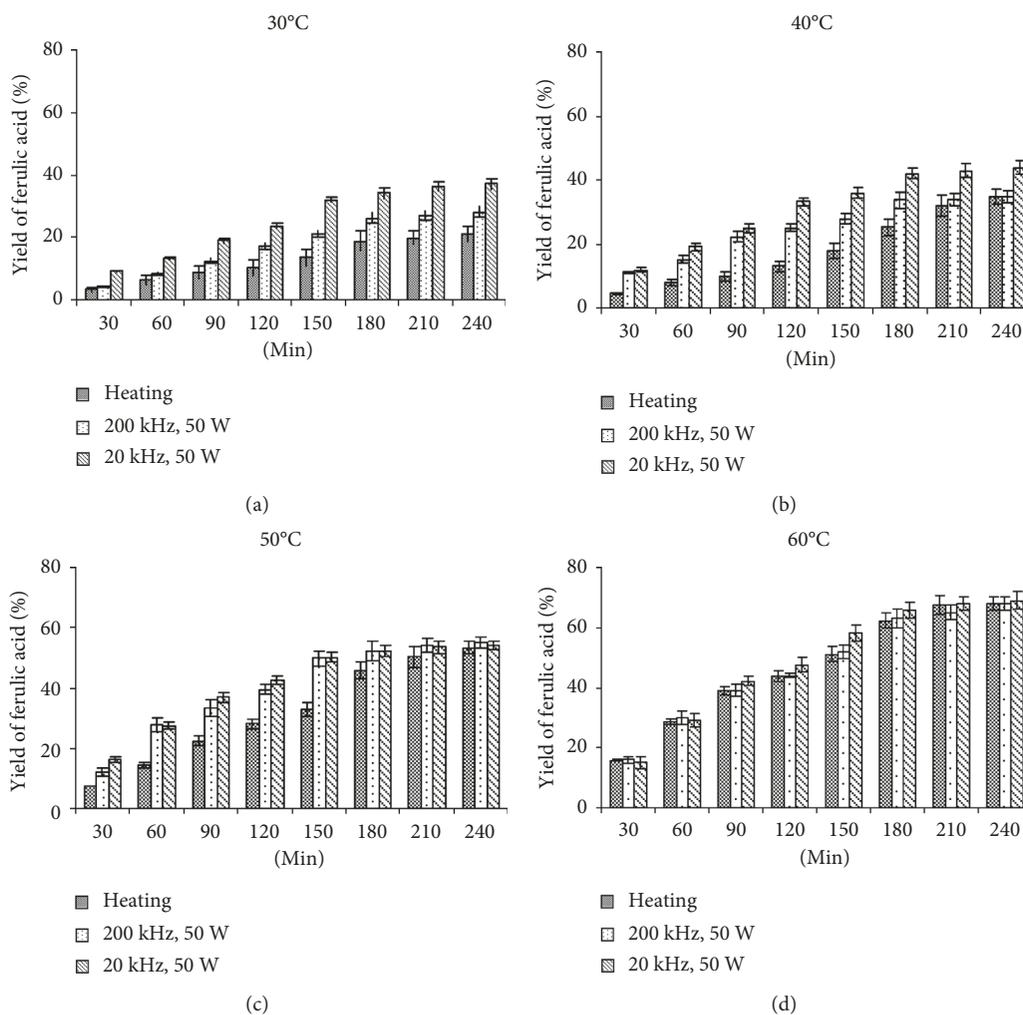


FIGURE 3: The yields of ferulic acid obtained by the heating method and the ultrasound-assisted method (20 and 200 kHz, 50 W) by varying reaction temperature from 30 to 60°C (A20).

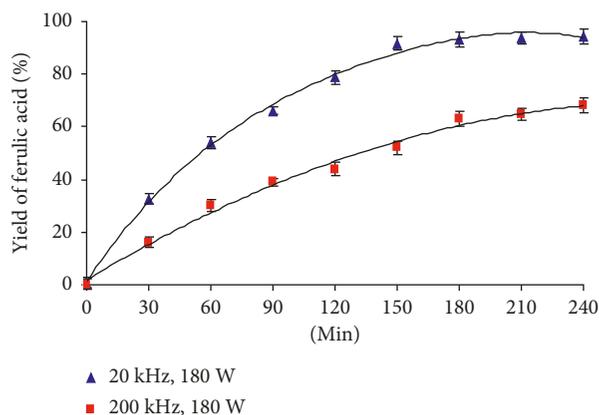


FIGURE 4: The yields of ferulic acid obtained by the ultrasound frequencies of 20 and 200 kHz at power of 180 W (A20).

heating method are shown in Figure 3. With increasing reaction temperature and reaction time, the yield of FA increased when either 20 kHz or 200 kHz irradiation was used. FA yields of 63–65% were obtained using 20 kHz or 200 kHz irradiation at 60°C for 3 h with a power of 50 W. By 20 kHz irradiation with a high power of 180 W, greater than 90% yield of FA was obtained, while by 200 kHz irradiation with the power of 180 W, the yield was 63.8% (Figure 4). The cavitation bubble size is inversely proportional to the frequency [31]; therefore, larger bubbles were produced at 20 kHz. These promoted the hydrolysis reaction more powerfully than did the smaller bubbles produced at 200 kHz. This is because large bubbles expand and collapse violently that helps to accelerate the reaction.

3.5. Activation Energy of γ -Oryzanol Hydrolysis. The kinetic parameters for alkaline hydrolysis of γ -oryzanol (A20) using the heating method and the ultrasonic irradiation methods at 20 and 200 kHz (50 W) were evaluated. As discussed in Section 2.5, the activation energies were estimated by plotting $\ln k$ versus $1/T$ (5) using the k values calculated using (3). The linear regression curves and R^2 values obtained for different methods are shown in Figure 5. The linear relationships between $\ln k$ and $1/T$ were $y = -5248x + 10.49$ (R^2 : 0.9878) for the heating method, $y = -3144x + 4.280$ (R^2 : 0.9889) for 20 kHz irradiation, and $y = -4205x + 7.450$ (R^2 : 0.9828) for 200 kHz irradiation. These linear correlations show that alkaline hydrolysis of γ -oryzanol is a pseudo-first-order reaction.

The estimated activation energies (E_a , J/mol) and rate constants are listed in Table 2. The activation energies for γ -oryzanol hydrolysis using the heating method, 20 kHz irradiation, and 200 kHz irradiation are 43.6, 26.1, and 34.9 kJ/mol, respectively. These results indicate that ultrasonic irradiation reduced the hydrolysis activation energy, and the lower frequency reduced it more effectively. Acoustic cavitation during sonolysis enhances mass transfer and the diffusion of chemical species and therefore increases the reaction rate [32, 33].

The rate constants at 30, 40, 50, and 60°C for the heating method (k_{heat}), irradiation at 20 kHz (k_{sonic20}), and irradiation

at 200 kHz (k_{sonic200}), and their ratios of $k_{\text{sonic20}}/k_{\text{heat}}$ and $k_{\text{sonic200}}/k_{\text{heat}}$ are summarized in Table 2. The ratios can be used to evaluate the contribution of ultrasound irradiation. The ratios increased with decreasing reaction temperature. At 30°C, the ratios of ultrasonic irradiation at low (20 kHz) and high (200 kHz) frequencies versus those of the heating method increased by 2.0- and 1.4-fold in comparison with those at 60°C, respectively. Furthermore, the contribution of ultrasonic irradiation to the hydrolysis reaction became decreasing with increase of temperature, as the averaged rate constant among three methods was $5.64 \pm 0.28 \times 10^4 \text{ min}^{-1}$ at 60°C. These inverse relationships between the ratios of the rate constants and the reaction temperatures are related to the solvent vapor pressure [25]. Cavitation occurs easily at low temperatures [31]. As the solvent temperature increases, its vapor pressure rises, and the solvent vapor fills the cavitation bubbles. The bubbles then tend to collapse less violently; that is, the sonication effect becomes less intense with increasing temperature. The effect of sonication on the reaction therefore depends on a combination of the reaction temperature and cavitation at a given frequency and power.

4. Conclusions

The alkaline hydrolysis of γ -oryzanol was investigated using two homogeneous reaction systems (Type A and B) and a heterogeneous one (Type C). In the experiments, the KO ratios (KOH/ γ -oryzanol (wt/wt)) and reaction temperatures were varied, and ultrasonic irradiations at 20 kHz and 200 kHz were used. The reaction was promoted by the homogeneous reaction system with ethanol as a cosolvent (Type A); the water used for a solvent of the KOH catalyst in the hydrolysis reaction. A kinetic study showed that alkaline hydrolysis of γ -oryzanol is a pseudo-first-order reaction and the activation energies were in the range of 26–44 kJ/mol. Although the contribution of ultrasonic irradiation to the hydrolysis reaction decreased with increasing temperature, the FA yield reached 94% at 60°C in 3 h using low-frequency (20 kHz) irradiation at a high power of 180 W: this is better than the results achieved using a conventional heating method. This method can be used to produce FA from

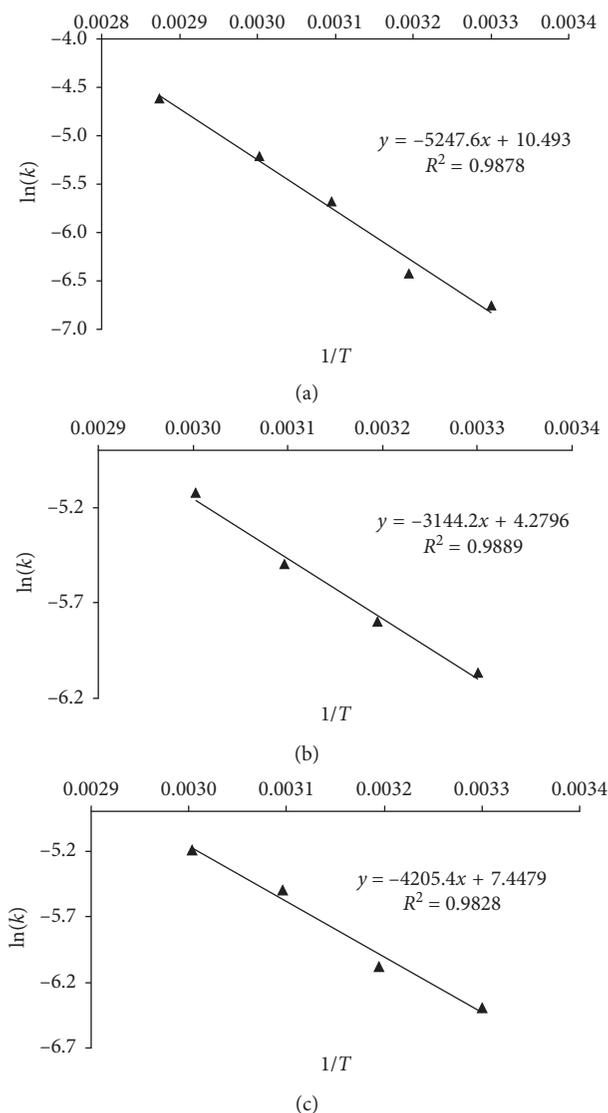


FIGURE 5: Arrhenius plot for the hydrolysis of γ -oryzanol (A20) by the heating method and ultrasonic irradiations. (a) Heating method. (b) 20 kHz ultrasonic irradiation. (c) 200 kHz ultrasonic irradiation.

TABLE 2: The kinetics parameters of γ -oryzanol hydrolysis obtained by the heating method and the homogeneous system of Type A with assistance of ultrasonic irradiation.

Method of hydrolysis	Rate constant ($k \times 10^4$ (min^{-1}))					E_a (kJ/mol)	$\ln A$
	30°C	40°C	50°C	60°C	75°C		
Heating method (k_{heat}) ¹	1.16	1.61	3.40	5.42	9.92	43.6	10.493
US 20kHz							
$(k_{\text{sonic20}})^2$	2.33	3.04	4.10	5.96	—	26.1	4.2796
$(k_{\text{sonic20}}/k_{\text{heat}})^3$	(2.00)	(1.88)	(1.21)	(1.10)			
US 200 khz							
$(k_{\text{sonic200}})^4$	1.67	2.29	4.08	5.54	—	34.9	7.4479
$(k_{\text{sonic200}}/k_{\text{heat}})^5$	(1.44)	(1.42)	(1.20)	(1.02)			

Reaction system of A20. Type A: consists of ethyl acetate/H₂O/ethanol. ¹Heating method (k_{heat}): rate constant of the heating method. ²Ultrasonic irradiation, 20 kHz, 50 W (k_{sonic20}). ³In parenthesis: ratio of k_{sonic20} versus k_{heat} . ⁴Ultrasonic irradiation, 20 kHz, 50 W (k_{sonic200}). ⁵In parenthesis: ratio of k_{sonic200} versus k_{heat} .

γ -oryzanol in soapstock from rice bran oil processing at a low temperature and in a short time using low-frequency and high-power irradiation.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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