Hydrolysis of Palm Oil Catalyzed by Macroporous Cation-Exchanged Resin

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ABSTRACT: Hydrolysis of palm oil was studied using four types of commercial H^+-exchanged resin with acidity in the region of 5×10^{-3} eq g^{-1} but with different pore volumes, specific surface areas, and pore diameters. The reaction was carried out in a stirred batch reactor in the liquid phase with continuous steam injection for up to 14 h. The rate of hydrolysis did not depend on total pore volume and specific surface area but did depend on pore diameter. On exchanging H^+ with La^{3+}, Co^{2+}, and Na^+, the rate of reaction decreased markedly and was dependent on the degree of exchange, demonstrating that hydrolysis was catalyzed by H^+ sites. The activation energy for the hydrolysis of the triglycerides was estimated to be 240 kJ mol^{-1}. A procedure to estimate the rates of the different stages of hydrolysis and hence the individual rate constants of the forward and reverse reactions is described. The procedure yielded reasonable parameters for the reaction at 155°C up to 6 h of reaction time, when about 75 mol% of triglycerides was hydrolyzed.

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KEY WORDS: Cation-exchanged resin, fatty acids, hydrolysis, kinetics, palm oil, triglycerides.

Continuous high-pressure fat splitting with superheated steam is still the preferred technology for fatty acid production since its invention in the 1930s. Hydrolysis is usually carried out at ~250°C and 3000–5000 kN/m^2 pressure with countercurrent flow of water and oil. About 96–98% of hydrolysis takes place within 2 h (1). The process involves high capital cost because of the corrosive nature of the acid produced at such high temperatures and pressures; high steam pressure also requires high energy input and costs. Due to rising energy and capital costs, renewed interest in ambient temperature enzymatic fat splitting using lipase as catalyst emerged around 1980 (1,2). The lipase process is suitable for small-scale production of fatty acids from heat-sensitive oils. The problems of catalyst recovery and the low rate of attaining equilibrium prevent commercialization of the process for large-scale production, although efforts to immobilize the enzyme on solid supports and to carry out the reaction at temperatures above ambient have resulted in some success (3).

Catalyzed hydrolysis of fats and oils in batchwise fatty acid production was used even before steam splitting. The Twitchell process, which uses a sulfonic acid as catalyst, was first patented in 1898 (4). Other catalysts involving solid acids and bases, such as supported alkylbenzene sulfonic acid, ZnO, and lime, have also been used (5). Cation-exchanged resins have been used for hydrolysis of esters (6–8), and the hydrolysis kinetics of triglycerides catalyzed by cation-exchanged resins has also been reported (6). It is well established that the hydrolysis of triglycerides is a stepwise process catalyzed by acid/base; however, there are insufficient kinetic data on the process in current literature. This report aims to fill the gap.

EXPERIMENTAL PROCEDURES

Four samples of polystyrene sulfonic acid cation-exchanged resins, CT-110, CT-151, CT-165, and CT-175, were gifts from Purolite International Limited (Pontyclun, United Kingdom). CT-110 is a gel-type resin whereas the others are macroporous resins. The resins with the H^+ cation-exchanged with La^{3+}, Co^{2+}, and Na^+ were prepared by repeated (4 times) equilibration of the resin with fresh nitrate solutions of the respective cation. It was estimated that more than 90% of the cation sites were exchanged. Resins with different H^+ fraction were prepared by adding to a series of different concentrations of sodium nitrate in conical flasks. The conical flasks were stoppered and then shaken for a few hours. The resin was filtered and washed with distilled water until the effluent was neutral to methyl orange.

The H^+ fraction was determined according to a standard method (9). A 1-g sample was weighed and placed in a 250-mL conical flask. Standardized 0.1 M NaOH in 5% NaCl (200 mL) was then pipetted into the flask. The flask was stoppered and allowed to stand overnight. A 50-mL sample of the supernatant liquid was then back-titrated with standardized 0.1 M HCl using phenolphthalein as an indicator to calculate H^+ capacity. The H^+ fraction was calculated by taking the ratio of H^+ capacity of a Na^+–exchanged resin and H^+ capacity of an unexchanged resin.

The hydrolysis experiments were carried out in a 250-mL three-necked round-bottom flask immersed in a constant temperature bath. Typically, about 5 g of the catalysts for 100 mL of the preheated refined palm olein was used. Steam was continuously injected. The reaction mixture was continuously

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stirred with a mechanical stirrer for up to 14 h. Samples were withdrawn at regular intervals.

Samples were analyzed by the following procedure. To 1 mL of sample, 1 mL of pyridine and 1 mL of chloroform were added and mixed well. From the mixture, 0.3 mL was withdrawn and mixed with 0.2 mL of hexamethyldisilazane followed by 0.1 mL of trimethylchlorosilane (10). The mixture was allowed to stand for at least 5 min before being injected into the gas chromatograph fitted with a 50-cm glass column with an internal diameter of 3 mm packed with 1% Dexil 300 (Supelco, Bellefonte, PA).

RESULTS AND DISCUSSION

Figure 1 shows a typical result of the hydrolysis of palm oil triglycerides catalyzed by macroporous resin (CT-165 resin) at 155°C. The disappearance of the triglycerides proceeded slowly at first, then accelerated after 30 min until after about 70 mol% was hydrolyzed, typically 4 h of reaction time. At the same time, concentrations of free fatty acids and diglycerides increased slowly at first, then accelerated, and eventually slowed. The monoglyceride concentration gradually increased, reaching a maximum at about the time when the hydrolysis of the triglycerides began to slow; thereafter, the concentration decreased. The initial induction period observed may be explained as follows: As water entered the pores of the resin and became trapped together with the triglycerides, reaction proceeded within the pores. Diffusion of the products out of the internal pores took time, hence a delay in the appearance of the products was observed.

The accelerated rate of reaction after the initial induction but before the slowdown, which followed first-order kinetics, may have been assisted by the formation of diglycerides and monoglycerides which helped emulsify the reaction mixture by bringing them into more intimate contact within the pores.

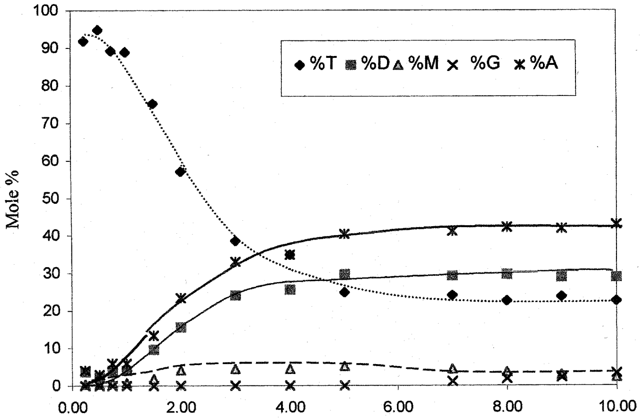

FIG. 1. Changes in the concentration of triglycerides (T), diglycerides (D), monoglycerides (M), fatty acid (A), and glycerol (G) with time of hydrolysis catalyzed by CT-165 (polystyrene sulfonic acid cation-exchanged resin; Purolite International Ltd., Pontyclun, United Kingdom) at 155°C. The symbols are experimental data, while the curves are simulated from Equations 4–7.

The expected maximum in diglycerides concentration was not observed, presumably because the concentration of triglycerides remained appreciable even after a reaction time of 14 h.

The monoglyceride concentration decreased after reaching a maximum which was not observed for homogeneous hydrolysis. Initially, the rate of monoglyceride formation from the hydrolysis of the diglycerides within the pores was higher than its rate of decomposition when the rate of formation of diglycerides was accelerating. Later, the rate of formation of monoglycerides slowed due to the decreased diglyceride concentration within the pores. The monoglyceride concentration decreased.

Relationship between activity and physical characteristics. Table 1 tabulates the physical characteristics of the various resins and the product concentrations of the reaction after 5 h at 140°C. For the reactions carried out with the four resins, which have approximately the same acidity, no correlation between the activities and surface area and pore volume was found. Catalysts with larger average pore diameters seem to have the higher activities. However, this correlation is not conclusive since all resins, except for CT-110, which is a gel, have average pore diameters greater than 350 Å, which is large enough to accommodate many molecules of the reactants as well as the products.

Effect of cation and H^+. It is well established that the hydrolysis of esters is catalyzed by acids. Thus, we performed the reaction on a number of cation-exchanged resins (Table 1). The original resin that contained H^+ was much more active than the other cation-exchanged resins. Although La^{3+}- and Co^{2+}-exchanged solids are known to possess appreciable acidity, these were also not very active compared to the H^+ resin. Despite this observation, it is still reasonable to conclude that the reaction is catalyzed by Brønsted acids. Figure 2 shows the percentage hydrolysis at the fifth hour as a function of the H^+ fraction (partially replaced by Na^+) at 155°C. The percentage hydrolysis using unexchanged H^+ resin was 75%; the percentage hydrolysis dropped dramati-

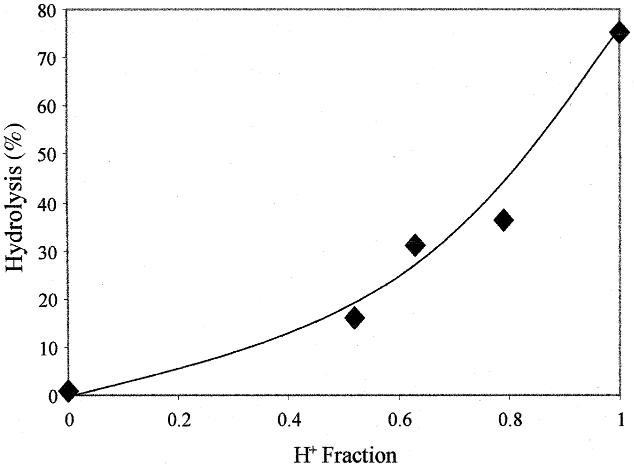

FIG. 2. Percentage hydrolysis after 5-h reaction time as a function of H^+ fraction for hydrolysis catalyzed by CT-165 at 155°C. For manufacturer see Figure 1.

TABLE 1
Effect of Resin Characteristics on Hydrolysis of Triglycerides After 5-h Reaction Time at 140°C

Sample	CT-110 Granular (H^+)	CT-165 Granular (H^+)	CT-175 Granular (H^+)	CT-151					
				Granular (H^+)	Powder (H^+)	Granular (Na^+)	Granular (Co^{2+})	Granular (La^{3+})	
Total capacity H^+ [a] (eq/kg)	4.9	5	5	5.1	5.1	5.1	5.1	5.1	
Specific surface[a,b] (m^2/g)	—	2.5	30	20	20	20	20	20	
Pore volume[a,c] (mL/g)	—	0.15	0.5	0.2	0.2	0.2	0.2	0.2	
Median pore diameter[a,c] (Å)	—	>1000	650	350	350	350	350	350	
	Product concentration (w/w %)								Average % deviation[d]
Triglycerides	96.6	78.1	86.4	84.5	85.4	99.6	98.3	96.2	±2.2
Diglycerides	3.2	12.9	6.0	6.0	6.3	0.2	0.9	2.2	±10.2
Monoglycerides	0	1.7	1.1	1.3	1.4	0.1	0.4	0.2	±4.6
Free fatty acids	0.2	7.3	6.4	8.2	6.9	0.1	0.4	1.4	±4.3

[a] Data from the manufacturer.
[b] Hg intrusion method.
[c] N_2 adsorption.
[d] Average % deviation, calculated from $[\Sigma(\Delta C/C)]/8 \times 100$ where ΔC and C are the difference in concentrations and the average concentration from duplicate experiments, respectively.
CT, polystyrene sulfonic acid cation-exchanged resins (Purolite International Ltd., Pontyclun, United Kingdom).

cally to 15% using sample with 48% of the H^+ exchanged. This showed that the H^+ sites were responsible for catalytic function.

Effect of temperature. As mentioned earlier, the reaction is first-order with respect to triglyceride concentration. The first-order plot for triglyceride hydrolysis catalyzed by CT-165 at 155°C is shown in Figure 3. Although the change in triglyceride concentration with time fit fairly well with first-order kinetics, hydrolysis is actually a composite of forward and reverse rates. The reaction constant is an overall rate constant and the first-order kinetics obtained is an approximation.

The reaction was carried out at temperatures between 120 and 155°C (the highest temperature possible before decomposition of the resin). From the Arrhenius plot (Fig. 4), the activation energy for the hydrolysis was 240 kJ mol^{-1} which is rather high for a catalyzed reaction.

Kinetic parameters. The mechanism of the hydrolysis has long been established to consist of the following steps:

$$\text{triglyceride (T)} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{diglyceride (D)} + \text{fatty acid (A)} \qquad \text{rate} = r_1 \qquad [1]$$

$$\text{diglyceride (D)} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{monoglyceride (M)} + \text{fatty acid (A)} \qquad \text{rate} = r_2 \qquad [2]$$

$$\text{monoglyceride (M)} + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{glycerol (G)} + \text{fatty acid (A)} \qquad \text{rate} = r_3 \qquad [3]$$

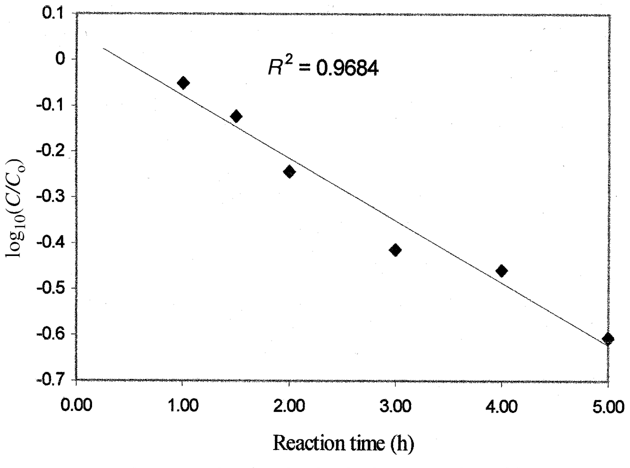

FIG. 3. First-order rate plot for the hydrolysis catalyzed by CT-165 at 155°C, where C_0 = initial concentration and C = concentration at time t. For manufacturer see Figure 1.

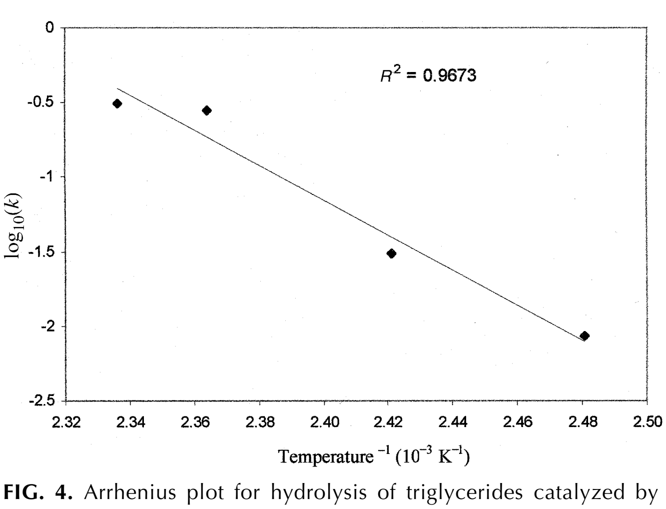

FIG. 4. Arrhenius plot for hydrolysis of triglycerides catalyzed by CT-165. For manufacturer see Figure 1.

TABLE 2
Rates of Change in Concentrations of Glycerides and Free Fatty Acids Catalyzed by CT-165 at 155°C[a]

Reaction time (h)	d[T]/dt	d[D]/dt	d[M]/dt	d[A]/dt	r_1	r_2	r_3
0.25	−1.5582	0.2429	0.8183	0.2289	0.5	0.3	−0.6
0.50	−6.0423	1.3247	0.9509	4.3330	2.6	1.3	0.4
0.75	−12.6844	3.4462	1.0956	7.9423	5.3	1.9	0.8
1.00	−19.9131	6.3641	1.2495	11.3298	8.4	2.1	0.8
1.50	−28.9435	11.4568	1.5598	14.8270	13.1	1.6	0.1
2.00	−27.0175	11.5183	1.8031	13.6341	12.8	1.3	−0.5
3.00	−13.4282	5.2282	1.6506	7.4268	6.5	1.3	−0.4
4.00	−5.7926	1.9406	0.5620	3.5796	2.7	0.7	0.2
5.00	−2.6865	0.7934	−0.4046	1.8162	1.0	0.2	0.6
6.00	−1.3733	0.3667	−0.7353	0.9964	0.3	0.0	0.7
7.00	−0.7645	0.1880	−0.7102	0.5872	0.1	−0.1	0.6

[a] T, triglyceride; D, diglyceride; M, monoglyceride; A, fatty acid. For manufacturer see Table 1.

TABLE 3
Reaction Rate Constants for Hydrolysis Catalyzed by CT-165 at 155°C[a]

Reaction time (h)	k'_1	k_{-1}	k'_2	k_{-2}	k'_1/k_{-1}	k'_2/k_{-2}
3.00–3.25	0.2328	0.0051	0.1245	0.0120	51.53	10.38
3.25–3.50	0.2844	0.0060	0.1212	0.0116	47.40	10.45
3.50–3.75	0.2598	0.0051	0.1944	0.0221	50.94	8.80
3.75–4.00	0.2739	0.0056	0.2351	0.0277	48.91	8.49
Average	0.26 ± 0.02	0.0055 ± 0.0005	0.17 ± 0.06	0.018 ± 0.008	50 ± 2	10 ± 1

[a] Where k'_1 is the rate constant that has incorporated water concentration.

It was nearly impossible to obtain the individual rate constants unless precise concentrations were determined for all the reactants and products. We simplified the process by determining the rate of each of the overall steps, r_1, r_2 and r_3, where $r_1 = k_1[\mathrm{T}][\mathrm{H_2O}] - k_{-1}[\mathrm{A}][\mathrm{D}]$, $r_2 = k_2[\mathrm{D}][\mathrm{H_2O}] - k_{-2}[\mathrm{A}][\mathrm{M}]$, and $r_3 = k_3[\mathrm{M}]\,[\mathrm{H_2O}] - k_{-3}[\mathrm{A}][\mathrm{G}]$ (11).

To determine the values of the various rate constants, we devised the following procedure: The average concentrations from two experiments for T, D, and A during the course of the reaction were first fitted by least squares to the following equations for the reactions catalyzed by CT-165 at 155°C:

$$[\mathrm{T}] = \frac{2.47 + 94.05t^{-2.99}}{0.11 + t^{-2.99}} \qquad R = 0.9982 \qquad S = 2.0437 \qquad [4]$$

$$[\mathrm{D}] = \frac{35.34 + 29.52t^{3.47}}{12.5 + t^{3.47}} \qquad R = 0.9983 \qquad S = 0.7355 \qquad [5]$$

$$[\mathrm{A}] = \frac{20.87 + 43.62t^{2.69}}{7.56 + t^{2.69}} \qquad R = 0.9976 \qquad S = 1.2825 \qquad [6]$$

$$[\mathrm{M}] = \frac{-0.01 + 0.70t}{1 - 0.32t + 0.05t^2} \qquad R = 0.9956 \qquad S = 0.1281 \qquad [7]$$

where t is the time of reaction in hours, R is the correlation coefficient, and S is the standard error.

The rates of reaction at various times were then obtained from the differentiation of these equations (Table 2). The r values were calculated using $r_1 = 1/3(d[\mathrm{A}]/dt + d[\mathrm{M}]/dt) + 2/3(d[\mathrm{D}]/dt)$, $r_2 = r_1 - d[\mathrm{D}]/dt$, and $r_3 = r_2 - d[\mathrm{M}]/dt$ (11). The values of r_1 and r_2 increased as the reaction proceeded, initially reaching maximal values at 1.5 and 1.0 h, then decreasing.

Since the concentrations [T], [D], [M], and [A] were known, concentration [G] can be calculated. If we assume that the solubility of water in the reaction mixture remained constant, the values of k_i can be calculated. The results were tabulated in Table 3, for the reaction between the third and fourth hours when the concentrations were changing moderately. We noticed that while the rate constants were relatively constant for the first stage of hydrolysis, the rate constants for both the forward and reverse reactions of the second stage continued to increase. However, the ratio of these constants remained nearly unchanged.

The average value for k'_i/k_{-i} within the third to fourth hour was obtained: $k'_1/k_{-1} = 50$ and $k'_2/k_{-2} = 10$. The value k'_3/k_{-3} was not determined, as we did not determine the concentration of glycerol. The ratios determined were also an approximation as the assumption of constant [$\mathrm{H_2O}$] in the oil may not be true since the presence of an emulsifying agent could affect the solubility of water. However, we think that the value obtained seems reasonable when the concentration of the partial glycerides was appreciable.

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