Kinetics of the Catalytic Esterification of Castor Oil with Lauric Acid Using *n*-Butyl Benzene as a Water Entrainer

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ABSTRACT: The esterification of castor oil with lauric acid was investigated using tetra *n*-butyl titanate (TBT), $SnCl_2 \cdot 2H_2O$ (stannous chloride), $CoCl_2 \cdot 6H_2O$ (cobalt chloride), and $(CH_3COO)_2Zn \cdot 2H_2O$ (zinc acetate dihydrate) as catalysts. Effects of catalyst concentration and reaction temperature on the progress of the reaction were investigated. TBT was the best catalyst for the esterification of castor oil with lauric acid at temperatures lower than 200°C. The reaction was first order with respect to each reactant. The activation energy for the esterification reaction of castor oil with lauric acid using TBT was 26.69 kcal/mol. The rate constants obtained for the esterification of castor oil with decanoic, lauric, palmitic, and stearic acids were nearly the same (15.80, 15.44, 15.06, and 14.67 mL $mol^{-1}min^{-1}$), as were the rate constants obtained for the reaction of castor oil and hydrogenated castor oil.

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KEY WORDS: Castor oil, decanoic acid, kinetics of esterification, lauric acid, palmitic acid, stearic acid, tetra *n*-butyl titanate.

Castor oil is a major source of specialty fats. Ricinoleic acid is the major FA in this oil. The hydroxyl group at the 12th carbon atom of ricinoleic acid can form secondary ricinoleyl esters with FA (1,2). Specialty fats consisting of esters of castor oil with their own FA have been reported. These esters undergo thermal dissociation at 260°C, leading to formation of dehydrated castor oil having an additional double bond adjacent to the hydroxyl group originally present and to unsaturation of conjugations up to 30% (2).

The rate of formation of estolides from castor oil FA and their decomposition at different temperatures have been studied (3). For the same purpose, esterification of castor oil with oleic acid was carried out using tin chloride, *p*-toluene sulfonic acid (*p*-TSA), and potassium hydroxide as catalysts, and the kinetics were established. The splitting of the ester was reported with *p*-TSA at 250°C (4). The mechanism and kinetics of the $CoCl_2$-catalyzed esterification reaction of castor oil with oleic acid has been reported (5). The effects of two Lewis acid catalysts, tin chloride and cobalt chloride, on the kinetics of esterifying castor oil and oleic acid have been investigated (6). Uncatalyzed and catalyzed reactions were carried out in the presence of excess oil and with equivalent amounts of reactants at various temperatures. The order of reaction varied with the initial ratio of oil to acid in the range used (1:1 to 20:1) and stabilized around second order with respect to acid when the amount of oil in the starting mixture was about 15 times the amount of acid or more at 225°C. The reaction was found to be first order with respect to castor oil in all cases, whereas with acid concentration the reaction was observed to change from second order for the uncatalyzed reaction to first order for the tin chloride-catalyzed reaction and to zero order for the cobalt chloride-catalyzed reaction.

TG estolides were synthesized by reacting the hydroxy moieties of lesquerella and castor oil with oleic acid. The optimal conditions for the reaction were found to be 200°C for 12 h for lesquerella oil and 24 h for castor oil, both under vacuum. The use of a mineral or Lewis acid catalyst increased the rate of TG estolide formation at 75°C but resulted in the formation of a dark oil, and the reaction did not go to completion in 24 h. Interesterification or dehydration of the resulting estolides to conjugated FA was not a significant side reaction, with only a slight amount of dehydration occurring at the highest temperature, 250°C (7).

The esterification of castor oil and hydrogenated castor oil with saturated FA such as myristic, palmitic, hystric (a mixture of 55% palmitic and 45% stearic acids), and behenic using *p*-TSA and sulfuric acid as catalysts has been studied, as have the physical properties of these specialty fats (8). Some of these esters did not crystallize even at 8°C. Castor oil esters are used as plasticizers in textile lubricating oils (9).

Direct esterification in the absence of a solvent requires temperatures in the range of 230–250°C, and the product obtained has a poor color.

Tetra *n*-butyl titanate (TBT) is a well-known catalyst for many reactions including esterification (10,11). Although TBT is a good catalyst for esterification, particularly at high reaction temperatures, its exploitation in fatty ester synthesis is rare. Therefore, it was desirable to investigate esterification with TBT for fatty esters, particularly when reducing the reaction temperature from 230–250°C to lower than 200°C.

In the present work, we studied the kinetics of the esterification reaction between castor oil and lauric acid using TBT, $SnCl_2 \cdot 2H_2O$ (stannous chloride), $CoCl_2 \cdot 6H_2O$ (cobalt chloride hexahydrate), and $CH_3COO)_2Zn \cdot 2H_2O$ (zinc acetate dihydrate) catalysts and using *n*-butyl benzene (*n*-BB) as solvent.

MATERIALS AND METHODS

Materials. Castor oil (commercial grade) and hydrogenated castor oil (commercial grade) were obtained from Jayant Oil Mills Ltd., (Mumbai, India). Lauric acid (98% purity),

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$CoCl_2·6H_2O$, $(CH_3COO)_2Zn·2H_2O$, $SnCl_2·2H_2O$ (laboratory reagent grade) were purchased from S.D. Fine-Chem. Ltd. (Mumbai, India). Palmitic acid (98% purity) and stearic acid (98% purity) were a gift from Godrej Soaps Ltd. (Mumbai, India). TBT was obtained from Coatwell Paints (Mumbai, India). *n*-BB was obtained from Vinati Organics Ltd. (Mumbai, India).

Experimental procedures. FA (0.148 mol) and *n*-BB (150 mL) were added to castor oil (50 g) in a three-necked flask. The flask was then fitted with a Dean–Stark assembly, and the reaction mixture was heated by using a heating mantle. Catalyst was added when the desired reaction temperature was reached. A sample was immediately withdrawn for analysis. The water formed during the reaction was separated from the reaction zone and collected in the Dean–Stark assembly. Progress of the reaction was monitored by determining the acid value of the reaction mixture.

The reaction was also carried out at lower temperatures of 160 and 170°C instead of 185°C under appropriately reduced pressure so that the reaction mixture boiled at the reaction temperature. This enabled water to be removed from the reaction mixture using the Dean–Stark assembly.

The reaction was then carried out at the same reactant concentration in a three-necked flask but without a solvent and with sparging through the reaction mixture to strip off water formed during the reaction. The temperature was maintained at 210°C using a heating mantle.

Analysis. Samples of the reaction mixture were withdrawn at regular time intervals and analyzed for their acid value (12). A decline in acid value was related to conversion of the FA.

RESULTS AND DISCUSSION

Experiments were carried out to determine the conditions for maximal conversion of acid in the reaction of castor oil with lauric acid. The hydroxyl value of the commercial-grade castor oil was 166. To completely esterify 50 g of oil, 0.148 mol of lauric acid was required. Table 1 shows the results of these preliminary experiments. At a 148°C reaction temperature and using $SnCl_2·2H_2O$ as a catalyst, as much as 48% conversion of acid was achieved. With *n*-BB as a solvent, the reaction temperature could be increased to 185°C at atmospheric pressure. Experiments 3, 4, and 5 indicate that about 65% of the acid could be converted to the corresponding ester. Attempts to increase it significantly by increasing the catalyst loading or by removing dissolved water by distilling the solvent followed by adding fresh solvent did not result in increased conversion.

Changing the catalyst ($SnCl_2·2H_2O$ to TBT, Experiments 3 and 6) did not significantly improve the conversion, nor did increasing the reaction temperature to 210°C and using N_2 to remove the reaction water substantially increase the conversion of the acid. Because the maximal conversion obtained was around 65 to 70%, we hypothesized that the –OH group of ricinoleic acid attached to the 1- and 3-positions at the backbone of the glyceride was easily esterified, whereas the –OH group of ricinoleic acid on the 2-position was difficult to esterify because of steric hindrance. Hence, only about two-thirds of the acid was converted to the ester. Similar results were reported in the literature (4). Subsequent experiments were carried out with a 1:0.67 mole ratio of castor oil to FA to achieve maximal conversion of the acid, with all other conditions remaining unchanged.

In the present work, the major experimental work was carried out in the temperature range of 148–185°C.

In Experiment 6 where the conversion of acid was maximal at about 67% and did not increase thereafter, the unreacted acid was neutralized and removed as its sodium salt in the aqueous phase. The acid was precipitated from the aqueous phase by acidification. The acid thus obtained was found to be lauric acid, indicating that there was no interesterification.

At higher temperatures (>250°C), estolides split to form dienes (2,6,9,13). Since, in the present case, the reaction temperatures used were much lower, the chances of dehydration leading to the formation of dienes were much less. In monitoring the water separated during the reaction and that present in the reaction mixture, we found that the total quantity of water was always marginally less than the acid consumed in

TABLE 1
Preliminary Experiments in the Reaction of Castor Oil with Lauric Acid Under Different Conditions

Exp. no.	Initial mole ratio of OH/COOH	Solvent	Catalyst	Temperature (°C)	Time (h)	% Conversion of lauric acid
1	1:1	Xylene	4% $SnCl_2·2H_2O$	148	8	41
2	1:1	Xylene	6% $SnCl_2·2H_2O$	148	8	48
3	1:1	*n*-BB	4% $SnCl_2·2H_2O$	185	6	65
4	1:1	*n*-BB	4% $SnCl_2·2H_2O$	185	2 + 1[a]	65
5	1:1	*n*-BB	4 + 2% $SnCl_2·2H_2O$	185	2 + 4[b]	65
6	1:1	*n*-BB	4% TBT	185	6	68
7	1:1	—	4% TBT	210	3[c]	70

[a] After 2 h, 75 mL of solvent was distilled out and 75 mL of fresh solvent was added. The reaction was continued of another 1 h.

[b] After 2 h, another 2% of the catalyst was added and the reaction was continued for another 4 h.

[c] The reaction carried out under N_2 sparging. *n*-BB, *n*-butyl benzene; TBT, tetra *n*-butyl titanate.

TABLE 2
Effect of Different Catalysts and Catalyst Concentrations on the Conversion of Lauric Acid[a]

Time	Conversion (%)								
	$CoCl_2·6H_2O$	$(CH_3COO)_2Zn·2H_2O$	TBT			$SnCl_2·2H_2O$			
(min)	4%	4%	0.13%	0.25%	0.5%	0.25%	0.5%	1%	2%
0	0	0	0	0	0	0	0	0	0
20	—	—	—	—	19.73	—	—	—	—
30	4.17	16.34	—	—	—	—	—	18.6	—
40	—	—	—	—	—	—	6.2	—	—
45	—	—	—	—	—	—	—	—	27.71
60	19.66	29.55	7.26	15.7	32.11	8.2	—	33.7	39.4
90	26.15	35.2	—	—	—	—	31.1	—	59.09
120	29.33	41.84	—	29.67	57.21	22.93	43.22	56.17	—
130	—	—	—	—	—	—	—	—	78.17
180	44.9	53.81	30.46	43.43	69.45	36.39	58.53	—	85.65
215	—	—	—	—	—	—	—	82.3	—
270	57.81	66.56	—	—	—	50.95	78.97	—	—
300	—	—	45.06	65.2	—	—	—	—	92.96
340	—	—	—	—	85.26	—	—	—	—
360	69.27	74.75	53.6	69.45	—	58.71	92.94	—	—
480	—	—	66.63	—	—	—	—	—	—

[a] Initial conditions: 50 g (0.049 mol) castor oil, 0.099 mol lauric acid, 150 mL *n*-BB, 185°C. For abbreviations see Table 1.

the reaction. This clearly indicates that no dehydration was taking place under the experimental conditions. Further, when castor oil in *n*-BB was heated to 200°C for 4 h in the presence of 0.5% TBT, water was not formed. This also indicates that no dehydration of castor oil took place under experimental conditions.

Effects of the following variables on the conversion of acid were investigated: (i) catalyst, (ii) catalyst concentration, (iii) temperature, (iv) FA, and (v) substrate.

Effect of catalyst. Experiments were carried out at 185°C with four different catalysts: TBT, $SnCl_2·2H_2O$, $CoCl_2·6H_2O$, and $(CH_3COO)_2Zn·2H_2O$. Loading of catalysts was 4% w/w based on castor oil for $CoCl_2·6H_2O$ and $(CH_3COO)_2Zn·2H_2O$. For TBT and $SnCl_2·2H_2O$, loading was 0.5% w/w based on the castor oil is used.

Table 2 shows the conversion of acid over time. For the four catalysts, the lowest conversion was obtained when $CoCl_2·6H_2O$ was used as a catalyst (4% based on castor oil). $(CH_3COO)_2Zn·2H_2O$ showed slightly higher conversion than $CoCl_2·6H_2O$ when used at the same concentration. When TBT and $SnCl_2·2H_2O$ were used as catalysts, higher conversion was obtained in the minimum time with 0.5% catalyst. The initial reaction rate was very high when TBT was used. For further kinetic studies, TBT and $SnCl_2·2H_2O$ were used as catalysts.

Effect of catalyst loading. The effect of catalyst loading was investigated for two different catalysts, TBT and $SnCl_2·2H_2O$. For TBT, 0.13, 0.25, and 0.50% w/w catalyst loadings (based on castor oil) were used. Conversion of acid for a given batch time increased with increasing catalyst concentration, and the initial reaction rate also increased with increasing catalyst concentration (Table 2).

For $SnCl_2·2H_2O$, 0.25, 0.50, 1, and 2% w/w catalyst loadings were used. The conversion of acid increased with increasing $SnCl_2·2H_2O$ concentration (Table 2). The concentration of TBT required to achieve comparable conversion under identical conditions was much less than the concentration of $SnCl_2·2H_2O$.

Effect of temperature. The reaction was carried out at 160, 170, and 185°C. For the first two reaction temperatures, reduced pressure was used to maintain refluxing conditions and facilitate water removal by using the Dean–Stark assembly. The TBT concentration used in this reaction was 0.5% w/w of the castor oil. The effect of temperature on the conversion of acid is shown in Figure 1. The conversion profile of the acid depended on the reaction temperature, and the conversion rate of the acid increased with an increase in reaction

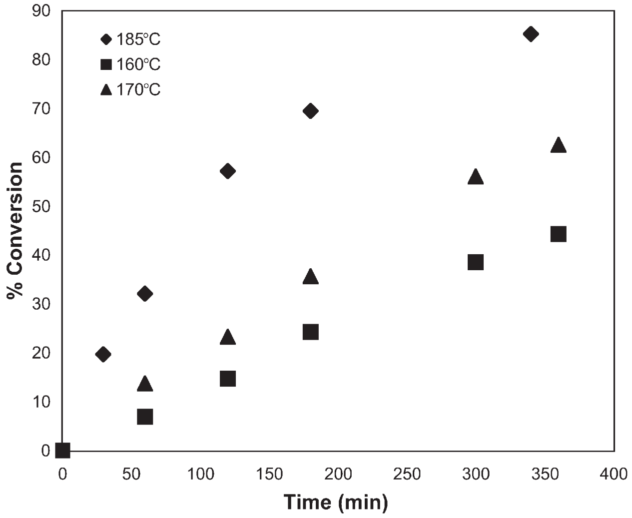

FIG. 1. Effect of temperature on the conversion of acid. Initial conditions: 50 g (0.049 mol) castor oil, 0.099 mol lauric acid, 0.5% tetra *n*-butyl titanate on the basis of oil weight, and 150 mL *n*-butyl benzene.

TABLE 3
Effect of Different FA and Hydrogenated Castor Oil on the Progress of the Reaction[a]

Time (min)	% Conversion of acid Castor oil + decanoic acid	Castor oil + lauric acid	Hydrogenated castor oil + lauric acid	Castor oil + palmitic acid	Castor oil + stearic acid
0	0	0	0	0	0
20	—	19.73	—	—	—
30	18.16	—	20.9	—	—
60	33.34	32.11	38.92	28.49	28.49
90	—	—	—	—	—
120	59.73	57.21	-	55.95	57.21
150	—	—	66.19	—	—
180	71.27	69.45	—	66.72	69.45
300	—	—	—	—	—
340	—	85.26	—	—	85.26
360	—	—	—	86.33	—
420	—	—	90	—	—

[a]Conditions: For both castor oil and hydrogenated castor oil reactions, 0.5% TBT and 150 mL *n*-BB were used. Temperature was maintained at 185°C. For the castor oil reaction, 50 g (0.049 mol) castor oil and 0.099 mol FA were used. For the hydrogenated castor oil reaction, 50 g (0.047 mol) of hydrogenated castor oil and 0.095 mol FA were used. For abbreviations see Table 1.

temperature. The reaction could thus be carried out with TBT as a catalyst at lower temperatures (<200°C).

Effect of FA. To investigate the effect of different FA, castor oil was esterified with decanoic acid, lauric acid, palmitic acid, and stearic acid. The reaction was carried out using TBT as a catalyst at 185°C with the other parameters remaining the same. With different FA, no significant change in the progress of the reaction was observed (Table 3).

Effect of substrate. The esterification reaction was carried out by using hydrogenated castor oil (instead of castor oil) and lauric acid using TBT as a catalyst. The reaction temperature was maintained at 185°C. The progress of the esterification reaction was identical for castor oil and hydrogenated castor oil (Table 3).

Kinetics. For the irreversible, bimolecular-type second-order reaction,

$$A + B \xrightarrow{\text{catalyst}} \text{product} \quad [1]$$

the rate of consumption of A, $(-r_A)$, is given by

$$-r_A = kC_C C_A C_B \quad [2]$$

The concentration of catalyst was constant throughout the reaction. Therefore,

$$-r_A = k' C_A C_B \quad [3]$$

where $k' = kC_C$, C_A = concentration of FA, and C_B = hydroxyl group concentration.

The integrated form of Equation 3 is

$$\ln\left[(1 - X_B)/(1 - X_A)\right] = (C_{B0} - C_{A0})k't \quad [4]$$

where X_A = fractional conversion of the FA; X_B = fractional conversion of the –OH group; C_{A0} = initial concentration of the FA (mol/mL); C_{B0} = initial hydroxyl group concentration (mol/mL); and k' = the second-order rate constant.

Figures 2 and 3 show the pertinent plots for Equation 4. The linearity of the data indicate the validity of Equation 4 and a first-order rate dependence on both the acid and the –OH group concentrations. The slope of each line was equal to $(C_{B0} - C_{A0})k'$, from which k' can be calculated (Table 4).

The rate constants (k') obtained for TBT and $SnCl_2{\cdot}2H_2O$ were then plotted against the catalyst concentration (Fig. 4). The straight line obtained indicates that the reaction was first order with respect to catalyst concentration.

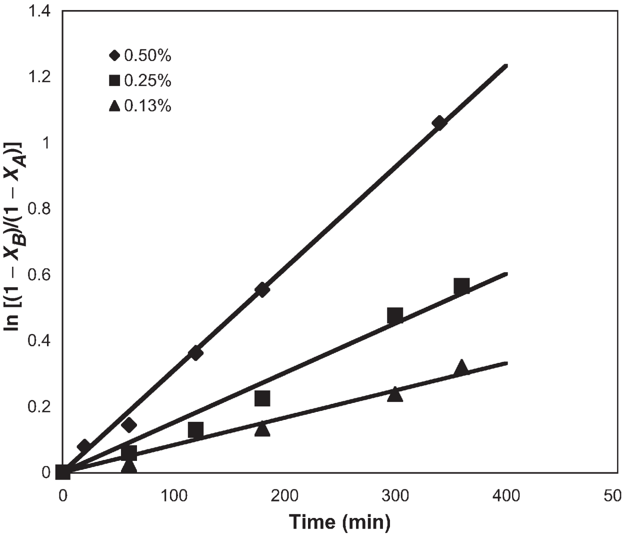

FIG. 2. Second-order plot for the esterification reaction using tetra *n*-butyl titanate as a catalyst (where X_A = fractional conversion of the FA and X_B = fractional conversion of the –OH group). Initial conditions: 50 g (0.049 mol) castor oil, 0.099 mol lauric acid, 150 mL *n*-butyl benzene, 185°C.

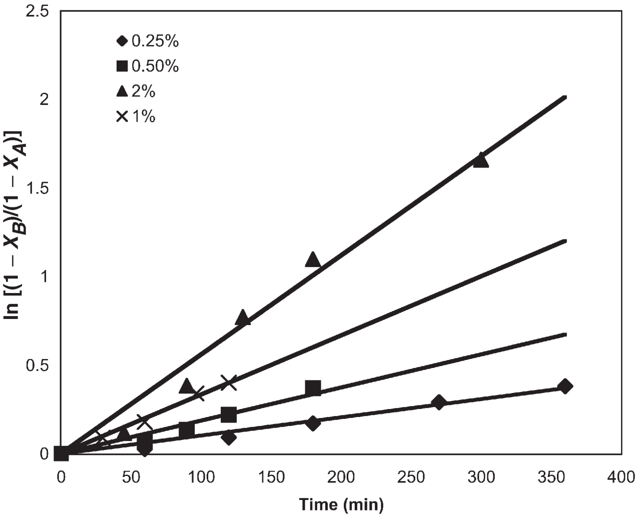

FIG. 3. Second-order plot for the esterification reaction using $SnCl_2 \cdot 2H_2O$ as a catalyst. Initial conditions: 50 g (0.049 mol) castor oil, 0.099 mol lauric acid, 150 mL *n*-butyl benzene, 185°C.

By using the equation $k' = kC_C$ and Figure 4, the values of the rate constant (k) were calculated for TBT- and $SnCl_2 \cdot 2H_2O$-catalyzed reactions. The rate constant obtained for $SnCl_2 \cdot 2H_2O$ was 1.62×10^6 mL^2 mol^{-2} min^{-1} and that for TBT was 5.15×10^6 mL^2 mol^{-2} min^{-1}, which is almost three times that for $SnCl_2 \cdot 2H_2O$.

An Arrhenius plot of the reaction of castor oil and lauric acid with TBT (0.5%) is presented in Figure 5. The activation energy for the reaction was 26.69 kcal/mol. The k' obtained for the reaction of castor oil with different FA and 0.5% TBT are shown in Table 4. The k' values were practically the same for all acids. The k' for the reaction of castor oil and lauric acid was 15.44 mL mol^{-1} min^{-1}, and the k' for the reaction of

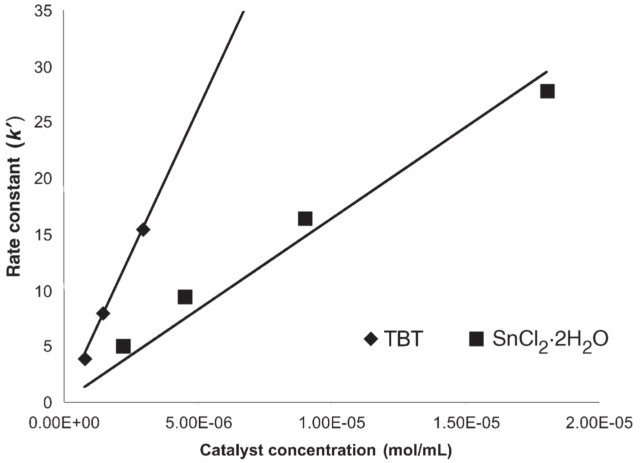

FIG. 4. Plot of rate constants (k') for tetra *n*-butyl titanate (TBT) concentration vs. $SnCl_2 \cdot 2H_2O$ concentration.

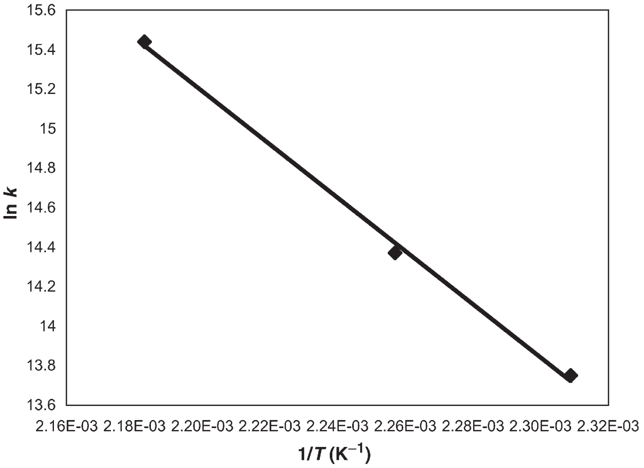

FIG. 5. Arrhenius plot for the esterification of castor oil with lauric acid using tetra *n*-butyl titanate as a catalyst.

TABLE 4
Rate Constants (k') for Different Catalyst Concentrations and Reaction Temperatures[a]

			Rate constant (k') (mL mol^{-1} min^{-1})		
			Reaction temperature (°C)		
Catalyst	FA	Loading (%)	185	170	160
TBT	Lauric acid	0.13	3.97	—	—
		0.25	7.98	—	—
		0.5	15.44	5.39	2.91
	Decanoic acid	0.5	15.80		
	Palmitic acid	0.5	15.06		
	Stearic acid	0.5	14.67		
$SnCl_2 \cdot 2H_2O$	Lauric acid	0.25	4.98	—	—
		0.5	9.46	—	—
		1	16.43	—	—
		2	28.88	—	—
$CoCl_2 \cdot 6H_2O$	Lauric acid	4	6.97	—	—
$(CH_3COO)_2Zn \cdot 2H_2O$	Lauric acid	4	8.96	—	—

[a] For abbreviation see Table 1.

hydrogenated castor oil and lauric acid was 15.80 mL $\text{mol}^{-1}\ \text{min}^{-1}$ when the reaction was carried out at 185°C and 0.5% TBT was used as a catalyst.

Of all the catalysts used, TBT was the best catalyst for the esterification of castor oil with lauric acid, and the esterification reaction was successfully carried out at a reaction temperature of 200°C or less. There was not much change in the k' of the castor oil and hydrogenated castor oil reactions. Basically, these were reactions between the –OH group of these oils and the –COOH group of the FA. The activity of the –OH group of both these oils was similar because these oils are structurally similar. With different FA, no significant change in the progress of the reaction was observed.

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