Reaction of glycerol with fatty acids in the presence of ion-exchange resins
Preparation of monoglycerides

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Abstract

The preparation of monoglycerides from glycerol and fatty acids in the presence of ion-exchange resins is studied. A preliminary swelling in the glycerol inhibits the reaction, whereas a swelling of the resin in the oleic acid, before the reaction, increases the activity and the selectivity. This result shows that the competitive adsorption of glycerol and fatty acid influences greatly the esterification rate. Generally, water is an inhibitor of the esterification reaction (catalyst poisoning and thermodynamic equilibrium) and different procedures have already been suggested for its elimination. By using a molecular sieve as a water trap, the oleic acid conversion increases up to 90% without any change of the monoglyceride selectivity (85%). Moreover, owing to the pore structure of the catalyst, it has to be expected that the hydrocarbon chain length of the fatty acid will influence the activity and the selectivity, evidence of which we give in the present study. Finally, if an excess of glycerol increases the selectivity of the monoglycerides, it decreases the activity and can be considered as a selective inhibitor. © 1999 Elsevier Science B.V. All rights reserved.
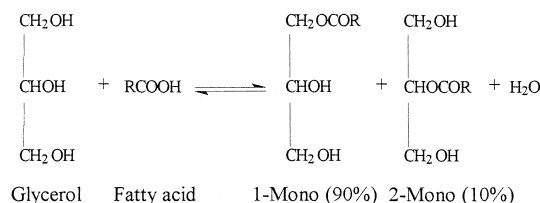
Keywords: Esterification; Monoglycerides; Fatty acids; Ion-exchange resins

1. Introduction

Monoglycerides are extensively used as emulsifiers [1] or stabilization agents [2] in cosmetics, in detergents and in food industries.

The three most important processes for the preparation of monoglycerides are the glycerolysis, the hydrolysis of triglycerides and the direct esterification of glycerol with fatty acids [3].

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\underset{\substack{\text{Glycerol}}}{\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\substack{\text{Fatty acid}}}{RCOOH} \rightleftharpoons \underset{\substack{\text{1-Mono (90\%)}}}{\begin{array}{c} CH_2OCOR \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\substack{\text{2-Mono (10\%)}}}{\begin{array}{c} CH_2OH \\ | \\ CHOCOR \\ | \\ CH_2OH \end{array}} + H_2O
$$

Nevertheless, at the end of the reaction, there is a mixture of glycerol, fatty acid, monoglycerides (35% to 40%), diglycerides (40% to 50%), triglycerides (10% to 15%) and secondary products (acrolein, polyethers or polyesters of glycerol). Before their use in industry, a separation step is necessary in order to obtain a pure product. In our laboratory, we investigated different ways of increasing the selectivity to monoglycerides, by using solid catalysts.

Indeed, the esterification reaction is generally catalyzed by homogeneous acid catalysts (sulfuric acid, AMS or APTS) [4–7] but the selectivity to monoglycerides is low. Furthermore, the use of such catalysts creates environmental problems (corrosion, difficulty of catalyst recycling) or chemical problems (secondary reactions). Among these catalysts, Lewis acids [6,8,9], heteropolyacids [10–12], enzymes [3,13–15], zeolites [9,16–20] or ion-exchange resins [21,22] can be listed. The cationic acid resins seem to be very interesting because they are active at low temperature and could act as shape selective materials [23]. Indeed, among all these materials, we can distinguish between the resins (gel-type), not really porous, and the macroporous resins. Moreover, Dorfner [24] shows that the swelling properties of a resin are due to the formation of hydrogen bonds between the sulfonic groups of the resin and the water or the alcohol molecules of the reaction mixture [25].

In a non-polar medium, a type I structure can be observed. On the other hand, when polar compounds (water or alcohol) are added to the medium, there is a partial modification of the protonic bonds (type II structure). A complete protonation of the solvent and a homogenization of the catalyst (type III structure) can be observed. With this type of structure, the resins appear as aqueous solutions of a strong acid.
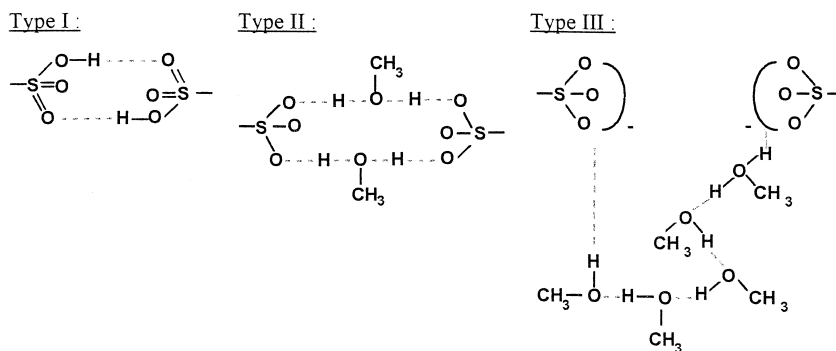
The degree of crosslinking has a direct effect on the resin swelling; when there is an increase of the crosslinking rate, the structure becomes more rigid and the resin does not swell [26].

A previous study [27] shows that, under mild experimental conditions, the gel resin (Amberlyst 31) is the best catalyst for the selective preparation of monooleyl glyceride. Indeed, a selectivity of about 90% for an oleic acid conversion above 50% is obtained. In the present paper, we present a detailed

Table 1
Physical characteristics of the resins

Resins	Structure	Particle size (mm)	Exchange capacity ($m_{eqH^+} / g_{dry\ resin}$)	Crosslinking degree (%)	Pore size diameter (Å)
Amberlyst 31	gel	0.4 to 1.2	4.8	4	–
Amberlyst 16	macroporous	0.3 to 1.2	5.0	12	20
Amberlyst 15	macroporous	1.2 to 1.6	4.7	20	12
K1481	gel	< 0.05	4.8	8	–

study of the esterification of glycerol with oleic acid over different resins; especially the effect of swelling and the influence of different experimental parameters.

2. Experimental

2.1. Materials

The ion-exchange resins used in the esterification reaction were supplied by Bayer (K1481) and Rohm & Haas (Amberlyst). Their principal physical characteristics are given in Table 1. Prior to using them in an esterification reaction, only the resin Amberlyst 31 was pretreated: the resin, supplied in a wet form, was first washed with ethanol and then dried under nitrogen at 100°C for 8 h.

Glycerol (Prolabo) and oleic acid (Prolabo) with a purity of 99% were used without further purification.

2.2. Reaction procedure

The esterification reaction was performed in a glass batch reactor equipped with a condenser. The glycerol (9 g) and the fatty acid (4.5 g) (molar ratio glycerol/fatty acid equal to six) were stirred at 800 rpm and heated in an oil bath at the required temperature (90°C generally). When the desired temperature was reached, the catalyst was added to the reagents (zero reaction time).

Table 2
Gradient profile used for the eluents

Time (min)	Eluent (% A)
0	100
13	80
17	50
19	100
25	100

Eluent A: chloroform (stabilized with ethanol).
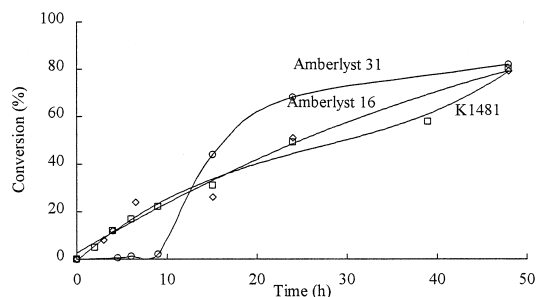Eluent B: mixture of methanol (92%), water (5%), chloroform (2.5%) and ammonia (0.5%).

Fig. 1. Oleic acid conversion over various resins.

After cooling down the reaction products (after about 15 min), ethanol (40 cm^3) was added in order to homogenize the mixture from which a sample of 2 cm^3 was taken, dissolved in 25 cm^3 of ethanol and analyzed by HPLC.

2.3. Analytical method

The reaction mixture was analyzed with high performance liquid chromatography (Touzart et Matignon) equipped with a light scattering detector (DDL 21), used for the detection of high molecular weight compounds (above 200) such as fatty compounds.

The chromatographic column was a silica column (type Kromasil silica 100 Å, $l = 25$ cm) and two types of eluents (1.2 ml min^{-1}) were used (see Table 2).

By a calibration method using cholesterol as an internal standard, the percentage of the reagents and products of the reaction medium was determined. The conversion was expressed with regard to the oleic acid transformation using the reaction coefficients for the formation of mono-, di- and triglycerides,

$$\text{Conversion } (\%) = \frac{S_{\text{monooleate}} + 2S_{\text{dioleate}} + 3S_{\text{trioleate}}}{S_{\text{monooleate}} + 2S_{\text{dioleate}} + 3S_{\text{trioleate}} + S_{\text{acid}}} \times 100$$

where S is the chromatographic surface corrected by response factor of different product.

In the same way, the selectivity of a specific ester (mono-, di- or triester) expressed by the ratio of the ester to all the various reaction products (corrected by the reaction coefficients).
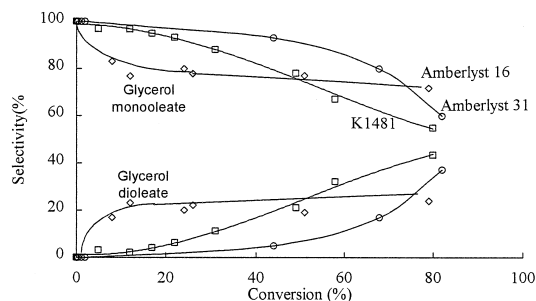

Fig. 2. Selectivity evolution over various resins.

$$\text{Monoglyceride selectivity } (\%) = \frac{S_{monooleate}}{S_{monooleate} + 2S_{dioleate} + 3S_{trioleate}} \times 100$$

$$\text{Diglyceride selectivity } (\%) = \frac{2S_{dioleate}}{S_{monooleate} + 2S_{dioleate} + 3S_{trioleate}} \times 100$$

$$\text{Triglyceride selectivity } (\%) = \frac{3S_{trioleate}}{S_{monooleate} + 2S_{dioleate} + 3S_{trioleate}} \times 100$$

3. Results and discussion

3.1. Activity and selectivity of some resins

A comparison between different cationic resins (K1481, Amberlyst 16 and 31) in the esterification of glycerol with oleic acid (Fig. 1) shows that the catalytic properties depend on the structure of resins (gel-type or macroporous-type). Fig. 1 shows that the activities of the K1481 and Amberlyst 16 resins are similar. These results indicate that the active sites are located on the surface of microparticles (K1481) or in the macropores of the Amberlyst 16 which are easily accessible to the reactants.

On the contrary, the induction period of 9 h observed over the Amberlyst 31 is due to the gel structure of the resin (a low crosslinked material) which limits the accessibility of reactants to the active sites located in the pores. Moreover, after the swelling of the matrix in a polar solvent, the initial activity is greater than the one observed in the presence of K1481 or Amberlyst 16.

On the other hand, the selectivity to monooleyl glyceride is above 90% at a conversion of 50% over the gel resin Amberlyst 31 whereas the structure of K1481 leads to a decrease of the selectivity to monoglyceride (Fig. 2).

In order to identify the effects of the swelling properties, we have studied the influence (i) of the swelling of resin either in glycerol or in oleic acid, (ii) of a reagent (water) or of an inert solvent (octane).

3.2. Influence of the reactants

3.2.1. Swelling in glycerol

These experiments were performed at different temperatures and the results are presented in Table 3. Owing to a strong adsorption of the glycerol over the resin (Amberlyst 31), the swelling of the resin in glycerol has an inhibitor effect without any change in the monoglyceride selectivity.

Table 3
Effect of the swelling properties of the resins in the esterification of glycerol with oleic acid

Resins	Swelling in glycerol	Oleic acid conversion (%)	Selectivity (%)		
			Mono	Di	Tri
Amberlyst 31	without	68	80	17	3
	at 70°C for 7 h	6	98	2	0
K1481	without	49	78	21	0
	at 55°C for 4 h	36	86	14	0

Experimental conditions—molar ratio: glycerol/oleic acid = 6, reaction time = 24 h, catalyst weight = 1 g, $T = 90$°C.

P : Ion-exchange resin
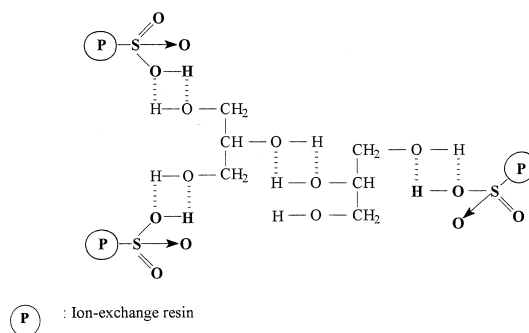
Indeed, after a 24-h reaction, the conversion of oleic acid is below 10%. Furthermore, both the fatty acid diffusion and the accessibility to active sites decrease and become the limiting steps of the esterification. Moreover, we believe that glycerol adsorption on active sites weakens the acid strength of the resin.

Experiments performed with Amberlyst 16 and 31, reported in Table 4, show clearly that the Amberlyst 31 resin swells in glycerol as well as in light alcohols and water but not in oleic acid. The swelling in glycerol is much more significant than the one observed for the Amberlyst 16 resin. This effect has already been observed by Dorfner [24] who studied resin swelling in different solvents and especially in glycerol (Table 5). These results show that the use of polar solvents like alcohol increases significantly the swelling percentage of a resin.

3.2.2. Swelling in oleic acid

Whatever the resin studied, when it swelled in oleic acid (Amberlyst 16 and 31), the acid conversion increased (Table 6). The K1481 resin does not swell in oleic acid nor in glycerol. On the other hand, the induction period of about 8 h, observed over Amberlyst 31, is suppressed (Fig. 3). We can also observe that the slopes of the conversion/time curves are practically the same before and after the resin swells in oleic acid. These changes suggest that the induction period is due to the oleic acid diffusion in the resin micropores before adsorption.
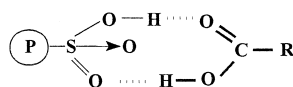
Apparently, the swelling step induces a high monoglycerides selectivity. For instance, after 24 h, for an oleic acid conversion of 75%, a glycerol monooleate selectivity above 80% is obtained over Amberlyst 31.

Table 4
Solvent effect on the swelling of resins after 96 h

Solvent	Swelling (%)	
	Amberlyst 31	Amberlyst 16
Glycerol	180	53
Oleic acid	6.7	0
Water	197	133
Propanol	193	190
Methanol	160	143

Table 5
Solvent effect on the swelling of various ion-exchange resins

Type of resin	Swelling percentage in					
	Water	Ethanol	Glycerol	Acetone	Acetic acid	Benzene
IR-120 (H$^+$)[a]	43	38	24	18	8	0
IR-105 (H$^+$)[b]	107	100	120	73	55	0

[a] Styrene–DVB polymer (gel-type).
[b] Formo-phenolic resin.

Table 6
Esterification of glycerol with oleic acid over various resins

Catalyst	Swelling	Conversion (%)	Selectivity (%)		
			Mono	Di	Tri
Amberlyst 31	without	68	80	17	0
	with	75	82	14	4
K1481	without	49	78	21	0
	with	45	83	17	0
Amberlyst 16	without	37	83	12	5
	with	42	77	19	4

Experimental conditions—molar ratio: glycerol/oleic acid = 6, $T = 90°C$, reaction time = 24 h, catalyst weight = 1 g.

3.2.3. Octane addition in the medium

In order to confirm the effect of the swelling properties on the activity, certain experiments were carried out in an apolar solvent. The results show the significant contribution of the gel phase in the catalytic process over different resins (gel or macroporous) (Table 7).

In the case of the K1481 resin and Amberlyst 15, the reaction occurs mainly at the surface of the microspheres: the addition of octane does not affect the activity of the resin. Whereas, in the case of Amberlyst 31 or 16, the addition of octane or the swelling of the resin in the solvent, modifies the oleic acid conversion. Indeed, the addition of octane limits the swelling of the resin. In the same way, at the first contact of the resin with the hydrocarbon, there is a contraction of the gel matrix which limits the accessibility to the active sites. This phenomenon can increase the induction period as could be observed with the Amberlyst 31 resin.

3.2.4. Water effect

One of the reaction products of the esterification between glycerol and oleic acid is water, a well-known poison or inhibitor of acid catalysts. The poisoning effect of water is demonstrated by the results presented in Table 8.
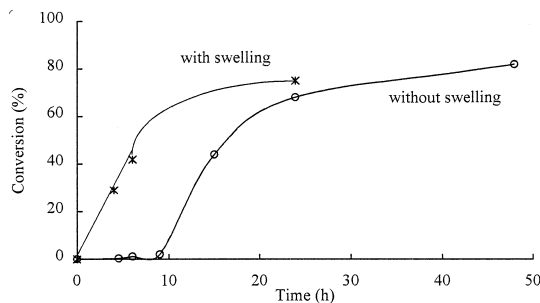

Fig. 3. Effect of the swelling of the ion-exchange resin (Amberlyst 31) in oleic acid before the esterification reaction.

Table 7
Octane effect in the medium

Resin	Type	Treatment	Conversion (%)	Selectivity (%)		
				Mono	Di	Tri
K1481	gel	without	49	78	21	1
		octane[a]	43	85	15	0
Amberlyst 31	gel	without	54	90	7	3
		octane[a]	19	95	2	3
		swelling in octane[b]	28	94	3	4
Amberlyst 16	macroporous	without	51	77	19	4
		octane[a]	11	95	2	3
		swelling in octane[b]	20	82	13	5
Amberlyst 15	macroporous	without	31	85	10	5
		octane[a]	22	84	12	4
		swelling in octane[b]	29	82	13	4

Experimental conditions—molar ratio: glycerol/oleic acid = 6, reaction time = 24 h, catalyst weight = 1 g, $T = 90°C$.
[a]Solvent volume (20 ml).
[b]At room temperature during 24 h before solvent evaporation.

Table 8
Water effect in the esterification reaction over Amberlyst 31

Additive	Reaction time (h)	Conversion (%)	Selectivity (%)		
			Mono	Di	Tri
Without	10	10	100	0	0
	24	68	80	17	9
With water (2 g)	24	11	98	2	0

Experimental conditions—molar ratio: glycerol/oleic acid = 6, $T = 90°C$, catalyst weight = 1 g.

In order to suppress or minimize the effect of water, a solid molecular sieve (pore size diameter of 3 Å), quite inactive in the esterification reaction, was added to the reaction medium (Table 9). Over such materials, after a long time reaction period, i.e., a conversion of oleic acid of about 20%, the monoglyceride selectivity decreased significantly to 40% [23,24]. The results presented in Table 8 show clearly that the elimination of water in the reaction mixture increases the activity of the Amberlyst 31 resin (up to 90%) while conserving a great glycerol monooleate selectivity (85%).

Table 9
Molecular sieve effect in esterification reaction

Catalyst and trap	Reaction time (h)	Conversion (%)	Selectivity (%)		
			Mono	Di	Tri
Molecular sieve (3 Å)	24	9	100	0	0
Amberlyst 31	24	68	80	17	4
	48	82	60	37	2
Amberlyst 31 + molecular sieve	24	90	85	12	3

Experimental conditions—molar ratio: glycerol/oleic acid = 6, $T = 90°C$, catalyst weight = 1 g, molecular sieve = 0.3 g.

Table 10
Influence of the hydrocarbon length of the acid in the esterification reaction

Acid	Conversion (%)	Selectivity (%)		
		Mono	Di	Tri
Oleic	14	65	33	1
Lauric	65	83	16	1

Experimental conditions—molar ratio: glycerol/oleic acid = 6, reaction time = 4 h, catalyst weight = 0.2 g, $T = 140°C$.

3.2.5. Influence of the hydrocarbon chain length of the acid

The influence of the hydrocarbon chain length on the diffusion rate of the acid inside the resin was studied. The dodecanoic acid (lauric acid: saturated acid with 12 carbon atoms) was chosen as the model molecule.

The results, presented in Table 10, show clearly that the nature of the acid influences very much the activity of the resin: the esterification reaction is more rapid with lauric acid (C_{12}) than with oleic acid ($C_{18:1}$) (see also the works of Petrini et al. [30]). These authors suggest that (i) the diffusion of the lauric acid is easier within the gel phase of the resin, (ii) its adsorption on the strong protonic sites is facilitated and (iii) the adsorption and diffusion of the monoesters outside the resin are also more rapid.

In order to obtain more information, the esterification between glycerol and lauric acid was carried out at 90°C over 0.2 g Amberlyst 31. In this case, compared to the results obtained with glycerol and oleic acid (Fig. 4), the formation of monoesters is quite rapid with lauric acid (C_{12}) while in the presence of oleic acid, a long induction period can be observed, even if the catalyst weight is more significant (weight five times heavier). This corroborates the suggestions made by Petrini.

3.3. Influence of reaction variables: R = glycerol/fatty acid (molar ratio) in the esterification of glycerol over an Amberlyst 31 resin

3.3.1. Fatty acid = oleic acid

The variation of the acid conversion presents a maximum for a R value of about 3 (Fig. 4) which could be explained by two different causes:

-need of a critical content of glycerol for the swelling of the gel matrix and the solvation of the sulfonic groups,
-esterification reaction.

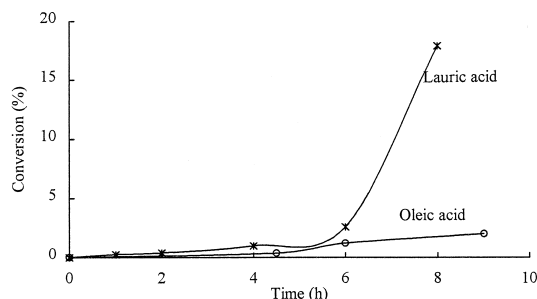

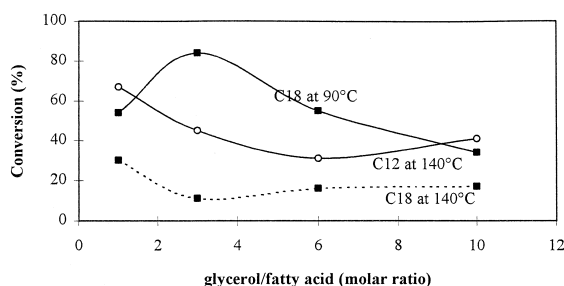Fig. 4. Esterification of lauric and oleic acid over Amberlyst 31 at 90°C.

Fig. 5. Esterification of glycerol with fatty acids over Amberlyst 31.

Ihm and Oh [28] obtained the same result for the esterification reaction of the oleic acid with *n*-butanol.

For a low value of R ($R = 1$) the small content of glycerol in the reaction mixture was used for a partial swelling of the resin, the acid conversion was low (Fig. 5). On the contrary, when the value of R was high ($R = 10$), the increase of the partial pressure of the glycerol in the pores inhibited the reaction. Owing to the hydrophobicity of the resin [29], the oleic acid diffusion towards acid sites was more difficult.

As far as the selectivity of monoglycerides is concerned (Fig. 6), there is a significant increase of their formation when the value of R varies from 1 to 3. This result could mean that, for a low value of R, the reaction occurs only at the surface of the resin particles, while by increasing the value of R to 3 and above, the esterification reaction occurs over the sites in the pores.

3.3.2. Fatty acid = lauric acid

Contrary to the above results, there is no diffusional limitation of lauric acid in the pores of the gel and the acid conversion is maximum for low values of R (Fig. 5). By increasing the glycerol concentration, the solvation of acid sites could decrease the strength of acid sites and therefore the activity of the resin. Owing to the formation of glycerol dioleate, the selectivity is small for $R = 1$ but much greater than the one obtained with oleic acid. Indeed, in the presence of oleic acid, the formation of polyglycerols (from the polycondensation of glycerol) and of esters of polyglycerols (from the esterification reactions) can be observed.
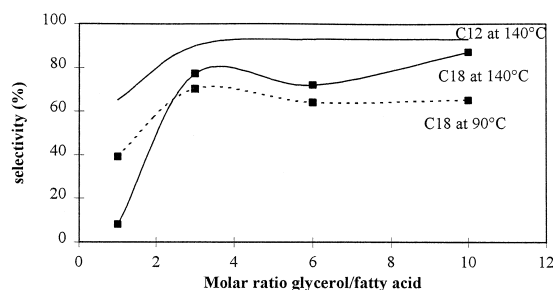

Fig. 6. Esterification of glycerol with fatty acids over Amberlyst 31. Selectivity to monoglycerides.

4. Conclusion

The selective esterification of glycerol, with fatty acid, into monoglycerides was studied in the presence of ion-exchange resins. If the activity and the selectivity to monoglycerides are influenced by the resin structure, the catalytic properties of these polymers are strongly influenced by the nature of the reagents. Indeed, if the catalyst activity depends on the adsorption rate of glycerol and oleic acid on the catalyst surface, this study shows the following.

(i) The strong adsorption of glycerol before the reaction inhibits very much the esterification of oleic acid because of a strong solvation on the sulfonic groups of the resins.

(ii) The swelling of the resin in the oleic acid favours the reaction without modifying the selectivity to monoglycerides. For a resin with a low degree of crosslinking, the induction period, observed at the beginning of the reaction, disappears after swelling in the fatty acid, without any change in the initial activity.

(iii) The elimination of water during the reaction by using a molecular sieve shifts the reaction equilibrium towards the formation of monoglycerides with an increase of the conversion (conversion: 90%, selectivity to monoglycerides: 85%).

(iv) The decrease of the hydrocarbon chain length of the fatty acid increases the reaction rate because of the greater accessibility to the active sites in the pores. The esterification rate of the lauric acid is greater than the one of oleic acid.

(v) An excess of glycerol, as can be expected, favours the formation of monoglyceride, lowers the degree of acid conversion.

Lastly, all the results indicate that, over catalysts like resins, the esterification of glycerol with fatty acids varies with the nature of their catalysts with various parameters in agreement with what was expected. But owing to the specific solvation properties of resins in the presence of polyols or/and water, the right procedure must be found in order to obtain the right catalytic properties.

Acknowledgements

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