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Reaction kinetics of the esterification of myristic acid with isopropanol and *n*-propanol using *p*-toluene sulphonic acid as catalyst

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ABSTRACT

The reaction kinetics of the esterification of myristic acid with isopropanol with *n*-propanol were determined, using *p*-toluene sulphonic acid (*p*TSA) as catalyst, for a temperature range of 343–403 K. The reactions follow first order kinetics in all components. The kinetic model corresponds with the results for the esterification of myristic acid with isopropanol reported in literature for 333–353 K. As expected, the reaction rate increases with increasing amount of catalyst and with increasing temperature. The reaction rate and equilibrium conversion increases with an increasing alcohol to myristic acid feed ratio. The reaction with *n*-propanol is considerably faster (at 373 K about 3.8 times) than the reaction with isopropanol.

1. Introduction

Fatty acid esters are (natural-based) chemicals used in a broad range of different fields of application, such as the cosmetic industry, the food industry, solvents and plasticisers, the coating industry, lubricants, biodiesel et cetera [1,2]. The fatty acid esters include methyl esters, partial glycerides, wax esters (esters of fatty acids with long-chain fatty alcohols), and ester oils (esters of fatty acids with poly alcohols). The main part of this research focuses on isopropyl myristate, which is used in cosmetics as the oil component and is one of the most common used fatty acid esters [1–3]. Because the reaction with isopropanol is very slow due to steric hindrance, also the esterification with *n*-propanol is studied for comparison.

Nowadays the fatty acid esters are produced in batch reactors using strong acids like sulphuric acid [4,5]. Their production processes involve costly separations, large energy consumption and the production of polluting by-products. Because of equilibrium limitations, high conversions can be only obtained by using a large excess of alcohol. To accelerate the reaction rate, a catalyst is used.

For a more competitive process it is preferable to produce fatty acid esters in a continuous way, at higher yields, in multi-product equipment, preferably using a heterogeneous catalyst. Reactive distillation is considered a promising technique because the integration of reaction and separation in one unit means significant savings in equipment and operating costs [6,7]. In order to model reactive distillation for the esterification of myristic acid with isopropanol, the reaction kinetics should be known.

To our knowledge, one kinetic study has been reported in the literature for the esterification of myristic acid with isopropanol using *p*TSA, H_2SO_4, Amberlyst 15 and a Degussa silica based catalyst [8]. In this study, the kinetics were measured at 60–80 °C, but for reactive distillation higher temperatures are needed to obtain sufficiently high conversions. Therefore, we study the reaction at a more appropriate range of 70–130 °C. Also a number of studies discussed the esterification reactions of other fatty acids using homogenous and heterogeneous catalysts [9–17]. An overview is given in Table 1.

In other research [18,19], which was part of the same project, different heterogeneous catalysts, like ion exchange resins, zeolites and sulphated metal oxide (zirconia, titania an tin oxide) were compared, based on their activity and selectivity. Sulphated zirconia showed high activity and selectivity for the esterification of lauric acid with a variety of primary alcohols ranging from 2-ethylhexanol to methanol [18,19], but appeared not successful for the esterification of myristic acid with isopropanol. This is illustrated in Fig. 1, where it can be seen that Sulphated Zirconia, Nafion SAC13 and Amberlyst 15 do not increase the rate compared to the uncatalysed reaction at the chosen conditions.

Yalçinyuva et al. [8] investigated the same reaction with Amberlyst 15 and a silica-based Degussa catalyst, which were reported to be successful in the esterification of carboxylic acids with short alkyl chains [20,21]. However, in the esterification of

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E_a	activation energy (J mol^{-1})
k	rate constant (L mol^{-1} s^{-1})
K_{eq}	equilibrium constant
r_E	reaction rate (mol L^{-1} s^{-1})
R	gas constant (J mol^{-1} K^{-1})
T	temperature (K)
[A]	fatty acid concentration (mol L^{-1})
[B]	alcohol concentration (mol L^{-1})
[E]	ester concentration (mol L^{-1})
[W]	water concentration (mol L^{-1})
[cat]	catalyst concentration (M)

myristic acid with isopropanol very low conversions (5–10% after 5 h) were found. They explained this phenomenon by the diffusion problem of myristic acid into the pores of the catalyst. In Fig. 1 it can be seen that comparable results are found in this research.

From the above results it can be concluded that none of the investigated heterogeneous catalysts is suitable for the esterification of myristic acid and isopropanol at the desired conditions. Therefore the focus will be on a homogeneous catalyst: *p*-toluene sulphonic acid.

The aim of the present research is to extend the previous work of Yalçinyuva et al. [8] to the higher reaction temperatures related to reactive distillation, using *p*TSA as catalyst for a temperature range of 343–403 K, and compare this with the reaction with *n*-propanol. McCracken and Dickson [22] found that with a homogeneous catalyst the esterification of acetic acid with cyclohexanol is second order in acid and first order in alcohol.

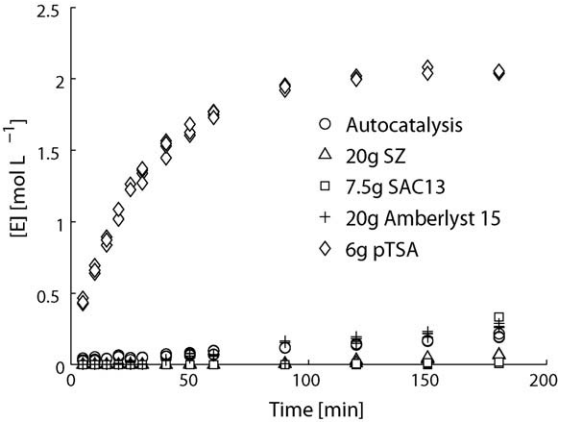

Fig. 1. Comparison of the reaction rate of the esterification of myristic acid with isopropanol for (a) autocatalysis and 10 g of Sulphated Zirconia catalyst at 130 °C and a equimolar ratio of isopropanol to myristic acid and for (b) autocatalysis, Sulphated Zirconia, Nafion SAC13, Amberlyst 15 and *p*TSA at 100 °C and a equimolar ratio of isopropanol to myristic acid.

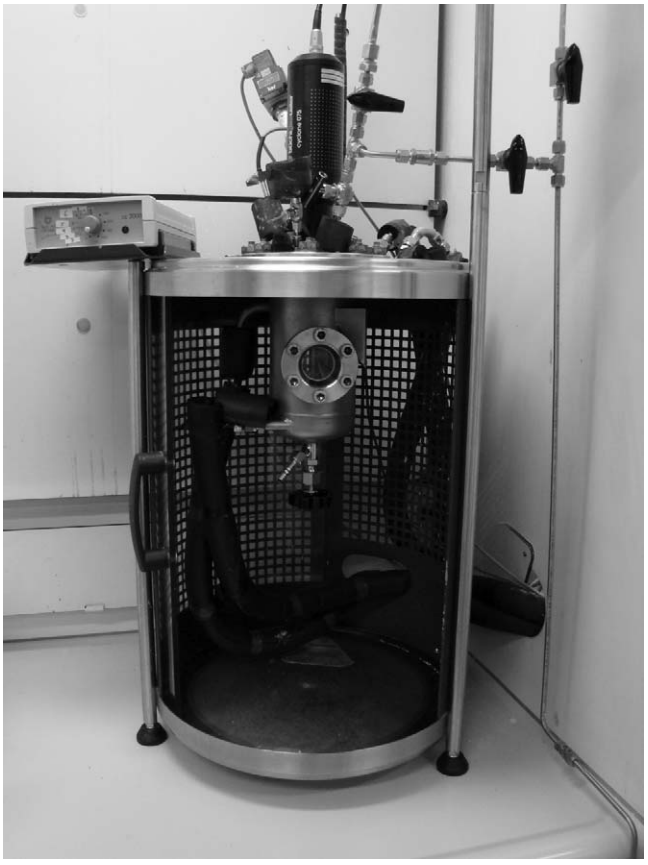

Fig. 2. Experimental setup for measuring the reaction kinetics.

Vieville et al. [15] reported that the esterification of oleic acid with methanol is only first order in acid. However, the majority of the researchers report that an esterification reaction follows second order reversible kinetics (first order in all components). For example, Dhanuka et al. [23] showed that the esterification could be expressed by second order (first order in both reactants) reversible kinetics. The same approach was used by other researchers for fatty acid esterification reactions [8–12,24]. Therefore the experimental kinetic data were analysed on the basis of a homogeneous model. The reaction parameters for both reactions were obtained and compared.

2. Experimental

2.1. Apparatus

The experiments are conducted in an autoclave from Büchi Glas Uster (ecoclave075) purchased at Autoclave. A picture of the set-up can be found in Fig. 2. The autoclave has a thermostated steel vessel

Table 1
Esterification of fatty acids with various catalysts.

Reaction	Catalyst	Reference
Decanoic acid + methanol	Amberlyst 15	Steinigeweg and Gmehling [13]
Myristic acid + isopropanol	*p*TSA, H_2SO_4, Amberlyst 15, Degussa	Yalçinyuva et al. [8]
Myristic acid + isobutanol	H_2SO_4	El-Kinawy et al. [12]
Palmitic acid + isopropanol	*p*TSA, zinc ethanoate	Aafaqi et al. [9]
Palmitic + isobutanol	H_2SO_4	Goto et al. [11]
Stearic acid + isobutanol	H_2SO_4	El-Kinawy et al. [12]
Oleic acid + methanol	*p*TSA, H_2SO_4, K2411, K1481	Unnithan and Tiwari [10], Othmer and Rao [14], Vieville et al. [15]
Oleic acid + 2-ethylhexanol	*p*TSA	Lacaze-Dufaure and Mouloungui [16]
Oleic acid + glycerol	K1481, Amberlyst 16, Amberlyst 31	Pouilloux et al. [17]