

Anhydrous Esterification of Myristic Acid with Propylene: Ion Exchange Resin and Acid-Treated Clay as Catalysts

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Anhydrous esterification of myristic acid with propylene was carried out in the temperature range of 110–145°C and pressure from 190–195 psig in the presence of Amberlyst-15 (cation exchange resin) and Filtrol-24 (acid-treated clay) as catalysts. The product ester, isopropyl myristate finds use in cosmetic and topical medicinal preparations where good absorption through the skin is desired. Filtrol-24 is the catalyst of choice, and the recommended operating temperature is 130°C with a pressure of 190 psig.

KEY WORDS: Acid-treated clay, cation exchange resin, isopropyl myristate, myristic acid, propylene.

The esters of fatty acids are generally manufactured by refluxing the fatty acid with the desired alcohol in the presence of some homogeneous catalyst, such as H₂SO₄. Esterification with secondary alcohols may be accomplished advantageously by using the corresponding olefin in the presence of a solid acid catalyst, such as cationic ion exchange resins or acid-treated clay. With olefins like propylene or butenes, almost complete conversion of the acid may be realized, which makes the separation of the pure ester much easier than with the conventional processes.

In this work, anhydrous esterification of myristic acid with propylene was carried out in the presence of a cation-exchange resin or an acid-treated clay as catalyst. These catalysts can be used repeatedly without further processing and without affecting the activity and selectivity.

No literature seems to be available on the anhydrous esterification of fatty acid with olefin in the presence of ion exchange resin or acid-treated clay as catalyst. However, some related literature is available (1–4).

MATERIALS AND METHODS

Myristic acid was obtained from a firm of repute (Godrej Soaps Ltd., Bombay, India) and it was more than 95% pure. Propylene was obtained from BOC Ltd. (London, U.K.). *n*-Heptane and methanol were reagent grade and were obtained from S.d. Fine-Chem Ltd. (Boisar, India). Amberlyst-15 was obtained from Rohm and Haas (Philadelphia, PA). Filtrol-24 was obtained from Filtrol (Los Angeles, CA). The physical properties of Amberlyst-15 and Filtrol-24 are given in Table 1.

Experiments were carried out in a 1-L stainless steel autoclave equipped with heating jacket, thermowell, internal cooling coil, sampling valve, pressure gauge and a vent. Solution of myristic acid in *n*-heptane (25% w/w) and catalyst were first charged into the autoclave. After tightening the autoclave, heating was started while stirring. When the temperature reached the desired reaction temperature, propylene gas was charged into the autoclave. A constant pressure was maintained during the reaction by adjusting the gas valve. The time of introduction of the gas was considered as the starting time of the

TABLE 1

Physical Properties of the Catalysts

Property	Amberlyst-15	Filtrol-24
Shape	Beads	Granular
Internal surface area, m ² /g	55	358
Weight capacity	4.75 meq/g	8.4 mg KOH per gm of catalyst at phenolphthalein end point
Temperature stability, °C	120	Data not available

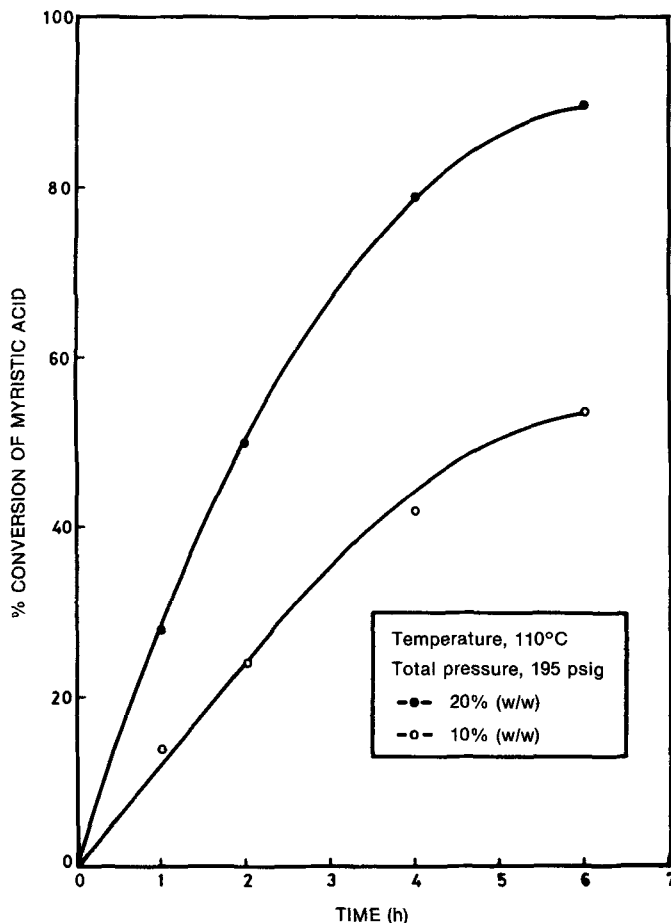


FIG. 1. Effect of catalyst loading on the rate of reaction of myristic acid in the presence of Amberlyst-15 as catalyst.

reaction. The temperature was maintained at the desired temperature ($\pm 2^\circ\text{C}$) by adjusting the heating rate and the flow rate of the cooling water.

For analytical purposes, 1 mL of the sample was pipetted out from the sample-collecting bottle, and 50 mL of methanol was added to it to ensure that no acid precipitated from the sample. It was then titrated against

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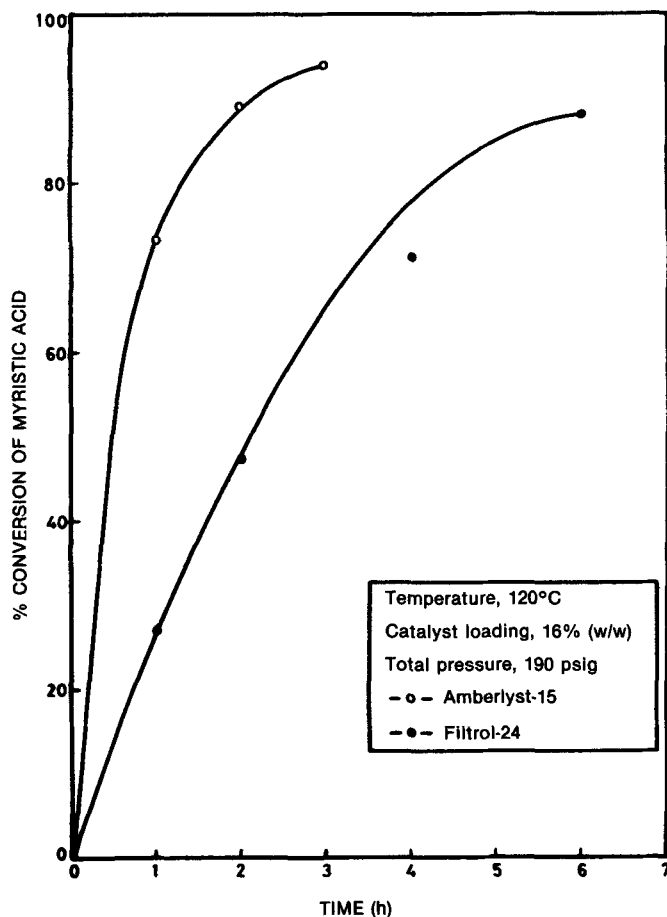


FIG. 2. Effect of different catalysts on the rate of reaction of myristic acid.

standard caustic soda solution. A typical sample of the reaction mixture was neutralized with aqueous caustic soda solution and was extracted with excess *n*-heptane. The solvent was then distilled from the organic layer, and the remaining material was used for confirmation of the product by gas chromatography and Fourier-transform infrared spectrophotometry (Bruker IFS 88, Bruker, Karlsruhe, Germany).

RESULTS AND DISCUSSION

The reaction was carried out in the temperature range of 110–145°C in the presence of Amberlyst-15 or Filtrol-24 as catalyst. The mole ratio of propylene to myristic acid was varied from 2.3:1 to 1:1 by varying the temperature of the reaction and partial pressure of propylene. The solubility of propylene at any particular temperature at one atmospheric partial pressure of propylene was determined by extrapolating the solubility (expressed as mole fraction of propylene) data of propylene in *n*-octane as reported in the literature (5) (solubility of propylene in *n*-heptane was assumed to be the same as that in *n*-octane). The solubility of propylene in the liquid phase at higher pressures was calculated by applying Henry's law. The solubilities of propylene in hydrocarbons like *n*-heptane, *n*-octane, etc., are expected to follow thermodynamic rules. The rate of reaction was directly proportional to the

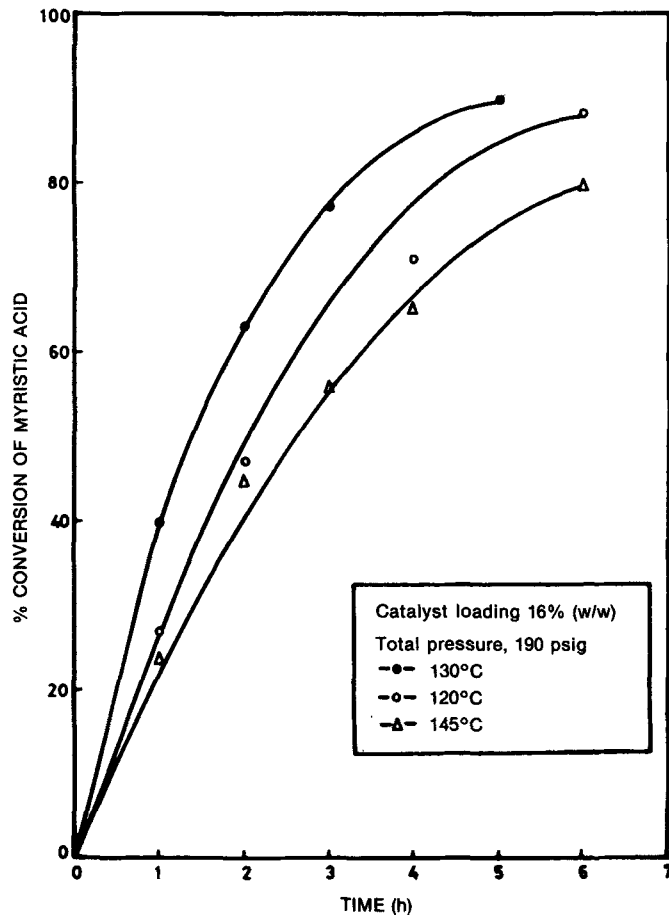


FIG. 3. Effect of temperature on the rate of reaction of myristic acid in the presence of Filtrol-24 as catalyst.

catalyst loading in the range employed (Fig. 1). With an increase in catalyst loading, as in the case of Amberlyst-15, the number of SO_3H groups increases, resulting in the formation of more carbonium ions (corresponding to the olefin) per unit time, which leads to an increase in the reaction rate. Amberlyst-15 was the best catalyst amongst those tried as far as activity was concerned (Fig. 2). The comparison was based on the same weight of the catalyst. Both catalysts were reusable at least three times without any observed drop in activity. Ion exchange resins are used as catalysts for esterification reactions in continuous processes (6). Figure 3 shows the effect of temperature on the rate of reaction of myristic acid. It is clear from Figure 3 that the best operating temperature (with Filtrol-24 as catalyst) is 130°C. At 145°C, although the rate constant for the reaction is highest, the overall reaction rate is slowest, due to the lower solubility of propylene at that temperature. The rate constant is found from the overall rate by dividing it by the concentration of propylene. The values of rate constant at 145, 130 and 120°C are $5.59 \times 10^{-5} \text{ s}^{-1}$, $4.98 \times 10^{-5} \text{ s}^{-1}$ and $2.99 \times 10^{-5} \text{ s}^{-1}$, respectively. No side reaction was observed in the temperature range employed.

This route of making isopropyl myristate has an additional advantage as far as the purification of the ester is concerned. The reaction was continued until complete conversion of myristic acid was realized. The reaction mix-

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ture was then filtered to remove the solid catalyst and was cooled to room temperature. Nitrogen was then passed through the mixture to free it from dissolved propylene (in practice, low-pressure stripping can be done). The remaining material was then distilled to separate *n*-heptane and pure ester. In practice, the reaction can be carried out without solvent because the isopropyl myristate formed will act as a solvent in which the solubility of propylene will be sufficiently high to drive the reaction forward toward the end.

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