



## Short Communication

# Butyric acid esterification kinetics over Amberlyst solid acid catalysts: The effect of alcohol carbon chain length



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## HIGHLIGHTS

- Rates of butyric acid esterification are characterized for linear alcohols.
- Alcohol steric effect, polarity, and hydroxyl concentration affect esterification rate.
- Kinetic model presented for butyric acid esterification with 2-ethylhexanol.
- Biodiesel cloud point substantially reduced by addition of butyrate esters.

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## ABSTRACT

The liquid phase esterification of butyric acid with a series of linear and branched alcohols is examined. Four strong cation exchange resins, Amberlyst™ 15, Amberlyst™ 36, Amberlyst™ BD 20, and Amberlyst™ 70, were used along with para-toluenesulfonic acid as a homogeneous catalyst. The effect of increasing alcohol carbon chain length and branching on esterification rate at 60 °C is presented. For all catalysts, the decrease in turnover frequency (TOF) with increasing carbon chain length of the alcohol is described in terms of steric hindrance, alcohol polarity, and hydroxyl group concentration. The kinetics of butyric acid esterification with 2-ethylhexanol using Amberlyst™ 70 catalyst is described with an activity-based, pseudo-homogeneous kinetic model that includes autocatalysis by butyric acid.

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## 1. Introduction

Esterification of carboxylic acids is a widely studied and industrially important reaction. Carboxylic acid esters can be used as plasticizers, solvents, in specialty applications, and as biofuel components (Mbaraka and Shanks, 2005). The traditional route for preparing esters is via reaction of the carboxylic acid with an alcohol using homogeneous catalysts such as sulfuric acid (Grob and Hasse, 2006) or para-toluenesulfonic acid (de Jong et al., 2009). Use of esters as biorenewable chemicals and as “green” solvents has encouraged the study of esterification reactions using acidic heterogeneous catalysts such as ion exchange resins (Engin et al., 2003; Kolah et al., 2006, 2008), Nafion/silica nanocomposite SAC-13 (Liu et al., 2006a,b), or modified zirconia (López et al., 2008).

There is growing interest in producing butyric acid (butanoic acid, herein BA) by fermentation from biorenewable resources (Zhang et al., 2009). Using BA as a platform molecule, n-butanol can be synthesized by hydrogenolysis (Gaertner et al., 2009); 2-ethylhexanol (herein 2-EHA) can be produced by condensation of n-butanol or butyraldehyde (Kim et al., 2011), and the secondary alcohol 4-heptanol can be made via ketonization of BA followed by hydrogenation (Gaertner et al., 2009; Kim et al., 2011; Murkute et al., 2011). Esters of BA made with these alcohols have potential as biofuel constituents.

The effect of alcohol chain length and branching on esterification rate of several carboxylic acids has been reported by Erdem and Cebe (2011), who examined esterification of propanoic acid with different alcohols in dioxane. They observed that esterification rate rapidly decreased as alcohol chain length and degree of branching increased, because of steric hindrance, and described the steric hindrance in terms of the Taft equation (Newman, 1956).

Ju et al. (2011) reported esterification kinetics of BA with n-butanol, but little information exists for the behavior of BA in

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