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Ultrasound assisted synthesis of methyl butyrate using heterogeneous catalyst

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ABSTRACT

Ultrasound assisted esterification of butyric acid with methanol was investigated in an ultrasound irradiated isothermal batch reactor using acid ion-exchange resin (amberlyst-15) as a catalyst. Effect of parameters such as temperature (323–353 K), catalyst loading (0–8.5% w/w), alcohol to acid ratio, *M* (2–6), ultrasound power (0–145 W), duty cycle (0–85%) and amount of molecular sieves added (0–11% w/w) on the rate of reaction was studied. At optimized parameters, a maximum conversion of 91.64% was obtained in 120 min in presence of ultrasound. Experimental kinetic data were correlated by using Eley–Rideal (ER) and Langmuir–Hinshelwood–Hougen–Watson (LHHW) models taking into account reverse reaction. Studies showed that single site LHHW with reactants and products both adsorbing on catalyst surface was most suited for the obtained experimental data. Activation energy determined based on heterogeneous kinetics was in the range 49.31–57.54 kJ/mol while it was 18.29 kJ/mol using homogeneous model.

1. Introduction

Organic esters are used widely in the manufacturing of flavors, adhesives, pharmaceuticals, pesticide, plasticizers, polymerization monomers, and emulsifiers in the food and cosmetic industries. Derivatives of many esters form variety of useful chemical intermediates and monomers for high molecular weight polymers and resins. In general, esters can be defined as the products of reaction between carboxylic acids and organic alcohols. Chemically, an ester is formed as the condensation product when a carboxylic acid is reacted with an alcohol [1]. Esterification of carboxylic acids with alcohols represents a well-known class of liquid-phase reactions of considerable industrial interest owing to its wide industrial uses [2,3]. Methyl butyrate or methyl ester of butyric acid is an ester with a fruity odor of apple, pineapple, and strawberry. Present in trace amounts in several plant products, especially pineapple flavor is produced by distillation of oils from vegetable origin. This ester is also manufactured on a small scale for use in perfumeries or flavoring food [4,5].

Organic esters can be synthesized by several routes, most of which have been briefly reviewed by Yadav and Mehta [5]. The traditional route for preparing esters is by the reaction of the carboxylic acid with an alcohol using homogeneous catalysts such as sulfuric acid or para-toluene-sulfonic acid [6,7]. Although, homogeneous catalysts provide faster reaction rates, separation and recovery of the catalyst from the reaction mixture is major issue [6,8]. In addition, the homogeneous acid catalysts are responsible for equipment corrosion, side reactions and additional neutralization cost of treatment of salt produced [9,10,13]. These limitations of homogeneous catalysts can be circumvented by the use of heterogeneous catalysts such as sulfonic acid based ion-exchange resins. The solid type of material has good physical and chemical properties with enhanced catalytic activity in esterification [3,7,11]. Solid catalyst can be mechanically separated from the reaction mixture and subjected to possible reuse [12]. Heterogeneous route offers promising option owing to its advantages as compared with the methods using homogeneous catalyst. Significant work is reported in the literature using variety of solid acid catalysts [7,11,14,15].

Despite advantages of heterogeneous method for the synthesis of organic esters, the reaction time is a concern which can be substantially reduced by using newer techniques. Use of ultrasound waves and microwaves in ester synthesis is still an evolving area and detailed studies are needed to shed some light on their applicability in heterogeneous catalysis. Therefore, an alternative esterification method is required to reduce processing time, to lower amount of catalyst and un-reacted raw materials and also to increase the mass transfer. The use of cavitation resulting from ultrasound waves appears to be an appealing option for heterogeneous synthesis of ester.

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Nomenclature

A	butyric acid
B	methanol
C_{A0}	initial concentration of butyric acid (mol/m^3)
C_A, C_B, C_E and C_W	concentration of butyric acid, methanol, methyl butyrate and water respectively at any time, t (mol/m^3)
C_p	specific heat of methanol at constant pressure (J/kg K)
E	methyl butyrate
E_a	activation energy(kJ mol^{-1})
E_d	sound waves dissipated energy (J/s)
E_i	input electrical energy, E_i = VI (J/s)
i	variable index indicative of species participating in the reaction (dimensionless)
I	electrical acoustic intensity (W/cm^2)
k_f	forward rate constant (l mol^{-1} min^{-1})
k_r	reverse rate constant (l mol^{-1} min^{-1})
k_s	surface reaction rate constant (l^2/mol gcat min)
K_A, K_B, K_E and K_W	adsorption equilibrium constant for butyric acid, methanol, methyl butyrate and water respectively (l/mol gcat s)
K_e	equilibrium rate constant
K_S	surface equilibrium rate constant
m	mass of methanol (kg)
M	methanol to butyric acid ratio (C_{B0}/C_{A0})
n	number of species involved in esterification (dimensioness)
p	index in Eq. (5) (dimensionless)
$(-r_A)$	reaction rate obtained based on butyric acid consumed (mol l^{-1} min^{-1})
(r_{exp})	experimental reaction rate (mol l^{-1} g^{-1} min^{-1})
(r_{pred})	reaction rate predicted by heterogeneous models (mol l^{-1} g^{-1} min^{-1})
R	universal gas constant (8.314 kJ/mol K)
T	temperature (K)
W	water
x_A	conversion of butyric acid $[(C_{A0} - C_A)/C_{A0}]$
x_{AE}	equilibrium conversion of butyric acid at equilibrium

Ultrasound (frequency ~20 kHz to l0 MHz) is cyclic sound pressure with a frequency greater than the upper limit of human hearing [16]. The main principle behind the application of ultrasonic waves to the reaction is a phenomenon known as cavitation. The ultrasonic waves technique has two cycles i.e. compression and rarefaction. During rarefaction a vacuum pressure creates a cavitation bubble and when the compression cycle occurs the bubble implodes in a very short period of time, producing localized heating, high pressures and liquid jet sprays with high velocities [17]. The ultrasound assisted techniques are playing an important role in chemical processes, especially in cases where conventional methods require extended reaction times. Applying Ultrasound to the chemical reaction process enhances mixing, shearing, transfer of materials and the rate of chemical reactions effectively reducing the reaction time [18–20]. Use of ultrasound irradiation is a promising and untapped technology for chemical reactions, though it was in use for last few decades. It can improve the reaction conditions, accelerate the rate of reaction and produce a higher yield [21,22]. Recently, synthesis of methyl butyrate was carried out using conventional heterogeneous route with amberlyst-15 as a catalyst [11]. The equilibrium conversion reported was greater than 90% using amberlyst-15 catalyst under optimal reaction conditions. However, the time required to achieve this equilibrium conversion was longer (about 4 h) which needed to be reduced further.

The objectives of this study were to test the suitability and efficacy of heterogeneous catalyst in presence of ultra sound irradiation for the synthesis of methyl butyrate and determine suitable kinetic model. Effects of time, temperature, catalyst loading, alcohol to acid ratio, addition of molecular sieves, ultra-sound power and duty cycle on esterification reaction were also undertaken.

2. Materials and methods

2.1. Materials

Butyric acid and methanol of 99.98% purity (w/w) were supplied by Merck. Both these chemicals were used as supplied. The acidic ion exchange resin (Amberlyst-15) was supplied by Alfa Aesar, USA. A cation exchange resin catalyst is insoluble polymer matrix which can exchange ions with the adjacent reacting mixture. It is a macro-porous type styrene DVB (20%) resin. The resin is formed by the copolymerization reaction between styrene and divinyl-benzene which acts as cross-linking agent. For cation exchange resins, acid sites are deposited on the polymer matrix by the treatment of strong acids such as sulfuric acid which gives sulphonated cation exchange resins.

2.2. Batch experiments

Esterification reactions were performed in a 100 mL batch reactor made of borosilicate glass. The three necked reactor was equipped with sample port, provision for ultrasound probe and condenser to recycle back liquid after vapors condensed during reaction runs. Water bath fitted with automatic temperature control was used to ensure constant reaction temperature. Sound waves (by ultrasonic horn) generated at 22 kHz were used to ensure adequate mixing of reaction contents. Ultrasonic horn was supplied by Dakshin Ultrasonics, Mumbai, India with maximum power rating of 120 W, input supply voltage 230 V (50 Hz AC). Vertically mounted probe tip was made up of SS 304 with 11 mm diameter and 10 cm height.

In a typical experiment, a measured quantity of methanol and catalyst (amberlyst-15) were charged into the reactor with no initial water present in the reaction mixture. The reactor was sealed and heating was started with condenser water on. To optimize parameters, ultrasound generator was used on varying power inputs and duty cycles. The type of reactor and ultrasonic probe distance from the surface of reaction mixture was used based on earlier reported work so as to ensure maximum cavitation (bubble generation) [23]. Thus, ultrasound probe was adjusted in such a way that the tip length of 0.5 cm dipped into the reaction mixture from the top liquid surface [23]. Once the desired temperature was reached, the required amount of butyric acid was injected into the reactor via syringe and sonication was initiated – the instant was marked as zero reaction time. Small amount of samples (0.2 mL) were withdrawn at specified time intervals over the first 2.5 h of reaction. Reaction mixture was filtered in the end to separate the sample solution from the used solid catalyst. All experiments were performed three times and average values have been reported with standard deviations.

2.3. Electrical acoustic intensity and dissipation rate of sound energy

Electrical acoustic intensity (I) can be defined as the ratio of electrical energy supplied to the cross sectional area of probe tip.