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Research paper

Equilibrium and thermodynamic parameters for heterogeneous esterification of butyric acid with methanol under microwave irradiation

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Abstract

Synthesis of methyl butyrate was investigated in a microwave irradiated batch reactor in presence of acid ion-exchange resin catalyst, amberlyst-15. Methyl ester was heterogeneously produced by the reaction between butyric acid and methanol. Effect of reaction parameters of temperature (323–343 K), catalyst loading (0–10.5% w/w), alcohol to acid ratio, M (1–5), and amount of molecular sieves added (0–13.5% w/w) on conversion were studied. Equilibrium conversion of 92.6% was achieved in 60 minutes under microwave irradiation. Equilibrium constants at varied temperatures and dependency of equilibrium constant on temperature were studied. Equilibrium constant and equilibrium conversion showed increase with the increase in temperature as expected as per le-Chatelier principle. Van't Hoff plot for esterification of butyric acid was linear with negative slope indicating that reaction was endothermic. Comparative study showed that microwave irradiated method for methyl butyrate synthesis to be very efficient and fast compared with conventional and ultrasound assisted routes under optimized reaction conditions.

Keywords: Microwave; Esterification; Butyric acid; Methanol; Amberlyst-15; Equilibrium constant

1. Introduction

Esterification is a reversible reaction between carboxylic acid and organic alcohol producing ester and water. The desired product, ester, is a useful product which has applications in chemical industry as solvents, emulsifiers, plasticizers, medicinal agents, flavors, fragrances, and polymerization monomers [1–3]. Methyl butyrate, the methyl ester of butyric acid has a fruity odor largely resembling apples or pineapples. It is produced by distillation of essential oils of vegetable origin, but is also synthesized for the use in perfumes and as a flavoring agent in food industry [4]. Methyl butyrate is produced by the liquid-phase reaction of butyric acid and methanol catalyzed by sulfuric acid or sulfonic acid ion-exchange resins. Use of sulfuric acid generally shows weak catalytic activity, requires high reaction temperatures and long reaction time. In addition, homogeneous catalyst is corrosive, difficult to separate from reaction mixture and requires special energy-inefficient processes for the treatment of the waste acid [5]. The ion-exchange resin is a promising substitute material for homogeneous acid catalysts owing to its advantages. The solid material has desirable physical and chemical properties, and exhibits excellent performance as a heterogeneous catalyst in ester synthesis reaction [6–8]. Despite advantages of heterogeneous method for the synthesis of organic esters, the reaction time and alcohol to acid mole ratio is a concern which can be substantially reduced by using novel techniques such as ultrasound and microwave irradiation. Ultrasound assisted esterification has been studied by several researchers [9–12]. The use of ultrasound waves demonstrated that the reactions are fast and take considerably less time in comparison with conventional heterogeneous route. The studies show that ultrasound irradiated esterification demands excess of alcohol to prevent hydrolysis of ester produced and there is scope for further reduction of reaction time [13]. Therefore, investigations for alternative synthesis method for the esterification are required to ascertain reduced processing time, lower alcohol to acid ratio and enhanced mass transfer rates. The use of microwaves for assisting esterification is still an evolving area and detailed studies are needed to find out its applicability in heterogeneous catalysis.

Studies on microwave-irradiated reactions begun in the year 1986, when pioneering investigations were reported [14]. Microwaves are electromagnetic waves having frequency range

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Nomenclature

A	butyric acid
B	methanol
C	methyl butyrate
C_{A0}	initial concentration of butyric acid [mol.lit^{-1}]
C_A, C_B, C_C and C_D	concentration of butyric acid, methanol, methyl butyrate and water respectively at any time, t [mol.lit^{-1}]
D	water
f	frequency [Hz]
ΔG	change in Gibbs free energy of reaction [kJ.mol^{-1}]
ΔH	change in enthalpy of reaction [kJ.mol^{-1}]
k_f	forward rate constant [lit.mol^{-1}.min^{-1}]
k_r	reverse rate constant [lit.mol^{-1}.min^{-1}]
K_{eq}	equilibrium rate constant (dimensionless)
M	methanol to butyric acid ratio [C_{B0}/C_{A0}] (dimensionless)
P_D	dissipated power [W.m^{-3}]
$(-r_A)$	reaction rate obtained based on butyric acid consumed [mol.lit^{-1}.min^{-1}]
R	universal gas constant [8.314 kJ.kmol^{-1}.K^{-1}]
ΔS	entropy change in reaction [kJ.mol^{-1}.K^{-1}]
T	temperature [K]
V	electrical field strength in [volt.m^{-1}]
x_A	conversion of butyric acid [(C_{A0}-C_A)/C_{A0}] (dimensionless)
δ	loss angle (radians)
Є’	relative dielectric constant (dimensionless)
Є”	relative dielectric loss (dimensionless)

of 0.3 to 300 GHz, corresponding to wavelengths of ~1 m to 1 cm, respectively. This region of the electromagnetic spectrum lies between the far infrared and radio frequencies. A frequency of 2.45 GHz is generally used, from among several frequency bands that are present in market for domestic and scientific applications [15]. Basic principle of microwave reactors is based on conversion of electromagnetic (EM) energy into heat efficiently, so that extremely fast heating rates are achieved in a reproducible way. Microwave irradiation results in an instantaneous localized superheating owing to induced dipole rotation. The energy transfer takes place within 10^{-9} s with each cycle of electromagnetic energy resulting in non-equilibrium state and instantaneous high temperatures. An increase in temperature causes greater movement of molecules leading to increased number of energetic collisions [16]. Initial studies of several reactions revealed an enhancement of reaction rates in presence of microwave irradiation, as compared to identical reactions heated by conventional methods. Microwave activation of a large number of organic synthesis and metal catalyzed reactions has been reported amply in the past investigations [17–19]. The effects usually were rate enhancements, abnormal increase in boiling temperature of organic solvents, modified reaction path in organic synthesis, yield or selectivity improvements, and less polluting processes [20–22].

The objectives of this experimental study were to test intensification of the process and efficacy of heterogeneous catalyst in presence of microwave irradiation for the synthesis of methyl butyrate. Effects of temperature, catalyst loading, alcohol to acid ratio and amount of molecular sieves added for the ester synthesis were also undertaken.

2. Experimental

2.1. Materials

Methyl alcohol and butyric acid 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 imported from by Alfa Aesar, USA. Amberlyst-15 is a micro porous polystyrene based ion exchange styrene-DVB (20%) resin with attached sulfonic groups on its polymer matrix. Sulfonated cation exchange resins are formed by the treatment of strong acids like sulfuric acid and subsequent deposition of acid sites on the polymer matrix. A resin catalyst is insoluble polymer matrix which exchanges ions with the adjacent reacting mixture. The resin catalysts are excellent source of strong acids that can exchange ions with the surrounding reaction mixture. This solid catalyst can be separated after completion of reaction and can also be reused several times.

2.2. Batch experiments

Esterification reactions were performed in a Multiwave PRO microwave reactor having dimensions of height, width, diameter as 760, 600, and 720 mm respectively. The reactor was equipped with a rotor mechanism to hold 16 reaction vessels (vials) of 100 mL capacity each and could be operated in batch mode. Reaction vessels were made up of a PTFE-TFM liner, supported by a ceramic vessel jacket and closed with a self-sealing lip-type seal. Microwave reactor was supplied by Anton Paar GmbH, Graz, Austria. Two standard magnetrons of 850 W delivered up to 1500 W microwave power in an un-pulsed mode over the full power range. Its integrated software prevented thermal overshoots and the design of microwave applicator provided maximum field density with enhanced degree of homogeneity, which paved the way for efficient heating. The sensor mechanism ensured actual temperature of the reaction mixture during the course of reaction.

In a typical experiment, measured quantity of methanol, catalyst (amberlyst-15) and molecular sieves were charged into