Bioresource Technology 102 (2011) 10094–10103

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Potential biofuel additive from renewable sources – Kinetic study of formation of butyl acetate by heterogeneously catalyzed transesterification of ethyl acetate with butanol

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ARTICLE INFO

Article history:
Received 16 May 2011
Received in revised form 4 August 2011
Accepted 6 August 2011
Available online 16 August 2011

Keywords:
Amberlyst 15
Amberlite IR 120
Butyl acetate
Kinetics
Transesterification

ABSTRACT

Butyl acetate holds great potential as a sustainable biofuel additive. Heterogeneously catalyzed transesterification of biobutanol and bioethylacetate can produce butyl acetate. This route is eco-friendly and offers several advantages over the commonly used Fischer Esterification. The Amberlite IR 120- and Amberlyst 15-catalyzed transesterification is studied in a batch reactor over a range of catalyst loading (6–12 wt.%), alcohol to ester feed ratio (1:3 to 3:1), and temperature (303.15–333.15 K). A butanol mole fraction of 0.2 in the feed is found to be optimum. Amberlite IR 120 promotes faster kinetics under these conditions. The transesterifications studied are slightly exothermic. The moles of solvent sorbed per gram of catalyst decreases (ethanol > butanol > ethyl acetate > butyl acetate) with decrease in solubility parameter. The dual site models, the Langmuir Hinshelwood and Popken models, are the most successful in correlating the kinetics over Amberlite IR 120 and Amberlyst 15, respectively.

1. Introduction

Butyl acetate holds good potential for enhancing biodiesel properties. This ester has a very low freezing point (200.15 K) and adding it to biodiesels, is expected to result in considerable improvement of cold flow properties without causing a significant decrease in the mixture's heat of combustion and cetane number values. Furthermore, its high flash point (295 K) makes it safer to use than ethyl acetate (flash point, 269 K) the other ester commonly used as a biodiesel additive (Burgazli et al., 2009; Ruiz, 2009).

The production of butanol (Swana et al., 2011), ethanol (Sáncheza and Cardonaa, 2008), and ethyl acetate (Christen et al., 1999) from renewable sources has been extensively studied. Recent advances in biotechnology and bioprocessing have made the production of fermentation derived- butanol (www.butanol.com) and -ethyl acetate (www.davyprotech.com) economically viable. The tranesterification of biobutanol with bioethylacetate is therefore a sustainable option for butyl acetate production. The co-product formed, ethanol, can undergo Davy dehydrogenation once again to form ethyl acetate, and get recycled back for transesterification. This route is eco-friendlier and avoids the disadvantages of the widely used Fischer and Speier (1895) esterification, as it does not require special grade (acetic acid resistant) stainless steel equipments and is devoid of serious contamination (associated with the use of homogeneous catalysts) and waste water (formed as product) disposal problems. Transesterification reactions are slow and can be catalyzed by heterogeneous ion exchange resins (Bozek-Winkler and Gmehling, 2006; Xu et al., 2009; Pappu et al., 2011). The heterogeneously catalyzed transesterification of biobutanol with bio ethyl acetate thus appears to be viable green option for the manufacture of bio-butyl acetate. Knowledge of the involved kinetics is necessary for the optimal design of such a process. Though several kinetic studies involving the formation of butyl acetate by heterogeneously catalyzed transesterification of butyl alcohol with methyl acetate are available in literature (Jiménez et al., 2002, Jiménez and Costa-López, 2002; Steinigeweg and Gmehling, 2004; Lin et al., 2006; Bozek-Winkler and Gmehling, 2006; Wang et al., 2008; Xu et al., 2009; He et al., 2010) corresponding studies with ethyl acetate appear to be limited (Ogawa et al., 2004).

Consequently, in this study, butanol is transesterified with ethyl acetate using Amberlyst 15 and Amberlite IR 120. These cation exchangers are eco-friendly, noncorrosive, and have good thermal stability. Moreover, the work of Ali (2009) has proved that Amberlyst 15 can catalyze reactions with butanol and other studies (Ali and Merchant, 2006; Ali et al., 2007) have shown that both Amberlyst 15 and Amberlite IR 120 can efficiently catalyze reactions with isopropanol and propanol (alcohols with molar volumes comparable to butanol). Hence, these catalysts are considered good candidates for the transesterification of butanol with ethyl acetate. This heterogeneously catalyzed transesterification is studied over

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doi:10.1016/j.biortech.2011.08.033

a wide range of temperature, feed compositions, and catalyst loading.

2. Methods

All the chemicals and catalysts utilized in this study were procured from Sigma–Aldrich. Butanol (Sigma–Aldrich 360465), ethyl acetate (Sigma–Aldrich 270989), butyl acetate (Sigma–Aldrich 402842), 1-decene (Fluka 30649), and ethanol (Sigma–Aldrich 459836) were of high purity and were used as such. GC analysis showed their respective purity values to be greater than 99%. The catalysts used, Amberlite IR-120 (Aldrich 216534) and Amberlyst 15 (Sigma–Aldrich 216380) were dried at 330.15 K in a vacuum oven for 48 h. Important properties of these catalysts have been compared and characterized in previous works (Ali and Merchant, 2006, 2009).

A one liter glass Lab–Max reactor system was used for carrying out the kinetic runs. The details of the reactor set up can be obtained from the work of Ali and Merchant (2009). Required amounts of separately preheated (to required temperatures) ethyl acetate, butyl alcohol, 1-decene (the internal standard) along with measured amounts of the catalyst were added to the reactor. The temperature of the reactor was maintained at the reaction temperature with the help of a water batch. The transesterification was studied over a temperature range of 303.15–333.15 K, an alcohol to ester molar ratio range of 3:1 to 1:3 and a catalyst loading range of 6–12 wt.%. Details of the conditions, under which the experiments were carried, and their corresponding Run numbers are shown in Table 1. Each experimental run was repeated thrice. Data acquisition is in terms of concentration–time measurements. Samples of the reaction mixture were withdrawn at zero-time (time corresponding to the addition of the reactants to the reactor) and at predetermined time intervals for the next 21,600 s. The samples were analyzed by GLC using a 25 m × 0.032 mm CP-Wax52CB column and a Thermal Conductivity Detector. The oven temperature was maintained at 323 K for 0.8 min, followed by a temperature increase of 10 K/min, till the temperature reached 383 K. This technique is capable of separating and quantifying the components of the reaction mixtures.

Table 1
Experimental conditions of studied kinetic runs.

Run #	Temperature (K)	Rounded molar ratio of alcohol:ester	Catalyst loading (wt.%)	Stirrer speed (rpm)	Catalyst
1	323.15	1:1	10	100	Amberlite IR 120
2	323.15	1:1	10	200	Amberlite IR 120
3	323.15	1:1	10	400	Amberlite IR 120
4	323.15	1:1	10	800	Amberlite IR 120
5	323.15	1:1	6	800	Amberlite IR 120
6	323.15	1:1	8	800	Amberlite IR 120
7	323.15	1:1	12	800	Amberlite IR 120
8	323.15	1:3	10	800	Amberlite IR 120
9	323.15	1:2	10	800	Amberlite IR 120
10	323.15	2:1	10	800	Amberlite IR 120
11	323.15	3:1	10	800	Amberlite IR 120
12	303.15	1:1	10	800	Amberlite IR 120
13	313.15	1:1	10	800	Amberlite IR 120
14	333.15	1:1	10	800	Amberlite IR 120
4′	323.15	1:1	10	800	Amberlyst 15
5′	323.15	1:1	6	800	Amberlyst 15
6′	323.15	1:1	8	800	Amberlyst 15
7′	323.15	1:1	12	800	Amberlyst 15
8′	323.15	1:3	10	800	Amberlyst 15
9′	323.15	1:2	10	800	Amberlyst 15
10′	323.15	2:1	10	800	Amberlyst 15
11′	323.15	3:1	10	800	Amberlyst 15
12′	303.15	1:1	10	800	Amberlyst 15
13′	313.15	1:1	10	800	Amberlyst 15
14′	333.15	1:1	10	800	Amberlyst 15

3. Theory

3.1. Reaction kinetics

The transesterification studied can be represented by the following reaction:

$$\mathrm{CH_3CH_2CH_2CH_2OH + CH_3COOCH_2CH_3} \leftarrow \frac{k_1}{k_2} \rightarrow \mathrm{CH_3CH_2OH + CH_3COOCH_2CH_2CH_2CH_3}$$

Transesterification rate and the equilibrium product composition depend on the reaction conditions. The commonly applied model to describe the transesterification rate catalyzed by macroreticular ion-exchange resins (Amberlyst 15, NKC-9) is the pseudo-homogeneous (PH) model (Bozek-Winkler and Gmehling, 2006; He et al., 2010; Jiménez et al., 2002; Steinigeweg and Gmehling, 2004; Wang et al., 2008; Xu et al., 2009). The PH model rate expression for the reaction being studied takes the form of Eq. (1) in Table 2.

Besides the PH model, the Popken, Langmuir Hinshelwood (LH), and Eleay Rideal (ER) models will also be tried to correlate transesterification kinetics as earlier work has shown that these models can correlate esterification (Ali, 2009; Ali and Merchant, 2006, 2009; Ali et al., 2007; Gangadwala et al., 2003; Pöpken et al., 2000) and transesterification (Alonso et al., 2009) kinetics, catalyzed by macro- and micro-reticular ion exchange resins, remarkably well. For easy reference the corresponding rate expressions are tabulated in Table 2.

3.2. Accounting for non-idealities

Though earlier workers have been successful in predicting non-idealities involved in the heterogeneous transesterification of butanol with methyl acetate using the UNIQUAC (Bozek-Winkler and Gmehling, 2006; Steinigeweg and Gmehling, 2004) and UNIFAC (He et al., 2010; Wang et al., 2008; Xu et al., 2009) methods, the Modified UNIFAC (Dortmund) (Weidlich and Gmehling, 1987) method has been employed in this study. This is because the latter method is integrated into commercially available simulators (unlike the UNIQUAC method) and predicts many thermodynamic system properties (Jakob et al., 2006) more accurately than the UNIFAC method. The UNIFAC groups of the different components, the Modified UNIFAC (Dortmund) R_k & Q_k values are shown in Table 3.

3.3. Diffusion

Meaningful kinetic studies cannot be carried out in the presence of either external or internal diffusion limitations. Carrying out the kinetic runs at sufficiently high, experimentally determined optimum agitation rates ensures absence of external diffusion limitations for heterogeneous solid–liquid catalytic systems. A strong influence of temperature on initial reaction kinetics is a good indication of the absence of internal diffusion limitations (Ali and Merchant, 2009; Fogler and Scott, 1999). Some workers (Ali and Merchant, 2006; Ali et al., 2007; Bart et al., 1996; Krishnaiah and Rao, 1984; Yadav and Thathagar, 2002) have used the Weisz–Prater criterion (C_{wp}) (Hicks and Weisz, 1962), to judge the effect of internal diffusion on the overall reaction rate. C_{wp} values significantly smaller than unity indicate the absence of internal diffusion limitations in the system (Hicks and Weisz, 1962).