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Experimental studies on hydrogenation of anthraquinone derivative in a microreactor

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Abstract

Microreactors provide a novel means for chemical synthesis in a highly controlled way to obtain better yield and selectivity. In the present work hydrogenation of ethylanthraquinone, which is the first step in the commercial production of hydrogen peroxide by Reidl–Pfleiderer process, is carried out in a microreactor packed with supported palladium catalyst. The effects of reaction temperature, hydrogen to liquid reactant flow rate ratio, reactor pressure, ethylanthraquinone concentration and fluid velocity on conversion and reactor space-time yield were studied. The performance data obtained from this microreactor study were compared with the data from conventional reactors reported in the literature. The data show that the reactor space-time yield is much higher in the microreactor than in conventional reactors.

Keywords: Microreactor; Hydrogen peroxide; Ethylanthraquinone; Supported palladium catalyst

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1. Introduction

Hydrogen peroxide is being increasingly used in many green chemistries for its environmentally friendly properties. For example, traditional bleaching of pulp and paper by chlorine or sodium hypochlorite solutions produces a large amount of trihalomethanes, mainly chloroform, which are released to the atmosphere. These trihalomethanes are known to be carcinogenic in nature and our atmosphere is thus polluted by the traditional pulp and paper bleaching process. Bleaching of pulp and paper by hydrogen peroxide produces no pollutants and today about 50% of the hydrogen peroxide produced in the world is used in pulp and paper bleaching [1]. Other uses of hydrogen peroxide include treatment of water and wastewater.

Hydrogen peroxide is commercially produced by a process known as Reidl–Pfleiderer process. In this process 2-ethylanthraquinone (EAQ) in an organic solvent is first hydrogenated in the presence of a supported Pd catalyst to yield 2-ethylanthrahydroquinone ($EAQH_2$). The $EAQH_2$ is then oxidized by molecular oxygen to produce hydrogen peroxide regenerating EAQ in the process. Hydrogen peroxide is then extracted with water to obtain an aqueous solution of hydrogen peroxide. The reaction scheme is presented as Scheme 1 given by Drelinkiewicz et al. [2]. The heat of reaction for the hydrogenation of EAQ is 104 kJ/mol while that of the oxidation step is 85 kJ/mol as given by Kirk–Othmer [3].

The regenerated EAQ is again hydrogenated in the next cycle to obtain another molecule of H_2O_2.

Although starting with EAQ the main reaction is as shown above, some $EAQH_2$ on further hydrogenation is converted to tetrahydro-2 ethylanthrahydroquinone (H_4EAQH_2). When H_4EAQH_2 is oxidized it produces one molecule of H_2O_2 and one molecule of tetrahydroanthraquinone (H_4EAQ). Like EAQ, this H_4EAQ is also used again and again to produce H_2O_2. Some other side reactions involving $EAQH_2$ also occur in which the products do not yield H_2O_2 and are termed degradation products. The degradation products include ethyloxanthrone, octahydro-ethylanthrahydroquinone, ethylanthrone and ethylanthracene. The routes for formation of degradation products are as shown below in reaction Scheme 2 as given by Drelinkiewicz et al. [2].

In the present study, fresh EAQ solution is used in all the runs to avoid the degradation products.

Santacesaria et al. [4] reported that hydrogenation of anthraquinone derivatives on Pd catalyst is a fast reaction, and mass transfer resistance controls the reaction rate in conventional

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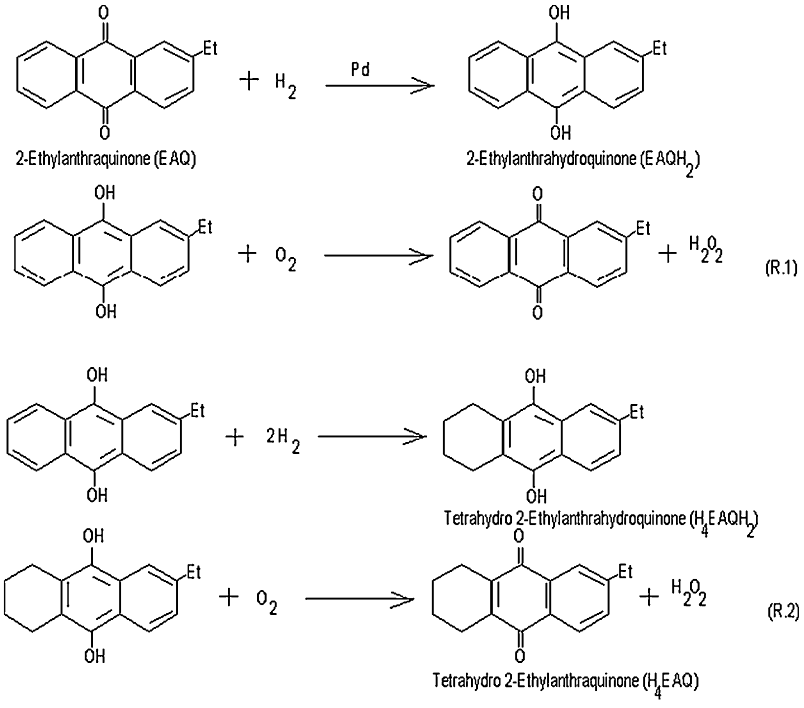
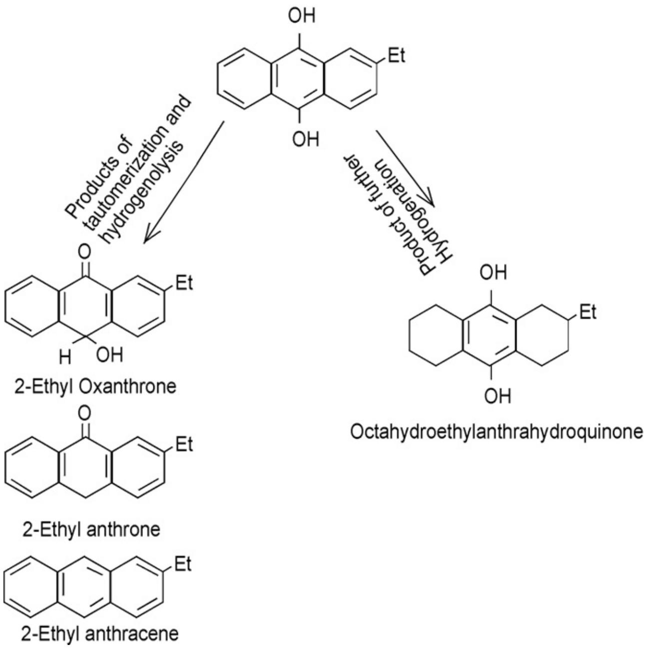


Scheme 1. Production routes for hydrogen peroxide.

reactors. Microreactors are known to have enhanced mass transfer rates compared to conventional reactors for multiphase reactions where the development of Taylor slug flow or pulsing flow has been shown to lead to orders of magnitude improvement in the mass transfer rates across the gas–liquid interface as shown by Losey et al. [5]. Since in this hydrogenation reaction mass transfer rate controls the reaction rate in conventional reactors, the reactor space-time yield can be increased to a great extent by using a microreactor. Also, microreactors have very high surface area to volume ratio thus enabling the control of exothermic reactions such as this hydrogenation reaction very efficiently. In this study, the hydrogenation reaction of anthraquinone derivative is experimentally conducted in a microreactor in order to demonstrate that the reactor space-time yield for this reaction is superior to that in conventional reactors.



Scheme 2. Production routes of degradation products.

2. Experimental

2.1. Chemicals

The solid EAQ is dissolved in a solvent mixture containing a polar and a non-polar solvent. The non-polar solvent is 1,3,5 trimethylbenzene, and the polar solvent is trioctyl phosphate. The EAQ, 1,3,5 trimethylbenzene and trioctyl phosphate (all reagent grade), were purchased from Sigma–Aldrich. The weight ratio of the trioctylphosphate and the trimethyl benzene used in the solvent mixture was 1:2.6. The concentration of the EAQ employed in the solution was in the range 0.22–0.44 mol/l.

Hydrogen gas used in this study was obtained from a cylinder and was of ultra high purity grade (99.9999%). The catalyst used in this work is 1% Pd supported on silica and, supplied by Johnson Matthey. The properties of the catalyst are given below:

- BET surface area = 320 m^2/g.
- Pore volume = 1.6 cm^3/g.
- Average pore diameter = 20 nm.

2.2. Experimental set-up and procedure

A sketch of the experimental set-up used for the present study is shown in Fig. 1. The EAQ solution was pumped at a