Electrochemical oxidation of isobutanol to isobutyric acid in a flow cell

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A systematic study of oxidation of isobutanol to isobutyric acid over a nickel oxide anode was carried out in a flow cell with well defined geometry. Various procedures for the activation of the anode were studied regarding their effect on the current efficiency and anode life. An attempt was made to optimize the other relevant operating parameters.

1. Introduction

Isobutyric acid is an important intermediate widely used in the perfumery and medicinal fields. It is synthetically prepared from isobutanol by oxidation. Although a number of methods for oxidation of alcohol to corresponding carboxylic acids have been reported [1], the general problem cannot be considered as definitely settled. This is due to the relative difficulty in the preparation of the reagents and in the working up of the reaction mixture [2]. Thus, there is scope for a new oxidation procedure which is versatile and selective. As oxidation is simply an electron transfer process, electrochemical anodic oxidation of alcohol appears to be an interesting alternative.

Electrochemical oxidation of alcohols can be carried out at a platinum electrode, but this is of limited value due to the high oxidation potentials required [3]. Oxidation of alcohols at lead oxide in acid solution normally yields considerable amounts of esters and seems to be better only for alkynols [4], whereas oxidation at a nickel oxide electrode results in carboxylic acid yields that are comparable, or even higher than those obtained by permanganate or nickel peroxide oxidation [5]. This can also be applied to alcohols having double bonds as double bonds in the compounds are not affected [5].

There is a wealth of information on electroorganic synthesis (EOS) [3, 6]. However, in a number of cases where the laboratory scale results were highly encouraging, failure was encountered on the large scale [7]. The main reason for these failures has been the lack of reliable scale-up procedures. The scale-up of electrochemical reactors (ECR) is complicated by the fact that for two dimensional electrodes, the electrode area increases as the square of the linear dimension, L^2, whereas the electrolyte volume increases as L^3. In view of this, laboratory studies using a tank cell could not be successfully scaled-up. In the last 15 years considerable attention has been devoted to the development of hardware for EOS. The success of the plate and frame type ECR in the Chlor–Alkali industry as well as the largest industrial EOS of adiponitrile from acrylonitrile [8] paved the way for the choice of this ECR for the newer applications. These plate and frame type reactors are versatile flow cells with a well defined geometry, flow structure and hence have well defined transport properties. Since many EOS are mass transfer controlled, a well defined flow structure and mass transfer performance is critical for successful scale-up. The ideal laboratory scale ECR should have the same electrode area/volume ratio (area of the electrode per unit volume of liquid between two electrodes) and mass transfer performance as the large scale counterpart. Newer designs of ECR which satisfy these criteria are therefore recommended for laboratory work. The present work describes the electrochemical oxidation of isobutanol to isobutyric acid in one such type of ECR over a nickel oxide electrode.

2. Previous studies

Initial research regarding oxidation of alcohols over nickel hydroxide electrodes by Vertes [9] and later by Fleischmann et al. [10] and Amjad et al. [11] mainly dealt with the mechanistic and electroanalytical aspects of the reaction. The preparative applications remained limited to simple aliphatic alcohols [11] and di-O-isopropylidene-L-sorbose [9, 12]. Kaulen and Schäfer [13] have carried out oxidation of short chain and long chain alcohols, diols and hydroxy steroids at a nickel oxide hydroxide electrode. These investigators have observed that oxidation of short chain alcohols takes place efficiently at room temperature. However, for long chain alcohols higher temperatures are required. These investigations were carried out in a glass beaker electrolyser
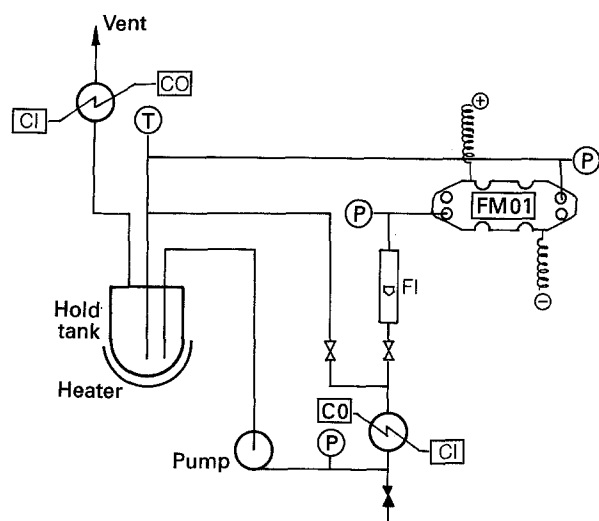

Fig. 1. Electrolyser setup: (CI) coolant in, (CO) coolant out, (T) thermometer, (P) pressure tapping and (FI) flow indicator.

under the constant current mode of operation. The cell used had an undivided configuration. Remorov and coworkers [14–17] have extensively studied oxidation of different types of primary alcohols in a flow cell (divided) over platinum, lead oxide, nickel oxide, platinum oxide and cobalt oxide electrodes and maximum yield was obtained with a cobalt oxide anode. Fioshin et al. [18] have reported a current efficiency of 90% and yield > 95% for isobutyric acid on a nickel oxide anode. However, optimization of the process parameters has not been attempted.

Fleischmann and Pletcher [10] proposed a mechanism of oxidation which was subsequently confirmed by Robertson [19]. A black surface layer of nickel(III) oxide hydroxide, similar to the well known oxidant, nickel peroxide [20] is continuously electrogenerated from nickel(II) hydroxide deposited on a nickel electrode. Oxidation takes place through a heterogeneous chemical reaction between the oxide hydroxide and adsorbed alcohol. An α-hydroxy radical is produced as an intermediate by radical hydrogen abstraction in the rate determining step. This intermediate is readily oxidized to a carboxylic acid in the case of primary alcohols. The above survey clearly indicates the feasibility of electrochemical oxidation of isobutanol to isobutyric acid. However, considerably more information, particularly regarding optimum operating parameters, is required for commercialization. The information required should be generated in a cell with well defined geometry and transport characteristics and should discern the effect of current density, hydrodynamic conditions etc., on current efficiency. For the electrooxidation of isobutanol an electrodeposited layer of nickel oxide as anode has been suggested. However, no information is available on the life of the layer once deposited. In view of this it was thought desirable to carry out a systematic study of oxidation of isobutanol to isobutyric acid with a view to optimizing the process and operating parameters.

3. Experimental details

3.1. Electrolyser

The FM01-LC laboratory process package, supplied by ICI Chemicals and Polymers (UK), was used in this work. This package comprised the FM01-LC flow cell, electrolyte flow circuits and DC stabilized power supply capable of constant current/constant voltage operation. The FM01-LC cell is designed on the lines of the FM21-SP electrolyser. Along with other advantages its mass transfer behaviour closely resembles that of the FM21-SP electrolyser under identical hydrodynamic conditions [21]. All experiments were carried out in an undivided cell with nickel oxide deposited on a nickel electrode $(0.0064\,m^2)$ as anode and stainless steel electrode $(0.0064\,m^2)$ as cathode. The interelectrode gap was maintained at 6 mm. The flow diagram of the electrolyser is shown in Fig. 1.

3.2. Materials

Analytical grade isobutanol, nickel sulphate, sodium acetate and sodium hydroxide supplied by Loba Chemie, India, were used.

3.3. Activation procedure

Before each electrolysis, a thin layer of nickel oxide was deposited on the nickel anode from an aqueous solution containing 0.1 M nickel sulphate, 0.1 M sodium acetate and 0.005 M sodium hydroxide at a current density of $6.25\,A\,m^{-2}$ [22]. By manual polarity changing, the nickel electrode was alternately used as anode and cathode for 1 min. This constitutes one cycle. Four such cycles were used followed by two cycles where polarity was changed after two minutes [22]. Beyond this point three different activation procedures were used.

Procedure 1: Keeping the nickel electrode as anode, activation was continued for a total time of 30 min at a current density of $7.81\,A\,m^{-2}$.

Procedure 2: Same as procedure 1 but activation was continued for a total time of 1 h.

Procedure 3: After 1 h of activation (when procedure 2 is complete), the used electrolyte was replaced with a fresh electrolyte (aqueous solution containing 0.1 M nickel sulphate, 0.1 M sodium acetate and 0.005 M sodium hydroxide) and activation was continued without change in polarity of the electrodes (keeping nickel oxide electrode as anode) for the next 1 h.

These three procedures were used to determine their effect on the current efficiency.

3.4. Conditions of electrolysis

Experiments were conducted under the constant current mode of operation using isobutanol dissolved in aqueous sodium hydroxide as electrolyte.
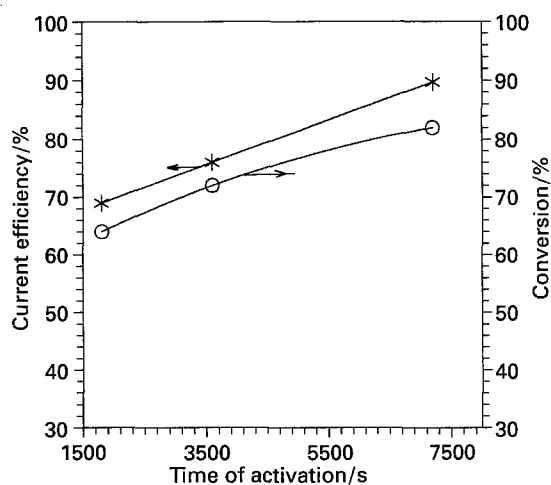
Fig. 2. Effect of time of activation of anode on current efficiency and conversion. Conditions: current density 546.8 A m^{-2}, charge passed 40 A h, isobutanol 0.404 mol, NaOH 0.5 mol, temperature 33° C and $Re = 2063$. Curves: (∗) current efficiency and (○) conversion. Mole ratio 0.74.

Fig. 3. Effect of operating (cycles) time on electrode activity. Conditions: current density 546.8 A m^{-2}, charge passed 28 A h, isobutanol 0.404 mol, NaOH 0.5 mol, temperature 33° C and $Re = 2063$. Curves: (∗) current efficiency and (○) conversion. Mole ratio 0.48.

Isobutanol concentration in the electrolyte was below the solubility limit, thus yielding a homogeneous electrolyte. The reaction mixture (500 ml 1 molar NaOH and 37.5 ml isobutanol) was taken in a three necked flask fitted with a condenser. The flask was placed in an electromantle which was used for temperature variation. The reaction mixture from the flask was pumped into the electrolyser with a magnetically driven PTFE pump. The flow rate was measured with a rotameter. The range of current density covered was 312.5–546.8 A m^{-2}.

3.5. Analysis

Unreacted isobutanol was extracted from the alkaline electrolyte with ether. The alkaline electrolyte was then acidified with 12 M HCl and the isobutyric acid liberated was extracted with ether [13]. Quantitative analysis was performed on a gas chromatograph (Chemito 8510) with a flame ionization detector using 1.8 m long and 1.3 mm diameter SS 304 high performance carbowax 20 M column. The injector, detector and oven temperatures were maintained at 220° C.

4. Results and discussion

4.1. Effect of time of activation of anode on current efficiency

For the process to have maximum current efficiency, it is necessary that the anode retains its activity. With increase in the anode activation time, the thickness of the nickel hydroxide layer deposited on the electrode surface increases [22]. Thus, anode activation time plays an important role in determining the life and activity of the electrode. The activity determines the conversion and current efficiency of the process. The current efficiency was defined as the fraction of charge effective in producing the desired product, and conversion was defined as the ratio of the
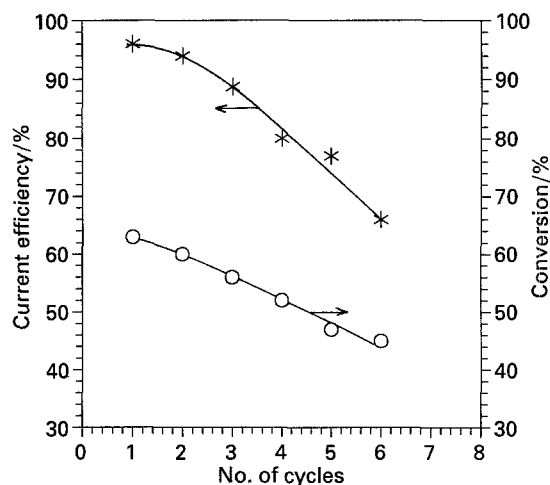
number of moles consumed in the reaction to the initial number of moles. Work done in the past indicates that fresh activation is required for each experiment. Use of a procedure [22, 13] for anode activation in this work resulted in low current efficiency and the electrode life was limited to one batch experiment only. Results for electrodes prepared by the three procedures described in Section 3.3 show that for the same charge, current efficiency increases with the time of activation as shown in Fig. 2. It is evident that a relatively high (90%) current efficiency is obtained with procedure 3 indicating that increase in the activation time beyond this may lead to only marginal increase in the current efficiency. All subsequent experiments were conducted using procedure 3 for anode activation.

4.2. Effect of operating time (cycles) on electrode activity

Different electrolysis experiments were conducted with the same anode without reactivation. In each experiment, charge equivalent to 90% conversion (on 100% current efficiency basis) of the isobutanol taken, was passed. Each experiment was denoted as one cycle. Figure 3 shows the effect of number of cycles on the current efficiency. It is evident that initially there is a slow decrease in the current efficiency. After the third cycle however, there is a rapid decrease in the current efficiency. It thus appears that the coating obtained using procedure 3 can be safely used for 2–3 batches.

4.3. Effect of current density on current efficiency

Over the range of current density (312.5–546.8 A m^{-2}), no change in current efficiency was observed. Similarly, no other products (e.g., acetone, acetic acid, etc.) were detected. It is possible that at higher current densities than those employed in this work competitive reactions [16] leading to the above products may occur.
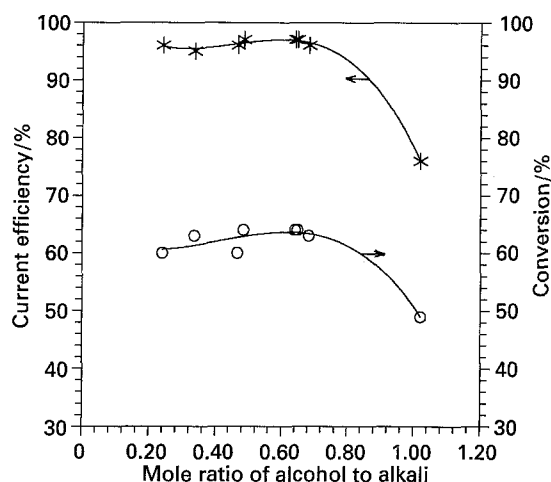
Fig. 4. Effect of alcohol to alkali mole ratio on current efficiency and conversion. Conditions: current density 546.8 A m^{-2}, temperature 33° C and $Re = 2063$. Curves: (∗) current efficiency and (○) conversion.

4.4. Effect of hydrodynamic conditions on conversion

Electrochemical reactions are heterogeneous in nature. Transport of species to and from the electrode surface plays an important role. The hydrodynamic conditions defined in the form of Reynolds number Re, decide the transport process rate. For the plate and frame geometry Re is defined as [23]

$$Re = \frac{d_e U_{av} \rho}{\mu}$$

where $d_e = 2BS/(B + S)$. The symbols are as follows: d_e is the equivalent diameter of the flow channel; B the electrode width (m) (which is 0.04 m in the present case); S the interelectrode gap (m) (which is 0.006 m in this case); $U_{av} = Q/BS$; U_{av} the average solution velocity (m s^{-1}); Q the electrolyte flow rate (m^3 s^{-1}); μ the electrolyte viscosity (7×10^{-4} kg m^{-1} s^{-1}); and ρ the electrolyte density (kg m^{-3}).

To discern whether the system is working above mass transfer limitation, experiments were carried out at different flow rates under otherwise identical conditions. A turbulence promoter in the form of a Teflon mesh was used in all the experiments. The Reynolds numbers covered were in the transition region. The results indicated a negligible effect of Reynolds number on the current efficiency for $1800 < Re < 2400$. It is therefore evident that there is no mass transfer limitation.

4.5. Effect of mole ratio of alcohol to alkali on current efficiency and conversion

Oxidation takes place through a heterogeneous chemical reaction between the black layer of NiOOH deposited on the anode surface and the adsorbed alcohol. NiOOH is continuously regenerated from the black Ni(OH)$_2$ on the electrode by hydroxide ions [10, 13]. Alkali, essential for the reaction to proceed (regeneration of NiOOH), is also consumed in neutralization of the acid formed. Thus NaOH concentration is an important parameter whose

deficiency affects current efficiency and conversion, especially at high conversion levels. At the same time large quantities of NaOH increase the reagent cost both in terms of the cost of the alkali and the cost of neutralizing acid required for liberating isobutyric acid. Further, there is an increase in the amount of salt produced which may not be desirable. Therefore, the optimum quantity of alkali to be used should be the minimum quantity which yields the highest current efficiency. The optimum alkali concentration can be best visualized in terms of the alcohol to alkali mole ratio where moles of alcohol represents quantity of alcohol consumed equivalent to the total charge passed during electrolysis and moles of alkali represents quantity of NaOH taken. To determine the effect of mole ratio of alcohol to alkali on the current efficiency and conversion, experiments were carried out at different mole ratios. The results are presented in Fig. 4. Conversion and current efficiency are relatively insensitive to the mole ratio for a mole ratio range of 0.2 to 0.68. Above a mole ratio of 0.68, there was a rapid decrease in the current efficiency. This was not accompanied by formation of by-products. Further, the material balance for alcohol was within ±2%, thus decarboxylation is unlikely. The only other possibility is that of oxygen evolution. However, this could not be observed in the closed cell construction employed. Therefore a mole ratio of 0.68 which yields the highest current efficiency and provides the maximum stability to the anode, is recommended.

4.6. Effect of temperature on current efficiency

Kaulen and Schäfer [13] observed that oxidation of α-branched and long chain alcohols require a higher temperature and also found that small amounts of (less than 0.2%) lower homologs of carboxylic acids are formed. Experiments were carried out at different temperatures to determine the decrease in current efficiency due to by-product formation. At the highest temperature employed (53° C) no by-products (lower homologs of carboxlylic acid) resulting from bond breakage were observed. For ease of operation and lower operating cost, it is preferable to work at ambient temperatures.

5. Conclusion

Oxidation of isobutanol was carried out over a nickel oxide electrode in flow cell of well defined geometry. Electrode activity is a key factor while considering the economic aspects of the process. The reported activation procedure for the anode was evaluated and modified so as to obtain current efficiency of the order of 90% without significant loss of activity up to three cycles. Alkali concentration, which determines the current efficiency of the process and cost of the reagent, was optimized. No side reaction was observed over the entire range of current density studied. Further, the reaction does not require higher

temperature for maximum current efficiency. The optimum conditions determined are: activation procedure 3 (as described in the Section 3.3), temperature 25–35° C and alcohol to alkali mole ratio 0.68.

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