SYNTHESIS OF DOCOSANOIC AND TETRACOSANOIC ACID FROM ALCOHOLS USING A TASK-SPECIFIC IONIC LIQUID CATALYST

N. GUAJARDO and C. CARLESI†

Abstract—Catalytic batch oxidation of docosanol to docosanoic acid and tetracosanol to tetracosanoic acid was performed using hydrogen peroxide as oxidant and a functionalized ionic liquid composed of an Aliquat® cation and a peroxotungstophosphate anion acting as catalyst.

Conversion of 76% and selectivity of 60.2% were obtained after 6 hours for docosanol oxidation at optimal operational conditions (temperature of 90°C; total-H₂O₂/alcohol molar ratio = 3; alcohol/catalyst mass ratio = 300). In the case of tetracosanol oxidation 85% conversion and 68% selectivity were reached in the same time interval at optimal operational conditions (temperature of 90°C; total- H₂O₂/alcohol molar ratio = 5; alcohol/final-catalyst mass ratio = 50). In both cases the oxidant and the catalyst were continuously added throughout the reaction time, thus enabling continuous reaction performance.

The batch results obtained in this study confirm the technical feasibility of operating a process to produce both these high molecular acids from alcohols as renewable raw materials.

Keywords - Docosanol, Docosanoic Acid, Tetracosanol, Tetracosanoic Acid, Quaternary Ammonium Peroxotungstophosphate Catalyst, Ionic Liquid.

I. INTRODUCTION

Traces of docosanoic and tetracosanoic acid are found in vegetable oils from different sources, reaching a maximum content of 1% in peanut oil (Beare-Rogers et al., 2001) and in peanut hulls (Lee, 2008). Docosanoic acid has natural humectants and smoothing properties that are of particular interest to the cosmetics and pharmaceutical industry, as indicated by US agricultural research (Lee; 2008; Coupland and Smith, 1989). The use of docosanoic acid (a 22 carbon chain acid) in cosmetic applications has been seen extensively due to its commercial availability (Lee, 2008). On the other hand, tetracosanoic acid is not produced on an industrial scale at the present, and the natural sources from which it could be extracted have a high added value themselves, therefore extraction is not cost effective. Among the renewable sources of tetracosanol we can find: the red sandalwood tree (Adenanthera pavonina), for which concentration can reach a maximum of 25% (Markley, 1960; Beare-Rogers et al., 2001).

Catalytic oxidation of alcohol has been studied to obtain these valuable types of acid (Venturinello and Gambaro, 1991; Bortolini et al., 1986; Bi et al., 2001; Kan et al., 2001; Hong et al., 2004). This synthetic route could be of industrial interest as it involves the use of potentially renewable and widely available natural resources in the form of long chain alcohols such as wax from sugar cane, aliphatic alcohols from tail oils, and mixed synthetic alcohols generated in the oxidation of paraffin (Guajardo, 2007; Markovits et al., 2009).

The present paper deals with the study of the oxidation of both docosanol and tetracosanol, using a peroxytungstinate functional group of an Ionic Liquid as catalyst.

The reaction medium includes the aliphatic substrate (alcoholic phase) and an aqueous phase containing the oxidant (hydrogen peroxide). The catalyst acts as active oxygen transfer between the two phases of the reaction system. In this case the catalyst belongs to the family of ionic liquids, a family of low temperature molten salts which offer properties (particularly low vapor pressure and high oxidative resistance) that allow efficient separation and recycling of the catalyst when working in highly oxidative aqueous media.

These and other tunable properties of ionic liquids solvents render them a key operative factor for many industrial applications (Plechikova and Seddon, 2008).

II. MATERIALS AND METHODS

A. Chemical reagents

The following reagents were used as purchased without further purification: Sodium sulphate from Scharlau (code SO0665), Phosphoric acid, dichloromethane and hydrogen peroxide from Merck (codes 815058, 106051 and 386790 respectively), Docosanol (95%) from Sasol and docosanoic acid (98%) from Aldrich, Sodium tungstate dihydrate (Na₂WO₄·2H₂O), methyltricaprylammonium chloride [(C₈H₁₇)₃CH₃N⁺ Cl⁻] (Aliquat 336), phosphotungstic acid (PTA) (H₃PW₁₂O₄₀), tungstosilicic acid (H₂SiW₁₂O₄₀), and tetrabutylammonium hexafluorophosphate (TBA) from Sigma.

B. Reactor set-up

The oxidation tests were carried out in a batch mode, using a thermostated reactor (Ika Eurostar, maximum volume of 2 liters), with mechanical stirring and in vapor reflux mode. The reactor was first loaded with the alcohol (docosanol or tetracosanol) followed by the addition of the aqueous phase containing the catalyst, thus forming a two phase system. The reaction starts with the addition of the oxidant drop by drop. The reaction
volume was 500 ml. Samples were collected regularly and then analyzed by gas chromatography (GC HP 6890) in order to follow the reaction paths. Molar conversion (C) and selectivity (S) were calculated using expressions 1 and 2, respectively.

\[ C = 100 \times \frac{n_{Alc(i)} - n_{Alc(t)}}{n_{Alc(i)}}, \quad (1) \]

\[ S = 100 \times \frac{n_{Ac(t)}}{n_{Alc(i)}}, \quad (2) \]

where \( n_{Alc(i)} \), \( n_{Alc(t)} \), and \( n_{Ac(t)} \) represent the molar concentration of the alcohol at reaction time (\( t \)), the initial concentration of the alcohol and the concentration of the acid over time.

The catalyst was recovered from the organic phase through distillation (at the bottom) at the end of each run. This is due to the large difference in the vapor pressure of the ionic liquid catalyst in relation to the reaction products and un-reacted reactants.

C. Catalyst synthesis

The ionic liquid catalyst (Acronym: \( Q^+3PW^-3 \)) was prepared by replacing the chloride anion of the Aliquat 336 reagent with peroxytungstophosphate anion (\( PW^-3 \)), following the procedure reported by Venturello and D’Aloisio (1988): 90 g sodium tungstate dihydrate (\( Na_2WO_4*2H_2O \)) as tungsten precursor was diluted into 252 ml of hydrogen peroxide solution (8% V/V) forming a suspension. This was then heated at 60ºC and stirred until a color transition took place (from pale yellow to white); this is an indication of the oxidation reaction. The solution was then cooled and filtered and 22.33 ml of \( H_3PO_4 \) solution (40% V/V) was added to the solid remaining in the filter and completed to a volume of 1080 ml with distilled water. This prepared solution was then mixed with a second solution composed of 75.3 g of Aliquat 336 dissolved in 440 ml of dichloromethane. The mixture of solutions was vigorously stirred for 15 minutes and left stand until two liquid phases were formed. After separation the organic phase containing the catalyst was dried over sodium sulphate, and the dichloromethane solvent was then extracted by means of a molecular distiller (KDL5 UIC) operated at 55ºC. The obtained solid was analyzed by FT-IR spectroscopy (Perkin Elmer - Spectrum One).

III. RESULTS AND DISCUSSION

A. Catalysis characterization

The principal signals from the FT-IR analysis were (wavelength in cm\(^{-1}\)): 3677.14; 3391.60; 2955.84; 2925.01; 2855.16; 1637.53; 1467.03; 1378.04; 1120.15; 756.79; 726.06; where the absorbance related to the \( Q^+3PW^-3 \) catalyst corresponds to: 889.67 cm\(^{-1}\) (W-O-W); and the zone between 1079.84 and 1040.77 cm\(^{-1}\) is related to (P-O) vibration; the 852.46 cm\(^{-1}\) signal is related to (O-O) bond (Alizadeh and Tayebee, 2005; Aubry et al., 1991).

Table 1: Summary of results for docosanol oxidation, under different operational conditions, after 6 h of reaction.

<table>
<thead>
<tr>
<th>Molar ratio H(_2)O(_2)/alcohol</th>
<th>Weight Ratio Alcohol/Catalyst</th>
<th>Temperature (°C)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>90</td>
<td>42.5</td>
<td>20.1</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>120</td>
<td>58.7</td>
<td>13.7</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>90</td>
<td>66.5</td>
<td>46.4</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>120</td>
<td>84.5</td>
<td>37.7</td>
</tr>
<tr>
<td>1</td>
<td>21</td>
<td>90</td>
<td>58.4</td>
<td>18.3</td>
</tr>
<tr>
<td>1</td>
<td>21</td>
<td>120</td>
<td>57.1</td>
<td>9.6</td>
</tr>
<tr>
<td>3</td>
<td>21</td>
<td>90</td>
<td>81.2</td>
<td>49.6</td>
</tr>
<tr>
<td>3</td>
<td>21</td>
<td>120</td>
<td>86.2</td>
<td>42.1</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>90</td>
<td>66.4</td>
<td>49.5</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>90</td>
<td>70.6</td>
<td>60.2</td>
</tr>
</tbody>
</table>
In Fig. 3, an improvement in reaction performance can be observed when the relative amount of catalyst is raised to more than 90% of conversion after seven hours of operation. As in the case of docosanol oxidation the performance is better when the catalyst is added continuously over the reaction time.

The results show that the variation in the ratios observed between the catalyst and the alcoholic substrate does not have a proportional effect on the performance of the reaction. This may be due to rapid regeneration of the catalyst. On the other hand, the relative amount of oxidant (H₂O₂) does have a marked effect on the performance of the reaction.

After verifying the technical feasibility of the proposed reactions and the quantitative separation and recycling of the catalyst, a basic process scheme was proposed, as presented in Fig. 4, for the production of the high molecular aliphatic acids from the corresponding alcohols. Each principal component of the process is specified in the caption of the Fig. 4 (adapted from Markovits et al., 2009).

IV – CONCLUSIONS

The oxidation reaction of docosanol and tetracosanol to docosanoic and tetracosanoic acids was studied with the aim of identifying an appropriate oxidant and catalyst to perform a bi-phasic batch process. Peroxotungstophosphate can actively transfer the active oxidant oxygen from the aqueous to the organic phase. This catalyst was rendered available for the reaction in its anionic form as an ionic liquid. The efficient performance of this kind of reaction is assured by the good chemical stability of the IL when exposed to high oxidizing media.

76% conversion and 60.2% selectivity were obtained after 6 hours for docosanol oxidation under optimal operational conditions (temperature 90ºC; molar ratio of total-H₂O₂/alcohol = 3; mass ratio of alco-
hol/catalyst = 300). In the case of tetracosanol oxidation 85% conversion, 68% selectivity were attained in the same time interval under best operational condition (temperature 90ºC; molar ratio of total-H2O2/alcohol = 5; mass ratio of alcohol/final-catalyst = 50). Both the oxidant and the catalyst should be added continuously throughout the reaction, thus enabling continuous reaction performance.

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