ELECTROLYTIC REDUCTION OF LEMON GRASS OIL

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INTRODUCTION

Lemon grass oil contains citral, which is the most important member of the group of aliphatic terpenes[1], possessing properties of great scientific interest and also being of considerable technical importance. Law[2] has attempted to reduce citral electrolytically in alkaline solution and a viscid oily substance was obtained. During the course of our investigation on the polarographic behaviour of lemon grass oil[3] at the dropping mercury cathode, it was thought worthwhile to study the electrolytic reduction of lemon grass oil and the results obtained are presented in this paper.

EXPERIMENTAL

Material :

Lemon grass oil is available in plenty in Travancore and it is purified by distillation under reduced pressure. The portion boiling in the range of 130–140°C at a pressure of 8.5 cms of mercury is collected and used for the investigation. The citral content of the lemon grass oil was 83 6% and citral content in the purified oil was 96%.

Cathode :

Mercury and amalgamated copper have been studied as cathodes

Electrolytic cell :

A glass beaker of diameter 10 cm and 16 cm height with a suitable perspex lid carrying holes for the electrodes, diaphragm and thermometer respectively was used as electrolytic cell. Cylindrical amalgamated copper cathode with an effective area of 0.24 sq. dm was used as rotating cathode. Two ceramic diaphragms of outer diameter 2 cm and height 12 cm were used and two narrow lead strips of 1 cm width and 14 cm long were used as anodes. In the case of investigations by the use of stationary electrode with the same cylindrical amalgamated copper cathode, a glass stirrer was used for effective agitation in the cell. The cathode potential was measured in a few experiments by Crompton potentiometer against a saturated calomel electrode. While investigating with mercury cathode, a pool of pure mercury was used in the cell and contact was given by means of glass tube fused with plantium wire. The other experimental conditions employed are given in the Tables.

Analysis :

When electrolysis was over, the unreduced citral in the lemon grass oil was estimated polarographically[3] and the current efficiency was calculated on the basis of the reduced cirtal content in the electrolysis. No attempt was made to isolate and analyse the reduction products.

Results and Discussions

Influence of the catholyte composition on the current efficiency for the reduction of citral content in lemon grass oil.

The effect of bath composition of the catholyte on the current efficiency is given in Table I and it can be seen from the table that a good current efficiency is obtained using 15% ammonium sulphate as catholyte.

Effect of cathode rotation on the current efficiency :

The current efficiency for the electrolytic reduction of lemon grass oil obtained by a rotating cathode is compared with a stationary cathode and the results are given in Table II. From the table it can be seen when the cathode is stationary there is a sharp fall[4] in current efficiency as the current density is increased. But in the case of a rotating cathode as shown in Table II the fall in current efficiency when the current density is increased, is not so sharp as in the case of a stationary cathode. Efficient agitation of the catholyte reduces the thickness of the diffusion layer while the current efficiency of the process is raised considerably as a result of the increase in the limiting current density. Agitation by

means of an auxiliary stirrer is not as efficient as in the case of a rotating cathode, where the stirring at the vicinity of the cathode, surface is more efficient, so that it reduces the thickness of the diffusion layer. The rate of the cathodic reaction could be increased either by efficient agitation or by increasing the concentration of the depolariser. Rotation of the cathode in this process helps access of the depolariser to the cathod surface and makes possible a slightly higher current efficiency without the danger of hydrogen evolution.

Effect of the temperature on the current efficiency :

The influence of temperature on the current efficiency of the process is given in Table III and it can be seen that a temperature range of 30–35°C can be advantageously employed for the cathodic reduction of lemon grass oil.

TABLE I

Effect of catholyte composition on the current efficiency of reduction of citral in tbe lemon grass oil.

Cathode	—	—	Mercury pool
Anolyte	—	—	5% sulphuric acid
Temperature	—	—	25–30°C
Lemon grass oil in the catholyte	—	—	5 cc (4.272 g)

Catholyte Composition	Cell Voltage (v)	Wt. of unreduced citral (g)	Current efficiency (%)
65 cc of 10% sodium hydroxide solution and 35 cc of methyl alcohol	6—7	4.053	5
65 cc of 5% sodium hydroxide solution and 35 cc of methanol	6—7	3.845	10
65 cc of 5% sulphuric acid and 35 cc of methanol	6—7	2.734	36
65 cc of 15% ammonium sulphate and 35 cc of methanol	6—7	1.281	70
65 cc of 10% sodium sulphate and 35 cc of methanol	10—15	1.025	76

TABLE II

Effect of cathode reaction on the current efficiency of reduction of citral in lemon grass oil.

Catholyte	—	20 cc of lemon grass oil in 180 cc of ammonium sulphate solution and 50 cc of alcohol.
Cathode	—	Amalgamated copper cathode.
R. P. M. of cathode	—	1000 when the same cathode was stationary a stirrer was included.
Effective area of cathode	—	0.24 dm^2
		all other conditions as in Table I

Cell Voltage	Duration of electrolysis (hrs)	Current (amp)	Current density (amp/dm^2)	Cathode motion	Current efficiency (%)
8—9	5	1.2	5	Stationary	79.8
7—8	5	1.2	5	Rotation	92 0
10—12	2.5	2.4	10	Stationary	58.0
9—11	2.5	2.4	10	Rotation	90.0
13—15	1.7	3.6	18	Stationary	36.0
12—14	1.7	3 6	15	Rotation	58.0

TABLE III

Effect of temperature on the Current efficiency

Catholyte	—	5 g of lemon grass oil in 180 cc of 15% ammonium sulphate solution.
		All other conditions same as in Table I.

Temperature (°C)	Cell Voltage	Cathode potential Vs N. H. E. (V)	Current efficiency (%)
50—53	4.4	2.14	42.50
30—35	4.6	1.34	83.73
20—25	4.9	1.64	77.50

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