OXIDATION OF MOLASSES TO PRODUCE OXALIC ACID

Abdul Sattar, Din Muhammad, M. Ashraf, Shafiq A. Khan and M. K. Bhatty

PCSIR Laboratories, Lahore-16

Oxalic acid was produced on laboratory scale by the oxidation of sugar cane molasses in 65.3 % yield. The oxidation was carried out with nitric acid (65 %) at 60-65° in the presence of catalytic amounts of vanadium pentaoxide (0.005-0.01 %) and tungstun oxide (0.05-0.06 %) as a co-catalyst. The reaction conditions were optimised first on sucrose and then the standardised oxidation procedure was applied on purified molasses. The studies were aimed at producing oxalic acid on industrial scale in the country. The difficulties involved and the conditions of the oxidation reaction are discussed here.

Key words: Oxalic acid, Molasses, Oxidation.

INTRODUCTION

Ethanedioic acid, commonly known as oxalic acid is an important industrial chemical. The acid and its salts are extensively used in the production of finished products such as celluloid, rayon, explosives, tanning and calicoprinting materials and certain dyes. The acid is also employed in the bleaching of straw, cork and rosin and in the extraction of rare earths. Laundry consumes a large amount of the acid for 'acid rinse' to neutralize the deterimental alkalinity usually present in the laundry soaps. It is also an important ingredient of corrosion inhibitor and removal compositions for automobile radiators and boilers. Total demand of oxalic acid in Pakistan has been reported to be 0.6 million Kg at an estimated price of Rs. 6.1 million [1].

Several methods have been used for the production of oxalic acid. The most important ones are (i) alkalifusion of cellulose [2] (ii) microbial fermentatation of carbohydrates by specific microbes [3] (iii) synthesis from sodium hydroxide, carbon monoxide, lime and sulphuric acid through the formation of sodium formate [4] (iv) oxidation of carbohydrates with nitric acid alone or in combination with catalysts and sulphuric acid [5]. The carbohydrates include [6] cellulosic residues and wastes, sucrose and sucrose containing materials and monosaccharides such as glucose and fructose. A variety of catalysts have been described for promoting and enhancing the oxidation process. Oxides of vanadium and molybdenum in combination with ferrous sulphate have extensively been used [6]. Our selection of the oxidation of carbohydrates, particularly of molasses was motivated because of the abundant availability of the raw material (0.3 million tonnes of molasses per annum). During these studies, the main objective was to study the oxidation parameters, so that the production is economical and commercially feasible.

EXPERIMENTAL

Reaction Vessel. The reaction vessel was a cylindrical vessel (30 in. by 12 in. dia) of Stainless steel and fitted with a slow speed stirrir (28 rpm). The vessel was jacketted outside and internally provided with stainless steel colooing/heating coils. The temperature of the reaction mixture was controlled by running cold water through these coils and the outer jacket. Besides the stirrir in the centre there was sugar feed arrangement by screw, a feed pipe for the acids and a gas outlet for the oxides of nitrogen formed during the reaction. The nitrogen oxide fumes were led out with a slow stream of air into two glass absorption columns joined in sequence and packed with broken glass pieces. Water would trickle down through the glass columns against the rising fumes to affect maximum absorption of nitrogen oxides. A safety vent also was provided at the top of the vessel to carry off any uncontrolled reaction mass. At the bottom of the reaction vessel there was an outlet to drain off the reaction product. The vessel was cleaned thoroughly after every reaction charges.

Purification of Molasses. Molasses (1 Kg) were dissolved in equal amount of water (1 litre) and 100 ml. of 10 percent solution of oxalic acid added with stirring. The mixture was boiled for 5 minutes and then allowed to cool down. Precipitated calcium oxalate alongwith other impurities was filtered. The slight excess of oxalic acid was accepted without further purification. The filtrate was concentrated back to original volume under vacuum to obtain light coloured thick syrup of molasses.

Oxidation Procedure. The acid mixture consisting of the required amount of 65 % nitric acid, conc. sulphuric

acid and water was added to the reaction vessel. Carbohy-drate material (sucrose or molasses) together with the catalyst was then gradually added through the screw feed arrangement and the mixture was stirred. After about 15 min, the temperature of the reaction mixture started rising rapidly. Cold water was circulated through the coils and the outer jacket of the vessel at a rate that a temperature was maintained at 60-65° in the reaction vessel. After about 2 hr. the temperature of the reaction mixture started falling. The vessel was then externally heated to maintain a temperature of 65-70° for another 5-6 hr., at the end of which, the product was drained off from the bottom in an open tray. The solution was chilled and was allowed to stay to crystallize. The crystals were filtered and the mother liquor was concentrated to obtain second and third crop of crystals. The crude material was dissolved in water at about 90° and after hot filtration, was allowed to crystallize to give pure (nearly 99.9 %) oxalic acid m.p. 101.5°C.

DISCUSSION

The experimental conditions were optimised first on sucrose and then employed on molasses for the production of Oxalic acid. Sucrose was oxidized with nitric acid under different conditions with and without the use of catalysts.
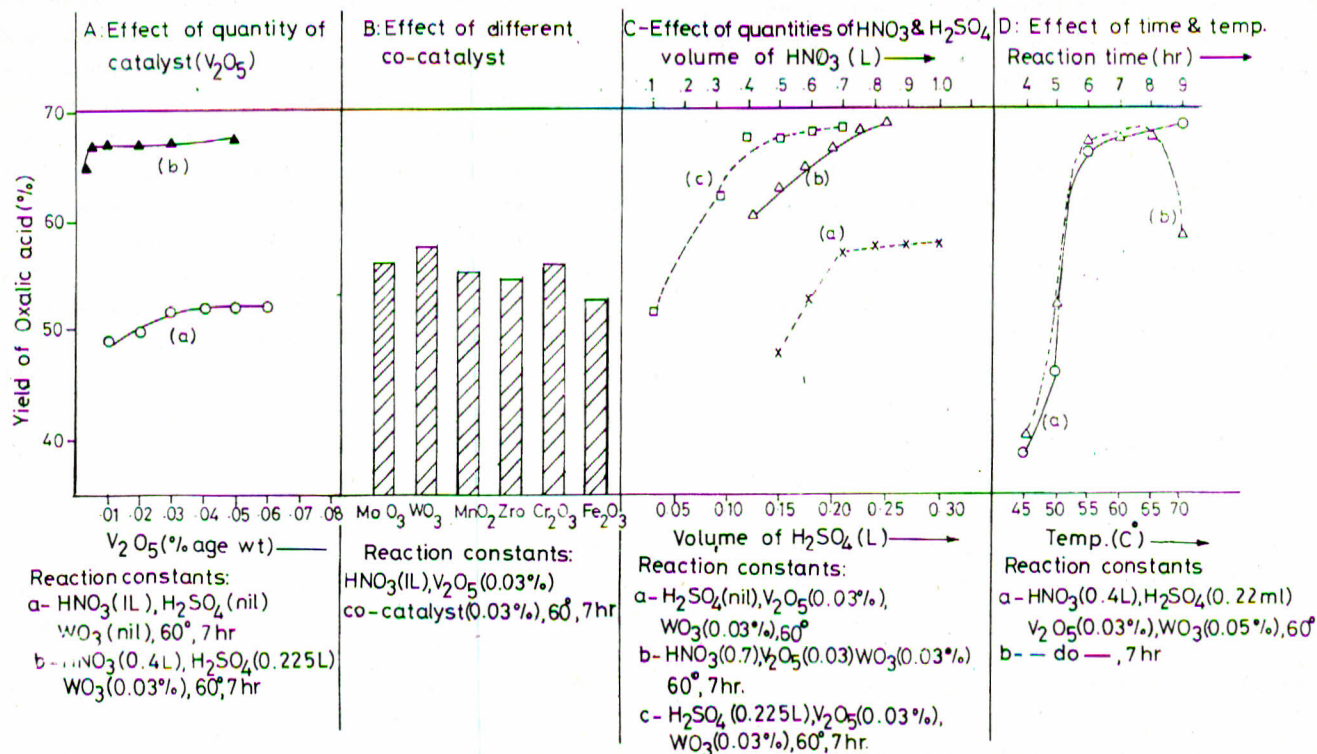
Nitric acid (65 %) alone gave poor yields of oxalic acid even on heating to 70-75°C. Even at 60° in the presence of catalytic amounts (0.01 %) of various transition metal oxides (MoO_3, WO_3, MnO_2, TiO_2, ZrO, Fe_2O_3, $Cu\,O$, NiO, SeO_2, Cr_2O_3 and CoO) poor yields were obtained except for V_2O_5 which showed an average yield of 52 %. This study of catalysts indicates that probably they do not form required intermediate complexes with nitric acid at the working temperatures. In the case of V_2O_5, this complex formation is easier and occurs at suitable tem-peratures.

Combination of oxides of transition metals also did not improve the yield but when MoO_3; WO_3, MnO_2, ZrO, CR_2O_3 and Fe_2O_3 (0.03 %) each were used as cata-lyst with V_2O_5, the yield of oxalic acid improved from 52 % to 56.0, 57.1, 55.4, 54.2, 55.8 and 52.4 % (Table 1; Graph-B) Vanadium pentaoxide in nitric acid (65 %) alone

Table 1. Effect of the addition of a Cocatalyst with V_2O_5.

Sucrose, 0.1Kg; HNO_3 IL; V_2O_5, 0.03 %;
Cocatalyst, 0.03 %; Temp., 60; time, 7 hr.

Cocatalyst	MoO_3	WO_3	MnO_2	ZrO	Cr_2O_3	Fe_2O_3
Yield of Oxalic acid %	56.0	57.1	55.4	54.2	55.8	52.4

Graph. Effect of variation of different parameters on the yield of oxalic acid from sucrose (0.1 Kg).

gave poor yields of oxalic acid (Graphs Aa & Ca). When a mixture of nitric acid (65 %) and sulphuric acid (60 %) were used, the yield improved tremendously (Graphs Ab & Cb). Moreover, the amount of nitric acid required to afford the same kind of yields decreased as well (graphs Cb & Cc). The oxidation of sucrose was maximum after about 6 hr. and then it levelled off to give almost constant yields (Graph Da). Increase in temperature of the oxidation reaction had a positive effect and at about 65°, the yield of oxalic acid was maximum but beyond this point the yield started dropping (Graph Db).

In the light of these observations the optimum conditions required for effecting maximum oxidation of mono-

Table 2. Effect of Catalyst, cocatalyst, acids, time and temperature variation in the yield of oxalic acid.

Catalyst (% V_2O_5)	Catalyst (% WO_3)	HNO_3 (65 %)	H_2SO_4 (60 %)	Time (hrs)	Temperature ^oC	Yield (%)
0.01	–	1L	–	7	60	49.0
0.02	–	”	–	”	”	49.8
0.03	–	”	–	”	”	51.6
0.04	–	”	–	”	”	51.9
0.05	–	”	–	”	”	52.0
0.06	–	”	–	”	”	52.1
0.03	0.03	0.5L	–	”	”	47.5
”	”	0.6L	–	”	”	52.4
”	”	0.7L	–	”	”	56.9
”	”	0.8L	–	”	”	57.2
”	”	0.9L	–	”	”	57.4
”	”	1.0L	–	”	”	57.3
”	”	0.7L	125ml	”	”	60.3
”	”	”	150ml	”	”	62.8
”	”	”	175ml	”	”	64.4
”	”	”	200ml	”	”	66.3
”	”	”	225ml	”	”	68.1
”	”	”	250ml	”	”	68.8
”	”	”	225ml	”	”	67.8
”	”	”	250ml	”	”	67.5
”	”	0.6L	225ml	”	”	67.4
”	”	0.5L	”	”	”	62.1
”	”	0.4L	”	”	”	67.6
”	”	0.3L	”	”	”	67.0
0.05	”	”	”	”	”	67.1
0.01	”	”	”	”	”	66.8
0.005	”	”	”	”	50	52.1
0.001	0.05	”	”	”	55	67.0
”	”	”	”	”	60	67.4
”	”	”	”	”	65	67.8
”	”	”	”	”	70	58.4
”	”	”	”	5	60	45.8
”	”	”	”	6	”	65.9
”	”	”	”	8	”	68.0
”	”	”	”	9	”	68.3

and disaccharides to oxalic acid with 0.1 Kg of sucrose as the standard raw material (Table 2, Graphs A to D) were: Catalyst (V_2O_5), 0.01 %, co-catalyst (WO_3), 0.05 %; 65 % HNO_3 (4 times V/W of sugar); 60 % H_2SO_4, 225 ml; Temperature 60-65°C and time for oxidation 7 to 8 hr. These reaction conditions were then employed on molasses to produce oxalic acid.

Molasses, a waste of sugar industry, usually contain 40-45 % sugars including 30-36 % sucrose, 15-20 % invert sugar and 21-25 % water besides containing other organic and inorganic compounds. Among these impurities, calcium salts are prominent and they interfere in the oxidation process and must therefore, first be removed. The molasses were thus freed from calcium salts by precipitating them as calcium oxalates. The standard oxidation procedure was then applied on the purified molasses except for the water that was added to dilute sulphuric acid by adjusting the already present water in the molasses (23 % on the average). When the amount of the mono and the disaccharides averagely present in molasses was taken into consideration, the yield of oxalic acid obtained from molasses was comparable (65.3 % on the basis of sugars present) with those derived from sucrose.

The major difficulty in the oxidation procedure lies in the absorption of nitrogen oxide fumes which evolve in large quantities. The NO_2 vapours are absorbed easily and can be utilised for the manufacture of sodium nitrite, but NO vapours need to be oxidised to NO_2 before being trapped and absorbed for use. The economics of the oxidation process depend on the absorption of NO_2 and NO gases.

REFERENCES

1. Foreign Trade, *Statistic of Pakistan* (Imports), Federal Bureau of Staistics of Pakistan, Karachi (1985).

2. (a) D.F. Othmer, C.H. Gamer and J.J. Jacobs, Jr; Ind. Eng. Chem., **34**, 262 (1942).

   (b) W.L. Faith; D.D. Keys and R.L. Clark, Industrial Chemicals, (Wiley, New York, 1950), pp. 446-452.

3. V.W. Cochrane; Economic Botany, 2, 145 (1948).

4. Kirk Othmer; *Encyclopedia of Chemical Technology*, (Interscience Publishers, New York, 1967) pp. 356-365.

5. (a) N.V. Vaveer, T.E. Lipkina, I.V. Petrov and P.F.

Sopin; Otkrytiya, Izabret, Prom. *Obraztsy Tovarnye Znaki,* U.S.S.R. **13**, 89 (1979), **CA**, **91**, 23429q (1979).

  (b) G.H. Fuchs and W.E. Watson; Br. Pat. 1198955 dt. 03.01.1969, J. App. Chem. 410 (1970).

6. (a) Poucini Laurence; Sch. Sci. Rev. **62**, 515 (1981); **CA**. **94**, 155763 (1981).

  (b) B. Karunanidhi and T.V. Subramanium; Chem.

Petro-Chem. J. **11**, 13 (1980); **CA**. **94**, 156255 p. (1981).

  (c) S. Boss, K.C. Gupta and S. Mukherjee; Indian Sugar **28 (7)**, 405 (1978), **CA**, **90**, 206206p (1979).

  (d) Mehboob Elahi and A. Ali Hussain, Bull. Fac. Sci., Riyadh University, KSA; **5**, 71 (1973), **CA, 81**, 107750 (1974).