AN EXPERIMENTAL INVESTIGATION FOR THE SYNTHESIS OF OXALIC ACID BY NITRIC ACID OXIDATION OF DATES FRUIT AND SYRUP

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ABSTRACT

An experimental investigation was conducted to study the various parameters affecting the production of oxalic acid by the action of concentrated nitric acid on carbohydrates. Two feedstocks were studied, viz., dates fruit and dates syrup. The study also covered the effect of the amount of nitric acid and catalyst used in addition to employing two acid concentrations (67 wt.% and 98 wt.% acid).

The results showed that when using 67 wt.% nitric acid, dates syrup was best suited as a raw material. And the best amount of nitric acid and V_2O_5 catalyst were in the ratio of 150 mls: 25 mg per 50 g feedstock.

When using 98 wt.% nitric acid, no catalyst was required for the reaction and the reaction proceeded violently with the evolution large amount of the nitrogen oxides.

الخلاصة

تم في هذا البحث اجراء تجارب مختبرية لدراسة تاثير العوامل المختلفة الموثرة على انتاج حامض الاوكزاليك من اكسدة الكربوهيدرات بواسطة حامض النتريك. اما العوامل التي تمت دراستها فهي :

- المادة الاولية وشملت التمر والدبس.
- تركيز حامض النتريك حيث استخدم حامض بتركيز 67 % و 98 % .
- كمية حامض النتريك .
- كمية العامل المساعد .

دلت النتائج على إن افضل انتاج لحامض الاوكزاليك عند إستخدام حامض النتريك 67 % كانت باستخدام الدبس كمادة اولية وبكميات الحامض والعامل المساعد حسب النسب التالية :-

الدبس :50 غم / حامض النتريك : 150 مل / العامل المساعد :25 ملغم .

كذلك وجد عند استخدام حامض النتريك المركز (98 %) يمكن الاستغناء عن العامل المساعد وإن التفاعل كان شديدا حيث تحررت كميات كبيرة من غازات اكاسيد النيتروجين .

KEY WORDS
Oxalic acid from dates., Oxalic from date syrup.

INTRODUCTION

Oxalic acid was first synthesized in 1776 by Scheele from the oxidation of sugar by nitric acid (Process Evaluation, 1974) Since then different processes were developed, e.g. alkali fusion of cellulose, synthesis from sodium formate...etc. However, only oxidation by nitric acid is still in use. The others have become obsolete or uneconomical. In the oxidation by nitric acid different raw materials may be employed depending on economy and availability (Process Evaluation, 1974; Oxalic acid, 1978). These raw materials include sugar, starch, ethylene and propylene, acetylene and acetaldehyde.

In the US, oxalic acid is primarily produced from corn starch and to a lesser extent from ethylene glycol. In the USSR and India from sugar. In France from propylene. Other countries such as China, Brazil, uses their locally available carbohydrates (Kuznetsov, et al,1976; Deshpande, et al, 1979).

When using starch in making oxalic acid, the starch is first hydrolyzed to glucose. The latter is then converted to oxalic acid at a temperature of 63°C in an agitated, cooled reactor using V_2O_5/Fe^{+3} as a catalyst. The reaction is:

$$C_6H_{12}O_6 + 12HNO_3 \rightarrow 3C_2H_2O_4.2H_2O + 3H_2O + 3NO + 9NO_2$$

In the ethylene glycol process, the reaction pressure is, mostly, atmospheric and the temperature is 57-60°C, then raised to 77°C for the last 20% of the reaction time. Oxalic acid is produced according to (US Patent 3531520, 1970):

$$3C_2H_6O_2 + 20HNO_3 \rightarrow 3C_2H_2O_4.2H_2O + 10H_2O + 2NO + 18NO_2$$

The oxalic acid manufactured from propylene involves a two step oxidation process using nitric acid and, preferably, in the presence of oxygen and a catalyst.

The two step reaction is as follows (Oxalic Acid, 1978):

(i) $CH_3CH{=}CH_2 + 3HNO_3 \rightarrow CH_3\underset{\displaystyle ONO_2}{\underset{|}{C}}HCOOH + 2NO + 2H_2O$

(ii) $CH_3\underset{\displaystyle ONO_2}{\underset{|}{C}}HOOH + 5/2O_2 \rightarrow C_2H_2O_4 + CO_2 + HNO_3 + H_2O$

Another process to synthesize oxalic acid is from carbon monoxide and water. But this process is very costly (Process Evaluation, 1974; Ger. Offen 2213935, 1973).

Oxalic acid has also been produced by pumping nitrogen dioxide directly into sugar or starch hydrolyzate in the presence of V_2O_5 and H_2SO_4. The process claimed to reduce nitric acid consumption (China Patent 1043494, 1990).

In another process, starch is oxidized with nitric acid and nitrogen dioxide simultaneously using V_2O_5-$FeSO_4$-$MnSO_4$ mixture as catalyst, at 40°C and reaction time of 3.5-4 hours (China Patent 1047854, 1990).

The one-step method for producing oxalic acid from starch claims 1.25 part oxalic acid for every part of the raw material starch. And that the consumption of nitric acid is 0.35-0.5 parts nitric acid for every part of oxalic acid produced (China Patent 1079731, 1993).

A recent development is to produce oxalic acid from sugar beet molasses by mixed nitric acid and sulphuric acid, where the sulphuric acid removes the water produced thus enhancing the reaction to give a good yield (Guru, et al, 2001).

It should be noted that the major by-products of oxalic acid synthesis are the oxides of nitrogen. The amount and type of oxides depend mainly on the strength of the nitric acid used. In any case the principle operating conditions that affect the yield of oxalic acid and the nitrous fumes are: reaction temperature, rate of nitric acid addition, rate of agitation, and the strength of nitric acid as well as the catalyst type.

EXPERIMENTAL WORK

Certain amounts of nitric acid and the catalyst as shown in **Tables (1) and (2)** were placed in a flask. The raw material, viz., dates fruit or dates syrup, was added gradually until the total desired amount was reached. During the addition, a violent reaction takes place with the evolution of nitrogen oxide gases. These gases pass through a condenser where they are collected as liquid at low temperature. At the end of the reaction, the amount of oxalic acid formed in the flask was filtered, dried and weighed.

RESULTS AND DISCUSSIONS

In the design of a batch liquid phase reactor, some of the design parameters must be available to the designer. These are: type and amount of reactants; in the present study these are the feedstock and the oxidizing agent nitric acid and the amount of the suitable catalyst (if required).
Thus, this study was set out to study those parameters affecting the synthesis of oxalic acid and the results are discussed below.

Feedstock

The results shows that using dates fruit required cumbersome purification operations to remove the skin, tissues and seeds of the fruit from the final oxalic acid product. Thus dates syrup was used where such problems do not arise. Sugar was also used as feedstock and the results showed that the yield of oxalic acid from dates syrup was 5 times greater than that obtained from sugar (Iraqi Patent 2688, 1997).

Amount of 67 wt.% Nitric Acid

For a given weight of dates, syrup feedstock (50g) and catalyst V_2O_5 (100g) increasing the amount of acid from 100 mls up to 300 mls, oxalic acid yield increased. However the yield increased dramatically from 100 mls to 150 mls nitric acid and the increase rate was lower at higher values and nearly leveled off at 250 mls nitric acid added. This effect is shown in **Table (1),** which also shows the concentration of the spent nitric acid. From these results, the best amount of nitric acid to be added under the prevailing conditions is 150mls.

Table (1) Effect of HNO_3 (67%) on the $H_2C_2O_4$ yield (Dates syrup 50 g, V_2O_5 100 mg)

HNO_3 (ml)	HNO_3 conc. post reaction (mol)	$H_2C_2O_4$ (g)
100	5.5	23
150	8.5	33
200	1.05	39
250	12.5	42
300	13.3	43

Amount of Catalyst

Table (2) shows the effect of the amount of V_2O_5 catalyst used on the yield of oxalic acid. It can be clearly seen that increasing the catalyst quantity, the yield was reduced. The highest value of the

yield obtained was at 25 mg catalyst, when using 50 g feedstock 150 gm nitric acid. This amount of nitric acid was obtained from the previous section.

Table (2) Effect of catalyst on the $H_2C_2O_4$ yield (Dates syrup: 50 g, 67% HNO3:150 ml.)

Catalyst V_2O_5 (mg)	HNO_3 conc. post reaction (mol)	$H_2C_2O_4$ (g)
25	9.0	51
50	9.0	35
100	9.1	31
150	9.1	29
200	9.1	21

Nitric Acid Concentration

Employing 98 wt.% nitric acid did not require the use of catalyst as compared to when employing the 67 wt% acid. Another difference observed is that the highly vigorous reaction with evolution of large amount of nitrous oxides. While the reaction was milder with less oxide gases using the 67 wt% weaker acid.

CONCLUSIONS

From the present study, these conclusions may be drawn :

1- Date syrup was a better feedstock than date fruit with respect to yield and quality of oxalic acid produced. And it is far better than sugar with respect to yield.
2- The optimum quantity of reactions and catalyst are as given in the ratio of 50 g: 150 ml: 25 ml date syrup: nitric acid: catalyst.
3- No catalyst was needed when using 98 wt% nitric acid.
4- larger quantities of nitrous oxides were obtained when using the 98% nitric acid compared to the 67 wt.% acid.

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