COMPARATIVE ANALYSIS OF OXALIC ACID PRODUCED FROM RICE HUSK AND PADDY

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ABSTRACT

In this research work, comparative analysis of Oxalic acid produced from Rice husk and Paddy was carried out in order to ascertain which waste sample produced a better yield. Nitric acid oxidation of carbohydrates was the method adopted in the production. The variable ratios of HNO_3:H_2SO_4 used were 80:20, 70:30, 60:40, and 50:50. The variable ratio of 60:40 gave the maximum yield and at a maximum temperature of 75^{o}C. Rice husk sample gave a percentage yield of 53.2, 64.4, 81.0, and 53.3 at temperatures of 55 ^{o}C, 65 ^{o}C, 75 ^{o}C, and 85 ^{o}C respectively. In the case of paddy a percentage yield of 53.1, 64.0, 79.9, and 52.8 at temperatures of 55 ^{o}C, 65 ^{o}C, 75 ^{o}C, and 85 ^{o}C were obtained respectively. The plots between yield and temperature at different variable ratios illustrate the dependence of yield on temperature, which was similar to a parabolic relationship and the peak value (yield) was at 75 ^{o}C above which it decreased. The properties of oxalic acid from both sources were very close and compared favourably with literature. In comparing the yield, oxalic acid produced from Rice husk gave higher yield than that from Paddy.

Keywords: Rice husk, paddy, oxalic acid, temperature, properties acid ratio and yield.

1.0 INTRODUCTION

Oxalic acid, $C_2H_2O_4$, or ethanedioic acid, molecular weight 90.04g/mol, is the simplest of the dicarboxylic acids (Kirk-Othmer, 1981). The anhydrous form is odourless, hygroscopic, and white to colorless. Oxalic acid is available commercially as a solid dihydrate, $C_2H_20_4$. $2H_20$, molecular weight 126.07g/mol (Sulberg, 2009). Oxalic acid can be manufactured using cellulosic materials, usually waste products such as sawdust, grain hulls, and others (kirk-Othmer 1981).The raw materials used in this work are Rice husk and Paddy. Rice (*Oriza sativa*) belong to the class of cereals. Rice that still contains it husk is called Paddy. These are harvested directly from the nursery, winnowed and milled to produce rice. The waste obtained during milling is called rice husk. These rice husks are usually dumped at a site as waste materials which constitute nuisance to the environment. Some people burn then to generate steam for power, but this can lead to environmental air pollution.

However, the objective of this project is to determine the optimum yield of oxalic acid and its properties by comparing the yields and characteristics of the oxalic acids produced from Rice husk and Paddy. Furthermore, this will curb the wastefulness of husk and paddy, which will also abate the environmental decay. Thus the essence of the study is to convert waste into useful resources. Anhydrous oxalic acid has an appreciable vapour pressure, sublimation starts at a temperature somewhat below 100 ^{0}C and proceeds rapidly at 125 ^{0}C. Partials decomposition takes place before the acid melts at 185 ^{0}C -190 ^{0}C, and its decomposition products include formic acid, carbon monoxide, carbon dioxide, and water. Dehydrating agents, such as sulphuric acid, accelerates the thermal decomposition of all forms of the acid. The anhydrous acid is quite soluble in anhydrous ethyl ether, 23.6 g per 100 g of solvent, while, the corresponding value for the dihydrate is 1.47 g per 100 g. Anhydrous oxalic acid may be crystallized from warm nitric or sulphuric acid (Sullivan, 2001).

Table 1: Physical and chemical properties of oxalic acids (http://webbook.nistgov)

Property	Values
Oxalic acid, anhydrous $(COOH)_2$	
Melting point, ^0C	187.0
Specific heat, cal/g, solid range, -200 to $+50^0c$	Cp=0.259 + 0.00076t
Heat of combustion, kcal, mole	60.1
Heat of formation at 18^0c, kcal/mole	195.36
Heat of solution in water, KJ/mol	-9.58
Heat of sublimation, Kcal, mole	21.65
Heat of decomposition, kcal/,mole	197.60
$Watt/cm^2$ ($^0c/cm$)	$9.0x10^{-3}$
Ionization constant, K1	$6.5\ x10^{-2}$
K2	$6.0x10^{-5}$
Coefficient of expansion at 25^0c,m/(kg^0c)	$1.784x10^{-4}$
OXALIC ACID, DIHYDRATE, $(COOH)_2.2H_20$	
Melting point ^0C	101.5
Density g/ml	1.653
Refractive index	1.475
Heat of solution (in water,),KJ/mole	-35.5

Oxalic acid can be manufactured by four general methods depending on the nature of raw materials (Kirk-Othmer, 1981). These methods are: alkali fusion of cellulose, fermentation process for carbohydrates, synthetic process from formates, and oxidation by nitric acid. For the oxidation of nitric acid, carbohydrate such as sugar, cellulose are oxidized with concentrated nitric acid with vanadium catalyst (Greenwood and Earnshaw, 2007). Among these methods, the latter two have been considered important for the commercial production of oxalic acid. However, the most widely acceptable commercial method for the manufacture of oxalic acid is nitric acid oxidation. The others have become obsolete and/or uneconomical.The potential production of oxalic by the nitric acid oxidation of waste cellulosic materials has long been recognized (Kirk-Othmer, 1981). Numerous patents and papers concerning this process have appeared in the literature and temperature range of 66-75^{0}C.The oxidation of saw dust with fuming nitric acid, ammonium vanadate catalyst(0.003%) temperature of 70-75^{0}C and a reaction time of 2 hrs resulting in a yield of 85 % of oxalic acid dihydrate have been reported (Boat,1926; Iyoti, 1988 http://pubs.acs.org/). Most of these processes involved prior hydrolysis of the cellulosic materials to produce a glucose solution, which in turn is oxidized in a nitric acid or a nitric acid/sulphuric acid medium according to equation 1.

$$C_6H_{12}0_6 + 6HN0_3 \longrightarrow 3H_2C_20_4 + 6NO + 6H_2O \ldots\ldots\ldots(1)$$

However, nitric acid is capable of affecting the simultaneous hydrolysis and oxidation of solid cellulosic materials according to equation 2 (Weast, 1980).

$$(C_6H_{10}0_5)_X\ H_20 + (x\text{-}1)\ H_20 + 6xHNO_3 \longrightarrow 3xH_2C_20_4 + 6xN0 + 6xH_20 \ldots\ldots.(2)$$

In order to make the process economically viable it is necessary to recover the oxides of nitrogen produced during the reaction. Sullivan , 2001 have investigated that nitric acid and mixed nitric acid/sulphuric acid (a variable ratio of nitric acid and sulphuric acid) in the oxidization of various cellulosic materials (wastes paper, wheat straw, ground oats, and sawdust) to produce oxalic acid. Oxalic acid is use in the processing of phosphate rock and as an intermediate in the production of oxamide, a potentially valuable source of nitrogen fertilizer. Oxalic acid's main applications include cleaning or bleaching, especially for the removal of rust (iron complexing agent). About 25% of produced oxalic acid is used as a mordant in dyeing processes. It is used in bleaches, especially for pulpwood and also used in baking powder (Wilhelm and Minoru, 2002). Oxalic acid is also an important reagent in lanthanide chemistry. Hydrated lanthanide oxalates form readily in strongly acidic solutions in a densely crystalline, easily filtered form, largely free of contamination by nonlanthanide elements. Lanthanide oxalates is importantly useful in commercial processing of lanthanides, and are used to recover them from solution after separation. After thermal decomposition and oxalate combustion, lanthanide oxalates convert to the oxides, which are the most common form in which they are marketed. Oxalic acid is used in the restoration of old wood. Its reducing properties are used in platinotype, the early photographic platinum/palladium printing process. Oxalic acid is also used for cleaning 'grubbiness' from dirty leather to get back to the flesh of the leather, before reintroducing preservatives. It is used in the cleaning of fiberglass boat hulls to remove water and tannin stains.

In humans, oxalic acid has an oral LD_{Lo} (lowest published lethal dose) of 600 mg/kg. The main toxicity of oxalic acid is due to kidney failure, which arises because it causes precipitation of solid calcium oxalate (the main component of kidney stones). Contact with oxalic acid can also cause joint pain due to the formation of similar precipitates in the joints. Oxalic acid can also be ingested indirectly in the form of ethylene glycol. In the body, ethylene glycol is metabolised (i.e., degraded) to oxalic acid. Use of the alternative antifreeze compound propylene glycol avoids this hazard (Safety Officer in Physical Chemistry , 2009).

2.0 MATERIALS AND METHOD

The materials used in the experiment are as follows: Rice husk, Paddy, H_2S0_4- Tetraoxosulphate (vi) acid (98%), $HN0_3$- Nitric acid (68%), 250 ml Beakers, Manganese (catalyst), Oven, Distillation apparatus, Electric weighing balance, Centrifuge, Test tubes, Spatula, 500ml Measuring cylinder, Sieve, Grinder, Thermometer, Fume cupboard, Refractometer, Heating mantle (Electro mantle), Funnel, pour point beaker and pH meter.

The samples (Rice husk and paddy) were screened and sieved to remove unwanted materials like stone, weeds, sticks, straws, dead seeds, dust, etc. The sieved rice husk and paddy were charged into the oven for drying at a of temperature of 70 ^{0}C to evaporate moisture for 24 hrs. The dried paddy was ground to reduce particles size to 100μm, which increased surface area.

All instruments/apparatus were washed with distill water and dried. 10 g of rice husk was weighed using electric weighing balanced. The sample was poured in a distillation apparatus. 50 ml of H_2SO_4 (98%) and $HN0_3$ (68%) was measured respectively using measuring cylinder and both were emptied into the distillation apparatus. 0.5 g of manganese was added to speed-up the reaction and was heated in an electro mantle at a temperature of 55 ^{0}C,measured by a thermometer. The experiment lasted for 1.30 hrs and was conducted in a fume cupboard. At the end, colourless liquor was obtained, which was allowed to cool for 2 hours and then transferred into a centurion centrifuge to enhanced crystallization. The centrifuge was set at 3500 rpm for 15 minutes. At the elapse of 15 minutes, crystals of oxalic acid were obtained. During the reaction, evolution of brownish gas was observed, which was suspected to be Nitrogen oxide (NO_x).

This procedure was repeated for various $HN0_3$:H_2SO_4 ratios and with same gram of catalyst, and the same step was adopted for Oxalic acid from Paddy. The Oxalic acid produced from each feedstock was characterized to determined its density, melting point, flash point, refractive index, solubility in water, pH and concentration etc.

3.0 RESULTS

The following Tables were results obtained from the experimentation.

Table 2: Yields of Oxalic acid produced from Rice husk at varying temperatures and acid variables.

Variable HNO_3:H_2SO_4	% Yield at different temperatures			
	55^{o}C	65^{o}C	75^{o}C	85^{o}C
80:20	52.4	63.4	79.0	52.0
70:30	52.7	63.8	79.6	52.7
60:40	53.2	64.4	81.0	53.3
50:50	53.0	64.0	79.9	53.0

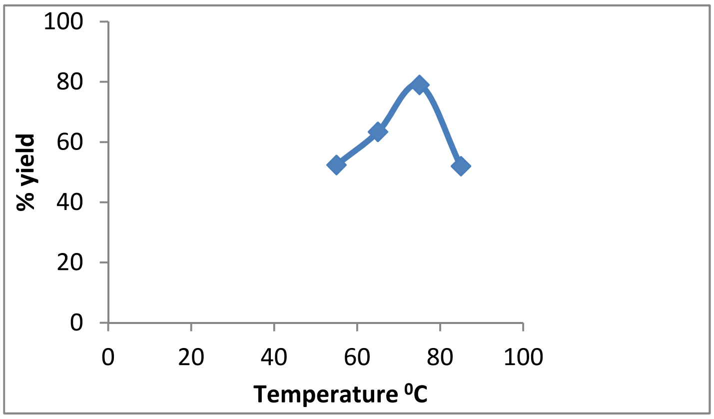

Figure 1:Yield of Oxalic acid from Rice husk with temperature at acid ratio 80:20

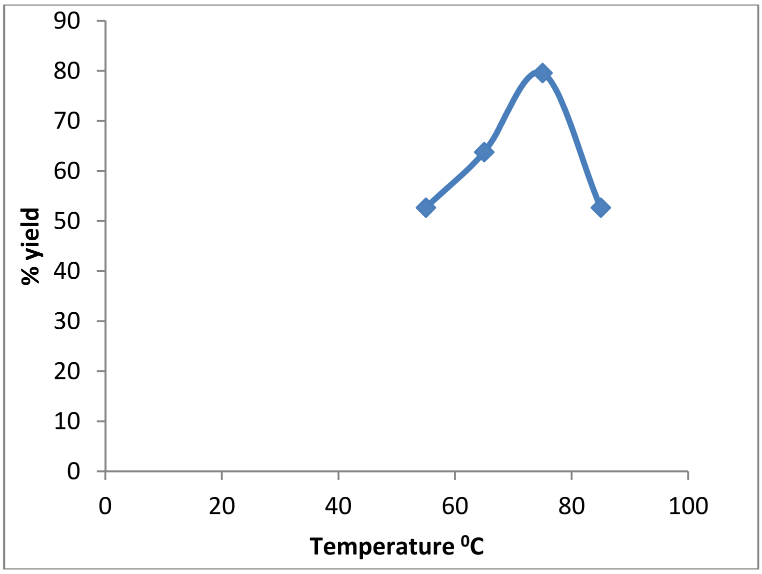

Figure 2:Yield of Oxalic acid from Rice husk with temperature at acid ratio 70:30

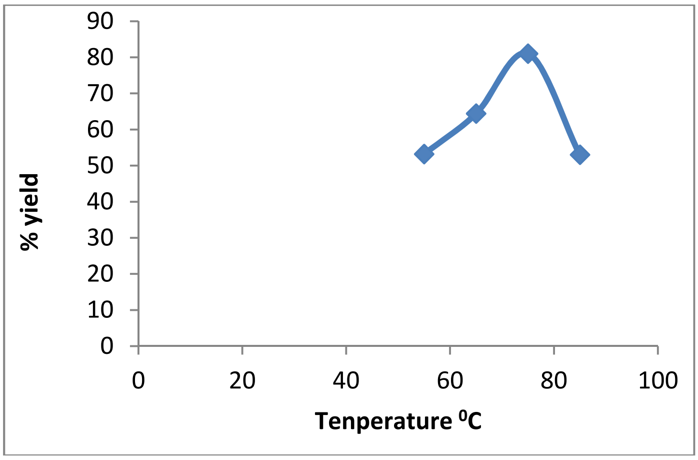

Figure 3:Yield of Oxalic acid from Rice husk with temperature at acid ratio 60:40

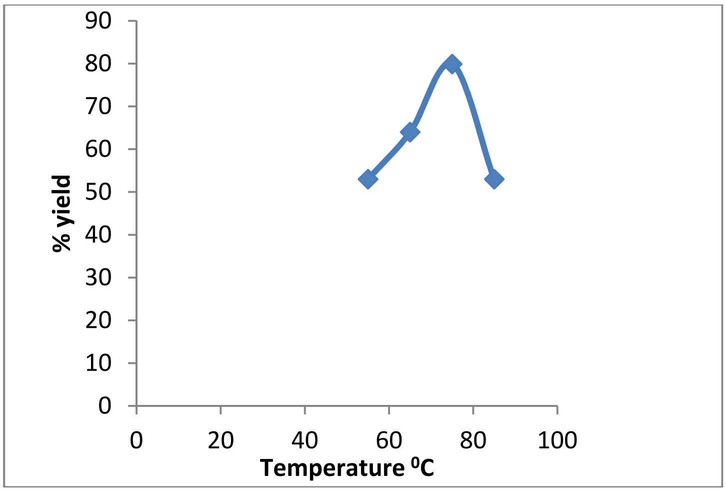

Figure 4:Yield of Oxalic acid from Rice husk with temperature at acid ratio 50:50

Table 3: Yields of Oxalic acid produced from Paddy at varying temperatures and acid variables.

Variable HNO_3:H_2SO_4	% Yield at different temperatures			
	55°C	65°C	75°C	85°C
80:20	52.2	63.0	78.9	51.5
70:30	52.6	63.3	79.0	52.0
60:40	53.1	64.0	79.9	52.8
50:50	52.8	63.7	79.4	52.7

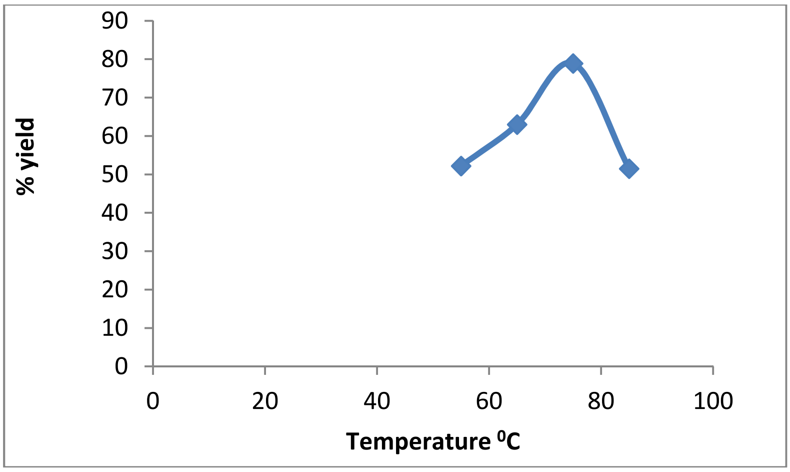

Figure 5:Yield of Oxalic acid from paddy with temperature at acid ratio 80:20

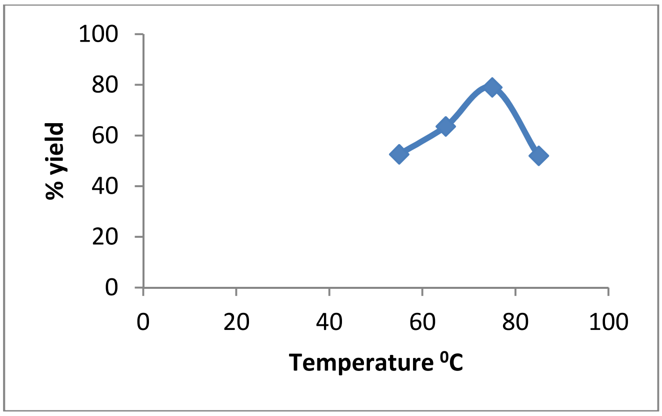

Figure 6:Yield of Oxalic acid from paddy with temperature at acid ratio 70:30

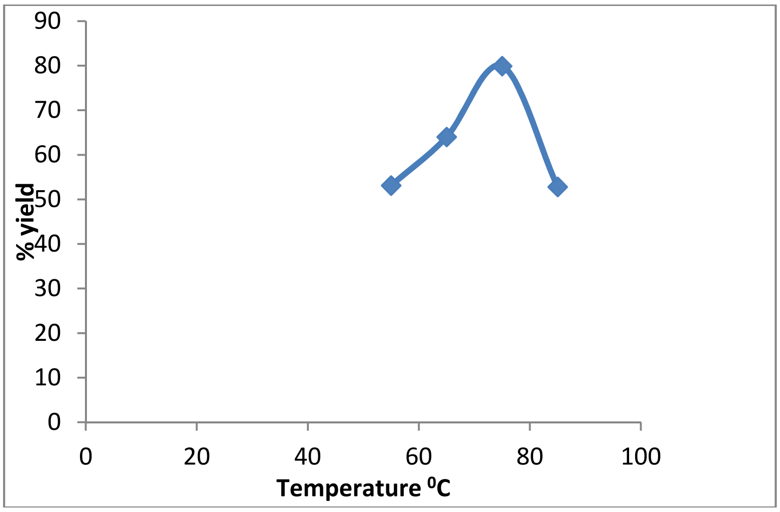

Figure 7:Yield of Oxalic acid from paddy with temperature at acid ratio 60:40

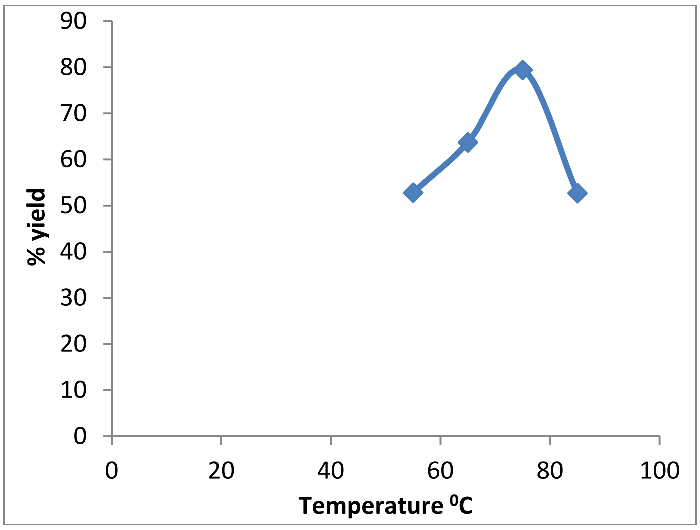

Figure 8:Yield of Oxalic acid from paddy at acid ratio 50:50

Table 4: Properties of Oxalic acid Produced from Rice Husk

Molecular formula:	$C_2H_20_4$:$2H_20$ (dihydrate)
Molar mass:	126.07 g/mol
Appearance:	white crystals
Density:	1.640 g/cm^3
Melting point:	102.5 ^{0}C
Concentration:	0.05 M
Solubility in water:	11 g/100 ml (25^{0}C)
	90 g/100 ml (100^{0}C)
Flash point:	168 ^{0}C
pH:	0.89
Refractive index:	1.49

Table 5: Properties of Oxalic acid Produced from Paddy

Molecular formula:	$C_2H_20_4$:$2H_20$ (dihydrate)
Molar mass:	126.07 g/mol
Appearance:	white crystals
Density:	1.633 g/cm^3
Melting point:	101 ^{0}C
Concentration of Oxalic acid:	0.05 M
Solubility in water:	9.5 g/100 ml (25^{0}C)
	82 g/100 ml (100^{0}C)
Flash point:	162 ^{0}C
pH:	1.1
Refractive index:	1.52

4.0 DISCUSSION

The result of the comparative analysis of oxalic acid from rice husk and paddy are represented Tables 2-5 The yield at various temperature and acid ratios for oxalic acid from both materials used in this study are shown in Tables 2 and 3 respectively. The values obtained revealed that yield increases with temperature to an maximum temperature of 75 ^{0}C and decreases at acid ratio 80:20.At 55^{0}C and 85 ^{0}C,the yield for acid ratios 80:20,70:30,60:40 and 50:50 are approximately the same for oxalic acid from rice husk (Table 2). A maximum yield of 81.0 % oxalic acid from rice husk was obtained at acid ratio 60:40 at 75 ^{0}C as shown in Table 2 and Figure 3 A similar trend of yield with temperature at various acid ratio are shown in Figures 1,2 and 4 for rice husk. From Table 3 and Figure 7, maximum yield of oxalic acid from paddy was 79.9% at the same operating conditions for rice husk. The yield obtained at 55^{0}C and 85^{0}C are also very closed as observed in rice husk (Table 3 and Figures 5,6 and 8).However, at 85 ^{0}C there was a decrease at all acid ratios. The observation was that yield increases with decrease in acid ratio. The lowest yield occurred at acid ratio 80:20 and 85 ^{0}C for both rice husk and paddy.

By comparing the properties of oxalic produced from both raw materials used (Tables 4and5), the values were very close. The appearance, density and melting point are the same. Oxalic acid from rice husk exhibit slightly more solubility, flash point and pH of 1.1g/100ml (25 ^{0}C); 99g/100ml (100 ^{0}C), 168 ^{0}C and 0.89 respectively. But that from paddy are solubility 95g/100ml (25 ^{0}C); 82g/100ml (100 ^{0}C), flash point 162 ^{0}C and pH 1.1. The refractive of the oxalic acid from rice husk and paddy are 1.49 and 1.52 respectively. These properties compared farvourably with those in literature. The percentage yield in Tables 2 and 3 were represented graphically in Figures 1-8. At temperature range of 55-85 ^{0}C,the percentage amount of oxalic acid from rice husk and paddy does not show appreciable variation; though a little higher in rice husk. Also the percentage yield and temperature plot is similar to a parabolic relationship whose maximum was 75^{0}C above which the yield decreased (Figure 1 to 8). Thus, it is pertinent to state that rice husk is a better feedstock for the production of oxalic acid in comparison with paddy. The maximum conditions of temperature 75^{0}C and acid ratio ($HN0_3$:H_2SO_4) 60:40 is recommended based on this research findings.

5.0 CONCLUSION

In this work, comparative analyses of oxalic acid from two samples (Rice husk and paddy) were carried out in order to ascertain which sample produced a better yield. Nitric acid oxidation of carbohydrates was the method applied in carrying out these analyses. The variables ratio of $HN0_3$:H_2SO_4 that gave the maximum yield was 60:40 and at a maximum temperature of 75^0C. Rice husk source appeared to be better as shown in the results, but paddy is also a good source of oxalic acid. The use of these materials will minimize environmental pollution

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