

# ACID HYDROLYSIS TREATMENT OF NUTMEG SHELL WASTE

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## ABSTRACT

*Milled nutmeg shell waste was treated with three selected acids. These were Nitric, Sulphuric and Hydrochloric acids. The nitric acid oxidation of the shells to Oxalic acid was facilitated by the usage of a Vanadium Pentoxide catalyst. Azeotropic hydrochloric acid vapour hydrolysis was used in the HCl hydrolysis of the material to simple sugars. Varying concentrations of Sulphuric acid were used for the Sulphuric acid hydrolysis to simple sugars. These sugars can in turn be fermented to produce ethanol for fuel purposes. Lignocellulose provides a basis for the extensive development of a new biotechnology for the production of chemicals and fuels. Nutmeg shell waste is one such material that is readily available in Grenada, a West Indian country.*

*The better yields of oxalic acid were in the region of 42%. Conditions favouring this type of yield were a reaction time of two hours and an acid to sample ratio of 8:1. Temperatures above 80°C are not recommended as the yields decrease considerably. The nitric acid recovery was 39% of initial nitric acid.*

*The maximum Hydrochloric acid saccharification of 24% was better than that of the Sulphuric acid saccharification process (19%). A typical packed bed biomass reactor was used in the hydrochloric acid conversions. Technologically, HCl hydrolysis is the more promising.*

## 1.0 INTRODUCTION

The Nutmeg plant (*Myristic fragans*) was introduced into Grenada in 1843. Nutmegs have become the premier export crop of Grenada. Processing involves the drying and cracking of the seeds to liberate the kernels. These shells are normally waste materials which can pose problems in disposal. Some 1,800

tonnes of shelled nutmegs were produced in 1980 (1). Studies are currently underway in the use of these shells for energy purposes. This work investigates the potential of these shells as a raw material for hydrolysis processes. The industry in Grenada provided the shells for these investigations. The purpose was to look at the production of more value added products from nutmeg shells.

It may be noted that the factors which influence the hydrolysis process are of two principal types viz:

1. Factors inherent to the process which include;
  - (a) The equipment used.
  - (b) The general operating conditions (temperature, pressure, etc.)
  - (c) The type of acid being used and its concentration.
2. Factors independent of the process which include;
  - (a) The material being hydrolysed.
  - (b) Factors which may be used to enhance the yields from hydrolysis processes (the use of ultra-sound).

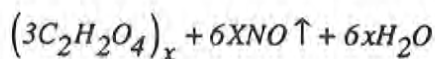
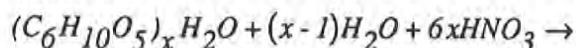
Crystalline or amorphous cellulose and hemicellulose can all be hydrolysed to their component sugars. If high temperatures and dilute acids are utilised, the product sugars may undergo degradation into furan compounds and tars. Low temperature and concentrated acids can produce higher sugar yields as a result of the conversion of crystalline cellulose into an amorphous form, which is readily hydrolysable.

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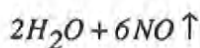
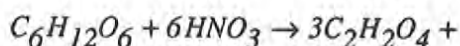
## 1.1 Acid Hydrolysis Processes

### 1.1.1 Nitric Acid Hydrolysis

Oxalic acid may be produced by nitric acid treatment of carbohydrates such as glucose, sucrose and starches. The choice of carbohydrate material depends on availability, economics and process operating characteristics. Nutmeg shells as a waste material is readily available in Grenada and was therefore considered to be a suitable raw material for this investigation. This material had not been previously investigated. Sugar was used by Deshpande (1) to produce oxalic and tartaric acid. Kothalkar (2) treated tuvar sticks in conjunction with Nitric/Sulphuric acid mixtures at 75°C in the presence of the catalyst Vanadium pentoxide. Yields of oxalic acid were in the region of 44%. Prabhu (3) used *Eucalyptus* hybrid bark and obtained a yield of oxalic acid between 40 - 45% at reaction temperatures of 75 - 80°C. Bailey (4) reported a yield of 85% oxalic acid at 60 - 64°C with Ammonium vanadate as catalyst. Mane (5) developed a method for the production of oxalic from sugarcane trash, groundnut shells, corn cobs and rice husks. A possible mechanism for conversion is that cellulose is first converted to glucose, which in turn is oxidised to Oxalic acid. A similar mechanism for hemicellulose is proposed. Braum (6) has postulated that the lignin molecule is hydrolysed to give a hydroxy propanol group. This group then undergoes condensation to yield an isoeugenol. This compound then undergoes oxidative cleavage of the double bond to give Oxalic acid.



The cellulose is hydrolysed to glucose and then oxidised.



### 1.1.2 Dilute Hydrochloric and Sulphuric Acid Hydrolysis

In general, dilute acid hydrolysis is conducted at acid concentrations of less than 2%, at temperatures between 160°C and 250°C, and at reaction times of less than one hour. The reaction of cellulose is a four-step sequence consisting of:

1. A rapid conversion of native cellulose to a stable hydrocellulose fraction.
2. A first order cleavage of the hydrocellulose to soluble polyaccharides.
3. A rapid hydrolysis of the soluble polysaccharides to simple sugars.
4. A first order decomposition to a degraded product.

The values of the kinetic parameters for the hydrolysis of cellulose are dependent on the type of acid used in the hydrolysis. For example, the rate of hydrolysis of Solka Floc (Delignified wood pulp) increases at a given molar concentration of acid in the order  $HCl > H_2SO_4 > H_3PO_4$  (7). The hemicellulose fraction is more rapidly hydrolysed than the cellulosic fraction and the soluble sugars is consequently limited by the loss of degradation products such as furfural, hydroxymethyl furfural, levulinic, formic and acetic acids. Yields of soluble sugars of no more than 65 - 70% are obtainable under isothermal conditions. Prolonged reaction times increases the decomposition of the soluble sugars.

Dilute sulphuric acid has formed the basis of several commercial processes. Sugar yields range between 55 - 72% of the hemicellulose and cellulose. Reducing sugar concentrations in the product streams prior to evaporative concentration vary between 4 - 6% (8).

### 1.1.3 Concentrated Acid Hydrolysis

These processes may be divided into two types (9):

1. Those with strong acids such as sulphuric, hydrofluoric or hydrochloric.

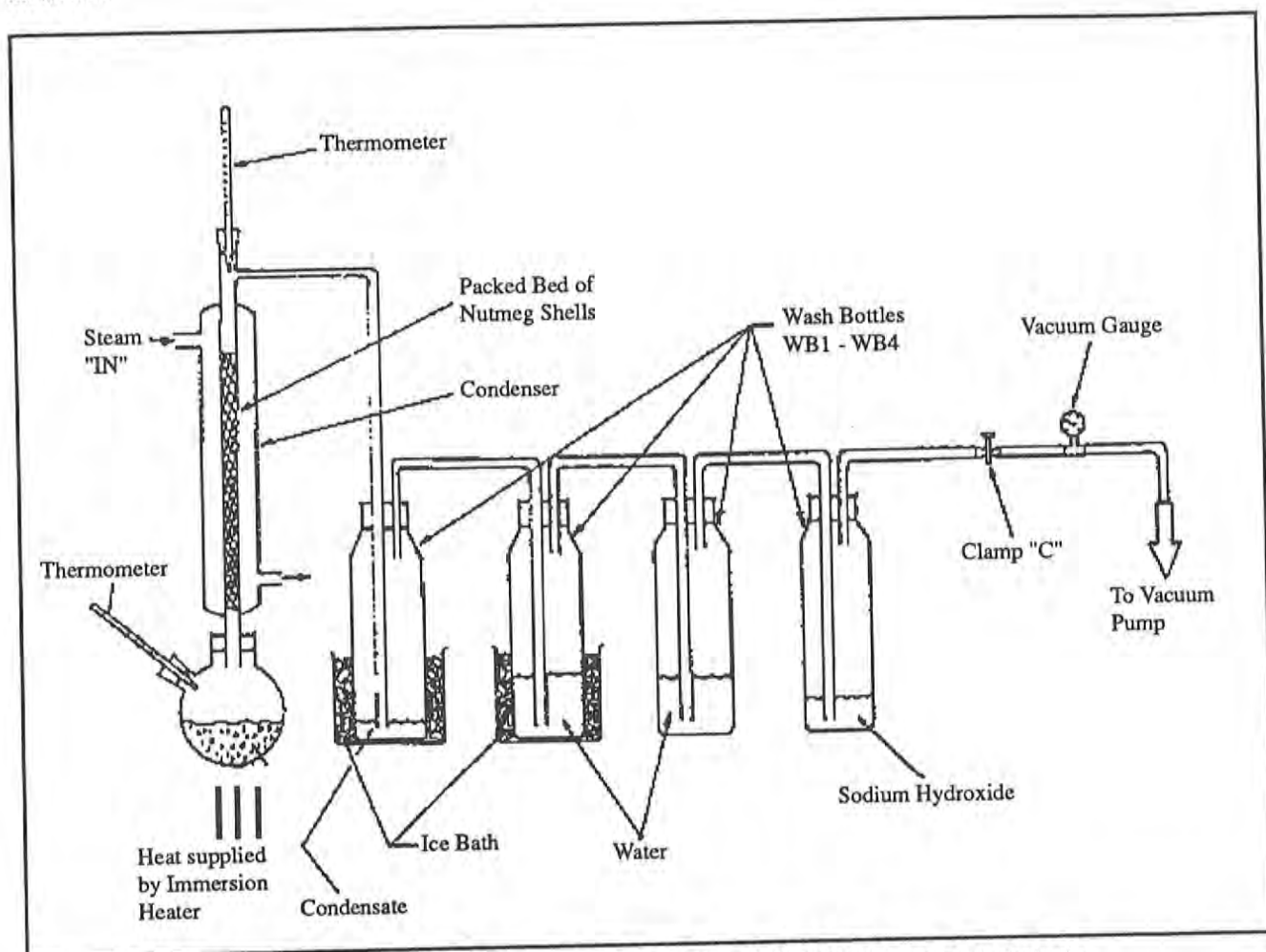


Figure 1: Schematic Diagram of Gas Phase 20.2% W/W HCl Vacuum Hydrolysis

2. Those with liquid organic acids such as acetic acid.

These processes are plagued by problems of corrosion and expensive acid recovery systems. Concentrated acid processes have the highest yield (80% or more of the available sugars), but suffer from high acid consumption (10).

Concentrated acid hydrolysis is conducted at more moderate temperatures (20 - 100°C), high acid concentrations (35% HCl; > 60% H<sub>2</sub>SO<sub>4</sub>) and for times varying between ten minutes and six hours. In a pilot scale, plant production of 10 - 12% obtained from agricultural residues (11). M. Ladisch (12) has outlined the various HCl processes available.

## 2.0 METHODOLOGY

### 2.1 Nitric Acid Hydrolysis

The method of Mane (5) was followed for the

hydrolysis of nutmeg shells. The acid to sample ratios were varied as well as reaction temperatures and times. The crystals obtained were purified by redissolving them and treating the solution with activated carbon. The mixture was then filtered. This was then evaporated under vacuum at 80°C. The concentrated solution was then cooled at 4°C. The pure crystals were separated by filtration. A standard chemical analysis was done to determine the purity of the oxalic crystals.

### 2.2 Hydrochloric Hydrolysis

The experimental procedure employed in the pre-hydrolysis of nutmeg shells, involved placing 100g of milled nutmeg shells in a jacketed reactor of the type shown in Figure 1, thus forming a packed bed. Steam was passed through the outer jacket of the reactor to maintain the reactor temperature. This process is similar to that used by Higgins (13) who compared the hydrolysis of cellulose by HCl between liquid and

gaseous phase processes. He used wheat straw, hulls and newspaper.

An azeotropic mixture of the Hydrochloric acid and water (20.2 wt% HCl) was heated to, and maintained at a temperature of 102°C using a heating mantle. A vacuum of sufficient magnitude to maintain the boiling temperature was then created by slowly closing clamp (C). This was initially open and connected via a T-junction to a vacuum pump as shown in Figure 1. Gauge (G) indicated the vacuum on the system. The vapour leaving the top of the column was passed through a series of four wash bottles. Wash bottle (WB1) enclosed in an ice bath was initially empty and served to condense as much as possible of the vapours leaving the reactor. Wash bottle (WB2) was also enclosed in an ice bath and wash bottle (WB3) originally containing 200ml distilled water each, served to condense as much as possible of the vapour not condensed in WB1. Wash bottle (WB4) initially containing 100ml of 0.5 Sodium Hydroxide was used primarily as a means of determining the unreacted acid.

After 15 minutes pre-hydrolysis time, the heating mantle and the bunsen burner were switched off and the clamp (C) slowly opened. The apparatus was then dismantled. The condensate from wash bottle WB1 was then taken and analysed for reducing sugars. The material in the column was removed with 300ml hot distilled water at 80°C. The resulting mixture was then vacuum filtered. The residue was oven-dried for 16 hours, weighed and stored. The filtrate was analysed for reducing sugars by the Layne-Eynon method. The mixture in wash bottle WB4 was titrated with 20.2 wt% HCl.

### 2.3 Sulphuric Acid Hydrolysis

Weighed samples of the ground shells were treated with measured quantities of 4.9% Sulphuric acid and heated under reflux for 45 minutes at 90°C. The mixture was filtered. The filtrate was retained and the residue was washed with distilled water. Washings were retained and the residue was vacuum dried at 100°C for 16 hours.

The pre-hydrolysis feedstock was treated with varying concentrations of Sulphuric acid for one hour at room temperature. The samples were then diluted to 8% wt. Sulphuric acid and heated under reflux for 10 minutes at 90°C. The slurry was vacuum filtered and the filtrate analysed for reducing sugars. The

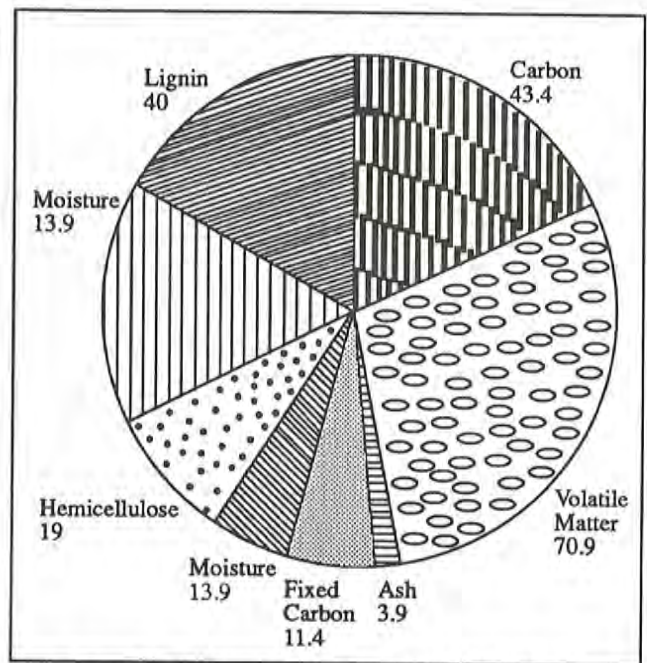


Figure 2: Proximate and Ultimate Analysis %

residue was dried at 75°C for 10 hours. This procedure was similar to that of Dunning (10).

## 3.0 RESULTS AND DISCUSSION

### 3.1 Raw Material Analysis

The analysis of the raw material is shown in Figure 2. This was done using standard ASTM methods. The shells were ground in a Wiley mill for fixed times. A typical sieve analysis of the particles used is shown in Figure 3.

### 3.2 Nitric Acid Hydrolysis

Results as shown in Figures 4 and 5 indicate that for the operating conditions, best results for the hydrolysis of nutmeg shells were as follows:

1. A reaction time of two hours.
2. A temperature less than 80°C.
3. An acid to sample ratio (W/W) of 8:1.

Under the above conditions, the yield was 42%. A similar result was obtained for work done by the author on coffee shells and guinea grass. Average yields for these various substrates were 43.6% and 36%

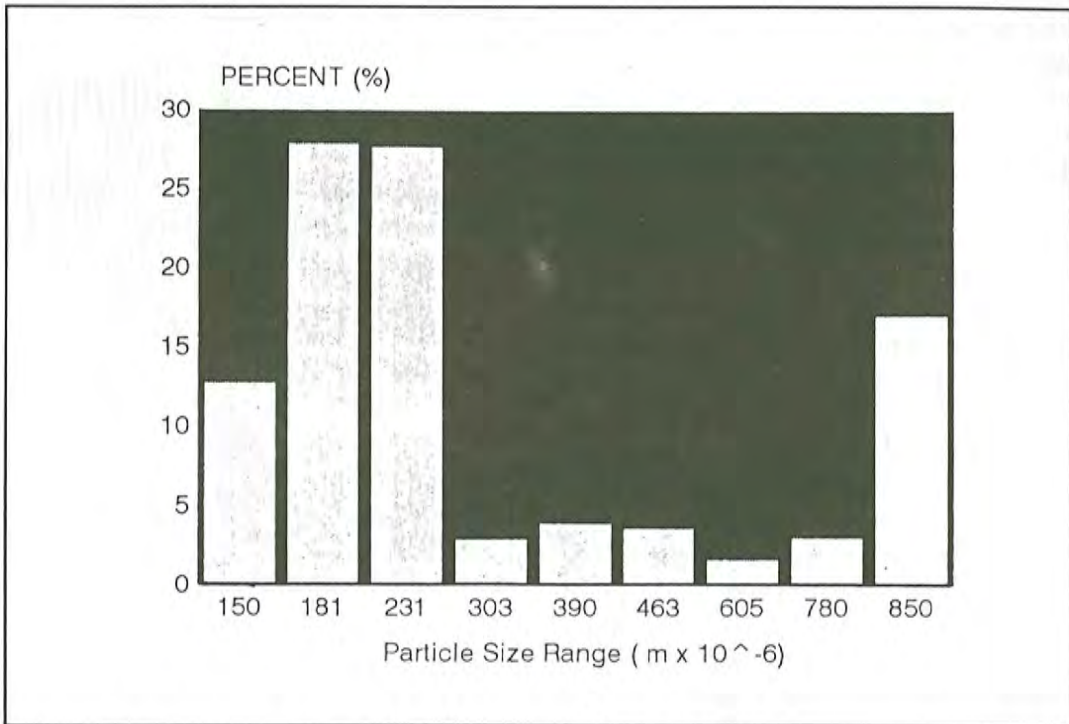


Figure 3: Nutmeg Shells Sieve Analysis Particle Size Distribution

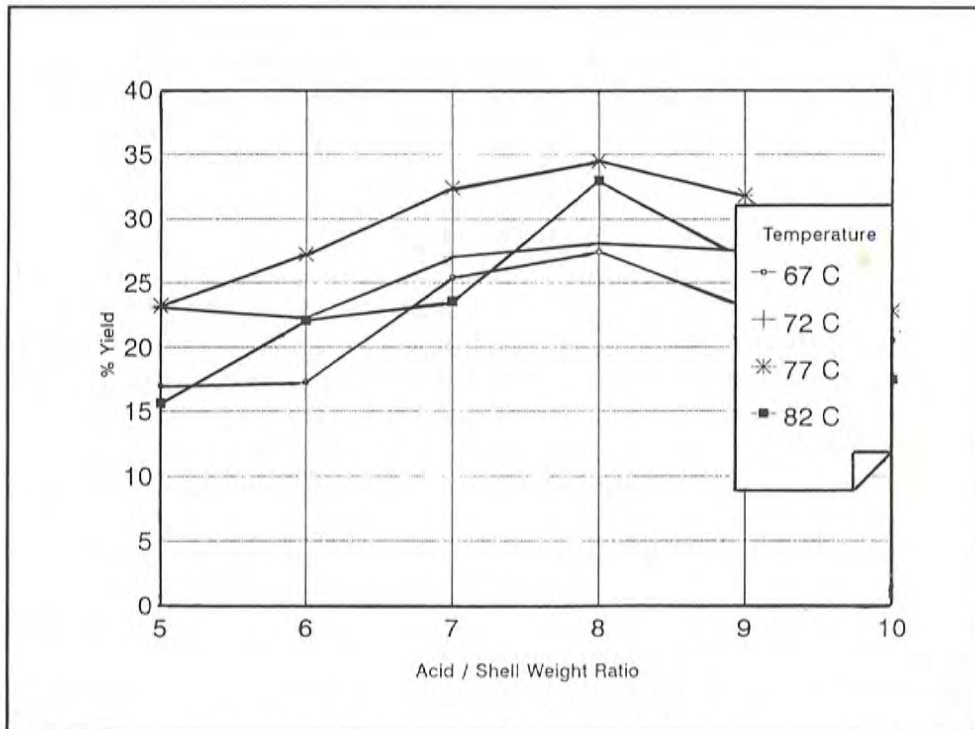


Figure 4: Percentage Yield of Oxalic Acid Hydrolysis Time 1 Hour

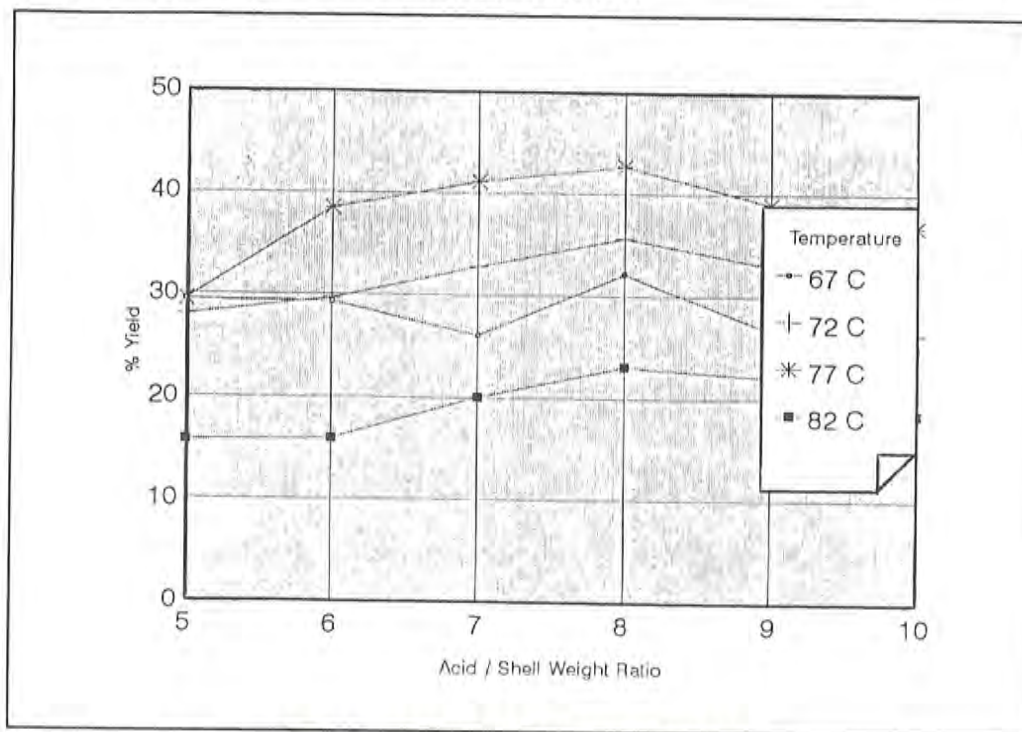


Figure 5: Percentage Yield of Oxalic Acid Hydrolysis Time 2 Hours

respectively. Such yields are comparable with that of Mane (6) who obtained yields of Oxalic acid of between 42.9% - 51.5% (W/W) using sugarcane trash as the preferred material. However, Mane's reaction times were for four hours. This may account for the yields in this case being at the lower end of the scale.

Dube et al (14) has shown that a type of grass grown in North India has proven to be a quite profitable raw material for Oxalic acid production, giving yields of 44.9%. Bailey (5) has reported yields of 85% for sawdust and fuming Nitric acid in the presence of 0.003% Ammonium vanadate at a ratio of 6:1. Such yields are unusual. He used the water sorption method. Finely powdered sawdust may have enhanced his yields.

At temperature values below 80°C, the yield increases. Beyond this, the yield decreased due possibly to the formation of degradation products such as carbon dioxide.

### 3.3 Prehydrolysis with Azeotropic HCl Vapour

A typical indication of the change in weight loss with time is shown in Figure 6. This shows a rapid increase followed by a levelling off. Higgins (13) obtained a

similar trend even though he operated at 50°C. The reducing sugars present in both filtrate and condensate are shown in Figures 7(a) and (b). The percentage reducing sugars has a maximum of 3.55. This was just below the values quoted by Ladisch (8). A maximum reducing content occurs at a reaction time of 30 minutes for the filtrate. The condensate shows a gradual increase with time for reducing sugar content. This is to be expected. Figure 8 shows how the reducing sugars per unit weight loss varies for condensate and filtrate. As expected, this showed only a gradual increase with time as this line should be close to horizontal.

The percentage saccharification defined as the ratio of the reducing sugars obtained to the hollocellulose (hemicellulose + cellulose) content expressed as a percentage. As illustrated in Figure 9, the saccharification closely follows the weight loss trend. This is a direct correlation. This indicated little sugar degradation as time increases at the azeotropic temperature.

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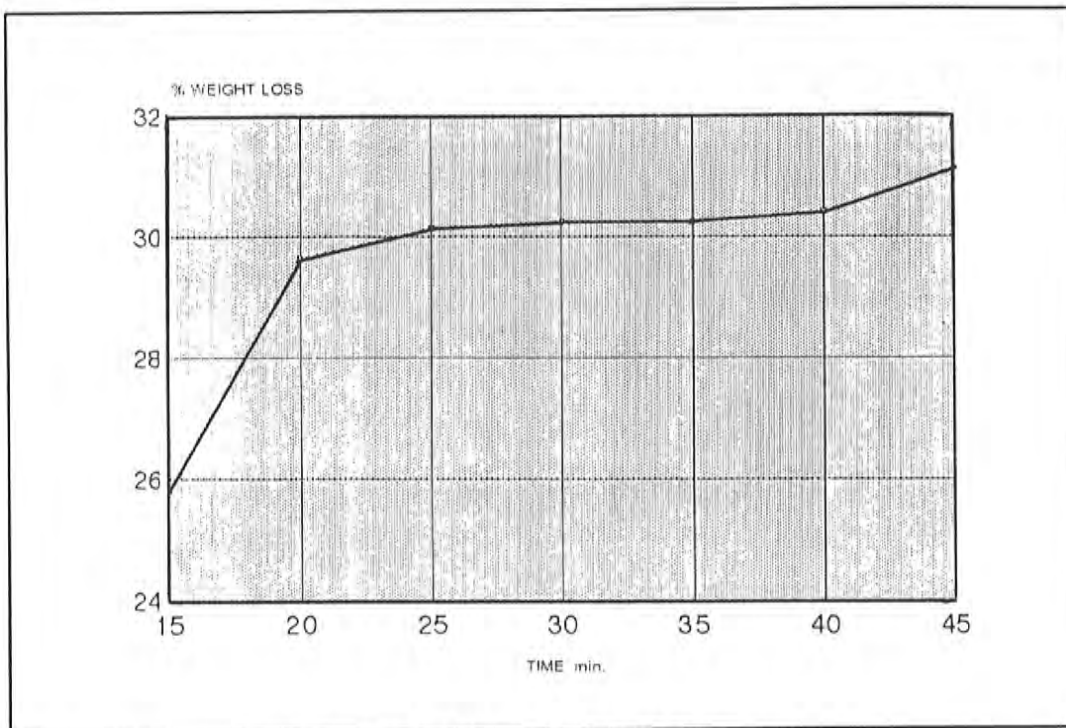


Figure 6: Pre-Hydrolysis 20.2% W/WHCl

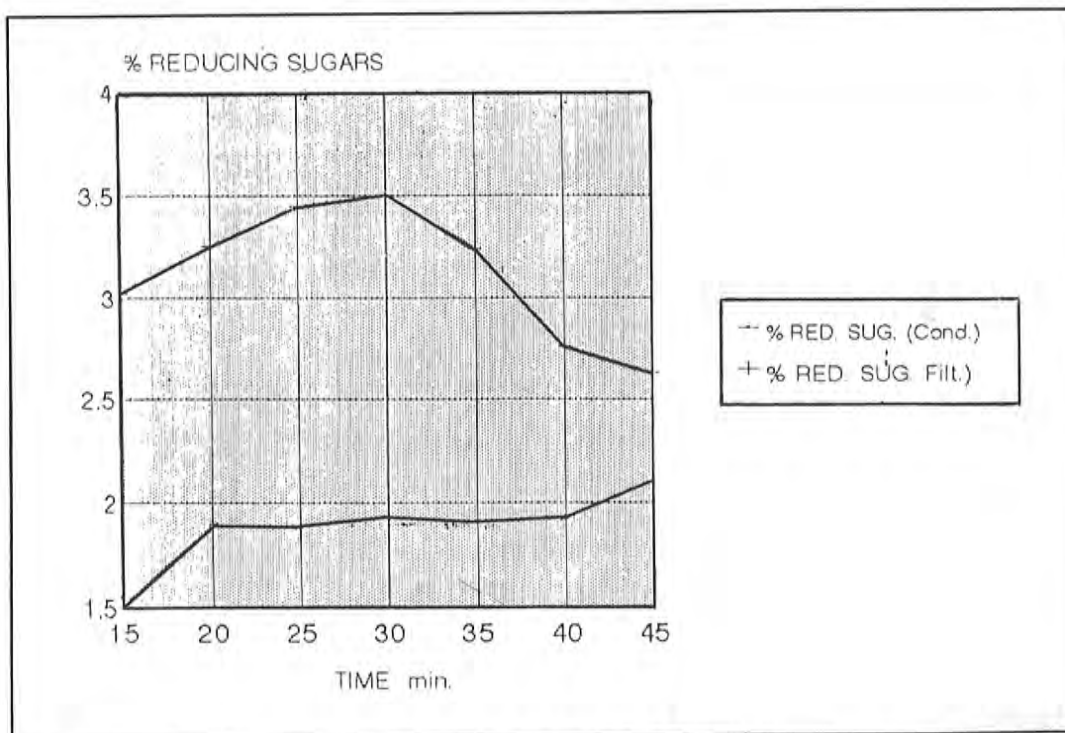


Figure 7: Pre-Hydrolysis 20.2% W/WHCl

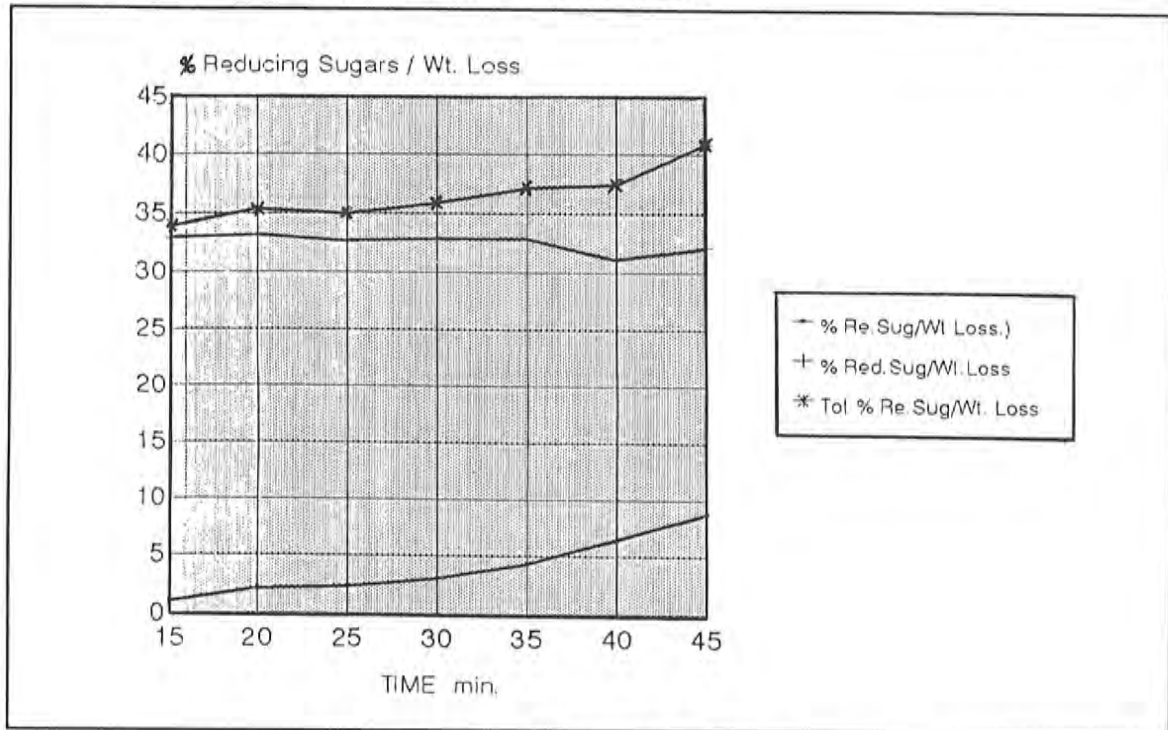


Figure 8: Pre-Hydrolysis 20.2% W/WHCl

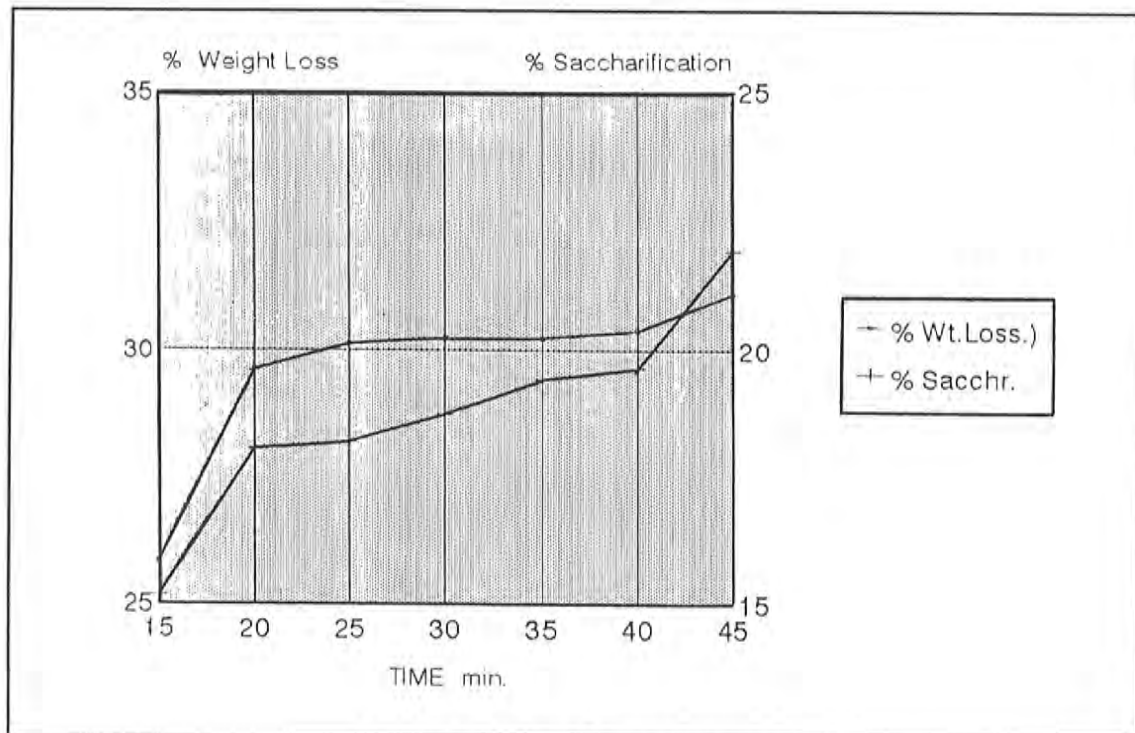


Figure 9: Pre-Hydrolysis 20.2% W/WHCl



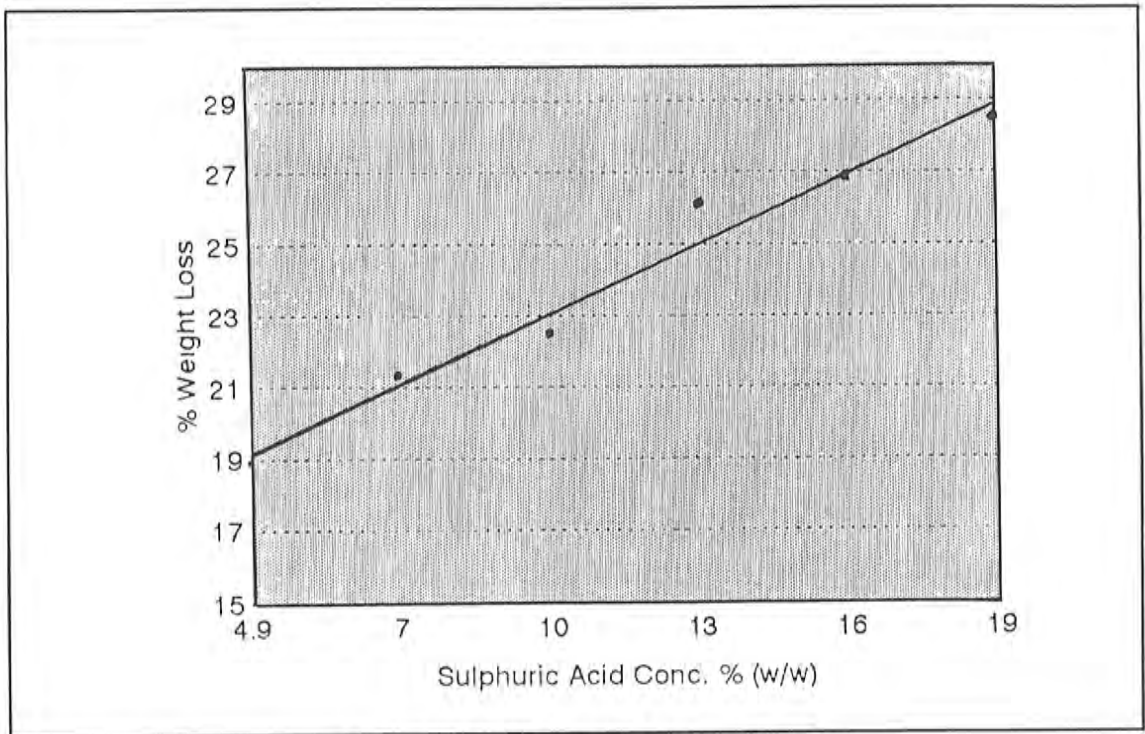


Figure 10: Pre-Hydrolysis Sulphuric Acid

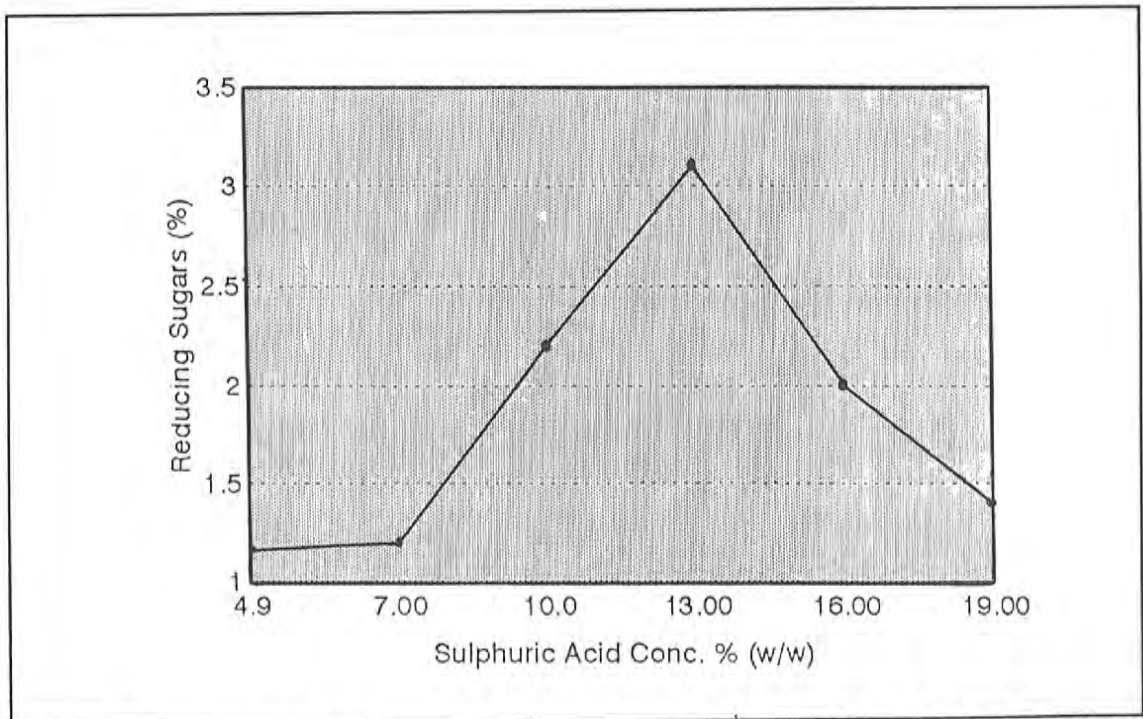


Figure 11: Pre-Hydrolysis Sulphuric Acid Filtrate Reducing Sug. vs. Acid Conc.

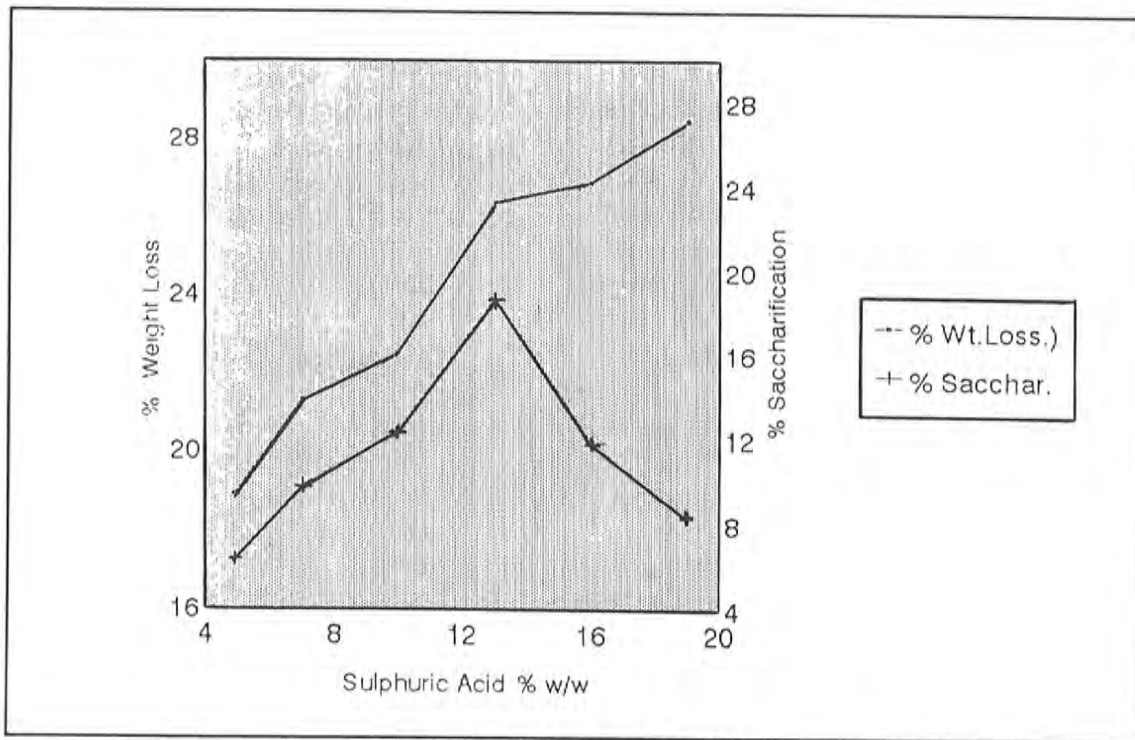


Figure 12: Pre-Hydrolysis (Sulph. Acid)

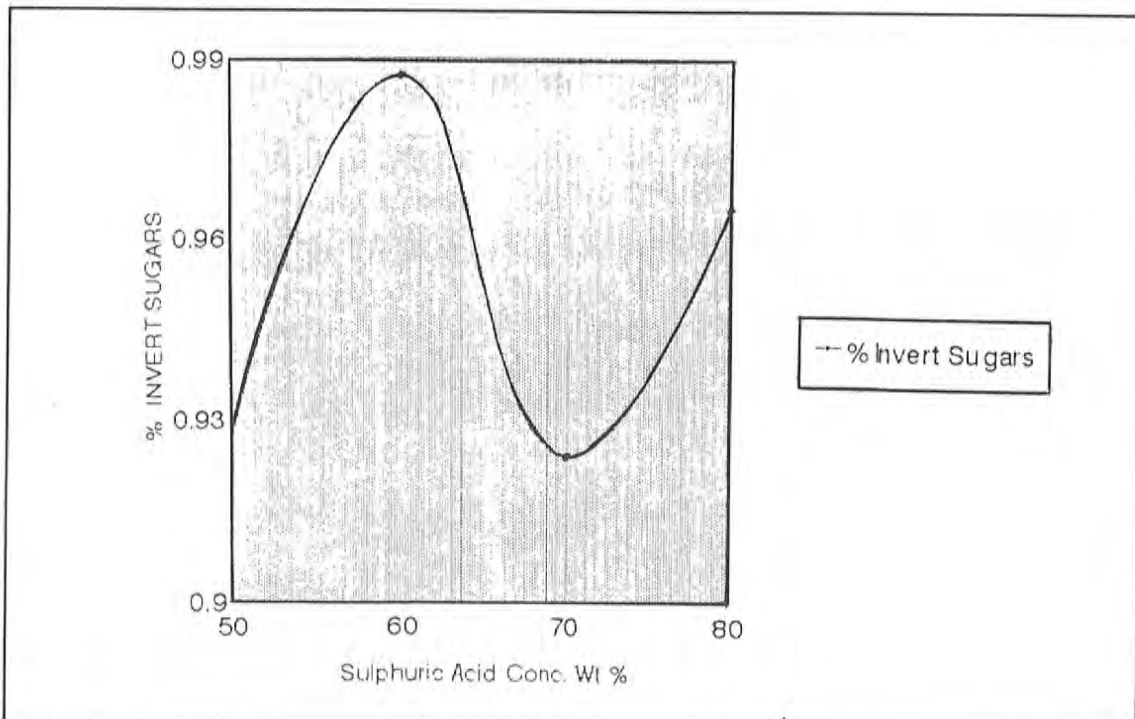


Figure 13: Acid Hydrolysis (Sulph. Acid)

### 3.4 Prehydrolysis with Varying H<sub>2</sub>SO<sub>4</sub> Concentration

As shown in Figure 10, the weight loss was found to increase linearly with increasing acid concentration. However, the reducing content reached a maximum at an acid concentration of 13% (Figure 11). This result was similar to that observed for related materials reported elsewhere (15). The maximum for these materials varied from 11% - 13%. At concentrations higher than these, there appears to be a breakdown of the reducing sugars into other compounds such as furfural.

A comparison between weight loss and saccharification is shown in Figure 12. Weight loss with increasing concentration continued even though saccharification decreased at the higher levels. It is evident that for higher concentrations of acid, there is significant degradation of the sugars. This is further supported by the fact that the brix (% Solids) of the filtrate showed a linear increase with increasing concentration even beyond 13%. Maximum saccharification values are around 19%. This is lower than the HCl prehydrolysis which gave saccharification values in the region of 24%.

The variation in reducing sugars with acid concentration is shown in Figure 13 for the concentrated acid hydrolysis of the prehydrolysed residue. This also shows a maximum around 60% concentration of Sulphuric acid. This was an inconclusive result indicating that more work has to be done in this area.

### 4.0 CONCLUSION

Nutmeg shells have potential to be converted into useful products such as Oxalic Acid and Fermentable Hydrolysates. An average yield of 42% Oxalic acid was obtained by Nitric acid oxidation/hydrolysis. This compares favourably with that obtained from other substrates. Percentage reducing sugars in hydrolysates of 3.5% also compares favourably with that found for other substrates, subjected to acid hydrolysis.

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