1. INTRODUCTION
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Carbohydrates constitute one of the most important group of natural products. They serve as a source of energy and also as a store of energy. Carbohydrates may be classified into two broad groups: Sugars and non-sugars or polysaccharides.

Polysaccharides have the properties typical of high polymers. Although they are tasteless, on hydrolysis, they yield many sweet monosaccharide molecules. The common and widely distributed polysaccharides correspond to the general formula \((C_6H_{10}O_5)n\), e.g., Starch, Cellulose etc. Other group of polysaccharides which are not so widely distributed in nature is the pentosans, \((C_5H_8O_4)n\). The important monosaccharides found in polysaccharides are glucose, xylose, and arabinose.

Xylose occurs in the form of the polymeric pentosans (xylan) which are the binding material of the fibres of cellulose in plants. Xylose is obtained by hydrolysis of pentosans from wood, straw, bran, oat hulls, sugar cane bagasse, cotton seed hulls, coconut shells, corn cobs etc. Later, xylose can be converted into XYLITOL, a product
sweeter than sucrose. The investigation has been undertaken with objectives to produce xylitol from corn cobs, which is an agricultural waste of no cost.

The corn cob contains about 38 to 40 percent xylan, a xylose polymer made up of D-xylose units, which can be converted to xylose (about 22 to 24 percent) by hydrolysis and then to xylitol (about 20 percent) by hydrogenation. (Table 1.1)

1.1 **IMPORTANCE OF XYLITOL:**

Several products that possess a low calorific value and are of dietetic value to the sufferers of diabetes have been proposed from time to time as artificial sweeteners. Saccharin known since 1879, has a sweetening power of about 400 times than that of glucose, but leaves a bitter metallic after-taste, which makes it objectionable to some users. It occupied a very prominent place in the market for sweeteners until the introduction of Cyclamates around the year 1950. The use of Cyclamates rose very rapidly until they were ordered off the market by the FDA in the year 1969 after indications were shown that they may induce bladder tumors.
Saccharin which is at present the largest selling artificial sweeteners, does not have any significant pharmacological effect and is not metabolized by the organism. Nevertheless, there is conflicting evidence that under certain conditions, it promotes cancer.

The fact remains that artificial sweeteners will continue to be needed by people who have to restrict their sugar intake. A possible candidate for this job can be XYLITOL (a penta alcohol obtained by the hydrogenation of xylose).

In European and American countries, the people are in habit of eating sugar made products, viz., confectionary and chocolates, due to which people suffer from tooth decay, dental caries, falling of teeth at early ages. This problem is due to sugar (sucrose). As per reports, if sugar is replaced by Xylitol, dental problems are not induced. Therefore, xylitol is a boon to those people who often suffers from dental problems.

1.2 **CHEMICAL STRUCTURES OF XYLAN, XYLOSE AND XYLITOL**

Details of chemical composition and structure of this hemicellulose fraction have since been discovered by
comparatively recent research which has, however, concentrated on the study of more homogeneous and purer substances such as araban, free xylan and these well characterized carbohydrate polymers are no longer classified with the hemicelluloses.

As more than 90 percent of hemicellulose (of sugar cane or corn cob) is composed of xylose, its polymer structure may be assumed to be essentially that of xylan, although the arabinose and glucuronic acid may be units of the polymer chains. The molecular weight of xylan is over 30,000 and it is not a long polymer chain of xylopyranose units, but rather consists of several shorter chains of some 40 units in length, linked to one another in a laminated structure, in the manner illustrated in figure 1.1. A xylose polymer is made up of D-xylose units, which can be converted to xylose by hydrolysis. Later xylose can be converted into xylitol by hydrogenation (Figure 1.1).

1.3 **NATURAL OCCURRENCE**

Natural and artificial sweeteners continue to be sought by people who have to restrict their sugar intake.
Possible candidates are the extracts from plants such as *Steviarebaudiana* and *Synepalum-dulcificum*, the dipeptide methyl ester L-aspartyl L-phenyl-alanine and the penta alcohol 'XYLITOL'.

Xylitol is a penta-valent alcohol (pentitol) of Xylose, a monosaccharide. It is a normal intermediary product of carbohydrate metabolism in man and animals and is also found in many fruits and vegetables, viz., Raspberries 268, Strawberries 362, Yellow Plums 935, Endives 258, Lettuce 131, Cauliflower 300, Spinach 107, Eggplant 180, Yellow Boletus Mushroom 128 mg per 100g. on dry basis respectively (A. Emodi, 1978). Extraction of xylitol from these sources, however, would not be economical, since the concentration of xylitol in plants is relatively low compared to the concentration of sucrose in sugar cane or sugar beets.

1.4 **PREPARATION OF XYLITOL:**

Xylitol can readily be prepared from xylose a by-product of agricultural wastes such as cotton seed hulls, rice husk, peanut shells, corn cobs, hard wood and sugar cane bagasse and prepared from plants that
contain xylan, the polymer of xylose (Table 1.1). Xylitol is prepared by hydrogenation of xylose. The xylitol is then purified and crystallized. Xylitol can also be made biologically by yeast fermentation but so far, only the chemical process has gained importance.

Corn cobs are the best source material overall if xylitol production is considered as an independent process. Corn cobs remaining after removal of corn (Maize) grains is a waste material which is presently used as a fuel. In India maize is an important cereal crop occupying fifth rank in being next to rice, wheat, sorghum and millets. In production it ranks fourth, while, in productivity it occupies third position. The normal maize is grown during kharif season in the eastern southern part of the country. Important corn products are corn flakes, starch, custard powder, dextrose etc. The annual production of corn is 9.07 million tonnes and corn cobs are near about 30 to 40 percent of total weight (Table 1.2 and Figure 1.2). Therefore the corn cobs are available in abundance and hence it can be exploited for the production of xylose and xylitol.
1.5 **UTILITY OF XYLITOL**

Xylitol is very soluble in water, 62.4 percent at 25°C. Its crystals resemble with those of sugar and it does not caramelize at elevated temperatures. It is a sweetener which is 20 to 25 percent sweeter than sugar (sucrose). Four hydroxyl groups should be free to participate in inter-molecular hydrogen bonding with the receptor site to give the sweet characteristics. In xylitol, four non-bonded hydroxyl groups have been tested and found to be sweeter than sucrose (Russo, 1976). It has no (or very little) insulin requirements, making it suitable for usage by diabetics (Lang, 1971).

It has a favourable effect on the fat balance of the body and does not elevate the sugar level in blood. It is non-cariogenic also.

It is realistic to expect only a relatively small future for replacement of sugar by xylitol. Health consciousness in the industrialized countries will, however, increase the demand for suitable sugar substitutes. The new alternative sweeteners are expected to be physiological substances (well tolerated, natural
or native identical). Their sweetnesses and tastes should be similar to those of sucrose as much as possible.

Diabetic patient should be able to consume them, when advised of their energy content, and they should not be cariogenic. In food processing, they should not pose unusual technological problems. Xylitol fulfills most of these requirements satisfactorily, which makes it not only a valuable alternative to sucrose and sucrose substitutes but also one of the few new discoveries in the field of foods today.

Xylitol's special characteristics, particularly its dental and metabolic aspects, justify its greater use. Consequently a realistic and useful application of xylitol in foods will be in confectionery and snack products, where the unique properties of Xylitol can be best utilized.

Xylitol is of special interest in as much as its chemical "back-bone" contains only 5- carbon atoms compared with 6- carbon back-bone of other saccharides and the sugar alcoholes. Xylitol is not utilized by most micro-organisms and products made from it are usually unaffected by microbial attack.
1.6 CARBOHYDRATE METABOLISM IN MAN:

Xylitol is a normal intermediate product of metabolism in man and animals. The earliest discovery of how pentitols are formed, was done by Hollmann & Touster (1956) who demonstrated the reduction of L-xylulose to xylitol by NADP linked system in mammalian liver. The formation of keto-pentoses in Candida utilis, an aerobic yeast, was shown by Horecker (1969) as a general indication of how polyols may arise (Figure 1.1).

Pentoses are produced by the pentose-phosphate pathway, either from glucose - 6-phosphate or from fructose - 6 - phosphate.

\[
\begin{align*}
\text{Glucose 6-P} & \quad \text{NADPH} \\
\uparrow \quad \uparrow & \quad \downarrow \\
\text{Fructose 6-P} & \quad \text{Gluconate 6-P} \\
\uparrow \quad \uparrow & \quad \downarrow \\
\text{Sedoheptulose 7-P} & \quad \text{Ribulose 5-P + CO}_2 \\
\uparrow \quad \uparrow & \quad \uparrow \quad \uparrow \\
\text{Xylulose 5-P} & \quad \text{Ribose 5-P}
\end{align*}
\]

The formation of ribose 5-phosphate and carbon dioxide from glucose 6-phosphate is an oxidative reaction, while that from fructose 6-phosphate is a non-oxidative reaction. In most cells, pentose phosphate is produced
by both reactions, since the oxidative pathway is insufficient to satisfy the needs for nucleotide synthesis. However, in mammalian cells much of the pentose phosphate for nucleic acid synthesis is produced through sedoheptulose 7-phosphate from fructose 6-phosphate (Horecker, et al. 1954); (Katz & Wood 1960); (Pontremoli et al. 1960). The pentose phosphate pathway is linked to the Embden Meyerhof Pathway (Conn & Stumpf 1972) at three points at the level of glucose 6-phosphate, fructose 6-phosphate, and glyceraldehyde 3-phosphate (Froesch & Jakob 1974).

A third pathway of carbohydrate metabolism was postulated by Touster et al. (1956) and Touster (1959), (1960), (1974). They were studying the conversion of L-Xylulose to D-xylulose via xylitol and elaborated the glucuronic acid pathway, which is converted to the pentose phosphate pathway metabolically by phosphorylation. Xylitol is converted to D-xylulose and joined to the pentose phosphate pathway through D-xylene - 5 Phosphate. The glucuronic acid pathway functions in the liver and kidney, and the administrated xylitol could be metabolized in tissue as a source of energy; this metabolism of
xylitol, in contrast to that of glucose, would require very little insulin.

1.7 PLAN OF WORK OF THE PROPOSED RESEARCH

The objective of the investigation is to prepared xylitol, exploiting corn cobs, an agricultural waste. The research work has been classed in two groups; firstly, xylan is extracted from corn cobs and then hydrolysed to xylose; Secondly, xylose is reduced to xylitol by hydrogenation. Keeping in view the objective, the process parameters have been optimized for both of the groups. More precisely, the proposed research plan includes the following:

(A) Analysis of corn cobs for its constituents.
(B) Extraction of xylan from corn cobs.
(C) preparation of xylose from xylan/corn cobs by acid hydrolysis.
(D) Conversion of xylose into xylitol by catalytic hydrogenation.
(E) Purification of xylitol.
TABLE 1.1

XYLOSE IN DIFFERENT AGRICULTURAL WASTES

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Agricultural Wastes</th>
<th>Xylose (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Wheat bran</td>
<td>10.8</td>
</tr>
<tr>
<td>2.</td>
<td>Rice husk</td>
<td>10.2</td>
</tr>
<tr>
<td>3.</td>
<td>Cotton seed hulls</td>
<td>13.6</td>
</tr>
<tr>
<td>4.</td>
<td>Corn Cobs</td>
<td>23.2</td>
</tr>
<tr>
<td>5.</td>
<td>Sugar Cane Bagasse</td>
<td>18.6</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>Wheat</td>
<td>54.52</td>
<td>49.65</td>
</tr>
<tr>
<td>Rice</td>
<td>74.59</td>
<td>74.95</td>
</tr>
<tr>
<td>Jowar</td>
<td>11.88</td>
<td>9.26</td>
</tr>
<tr>
<td>Bajra</td>
<td>5.91</td>
<td>6.62</td>
</tr>
<tr>
<td>Maize</td>
<td>9.07</td>
<td>9.41</td>
</tr>
<tr>
<td>Ragi</td>
<td>2.33</td>
<td>2.73</td>
</tr>
<tr>
<td>Small Millets</td>
<td>1.23</td>
<td>1.11</td>
</tr>
<tr>
<td>Barley</td>
<td>1.64</td>
<td>1.46</td>
</tr>
</tbody>
</table>

**SOURCE:** Thirty fourth Annual Progress Report
All India Co-ordinated Maize Improvement Project (1991).
FIGURE 1.1  Structures of Xylan, Xylose & Xylitol and Reactions.
Figure 1.2 - Area, production and productivity of maize during the seventh plan.