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Mini review on Corncob biomass: A potential resource for value-added metabolites

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ABSTRACT

Plant biomass is one of the major renewable raw material sources on earth.It is composed of carbohydrates and aromatic polymers. These carbohydrates (cellulose and hemicellulose) and aromatic polymers (lignin) are a potential resource for the industrial production of value-added products and biofuel. One under-utilized form of plant biomass is corncob. However, there are many difficulties in the industrial production of value added products from corncob hydrolysate. This literature summarizes the advantages and challenges in the various industrial methods for the production of value-added products from corncob biomass in a cost-effective manner.

Key words: Corncobs biomass, Xylose, Corncob fermentation, Hemicellulose detoxification

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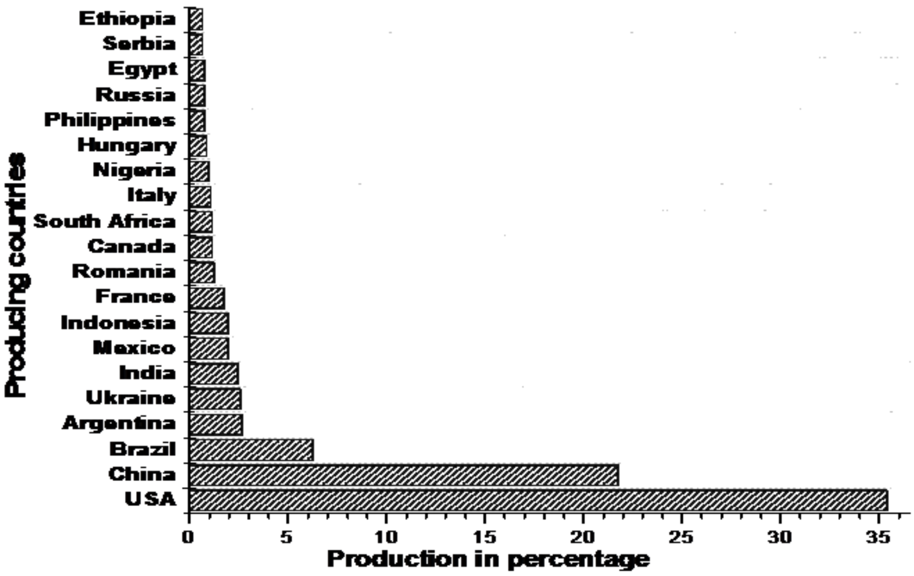
INTRODUCTION

Corn is one of the most extensively grown cereal crops with 885.3 million tones produced world wide in 2014. The leading producer is the United States with 313.9 million tonnes followed by China. India holds the 6th place [1] (Figure 1).

Corncob is the material remaining after removing the grains and is traditionally used as feedstock or fuel. It contains hemicelluloses, cellulose and lignin. Despite polymeric fibers consist of monomer molecules. Amidst cellulose is composed of C6 sugars and hemicelluloses are C5 sugars (xylose and arabinose). In most of the plant derived biomass cellulose, hemicellulose and lignin are wrapped in a complex matrix which is very resistant to enzymatic degradation [2]. Hence, the identification of suitable technique for the utilization of available cellulose and hemicelluloses matter in the corncob biomass is still the biggest task. Generally most of the plant biomass as useful industrial value added metabolites viz., glucose, xylose, acetate, furfural and hydroxymethyl furfural along with Lingin [3]. Furthermore, lignin will be converted in to co-products like vanillin, phenols and high octane hydrocarbon materials. Though, the utilization of corncob biomass is one of the major resources for these metabolites [4]. Also the bioconversion of these available metabolites by microbial fermentation is a novel research. Until the conversion technologies were identified as available corn biomasses which are used for house hold combustion purpose. The recent conversion strategy exhibits the microbial fermentation with native and mutant strains which has the ability to ferment the corncobs sugars in to value added metabolite. It's strategically includes processing of corn cobs, acid hydrolysis and metabolite estimation, fermentation process, substrate consumption by selected organism, product formation, quantification of products and co products [5].

Figure 1: worldwide production of Corncob

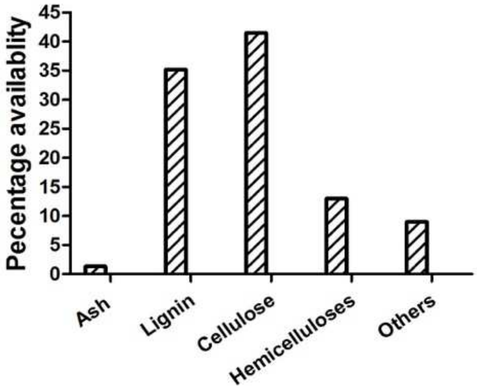


(Data resource: Food and Agriculture Organization of the United Nations, 2014)

1.1. Corncob Biomass Constitutions

The most widely available wastage in India is plant biomass. In particular,the corncobs are 40% available in over all biomass, while 10% products utilized for bioconversion process. Remaining surrogates utilizedconventionally in rural part of India as a fire starter, pot scrubber and animal bedding [6]. In recent years the researchers explored the importance of corncob biomasshydrolysate and its vital metabolites alsocan be utilized for the production of industrial value added productsdue to their natural properties. In general, the composition of lignocellulose depends on the source whether it is derived from hard wood, soft wood or plant (Figure 2).

Figure 2: Corncob biomass compositions

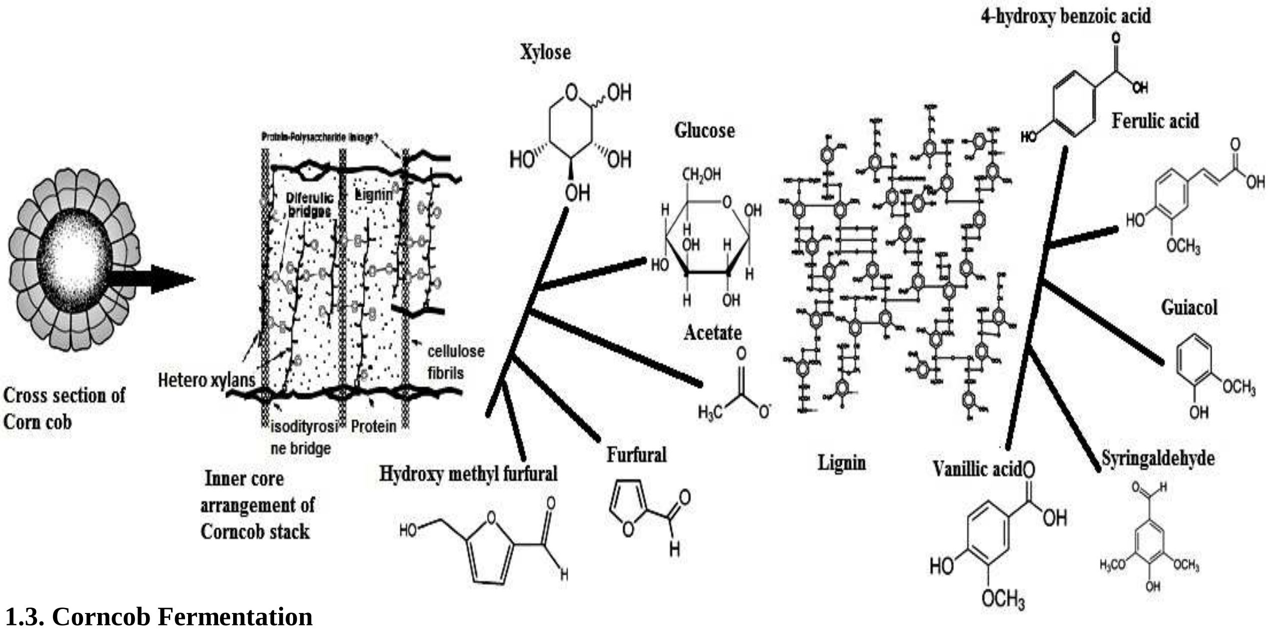


In Corncob hemicelluloses xylan is one of the complex heteroxylanshasß-(1, 4)-linked xylose residues [7]. It's made up of33–35% arabinose, 3-6% galactose, 6–16% glucuronic acid and 48–53% xylose. Generally the 80% of xylan is highly substituted with monomeric side chains of glucuronic acid or arabinose which is linked with O-2 or O-3 xylose residues. Moreover the oligomeric side chain has arabinose, xylose and few galactose residues [8] (Fig. 3). Xylose is one of the major constitutions in the hemicellulose hydrolysate of corncobs; hence the bioconversion of xylose to xylitol will be a useful process, which has a wide variety of industrial application. Chemical synthesis of xylose is possible but expensive and time consuming. The utilization of available plant biomass like corncobs will be the potential natural resource for the production of bulk quantity of xylose with less cost and less time. Whereas the commercial xylitol production is achieved by aerobic(presence of oxygen) fermentation of corncob hydrolysate with yeast (*Debaryomycesnepalensis*and *Debaryomyceshanseni etc.,*) is used as an artificial sweetener, dental application etc.,

1.2. Processing of Corncob for Fermentation

Primarily corncob cleansing begins with purified water to remove dirtand other impurities. Then, the washed shells are dried under shadow or oven dry. After dried shells was grinded mechanically or with ball mill technique. These grinded materials with particle size of 0.5 to 2 mm size is separated using appropriate sieves, where the size of the corncob particle plays a major role for holding the sugars. Particles sizerange between 0.02-0.1 cm for preparation of hydrolysates rich in glucose whereas 0.5-2 cm for hydrolysates rich in xylose. In order to obtain the various concentration of metabolite in the hydrolysate, size of the particle can be adjusted accordingly. This helps in the simple extraction of metabolites like glulcose, xylose, acteate, furfural and hydroxyl methyl furfural from ground material. Further, those ground matter will be acid hydrolysed with H_2SO_4 in the ratio of 1:20 W/V (Solid and liquid ratio), which is ideal for the breakdown of inner core of corncob embedded with combination of metabolites [9]. In addition numerous researchers studied to release/extract all the available composition of metabolite in acid hydrolysate material by vigorous agitation, which represents the level of metabolite release considerably higher amount [10].

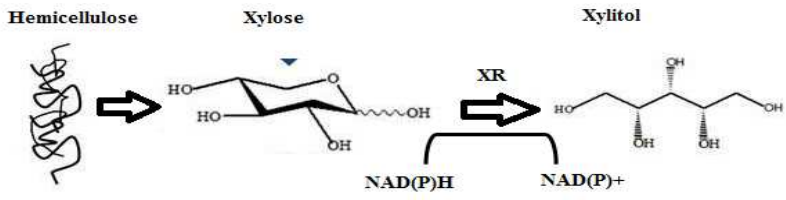
Figure 3: Schematic representation for frame work of Corncobhemicelluloses



1.3. Corncob Fermentation

Generally corncob hydrolysates posses rich in sugars like glucose and xylose. Depending on the type of fermentation and end product requirement the fermentation process has to be carried out. For example, the xylose fermentation the hydrolysate is called non detoxified hydrolysate which can be fermented by using yeast under aerobic condition at optimum temperature at 30^{o}C. Since, the microbes consume the sugar and produce end products like xylitol andethanol. Here the major disadvantage is the presence of inhibitors as lignin, furfural and hydroxymethyl furfural that may hinder the fermentation process by interference of bacterial xylitol metabolism. Therefore, the removal of such inhibitors will help to organismsfor produce rich amount of end products and co-end products. Bioconversion of xylose to xylitol is carried out by an enzyme called xylose reductase (XR) which is NADP dependent enzyme. The presence of inhibitors will deduct the activity of XR in the fermentation process [11] (Figure 3). Current bioprocess research focuses on decreasing the concentration of inhibitorin corn hydrolysate. By treating them with different absorbents namely activated charcoal, $CaCO_3$(Calcium carbonate) and other

Figure 4: Xylose fermentation in corn cob hydrolysate by yeast



suitable natural absorbents. These absorbents will absorb the fermentation inhibitor considerably. Meanwhile there is a possibility to lose the product of our interest where during this absorbent treatment process.Hence, an extensive research must be required to develop such process [12].

1.4. Estimation of Metabolite and Co-Metabolitein Corncob Hydrolysate

Generally, the quantification of metabolite analysis before and after hydrolysate for all kind of carbohydrate estimation can be analysed by HPLC. But, quantification of metabolite depends on the selection of suitable chromatography column. Specifically, for corncob hydrolysate metabolite estimation 'the sugar column' is well recognized techniquewith RID detector (UV detector). To quantify the presence of lignin content spectrophotometrically in the presence of strong alkali as base [13].

1.5. Detoxification of Corncob Hemicellulose Hydrolysate For Effective Fermentation

The main objective of detoxification of corn cob hydrolysate is to minimize the concentration of inhibitors, which can be done in many ways. Organisms which involved in the hemicelluloses corncob hydrolysate are highly sensitive to inhibitors. Event the presence of less concentration of inhibitors may disrupt fermentation process. Consequently the removal is essential for complete utilization of fermentable sugars in corncob hydrolysate. Some of the representative methods for removal of such process in detoxification are: (1) physical methods (2) physicochemical method (3) biological method. But the identification such a suitable method of detoxification solely depends on the source of biomass in each method. Even though, enormous methods have been reported for detoxification of hemicelluloses hydrolysate, still the identification of an exact method for corncob hydrolysate detoxification in industrial level is not identified till date. Each method of detoxification has their own short comings [12] (Table 2).

Table 1: Comparison of different methods for detoxification of hemicelluloses hydrolysate and their advantage and disadvantages

Methods	Process	Advantage	Disadvantage
	Physical Methods		
Concentration or Evaporation	Removal of toxic compounds by evaporation under vacuum concentrator based on the volatility	Reduction of volatile compounds as acetic acid, furfural, and vanillin	Increases the nonvolatile toxic compounds as extractives
Membrane filtration	Surface functional groups on membrane attached with their internal pores, which may remove metabolite inhibitors	Rejects the requirement to disperse one phase and reduces on entrainment of small amount of organic phase	- High costeffective - specific removal of inhibitors
	Physico Chemical Methods		
Ion Exchange Resin	Resins modify undesirable ions of the liquid phaseto be purified by saturating thefunctional group of resins.	- Can be reused and regenerated - Removal of polymeric inhibitor lignin and furfural - Removal of acids inhibitors acetic acid and furfural - Loss of sugar amount is high	- Pressure is high - Long time for processing - high chance of Possible degradation of fragile biological product - high scale up difficulty
Overlimming	Increase of pH followed by suddenpH fall	- Precipitate toxic compounds	- sugar loss is high - complexity in filtration
Activated Charcoal	Adsorption of toxic compounds by charcoal the charcoal activity is increased by contact surface	- Cheap - Removal of phenol and furfural effectively - very less amount of sugar loss	-complexity in filtration process
Extraction with Organic Solvents	Mix of liquid phase to be purified and a organic solvent. Separation of liquid phase is recovered by two phase system (organic and aqueous)	-Recycle of solvents for subsequent cycles - Removal rate of acetic acid, vanillin, 4-hydroxybenzoic acid, , furfural and low molecular weight phenolics are high	- High cost - Long time consuming process
Vegetable Polymer	Biopolymers are made up of tannins with fast binding properties that flocculate inhibitor compounds	- Less cost - Biologically degradable - reduces loss of sugar - Reduce toxic compounds	- Cell death is high when the concentration of tannin content is high - volume loss is significant
	Biological Method		
Microorganism	Microbes act on hydrolysate inhibitors and change their composition with the help of their enzyme	-Less waste formation - Eco friendly - Less energy process	- Long time process

1.6. Challenges Associated With Corncob Biomass Utilization For Industrial Fermentation

1. Availability of Corncobs for entire year is not possible
2. Available metabolite content may vary in each batch of corn after harvesting (Maturation of level of corn), so the formulation offermentation process needs to be optimized for bulk production. Biomass transportation and storage without losing the available hemicelluloses content is difficult.
3. Selection of suitable pretreatment process for corncob processing.
4. Selection of appropriate catalyst and possible recovery of the same.
5. Removal of recalcitrant polymers like lignin needs more effort during the process.
6. Prevention of phenolic compounds formation from lignin
7. Health of the plant and yield of biomass/hectare area.

8. Selection or identification of suitable pretreatment absorption process to remove the inhibitor concentration for successful detoxification process.
9. Identification of possible bioconversion strategies for the utilization and conversion of lignin to useful phenolic compounds in corncob biomass.
10. Recovery of fermented sugar products like xylitol and biofuel from fermented hydrolysate broth.
11. Removal of co-products and its influence/interference in microbial metabolism.

CONCLUSION

Corncob hemicellulose raw material is a vital fraction that reveals sustainable alternative for the production of commercially important value added industrial products, bi-products, industrial enzymes, lactic acid, succinic acid, ethanol etc. It can be readily converted into simple sugars by acid hydrolysis, and then resultant sugar hydrolysate is subjected to conditioning and detoxification, which can be converted into the beneficial products through bioprocess routes. Also the implementation of thermo chemical processes such as Shrinking bed reactor, Plug flow, and counter-current are responsible for enhancethe sugars recovery with less inhibitors formation. The detoxified hydrolysate can be used for production of value added products including second generation biofuel i.e., ethanol by appropriate microorganisms under aerobic and anaerobic fermentation process. In recent research progress has clearly proved that it is possible to utilize hemicelluloses hydrolysate into valuable products with desired percentage of yields. However, it is necessary to build a robust process to be employed at industrial scale. Biomass based derived products have potential to replace chemically synthesized products like xylitol and arabitol. Owing to this, biorefinery companies offer numerous opportunities to develop unique functionality and marketing benefits from the products derived from Corncobs biomass generating long term sustainability and green environment in developing countries like India.

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