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Synthesis of Furfural Alcohol from Bagasse

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Abstract: **Bagasse is a waste product from the sugar industry, which is usually used as energy source as well as primary fuel source in sugar industry at present. However, the amount of bagasse left is still high enough for more value-added product for example furfural. Bagasse is a good source of pentosan and containing about 25 to 27%. The main objective of the research was to produce furfural alcohol from bagasse. The main raw material for the production furfural was bagasse and some chemicals/ingredients were used H_2SO_4 (sulphuric acid), water, NaCl. Furfural is an important organic chemical, produced from agro industrial wastes and residues containing carbohydrates known as Pentosans (Five sugars mainly xylose). It is a basic chemical, which can be utilized in a variety of industries such as chemical industry, refining oil industry, food industry and agricultural industry also its been used in Rocketery as a fuel . In its pure state, it is a colourless or yellow oily liquid with the odour of almonds, but upon exposure to air it quickly becomes yellow then brown and finally black, it is commonly known as furfuraldehyde (OC_4H_3CHO).**

Keywords: **Bagasse, Furfural, Furfuraldehyde, and Pentosans, etc.**

I. INTRODUCTION

A) Bagasse

Bagasse is a waste product from the sugar industry, which usually includes Cellulose - 45–55%, Hemicellulose -20–25%, Lignin 18–24%, Ash 1–4%, Waxes <1 % It also, used as forage and raw material for production of pulp, paper making and particleboard. It has been reported that bagasse contains arabinoxylan. It is a basic chemical, which can be utilized in a variety of industries such as chemical industry, refining oil industry, food industry and agricultural industry. Furfural was first isolated in 1821 by the German chemist Johann Wolfgang Dobereiner In 1840, the Scottish chemist John Stenhouse found that the same chemical could be produced by distilling a wide variety of crop materials, including corn, oats, bran, and sawdust, with aqueous sulfuric acid, and he determined the empirical formula ($C_5H_4O_2$). In 1901, the German chemist Carl Harries deduced furfural's structure. Now days, it is also usually produced from agricultural wastes containing pentosan as the main component, such as, rice straw, Bagasse and rice hull . One of the application bagasse is the production of a valuable material called furfural. This material is used in synthesis and production of various chemical compounds.

Furfural has applications as a selective solvent in the refining of petroleum, lubricating oils, diesel fuels and vegetable oils. In the refining of lubricating oils, petroleum and diesel fuel, furfural has been used to separate aromatics and retain paraffinic-type compounds from the mixture to improve the viscosity index, ignition characteristics, oxidation stability, color, flash point, and to lower the carbon-forming tendency. It can also be used as the raw material for other by-products such as alcohol furfural and eruptions, which is the raw material for the production of many industrial resins. Moreover, the waste, after processing, is used as a light rich fertilizer. Every year, a large amount of waste is created throughout the processing of sugar canes (Bagasse). Collection and disposal of these wastes is not only very costly and causes an excessive amount of environmental pollution, but also it is a great loss of wealth that can be used in different industries. Since the main raw material, bagasse is easily found from those industries we are initiated to produce an important organic chemical, furfural that is used in a variety of industries such as chemical industry, refining oil industry, food industry and agricultural industry. The general objective of the research was to produce furfural from bagasse.

B) Furfural

Furfural is a liquid chemical that is sourced from renewable resources–it is created from the hemicellulose components (pentosans). It is also the only compound of the furan series being directly obtained from biomass (e.g. bagasse) at industrial scale. Furfural production is generally carried out by hydrolysis of hemicelluloses-derived pentosans into monomeric pentoses, and their subsequent acid-catalysed dehydration. In its pure state, it is a colourless or yellow oily liquid with the odour of almonds, but upon exposure to air it quickly becomes yellow then brown and finally black, it is commonly known as furfuraldehyde. It is an important organic chemical, produced from agro industrial wastes and residues containing carbohydrates known as Pentosans. As no commercial synthetic routes have been found so far, all furfural manufacturing activity is based on pentosan containing residues that are obtained from the processing of various agricultural and forest products. In commercial terms, the most important intermediate derived from furfural is furfuryl alcohol. Furfural is a hazardous chemical, being both toxic and flammable. Fortunately, incidents involving furfural are very rare, which is probably due to its low volatility; it has a boiling point of 170 ºC.

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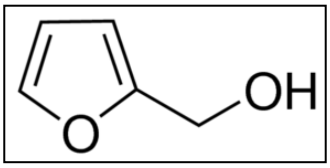

Fig. 1 Structure of Furfural Alcohol

In small doses furfural is not a problem and we all have a little furfural each day in our food and drink. It occurs naturally in sweet potatoes. It is imparted to wines and spirits by maturing in wood and is created by high temperature cooking processes such as baking, roasting, frying and grilling. The chemical formula for furfural is C5H4O2, in structure it is a heterocyclic compound consisting of a furan ring (four carbon atoms and an oxygen atom) plus an aldehyde group.The furan ring is common in nature, being a component of the sucrose molecule. Structure of Furfural is only partially soluble in water and with a density of 1160 kg/m^3, therefore when separation occurs the water layer is on the top. At 20°C the furfural layer contains 5wt% water while the water layer contains 8.3wt% furfural. During distillation of furfural/ water mixtures a low boiling azeotrope is formed. The azeotrope contains 35% furfural.

Table 1
Properties of Furfuraldehyde

Molecular Formula	$C_5H_4O_2$
Molar mass	96.08 g mol^{-1}
Appearance	Colourless Oil
Odor	Almond Like
Density	1.16 g/ml (20^0C)
Melting Point	-37^0C, -35^0F, 236^0K
Boiling Point	162^0C, 324^0F, 435^0K
Solubility in Water	83 g/L
Acidity	0.08 mol/l

C) Pentosan Content Of Various Raw Materials

The production of furfural requires raw materials rich in pentosan. The pentosan content of some material is given in table the pentosan content of various raw materials in percent of dry mass. The pentosan content is measured by converting the pentosan to furfural, and by then determining the furfural, usually by precipitation with barbituric acid.

Table 2
Pentosan Content in Raw Materials

Raw Material	Pentosan Content (%)
Corn Cobs	30 to 32
Oat hulls	29 to 32
Almond husks	30
Cottonseed hull bran	27 to 30
Birch wood	27
Bagasse	25 to 27
Sun flower husks	25
Beech wood	24
Flax shives	23
Hazelnut shells	23
Residue of oil extraction	21 to 23
Eucaplatus wood	20
Balsa Wood	18
Rice hulls	16 to 18
Spruce wood	11
Pine wood	7 to 9
Douglas fir wood	6

D) Objective Of The Study

The main objective of the study is to prepare furfural alcohol from bagasse.

II. METHODOLOGY

A) Reactions

The reaction leading to furfural is universally made from agricultural raw material rich in pentosan. By aqueous acid catalysis, the pentosan is hydrolyzed to pentose, and this pentose is dehydrated to furfural in a unified process.

B) Stoichiometry

The Stoichiometry of the two reactions reads as follows:

1) Hydrolysis of Pentason:

$$Pentason + n_x\ Water \xrightarrow{yields} n_x\ Pentose$$
$$(C_5H_8O_4)n + n(H_2O) \xrightarrow{yields} (C_5H_{10}O_5)$$

2) Dehydration of Pentose:

$$Pentose - 3x\ Water \xrightarrow{yields} Furfural$$

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C) Mechanisms

Pentosan consists of predominantly rings linked by oxygen bridges as shown in figure2.

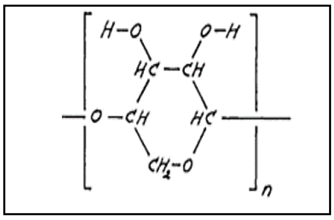

Fig. 2 Ring of Pentosan

The mechanism of the acid hydrolysis of pentosan is comprise in the following steps:

1) Protonation of an oxygen link, thus leading to trivalent oxygen.
2) Cleavage of a carbon/oxygen bond leading to a carbon onside of the oxygen bridge, and to a hydroxyl group on the other side of the oxygen bridge.
3) The carbocation takes up water.
4) The resulting H_2O + group liberates a hydrogen ion, thus leading a hydroxyl group behind. This sequence of process is repeated until all oxygen bridge has dispersed so that the rings have become individual pentose molecules.

D) Furfural Production Steps

Drying: Dryer is the first equipment in the furfural production which is used to remove the moister content of the bagasse from 45% to 15% at a temperature of 100 ºC.

Grinding: The dried bagasse is then entering to the grinding unit in order to grind the bagasse /in order to decrease its size.

Sieving: It is used to sieve the crushed bagasse to the particle size of 30 to 40mm (i.e. to remove course or larger materials and bagasse).

Reactors: Furfural is made from the pentosan contained in the fiber. The method consists of pressure cooking the fiber (bagasse) in the presence of acid. During the initial heating the solid pentosan reacts with water to form soluble pentose, when the temperature rises above 165 0C the pentose undergoes a dehydration reaction to yield furfural. There are three types of digesters for the commercial production of furfural at the present time.

Quaker batch process: The initial production process was developed by Quaker Oats at their Cedar Rapids plant. Though Quaker no longer produces furfural, their process continues in a number of plants including the largest at Central Romana. It is a batch process where the feedstock is mixed with sulphuric acid and then reacted in a rotating spherical digestor (up to 6 m in diameter) at 153 0C (515 kPag) while being sparged with superheated steam.

As furfural is formed it is stripped off by the steam passing through the bed. After 5 hours the process is stopped and the residue is emptied from the digestors. It consists of the cellulose and lignin fractions and in many cases is used as fuel. The steam and furfural vapors extracted from the digestor are condensed and then separated using decanting and distillation.

Chinese batch process: The Chinese process differs from the Quaker batch process in that the digestors do not rotate. They consist of large cylinders in which steam, at 5 bars, is passed through a static bed 1.5 m diameter and 8 m tall. Percolation of steam through the bed is assisted by ensuring that the size of the corn cobs is between 20 to 30 mm.

Rosenlew continuous process: The Rosenlew process is similar to the Chinese process in that vertical digestors are used however they are operated in a continuous fashion. The only Rosenlew plant operating at present uses sifted bagasse as the feedstock. The coarse fraction is admitted to the top of the digestors via a lock hopper and residue is discharged from the bottom through valves. Steam at 10 bars is fed into the bottom and flows upwards through the bagasse. Unlike other processes, sulphuric acid is not added to assist furfural production; instead, organic acids formed by side reactions concentrate within zones of the digestor and promote furfural production. Steam and furfural leave from the top of the digestor.

Distillation: Distillation of furfural all furfural reactors known so far to produce a vapour stream consisting of more than 90% water of up to 6% furfural and various by product. After liquefaction, commonly used to make secondary steam, and sometimes after a filtration or a centrifugal separation of solids, the products stream is fed in to an azeotrope distillation. A typical simple distillation plant is, used to make of the water/furfural azeotrope boiling point of 97.850c and a water content of 65%. The Column is commonly called the azeotrope column although this is unfortunate as in a subsequent column the same azeotrope is used for the dehydration of furfural, so that the attribute is not a unique feature of the column. The sump fraction of the column is water loaded with some carboxylic acid, mostly acetic acid. This fraction is sometimes discharged in to the sea or in to waste water treatment plant.

Decanters: From the azeotrope column, commonly a tray column fraction roughly corresponding to the azeotrope is withdrawn as a liquid side stream and fed into decanter where it separate the liquid phase, a light phase rich in water, and a heavy phase rich in furfural . The light phase is reflex in to the azeotrope column. The heavy phase of decanter consists typically of 94%frufural.

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It is passed through a neutralizer and then fed in to a randomly packed vacuum 5 energized by a reboiler as well as steam injection where the raw furfural from the neutralizer.

Neutralizers: The furfural from the decanter is passed through a neutralizer in order to neutralize the acidic media by adding NaOH and then fed in to a randomly packed vacuum energized by a reboiler as well as steam injection where the raw furfural and polymer are separated from the neutralizer.

Generally the production process of furfural is summarized as shown in the block diagram bellow:

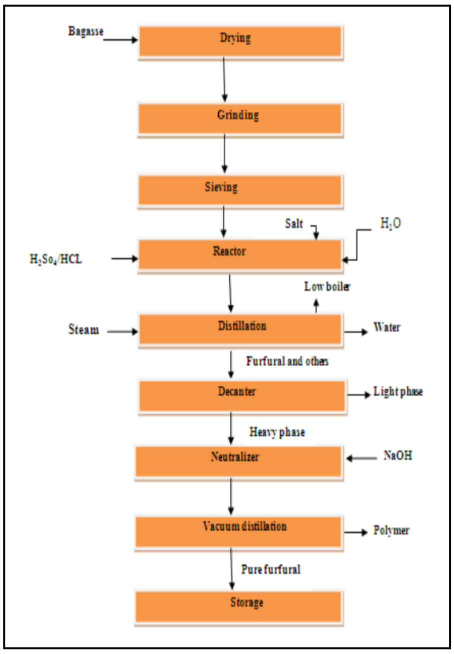

Fig. 3 Production of Furfural

III. Materials And Methods

The experiments of production of furfural from bagasse were carried out in the laboratory of Vishwakarma Institute of Technology, Pune.

A) Materials Use For The Experiments

The main raw material for the production of furfural is,

- Bagasse Chemicals that are used for the experiment are,
- Sulfuric acid (H2SO4): used as catalysts.
- Water :to dissolve the pentose
- Salt (NaCl): enhancing the furfural selectivity and rate of formation.

B) Main Equipment's For Furfural Production

- Grinder: to grind the bagasse.
- Sieve: to sieve the crushed sample to the particle size of 1mm
- Round bottom flask: as batch reactor for the solution
- Tube and condenser: to collect and cool the product
- Beaker: to store product.
- Shaker(stirrer): to shake sample
- Measuring cylinder: to dilute the concentrated acid
- Burette: for measuring the volume of the water and sulfuric acid
- Thermometer: Device to measure temperature.
- Oil bath: Device to boil the sample.

C) Experimental Procedure

In a 500ml round-bottomed flask are placed 0.015 kg of dry bagasse (ground to about the size of 1mm) 150ml diluted sulfuric acid, and 0.005kg of salt. The flask is shaken in order to secure a homogeneous mixture and is then connected with tube, water condense. Heat is applied from the oil bath, the flame being adjusted so that the liquid distils at a rapid rate. The distillation process is continued until practically no more furfural can be seen collecting in the distilling flask used as a receiver. The above operation requires 40 minutes. This experiment repeats 3 times at different temperatures, sample amounts (bagasse) and salt.

Fig. 4 Experimental Setup

IV. Result And Discussion

Table 3
Parameter for the Experiment at Different Temperature

No. of Samples	1	2	3
Mass of sample (g)	15	10	10
Mass of Salt (g)	5	10	7
Amount of Diluted Acid (ml)	150	100	100
Temperature (^{0}C)	170	200	190
Time (min)	40	40	40
Mass of Beaker (m1)	187.1	101.5	101.5
Mass of Product (m2) + Mass of Beaker (g)	211.6	132.3	129.2
Mass of Product (m2-m1)	24.5	30.8	27.7

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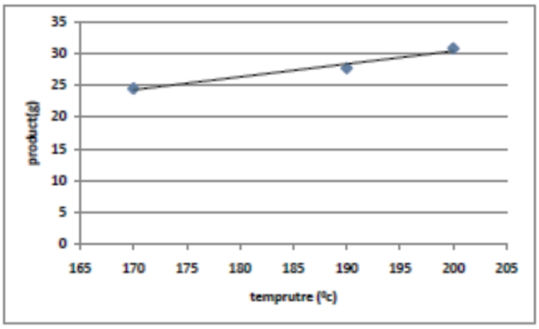

Fig. 5 Product Vs Temperature Graph

A) Effect Of Temperature On The Product

From the experiment we observed that as the temperature increases the amount of the product which is (furfural, water and others) increases and also observed that the colour was yellow which indicates one of the characteristics of the furfural.

B) Effect Of Salt On The Product

The salt has a positive effect on enhancing the rate of formation of furfural so that from the result that indicates in the table an increasing the amount of the salt it also increase the product and a colour change was observed.

C) PH

PH is the one that measure acidity, base characteristics of solution. Therefore, the PH of the products that was measured in the laboratory was 1.8, 0.5 and 1.23 respectively. From the result we observed that the acidity increases with the product .i.e. the increasing the acidity of the product indicates that amount of furfural is high in the product Furfural (product).

V. Conclusion

The study was aimed at synthesis of furfural from bagasse. The type of ingredients which are suitable for furfural synthesis specified in the experimental part during production process and what are the procedures to be considered and which order is come first for good final quality product were considered.

From the experiment the yields of furfural depend on the temperature and amount of salt because, salt has great effect on furfural formation. Many new developments would takes place in acid hydrolysis process and use of furfural for many applications such as for synthesizing a family of derived solvents like furfuryl alcohol and tetrahydrofuran and in the production of resins for moulded plastic and metal coatings. Furthermore, furfural has been used in the food industry for flavouring purpose too also it plays a big role in manufacturing of aero fuel as well.

Recommendations

Based on the gaps identified in this research work, the following recommendations are made for the future researchers to bring integrated and valuable knowledge contributions to the country.

- Further researches have to be done to improve the production of high quality and quantity of furfural from bagasse.
- Alternative extraction methods of furfural such as diluted hydrochloric acid extraction have to be done in order to investigate the variation that could be arise on the quality and quantity of the furfural yield.
- Extraction parameters such as time, temperature, and others shall be optimized in detail.

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