PREPARATION OF FURFURAL FROM AGRICULTURAL WASTE

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Abstract:

Furfural is basic chemical, which can be used in a variety of industries such as chemical industry, refining oil industry, food industry, pharmaceutical industry,paint indusry and agricultural industry. Furfural can be obtained from agricultural waste such as corn cobs, sunflower hulls, rice husk, bagasse etc. Furfural formation is based on pentosane content, higher the content of pentosane higher will be yield of furfural. Different raw materials have different pentosane content. Pentosan is a compound of polysaccharide group which can be hydrolysed into monosaccharides with five carbon atoms so called pentose. The aim of this research is to optimize the production process and maximize yield of furfural. Production processs has been optimized by using heating medium as electric heater instead of steam and yield is compared with different raw materials. Steps involved in process are pretreatment of raw material, hydrolysis and distillation/liquid liquid extraction. H_2SO_4 has been used as hydrolysis agent, and ether as solvent for extraction. Parameters which have been studied are effect of temperature PH, acidity, digestion time, effect of concentration of acid, salt, size of raw material, solid to liquid ratio etc. Furfural yield has been determined using titration method.

Keywords: Furfural, pentosan,Agricultural waste.

Introduction

Limited world reserves of petroleum have created huge interest in the development of physico-chemical processes for the production of chemicals and fuels.furfural can be obtained from the lignocellulosic biomass such as agricultural waste (corn cobs,rice husks etc.) and forest proceesing residues as well as hardwood trees.furfural was first isolated in 1821 by german chemist johann wolfgang dobereiner, produced as a byproduct of formic acid synthesis.In 1840,the Scottish chemist john stenhouse found the the furfural is also produced by a more variety of crop material such as corn,oats,bran and saw dust,he also made a empirical formula for furfural as $C_5H_4O_2$. An aldehyde (CHO) and a a conjugated system (C=C-C=C) this are two important functional groups of furfural.In 1920,that the first systematic research was conducted to produce furfural from corncobs[1,11].

Furfural is a selective solvent for separating saturated from unsaturated components in gas oil,disel fuel and petroleum refining and for the high of its derivative[2,19]. 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. Furfural is mainly produced from the pentosan in the cellulose of plant tissues,the most famous sources of furfural are corn cobs,bagasse,sunflower hulls,paper-pulp residue,rice husks,nut shells,cotton seed and wood.generally,furfural is produced from the corncobs and bassage. The main advantage of furfural is produced from the renewable sources.[2].

Lignocellulosic biomass has gains a lot of attention because of its high carbohydrate contents.lignocellulosic biomass contains approximately 23-36% hemicelluloses,42-54% celluloseand 22-28% lignin[3,8]. According to the U.S department of Energy furfural is one of the top 30 biomass-derived platform chemicals.usually furfural is mostly produced from xylose or xylane (hemicelluloses) using the acid catalyst[10,17].It is also produced using ionic liquids,ionic liquids(ILs) can be employed in the processed for furfural preparation as additives,as a catalysts and as a reaction media.depending on the ionic liquid use,externally added catalysts can be necessary to reach high reaction yields.[18]. Furfural can also be produced from autohydrolysis liquor by microwave technology.the use of microwave for carbohydrate or other products.the microwave method can be used at high pressure and temperature providing fast and constant heating for chemical transformation.[20]

Furfural is produced by agricultural waste such as corncobs, rice husks, sunflower hulls, bagasse etc. This waste consist of pentosan content in different proportion. On reaction with hydrolyzing agent this pentosan containing hemicelluloses undergo hydrolysis to produce xylose.pentosan are the aldose sugars, composed of a small rings formed from short five-member chains,which constitute a cmplex carbohydrate class,present in a cellulose of woody plants such as crn cobs,bassage, sugarcane,rice husk and oat hulls etc[4]. Furfural dissolves readily in most polar organic solvent,it is slightly soluble in water.furfural frequently called as 2-furancarbo-xaldehyde, 2-furaldehyde, furfurylaldehyde, furale, 2-furanaldehyde,is a chemical compound produced by means of acid hydrolysis and dehydration of pentoses [5].furfural is the natural precursor to furan-based chemical producs and has a potential to become important platform for biofuels.[14]

Furfural is produced industrially via batch or continuous operation. In this process, the pentosan content of agricultural waste is converted into monosaccharides(pentoses).After the dehydration of pentose furfural is produced.methanol ,acetic acid is the by products,depending upon the separation of process.the solid residure is separated from the liquid at the end of the reaction time and may be processed to recover the acid catalyst [6].The extraction method is also used to create a high-value product from renewable biomass and furfural is one of them[12].Acid hydrolysis of concentrated acid solutions creates a high yield of glucose from cellulose.In case of lignocellulosic hydrolysis from biomass,sulfuric acid is normally used,other acids also used such as phosphoric acid ,hydrochloric and nitric acid[13].

Currently, many research studies have been developed by using lignoceelulosic materials as a feedstock furfural and other chemical production. Prof. S.L.Bhagat et.al.(2015) was studied on the synthesis of furfural from corncobs by using membrane technology.in this process they studied on the pervaporation performance on the membranes with aqueous furfural as feed. They also studied the effect of the composition and temperature on the membrane performance[7].

For furfural production there are three main processes available in the market are known as quaker batch,Chinese batch and rosenlew.the quaker and rosenlew use sugarcane,baggase as a raw material and they are used in the first and second largest plant in the world.chinese batch process uses corncobs as feedstock perates in a small scale plants across china.[15]

Furfural is also known as a sleeping beauty of all biorenewable chemicals,bioplastic and polymers.furfural and its derivative has vast application in many industries such as plastics,pharmaceuticals and agrochemicals,etc.furfual is commonly used as a selective solvent for refining lubricating oils and resin and to improve the properties of diesel fuel [3].it is mainly used in the lagre scale industries as a base material for synthesizing a group of derived solvents like furfuyl alcohol and tetrahydrofuran and also in the preparation of resin for metal coating [12].furfural has many applications such as antiacids,fertilizers,plastics,inks,flavoring compound etc.[16]There are many analytical methods were developed in a recent years to determine furfural compounds in environment and food samples.UV spectral method is one which relatively simple and easy.UV technique is to monitor furans (furfural and HMF) produced in a dilute acid hydrolysate of biomass [9].

There are several factors which affect the furfural production including catalyst concentration,reaction temperature,pressure,time,agitation,liuid and solid ratio and size of the raw material. The stoichiometry of the two reactions reads as follows:

- Hydrolysis of pentosan:

PENTOSAN + nxWATER ⟶ nxPENTOSE

$(C5H_80_4)n + n\ H_20 \longrightarrow nC_5H_{10}0_5$

- Dehydration of pentose:

PENTOSE + 3xWATER ⟶ FURFURAL

$C_5H_{10}05 + 3\ H_20 \longrightarrow C_5H_40_2$

- Thus, the overall reaction can be said to be

PENTOSAN + 2 x WATER ⟶ FURFURAL

Pentosan content of various raw materials:

The production of furfural is depend on pentosan content. If raw material is rich in pentosan yield will more. Corncobs consists more pentosan content than others.

Raw material	Pentosan content (%)
Corncobs	30 to 32
Bagasse	25 to 27
Sunflower hulls	25
Rice husk	16 to 18
Oat hulls	29 to 32

Materials and methods :

1.Materials:

3 units of corn cobs collected from a new panvel market,Navi Mumbai.Hydrochloric acid (35-38% LR) were purchased from S.D fine chemicals.sulphuric acid (90%) and sodium hydroxide (97%) purchased from a Loba chemie pvt.ltd.potassium bromide(LR),sodium thiosulphate (LR),sodium sulphate(anhydrous) was obtained from research lab fine chem. Industries. Toluene,starch and potassium iodide was purchased from Sigma-Aldirich chemicals pvt.ltd.A niline and acetic acid were obtained from merck specialities pvt.ltd.. All the reagents were used as received from the supplier without any further purification.

Methods:

Experimental procedure:

- Corncob as raw material weighing 5gm is taken in crushed form.Diluted HCl(1.5M) is mixed with the powdered corncobs.This mixure is added into batch reactor equipped with stirrer and total reflux to carry out hydrolysis.This mixture in reactor is heated at temperature 80,90,100^{o}C for 2 hours.
- After hydrolysis mixture is filtrated to remove corncobs and toluene is added to filtrate in 1:1 ratio.
- Seperation of furfural toluene is carried out by decantation of liquids for 12 hours. After decantation furfural toluene is obtained at upper layer.
- To remove water content Na_2SO_4 is added to furfural toluene layer.
- Anhydried is separated by filtration and distillation is carried out to remove toluene at 110^{o}C and furfural is obtained as bottom product of yellowish colour.

Fig.a: Experimental set up

Methods of analysis of furfural:

1. Aniline method

Furfural can be analyzed by adding aniline and toluene into known amount of furfural, that gives red color. Furfural was analysed as following,

1) By using reagent the analysis of furfural is done.
2) Reagent was mixture of acetic acid and aniline of 1:1 ratio.
3) 1ml of furfural is added to 1ml of acetic acid and aniline each.
4) To obtain furfural colour should changes to red.

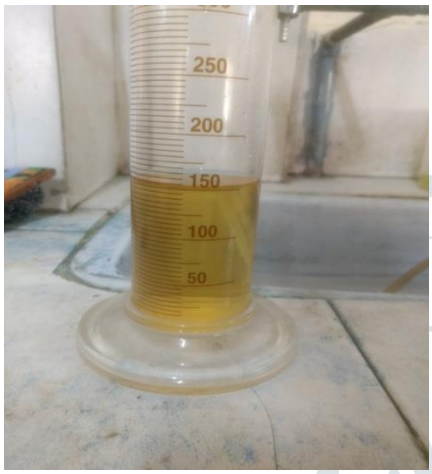

Fig.b Furfural (product)

Fig.c Analysis

2. Titration method :

To prepare 12% hydrochloric acid add 166.6 ml hydrochloric acid in 333.3 ml water. Take 200 ml 12% HCL solution add 25ml reagent (bromine-bromide) and known quantity of furfural in iodine flask and put it in dark light place for about 30 min. After 30min add 10ml 10% KI solution and 10 ml starch indicator. Titrate the solution with 0.1 N sodium thiosulphate solution. Take observation and calculate concentration of furfural.

Fig.d: Before Titration

Fig.e: After Titration

Results and discussion:

Feed as corncobs are taken in powdered form(120 mesh) because on size reduction area increases that gives good contact between reactant molecules. Pentosan hydrolyses into pentoses which on dehydration converts into

furfural. In order to determine yield of Furfural, Various experiments are carried out by changing solid to liquid ratio, changing concentration, changing acids. Furfural concentration is estimated by bromine-bromide method. Aniline acetic acid test is carried out to detect the formation of Fufural. Results have been tabulated in Table No.1

Table 1:

Sr. No	Type of acid	Solid to liquid ratio	Concentration of acid (M)	Concentration of furfural	Yield(%)
1	HCl	1/30	1.5	7.3036	7.3
2	HCl	1/20	1.5	8.649	11.027
3	HCl	1/20	2.5	7.447	6.7029
4	HCl	1/5	3.7	6.823	0.18
5	H_2SO_4	1/30	1.5	1.53	2.21
6	H_2SO_4	1/20	1.5	1.72	1.03
7	H_2SO_4	1/20	2.5	1.201	0.744
8	H_2SO_4	1/30	3..5	1.04	0.605

It has been observed from the obtained results that the hydrochloric acid gives more yield than sulphuric acid.. It is found that on decreasing solid to liquid ratio yield increases this is because with respect of feed volume of acid is more.

Effect of solid to liquid ratio, concentration of acid, type of acid on yield of furfural:

The experimental work is carried out by keeping temperature constant at 90^{o}C and acid concentration is varied i.e. for 1.5M and 2.5M . Also experiments are carried out with varying the ratio of solid to liquid. The obtained results are discussed below

1) For HCL – On keeping concentration same (1.5M) and decreasing solid to liquid ratio (in a range of 1:20, 1:30, 1:5) yield increases due to low dilution .(From run 1 & 2)

-On keeping solid to liquid ratio same and increasing concentration yield decreases because it is difficult to extract furfural. (From run 2 &3)

2) For H_2SO_4 - On keeping concentration same (1.5M) and decreasing solid to liquid ratio (1:30,1:20)yield decrease.(From run 5 & 6)

- On keeping solid to liquid ratio same and increasing concentration yield decreases. (From run 6 &7)

From results we come to know that HCL gives more yield than H2SO4.

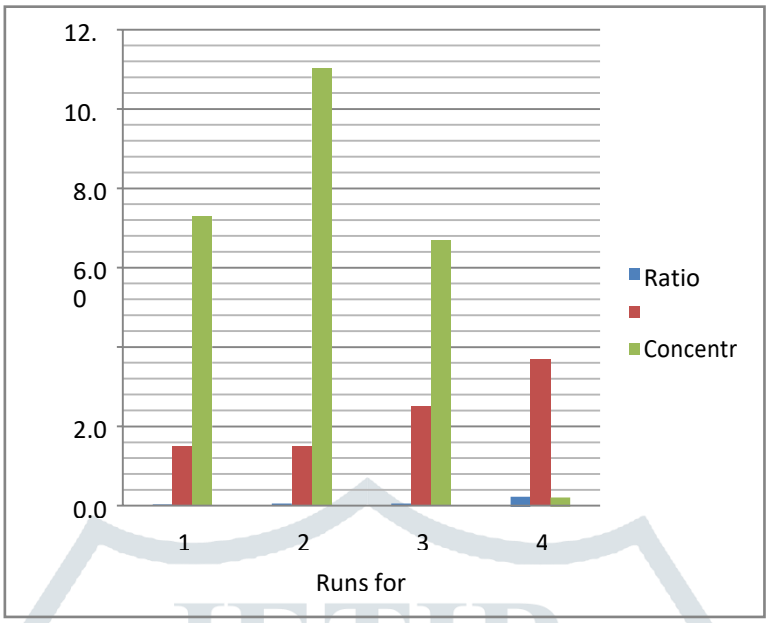

Fig.F. Ratio,concentration,yield vs runs for HCL

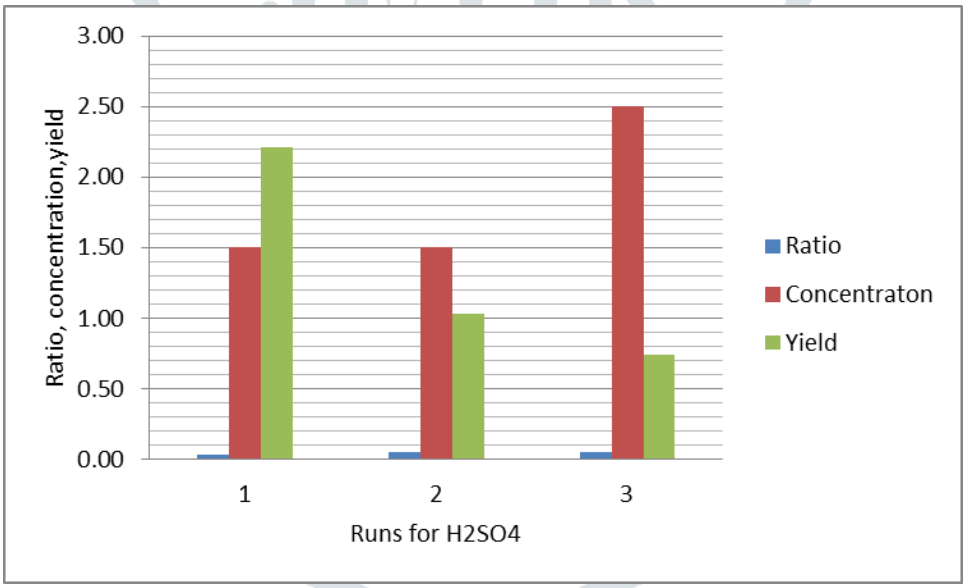

Fig.g. Ratio,concentration,yield vs runs for H_2SO_4

Conclusion:

Furfural obtained from corncobs contains 32% pentosan. In order to estimate the yield of Fufural various experiments are carried out by changing solid to liquid ratio, changing concentration, changing acids. It is observed from the obtained results that maximum yield of Fufural (11.027%) is obtained using 1:20 Solid to Liquid ratio and 1.5 M of HCl. This may be due to low solid to liquid ratio and concentration of HCl as compare to others. It is also observed that Fufural is difficult to extract at higher solid to liquid ratio as well as at higher concentration of acid. Furfural yield can be maximized using lower concentration of acid.

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