PREPARATION OF FURFURAL FROM AGRICULTURAL WASTE: REVIEW

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ABSTRACT

The interest for producing chemicals from renewable resource has increase in the last decade in direct relation to the decreasing reserve and increasing price of fossil fuels.furfural is produced from the lignocellulosic biomass which contains pentosan**,**pentosan is a polysaccharide composed of five carbon sugars called pentoses.There are various products that can be obtained from the agricultural waste which is a renewable resource,furfural is also one of them.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. 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. 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 produced industrially via batch or continuous operation. The extraction method is also used to create a high-value product from renewable biomass and furfural is one of them.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.In this sense,this article performs a review about mechanism ,various methods of furfural production.

Keywords: furfural,Agricultural waste, pentosane.

INTRODUCTION:

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, who 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 $C_5H_4O_2$. In 1901, the German chemist Carl Harries deduced furfural's structure [1].

Furfural is one of the platform chemicals which is also used as a starting reagent to produce a high value added products and which can be produced from various agricultural waste material.The main advantage of the lignocellulosic biomass as feedstock in the furfural formation is the sources are renewable.the main biomasses which is used for the furfural production such as,corn cobs,sugar cane ,bagasse,rice husk and wheat bran are the major sources used for furfural obtainment.It is normally shining and uncolored oil that when exposed to oxygen

from air undergoes an oxidation changing its colour.In one year,250000 tons are produced,which is used as solvent or starting material for the preparation of other organic solvants such as furfuryl alcohol and tetrahydrofuran.Lignocellulosic biomass is any organic matter that is available in arenewable form which includes normally energy crops,agricultural residues,aquatic plants,wood and wood residues and also a waste material.the interest in the used of agricultural residues in the aquire of renewable fuels,such as ethanol etc has been observed. Despite of the huge amount of ethanol production already existent,its production from alternative sources is an interesting with industrial process [2].

Industrial technology for production of furfural depends on batch or continuous reactors where the pentosan fraction of the lignocellulosic is converted into monosaccharides (pentoses)by acid hydrolysis.after dehydration reaction of the pentoses yield furfural.the yield loss reaction occurs while the furfural in the liquid phase,by polymerization and by reaction with pentose[3].

Lignocellulosic biomass has secure a lot of attention because of its high carbohydrate contents.lignocellulosic biomass contains approximately 23-36% hemicelluloses,42-54% celluloseand 22-28% lignin[4,5]. 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.

Furfural is a both toxic and flammable,and it is very rare,which is possibly due to its low volatility;it has a boiling point of 161^0C.a little amount of furfural each day in our food and drink.it occur naturally in nectarines and sweet potatoes.it is transmitted to wines and spirit by maturing in wood and is created by high temperature in cooking processes such as baking,roasting, frying, grilling etc.[6]

In 1921,F.A.Forge used corncobs as a the feedstock for synthesis of furfural using acid hydrolysis method.the corn cobs was heated with diluted HCL at a temperature of 180-185^0C in an stirred reactor for minimum time of 30-45 min.The yield of the furfural was obtained approximately 7.75%. After,year 1924,some other researchers uses a corn cobs and oat hulls as the raw material for synthesis of furfural using corn cobs where the hydrochloric acid (HCL) is used. In tthis process corn cobs was heated with dilute hydrochloric acid at a particular solid to liquid ratio at a temperature of 180^0C in an pressure digester for 30 min.the yield of the furfural obtained was 1-1.5% and adhesives was 40-45%[7].

Xiaofang Li et.al,was studied the production of furfural from bamboo by a two step method at atmospheric pressure.bamboo has more advantages,such as high output,capable of rapid growth that can avoid a future deforestration of our valuable tropical reinforests.In this method first hydrolysis step of bamboo hemicellulose was researches by an experimental factors such as reaction time,liquid-solid ratio, volume fraction of solvent and volume fraction of acid and so on.

At the first step i.e hydrolysis process,the hydrolysis of hemicellulose provides a feedstock for the production of furfural and extracts lignin to separate cellulose,an da t a second step a small amount of furfural was generated in the vapor phase,and xylose and intermediate products are stored in the liquid phase [8].

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].

Furfural has a renewable chemical and fuel as a precursor

Furfural has a attractive thermosetting properties,physical strength,and corrosion resistance.furfural is a natural precursor to a range of furan based chemicals and solvents,including methyl furan,furfuryl alcohol,tetrahydrofurfuryl alcohol,tetrahydrofuran,methyltetrahydrofuran and furoic acid.for the synthesis of longer chain hydrocarbon from furfural,adduct formation by aldol condensation and dimerization followed by hydrodeoxygenation can produce C_8 and C_{13} alkanes. Fig.1 shows the outline of these potential chemical products from furfural which have a high value advantage as a fuel additive.Hydrogenation of furan or aldehyde group remains most adaptable.

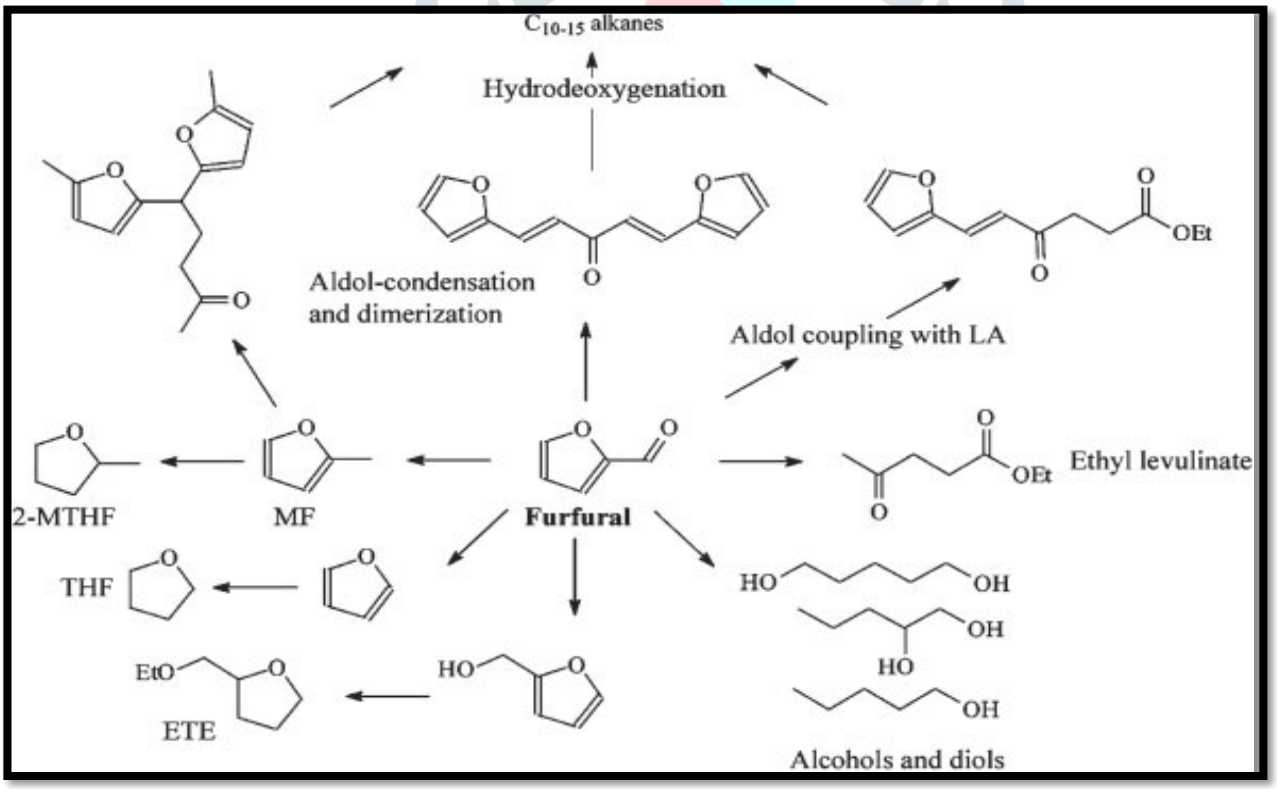

Fig.01, fuel derivatives and potential chemicals from furfural

Reaction to upgrade furanic components and can be employed to synthesize hydrocarbon fuels directly from furan directly from furan derivatives[10].

FURFURAL PRODUCTION PROCESS & METHODS :

The normally used feedstock for the furfural production are agricultural residues due to their homogeneity and prim availability in huge amount from food processing plants.furfural is usually produced from the lignocellulosic biomass i.e.agricultural waste by the dehydration of pentose.furfural also been produced from one step or two step method. In one step furfural production pentosans are hydrolysed into xylose and then dehydrated into furfural respectively.In two stage method,hydrolysis of pentosans occurs under gentle condition followed by dehydration of xylose into furfural[4]. when compared to the one step process large amount of furfural is produced in two stage process.

In any type of lignocellulosic material containing pentosans can be used as a raw material for furfural production.The first furfural production plant was a batch process originally started by quaker oat technology established in 1920s in the united states.In this process biomass is treated with acid 2.2% OD of biomass aqueous sulphuric or phosphoric acid and steam is used as a heating medium at a temperature of 153^0C in the hydrolysis step which could convert pentosans into pentoses.the pentoses which is formed is converted into furfural in a next stage and furfural was recovered by steam stripping from solution.the disadvantage of this process is the low yield sustential requirement,high effluent production and operating cost is also high.the low yield of this process because the first step was 50 times faster than the second step. Consequently,the various side reactions occurred because of the availability of monosugars in the process,the quaker oat technology is also used in a continuous mode.This method uses a fixed bed reactor and a azeotropic distillation refining process,which has to 4-12% production yield with respect to the initial weight of dried used (i.e.rice husk,corn cobs,bagasse etc)[15]

- The disadvantages of the quaker batch process are as follows:
  - A long residence time because of the low temperature.
  - A high requirement for sulfuric acid to somewhat compensate the low temperature.
  - Special measures against corrosion (cabon bricks).
  - An extremely acid residue.
  - Problem in processing fines which tend to be blown out by the steam as the tumbling of the charge invites such an effect.[12]

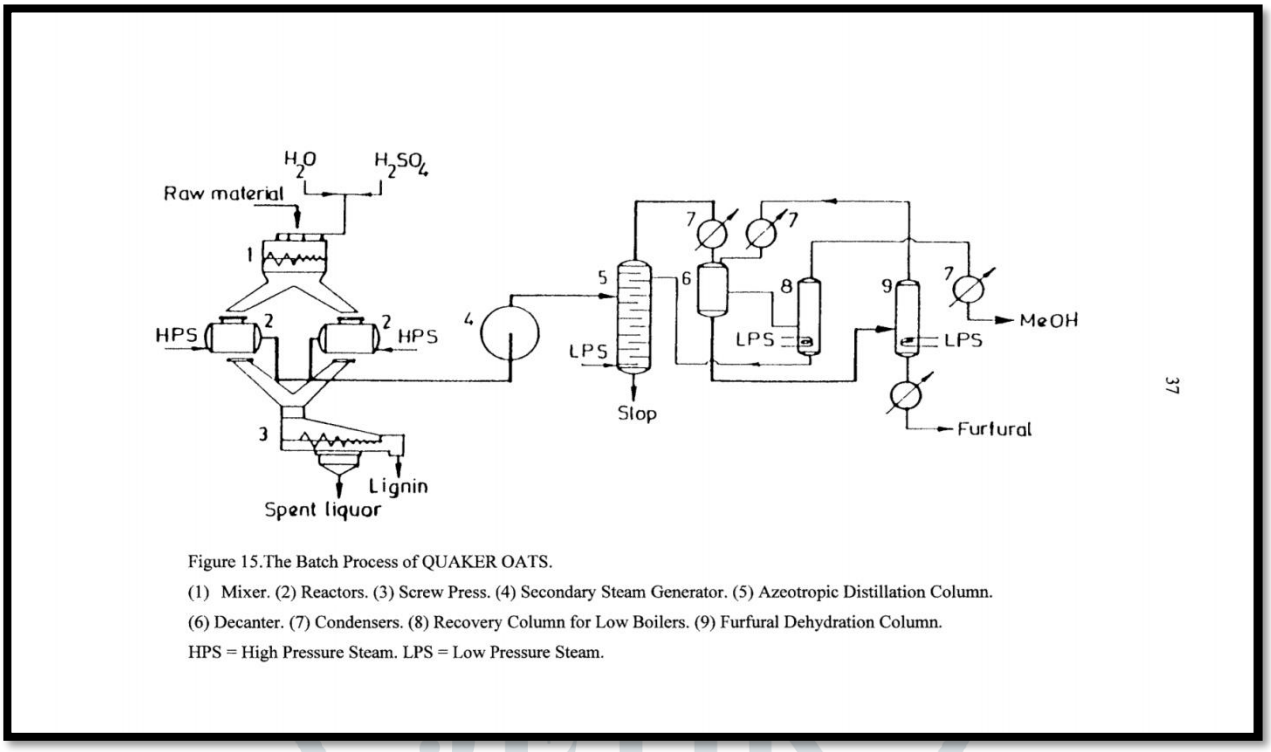

Figure 15.The Batch Process of QUAKER OATS.
(1) Mixer. (2) Reactors. (3) Screw Press. (4) Secondary Steam Generator. (5) Azeotropic Distillation Column.
(6) Decanter. (7) Condensers. (8) Recovery Column for Low Boilers. (9) Furfural Dehydration Column.
HPS = High Pressure Steam. LPS = Low Pressure Steam.

Fig.2. Quaker batch process [12]

Supra yeild is another method of furfrual production and it is also known as modified quaker oat technology introduces in 1990s.in this technology,lignocelluloses are hydrlysed in one stage and then pentoses are converted into furfrual in aquious solution at is boiling point.aftter that the product furfrual is adiabatically for flash distilltion which facilitates the tranfer of the furfural from aquous phase to the vapour phase.the process has production yield of 50-70% it is less costly as comapared to the traditional one.the high temperature of this process promotes conversion of monosugars to furfrual.

Vendernikov has patented a single-step furfural production process by using a concentrated H_2SO_4, sulphuric acid increases the rate of hydration compared to the conventional method of hydrolysis of pentosans. The main feature of the vendernikov's process are increased yield,from theroetical 55% maximum to 75% and maintainance of cellulosic part of the raw material for further chemical processing into other byproduct such as Bioethanol[14].

Another method adopted by china is Chinese batch process. In this process all the reactor has a diameter of 1.5m and aheight of 8m.reactor os made up of amild steeland have a enourmous wall thickness of 50 mm to sustain the corrosion.there is no lining but inside wall of the reactor is covered and protected also by furfural polymer naturally form in the in the process.the raw material used is ground corn cobs from which the fines where removed by shifting.in a feed screw the sulfuric acid is sprayed over incoming corncobs to give 1.5kg acid per 100 kg of liquid phase.instead of the secondary generator the process transfer vapour in the reactor directly through the reboiler of the azeotropic distillation column and latter are flashed into the atmosphere before distillation[12].

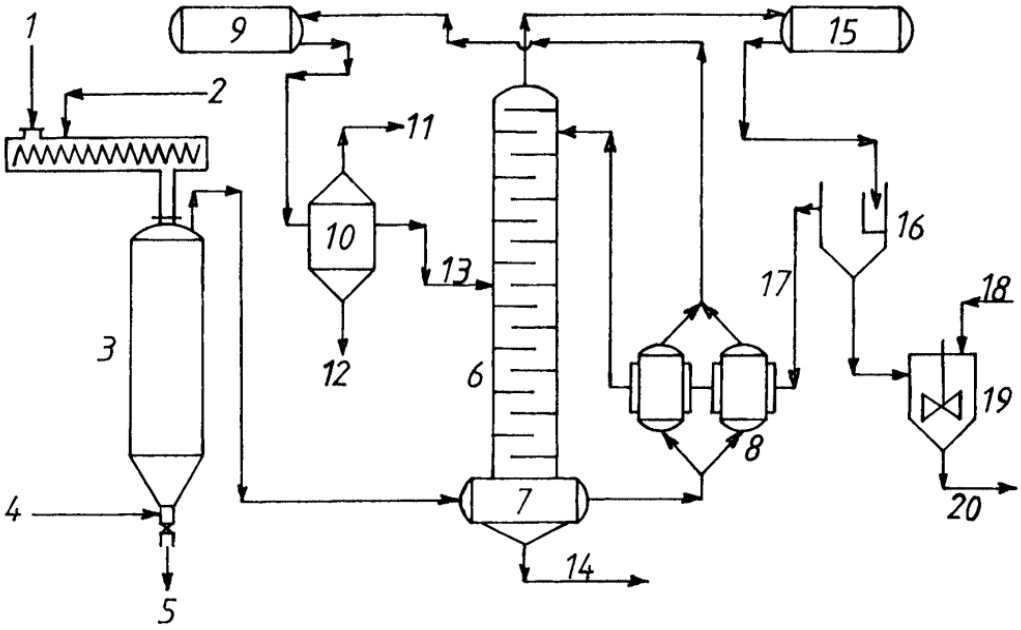

Figure 17. Schematic of the Chinese Furfural Process (Plant in Shanying, 2500 tons/a with 6 reactors).
(1) Ground corncobs. (2) Sulfuric acid. (3) Reactor. (4) Steam. (5) Residue. (6) Azeotropic distillation column. (7) Reboiler. (8) Heat exchangers. (9) Cooler. (10) Flash tank. (11) Noncondensible vapors. (12) Solids. (13) 5 % Furfural. (14) 2 % Acetic acid. (15) Condenser. (16) Decanter. (17) Aqueous phase. (18) 7 % Aqueous sodium carbonate. (19) Neutralizer. (20) Raw furfural to refining.

Fig.3. Chinese batch process [12]

APPLICATIONS OF FURFURAL

1. **Furfural as a solvent**

   Furfural and its derivative have a wide applications in many industries such as paint,plastic,pharmaceuticals,and agrochemicalsetc.furfrual is also known as a sleeping beauty of all the bio-renewable chemicals,bioplastic and polymers.

   The aldehyde group and furan ring in the furfural confirms the furfural molecule with effective properties as a solvent.furfural is widely used in industries for the extraction of aromatics from lubricating oils and diesel fuels or unsaturated compounds from vegetable oils and also in the waxy recovery [4]

2. **Abrasive wheels:**

   the new furfural is used in moulding material as a binder for adhesive particles was suggested by the fact that bakrlite,and particularly furfural phenol resin as well as other plastics such as hard rubber are also used extensively in abrasive wheels.[the application of furfural [13]

3. **Furfural as flavour enhancer for food and drinks**

   Furfural is a natural degradation of vitamin C and it is significant component of wines and fruit juices.the older the wine,the more the furfural. Furfural is present in some essential oils, foods, and cosmetic products[4].

CONCLUSION:

The study evaluate the production process as well as mechanism and application of furfural.the main advantage of the the lignocellulosic biomass as a raw material in the furfural formation is the source of renewable.New development of the production process feasible in the industrial sector including chemical,biofuels,and energy gain from the renewable sources as lignocellulosic biomass is very important.taking into consideration of environmental and economic aspects, furfural production from biomass provides a cost effective alternatives to commercial in many application.

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