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FURFURAL SYNTHESIS FROM CORN COB AND PINE WOOD

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Abstract: Furfural is a basic chemical which can be utilized in a variety of industries like Chemical, Refining Oil, Food and Agricultural Industries. This research work aims the use of Pine wood and Corn Cob for synthesis of furfural. The production of furfural by acid hydrolysis of Biomass is the focus area. Syntheses of the furanic compound at different Molar concentrations are used can product is analyzed by Gas Chromatography. We focused on the hydrolysis by using dilute HCL at specific temperature and reaction time using steam distillation. A result shows maximum furfural (2.5 M HCL) yield 7.954 % is obtained for Corn Cob in comparison with Pine Wood.
Keywords: Furfural, Acid Hydrolysis, Pine Wood, Corn Cob, GC–MS, Concentration

1. INTRODUCTION

Biomass is biological material derived from living, or recently living organisms. It most often refers to plants or plant–based materials which are specifically called ligno–cellulosic biomass. As an energy source, biomass can either be used directly via combustion to produce heat, or indirectly after converting it to various forms of biofuel. Conversion of biomass to biofuel can be achieved by different methods which are broadly classified into: thermal, chemical, and biochemical methods. Wood remains the largest biomass energy source to date; examples include forest residues (such as dead trees, branches and tree stumps), yard clippings, wood chips and even municipal solid waste. In the second sense, biomass includes plant or animal matter that can be converted into fibers or other industrial chemicals, including biofuel [5,7,40]. Industrial biomass can be grown from numerous types of plants, including miscanthus, switch grass, hemp, corn, poplar, willow, sorghum, sugarcane, bamboo and a variety of tree species, ranging from eucalyptus to oil palm (palm oil) [1,2,9].

Plant energy is produced by crops specifically grown for use as fuel that offer high biomass output per hectare with low input energy. Some examples of these plants are wheat, which typically yield 7.5–8 tons of grain per hectare, and straw, which typically yield 3.5–5 tons per hectare. The grain can be used for liquid transportation fuels while the straw can be burned to produce heat or electricity [25,26]. Plant biomass can also be degraded from cellulose to glucose through a series of chemical treatments, and the resulting sugar can then be used as a first generation biofuel. Biomass can be converted to other usable forms of energy like methane gas or transportation fuels like ethanol and biodiesel [25,27,33].

Rotting garbage, and agricultural and human waste, all release methane gas—also called "landfill gas" or "biogas." Crops, such as corn and sugar cane, can be fermented to produce the transportation fuel, ethanol. Biodiesel, another transportation fuel, can be produced from left–over food products like vegetable oils and animal fats. Also, biomass to liquids (BTLs) and cellulosic ethanol are still under research. There is a great deal of research involving algal, or algae–derived, biomass due to the fact that it's a non–food resource and can be produced at rates 5 to 10 times faster than other types of land–based agriculture, such as corn and soy[8,9,10]. Once harvested, it can be fermented to produce biofuel such as ethanol, butanol, and methane, as well as biodiesel and hydrogen [8,9,36].

2. BIOMASS SOURCES

Historically, humans have harnessed biomass–derived energy since the time when people began burning wood to make fire. Even in today's modern era, biomass is the only source of fuel for domestic use in many developing countries. Biomass is all biologically–produced matter based in carbon, hydrogen and oxygen. The estimated biomass production in the world is 104.9 petagram (104.9 * 1015 g) of carbon per year, about half in the ocean and half on land [26,28,30]. Wood remains the largest biomass energy source today; examples include forest residues (such as dead trees, branches and tree stumps), yard clippings, wood chips and even municipal solid waste. Wood energy is derived by using lignocellulosic biomass (second generation biofuel) as fuel. This is either using harvested wood directly as a fuel, or collecting from wood waste streams [3,4,28,29].

The largest source of energy from wood is pulping liquor a waste product from processes of the pulp, paper and paperboard industry. In the second sense, biomass includes plant or animal matter that can be converted into fibers or other industrial chemicals, including biofuel [14,15]. Industrial biomass can be grown from numerous types of plants, including miscanthus, switch grass, corn, poplar, sugarcane, bamboo. Based on the source of biomass, biofuel are classified into two major categories. First generation biofuel are derived from sources such as sugarcane and corn starch etc. Sugars present in this biomass are fermented to produce bioethanol, an alcohol fuel which furthermore can be used directly in a fuel cell to produce electricity or serve as an additive to gasoline. However, utilizing food based resource for fuel production aggravates food shortage problem. Second generation biofuel on the other hand utilize non–food based biomass sources such as agriculture and municipal waste. It mostly consists of ligno–cellulosic biomass which is not edible and is a low value waste for many industries [18,19,20].

Plant energy is produced by crops specifically grown for use as fuel that offer high biomass output per hectare with low input energy. The grain can be used for liquid transportation fuels while the straw can be burned to produce heat or electricity [35]. Plant biomass can also be degraded from cellulose to glucose through a series of chemical treatments, and the resulting sugar can then be used as a first generation biofuel. The main contributors of waste energy are municipal solid waste (MSW), manufacturing waste, and landfill gas. Energy derived from biomass is projected to be the largest non–hydroelectric renewable resource of electricity. Biomass can be converted to other usable forms of energy like methane gas or transportation fuels like ethanol and biodiesel. Rotting garbage, and agricultural and human waste, all release methane gas—also called "landfill gas" or "biogas." Crops, such as corn and sugar cane can be fermented to produce the transportation fuel, ethanol. Biodiesel, another transportation fuel, can be produced from left–over food products like vegetable oils and animal fats. Also, biomass to liquids (BTLs) and cellulosic ethanol are still under research. There is a great deal of research involving algae, or algae–derived, biomass due to the fact that it's a non–food resource and can be produced at rates 5 to 10 times those of other types of land–based agriculture, such as corn and soy. Once harvested, it can be fermented to produce biofuel such as ethanol, butanol, and methane, as well as biodiesel and hydrogen. Efforts are being made to identify which species of algae are most suitable for energy production. Genetic engineering approaches could also be utilized to improve microalgae as a source of biofuel [34,35,37].

Furfural, identified as one of the top 30 platform chemicals derived from biomass, as an important fuel precursor and can be converted to hydrocarbon fuels and fuel intermediates [21]. With current global production greater than 200,000 tons annually it is currently a high–value commercial commodity chemical, produced primarily from agricultural wastes such as corn cobs, and sugar cane bagasse and wood. Industrial processes for furfural production were developed in 1921 when Quaker Oats batch process was developed to produce furfural from oat hulls [22,23].

Since then, many alternative batch and continuous processes have been developed with most of the batch operations primarily using sulfuric acid as a homogeneous acid catalyst and temperatures ranging between 160 and 200 °C.6 High operating costs and low energy efficiency coupled with low furfural yield, on the order of less than 50%, resulted in the closure of batch process based plants in 1990s. Another significant industrial continuous process for furfural production was developed by Quaker Oats, which operated for 40 years in Belle Glade, Florida, until 1997 [24]. The continuous process utilized a traditional horizontal screw–style reactor, similar to the 1–ton per day horizontal reactor system (Metso, Norcross, GA) used at National Renewable Energy Laboratory (NREL) for dilute acid pretreatment. A slightly improved furfural yield (55%) was obtained in the continuous process developed by Quaker Oats using a residence time of 1 h. While this process was technically successful, the plant ultimately shut down due to the high maintenance cost of the continuous reactor system. Improving furfural yield beyond 55% in industrial production has been the subject of much research over the last 100 years [11,38].

This is a difficult task because furfural, once produced, rapidly degrades through resinification and condensation reactions. Furfural resinification is a reaction in which furfural reacts with itself, while condensation reactions occur when furfural reacts with xylose or one of the intermediates of xylose–to–furfural conversion to form furfural pentose or difurfural pentose [6]. The loss of furfural by condensation is significantly greater than the loss by resinification. Much research has been conducted in recent decades to try to minimize degradation and improve furfural yield. As a ligno–cellulosic waste material i.e. Corn Cob and Wood was hydrolyzed with acid to yield chemical i.e. furfural. Biomass residues available from agricultural and forest processing constitute a potential source for production of chemicals such as ethanol, reducing sugars and furfural by using enzyme or acid–catalyzed hydrolysis. Furfural 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. It is usually produced from agricultural wastes containing pentosan as the main component, notably corn cob, rice straw, bagasse and rice hull4 .In the past ten years. Furfural (FF) is a solvent produced from plant pentosans (xylan, arabinan and polyuronids), the complex carbohydrates contained in the cellulose of plant tissues. The product has attracted some interest because it helps in the converting the relatively abundant supplies of lignocelluloses feedstock's into ethanol and higher–valued co–product chemicals [7,9,10,16].

The World market for furfural is currently 200,000 to 210,000 tpa, which includes 120,000 to 130,000 tpa for use to make furfuryl alcohol. Currently there are four important and potentially significant applications of product furfural in the industry such as agrochemicals, clean Fuels/Bio–fuels, timber treatment. Corncobs as the raw material for synthesis of furfural using acid hydrolysis method. The corncobs were heated with dil hydrochloric acid at temperature of 180 –185^{0}C in an autoclave for 45 min. The yield of furfural was obtained approximate 7.75%. After that in 1924, researchers utilized corncobs and oat hull as the raw material for synthesis of furfural using acid hydrolysis method [17,31,32,39].

The corncob was heated with dil hydrochloric acid at temperature of 1800C in a pressure digester for 30 min. The yield of furfural obtained was 1–1.5% and adhesive was 40–45%. This paper gave the idea about the production of furfural from corncobs. The unit consists of a pressure digester unit and a continuous column still. The cobs are digested with water and high–pressure steam, the vapors being condensed to form a dilute furfural solution. Optimum operating conditions are: Pressure, 130 to 135 pounds (180°C); ratio of water to cobs, 4:1; digestion period, 2 hours. The furfural yield obtained is 6 % of the weight of cobs used. The chemicals formed during this process acetic acid, acetaldehyde, and methanol are by–products. After 1990 onwards, the various researcher described the process of hydrolysis of rice husks, wood and some edible plants species with different concentration of hydrochloric acid (HCl) and sulfuric acid (H2SO4), and in the presence of lactose, some metallic oxides as catalyst and mild oxidizing agents. A gas chromatography (GC), HPLC and a UV visible spectrophotometer are used to confirm the presence of furfural. The presence of mild oxidizing agents seems not to affect the yield of furfural but the presence of catalyst affect the yield of furfural [2–5].

3. MATERIALS AND EXPERIMENTAL METHODS

Specific amounts (1 kg each) of Corn Cob or Pine wood are collected from a Local Area (Morbi, Gujarat). It is dried in the oven temperature at 200°C for 48 hours. It is then grinded in to the mixture and sieved to a maximum size of 1mm and the sieved materials are stored in the autodesiccator. This Experiment is carried out in a batch reactor system. The apparatus is consisted of six main parts:3L capacity three–neck round bottom flask as batch reactor , 30 cm column and a condenser, a mechanical stirrer , extraction flask and device to measure temperature Figure [1]. The chemicals such as 1M aqueous HCl (1.50 liter) and 400 g (6.84 mole) NaCl are introduced into a 3L three–neck round bottom flask along with 20 gms of Biomass. Based on that different Molar Concentration of HCl has been prepared [11,12].

A column and a condenser are attached and the reaction mixture is heated and stirred with a mechanical stirrer. Steam distillation is observed after 15 minutes at the distilling temperature of 107°C. The distillate is set to flow into an extraction flask containing 250 ml chloroform Figure [2].

Two layers are formed with the aqueous layer at the top and the chloroform-furfural containing layer at the bottom of the flask Figure [3]. The stoichiometric equations for this reaction is as below.

$$(C_5H_8O_4)_n + nH_2O \rightarrow nC_5H_{10}O_5 \quad (1)$$
Pentosans Pentoses

$$nC_5H_{10}O_5 \rightarrow nC_5H_4O_2 + 3\,nH_2O \quad (2)$$
Pentoses Furfural

Figure 1. Acid hydrolysis of Biomass for Synthesis of Furfural

Figure 2. Process of Extraction after Acid Hydrolysis

Figure 3. Synthesized Product after Extraction

The chloroform–furfural layer is subjected to extraction to remove the chloroform, and a clear yellowish liquid remained. Product is then analysed by GC–MS and is determined as furfural Figure 4 [5].

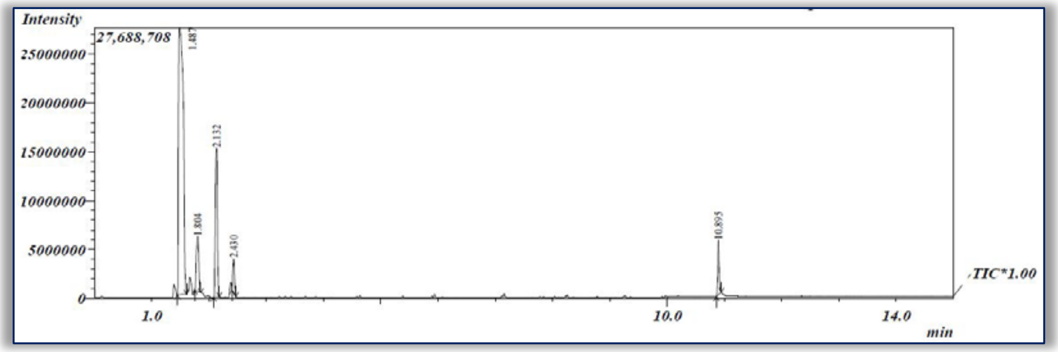

Figure 4. GC–MS Peak for Identification of Furfural Concentration

3. RESULTS AND DISCUSSION

Effect of Type of Acid

The effect of type of acid on the yield of furfural can be studied. The different types of acid used such as HCl and H_2SO_4 can be used in this method. Sulfuric acid shows more yield of furfural than hydrochloric acid as per literature survey [11,15,16].

Effect of Concentration of Acid

The effect of Concentration of acid on yield of furfural is studied. The different concentrations of acid can be used such as (0.5 M, 1.5 M and 2.5 M). Table [1] shows the effect on yield of furfural. Increase in the furfural production as increase in the concentration of furfural. Highest yield is obtained at 2.5M concentration of HCL when raw material is corn cob [11,16,17].

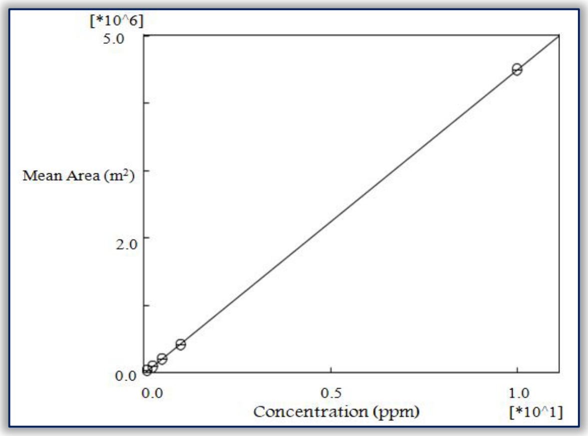

Figure 5. GC- MS Calibration Curve

Table 1. "Furfural Concentration Results for Different Biomass Samples"

Sr. No.	Different Biomass Samples	Wt% Furfural Concentration
1	0.5 M HCL + Corncob (20 gms)	1.092
2	1.5 M HCL + Corncob (20 gms)	2.489
3	1.5 M HCL + Wood (20 gms)	1.525
4	2.5 M HCL + Corncob (20 gms)	7.954
5	2.5 M HCL + Wood (20 gms)	1.570

4. CONCLUSION

Many new developments is 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 molded plastic and metal coatings. Furthermore, it plays a big role in the manufacture of insecticide as well. Recently, furfural has been used in the food industry for flavoring purpose too. Many of the researchers are worked on acid hydrolysis of rice hull, Lignocellulosic waste and Sorghum straw by using different metallic catalysts [40,42]. This experiment revealed a good yield of the 7.954 wt % furfural from Corn Cob which can be confirmed by the various tests. In a view of environmental and economic aspects, production of furfural from biomass may provide cost–effective alternative to commercial furfural in many applications [39,41].

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