PRODUCTION OF FURFURAL FROM SUGAR CANE BAGASSE BY DILUTE ACID-CATALYSED HYDROLYSIS

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ABSTRACT

The aim of this work was to study the production of furfural from sugar cane bagasse using dilute acid hydrolysis under variable parameters, were types of acid (nitric acid, sulfuric acid and phosphoric acid), concentration of acid (3%, 6%, and 9%) and pre-hydrolysis time (1, 2 and 3 hours). The results found that when increased concentration of acid and pre-hydrolysis time, nitric acid and phosphoric acid gave more yields of furfural. In contrast, when using sulfuric acid, yield of furfural decreased when increase pre-hydrolysis time. The optimal conditions for each acid type were 9% HNO_3 with 3 hours pre-hydrolysis time which furfural yield was 4.80%, 9% H_2SO_4 with 1 hour pre-hydrolysis time which furfural yield was 18.96%, and 9% H_3PO_4 with 3 hours pre-hydrolysis time which highest yield of furfural yield was 1.50%. In conclusion the suitable conditions to produce furfural was 9% H_2SO_4 with 1 hour pre-hydrolysis time.

Key word: furfural, sugar cane bagasse

หัวข้อวิทยานิพนธ์ การผลิตเฟอร์ฟูรัลจากชานอ้อยโดยปฏิกิริยาไฮโดรไลซิสด้วยกรดเจือจาง
นักศึกษา นาย ธีรวัฒน์ น้อยหมอ
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บทคัดย่อ

การทดลองนี้มีจุดประสงค์เพื่อศึกษาการผลิตเฟอร์ฟูรัลจากชานอ้อยโดยปฏิกิริยาไฮโดรไลซิสด้วยกรดเจือจางภายใต้สภาวะต่าง ๆ โดยตัวแปรที่ศึกษาได้แก่ ชนิดของกรด (กรดไนตริก, กรดซัลฟิวริก และกรดฟอสฟอริก) ความเข้มข้นของกรด (3%, 6% และ 9%) และเวลาที่ใช้ในการไฮโดรไลซิสเบื้องต้น (1, 2 และ 3 ชั่วโมง) จากผลการทดลองพบว่าเมื่อเพิ่มความเข้มข้นของกรด และเวลาที่ใช้ในการไฮโดรไลซิสเบื้องต้น กรดไนตริกและกรดฟอสฟอริกจะให้ปริมาณเฟอร์ฟูรัลเพิ่มขึ้นในทางตรงข้ามกรดซัลฟูริกจะให้ปริมาณเฟอร์ฟูรัลลดลงเมื่อเพิ่มเวลาที่ใช้ในการไฮโดรไลซิสเบื้องต้น สภาวะที่ดีที่สุดของกรดแต่ละชนิดคือ กรดไนตริกที่ความเข้มข้น 9% เวลาที่ใช้ในการไฮโดรไลซิสเบื้องต้น 3 ชั่วโมงจะให้ร้อยละผลได้ของเฟอร์ฟูรัล 4.80 กรดซัลฟิวริกที่ความเข้มข้น 9% เวลาที่ใช้ในการไฮโดรไลซิสเบื้องต้น 1 ชั่วโมงจะให้ร้อยละผลได้ของเฟอร์ฟูรัล 18.96 และกรดฟอสฟอริกที่ความเข้มข้น 9% เวลาที่ใช้ในการไฮโดรไลซิสเบื้องต้น 3 ชั่วโมงจะให้ร้อยละผลได้ของเฟอร์ฟูรัล 1.50 สรุปได้ว่าสภาวะที่เหมาะสมซึ่งให้ร้อยละผลได้ของเฟอร์ฟูรัลสูงสุดคือกรดซัลฟิวริกที่ความเข้มข้น 9% เวลาที่ใช้ในการไฮโดรไลซิสเบื้องต้น 1 ชั่วโมง

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Chapter 1

Introduction

1.1 Motivation

Thailand exports a lots of goods from agriculture industrial such as rice, sugar etc., so we have a lots of waste from agriculture production. Sugar cane bagasse, as waste in the process of sugar extraction, is an abundant and low-cost lignocellulosic material [1]. An adequate use of the sugar cane bagasse gives an added value for this material and a solution for the removal of this abundant waste, solving a problem of the sugar industry and increasing the economical yield of the process. Therefore, a double effect its obtained, economical and ecologic. The most frequent use for sugar cane bagasse is the energy production by its combustion [2]. This provokes a problem of pollution, increasing the emissions of CO_2. Other alternative uses of sugar cane bagasse are the production of chemical compounds such as furfural or hydroxymethylfurfural [3], the production of paper paste [4] or the biotechnological production of ethanol [5].

The hydrolysis of sugar cane bagasse to produce furfural solutions could be a good alternative use for this abundant resource. The worldwide furfural market reached around $3x10^{14}$ kg/yr with a market price of around US $1.7 per kg in 2002 [6]. Furfural and its derivated are important chemicals because it is a selective solvent for separating compounds in petroleum refining, gas, oil and diesel fuel. Their derivate furfuryl alcohol is a basic component for furan resins [7].

Furfural formation from sugar cane bagasses containing pentosans (25-27%) consist of two steps. The first step involves acid-catalysed hydrolysis, where the pentose chains are hydrolysed at high temperatures to monomeric pentose in aqueous media. In a second step pentoses are converted into furfural by the elimination of water. While the first reaction proceeds rapidly and at high yield, considerable losses of furfural occur during the dehydration step. Furfural generated by cyclization of xylose can be destroyed by the decomposition and condensation side reactions leading to reduction in yield. So, steam distillation is used to separate furfural from reaction to avoid furfural decomposition and condensation

1.2 Objectives

1. To produce furfural from sugar cane bagasse by hydrolysis with dilute acid and separate with steam distillation.
2. To investigate the effect of acid types, acid concentrations and pre-hydrolysis time on furfural yield.

1.3 Scope of study

1. Investigate the various parameters that effected on furfural yield under the following condition;
    - Types of acid are nitric acid, sulfuric acid and phosphoric acid
    - Concentration of acid are 3, 6, and 9%
    - Pre-hydrolysis time are 1, 2 and 3 hours.
2. Analyze furfural yield by using UV-visible spectrophotometer technique.
3. Determine the optimum condition for production of furfural.

1.4 Expected result

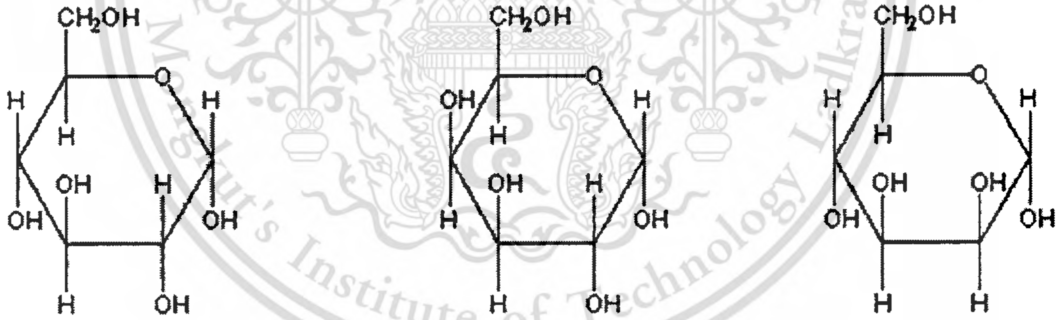
Obtain the best condition for production of furfural from sugar cane bagasse by hydrolysis with dilute acid.

Chapter 2

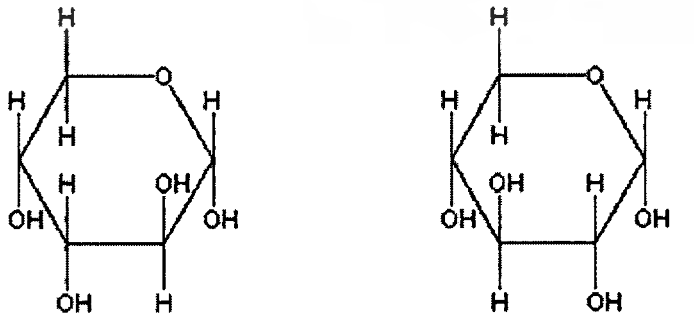
Theory and Literature Reviews

2.1 Constituent of biomass

2.1.1 Hemicellulose [18] can be any of several heteropolymers present in almost all cell walls along with cellulose. While cellulose is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base as well as myriad hemicellulase enzymes. Hemicellulose contains many different sugar monomers. In contrast, cellulose contains only anhydrous glucose. For instance, besides glucose, sugar monomers in hemicellulose can include xylose, mannose, galactose, rhamnose, and arabinose. Hemicelluloses contain most of the D-pentose sugars, and occasionally small amounts of L-sugars as well. Xylose is always the sugar monomer present in the largest amount, but mannuronic acid and galacturonic acid also tend to be present.



Glucose Galactose Mannose



Arabinose Xylose

Figure 2.1 Chemical structures of the main components of hemicelluloses [20]

2.1.2 Lignin[19] fills the spaces in the cell wall between cellulose, hemicellulose and pectin components, especially in tracheids, sclereids and xylem. It is covalently linked to hemicellulose and thereby crosslinks different plant polysaccharides, conferring mechanical strength to the cell wall and by extension the plant as a whole. It is particularly abundant in compression wood, but curiously scarce in tension wood.

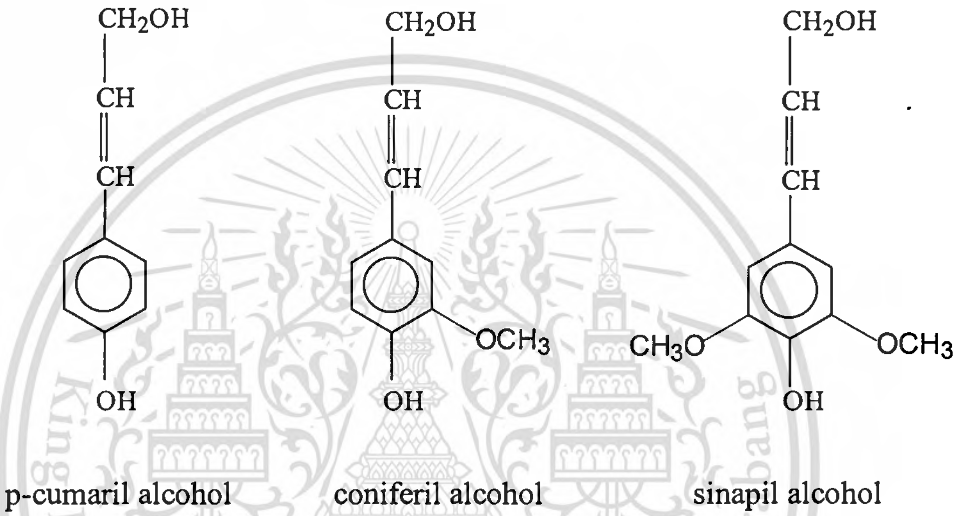


Figure 2.2 Chemical structures of the main components of lignin [21]

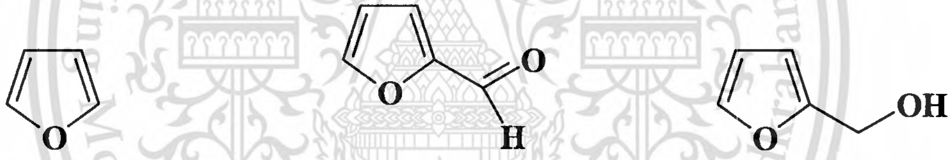
2.2 Furfural and a diverse derivatives [8]

Furfural was first isolated in 1832 by the German chemist Johann Wolfgang Döbereiner, who formed a very small quantity of it as a byproduct of formic acid synthesis. 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 sulphuric acid, and he determined that this chemical had an empirical formula of C_4H_3OCHO. In 1901, the German chemist Carl Harries deduced furfural's structure and 1922 the Quaker Oats factory at Cedar Rapids commenced the commercial production of furfural.

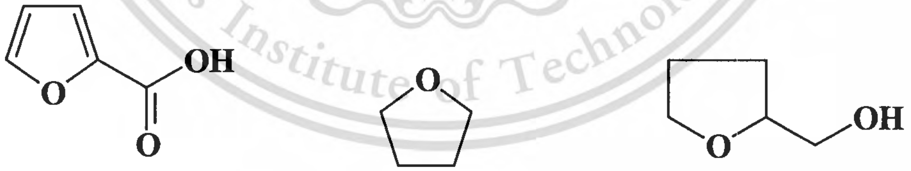
Furfural is produced from agricultural wastes that contain pentosans. Theoretically, almost any pentosan-containing material or combination of materials can be used for the production of furfural. The most common materials used for furfural production are corncobs, cottonseed hull bran, oat hulls (cleaned), cottonseed hulls, bagasse and rice hulls.

Furfural is important in terms of its presence, as a carbohydrate, in a chemical industry dominated by hydrocarbons. It seems to be one of the few renewable carbohydrate biomass products that can compete with hydrocarbon chemicals and without recourse to subsidize. Furfural is derived from the pentosan in the cellulose of plant tissues, the most prominent sources of which are corn/maize cobs, bagasse, paper-pulp residue, bamboo, kenaf, grain hulls, wheat and rice straw, nut shells, cottonseed and wood (soft and hardwood). Most furfural that is being produced today is derived from bagasse and corncobs

Figure 2.3 shows the structural formula of furfural and its derivative; furfuryl alcohol, furoic acid, tetrahydrofuran, tetrahydrofurfuryl alcohol. In addition, the derivative of furfural is shown in figure 2.4



Furan Furfural Furfuryl alcohol



Furoic acid Tetrahydrofuran Tetrahydrofurfuryl alcohol

Figure 2.3 Structural formula of furfural and its derivatives

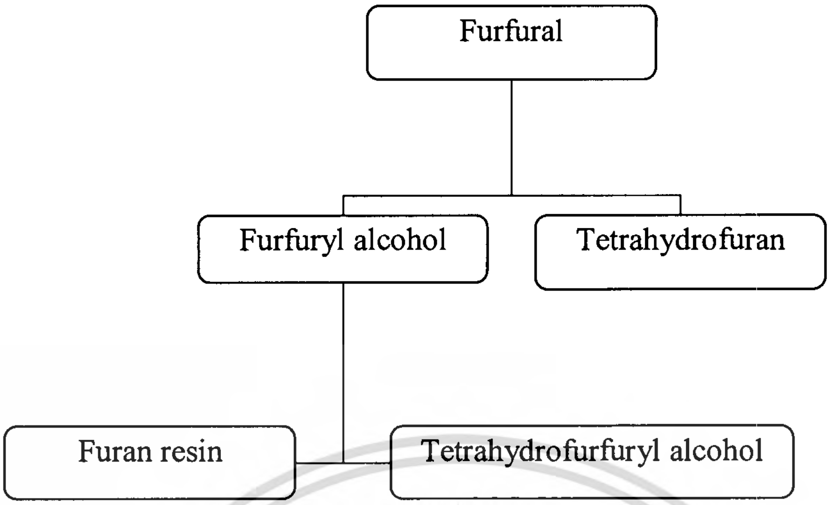


Figure 2.4 Diagram of furfural and its derivatives

A derivative of furan, it is prepared commercially by dehydration of pentose sugars obtained from cornstalks and corncobs, husks of oat and peanut, and other waste products. It is used in the manufacture of pesticides, phenolfurfural resins, and tetrahydrofuran. Tetrahydrofuran is used as a commercial solvent and is converted in starting materials for the preparation of nylon .

2.3 Physicochemical Properties [8]

Furfural, or Furan-2-carboxaldehyde, or Fural, Furfuraldehyde, or Pyromucic aldehyde is an aromatic aldehyde, and the chemical formula is $C_5H_4O_2$. It has properties similar to those of benzaldehyde. Furfural is a colorless oily liquid with the odor of almonds, but upon exposure to air it becomes dark brown, black, or yellow. Furfural dissolves readily in most polar organic solvents, but is only slightly soluble in either water or alkanes.

Furfural participates in the same kinds of reactions as other aldehydes and other aromatic compounds. The aromatic stability of furfural is not as great as in benzene, and furfural participates in hydrogenation and other addition reactions more readily than many other aromatics. The physical properties of furfural is shown in Table 2.1

Table 2.1 Physical properties of furfural

General Properties	
Molecular weight	96.08
Boiling point at 101.3 kPa (1 atm), °C	161.7
Freezing point, °C	-36.5
Refractive index, nD	
20°C	1.5261
25°C	1.5235
Density, d4 at 20°C, g/cm^3	1.1598
Vapor density (air=1)	3.3
Critical pressure, P_c, MPa	5.502
Critical temperature, T_c, °C	397
Solubility in, wt%	
Water	8.3
Alcohol; ether	∞

Thermodynamic Properties	
Heat of vaporization (liq), kJ/mol	42.8
Heat capacity (liq), J/(g.K)	
20-100°C	1.74
Heat of combustion (liq), kJ/mol	2344
Enthalpy of formation, kJ/mol	-155

Fluid Properties	
Viscosity, mPa.s, 25°C	1.49
Surface tension, mN/m (=dyn/cm)	
29.9°C	40.7

Electrical Properties	
Dielectric constant 20°C	41.9

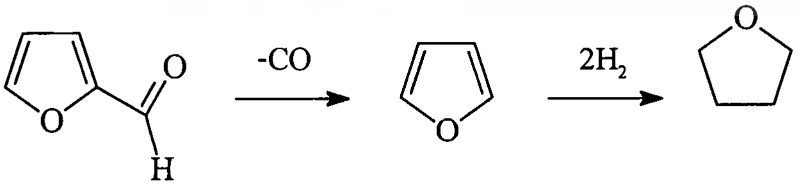
Flammability Properties	
Explosion limits (in air), vol%	2.1-19.3
Flash point, °C, tag closed cup	61.7
Auto ignition temperature, °C	315

2.4 Changing of furfural to its Derivatives [9,10]

The reaction leading from furfural to furfuryl alcohol and tetrahydrofurfuryl alcohol is adding hydrogen with catalyst.

furfural tetrahydrofurfuryl alcohol furfuryl alcohol

Tetrahydrofuran is the product of decarbonylation reaction. The catalyse is Zinc-Chromium-Molybdenum, *via* the hydrogenation of furan then a product is tetrahydrofuran.



furfural furan tetrahydrofuran

2.5 Industrial Applications of Furfural [8,10]

Furfural has the unique property to dissolve aromatics and other unsaturated olefins. It has large scale applications to its solubility characteristics and its easy recuperation by steam distillation.

2.5.1 A selective solvent in the refining of lubricating oils

Furfural is used as a solvent in petrochemical refining to extract dienes (which are used to make synthetic rubber) from other hydrocarbons.

2.5.2 Purification technology for C_4 and C_5 hydrocarbons

Separation and purification of C_4 hydrocarbons by extractive distillation with furfural. For the manufacture of synthetic rubber enormous quantities of pure 1,3-butadiene were needed. Corncobs and cottonseed hulls based plants were added as feedstocks to raise the furfural capacity.

2.5.3 Decolorizing agent to refine crude wood resin

In the industrial, wood resin purification with furfural by an extractive distillation technique are used.

2.5.4 The production of resin

Furfural, as well as it's derivative furfuryl alcohol, can be used either by itself or together with phenol, acetone, or urea to make resins. Such resins are used in the manufacture of casting moulds, fiberglass, some aircraft components, and automotive brake linings.

2.5.5 Cold-molding of resin-bonded abrasive wheels with furfural.

Furfural is unusually effective as a solvent for phenolic resins. In the manufacture of abrasive wheels, brake linings and refractory products for the steel industry furfural is known as a reactive solvent and excellent wetting agent.

2.5.6 Raw of Furfuryl alcohol production

Furfuryl alcohol is produced using a catalytic hydrogenation process at high pressure, the raw material being furfural. Furfuryl alcohol is used for the production of furanic resins in the foundry industry and in the production of tetrahydrofurfuryl alcohol (THFA), a solvent employed in the pharmaceutical industry.

2.5.7 Tetrahydrofuran production

Furfural is also used as a chemical intermediate in the production of the solvents furan and tetrahydrofuran, manufacture of pesticides, phenolfurfural resins, and tetrahydrofuran. Tetrahydrofuran is used as a commercial solvent and is converted in starting materials for the preparation of nylon .

2.6 Raw of furfural production [10,11]

Many plant materials contain the polysaccharide hemicellulose, a polymer of sugars containing five carbon atoms each. For crop residue feedstocks, about 10% of the mass of the original plant matter can be recovered as furfural. Furfural and water evaporate together from the reaction mixture, and separate upon condensation.

2.7 Production of Furfural [10,11]

Furfural is produced in a digester under high-pressure steam, from where it is recovered by steam distillation, followed by water-furfural separation and purification. The scheme illustrates all consecutive steps in the conversion of sugar cane bagasse into Furfural. In the first step pentosans are hydrolyzed by strong mineral acids to monomeric C_5-sugars. Subsequent cyclodehydration of the pentoses yields furfural.

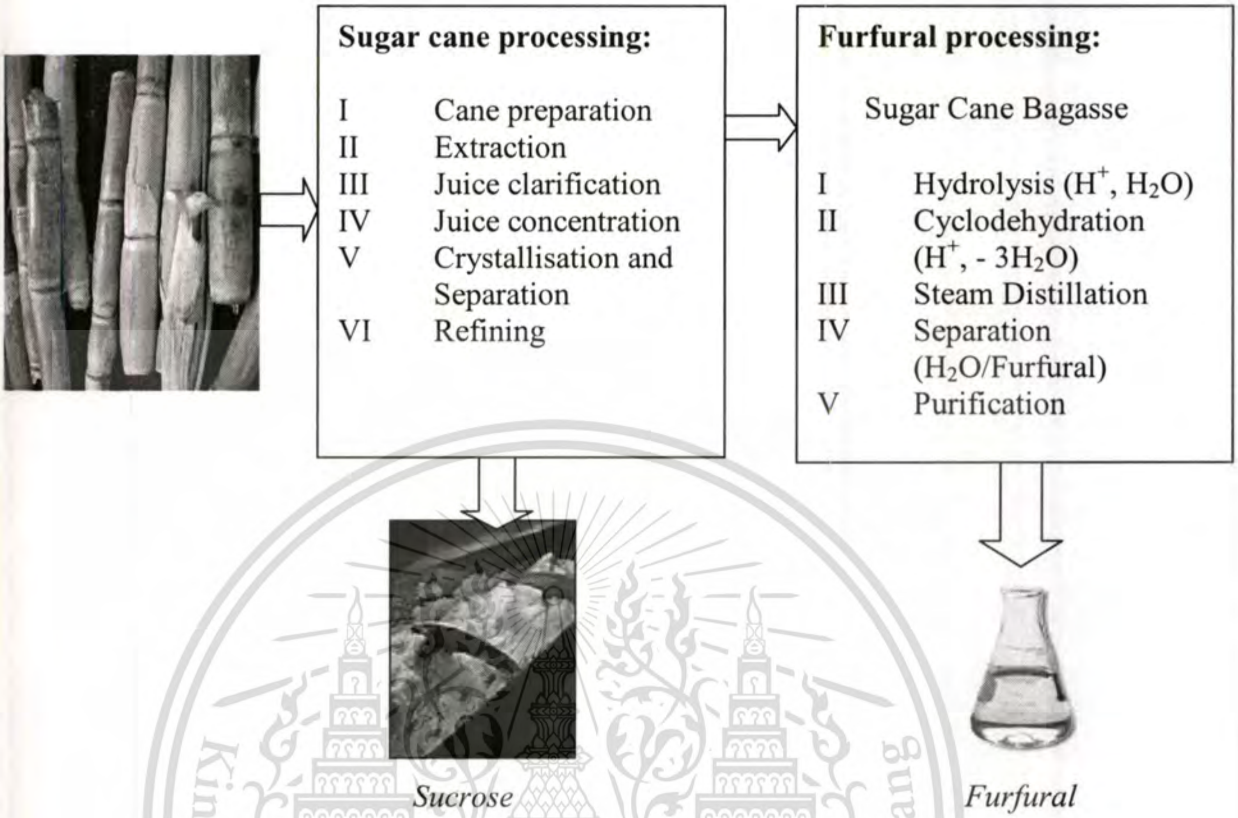


Figure 2.5 Diagram of furfural production

Furfural is formed from pentosan, a five-carbon cellulose which occurs prolifically in natural woody products such as oat hulls, corncobs, bagasse, wood chips and other vegetable waste. The reactions are simple. The acidified feedstock is heated, at 100°C the pentosan is hydrolyzed to pentose, and this pentose is dehydrated to furfural in a unified process.

The stoichiometric and mechanism of the two reaction show as follows:

(1) Hydrolysis of pentosan

Pentosan + nWater $\xrightarrow{\text{Acid (Catalyst), 100°C}}$ n Pentose

$(C_5H_8O_4)_n$ + n H_2O $\longrightarrow$ n $C_5H_{10}O_5$

n 132.114 + n 18.016 $\longrightarrow$ 150.130 g/mole

(2) Dehydration of Pentose:

Pentose - 3 Water $\xrightarrow{\text{Acid (Catalyst), 175°C}}$ Furfural

$C_5H_{10}O_5$ - 3 H_2O $\longrightarrow$ $C_5H_4O_2$

150.130 - 54.048 $\longrightarrow$ 96.082 g/mole

So that the stoichiometric yield of furfural from pentosan is 72.72 g per 100 g of pentosan.

This is the sacred figure against which all furfural plants are measured.

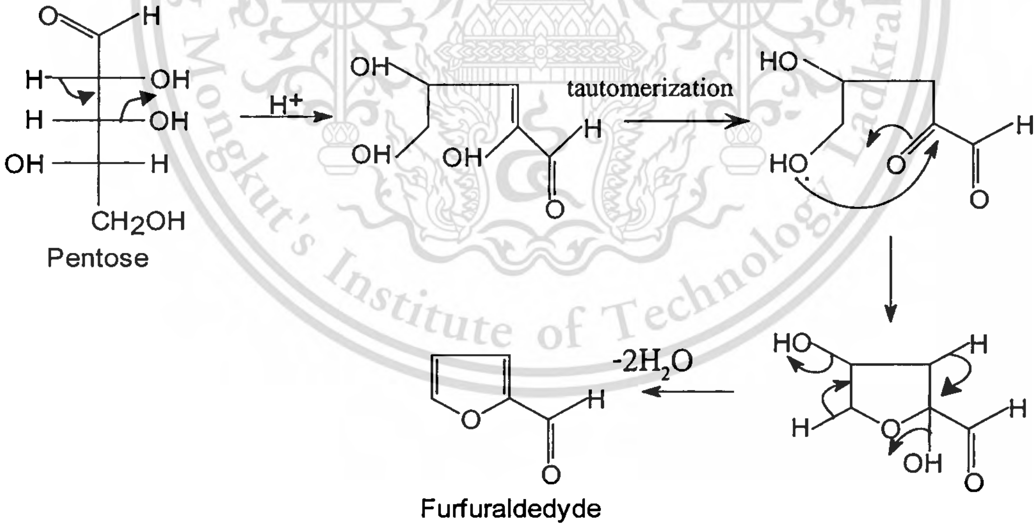


Figure 2.6 The mechanism for the dehydration of pentose to furfural

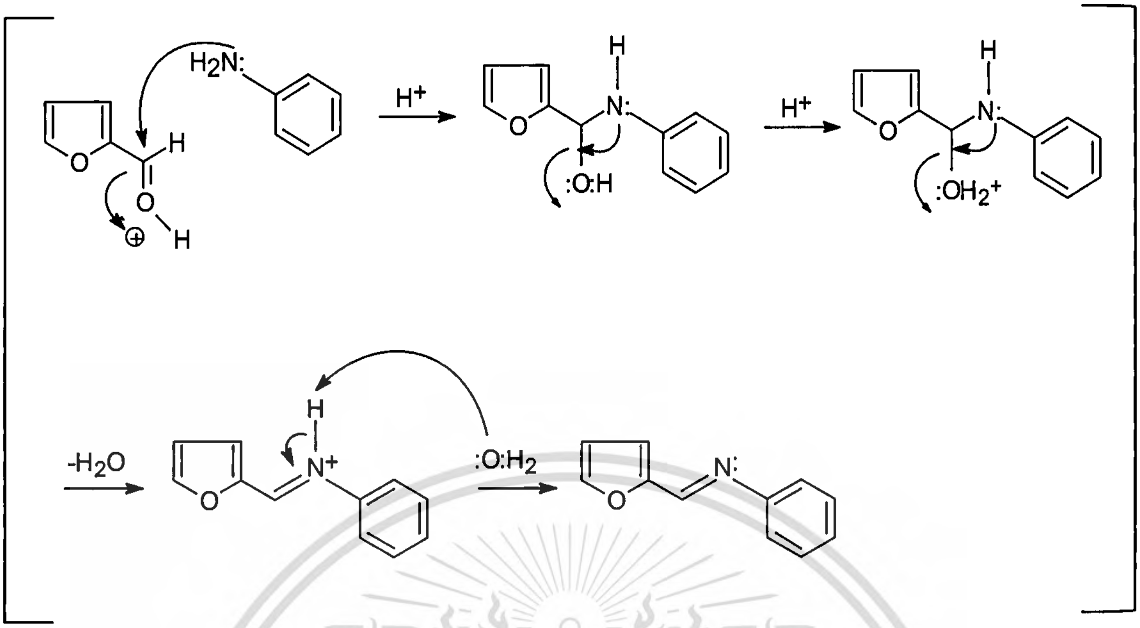


Figure 2.7 The mechanism for the reaction of furfural test with aniline

2.8 Literature Reviews

Mansilla et al.[7] studied the formation of furfural under the varying condition. This research was observed on an effectiveness of the furfural production from rice hull. There are two types of technologies to produce furfural. In one-stage technology, depolymerization of pentosans in xylose and dehydration to furfural occur simultaneously. In two-stage technology, a dissolution and depolymerization of pentosans occur under mild conditions, followed by dehydration of xylose to furfural. The parameters that influence yield in the autoclave are the acid concentration, liquid/solid ratio, particle size, and catalyse nature.

Manuel and Martha [12] had studied the furfural production by hydrolysis of sorghum straw with phosphoric acid at 134 °C. Several concentrations of H_3PO_4 in the range 2–6% and reaction time (range 0–300 min) were evaluated. Kinetic parameters of mathematical models for predicting the concentration of xylose, glucose, arabinose, acetic acid and furfural in the hydrolysates were found. Optimal conditions for furfural production by acid hydrolysis were 6% H_3PO_4 at 134 °C for 300 min, which yielded a solution with 13.7 g furfural/L, 4.0 g xylose/L, 2.9 g glucose/L, 1.1 g arabinose/L and 1.2 g acetic acid/L. The furfural yield of the process was 0.1336 g furfural/g initial dry matter was obtained. The results confirmed that sorghum straw can be used for furfural production when it is hydrolyzed using phosphoric acid.

Téllez – Luis et al.[13] had studied the mathematical modeling of hemicellulosic sugar production from sorghum straw. The aim of this research was to produce xylose from hydrolysis of sorghum straw at 122 °C, by using three concentrations of sulphuric acid (2%, 4% and 6%). Kinetic parameters of mathematical models for predicting the concentration of xylose, glucose, acetic acid and furfural were found and optimal conditions selected. These were 2% H_2SO_4 at 122°C for 71 min, which yielded a solution with 18.17 g xylose/L, 6.73 g glucose/L, 0.9 g furfural/L and 1.51 g acetic acid/L.

Chapter 3

Experimental Details

3.1 Materials

1. Sugar cane bagasse
2. 85% Phosphoric acid (H_3PO_4), analytical grade, from SR. LAB
3. 96% Sulfuric acid (H_2SO_4), analytical grade, from SR. LAB
4. 65% Nitric acid (HNO_3), analytical grade, from SR. LAB
5. Aniline ($C_6H_5NH_2$), analytical grade, from MERCK
6. Acetic acid (CH_3COOH), analytical grade, from LAB SCAN
7. Stannous chloride ($SnCl_2$), analytical grade, from MERCK
8. 95% Ethanol (C_2H_5OH), analytical grade, from LAB SCAN
9. 98% Standard furfural ($C_5H_4O_2$), analytical grade, from MERCK

3.2 Equipments

1. Three-necked round bottom flask 500 mL
2. Volumetric flasks 25, 50 and 100 mL
3. Pipettes 1, 5, 10 and 20 mL
4. Cylinders 100 mL
5. Beakers 50 mL
6. Condenser
7. Heating mantle
8. Thermometer
9. Separating funnel
10. Glass Tube
11. Erlenmeyer flasks 25 mL
12. String rod
13. Dropper
14. Glass funnel
15. UV-visible spectrophotometer (Jenway 6405 UV/vis Spectrophotometer)

3.3 Experimental Procedure

3.3.1 Preparation of raw material

The raw material using in experiments was sugar cane bagasse from the sugar extraction industry. The sugar cane bagasse were dried in an oven at 110 °C, milled, screened to select the fraction of particles with a size lower than 60 meshes, homogenized in a single lot and stored in desiccator to ensure low residual moisture content.

3.3.2 Preparation of acid solution

Acid were pipetted according to Table 3.1 and then it was diluted with distilled water by 1000 mL volumetric flask.

Table 3.1 Volume of acid for dilution

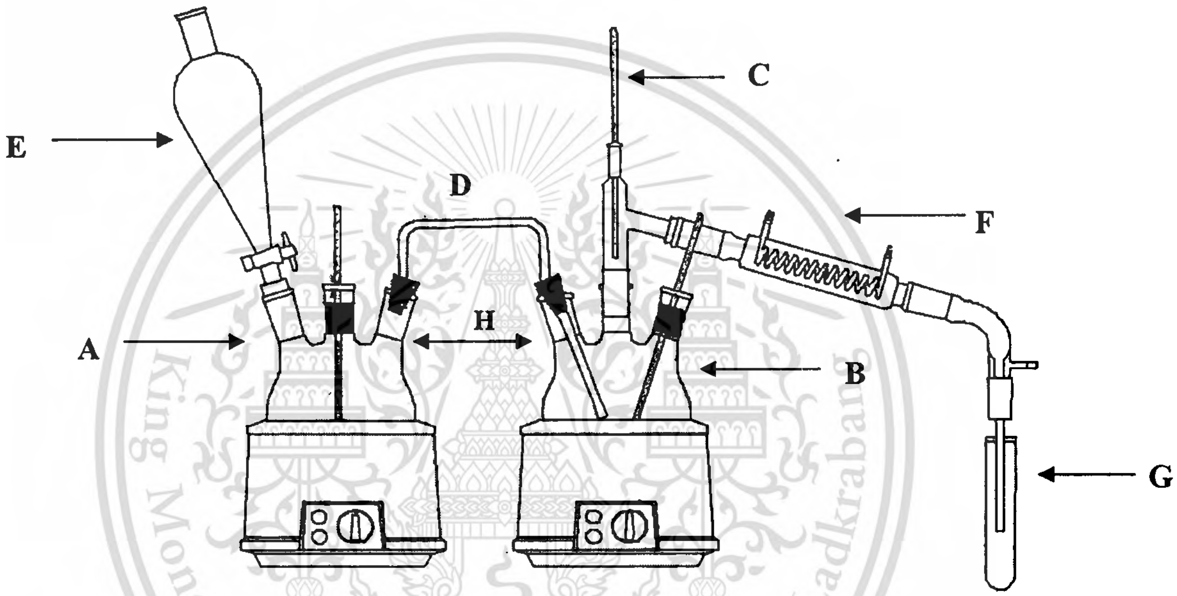
Types of acid	Volume (mL)		
	3%	6%	9%
HNO_3	46.15	92.31	138.46
H_2SO_4	31.25	62.50	93.75
H_3PO_4	35.29	70.59	105.88

3.3.3 Acid hydrolysis of sugar cane bagasse

The reaction were conducted in an experimental apparatus show in Figure 3.1 Production of furfural from sugar cane bagasse by dilute acid hydrolysis

1. 10 g of dry bagasse and 150 mL of acid solution were added into 500 mL of three-necked round bottom flask (B). Then, the solution were synthesized at different pre-hydrolysis time.
2. 200 mL distilled water was pour into another three-necked round bottom flask (A).
3. After reach the pre-hydrolysis time, both of three-necked round bottom flask were heated by heating mantle. The furfural was recovered by steam distillation and collected in test tube.
4. The nitrogen gas was flowed into test tube to reduce oxygen in air.

5. The synthesized furfural was determined using a Colourimetric method [14]. The analysis is based on the reaction of furfural with aniline in acetic acid and stannous chloride to stabilize the colour. Spectral analyses were done at 515 nm by UV-Visible spectrometer and compared with a calibration curve for pure furfural.



A: Round bottom flask (containing water)

B: Round bottom flask (containing sugar cane bagasse and acid)

C: Thermometer

D: Glass tube

E: Separating funnel

F: Condenser

G: Test tube (Collecting furfural)

H: Heating mantle

Figure 3.1 Experimental apparatus for acid hydrolysis of sugar cane bagasse

The condition of 27-runs of experiments listed in Table 3.1

Table 3.2 Design for experimental

Run	Type of Acid	Acid concentration	Pre-hydrolysis time (hours)
1	Nitric Acid	3%	1
2	Nitric Acid	3%	2
3	Nitric Acid	3%	3
4	Nitric Acid	6%	1
5	Nitric Acid	6%	2
6	Nitric Acid	6%	3
7	Nitric Acid	9%	1
8	Nitric Acid	9%	2
9	Nitric Acid	9%	3
10	Sulfuric Acid	3%	1
11	Sulfuric Acid	3%	2
12	Sulfuric Acid	3%	3
13	Sulfuric Acid	6%	1
14	Sulfuric Acid	6%	2
15	Sulfuric Acid	6%	3
16	Sulfuric Acid	9%	1
17	Sulfuric Acid	9%	2
18	Sulfuric Acid	9%	3
19	Phosphoric Acid	3%	1
20	Phosphoric Acid	3%	2
21	Phosphoric Acid	3%	3
22	Phosphoric Acid	6%	1
23	Phosphoric Acid	6%	2
24	Phosphoric Acid	6%	3
25	Phosphoric Acid	9%	1
26	Phosphoric Acid	9%	2
27	Phosphoric Acid	9%	3

3.3.4 Analytical method

Preparation of reagent

1. The 2 g of stannous chloride was weighted and diluted with 10 mL of 12N hydrochloric acid and heated for 5 minute to give 20% of stannous chloride solution
2. Dilute 10 mL of aniline with conc. acetic acid and then add 5 mL of 20% stannous chloride solution and set volume 100 mL with conc. acetic acid.

Preparation of calibration curve

1. Pipette 1.02 mL. of standard furfural and dilute into 100 mL. volumetric flask with distilled water
2. Pipette 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 mL. Then dilute into 100 mL. volumetric flask with distilled water will get 0.005, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035 and 0.040 %v/v furfural
3. Pipette 6 mL of furfural and add 3 mL of ethanol and 10 drops of reagent and then analyst by UV-Visible spectrometer at 515 nm.
4. Plot calibration curve between absorbance and furfural concentration (mg/L)

Chapter 4

Results and Discussion

Furfural was produced by hydrolysis of sugar cane bagasse with acid solution. The effects of acid type, acid concentration, and pre-hydrolysis time were investigated. The furfural concentration was analyzed by UV-spectrophotometer and standard calibration curve was prepared.

4.1 Preparation of calibration curve

Furfural was determined using a colorimetric method. The analysis is based on the reaction of furfural with aniline in acetic acid and stannous chloride to stabilize the color. Spectral analyses were done at 515 nm. The result is shown in table 4.1 and the calibration curve is plotted in figure 4.1

Table 4.1 Absorbance of Standard furfural solution at various concentrations.

Standard Furfural Concentration		Absorbance
%v/v	mg/L	
0	0	0
0.005	58	0.497
0.010	116	0.798
0.015	174	1.263
0.020	232	1.588
0.025	290	2.085
0.030	348	2.422
0.035	406	2.650
0.040	464	2.934

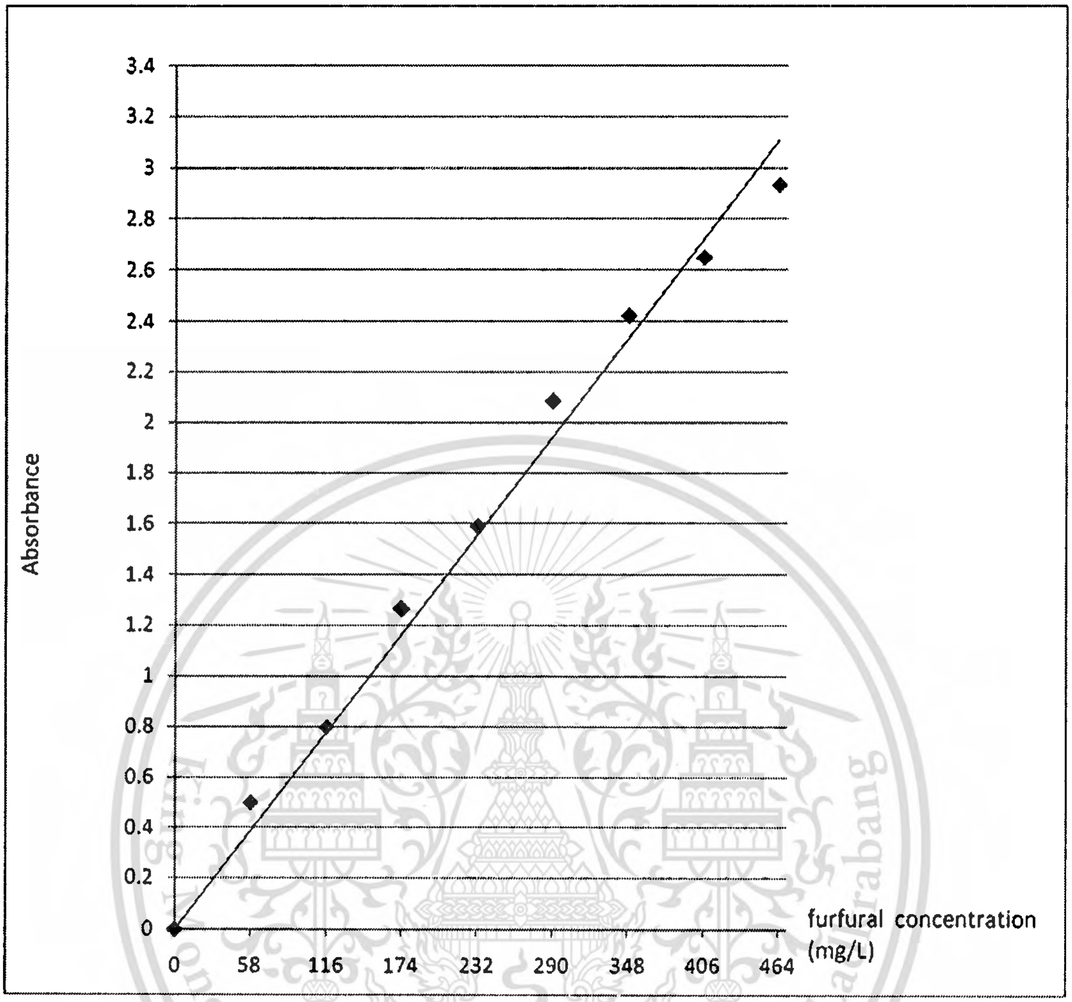


Figure 4.1 Calibration curve of standard furfural.

Calibration curve in figure 4.1 was used to determine the concentration of furfural that obtained from hydrolysis reaction of sugar cane bagasse.

4.2 Furfural production by hydrolysis of sugar cane bagasse.

In this work, sugar cane bagasse was hydrolyzed with different acid (HNO_3, H_2SO_4, and H_3PO_4) at a concentration of 3, 6, and 9 % with a pre-hydrolysis time of 1, 2, 3 hours. The concentration of furfural and furfural yield from the experiments are summarized in Table 4.2 and 4.3.

Table 4.2 Furfural concentration at different acid, concentration and pre- hydrolysis time.

Acid type	Acid concentration		Furfural concentration(mg/L)		
	%v/v	mol/dm^3	Pre-hydrolysis time 1 hour	Pre-hydrolysis time 2 hours	Pre-hydrolysis time 3 hours
Nitric acid	3	0.7189	9.17	15.83	38.33
	6	1.4378	10.83	18.83	52.33
	9	2.1567	12.67	32.33	87.33
Sulfuric acid	3	0.5628	54.17	26.33	15.67
	6	1.1256	113.17	85.17	77.00
	9	1.6885	344.67	320.67	266.33
Phosphoric acid	3	0.5158	12.67	17.83	25.33
	6	1.0316	14.00	18.50	25.83
	9	1.5474	15.00	20.17	27.33

Table 4.3 Percent yield of furfural at various concentrations.

Acid type	Acid concentration	Furfural yield (%)		
		Pre-hydrolysis time 1 hour	Pre-hydrolysis time 2 hours	Pre-hydrolysis time 3 hours
Nitric acid	3%	0.50	0.87	2.11
	6%	0.60	1.04	2.88
	9%	0.70	1.78	4.80
Sulfuric acid	3%	2.98	1.45	0.86
	6%	6.22	4.68	4.24
	9%	18.96	17.64	14.65
Phosphoric acid	3%	0.70	0.98	1.39
	6%	0.77	1.02	1.42
	9%	0.83	1.11	1.50

4.2.1 Effect of acid types

The concentrations of furfural in the product from hydrolysis of sugar cane bagasse at different acid types are shown in figure 4.2 - 4.4

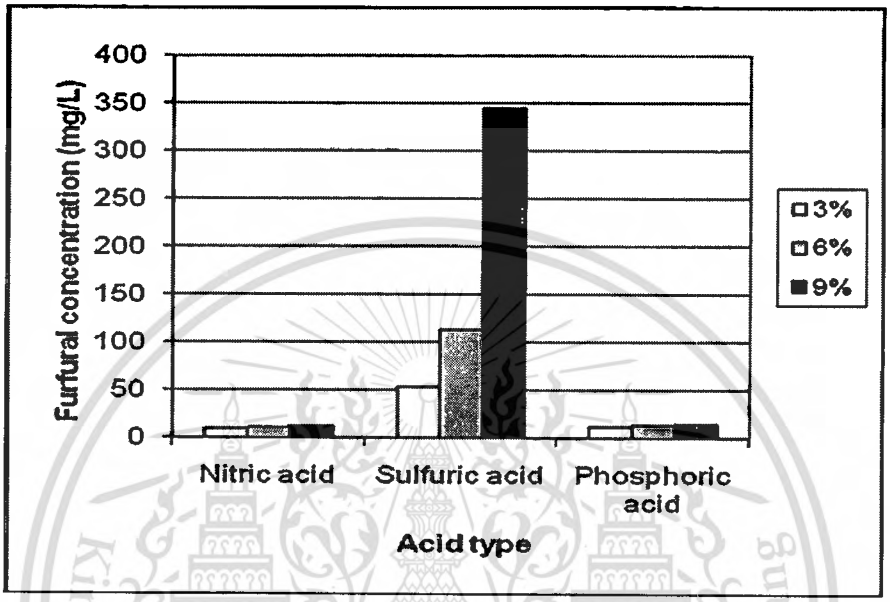


Figure 4.2 Effect of acid types on furfural concentration with a pre-hydrolysis time 1 hour

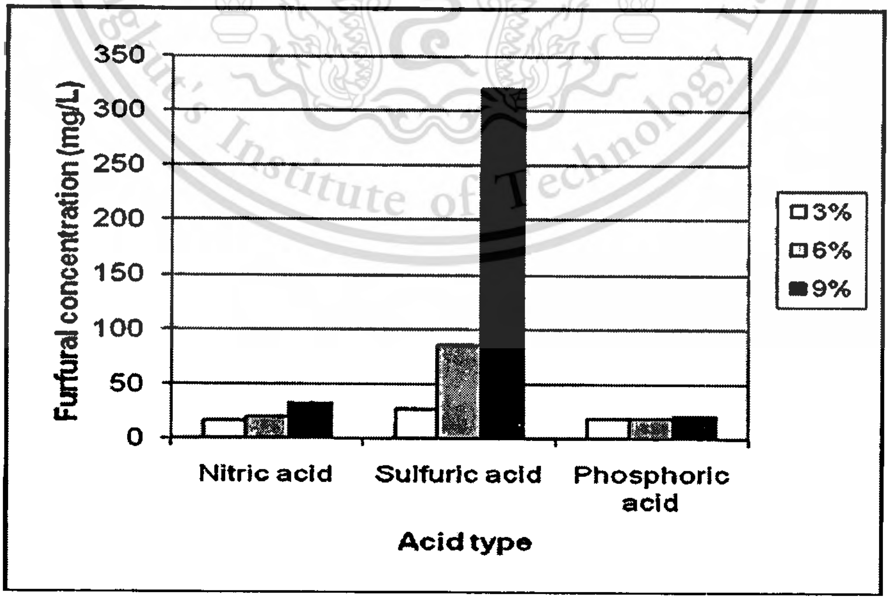


Figure 4.3 Effect of acid types on furfural concentration with a pre-hydrolysis time 2 hours

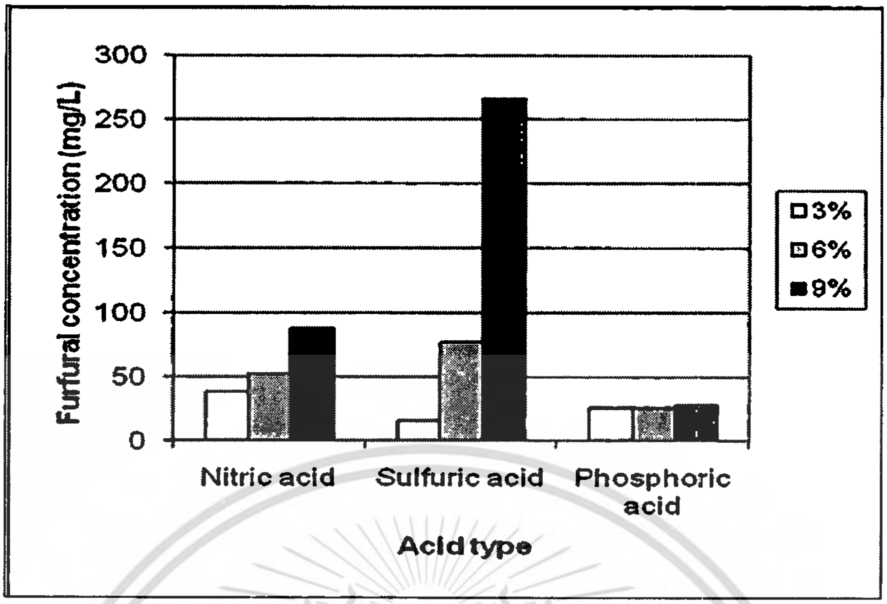


Figure 4.4 Effect of acid types on furfural concentration with a pre-hydrolysis time 3 hours

From figure 4.2 to 4.4, it was shown that sulfuric acid produced the higher furfural concentration than nitric acid and phosphoric acid, (54.17 mg/L at 1 hr, 113.17 mg/L at 2 hrs, and 344.67 mg/L at 3 hrs). Sulfuric acid and nitric acid were strong acid (pKa was -10 and -2 respectively) that different in the amount of proton. The protons of sulfuric acid were ionized from the molecules and dissolved in solution twice as that of nitric acid. Then more protons in acid will be reacted with pentose in sugar cane bagasse to get more furfural. For phosphoric acid, it was weak acid (pKa = 2.12), give the less proton than sulfuric and nitric acid, then, lowest furfural yield was obtained. It is important to remark that the experimental result of the study of acid type effect was in accordance with the earlier reported of Aguilar et al.[15], and Sara Gamez et al. [16].

4.2.2 Effect of acid concentrations

The furfural concentrations of the product from hydrolysis of sugar bagasse at different acid concentration are shown in figure 4.5 - 4.7

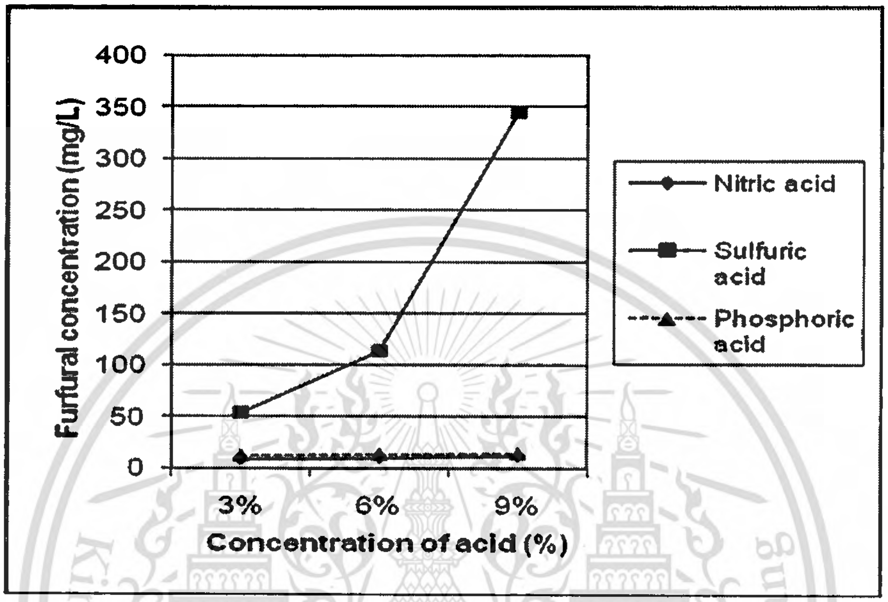


Figure 4.5 Effect of acid concentration on furfural concentration with a pre-hydrolysis time 1 hour

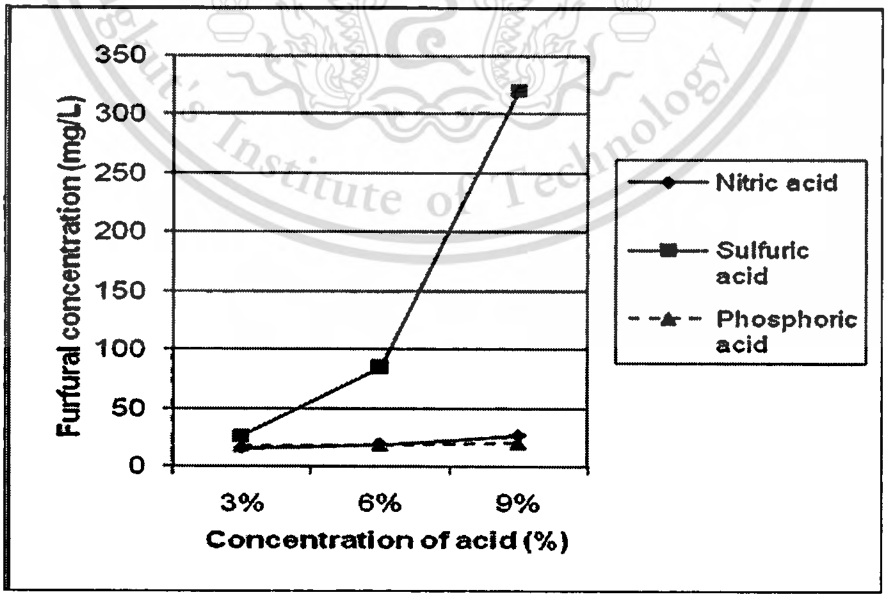


Figure 4.6 Effect of acid concentration on furfural concentration with a pre-hydrolysis time 2 hours

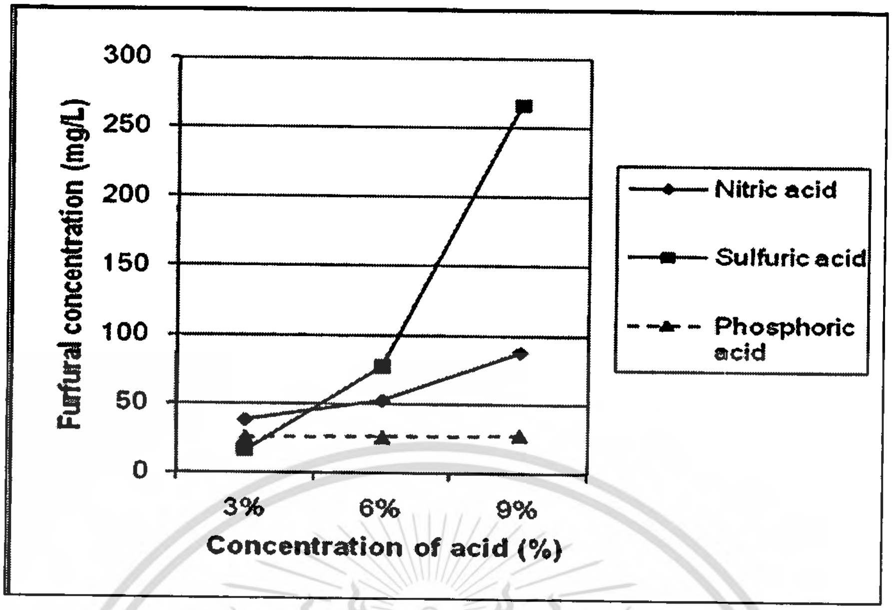


Figure 4.7 Effect of acid concentration on furfural concentration with a pre-hydrolysis time 3 hours

From figure 4.5 to 4.7, the furfural concentration was increased when acid concentration at all type of acids and pre-hydrolysis time were performed. Increasing of furfural concentration from hydrolysis with sulfuric acid was higher than that of nitric acid and phosphoric acid by which at an acid concentration at 9 % gave the maximum value of furfural concentration (344.67 mg/L at 1 hr, 320.67 mg/L at 2 hrs, and 266.33 mg/L at 3 hrs.). It can be described that the increasing of acid concentration, the concentration of proton was increased. Then, the large amount of proton can be diffused through the wet cellulosic metrix and reacted with pentose to produced highly yield of furfural. In addition, the experimental result from Mansilla et al. [7] summarized the effect of acid concentration in accordance with this work.

4.2.3 Effect of pre-hydrolysis time

In the experiment, pentose was converted from pentosan in a pre-hydrolysis step. In the second step cyclization and dehydration of pentose was occured. The effect of pre-hydrolysis on furfural concentration at different acid are shown in Figure 4.8 to 4.10

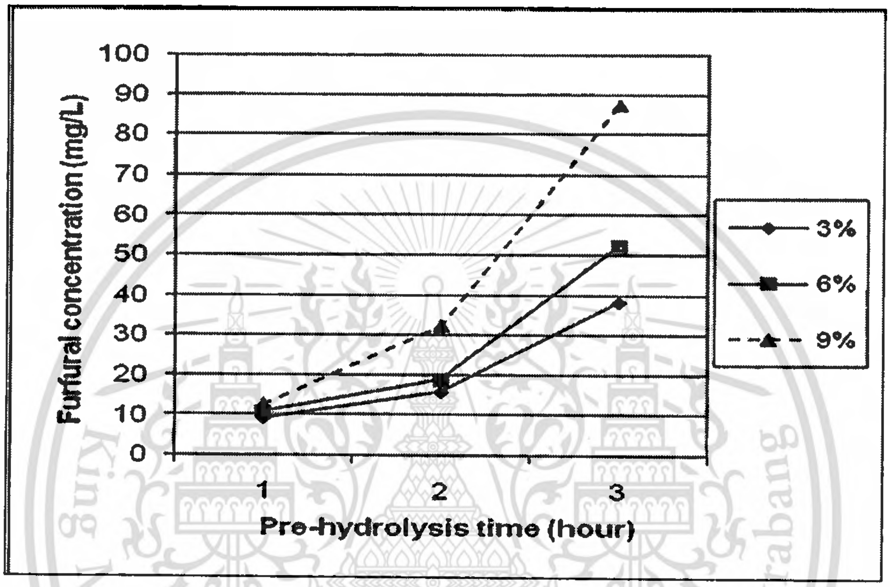


Figure 4.8 Effect of pre-hydrolysis time on furfural concentration using nitric acid (HNO_3)

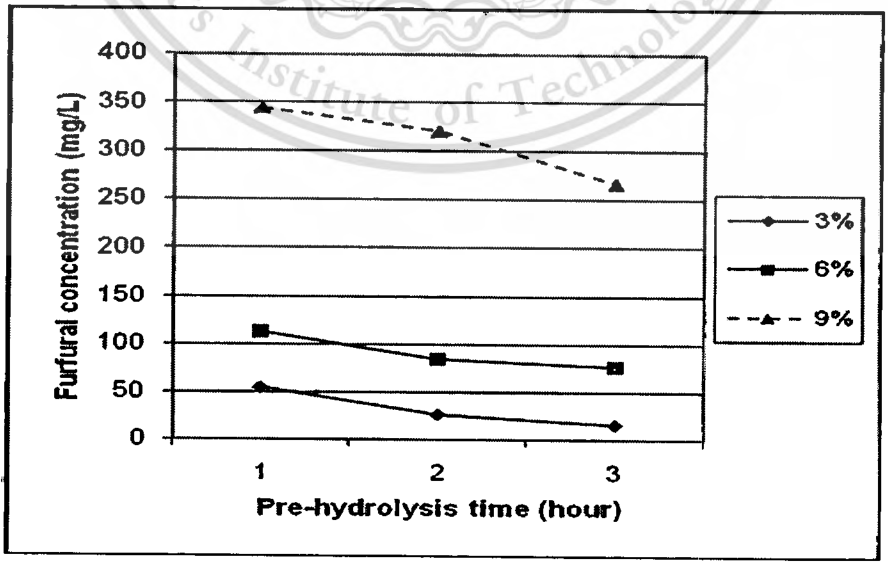


Figure 4.9 Effect of pre-hydrolysis time on furfural concentration using sulfuric acid (H_2SO_4)

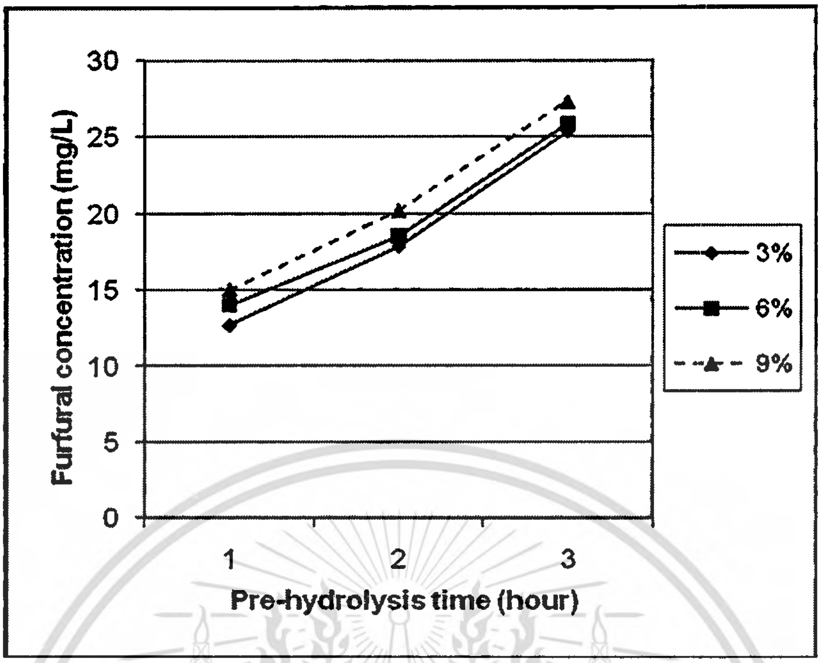


Figure 4.10 Effect of pre-hydrolysis time on furfural concentration using phosphoric acid (H_3PO_4)

It can be seen from Figure 4.8 and 4.10 that the furfural concentration was increased with increasing pre-hydrolysis time for hydrolysis with nitric acid and phosphoric acid. The results show that pentosan begins to convert and undergoes to pentose when the reaction time is longer result in the more pre-hydrolysis time, and the more contact time for pentosan to react with acid and converted to pentose. On the other hand, concentration of furfural was slighty decreased when increased the pre-hydrolysis time using sulfuric acid as acid medium.

It can be described that sulfuric acid was the strong acid and gave the more protons than other acid used in the experiment. At the longer pre-hydrolysis time, the decomposition of pentose was occurred from proton attach. Mansilla et al [7] studied effect of pre-hydrolysis time on furfural yield from hydrolysis of rice hull using 15% H_2SO_4. They found that beyond 30 minutes the furfural production decrease as a consequence of pentose decomposition during the pre-hydrolysis step. The result of this effect showed that a pre-hydrolysis time of 1 hour in sulfuric acid gave the highest yield of furfural.

In summary, the hydrolysis of sugar cane baggasse with sulfuric acid at a concentration of 9% and pre-hydrolysis time of 1 hour produced the highest concentration of furfural (344.67mg/L) and yield (18.96%) that is the optimum condition for this experiment.

4.3 Identification of furfural

Identification of furfural produced from hydrolysis of sugar cane bagasse was done by spectroscopic method, with Fourier Transformed Infrared spectroscopy (FT-IR).

Furfural product for FT-IR was prepared by sugar cane bagasse with sulfuric acid under acid concentration of 9% and pre-hydrolysis time of 1 hour.

In chemical structure of furfural (Figure 4.11) consisted of carbonyl function group and many chemical bonds. Carbonyl group and each of chemical bond will showed absorption band or peak at different absorption frequency. In figure 4.12, illustrated FT-IR spectrum of furfural, absorption bands or peak of furfural are listed in Table 4.4

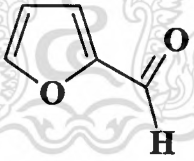


Figure 4.11 Chemical Structure of furfural

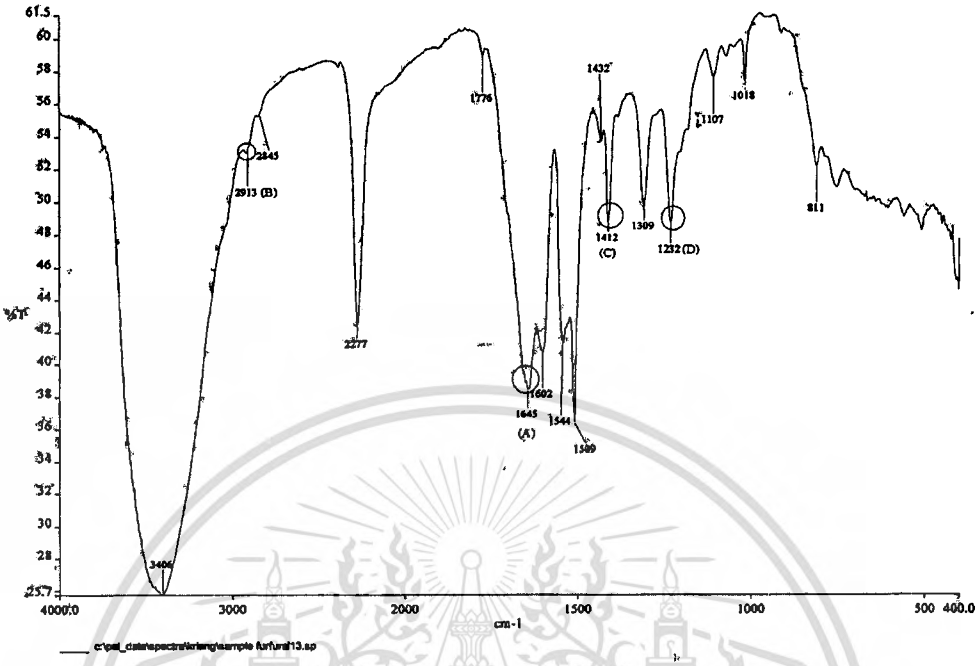


Figure 4.12 Infrareded spectroscopy of furfural (hydrolysis with 9% H_2SO_4 at 1 hour pre-hydrolysis time)

Table 4.4 Absorption frequencies of functional group and chemical bond on furfural [17], [23]

Position	Absorption frequency (cm^{-1})	Bond	Functional group
A	1645	C=O stretching	alpha, beta-unsaturated aldehydes
B	2913	C-H stretching of aldehyde	aldehydes
C	1412	C=C	aromatic
D	1232	C-O	aromatic ethers

All groups in Table 4.4 were interrupted with chemical structure of furfural.

Chapter 5

Conclusion and Recommendation

This special project was intended to produce furfural from sugar cane bagasse by dilute acid hydrolysis. To added value for waste material from agriculture by react with acid, therefore, this special project was aimed to get high quantity of furfural.

The goal of this research was to study the best condition for production of furfural by pre-hydrolysis with sugar cane bagasse with three types of acid below:

1. Nitric acid
2. Sulfuric acid
3. Phosphoric acid

The studying in each type of acid was tried to find optimal condition to produce furfural

1. Suitable condition of nitric acid was 9% HNO_3 with 3 hours pre-hydrolysis time which furfural yield of 4.80%.
2. Suitable condition of sulfuric acid was 9% H_2SO_4 with 1 hour pre-hydrolysis time which furfural yield of 18.96%.
3. Suitable condition of phosphoric acid was 9% H_3PO_4 with 3 hours pre-hydrolysis time which furfural yield of 1.50%.

To investigate parameters that effected on furfural yield we conclude that:

- For nitric acid and phosphoric acid, when more pre-hydrolysis time we get more yield of furfural because pre-hydrolysis is stepping that change pentosan to more pentose. So we get more yield of furfural. But for sulfuric acid if too long pre-hydrolysis, it makes by-reaction, that is decomposition of pentose which decrease in yield of furfural
- When increase concentration of acid, we got more yield of furfural because acid is important parameter that increase reaction of hydrolysis of pentosan but if it too much concentration, the yield of furfural will decompose because condensation and polymerization reaction.

The best condition to produce furfural was 9% H_2SO_4 with 1 hour pre-hydrolysis time.

5.2 Recommend Further Study

1. Study the using of supercritical carbon dioxide for recover furfural from the hydrolysis reaction instead of steam distillation.
2. Study the preparation of furfural from waste water of paper pulp industrial that it has cellulose in chemical structure.
3. Study by using heterogeneous catalyst to improve yield of furfural.

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Appendix-A

Data information

Table A-1 Absorbance of furfural from hydrolysis of sugar cane bagasse under various condition.

Acid		Absorbance (515 nm.)		
Types	Concentrations(%v/v)	Pre-hydrolysis time 1 hr	Pre-hydrolysis time 2 hr	Pre-hydrolysis time 3 hr
HNO_3	3	0.055	0.095	0.230
	6	0.065	0.113	0.314
	9	0.076	0.194	0.524
H_2SO_4	3	0.325	0.158	0.094
	6	0.679	0.511	0.462
	9	2.068	1.924	1.598
H_3PO_4	3	0.076	0.107	0.152
	6	0.084	0.111	0.155
	9	0.090	0.121	0.164

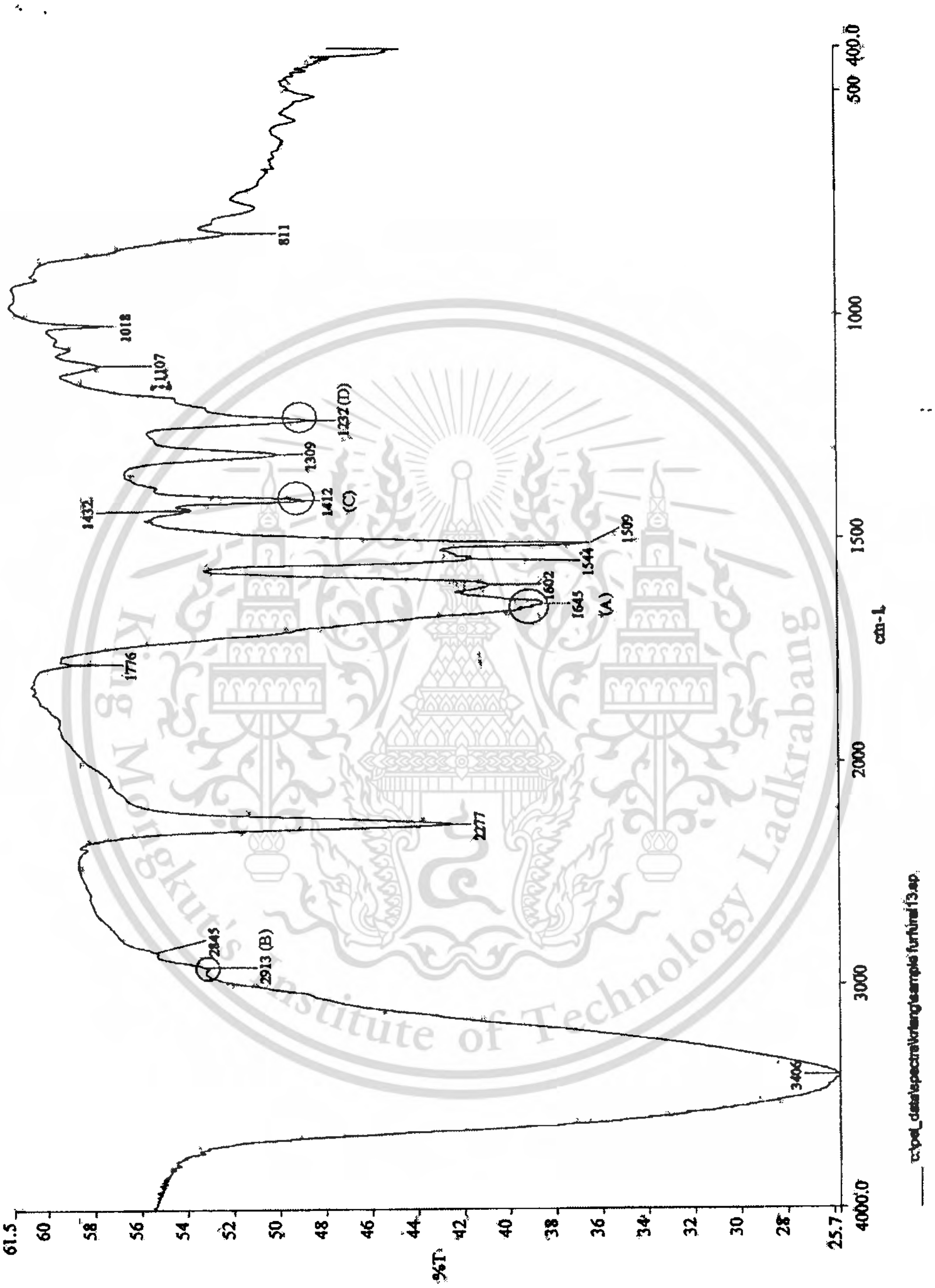

Figure A-1 FTIR Spectrum of 9% H_2SO_4 with pre-hydrolysis time of 1 hour

Appendix-B

Properties of acid and calculation of acid concentration

Table B-1 Properties of acid [22]

Acid type	Molecular weight (g/mol)	Density (g/cm^3)	pKa
H_2SO_4	98.078	1.84	-10
HNO_3	63.012	1.51	-2
H_3PO_4	98.000	1.685	2.12

B-1 Preparation of acid

Preparation of acid at difference concentration

Formula for calculation

$$M = \frac{10xCxd}{MW}$$

where: M = concentration of acid, mol/dm^3

C = percentage of acid, %

d = density of acid, g/cm^3

MW = molecular weight of acid, g/mol

$$C_1V_1 = C_2V_2$$

where: C_1 = concentration of conc. acid

V_1 = volume of conc. acid

C_2 = concentration of acid solution

V_2 = volume of acid solution

For example:

Preparation of 1000 mL of 3% HNO_3 from 65% HNO_3

1. Change 65% HNO_3 into mol/dm^3

$$M = \frac{10x65x1.51}{63.012}$$

$$M = 15.5764$$

2. Change 3% HNO_3 into mol/dm^3

$$M = \frac{10x3x1.51}{63.012}$$

$$M = 0.7189$$

3. Calculate volume of conc. nitric acid use to prepare 1000 mL of 3% HNO_3

$$C_1V_1 = C_2V_2$$

$$15.5764\ V_1 = 0.7189x1000$$

$$V_1 = 46.1531\ mL$$

so, use 46.15 mL to prepare 1000 mL of 3% HNO_3

Preparation of 1000 mL of 3% H_2SO_4 from 96% H_2SO_4

1. Change 96% H_2SO_4 into mol/dm^3

$$M = \frac{10x96x1.84}{98.078}$$

$$M = 18.0102$$

2. Change 3% H_2SO_4 into mol/dm^3

$$M = \frac{10x3x1.84}{98.078}$$

$$M = 0.5628$$

3. Calculate volume of conc. sulfuric acid use to prepare 1000 mL of 3% H_2SO_4

$$C_1V_1 = C_2V_2$$

$$18.0102\ V_1 = 0.5628x1000$$

$$V_1 = 31.2489\ \text{mL}$$

so, use 31.25 mL to prepare 1000 mL of 3% H_2SO_4

Preparation of 1000 mL of 3% H_3PO_4 from 85% H_3PO_4

1. Change 85% H_3PO_4 into mol/dm^3

$$M = \frac{10x85x1.685}{98}$$

$$M = 14.6148$$

2. Change 3% H_3PO_4 into mol/dm^3

$$M = \frac{10x3x1.685}{98}$$

$$M = 0.5158$$

3. Calculate volume of conc. phosphoric acid use to prepare 1000 mL of 3% H_3PO_4

$$C_1V_1 = C_2V_2$$

$$14.6148\ V_1 = 0.5158x1000$$

$$V_1 = 35.2930\ \text{mL}$$

so, use 35.29 mL to prepare 1000 mL of 3% H_2SO_4

Appendix-C

Calculation of Furfural Yield

C-1 Calculation of furfural yield

1. *Solution of standard furfural concentration.*

In solution 100 mL has furfural 0.005 mL

In solution 1000 mL has furfural $\frac{0.005}{100} x 1000$ mL

1.1 Convert to mg/L

Density of fufural is 1.16 g/mL

For example:

$$\frac{0.05\ \text{mL}}{1\text{L}} x \frac{1.16\ \text{g}}{1\ \text{mL}} = 0.058\ \text{g/L}$$

$$\frac{0.058\ \text{g}}{1\text{L}} x \frac{1000\ \text{mg}}{1\ \text{g}} = 58\ \text{mg/L}$$

2. *Solution of furfural concentration.*

From the calibration curve (figure 4.1)

$$y = 0.006\,x$$

where y = Absorbance

x = furfural concentration.

and a slope is 0.006

For example:

- Find concentrations of furfural (mg/L) in 9% H_2SO_4

At 1 hour pre-hydrolysis time $\frac{2.068}{0.006} = x$

$x = 344.67$ mg/L

At 2 hours pre-hydrolysis time $\frac{1.924}{0.006} = x$

$x = 320.67$ mg/L

At 3 hours pre-hydrolysis time $\frac{1.598}{0.006} = x$

$x = 266.33$ mg/L

3. *Solution % yield of furfural*

In dry baggase consisted of pentosan 25% by weight[15].

The stoichiometric yield of furfural is 72.72 g per 100 g of pentosan following equation

$$\text{Pentosan} + n\ \text{Water} \longrightarrow n\ \text{Pentose}$$

$$(C_5H_8O_4)_n + n\,H_2O \longrightarrow n\,C_5H_{10}O_5$$

$$\text{Pentose} - 3\ \text{Water} \longrightarrow \text{Furfural}$$

$$C_5H_{10}O_5 - 3\,H_2O \longrightarrow C_5H_4O_2$$

$$\%\ \text{yield} = \frac{\frac{\text{mg furfural}}{1000} x100}{0.25x0.7272x\text{Weight of sugar cane bagasse}}$$

For example:

- Find % yield of furfural in 9% H_2SO_4

At 1 hour pre-hydrolysis time

$$\% \text{ yield} = \frac{(443.67 \text{ mg}/1000)\, x100}{0.25x0.7272x10\text{g}}$$

$$= 18.96\ \%$$

At 2 hours pre-hydrolysis time

$$\% \text{ yield} = \frac{(320.67 \text{ mg}/1000)\, x100}{0.25x0.7272x10\text{g}}$$

$$= 17.64\ \%$$

At 3 hours pre-hydrolysis time

$$\% \text{ yield} = \frac{(266.33 \text{ mg}/1000)\, x100}{0.25x0.7272x10\text{g}}$$

$$= 14.69\ \%$$