Dadgar, Alireza Memaran, 1957-

Page Number 106

☐ Images

☐ Foldouts

☐ Maps

☐ Scanned

☐ Clean-up

☐ PDF

☐ Archive ☐

MSF Projects

TB

Verified

9/8/14

Date

PRODUCTION OF 5-HYDROXYMETHYL-2-FURALDEHYDE BY ACID HYDROLYSIS OF OAK SAWDUST AND SEPARATION FROM WATER

Thesis Approved:

Gary L Foutch
Thesis Adviser

Robert A. Wills

Robert H Heidersbach Jr

Norman N Durham
Dean of Graduate College

ACKNOWLEDGMENTS

I wish to express my most sincere thanks and appreciation to my major adviser Dr. G. L. Foutch for his valuable suggestions and the guidance provided by him.

I would like to thank Dr. B. Heidersbach and Dr. R. Wills as members of my examining committee. A special thanks is due Dr. R. Wills for his technical advice and for the use of his laboratory equipment.

I shall always be thankful to the Oklahoma State University School of Chemical Engineering which has provided space, facilities, materials, and financial assistance.

I am grateful to AMOCO Corporation for the financial assistance provided for the completion of this work.

I am deeply indebted to my parents, Mr. and Mrs. Memaran Dadgar, Mr. and Mrs. Ghoreishi, my sister and her husband, for their encouragement and understanding which provided the stimulus for this program.

Finally, I would like to thank all my friends for their understanding attitude and patience.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

The production of 5-hydroxymethyl-2-furaldehyde, also known as hydroxymethyl furfural (HMF), by the action of mineral acids on various kinds of wood has been known for over one hundred and fifty years. The process involves cellulose conversion to glucose by acid hydrolysis, followed by dehydration of glucose resulting in the formation of HMF. HMF can be further reacted to levulinic acid and formic acid.

The mechanism for the hydrolysis of cellulose to levulinic acid has been described by McKibbins (13). The overall reaction consists of a series of consecutive reactions as can be seen in Figure 1. The main species that constitute wood are cellulose, lignin, hemicellulose, and acetyl groups. When hemicellulose and cellulose are heated in the presence of mineral acid they decompose, resulting in the formation of hexoses and pentoses, which in turn are dehydrated to produce hydroxymethyl-2-furaldehyde and finally levulinic acid and formic acid. Hydroxymethyl furfural is found in many glucose solutions of industrial importance such as in hydrolyzed starch solutions and in the production of crystalline corn sugar. HMF also contributes to discoloration of sugar solutions during heating, a process known as "non-enzymatic browning" (9). The presence of large amounts of HMF is known to reduce the yield of sugar produced by the acid hydrolysis of wood.

A process that produces HMF should have several advantages over

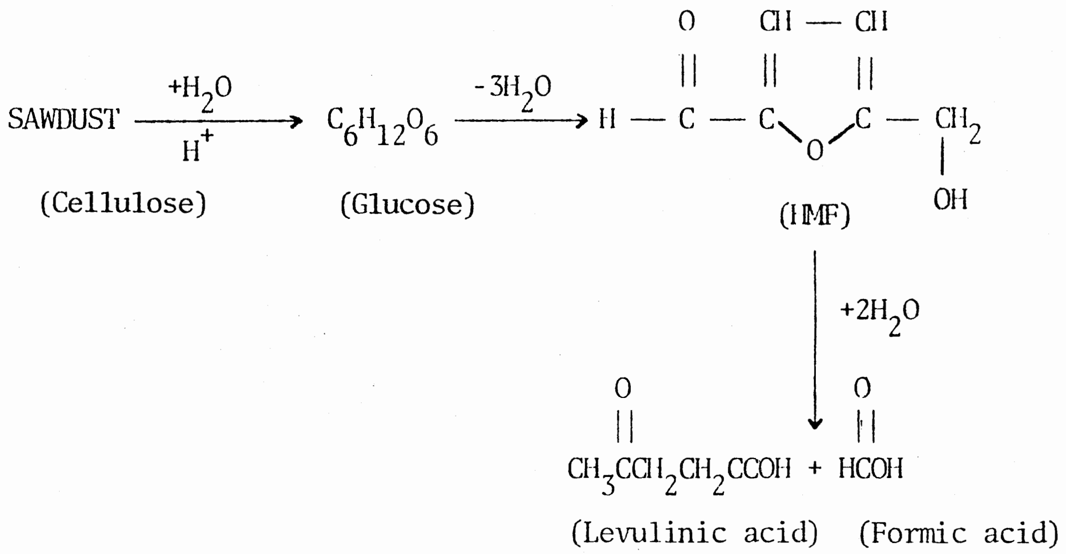


Figure 1. The Hydrolysis of Cellulose to Final Products (13)

other bioconversion schemes: (1) the raw material, wood, is readily available and inexpensive and (2) the poly-functional characteristics of HMF are of considerable industrial interest. HMF undergoes the expected reactions of alcohols and aromatic aldehydes as well as ring cleavage reactions resulting in unsaturated straight chain compounds. This versatility makes HMF a valuable compound for synthesis of chemicals such as ethers, glycols, dialdehydes, acetals, furfuryl alcohol (2), and other organic intermediates which in turn can be used to produce chemicals such as surfactants, plasticizers, resins, and agricultural chemicals (16).

The production of HMF from sawdust will be investigated to determine reaction and separation conditions necessary to obtain the optimum overall yield of HMF. Liquid-Liquid extraction will be considered as a separation technique for the recovery of HMF from water.

CHAPTER II

LITERATURE SURVEY

Acid hydrolysis of wood has been the subject of several investigations. In 1840, Mulder (18) experimented with the effects of mineral acids on sugar. He isolated and listed several properties of an acid which he called glucinic acid. Shortly afterward, Grote and Tollens (7) duplicated and enlarged Mulder's work and renamed the product levulinic acid.

Extensive studies were performed by Blanksma and von Eckenstein (1) on reactions of different sugars with acids. They concluded that both pentoses and hexoses react the same way when treated with acids. The reaction of pentoses yielded 2-furaldehyde while hexoses yielded an unstable intermediate, 5-hydroxymethyl-2-furaldehyde (HMF), which further degraded to levulinic acid and formic acid.

In 1919, Middendorp (16) published his study on HMF. He described an analytical procedure for HMF production from sucrose, and identified several physical and reactive properties of HMF. Notable among these properties is the high solubility of HMF in water, alcohols, acetone, ether, chloroform, and benzene which makes separation and recovery of HMF from solution a reasonable possibility.

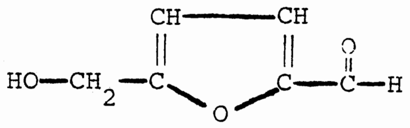
Sources of 5-Hydroxymethyl-2-Furaldehyde (HMF)

Starting materials for HMF production are numerous. Any material containing carbohydrates with six carbon monomeric units can produce HMF upon hydrolysis. Due to its abundance and low cost, wood is a logical choice to supply the necessary carbohydrate for the production of sugar, HMF, and levulinic acid.

Willey (28) concluded that wood and pulping wastes are the most economical raw materials for production of low cost hydrocarbons (sugars). He estimated that for every one hundred pounds of dry wood hydrolyzed, 30 lbs of lignin, 14 lbs of levulinic acid, 7 lbs of furfural, 5 lbs of acetic acid, and 4 lbs of formic acid can be expected.

Physical and Chemical Properties of
5-Hydroxymethyl-2-Furaldehyde
(HMF)

The structure of 5-hydroxymethyl-2-furaldehyde is:



The physical and chemical properties of HMF are given by Middendorp (16) and are listed in Table I. Unlike furfural, HMF is not volatile with steam. HMF forms oxime, aldazine, semicarbazone, and various amides (16). HMF also condenses with two moles of urea to give a diureide. Similarly, with the appropriate amide N, N-5-(hydroxymethyl) furfurylidenediacetamide, and dibenzamide are obtained (4). The Dische color produced by HMF is due to its reaction with diphenylamide-acetic acid-sulfuric acid reagent (4). It gives a yellow color with aniline acetate and a dark precipitate with phoroglucinol-

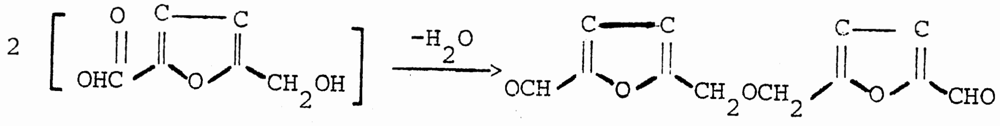
TABLE I

PHYSICAL AND CHEMICAL PROPERTIES OF 5-HYDROXYMETHYL-2-FURALDEHYDE (4, 16)

Light yellow to brown oily liquid or hygroscopic, colorless crystals

Molecular weight		126.1
Melting point		31 - 31.5 C
Boiling point		110 - 120 C at 0.2 - 0.5 mm. Hg.
Density	Liquid:	1.268
	Solid:	1.2629
Index of refraction	n	1.5627
Heat of combination		664.8 cal./mol.
Solubility		Easily soluble in water, alcohols, acetone, ether, chloroform, and benzene. Soluble with difficulty in carbon tetrachloride and petroleum ether.

hydrochloric acid. HMF condenses with loss of water to form oxybis (5-methylene-furfural) (4).



The colorless crystals of HMF turn yellow when exposed to light. HMF decomposes to Furan derivatives at atmospheric pressure and room temperature. Any samples of HMF, therefore, must be kept in a dark and cool environment.

Preparation of 5-Hydroxymethyl-2-Furaldehyde

A method for the preparation of HMF from sugar containing material was described by Middendrop (16), sucrose and oxalic acid are heated for three hours in water under three atmospheres of pressure. The black residue is removed and the filtrate is neutralized with calcium carbonate. Basic lead acetate is added to form a precipitate which is removed by filteration. The filtrate is extracted six times with ethylacetate and dried with sodium sulfate to prevent rehydration. Under high vacuum distillation an impure, pale yellow, oily HMF is obtained.

Haworth and Wiggins (11) described a procedure to make HMF and levulinic acid from glucose, sucrose, and sorbose. Sucrose was heated with oxalic acid hydrate at 150 to 170 C. The HMF produced was extracted several times with ethyl acetate for further purification. The residue when treated with bromic acid at 130 to 140 C yielded formic and levulinic acid.

Harris, Saeman, and Zach (9) described a method for obtaining experimental amounts of HMF from hydrolyzed sucrose. 30.6 lbs of water 30.6 lbs of sucrose and 9.2 lbs of sodium hydroxide were brought to the temperature of 107C. When boiling began, 350 ml of hydrochloric acid was added and the solution was stirred constantly. After 25 minutes the reaction was quenched by the addition of 7 lbs of ice. The solution was then neutralized with sodium hydroxide and filtered. The concentration of HMF was found to be 4 to 5 mg/ml of the solution. After 3 hours of continuous extraction, the concentrated extract was washed with a saturated solution of sodium carbonate and subjected to a high vacuum distillation. The first distillation yielded HMF with a purity of 85 to 95% Redistillation raised the purity to greater than 99%. Snyder (25) described a procedure for production of HMF from cellulosic materials. Oak wood chips were sprayed with a 0.6% sulfuric acid at ambient temperature for 30 minutes. The chips were drained and charged to a preheated reactor where the temperature and pressure were quickly raised to 546 F and 1000 psi by the introduction of steam. After 105 seconds, products were discharged into a dry blow-down drum. The principal component of the hydrolyzate liquor was HMF with a 50-80% theoretical yield. HMF concentration was determined by chemical analysis and infrared absorption.

The pH conditions of treatment are particularly important in the production of HMF. Snyder (25) concluded that unless the pH of the crude hydrolyzate liquor is below 3.0, the yield of HMF will be considerably reduced due to a tendency for HMF to polymerize or react to form resinous products. However, if the pH is 1.9, HMF is known to undergo rapid polymerization (25). Choudhury (3) performed a series of studies on the light-scattering of cellulose solutions treated with phosphoric and sulfuric acid. His studies indicated the formation and growth of a large and extensively branched polymer of a 5-Hydroxymethyl-2-Furaldehyde during the hydrolysis of cellulose. A similar experiment by Natesain (19) described the mechanism of polymerization of furfural and HMF in the presence of mineral and organic acids, by means of light scattering and viscometry. He isolated a linear polymer from a phosphoric acid catalyzed furfural solution just before gelation, when the solution became a very jelly-like mass. This was partially soluble in alcohol but was completely soluble in acetone and contained a very small amount of unchanged furfural. The end-product was a thermosetting material which was unaffected by high temperature, chemical reagents, and organic solvents.

Mechanism of the Reaction

Formation of HMF is known to take place by hydrolysis of a polysaccharide, cellulose, to a monosaccharide or hexose sugar, and then degradation of the sugar by dehydration to produce 5-hydroxymethyl-2-furaldehyde and finally levulinic and formic acids. According to Wiggins (27), the reaction is initiated when one molecule of sucrose is hydrolyzed to glucose and fructose. Both glucose and fructose form an enediol which loses three molecules of water to form HMF. This mechanism is shown in Figure 2.

Haworth and Jones (10) examined the preparation of HMF from sucrose. The glucose portion was unchanged for the most part. They proposed the scheme shown in Figure 3. The mechanism is by the way of the enol, III, to account for the conversion of fructose, I (furanose

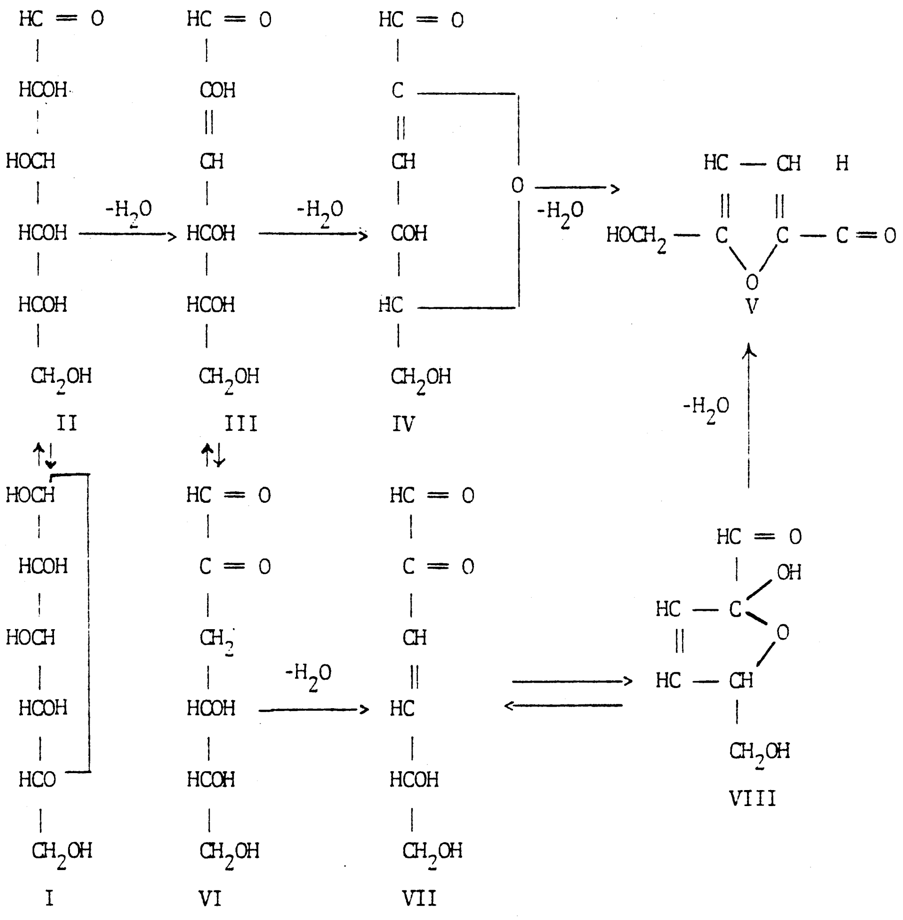


Figure 2. Mechanism of HMF Formation from Sucrose (27)

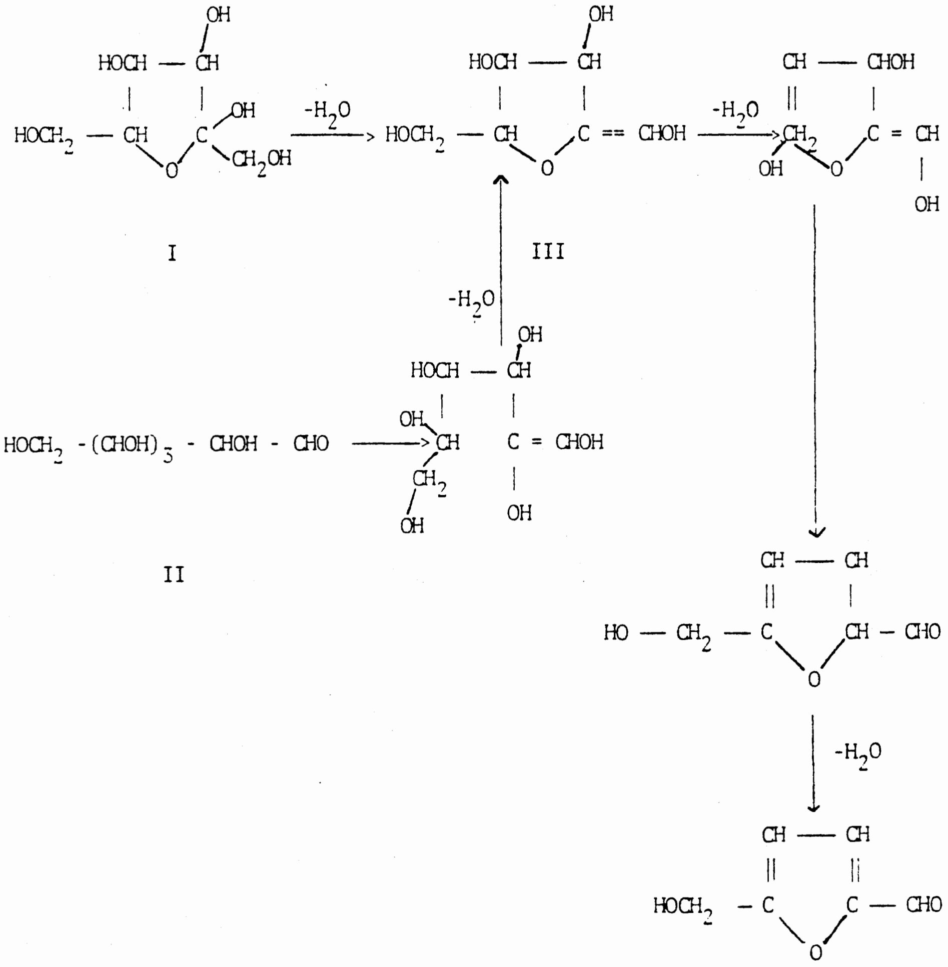


Figure 3. Mechanism of HMF Formation from Fructose and Glucose (10)

form). The same result is obtained from glucose, II, if it could react in the form of its ene-diol, IV, which could go through cyclodehydration to give III. To accomplish the proposed mechanism of HMF production, Haworth and Jones preheated glucose with aqueous calcium hydroxide and then with oxalic acid where HMF was obtained with a 13% yield.

Kinetics of the Reaction

Saeman (20) studied the kinetics for the consecutive reactions of cellulose to sugar, HMF, and levulinic acid. His analysis includes the effects of reaction time, temperature, and acid concentration. He concluded that the disappearance of glucose followed a first order mechanistic model.

Experimental results indicated that the relation of the first-order reaction constant, K, to acid concentration in decomposition of glucose at various temperatures followed a straight line. Saeman approximated that for every 10 C increase in temperature, the rate constant for the disappearance of glucose increases by a factor of 1.2. He determined the following relationship for the rate constant:

$$K = (1.86 \times 10^{14}) C_s^{1.02} \ \mathrm{Exp.}(-32700/RT)$$

where,

C_s = Sulfuric acid concentration, percent by weight

T = Temperature, K

R = Ideal gas constant, cal/gmole-K

A more complete work on the kinetics of the acid catalyzed conversion of glucose to HMF and levulinic acid is given by McKibbins (13). He studied the rate of disappearance of glucose and the simultaneous formation of HMF. He supported the results of Saeman and showed that glucose disappearance followed a first-order mechanism with HMF displaying growth and decay response with time. He concluded that the formation of HMF is essentially independent of catalyst concentration, but is increased by raising the temperature and by lowering the initial concentration of glucose. He studied the production of HMF from fructose and found that the maximum yield of HMF was twelve times higher than that obtained with glucose.

The data for the disappearance of glucose and the formation of HMF indicated the following equations:

$$\frac{dC_G}{dt} = -k_1 C_G$$

where,

k_1 = rate constant, $(9.27 * 10^{14})(A_G C_A$ Exp. $(-32689/RT)$

A_G = an activity coefficient for glucose formation

C_G = glucose concentration, moles per liter

C_A = acid concentration, normality

HMF formation:

$$C_H = C_{Go}\left(\frac{0.51}{A-1}\right)[\text{Exp.}(-K_1 t) - \text{Exp.}(-AK_1 t)]$$

where,

$$A = \frac{K_2}{K_1}$$

$K_2 = (2.4 \times 10^{11})(A_H C_A)[\text{Exp.}(-23110/RT)]$

C_{Go} = initial glucose concentration, moles per liter

A_H = an activity coefficient for HMF formation

Related Processes

Production of Sugar and Ethyl Alcohol from Wood Waste

The first commercial plants to produce sugar by acid hydrolysis of wood cellulose began in the Southern United States during World War I. Improvement of wood hydrolysis technology eventually evolved along two paths: (1) dilute acid hydrolysis at elevated temperatures (above 150 C), and (2) concentrated acid hydrolysis at low temperatures (60-100 C). Both systems have been practiced commercially with dilute acid receiving more attention.

Scholler Process

During the 1920's, Meiler (15) and Scholler (21) studied the hydrolysis of cellulose. On the basis of their investigations, the "Scholler" process for wood hydrolysis was established in the United States during World War II. The process, as first carried out in Germany, utilizes wood as the raw material for production of sugar, which is followed by fermentation of the sugar to ethanol. Wood chips were compressed in brick-lined steel percolators to 30-40 psi and then preheated with live steam to 265 F. Several batches of 2000 to 3000 gallons of 0.5% sulfuric acid were forced through the wood waste between pressures of 165 and 180 psi. After 45 minutes a dilute sugar solution was removed from the percolator, cooled, neutralized, and fermented to produce industrial ethyl alcohol. The qualities of major raw materials needed for one gallon of 190-proof ethanol indicated by Pilot plant (21) is shown in Table II.

TABLE II

MAJOR RAW MATERIAL TO PRODUCE ONE GALLON OF 190-PROOF ETHANOL BY SCHOLLER PROCESS (21)

Wood (Douglas Fir, dry basis), lb.	38.4
Sulfuric Acid (76%), lb.	2.3
Chemical Lime, lb.	2.2
Water, gal.	121.0

Rotary Digester

The Forest Products Laboratory (22) optimized wood hydrolysis to obtain the conditions required for maximum production of sugar. As a result, a plant consisting of an acid preparation unit, a rotary digester surrounded by a steam jacket, a series of tanks to wash partially converted sugar from sawdust by hot water, a neutralization unit, and a fermentation apparatus was designed.

The wood waste was introduced into the rotary digester. An acid solution was added along with steam to heat the revolving digester at 290 to 300 F and a pressure of 100 psi. After 4 to 6 hours, 350-400 pounds of sugar per ton of wood waste was produced. High yields of sugar at high concentrations proved difficult. The drawbacks of this process were: (a) process time (4-6 hours); (b) the amount of acid required; (c) formation of gums and caramels inside the digester; and (d) breaking of the lead lining of the rotary digester, an expensive factor contributing to delay in operation.

Stationary Digester

Dow Chemical Company carried out the pilot plant wood hydrolysis using a stationary digester (8). Sawdust, wood chips, or hogged wood was treated with 5.9 to 11.3% sulfuric acid at temperatures from 135 to 195 C for up to 9 hours. To prevent the decomposition of the simple sugars produced, it was necessary to remove sugar as fast as possible. Yields of reducing sugars ranged between 45 to 57% of the wood weight for softwoods and 45 to 52% for the hardwoods. The sugar solutions were then neutralized and fermented to give up to 2.9%

by volume alcohol. Forty to sixty gallons of alcohol were obtained per ton of wood from softwoods and 33 to 42 gallons from hardwoods.

Liquid-Liquid Extraction

Liquid extraction, also known as solvent extraction, is a separation process accomplished by treating the solution with an immiscible solvent in which one of the species of the solution is soluble. This process involves the contacting of the solvent and solution, separating the phases, and removing the solvent from each phase. Intimate contacting of the phases is required to ensure the best possible efficiency of the extraction process. Adequate contacting may be accomplished in agitated vessels, plate columns, or packed towers. Separation of phases may be done by gravity settling or by centrifugation. Recovery of the solvent from the solvent layer (extract) is usually accomplished by means of distillation.

Selection of the Solvent

Choice of the solvent is usually limited, due to factors described by Treybal (26):

A. Selectivity. A measure of the effectiveness of a solvent to separate the components of a solution. For a practical extraction process the selectivity must be greater than one.

B. Distribution Coefficient. Defined as the mole fraction of solute in the extract phase per mole fraction of solute in the raffinate (solution) phase. A distribution coefficient greater than one is desirable but not required.

C. Solvent Immiscibility. The influence of solvent solubility is due to the nature of particular solvent-solute system. The more solute can be dissolved, the less solvent is required to perform the extraction.

D. Recoverability. For an extraction process to be economically feasible, the solvent must be recovered for reuse. If a distillation process is used, the solvent should have a high relative volatility and must not form an azeotrope with the solute.

E. Density. The difficulty in phase separation is greatest when the difference of the densities of the two phases are small. A large difference in densities of solvent and solution makes the economic evaluation of the extraction process more feasible.

F. Interfacial Tension. This is the degree in which one liquid dispersed in the other. For a useful extraction process interfacial tension should be high.

H. Chemical Properties. The solvent sould be stable, nontoxic, nonflammable, and inert with respect to the solute.

Methods of Operation

Sherwood (24) divided the operation of extraction processes into three primary categories:

A. Single Contact. In this operation the solvent and the solution are brought into contact for a single-batch extraction. Figure (4) shows a single contact extraction process. The extent to which solute is transferred from the solution to the solvent is determined by the amount of the solvent used and the degree possible to reach equilibrium. The efficiency of a single-contact extraction is usually low.

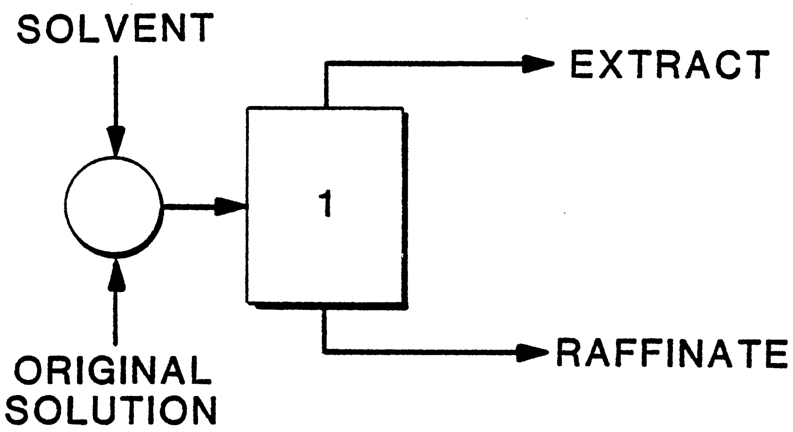


Figure 4. A Single Stage Extraction Process (24)

B. Cocurrent Multiple-Contact. The concentration of solute in the raffinate can be reduced to any desired extent by addition of number of contacts. Figure (5) shows a three stage extraction process where fresh solvent is used in each stage. Although a low concentration of solvent in the raffinate can be achieved, but this method requires a large volume of solvent.

C. Counter Current Multiple-Contact. This method avoids the uneconomical use of the solvent by utilizing the solvent with low solute concentration in place of the fresh solvent. This is the most efficient way to operation an extraction process. Figure (6) shows a counter current system consisting of five stages. Each stage is proceeded by an agitated vessel. Fresh solvent is introduced only into the last mixer. Counter current flow of solution and solvent improves contacting time.

Stage Efficiency

Extraction performance can be described to the extent that the extract and raffinate phases approach equilibrium. The Murphree stage efficiency, described by Treybal (26), is the weight fraction of the solute in the extract at equilibrium per weight fraction at the actual operating condition. An overall efficiency of the extraction process may be defined as the number of equilibrium stages per number of actual stages required to achieve the desired separation. The performance of several types of extraction equipment, the mixer-settler, the perforated-plate column, the baffle column, and the agitated tower are given in Table III.

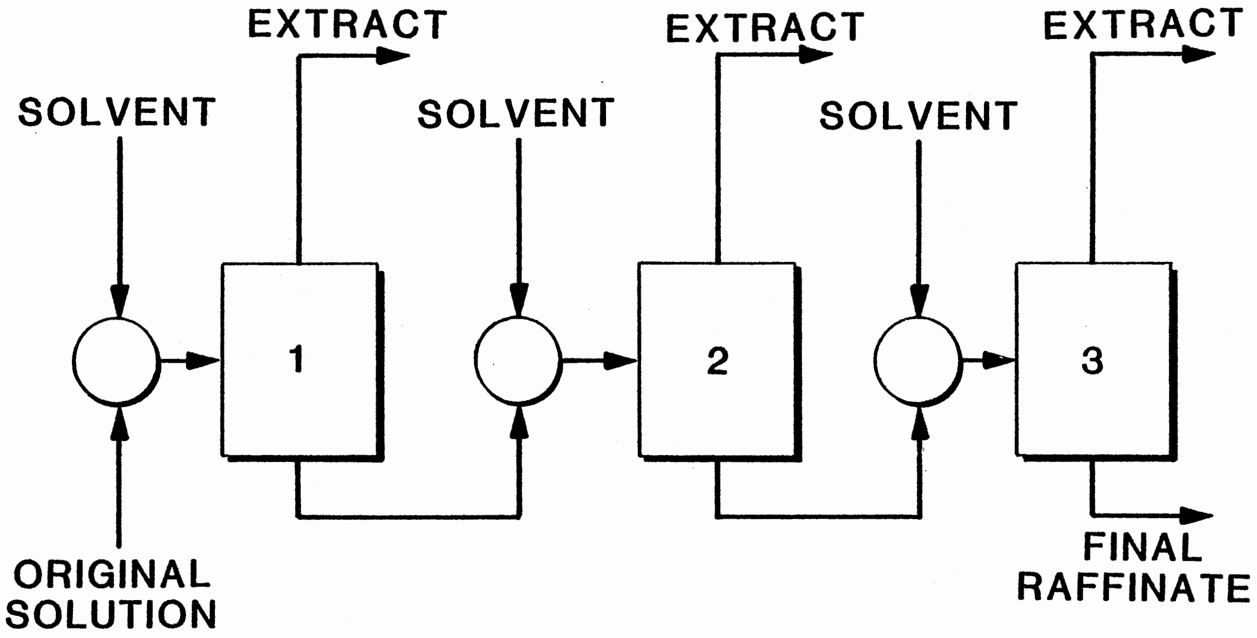


Figure 5. A Three Stage Cocurrent Extraction Process (24)

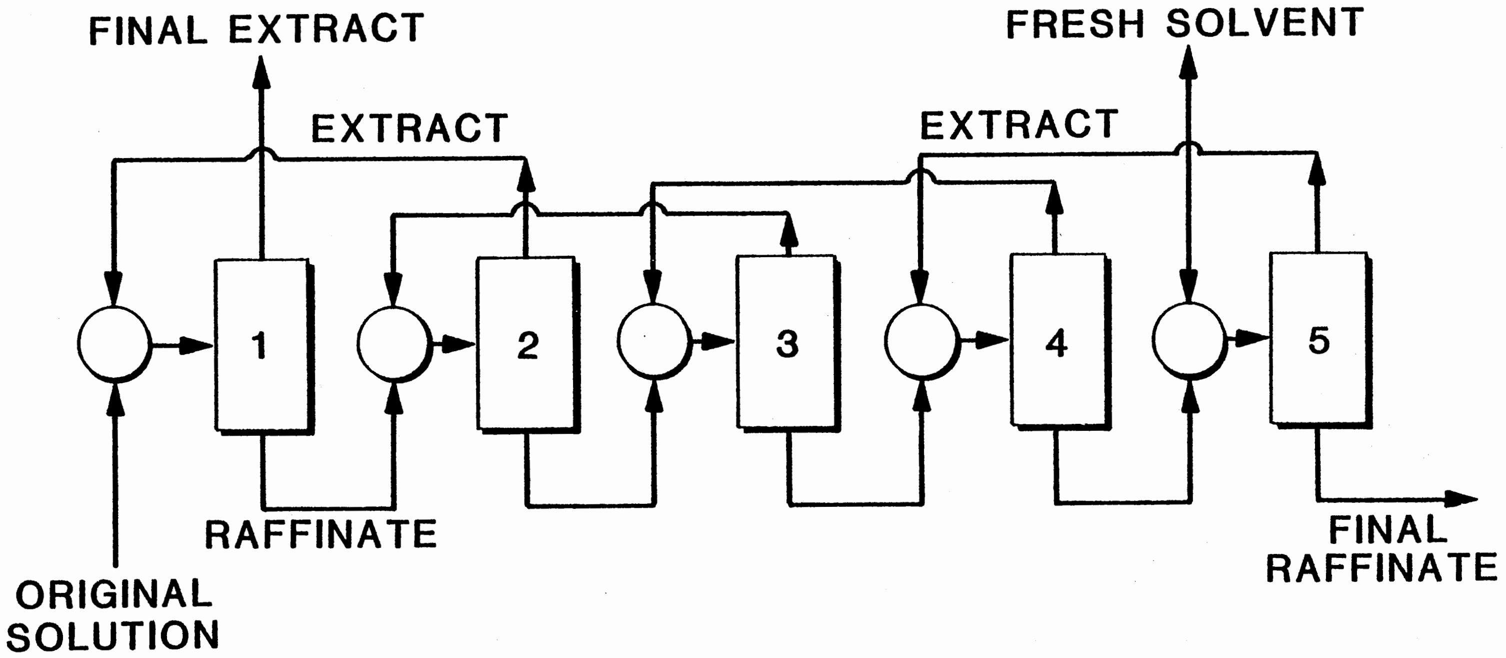


Figure 6. A Five Stage Counter Current Multiple-Contact Extraction Process (24)

TABLE III

ESTIMATED STAGE EFFICIENCY FOR SEVERAL EXTRACTION EQUIPMENT (12)

Type	Stage Efficiency, %
Mixer-Settler	75-100
Perforated-Plate Column	6-24
Baffle Column	5-10
Agitated Tower	80-100

Separation Methods of HMF From Water

The physical and chemical properties of HMF create difficulties in separating pure HMF from the other hydrolysis by-products. Middendorp (16) used high vacuum distillation where products were treated with a second distillation process to achieve 80 to 90% purity.

Column chromatographic methods for separation of carbohydrates, especially furan derivatives, are discussed by Philip Morris, Inc. (17). They indicate that the carbohydrate degradation products could be partitioned by column chromatography on activated aluminum oxide. The procedure consisted of a standard mixture containing 200 ml each of furfural, HMF, furfuryl alcohol, and fumaric acid, and a ten-hour aqueous reflux of fructose at pH 5.2. The solutions were chromatographed on a 4 cm x 33 cm column containing 450 gms of basic aluminum oxide. HMF was eluted with chloroform as a yellow-orange band.

Use of a sample applicator for chromatographic paper was considered by McKibbins, Harris, and Saeman (14). The solvent system used in the analysis of HMF was the organic layer which results from the mixing of equal volume of 5 molar formic acid and pentanol. The analytical procedure involved streaking the solution onto sheets of Whatman No. 3 chromatographic paper, irrigating at 30 C for 15 hours with the formic acid-pentanol solvent, and drying the band of HMF with the aid of an ultraviolet lamp.

The three methods for the separation of HMF described have several disadvantages which make them impractical. The distillation method results in a considerable decrease in the yield of HMF and has a high cost for operation. The column chromatograph and sample applicator methods are tedious, lengthy, and unimportant on an industrial scale.

Therefore, the establishment of an economical procedure for separation of HMF is needed. A separation method based on extraction of HMF from water will be described in the following chapter.

CHAPTER III

EXPERIMENTAL EQUIPMENT AND ANALYTICAL PROCEDURE

The purpose of this study was to produce and purify 5-hydroxymethyl-2-furaldehyde (HMF). Therefore, the total research program was divided into two parts:

Part I: Production of HMF from oak sawdust. In this study, HMF was produced by hydrolysis of oak sawdust. The affects of temperature, acid concentration, wood particle size, and reaction time on the production rate of HMF were investigated to establish a basis of comparison with the established literature.

Part II: Separation of HMF from water. Experimental equilibrium data for HMF in water for two solvents, dichloromethane (DCM) and isobutyl-metylketone (IMK) were obtained at 25 C.

The range for particle size, acid concentration, temperature, and reaction time are shown in Table IV. These ranges were somewhat limited due to the capability of the equipment.

Study I: Production of HMF

All experiments were carried out in batch reactors, 30 ml vials equipped with teflon lined caps. Vials were tested at 600 F and 1541 psi. Each vial was charged with 1.000 g of oak wood sawdust,

TABLE IV

RANGE OF VARIABLES FOR PRODUCTION OF HMF

Temperature (C)	Particle Size (MESH)	Acid Concentration (% Acid by weight)	Reaction time (hr)
	20		0.5
300	40	3.0	1.0
340	60	6.0	2.0

ground to either 20, 40, or 60 mesh. Hydrochloric acid at concentrations of 3 and 6% acid by weight were prepared. To each vial 15 ml of hydrochloric acid solution was added. Vials were placed in a stainless steel container, partially filled with water to equalize the pressure in the vials during heating. The container was preheated to temperatures of either 300 C or 340 C. Eight bolts secured the top of the container. After the specified heating time of 0.5, 1.0, or 2.0 hours had elapsed, the container was removed from the furnace and placed in an ice bath. The content of each vial was filtered and the filtrate centrifuged. One milliliter of filtrate was placed in a test tube and the pH of the solution was raised from 0.4-0.7 to 1.5-2.0 by dropwise addition of 5 N sodium hydroxide.

Method of Analysis

Carbon Analysis

A model 240 Perkin Elmer elemental analyzer equipped with a range recorder, an auto balance, and a sealer were used to analyze the content of the oak sawdust for carbon. The major components of the analyzer are the combustion tube, the reduction zone, and the detector unit. The sample was weighed, placed in a special aluminum capsule, and burned in an atmosphere of oxygen in the combustion zone at temperature of 650 to 700 C. High purity helium carried the gases produced through packing where sulfur oxides and halogens were removed. Gases were then passed through the reduction tube where nitrogen oxides were reduced to molecular nitrogen.

The exit gases from the combustion tube; water vapor, carbon dioxide, nitrogen, and helium, were passed through a series of thermal conductivity cells. The difference in thermal conductivities of the sample before and after a carbon dioxide trap gave the concentration of carbon dioxide and hence the carbon concentration in the sample. The carbon content of the oak sawdust used in all experiments was found to be 44.1% by weight averaged over several runs.

Sugar Analysis

The amount of sugar in the product was determined by means of its ultraviolet absorption. Scott (23) has described a procedure for the combined determination of glucose, mannose, and xylose by spectrophotometry. The method depends upon the dehydration of sugars to furans and uses chloride to distinguish the differences between the spectra. The procedure is divided into four parts:

A. Dehydration to Furans. 0.125 ml and 0.25 ml of sample are transferred to two test tubes. 0.125 ml of NaCl-H_3BO_3 solution (12 g of NaCl and 2 g of H_3BO_3 in 100 ml of water) are added to the smaller sample. The dehydration reaction is started by the addition of 2.0 ml of concentrated H_2SO_4 (96 %) to each test tube, immediately mixed by tilting, and placed in a 70 °C constant temperature bath. Each tube is removed after exactly 30 minutes and cooled by swirling for 15 seconds in water at room temperature.

B. Spectrophotometry. A spectrophotometer, [Lambda 3 Model, Perkin-Elmer], is utilized to read the absorbances of the 0.125 ml sample at 280, 310, and 340 nanometer. The absorbance of 0.25 ml sample is read only at 280 nanometer. Concentrated H2SO4 (96 %) is used as a blank sample. The characteristic absorbance used for calculations are those at 310, A_{310}, and at 340, A_{340}, nanometer for

0.125 ml sample and the absorbance difference between the two samples at 280 nanometer (ΔA_{280}). This difference is obtained by subtracting half of the 0.25 ml sample absorbance from the absorbance of the 0.125 ml sample.

C. Standardization. Separate standard solutions containing 0.1 g/l each of glucose, mannose, and xylose were prepared. The average characteristic absorbances for each solution is determined by repeating parts 1 and 2 three times. Absorptivity, the absorbance given by 1 mg/ml, is calculated for each average absorbance and inserted into a third-order determinant as follows:

$$\begin{array}{c|ccc|} (\Delta A_{280}) & g_1 & m_1 & x_1 \\ (A_{310}) & g_2 & m_2 & x_2 \\ (A_{340}) & g_3 & m_3 & x_3 \end{array}$$

The symbols g, m, and x are absorptivities of glucose, mannose, and xylose respectively.

D. Calculation. The three characteristic absorbances A280, A310, and A340 from an unknown solution, together with the standard matrix, are used to calculate the concentration of the three sugars. Each sugar concentration is calculated by a separate equation. The results of calibration and calculation of a standard matrix for 0.1 g/l glucose, 0.1 g/l xylose, and 0.1 g/l mannose are given in Appendix A. To facilitate the computation, a computer program along with the supplementary equations are given in Appendix B.

HMF Calibration

The calibration curve for HMF was obtained by using a Hewlett

Packard - 5880 A series gas chromatograph. The column was 5 feet long, 0.125 inch in diameter and packed with 15% diethylene glucol succinate (DEGS) on chromosorb W (AW-DMCS), 60-80 mesh. The oven temperature was programmed from 100 C to 210 C at a rate of 4 deg.c/min. Both injection and detection temperatures were set at 300 C. The gas flow rates were 30 ml per minute for nitrogen, 32 ml/min for hydrogen gas, and 450 ml/min for air. Different amounts of 5-hydroxymethyl-2-furaldehyde (HMF) were dissolved in water. Three microliters of the HMF - water solutions were injected into the gas chromoatograph. The calibration curve of HMF for several repeated runs is presented in Appendix C.

Furfural Calibration

The amount of furfural (2-furaldehyde) was calibrated in the same manner as HMF. Column packing and oven conditions were kept the same. The results are shown in Appendix D.

Levulinic Acid Calibration

For the case of complete dehydration of cellulose, a considerable amount of levulinic acid was obtained. To determine the amount of levulinic acid in a solution, known concentrations of levulinic acid-water solution were injected at the described conditions. Appendix E shows the calibration for levulinic acid as a function of peak area.

Study II: Separation of HMF Extraction

Samples containing 10, 5, 3 and 1.5 % by weight HMF were prepared. To 1.0 ml of sample in a test tube, 1.0 ml of dichloromethane was added. This was done under the hood with enough circuation to avoid any health hazards. The content of the test tube was mixed for 60 seconds. After 5 minutes, the content of the test tube had come to rest and the two distinguished phases, water (top) and dichloromethane (bottom), were carefully separated by means of a 0.25 ml pipet. Each phase composition was analyzed separately using the gas chromatograph.

Isobutyl-methylketone known as 4-Methyl-2-Pentanone (IMK) was also used in place of dichloromethane for additional extraction studies.

CHAPTER IV

RESULTS

Study I: Production of 5-Hydroxymethyl-2-Furaldehyde From Oak Sawdust

The data for the formation of 5-hydroxymethyl-2-furaldehyde (HMF) from Oak sawdust are listed in Tables V-VII. The concentration of HMF obtained experimentally is presented for 3% hydrochloric acid and reaction temperature of 300 C (Table V), 6% hydrochloric acid and 300 C (Table VI), and 3% hydrochloric acid and 340 C (Table VII) at 0.5, 1.0, and 2.0 hours reaction time. The data are plotted as concentration of HMF in mg/ml of solution versus process reaction time in hours in Figures 7-9. As a general approach to modeling and prediction of the behavior of the data, the overall rate of formation of HMF from glucose and simultaneous degradation of HMF to Levulinic and formic acid is considered. The rate constants are obtained from McKibbins (13) and Grethlein (6).

The primary factors effecting the formation of HMF are the process reaction time, acid concentration, and temperature with particle size having a lesser effect. A discussion of each one is as follows:

A. Process Reaction Time. For all cases studied, the formation of HMF shows a decay under the conditions of this study. In general, the concentration of HMF reaches a maxima and then follows a decay. As

TABLE V

EXPERIMENTAL DATA ON PRODUCTION OF 5-HYDROXYMETHYL-2-FURALDEHYDE (mg/ml) FROM OAK SAWDUST AND 3% BY WEIGHT HYDROCHLORIC ACID AT 300 C

Reaction Time (Hours)	Particle Size (Mesh) 20	40	60
	Concentration of HMF (mg/ml)		
0.5	0.49	0.51	0.52
1.0	0.87	0.99	1.12
2.0	0.61	0.65	0.68

TABLE VI

EXPERIMENTAL DATA ON PRODUCTION OF 5-HYDROXYMETHYL-2-FURALDEHYDE (mg/ml) FROM OAK SAWDUST AND 6% BY WEIGHT HYDROCHLORIC ACID AT 300 C

Reaction Time (Hours)	Particle Size (Mesh) 20	40	60
	Concentration of HMF (mg/ml)		
0.5	0.56	0.58	0.55
1.0	0.721	1.27	1.50
2.0	0.487	0.74	0.95

TABLE VII

EXPERIMENTAL DATA ON PRODUCTION OF 5-HYDROXYMETHYL-2-FURALDEHYDE (mg/ml) FROM OAK SAWDUST AND 3% BY WEIGHT HYDROCHLORIC ACID AT 340 C

Reaction Time (Hours)	Particle Size (Mesh)		
	20	40	60
	Concentration of HMF (mg/ml)		
0.5	0.58	0.60	0.64
1.0	1.36	1.51	1.84
2.0	0.80	0.82	0.91

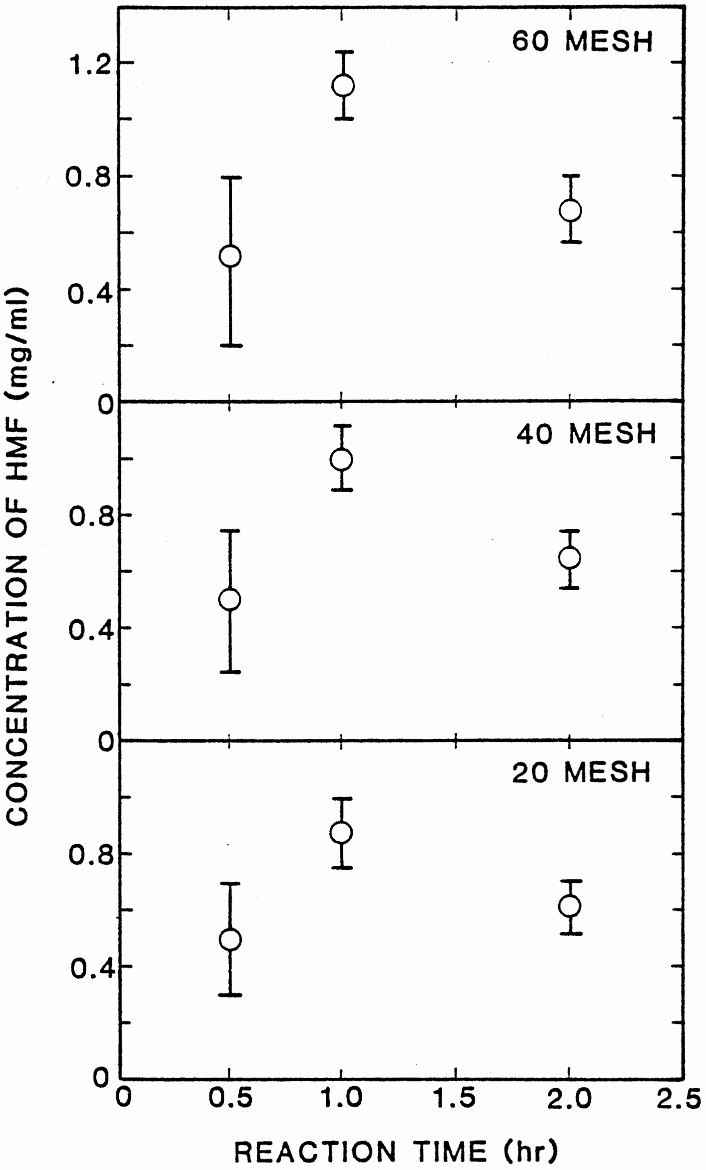


Figure 7. Effect of Reaction Time on Production of HMF at 300 C and 3% HCL

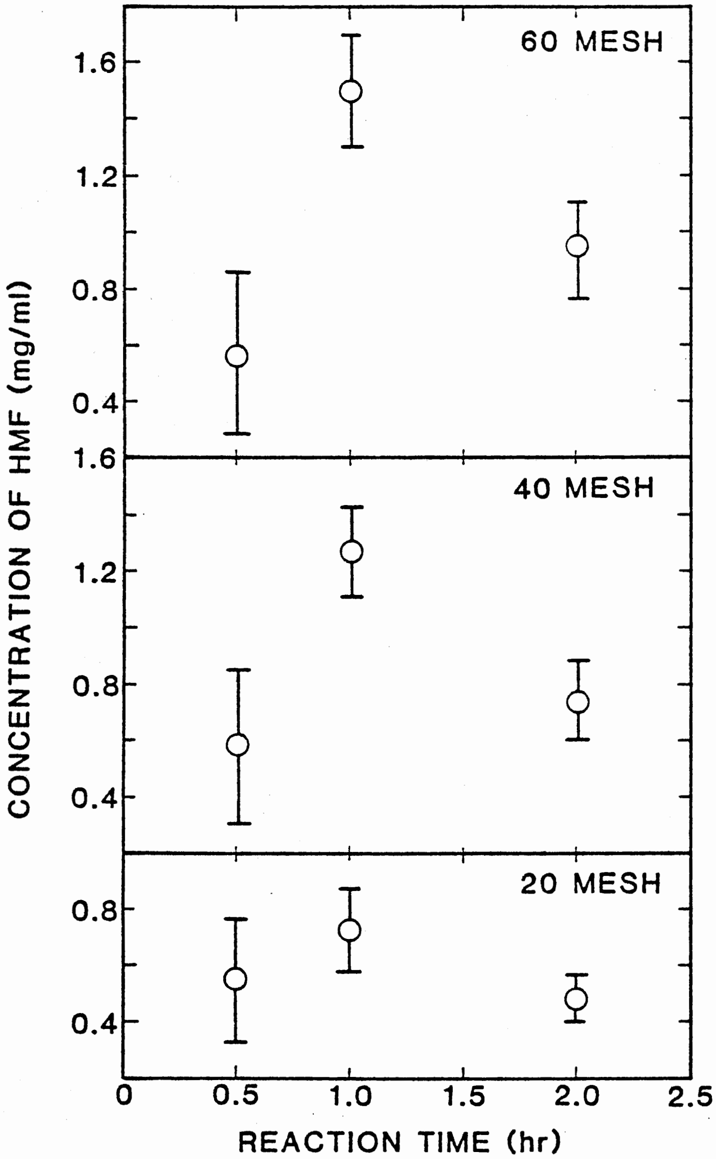


Figure 8. Effect of Reaction Time on Production of HMF at 300 C and 6% HCL

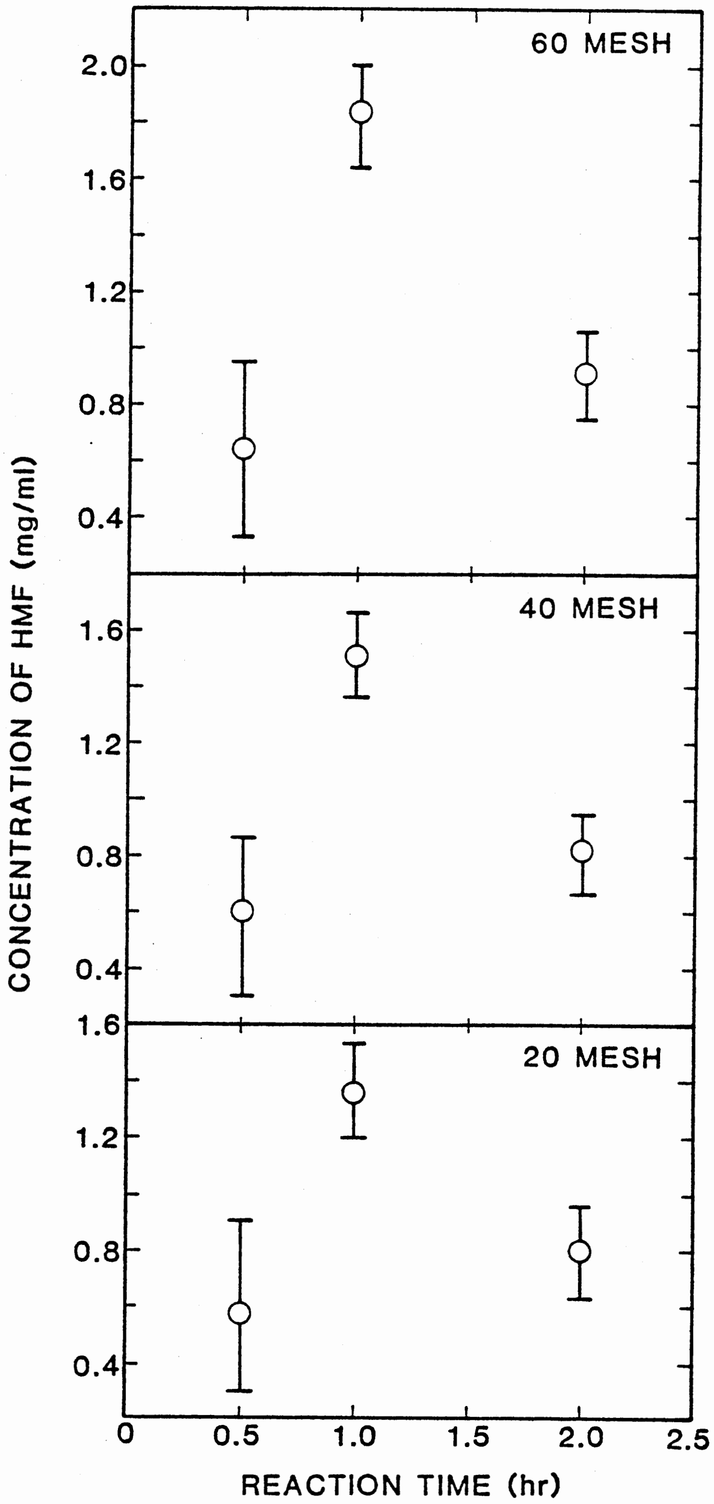


Figure 9. Effect of Reaction Time on Production of HMF at 340 C and 3% HCL

hydrolysis reaction proceeds, more glucose reacts to produce HMF. There is an increase in formation of HMF up to when the rate of degradation of HMF exceeds its rate of formation. For the first order reaction of cellulose to glucose to HMF and disappearance of HMF to final products, the following mechanism is experimentally verified (6, 13),

$$\text{cellulose} \xrightarrow{K_1} \text{glucose} \xrightarrow{K_2} \text{HMF} \xrightarrow{K_3} \text{L}$$

The rate of disappearance of cellulose is:

$$\frac{dC_c}{dt} = -K_1 t \qquad (1)$$

where,

C_C = concentration of cellulose, moles per liter

t = reaction time, minutes

K_1 = rate constant, $(\text{minutes})^{-1}$

The net rate of production of glucose and HMF are:

$$\frac{dC_G}{dt} = K_1 C_C - K_2 C_G \qquad (2)$$

$$\frac{dC_H}{dt} = K_2 C_G - K_3 C_H \qquad (3)$$

where,

C_G = concentration of glucose, moles per liter

C_H = concentration of HMF, moles per liter

K_2 = rate of disappearance of glucose, $(\text{minute})^{-1}$

K_3 = rate of dissociation of HMF, $(\text{minute})^{-1}$

Equation (1) can be integrated with the boundary condition that at

$t = to = 0$, $Cc = C_{CO}$ where,

C_{co} = initial concentration of cellucose at the start of the hydrolysis reaction, moles per liter.

Integrating Equation (1-3) by seeking the solutions of the first order differential equations yield,

$$C_C = C_{Co} \text{ Exp.}(-K_1 t) \tag{4}$$

$$C_G = C_{Co}\left[\frac{K_1}{K_2 - K_1}\right](\text{Exp.}(-K_1 t) - \text{Exp.}(-K_2 t)) \tag{5}$$

$$C_H = C_{Co}\left[\frac{K_1 K_2}{K_2 - K_1}\right]\left[\frac{\text{Exp.}(-K_1 t) - \text{Exp.}(-K_3 t)}{K_3 - K_1} + \frac{\text{Exp.}(-K_3 t) - \text{Exp.}(-K_2 t)}{K_3 - K_2}\right] \tag{6}$$

The value of rate constant K_1 is adapted from Grethlein (6) with K_2 and K_3 from McKibbins (13),

$$K_1 = 1.22 \times 10^{19} (C_A^*)^{1.16} \text{ exp.}(-42{,}500/RT) \tag{7}$$

$$K_2 = 9.27 \times 10^{14} (a_G C_A) \text{ exp.}(-32{,}690/RT) \tag{8}$$

$$K_3 = 2.4 \times 10^{11} (a_H C_A) \text{ exp.}(-23{,}110/RT) \tag{9}$$

where

C_A = acid concentration, normality

C_A^* = acid concentration, percent by weight

R = ideal gas constant = 1.9872 cal/gmole-K

a_G, a_H = activity coefficient, = 1.0 at C_A = .8N

The calculated concentration of HMF utilizing Equations (6-9) and the experimental data for 20 mesh particles are shown in Figure 10.

A. Acid Concentration. To investigate the effect of catalyst acid concentration, temperature was held constant at 300 C. Figures 11

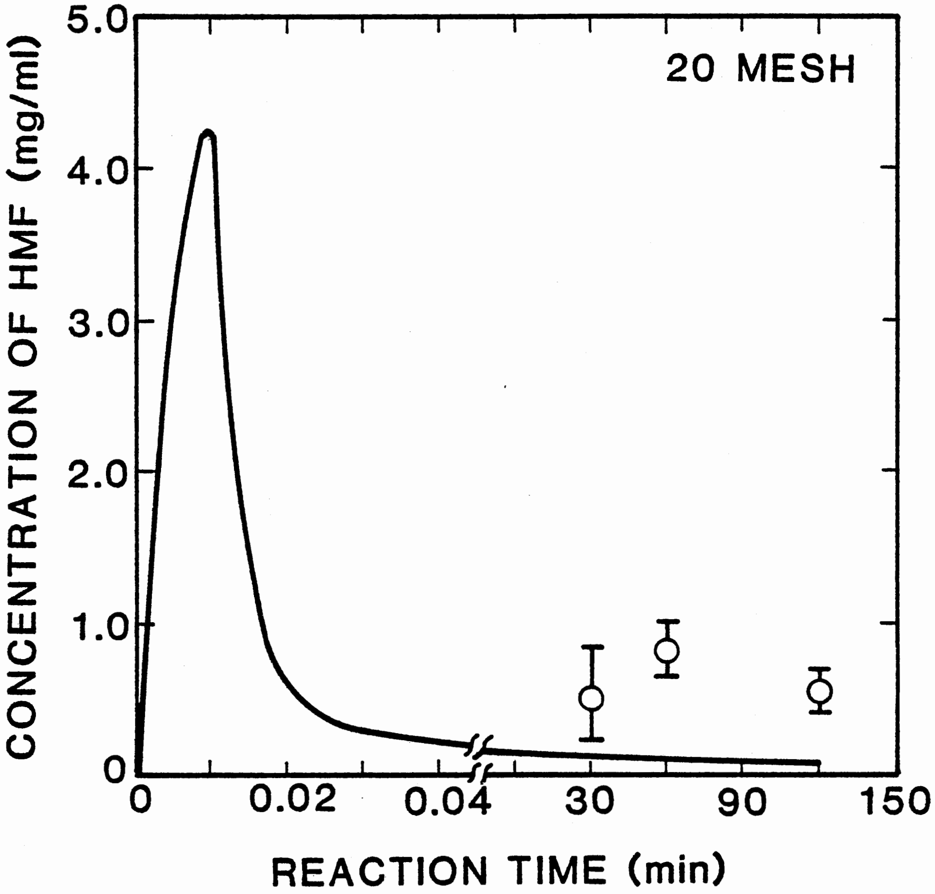


Figure 10. Formation of HMF as Predicted by the Rate Equation and as Obtained Experimentally at 300 C

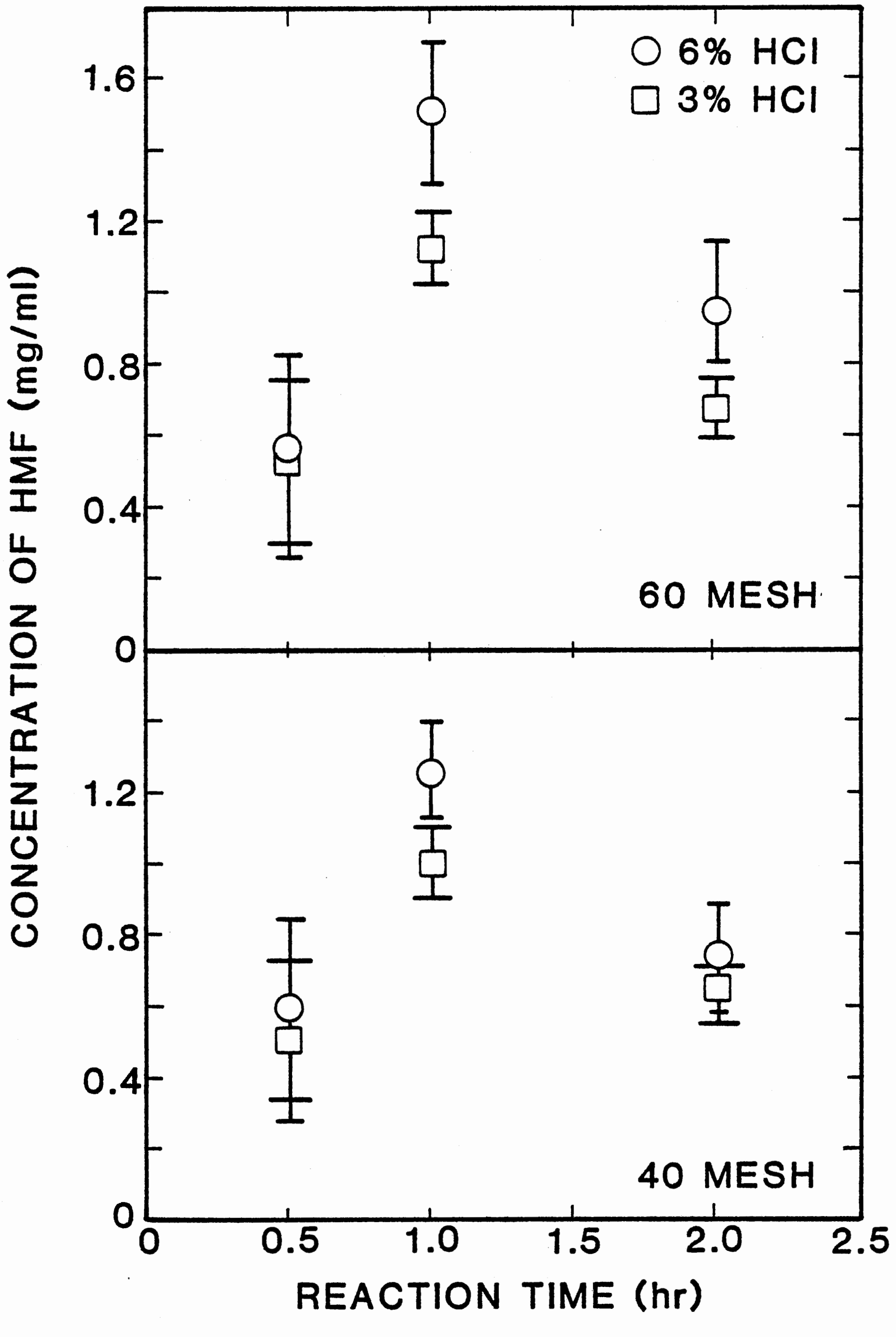


Figure 11. Effect of Hydrochloric Acid Concentration on Production of HMF at 300 C

shows a 25% increase in formation of HMF from 60 mesh or 40 mesh Oakwood particles as the concentration of hydrochloric acid increased from 3 to 6% by weight.

C. Temperature. The most important factor controlling the rate of function of HMF is the temperature of the hydrolysis reaction. The data reported in Figures 12-14 indicate that for a 40 C increase in temperature, HMF concentration increased by 44% for 60, 40, or 20 mesh particle sizes. The simplest relationship between temperature and the rate constant is described by the Arrhenius equation,

$$K = A\ \mathrm{Exp.}(-E/RT) \qquad (10)$$

where,

A = a constant

E = activation energy, cal/g-mol

T = absolute temperature, K

Equivalent to Equation (10) is,

$$\ln(K) = \ln(A) - (E/RT) \qquad (11)$$

at $T = T_1$

$$\ln(K)_{T_1} = \ln(A) - (E/RT_1) \qquad (12)$$

at $T = T_2$

$$\ln(K)_{T_2} = \ln(A) - (E/RT_2) \qquad (13)$$

Subtracting Equation (12) from (13),

$$\ln\left[\frac{(K)_{T_2}}{(K)_{T_1}}\right] = \frac{E}{R}\left(\frac{T_2 - T_1}{T_2 T_1}\right) \qquad (14)$$

or

$$\frac{(K)_{T_2}}{(K)_{T_1}} = \mathrm{Exp.}\left[\frac{E}{R}\left(\frac{T_2 - T_1}{T_2 T_1}\right)\right] \qquad (15)$$

For a 40 C (300 to 340 C) increase in temperature,

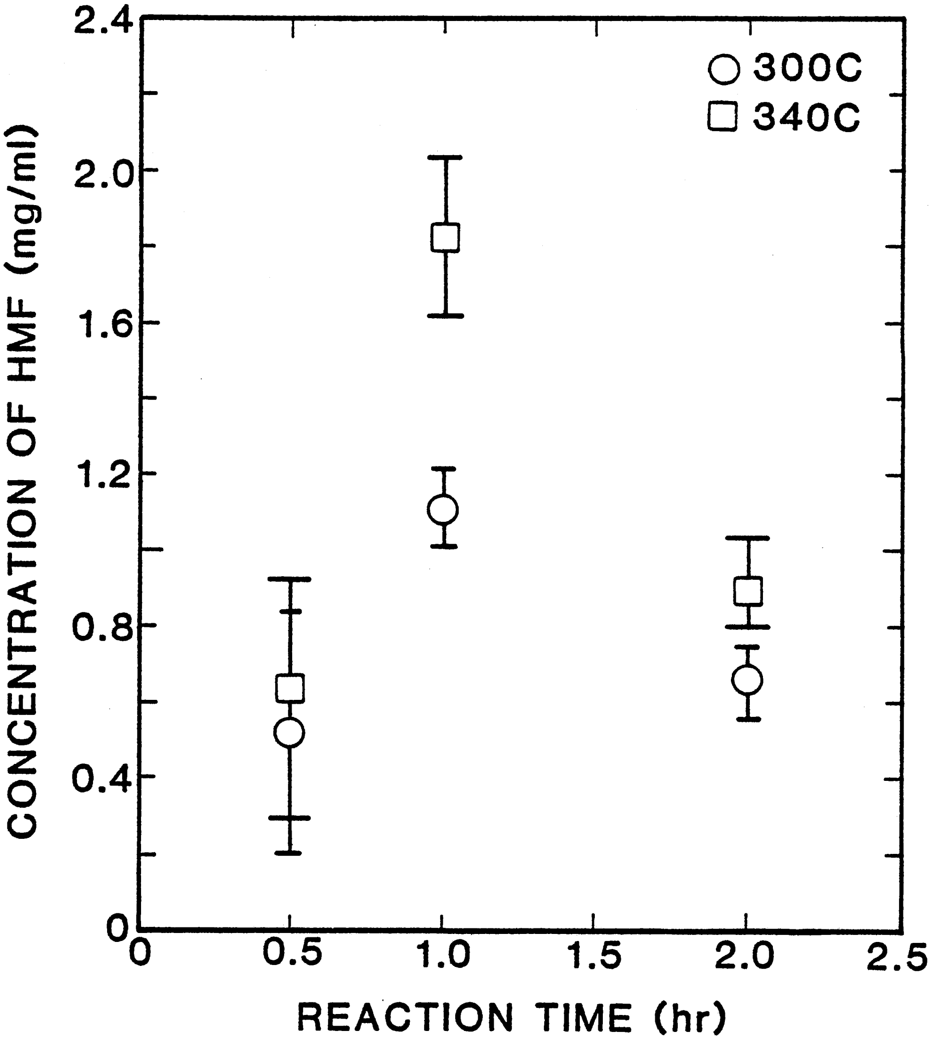


Figure 12. Effect of Temperature on Production of HMF for 60 Mesh Particles

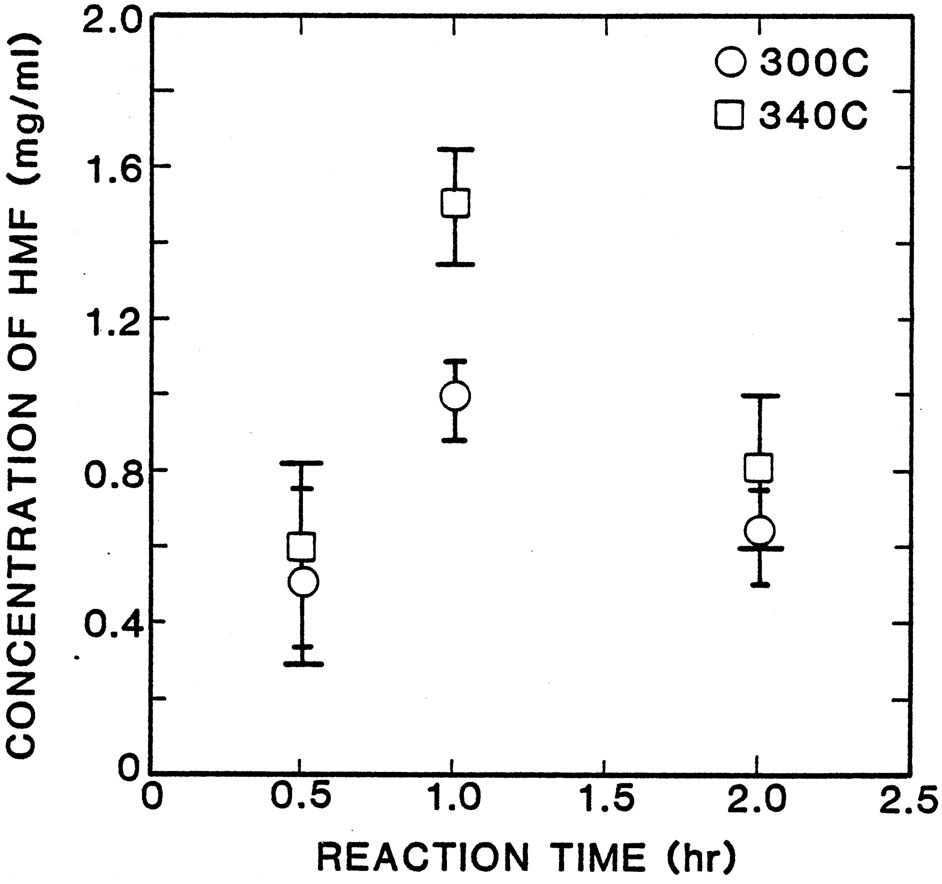


Figure 13. Effect of Temperature on Production of HMF for 40 Mesh Particles

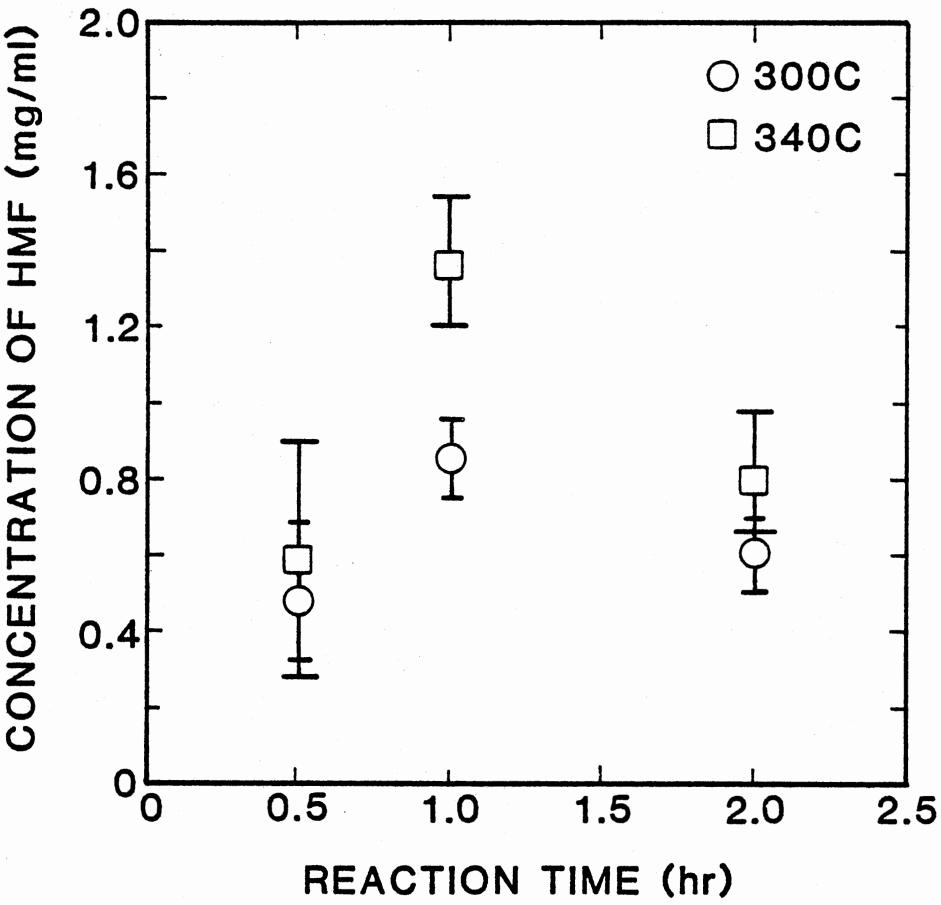


Figure 14. Effect of Temperature on Production of HMF for 20 Mesh Particles.

$$\frac{(K)_{T_2}}{(K)_{T_1}} = \text{Exp.}(5.73 \times 10^{-5} * E) \qquad (16)$$

Since the activation Energy, E, is always a positive number, Equation (16) indicates that the rate constant increases due to the rise of temperature.

D. Particle Size. Among the factors investigated in this study, the particle size showed a very mild effect on production of HMF. In all runs, the particle size of 60 mesh yielded a higher concentration of HMF than 40 mesh than 20 mesh. For example, for the reaction condition of 300 C and 3% hydrochloric acid the 60 mesh particles showed a 12% increase in HMF concentration over 40 mesh particles and a 18% increase over 20 mesh particles.

E. Other Products of Hydrolysis. Furfural and levulinic acid are the two products of acid hydrolysis that were obtained in measurable amounts. Figure 15 shows a selected curve of furfural concentration as a function of time at 300 C by action of 6% hydrochloric acid. Like HMF, the concentration of furfural displayed a decay with time under the experimental conditions of this study.

The levulinic acid concentration showed an increase with time with no indication of any decay. An example is provided in Figure 16. Equations of the form 1 through 3 could be developed to predict the concentration of levulinic acid as a function of time. That is,

$$\frac{dL}{dt} = K_3 C_H \qquad (17)$$

where

L = concentration of levulinic acid, mol/l

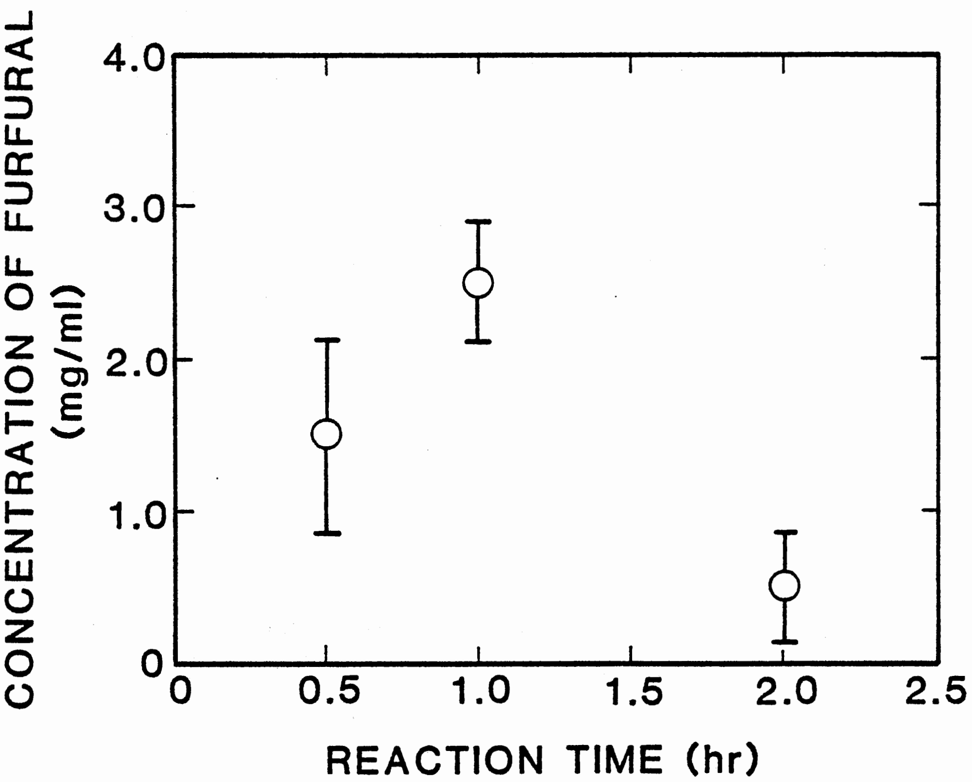


Figure 15. Formation of Furfural From 60 Mesh Oak Sawdust With 6% HCL at 300 C

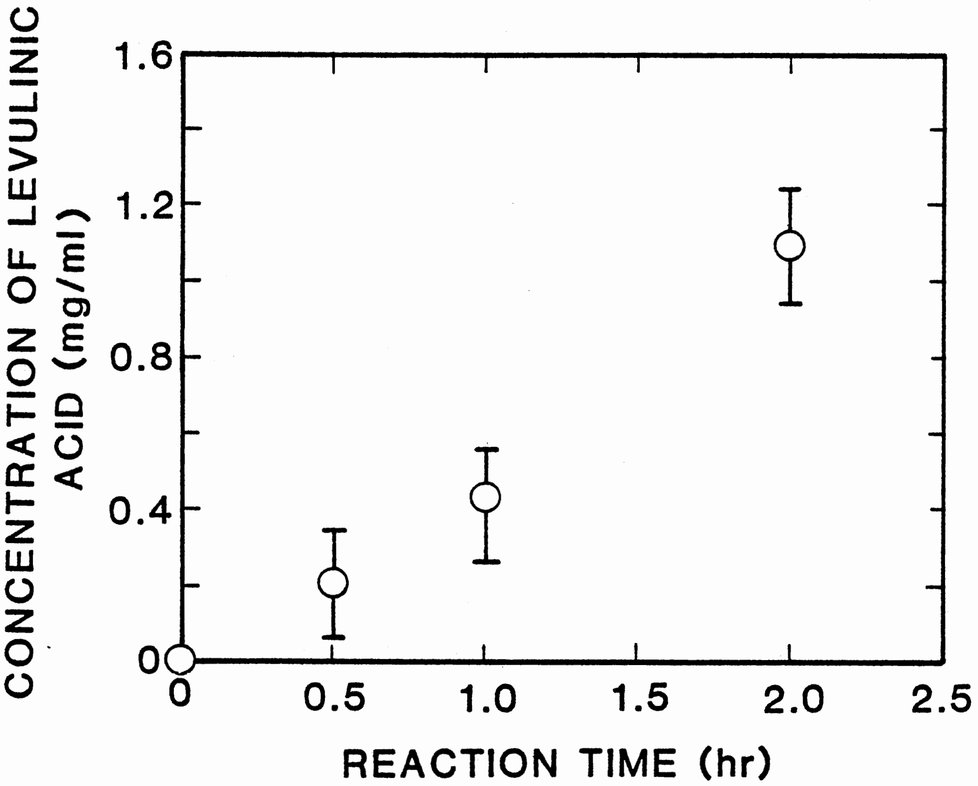


Figure 16. Formation of Levulinic Acid From 60 Mesh Oak Sawdust With 6% HCL at 300 C

and C_H is given by Equation (6). Substituting for C_H in Equation (17) and integrating,

$$L = C_{Co}\left[\frac{K_1K_2K_3}{K_2 - K_1}\right]\left[\frac{\text{Exp.}(-K_3t) - \text{Exp.}(-K_1t)}{(K_3 - K_1)^2} + \frac{\text{Exp.}(-K_3t) - \text{Exp.}(-K_2t)}{(K_3 - K_2)^2}\right] \tag{18}$$

McKibbins (13) experimental results on formation of levulinic acid from pure glucose displayed an increase in concentration of levulinic acid. Due to stability of levulinic acid at operating temperature of up to 220 C, McKibbins (13) concluded that the levulinic acid formation reached a plateau value.

Study II. Separation of HMF From Water by Extraction

The equilibrium data for extraction of HMF from water is obtained for two solvents: Dichloromethane (DCM) and isobutyl-methylketone (IMK). The data is listed in Tables VIII and IX and shown in Figures 17 and 18. The ordinate is reported as the solute (HMF) concentration in the extract (DCM or IMK) layer in mg of HMF per ml of solvent. The abscissa is the concentration in the raffinate (water) layer in mg of HMF per ml of water.

Phase Calculations

According to the distribution law (24), the equilibrium concentration of a solute in the raffinate and extract phases are

TABLE VIII

EQUILIBRIUM CONCENTRATION OF HMF IN DICHLOROMETHANE AND WATER AT 25 C

Percent HMF by Weight in the Original Solution	Extract $\frac{\text{mg HMF}}{\text{ml DCM}}$	Raffinate $\frac{\text{mg HMF}}{\text{ml Water}}$	Distribution Coefficient (K)
100	47.66	40.88	1.17
50	27.47	18.80	1.47
30	15.98	10.93	1.46
15	7.04	4.20	1.68

TABLE IX

EQUILIBRIUM CONCENTRATION OF HMF IN ISOBUTYL-METHYLKETONE (IMK) AND WATER AT 25 C

Percent HMF by Weight in the Original Solution	Extract $\frac{\text{mg HMF}}{\text{ml IMK}}$	Raffinate $\frac{\text{mg HMF}}{\text{ml Water}}$	Distribution Coefficient (K)
10	50.46	40.66	1.24
5	25.45	18.51	1.37
2.5	12.98	8.74	1.48
1.5	8.14	5.60	1.45

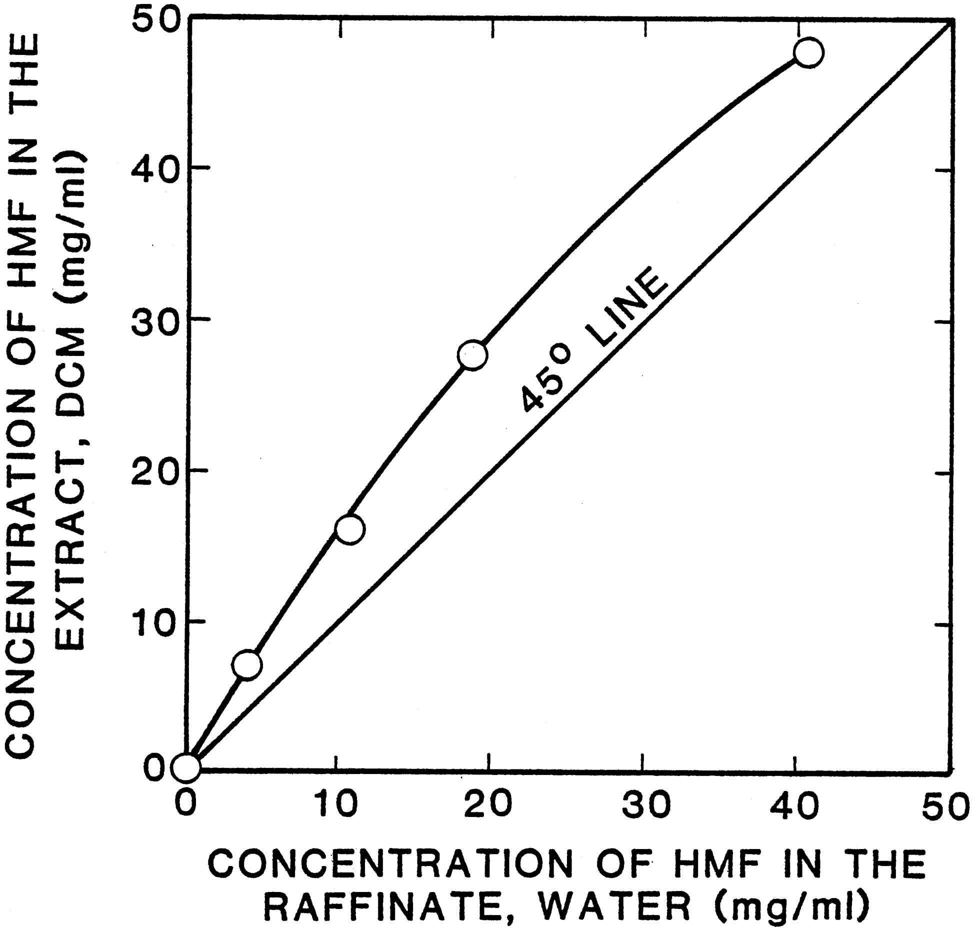


Figure 17. Equilibrium Concentration of HMF in Dichloromethane and Water at 25 C

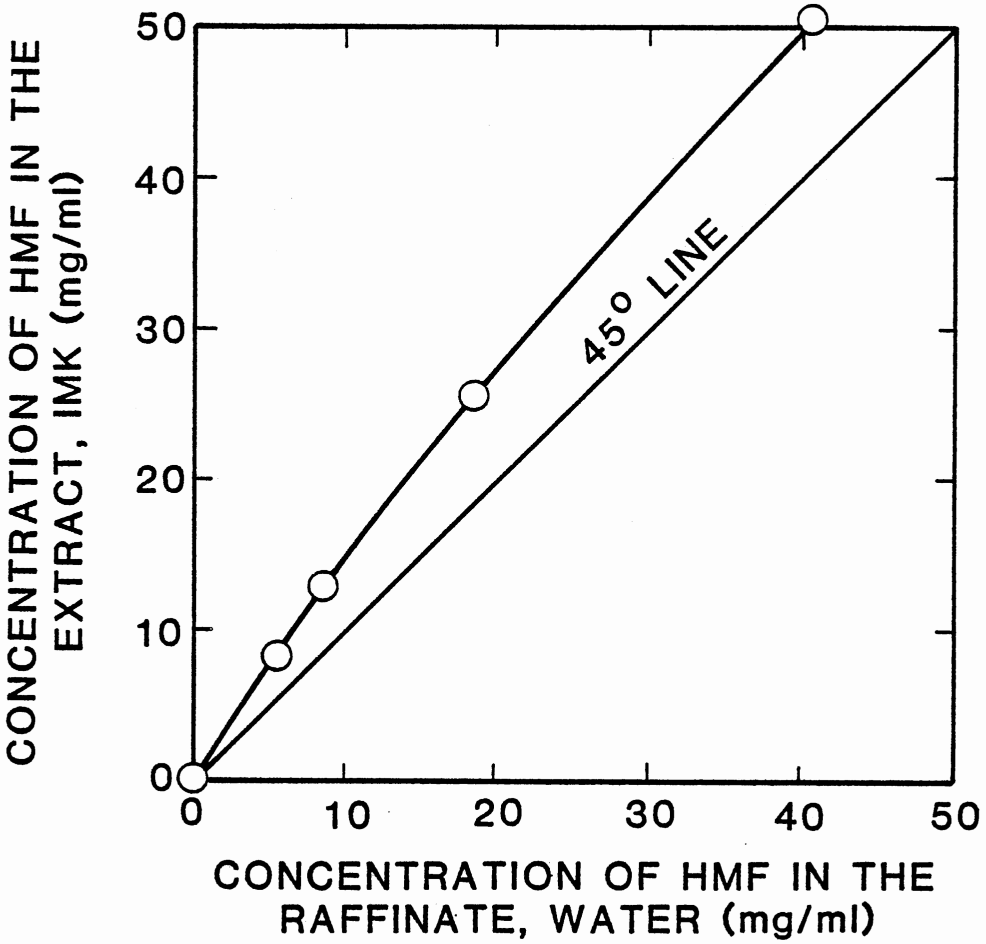


Figure 18. Equilibrium Concentration of HMF in Isobutyl-Methylketone and Water at 25 C

related by:

$$y = K\,x \qquad (19)$$

where,

y = solute concentration in the extract phase

x = solute concentration in the rafinate phase

K = the distribution coefficient

Graphical Construction of Extraction Process for the Immiscible Liquids

Cocurrent Multiple-Contact Extraction

Figure 19 shows the graphical presentation of this method of extraction. The equilibrium line is constructed experimentally. For an initial composition of x_o, where the ratio of solvent to solution is M/N, the compositions x_i and y_1 can be obtained at C by drawing a line with slope equal to -M/N passing through x_o. Further extraction, will result in compositions x_2 and y_2 accordingly.

Counter Current Multiple-Contact Extraction

Equation 7 suggests that the composition of the raffinate leaving the n^{th} stage is a linear function of the composition of the extract entering the n^{th} stage. Figure 14 shows the equilibrium line obtained experimentally for extraction of HMF from water using IMK as the solvent and the operating line with the slope M/N through the point (y_n, x_n). For an original solution with composition x_o, and final raffinate concentration x_n the compositions of extract and raffinate phase of each stage are determined by stepping off the intervals AB, CD, . . .,

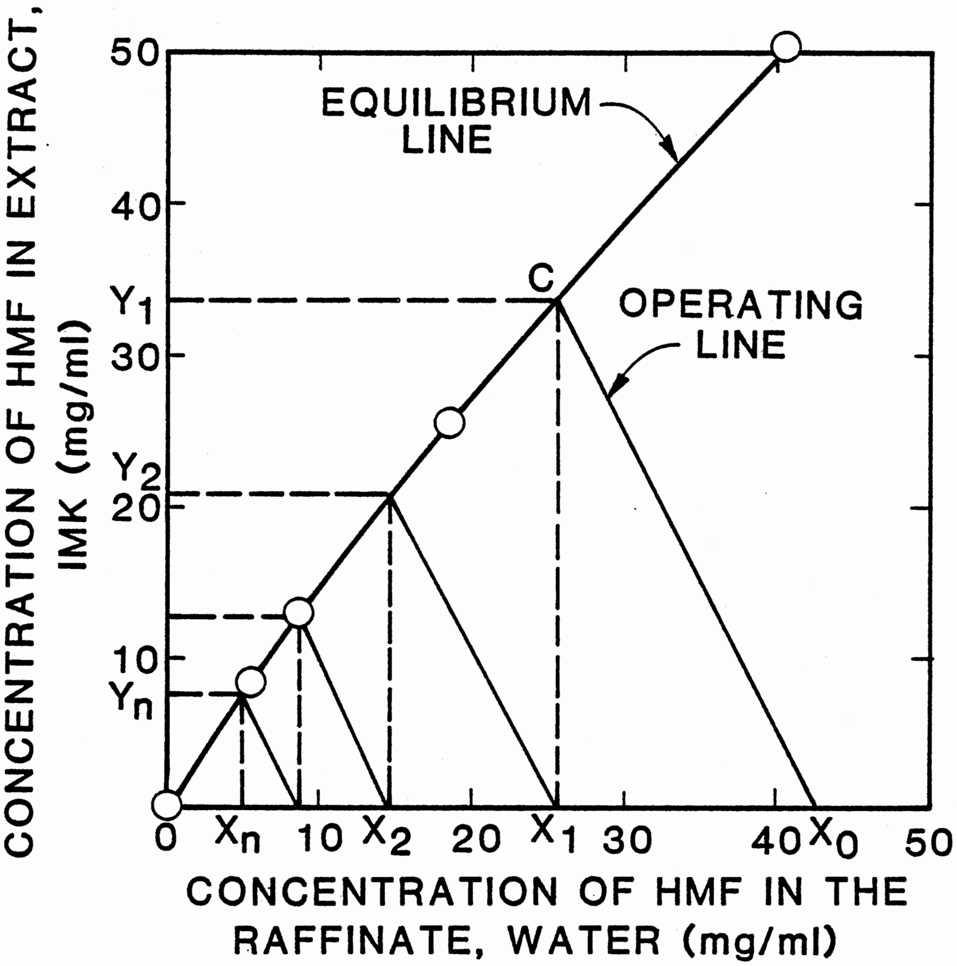


Figure 19. Graphical Construction for the Cocurrent Multiple-Contract Extraction of HMF From Water

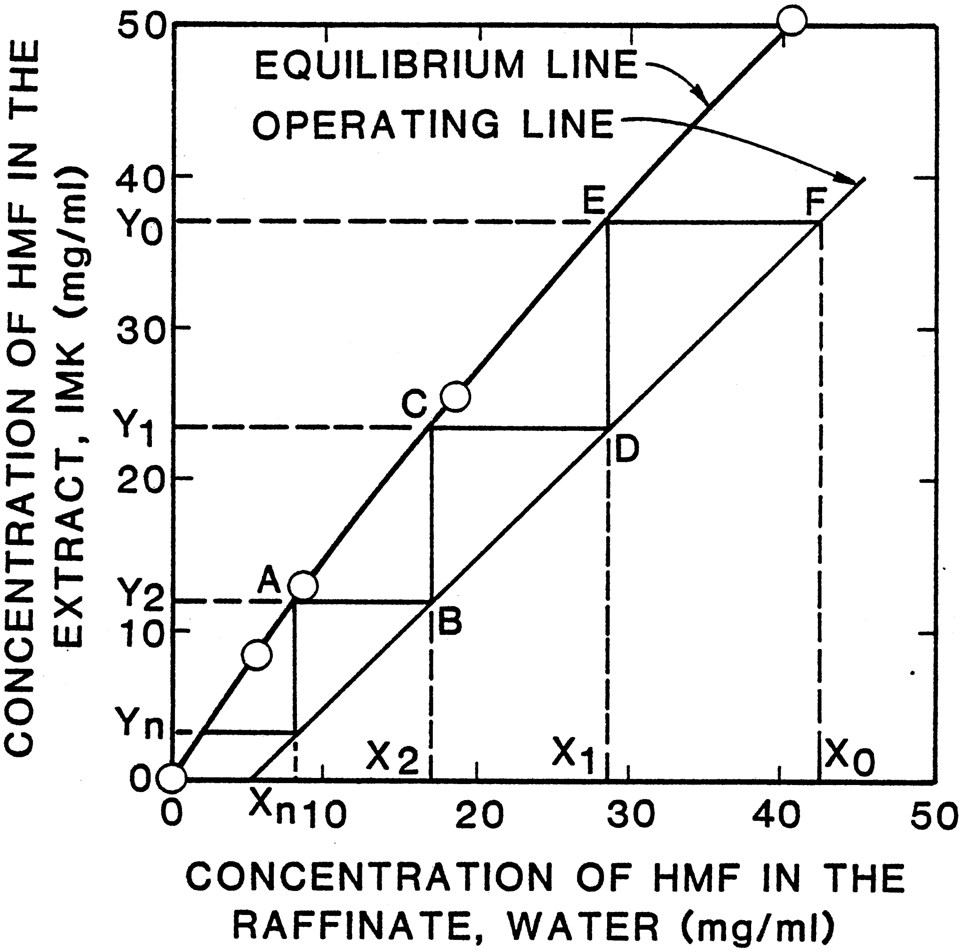


Figure 20. Graphical Construction for the Counter Current Multiple-Contact Extraction of HMF From Water

etc. The number of equilibrium stages is calculated by the number of intervals required to lower the initial concentration of x_o to the final desired x_n.

Numerical Method of Extraction Process for the Immiscible Liquids

The graphical method offers a simple and easy way of calculating the number of equilibrium stages but it is tedious and requires accurate drawing abilities. Experimental data indicates that Equation 19 holds true only for low concentrations of solute. For high solute concentration K is a strong function of concentration.

If an original solution with the composition x_o containing M grams of solvent R (water) is extracted with N grams of pure solvent E (DCM or IMK) in a cocurrent multi-contact extraction the material balance is,

$$Mx_o = Mx_1 + Ny_1 \tag{20}$$

or,

$$\frac{y_1}{x_1 - x_0} = - \frac{M}{N} \tag{21}$$

where

x_1 = Composition of the solute in the raffinate leaving the first stage

y_1 = Composition of the solute in the extract entering the first stage

If the above conditions were used in a counter current multiple-contact extraction, the material balances on the first stage requires,

$$Ny_2 + Mx_o = Ny_1 + Mx_1 \tag{22}$$

For the n^{th} stage,

$$Ny_{n+1} + Mx_{n-1} = Ny_1 + Mx_1 \tag{23}$$

Material balance around the first n^{th} stages results,

$$Mx_o + Ny_{n+1} = Mx_n + Ny_1 \tag{24}$$

Rearranging and solving for the extract composition entering the n+1 stage,

$$y_{n+1} = \frac{M}{N}(x_n - x_o) + y_1 \tag{25}$$

To facilitate computation and simplify possible trial and error solutions required in the graphical procedure, it is necessary to obtain a relationship between the concentration of solute in the extract and the raffinate phases. The equilibrium K values for solvents dichloromethane (DCM) and isobutyl-methylketone (IMK) are listed in Tables X and XI at 25 C. The data is reported as concentration of solute in the extract phase per concentration of solute in the raffinate phase. The variation in the equilibrium K values indicates that the distribution law does not hold for these systems. The equilibrium data, obtained experimentally, is fitted into a second order polynomial. For dichloromethane (DCM),

$$(C_{HMF})_{DCM} = 1.5701\ (C_{HMF})_w - 9.8891 \times 10^{-3}(C_{HMF})_w^2 \tag{26}$$

where,

$(C_{HMF})_{DCM}$ = Concentration of HMF in the extract phase in mg HMF/ml DCM

$(C_{HMF})_W$ = Concentration of HMF in the raffinate phase in mg HMF/ml water

For isobutyl-methylketone (IMK),

$$(C_{HMF})_{IMK} = 1.55196\ (C_{HMF})_w - 7.6473 \times 10^{-3}\ (C_{HMF})_w^2 \qquad (27)$$

where,

$(C_{HMF})_{IMK}$ = Concentration of HMF in the extract phase in mg HMF/ml IMK

Equation 25, 26, and 27 can be used to calculate the composition of phases leaving each stage as well as the number of equilibrium and actual stages required for a given solvent ratio. The computation procedure is given in Appendix F.

This method of calculating the extraction parameters (number of equilibrium stages, solvent to solution ratio, and so on) is suited for use by most of the computers and provides a fast and accurate answer.

In most cases, it is desirable to express the concentration of HMF in the raffinate and the extract phases in terms of weight percent. With this fact in mind, Figures 21 and 22 that are constructed from the information presented in Tables X and XI can be utilized to determine the number of equilibrium stages which are required for a specified HMF recovery.

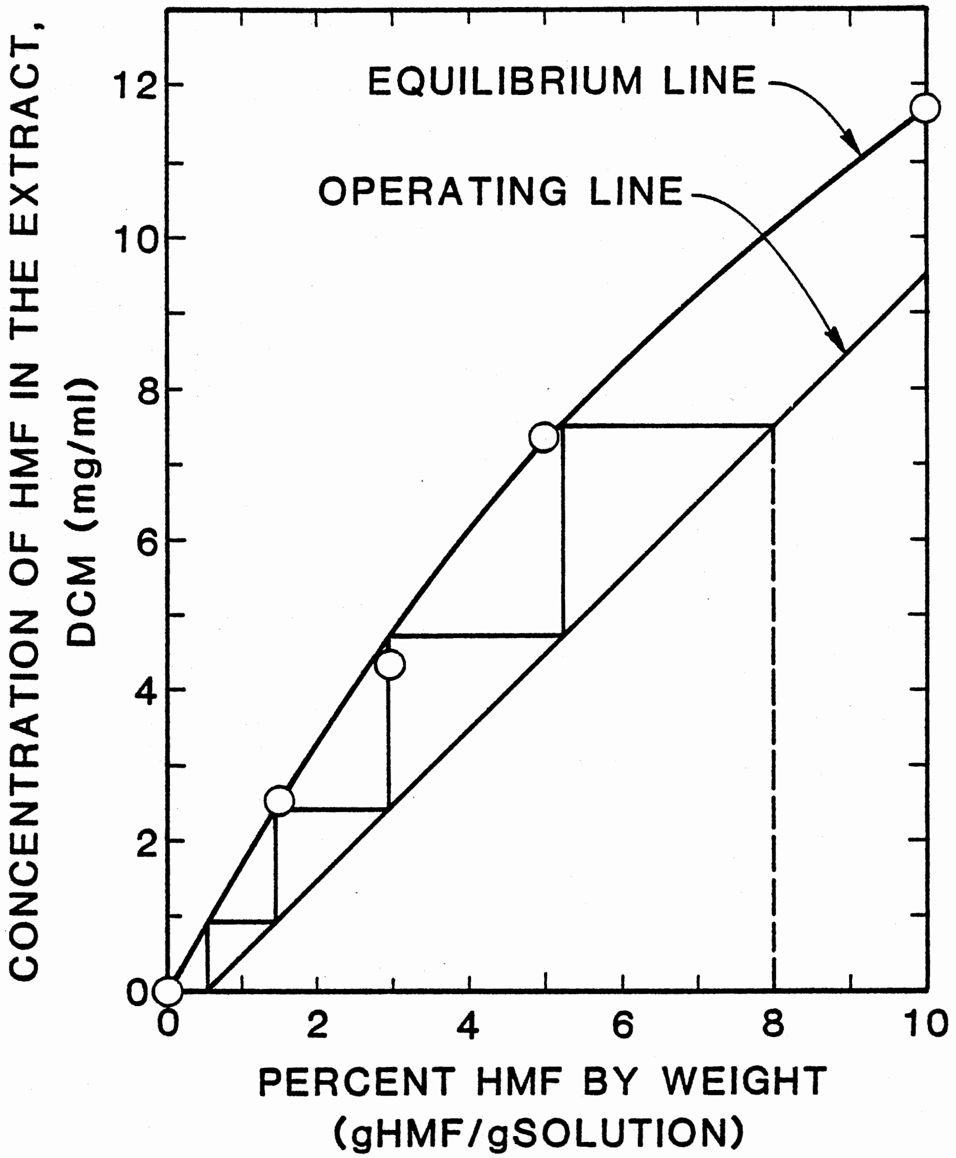


Figure 21. Graphical Determination of the Number of Equilibrium Stages for 95% Recovery of HMF by Dichloromethane

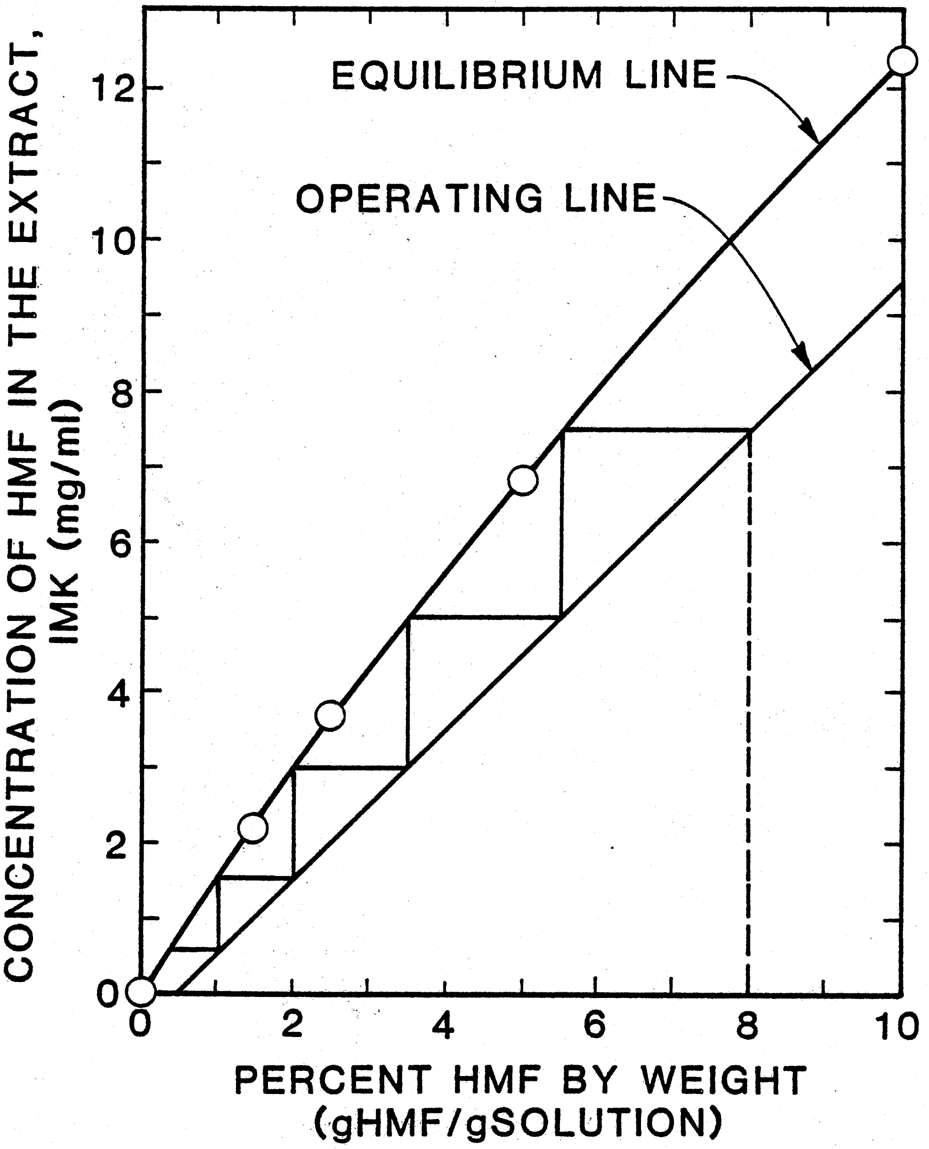


Figure 22. Graphical Determination of the Number of Equilibrium Stages for 95% Recovery of HMF by Isobutyl-Methylketone

CHAPTER V

DISCUSSION

The experimental data indicated that oakwood chips can be utilized as a source for the production of 5-Hydroxymethyl-2-furaldehyde (HMF). The concentration curve for HMF formation obtained experimentally, displayed a decay for reaction times between 0.5 and 2.0 hours. The calculated concentration of HMF from the rate equations indicated the maximum occuring within the first minute of the reaction time preceeding a rapid decay as shown in Figure 10. Within allowable error, the experimental results compare well with the calculated values. The differences between the two can be explained as a result of several factors:

A. Due to the limited capability of the equipment, it was not possible to heat up the content of the reactor instantaneously. Therefore the gradual addition of heat caused the actual process reaction time to be within ±15 minutes of the measured time.

B. The rate equations do not take into account the formation of other species during the hydrolysis and their inhibition role in relation to the formation of HMF.

C: The expressions for the rate constants, K_1, K_2, and K_3 adapted from Grethlein (6) and McKibbins (13) were applicable in the range of 180-240 C. These expressions were used to predict the behavior of the HMF formation at temperatures of 30 and 340 C.

D. The values for the activity coefficient in the McKibbins (13) rate constants, A_G and A_H, were asssumed to be one, since no other information was available.

Hence, the experimental results of HMF production must be used with care and caution. The emphasis of this research study was devoted to establishment of an efficient method to recover HMF from the solution in high overall yield.

The experimental search made possible an extraction process which could be utilized for HMF recovery from an aqueous solution. A counter current multiple-contact extractor was suggested to achieve maximum efficiency of the operation. The extraction process, operating at 77 F and 1 atm has the advantage of no addition of heat. The thermal degradation of HMF and a low overall yield is avoided under these conditions.

The two solvents used to perform the extraction, dichloromethane (DCM) and isobutyl-methylketone (IMK), were both equally effective in extracting HMF from water. Special care must be taken to avoid inhalation of dichloromethane. The operating environment must be highly ventilated even though it is assumed the system is airtight.

Economic Evaluation of an HMF Production Plant

In an attempt to determine the economic feasibility of an HMF producing plant, the information on HMF production from oakwood chips by Snyder (25) was utilized. The experimental data of this research study on extraction of HMF was applied to recover the 95% of the HMF. The process flow diagram of the proposed plant is presented in Figure

23. For the production of 5,000,000 lbs of HMF per year, 1.3 x 10^7 of oakwood chips as the raw material and 3.6 x 10^7 lbs of 0.6% solution of sulfuric acid as the catalyst are required. The oakwood chips are sprayed with 0.6% sulfuric acid for 30 minutes at ambient temperatures and are charged into a second reactor where saturated steam at pressure of 1000 psi is introduced. After 105 sec., the solids are collected in a lignin receiver tank and the liquid product is run through a heat exchanger to cool the product to 77 F. Sodium hydroxide is added to neutralize and quench the reaction. Any solid formed during the neutralization or carried by the hydrolysis reaction is removed through a filter. The solution containing 8% HMF by weight is fed into the top of a counter current extraction column where it is contacted with isobutyl-methylketone (IMK). For 95% recovery of HMF, 10 actual stages are required with estimated stage efficiency of 60%. The extract is then subjected to high vacuum distillation where HMF is collected as the bottom product and IMK is recovered in the overhead stream. The IMK stream is sent to a solvent make up tank for reuse. Appendix G shows the details of the heat and material balances for the described plant.

The economic feasibility of an extraction process is determined by the rate of recovery of the solvent for reuse. The wide range of the boiling points of HMF and either of the solvents utilized, made it easy to recover 98% of the solvent originally used.

The economic evaluation of the HMF plant is shown in Table X and XI. The capital cost of $734,500 and the annual operating cost of $1,696,800 are required to produce $3,000,000 revenue each year. If the plant is to be 70% financed over 5 years at an annual interest rate of 12%, the break even point for this process is about 1 year. The break even price of HMF, not including the interest on the capital investment, is $0.34/lb. of HMF produced. Table XII shows the effect of interest rate on economics of this plant.

The main concern in investing in an HMF production plant is the marketability of the HMF. The chemistry of HMF makes it a raw material for the synthesis of other valuable chemicals such as ethers, acetals, furfuryalcohol, and several other chemicals that are in great demand.

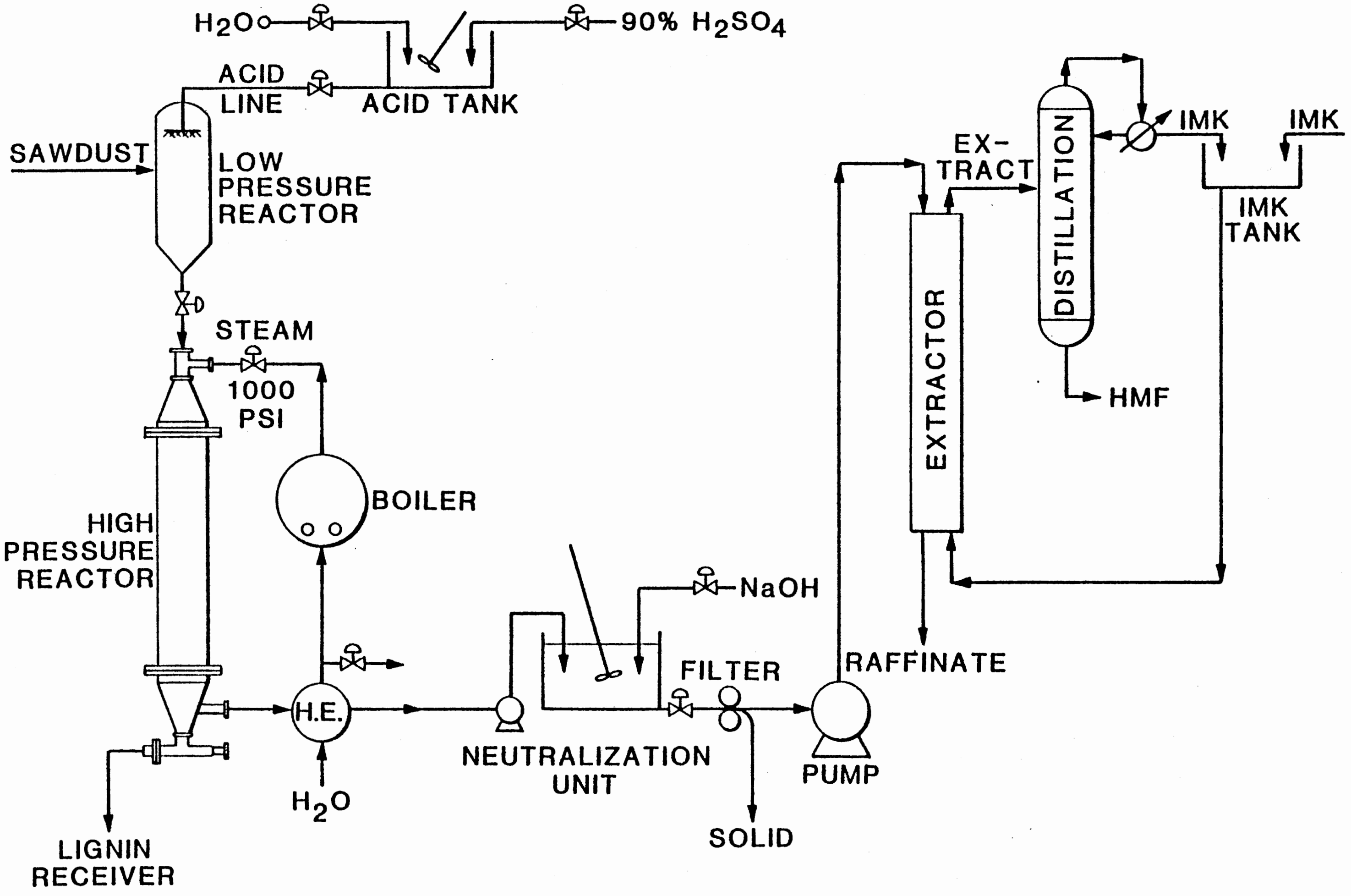


Figure 23. Process Flow Diagram for HMF Production and Recovery Plant

TABLE X

ECONOMIC EVALUATION OF THE HMF PROCESS (PLANT EQUIPMENT COST)

Description of Units		Price
Low pressure reactor		$ 57,000
High pressure reactor		142,000
Extraction column		164,000
Vacuum distillation unit		71,000
Acid tank		10,700
IMK make up tank		7,600
Boiler		82,000
Filter		66,000
Neutralization unit and pump		23,500
Heat exchanger		43,500
Pump		67,200
	Total	$734,500

*Based on Dec. 1982.

TABLE XI

ECONOMIC EVALUATION OF THE HMF PROCESS

Operating Cost	
Wood (\$50/ton)	\$300,000
H_2SO_4 (\$56/ton)	5,600
NaOH (\$684/ton)	55,200
IMK (\$0.51/lb)	536,700
Utilities	220,000
Labor and supervision	300,000
Maintenance (10%)	73,500
Depreciation (20%)	147,000
Taxes (8%)	58,800
Total	\$1,696,800
Revenue (5 M HMF/yr, \$0.6/lb)	\$3,000,000

TABLE XII

EFFECT OF ANNUAL INTEREST RATE ON ECONOMICS OF HMF PLANT

Interest Rate % Annually	Break Even Point Month
12	12
14	18
16	26
18	38

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The objectives of this study were to verify the production of 5-hydroxymethyl-2-furaldehyde (HMF) by action of dilute hydrochlroic acid (3 to 6%) on wood oak sawdust at elevated temperatures (300 - 340 C) and to establish a separation process for HMF recovery avoiding the thermal degradation of HMF. Conclusions drawn from this research study are:

1. The oakwood chips can be a source for the production of HMF.

2. Oakwood particle size did not show a significant improvement in the the yield of HMF production.

3. The rate of formation of HMF increased with an increase in temperature.

4. An extraction process can be utilized to recovery HMF with 76% of overall yield.

5. Dichloromethane or isobutyl-methylketone can be employed as a solvent to recover 95% of HMF in the hydrolyzate in 10 actual stages.

The following recommendations are made for the future studies:

1. Kinetics of steam hydrolysis should be establisned to determine the rate parameters of this reaction.

2. Additional experimental data on HMF production from other cellulosic material besides oakwood chips should be taken.

3. The possibility of enhancing the hydrolysis reaction by means

of a catalyst in addition to the acid solution should be considered.

4. Equilibrium data on distribution of HMF-water solution for the other solvents such as n-butanes, toluene, chloroform, etc., should be taken to choose the best solvent for the extraction process.

BIBLIOGRAPHY

1. Blanksma, J., and Von Ekenstein, W., Ber., 43, II, 2355 (1910).
2. Bunji, M., Brit. UK Appl. 2,025,337, Feb. (1980).
3. Choudhury, P. K., J. Sci. Ind. Res.(India) 16B, 289-94 (1957).
4. Dunlop, A. P., and Peters, F. N., The Furans (1953).
5. Faith, W. L., I&EC, 37, 1 (1945).
6. Grethlein, H. E. Proceedings - Annual Fuels From Biomass Symposium, 2nd (1978).
7. Grote, A., and Tollens, B., Ber., 7, 1375 (1874).
8. Harris, E. E., et al., I&EC, 37, 1 (1945).
9. Harris, J. F., Saeman, J. F., and Zoch, L. L., Forest Products J. 10, 125-8 (1960).
10. Haworth, W. N., and Jones, A. L., J. Chem. Soc., 667 (1944).
11. Haworth, W. N., and Wiggins, F., Brit. 591, 858, Sept. 1 (1947).
12. McCabe, W. L., and Smith, J. C., Unit Operations of Chemical Engineering, 3rd Edition, McGraw-Hill Book Company (1976).
13. McKibbins, S. W., Ph.D. Dissertation, Chemical Engineering Dept., University of Wisconsin, Madison, Wisconsin (1958).
14. McKibbins, S. W., Harris, J. F., and Saeman, J. F., Journal of Chromatography, 5, 207 (1961).
15. Meiler, L., Dissertation, Techn. Hochschule, Munich (1923).
16. Middendorp, J., Rec. Trav. Chim., 38 1 (1919).
17. Morris, P., Inc., Analytical Chemistry, 35, 10 (1963).
18. Mulder, G., J. Prakt. Chem., 21, 219 (1840).
19. Natesan, M. V., J. Indian Chem. Soc., 36, 215-20 (1959).
20. Saeman, J., Ind. Eng. Chem., 37, 43 (1945).

21. Scholler, H., Dissertation, *Techn. Hochschule*, Munich (1923).

22. Scherrad, E. C., and Kressman, F. W., *Ind. and Eng. Chem.*, *37*, 1 (1945).

23. Scott, R. W., *Analytical Chemistry*, *48*, 13 (1976).

24. Sherwood, T. K., *Absorption and Extraction*, McGraw-Hill Book Co. (1937).

25. Snyder, F. H., U.S. Patent 2,851,468, Sept. 9 (1958).

26. Treybal, R. E., *Mass Transfer Operation*, Third edition, McGraw-Hill Book Co. (1980).

27. Wiggins, L., *The Sugar Research Foundation Inc.*, England (1948).

28. Wiley, A., Harris, J., Saeman, J., and Locke, E., *Ind. and Eng. Chem.*, *47*, 1397 (1955).

APPENDIX A

CALCULATION OF THE STANDARD MATRIX FOR GLUCOSE, MANNOSE, AND XYLOSE DETERMINATION

TABLE XIII

GLUCOSE STANDARD (.1 g/1)

Sample	A_{280}	A_{310}	A_{310}	ΔA_{280}	$A_{310(avg)}$	$A_{340(avg)}$
A_1	.179	.535	.508			
A_2	.167	--	--	.0955		
B_1	.157	.497	.477			
B_2	.202	--	--	.0560	.5256	.4966
C_1	.171	.545	.505			
C_2	.143	--	--	.0995		

$\Delta A_{280(avg)} = .0836$

$A_{310(avg)} = .5256$

$A_{340(avg)} = .4966$

TABLE XIV

MANNOSE STANDARDS (.1 g/l)

Sample	A_{280}	A_{310}	A_{340}	ΔA_{280}	$A_{310(avg)}$	$A_{340(avg)}$
A_1	.370	.242	.156			
A_2	.323	--	--	.2085		
B_1	.342	.202	.128			
B_2	.277	--	--	.2035	.215	.1376
C_1	.342	.201	.129			
C_2	.282	--	--	.2010		

$\Delta A_{280(avg)} = .2043$

$A_{310(avg)} = .2150$

$A_{340(avg)} = .1376$

TABLE XV

XYLOSE STANDARDS (.1 g/l)

Sample	A_{280}	A_{310}	A_{340}	ΔA_{280}	$A_{310(avg)}$	$A_{340(avg)}$
A_1	.175	.807	.144			
A_2	.225	--	--	.0625		
B_1	.158	.771	.127	.0465	.7886	.1336
B_2	.223	--	--			
C_1	.158	.788	.130	.0495		
C_2	.217	--	--			

$\Delta A_{280(avg)} = .0528$

$A_{310(avg)} = .7886$

$A_{340}(avg) = .1336$

TABLE XVI

STANDARD MATRIX

ΔA_{280}	.0836	.2043	.0528
A_{310}	.5256	.2150	.7886
A_{340}	.4966	.1376	.1336

D = determinant = 5.71727×10^{-2}

APPENDIX B

SUPPLEMENTARY EQUATIONS AND THE COMPUTER PROGRAM FOR CALCULATING THE CONCENTRATION OF GLUCOSE, MANNOSE AND XYLOSE

$$G = \Delta A_{280}\frac{\begin{vmatrix} m_2 & x_2 \\ m_3 & x_3 \end{vmatrix}}{D} + A_{310}\frac{\begin{vmatrix} x_1 & m_1 \\ x_3 & m_3 \end{vmatrix}}{D} + A_{340}\frac{\begin{vmatrix} m_1 & x_1 \\ m_2 & x_2 \end{vmatrix}}{D}$$

$$M = \Delta A_{280}\frac{\begin{vmatrix} x_2 & g_2 \\ x_3 & g_3 \end{vmatrix}}{D} + A_{310}\frac{\begin{vmatrix} g_1 & x_1 \\ g_3 & x_3 \end{vmatrix}}{D} + A_{340}\frac{\begin{vmatrix} x_1 & g_1 \\ x_2 & g_2 \end{vmatrix}}{D}$$

$$X = \Delta A_{280}\frac{\begin{vmatrix} g_2 & m_2 \\ g_3 & m_3 \end{vmatrix}}{D} + A_{310}\frac{\begin{vmatrix} m_1 & g_1 \\ m_3 & g_3 \end{vmatrix}}{D} + A_{340}\frac{\begin{vmatrix} g_1 & m_1 \\ g_2 & m_2 \end{vmatrix}}{D}$$

where,

G = concentration of glucose, mg/ml

M = concentration of mannose, mg/ml

X = concentration of xylose, mg/ml

D = Determinant of the standard matrix

```
10     REM G refers to glucose, E1 to mannose, and X to xylose
20     DIM A1(10,10)
30     Let n = 3
40     For I1 = 1 to N
50     For I2 = 1 to N
60     Input "Array Element", A1(I1,I2)
70     Next I2
80     Next I1
90     Print
100    Print "G          M          X   Array"
110    For I1 = 1 to N
120    Print A1(I1,1), A1(I1,2), A1(I1,3)
130    Next I1
140    Print
150    Let D = A1(1,1)*A1(2,2)*A1(3,3)+A1(1,2)*A1(2,3)*A1(3,1)
160    Let D = D + A1(1,3)*A1(2,1)*A1(3,2)-A1(1,3)*A1(2,2)*A1(3,1)
170    Let D = D-A1(1,1)*A1(2,3)*A1(3,2)-A1(1,2)*A1(2,1)*A1(3,3)
180    Print "Determinant =", D
190    Print
200    Input "Delta A280", A2
210    Input "A310", A3
220    Input "A340", A4
230    Print
240    Let G = (A1(3,3)*A1(2,2)-A1(3,2)*A1(2,3))*A2/D
250    Let G = G + (A1(1,3)*A1(3,2)-A1(3,3)*A1(1,2))*A3/D
260    Let G = G + (A1(1,2)*A1(2,3)-A1(2,2)*A1(1,3))*A4/D
270    Let G = G/10
280    Print G; "mg glucose/ml"
290    Print
300    Let E1 = (A1(2,3)*A1(3,1)-A1(2,1)*A1(3,3)*A2/D
310    Let E1 = E1 + A1(1,1)*A1(3,3)-A1(1,3)*A1(3,1))*A3/D
320    Let E1 = E1 + (A1(1,3)*A1(2,1)-A1(1,1)*A1(2,3))*A4/D
330    Let E1 = E1/10
340    Print E1; "mg manose/ml"
350    Print
360    Let X = (A1(2,1)*A1(3,2)-A1(2,2)*A1(3,1))*A2/D
370    Let X = X + (A1(1,2)*A1(3,1)-A1(1,1)*A1(3,2))*A3/D
380    Let X = X + (A1(1,1)*A1(2,2)-A1(1,2)*A1(2,1))*A4/D
390    Let X = X/10
400    Print X; "mg xylose/ml"
410    Print
420    Input "Do you have new A-values? Enter (0 No, 1 Yes)", Q1
430    If Q1=1 then 190
440    Input "Do you have new A-Values? enter (0 No, 1 Yes)", Q2
450    Print
460    If Q2 = 1 then 40
470    End
```

APPENDIX C

CALIBRATION CURVE FOR 5-HYDROXYMETHYL-2-FURALDEHYDE (HMF) IN WATER AT 25 C

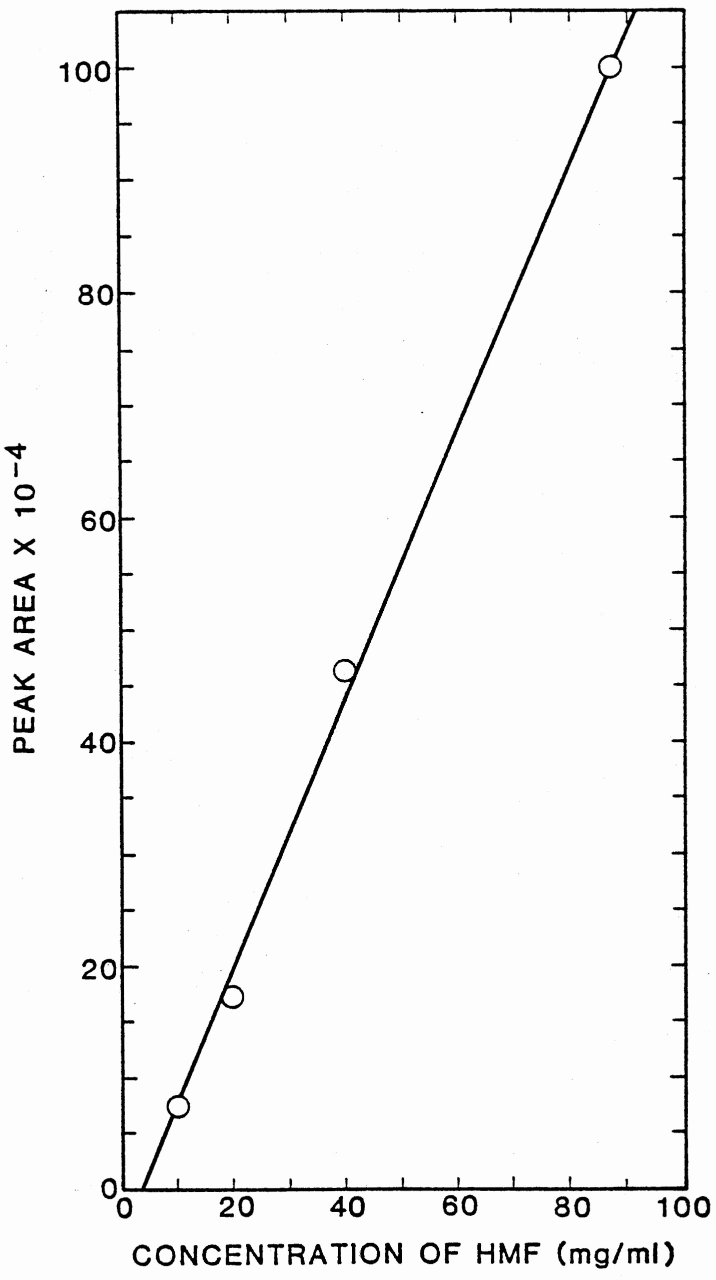


Figure 24. Calibration Curve of HMF

APPENDIX D

FURFURAL CALIBRATION CURVE IN WATER AT 25 C

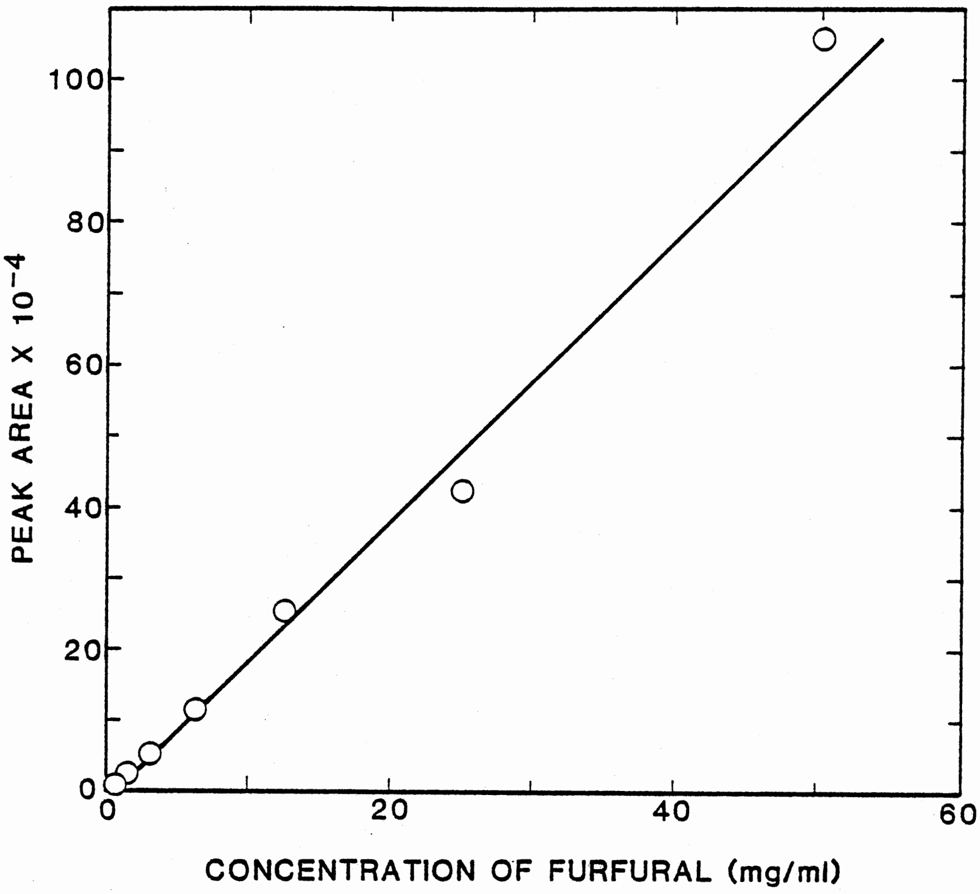


Figure 25. Calibration Curve of Furfural

APPENDIX E

CALIBRATION OF LEVULINIC ACID IN WATER AT 25 C

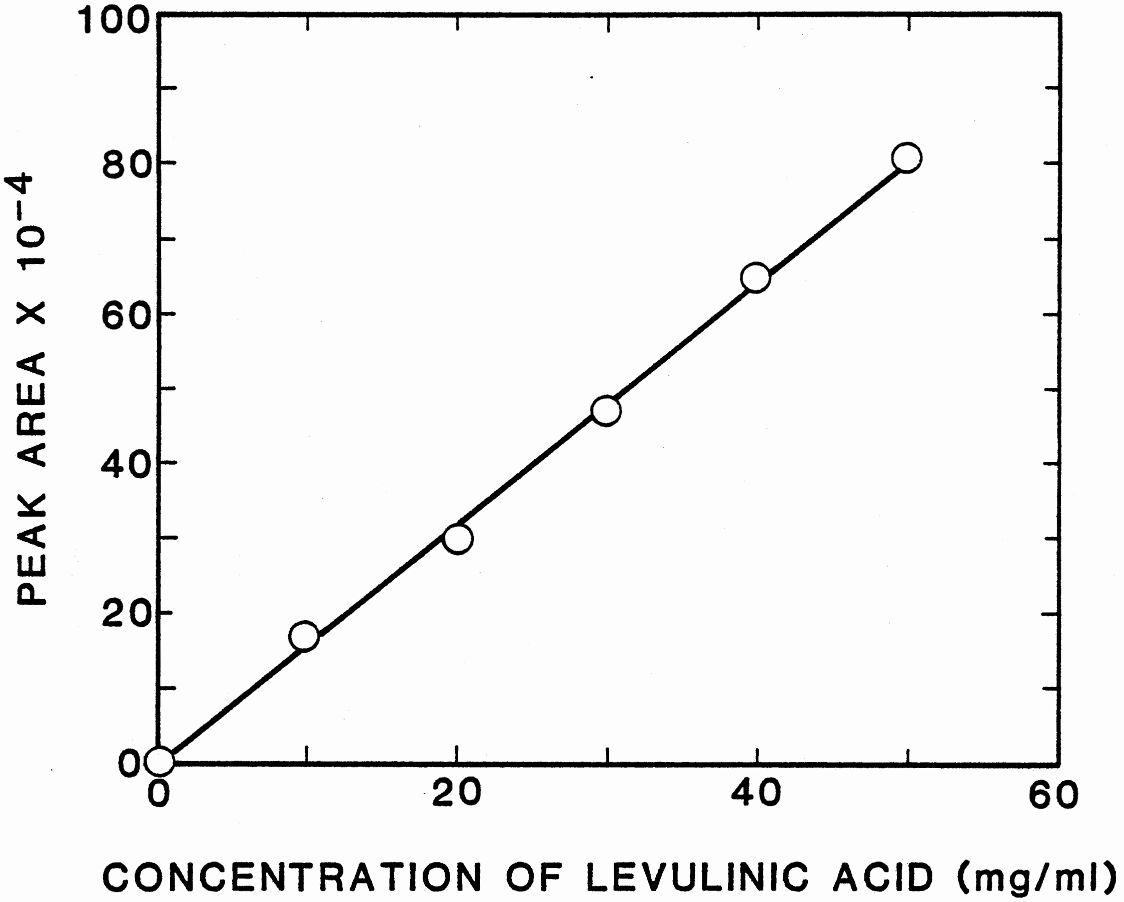


Figure 26. Calibration Curve of Levulinic Acid

APPENDIX F

THE COMPUTATION PROCEDURE FOR THE COUNTER CURRENT MULTI-CONTACT EXTRACTION PROCESS OF HMF FROM WATER

Tray-by-Tray Calculation of HMF Concentration for the Extraction Process

```
1.  Enter values of:
        $x_o$, $X_F$, $Y_F$, M, N, and K = 0
2.  Set the counter:
        $K = K + 1$
3.  Calculate $Y_1$:
        $Y_K = Y_F + M/N(X_F - x_o)$
4.  Compute $x_1$:
        If dichloromethane is the solvent,
            $*Y_K = 1.507\ (X_K) - 9.8891 \times 10^{-3}\ (x_K)^2$
        If isobuthyl-methylketone is the solvent,
            $*Y_K = 1.55196\ (x_K) - 7.6473 \times 10^{-3} (x_K)^2$
5.  Check:
        If $Y_K \leq Y_F$, or $x_K \leq x_F$, go to 6.
        Otherwise go to 2.
6.  Calculate number of equilibrium stages (NES):
        NES = K
7.  Estimate the tray efficiency, TE.
8.  Calculate number of actual stages (NAS):
        NAS = NES/TE
9.  Exit
```

APPENDIX G

THE FLOW DIAGRAM, HEAT AND MATERIAL BALANCE FOR THE PROPOSED HMF PRODUCTION PLANT

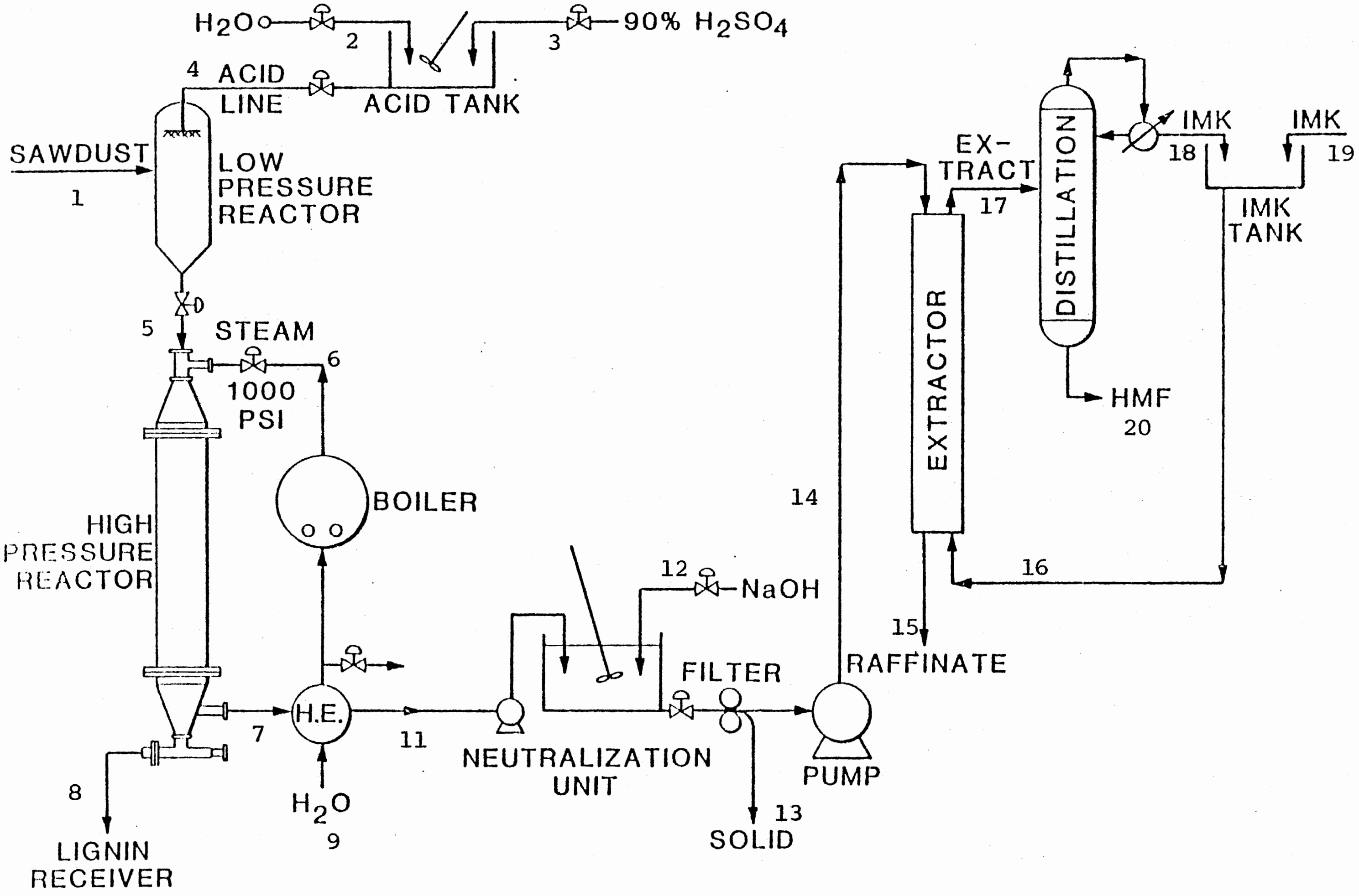


Figure 27. Process Flow Diagram for Material Balance of HMF Production and Recovery Plant

TABLE XVII

MATERIAL BALANCE FOR HMF PLANT

Basis: 5 M lb/yr HMF

Stream	Composition (lb/hr)
1	1524.3 sawdust
2	4237.56 H_2O
3	28.44 H_2SO_4 (90%)
4	.6% H_2SO_4 solution
5	1524.3 sawdust; 4266 H_2O-Acid solution
6	3652.8 steam at 1000 psi, 546 F
7	610 HMF; 7004.63 H_2O; 28.64 H_2SO_4
8	914.3 Lignin; 914.3 H_2O; 2.96 H_2SO_4
9	8000 H_2O (at 60 F)
10	4347.2 H_2O at 546 F
11	610 HMF; 7004.63 H_2O at 77 F; 22.64 H_2SO_4
12	18.48 NaOH
13	32.8 Na_2SO_4; 8.32 H_2O
14	610 HMF; 7004.63 H_2O
15	30.5 HMF; 7004.63 H_2O; 121.8 IMK
16	913 IMK (gal/hr) = 6089.62 IMK
17	579.5 HMF; 5967.82 IMK
18	5967.82 IMK
19	121.8 IMK
20	579.5 HMF

Heat Balance Calculations

Energy Required for Steam Generation

$Q_{st.}$ = (3652.8 lb/hr)[(1)(546 - 60) + $\Delta H_{vaporization}$]

$Q = 3652.8\ (486 + 650) = 4.15 \times 10^6$ Btu/hr

Assume 90% efficiency,

$$Q = \frac{4.15 \times 10^6}{.9} = 4.61 \times 10^6 \text{ Btu/hr}$$

Solvent Recovery

$Q_{sr.}$ (90 cal/g @ 92C)(912.9 gal/hr)(.8 g/cm^3)(30.48^3 cm^3/ft^3)

x(7.481 ft^3/gal)(252 Btu/cal) = $.987 \times 10^6$ Btu/hr

90% efficiency,

$$Q_{sr.} = \frac{.987 \times 10^6}{.9} = 1.1 \times 10^6 \text{ Btu/hr}$$

Process energy required,

$Q_{PE} = 1.0 \times 10^6$ Btu/hr

Heat exchanger (energy given off)

Q_{HE} = [(610)(.416) + (7004.63)(1)](546-77)

$= 3.4 \times 10^6$

90% efficiency

$Q_{HE} = 3.4 \times 10^6 * .9 = 3.06 \times 10^6$ Btu/hr

Solid energy recovery:

Q_{SE} = (914.3 lb/hr)(600 Btu/lb) = $5.48 \times 10^6 * .9 = 4.93 \times 10^6$ Btu/hr

Total energy balance:

$(4.61 + 1.1 + 1.0) \times 10^6 = 6.71 \times 10^6$ Btu/hr

Energy produced:

$(4.93 + 3.06) \times 10^6 = 7.99 \times 10^6$ Btu/hr

VITA

Alireza Memaran Dadgar

Candidate for the Degree of

Master of Science

Thesis: PRODUCTION OF 5-HYDROXYMETHYL-2-FURALDEHYDE BY ACID HYDROLYSIS OF OAK SAWDUST AND SEPARATION FROM WATER

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Zahdan, Iran, August 6, 1957, the son of Mr. and Mrs A. M. Dadgar.

Education: Graduated from Mehran High School, Zahdan, Iran, in May, 1975; received Bachelor of Science in Chemical Engineering degree from Oklahoma State University in 1981; completed requirements for the Master of Science degree in chemical engineering at Oklahoma State University in July, 1983. Currently enrolled in doctoral program at Oklahoma State University.

Professional Experience: Graduate teaching and research assistant, School of Chemical Engineering, Oklahoma State University, 1981-1983.