THESIS

This is to certify that the

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CATALYTIC DEHYDRATION OF SUGARS

presented by

Jinder Jow

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Major professor

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CATALYTIC DEHYDRATION OF SUGARS

By

Jinder Jow

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ABSTRACT

CATALYTIC DEHYDRATION OF SUGARS

By

Jinder Jow

The objective of this research was to explore the dehydration of sugars to levulinic acid using solid acid catalysts (such as zeolites and heteropoly acids). Sugar dehydration via solid acid catalysts has several potential advantages relative to fermentation and other acid-catalyzed sugar dehydration technologies for production of chemicals. Primary advantages are (1) high carbon conversion (2) no dilution required (3) short reaction time (4) ease of catalyst separation and recovery and (5) high feasibility for continuous process.

A lot of work has been reported on the dehydration of sugars to chemicals using inorganic acids (such as H_3PO_4, H_2SO_4, HCl, etc.) and strong ion-exchange resins (such as Diaion PK-208, Amberlyst XN-1010, Dowex MSC-1H, etc.) as catalysts in a solvent system (such as water, dimethyl sulphoxide, etc.). Two major products are produced during catalytic dehydration of sugars--levulinic acid and 5-hydroxymethyl-2-furaldehyde(HMF). Carbon conversion to major products is increased and reaction time is decreased relative to fermentation. However, most work with previous acid catalyzed dehydration of sugars studies resulted in

low conversions to levulinic acid, the requirement of a solvent for substrate, and requirement of a homogeneous catalyst system.

In this work, two basic experimental studies were conducted. They were designed to determine (1) if one step catalytic dehydration of sugars to gas phase hydrocarbons is possible and (2) the nature and yield of the dehydration products in the liquid phase.

In the first study, the aqueous sucrose solutions were reacted with several solid acid catalysts. The gas phase above the reaction system was analyzed to determine if hydrocarbons were produced. It was shown that there were no organic gas products, even though the reactions were carried with zeolite or heteropoly acid. Only the carbon dioxide was produced in the gas phase. But the changes both in the value of PH and in the color of liquid along with CO_2 generation indicated that the dehydration reactions occured.

In the second study, one gram of fructose was reacted with one gram of LZY zeolite under a nitrogen atmosphere. Three temperatures (95 ^{0}C, 120 ^{0}C, and 140 ^{0}C) and several reactions time (0.5hr, 1.0hr, 2.0hr, 5.0hr, and 15hr) were investigated in this nonsolvent system. In addition, two runs were designed to study the catalyst effect by using heteropoly acid as a catalyst and the solvent effect by using water as a solvent for one hour at 95 ^{0}C. The liquid phase of the reaction system was analyzed to determine the

nature and the yield of dehydration products. It was shown that high yields and selectivity of levulinic acid were obtained by using LZY zeolite at moderate temperatures. There was an increase in yield of levulinic acid by increasing either temperature or reaction time. HMF was observed as a reaction product for reaction times of 2 hours or greater at 140 ^{0}C. HMF was not observed at short reaction times, times less than two hours. This behavior is not characteristics of a reaction intermediate as observed in some homogeneous catalyst systems as reported in the literature. The order of the conversion rate of fructose in our work was higher than that of fructose in the solvent system as reported in the literature. Also, isomerization of hexose occured in this dehydration reaction.

This work demonstrates that the use of solid acid catalysts such as LZY zeolite to dehydrate sugars in a non-aqueous medium is potentially superior to other acid-catalyzed sugar dehydration systems including fermentation due to (1) the high yield and selectivity of levulinic acid, (2) the ability to separate and recycle catalysts easily, (3) elimination of the need for a high energy process to separate products, and (4) high feasibility for development of a continuous process. It is recommended that continued research be directed toward optimization of catalyst systems and evaluation of various overall process schemes for directly converting sugars to fuels and chemicals.

——Tomy dear parents,
Ching-Long Jow
Lai-How Jow

獻給我敬愛的父親，卓清龍
母親，卓來好

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CAP : Chromatography application Program Software

DMF : Dimethyl formamide

DMSO : Dimethyl Sulphoxide

FA : Formic Acid

G. C. : Gas Chromatography

HFBA : Heptafluoro Butyric acid

HMF : 5-Hydroxymethyl-2-furaldehyde

HPA : Heteropoly acid

HPLC : High Performance Liquid Chromatography

HUM : Humin

LA : Levulinic Acid

LZY : Linde Zeolite Y type

MIBK : Methyl Isobutyl Ketone

ODS : Octadecyl Sulfate

Rc : conversion factor of one compound to the internal standard

TCD : Thermal Conductivity Detector

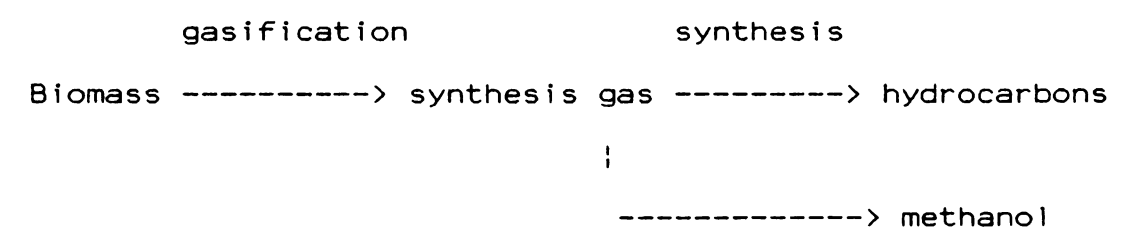
^ : Exponent notation

INTRODUCTION

Crude oil and natural gas are the primary resources for chemicals. The era of low price and readily availabe petroleum will likely draw to an end in the future. Chemical resources will eventually shift to coal and/or biomass. Even though coal has the potential to substitute for petroleum, it is nonrenewable and limited. In the very long term, biomass will be the main resource for hydrocarbons and organic chemicals. Biomass has several distinguishing features relative to coal: composition, renewable, distributed source, and human control of resource. A problem for biomass-to-chemicals system is whether biomass should be converted either to chemicals by destroying the chemical structure of the original biomass, or by maintaining chemical features in the products similar to the orginal biomass.

There are several technologies available for converting biomass to useful chemicals and fuels. These technologies are summarized below :

Thermal Conversion:



fast pyrolysis

Biomass ----------> olefins

pyrolysis

Biomass ----------> pyrolytic oils + char + gas

Microbial Conversion:

digestion

Biomass ----------> methane

Saccharification and Fermentation:

enzyme hydrolysis

Starch ----------> sugars

acid hydrolysis

Cellulose or Hemicellose ----------> sugar + ligin

fermentation

Sugar ----------> aqueous ethanol + CO_2 + Yeast

| distillation

-------> anhydrous ethanol

dehydration/ZSM-5

Anhydrous ethanol ----------> hydrocarbons

Mobil Process

Thermal conversion processes for converting biomass to fuels and chemicals involve energy intensive pyrolysis and gasification steps to produce products which can be converted to hydrocarbons and methanol. Gasification processes basically destroy the chemical structure of the original biomass to produce a synthesis gas which can be reacted over various catalysts to synthesize a spectrum of hydrocarbons and oxygenated chemicals such as methanol. Microbial conversion involves a very slow digestive reaction eventually converting biomass to methane.

Saccharification and fermentation processes convert biomass to sugars which are fermented to dilute alcohol solutions. These processes are attractive since the technology is well developed. But, the separation of ethanol from water by distillation is energy intensive.

The fermentation process is a traditional and well-known process to convert biomass into chemicals. But it has some disadvantages affecting the economics: (1) long reaction time, (2) low carbon conversion, (3) very dilute aqueous medium required, and (4) difficulty in continuous process development.

Our goal is to explore a catalytically continuous process for converting sugars to useful chemicals, which has short reaction time, high yield, high selectivity, high carbon conversion, and nondilute reaction medium.

Instead of fermenting sugars to dilute alcohol solution, our research approach is directly to convert

sugars to chemicals using a solid acid catalyst as the Mobil process[1] did on methanol. A major difference between our concept and the traditional process based on fermentation is that the reactions may take place either in a concentrated solution or in a nonsolvent system. Only the water produced by the reaction can be easily removed by evaporation. Whereas, in a fermentation process, dilute solutions of water/ethanol (7 % ethanol) are separated to produce anhydrous ethanol by distillation which is energy intensive. Basically, our process has the potential of converting sugars directly to chemicals without significant dilution as required by fermentation. Meanwhile, our research is stimulated by the desire to shorten the present long reaction time of dilute solution fermentation of sugars.

From fundamentals of chemistry, the dehydration of hexoses in acidic media produces 5-Hydroxymethyl-2-furaldehyde (HMF; also called as 5-hydroxymethyl-2-furancarboxaldehyde) and Levulinic acid (LA; also called as 4-oxo-pentanoic acid). HMF, a ring structural furan derivative, will be a good intermediate for the chemical industry due to the multifunctional groups on its structure. LA has both keto and carboxyl groups to be a potential intermediate in producing various pharmaceuticals, pesticides, dye, and plasticizes. Reid H. Leonard[2] has investigated and suggested most of the reactions as well as applications of levulinic acid as a

basic chemical raw material. It, also, has attractive applications as a source of three types of lactone solvents and maleic anhydride. The salt of levulinic acid could replace ethylene gycol as an antifreeze in the automobile system. LA can be catalytically converted to 1,4-pentanediol by hydrogenation or to methyl ethyl ketone by decarboxylation. It seems possible to convert sugars directly either to ketone or to hydrocarbons through the formation of levulinic acid by using suitable catalysts and favorable reaction conditions.

In our research system, both HMF and LA, which are dehydrated from sugars, can be extracted by methyl isobutyl ketone from the production phase. The remains are water removed by evaporation and the unreacted sugar solution recycled back to the primary reactor. HMF or LA can be continuously converted to ketone or hydrocarbons in the secondary reactor by another reaction scheme.

Basically, one mole of HMF by dehydration of one mole of hexose produces three moles of water. One mole of HMF can be further converted into one mole of LA and one mole of formic acid (FA) with two moles of water consumed. All the reaction schemes involve dehydration, hydrolysis, and decarboxylation. The ideal stoichiometric reaction scheme is shown below:

Individual Reaction

dehydration step

$$C_6H_{12}O_6 \text{ (hexose)} \xrightarrow{\text{acid}} C_6H_6O_3 \text{ (HMF)} + 3\ H_2O$$

hydrolysis step

$$C_6H_6O_3 \text{ (HMF)} + 2\ H_2O \xrightarrow{\text{acid}} C_5H_8O_3 \text{ (LA)} + CH_2O_2 \text{ (FA)}$$

decarboxylation / hydrogenation step

$$C_5H_8O_3 \text{ (LA)} \xrightarrow{\text{solid catalyst}} C_4H_8O \text{ (methyl ethyl ketone)} + CO_2$$

$$C_5H_8O_3 \text{ (LA)} + 3\ H_2 \xrightarrow{\text{Raney Nickel}} C_5H_{12}O_2 + H_2O$$

Total Stoichiometry for our process:

without decarboxylation/hydrogenation:

$$C_6H_{12}O_6 \xrightarrow{\text{acid}} \text{HMF} \xrightarrow{\text{acid}} C_5H_8O_3\text{(LA)} + CH_2O_2 + H_2O$$

$$\downarrow \text{ solid acid}$$

$$C_5H_8O_3\text{(LA)} + CH_2O_2 + H_2O$$

with decarboxylation/hydrogenation:

$$C_6H_{12}O_6 \xrightarrow{\text{acid/solid acid}} \text{LA} \rightarrow C_4H_8O + CH_2O_2 + CO_2 + H_2O$$

$$C_6H_{12}O_6 \xrightarrow[3H_2]{\text{acid/solid acid}} \text{LA} \rightarrow C_5H_{12}O_2 + CH_2O_2 + 2\ H_2O$$

compared to fermentation process:

$$C_6H_{12}O_6 \xrightarrow{\text{yeast}/H_2O} 2\ C_2H_5OH + 2\ CO_2$$

Apparently, our process has four advantages over fermentation in biomass-to-chemicals research:

(1) high carbon conversion.

(2) lower reaction time.

(3) without significant dilution for reaction.

(4) availability of continuous process development.

BACKGROUND

FUNDAMENTALS OF CHEMISTRY

A. CHEMISTRY OF SUGAR DEHYDRATION:

The dehydration of carbohydrates in alkaline or acidic aqueous solution has been discussed by J. F. Harris et al[3]. The final dehydrated products are determined by the character of the medium, the structures of the carbohydrates reacting, and the conditions of reaction.

For sugar dehydration, the structures of products depend on the character of the medium. In an acidic solution, sugars produce furan compounds. In a basic solution, sugars produce acyclic saccharinic acids. For various types of sugars, the dehydration rate depends on their structures. The dehydration rate of D-fructose is about 40 times higher than that of D-glucose[4]. If sucrose dehydrates in an acidic solution, only the portion of D-fructose molecule reacts, and D-glucose is completely recovered. It implies that keto-structure is more reactive than aldo-structure in the sugar structure.

Ring opening in the reaction mechanism is the first step for the acidic or basic reaction of cyclic sugar. Then the acyclic sugar goes through the Lobry de Bruyn-Alberda Van Ekenstein transformation. The transformation results from the simultaneous occurence of these three reactions :

epimerization of aldoses, epimerization of ketoses, and aldose-ketose isomerization.

The reactive acyclic species, principally 1,2- and 2,3-enediols will be formed through structure rearrangement of acyclic sugar. The rate of sugar dehydration is naturally dependent on both the ease of ring opening and the rate of formation of the reactive acyclic species, which are 1,2- and 2,3-enediols. By isotope-exchange experiments[5,6], the formation of acyclic enediols, which are the intermediates in the isomerization, is apparently the crucial step that leads to dehydration products. The dehydration of the enediols is the next step subject to general acid-base catalysis for sugar dehydration.

There are three forms of dehydrated products of sugars[7]:

(a) volatile products: carbon dioxide, acetone, water, etc.

(b) nonvolatile soluble products : HMF, LA, FA, etc.

(c) nonvolatile insoluble products : Humin, etc.

The products of dehydration of D-fructose in an acidic solution are given in Table 1[7,8]. The major components of the nonvolatile soluble products are 5-Hydroxymethyl-2-furaldehyde (HMF) and Levulinic acid (LA). The formation of Humin (HUM) parallel to HMF has been supposed to result from the copolymerization between HMF and the acyclic intermediates[9, 10, 11]. HUM is a nonvolatile insoluble solid whose color varies from brown to black and composition is C : 66.4% ; H : 3.9% determined by thermogravimetric analysis.

Table1[7,8] :products for acid-catalyzed reaction of fructose

compound	formula	m.p.(^{0}C)	b.p.(^{0}C)
5-hydroxymethyl--2-furaldehyde	$C_6H_6O_3$	31-31.5	110-120
levulinic acid	$C_5H_8O_3$	33-35	245.8
formic acid	CH_2O_2	8.6	100.8
acetic acid	$C_2H_4O_2$	16.7	118.1
alpha-Angelica lactone	$C_5H_6O_2$		
beta-Angelica lactone	$C_5H_6O_2$		
isomaltol	$C_6H_6O_3$		
furfural	$C_5H_4O_2$	-38.7	161.7
4-hydroxy-2,3,5,--hexanetrione	$C_6H_7O_4$		
5-methyl-2-furaldehyde	$C_6H_6O_2$		
2-(2-hydroxyacetyl)furan	$C_6H_6O_3$		
2-(2-hydroxyacetyl)--furan formate	$C_7H_6O_5$		
4-hydroxy-2-(hydroxymethyl)--5-methyl-3(2H)-furanone	$C_6H_{10}O_4$		
humin	$C_{2.3}H_{1.67}O$		
carbon dioxide	CO_2	-78.5	-56.6
acetone	C_3H_6O	-94.6	56.5

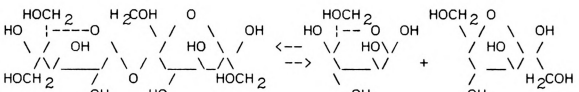
B. CHEMISTRY OF LEVULINIC ACID REACTION:

Levulinic acid (LA) is obtainable from sugars via dehydration and hydrolysis. The theoretical yield of LA from hexose is 64.5 % (Reid H. Leonard: 1956). The reactive nature of levulinic acid, which is a bifunctional intermediate, is shown by the keto and carboxyl groups. LA can be catalytically converted to 1,4-pentanediol by hydrogenation or to methyl ethyl ketone by decarboxylation. It also is very convertible to three types of lactones as solvents. General reaction of levulinic acid, the reduction of levulinic acid by catalytic hydrogena-tion, the oxidation, halogenation, general application, and its reaction as ketone were investigated by Reid H. Leonard (1956).

MECHANISM OF SUGAR DEHYDRATION

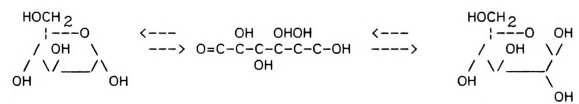
Consideration of mechanism indicates that most of these dehydrated products can be formed from sugars by a simple combination of hydrolysis, enolization, and dehydration steps. Several workers have proposed different mechanisms for the acid catalyzed dehydration of sugars shown as follows:

Hydrolysis: acid: dilute sulfuric acid



SUCROSE D-GLUCOSE + D-FRUCTOSE

Mutarotation of D-GLUCOSE:



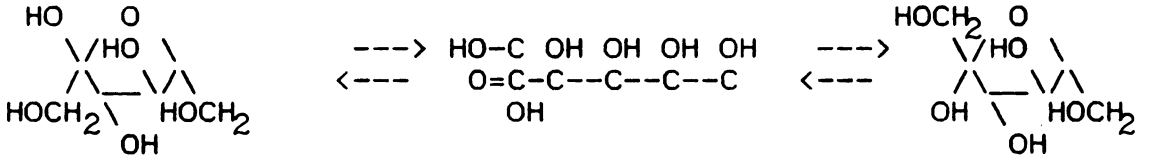
alpha-D(+)-GLUCOSE ACYCLIC GLUCOSE beta-D(+)-GLUCOSE

(36% at equilibrium) (64% at equilibrium)

There is an evidence indicating that the amount of open chain D-(+)-glucose in the solution is very small. Because the solution of D-glucose gives no observable ultraviolet absorption band for a carbonyl group, and the solution of D-glucose gives a negative test Schiff's reagent.

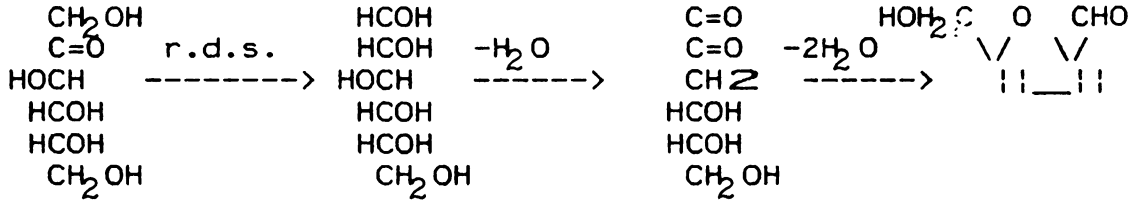
A. Anet [12] mechansim :

Isomerization of D-FRUCTOSE:



alpha-D-fructose ACYCLIC FRUCTOSE beta-D-fructose

Enolization and Dehydration of ACYCLIC FRUCTOSE:



D-FRUCTOSE	1,2-ENEDIOL	INTERMEDIATE	HMF
($C_6H_{12}O_6$)	($C_6H_{12}O_6$)	($C_6H_{10}O_5$)	($C_6H_6O_3$)

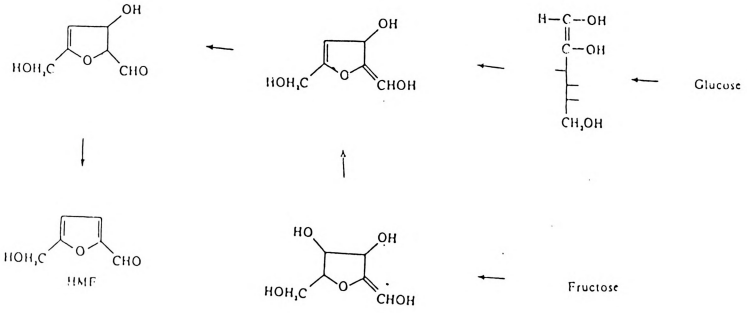
Feather[14] used labelled sugars to confirm the existence of a cyclic precursor to HMF in the dehydration of hexose. This gave a strong evidence for Scheme 1 and Scheme 2.

B. Haworth and Jones[13] mechansim:

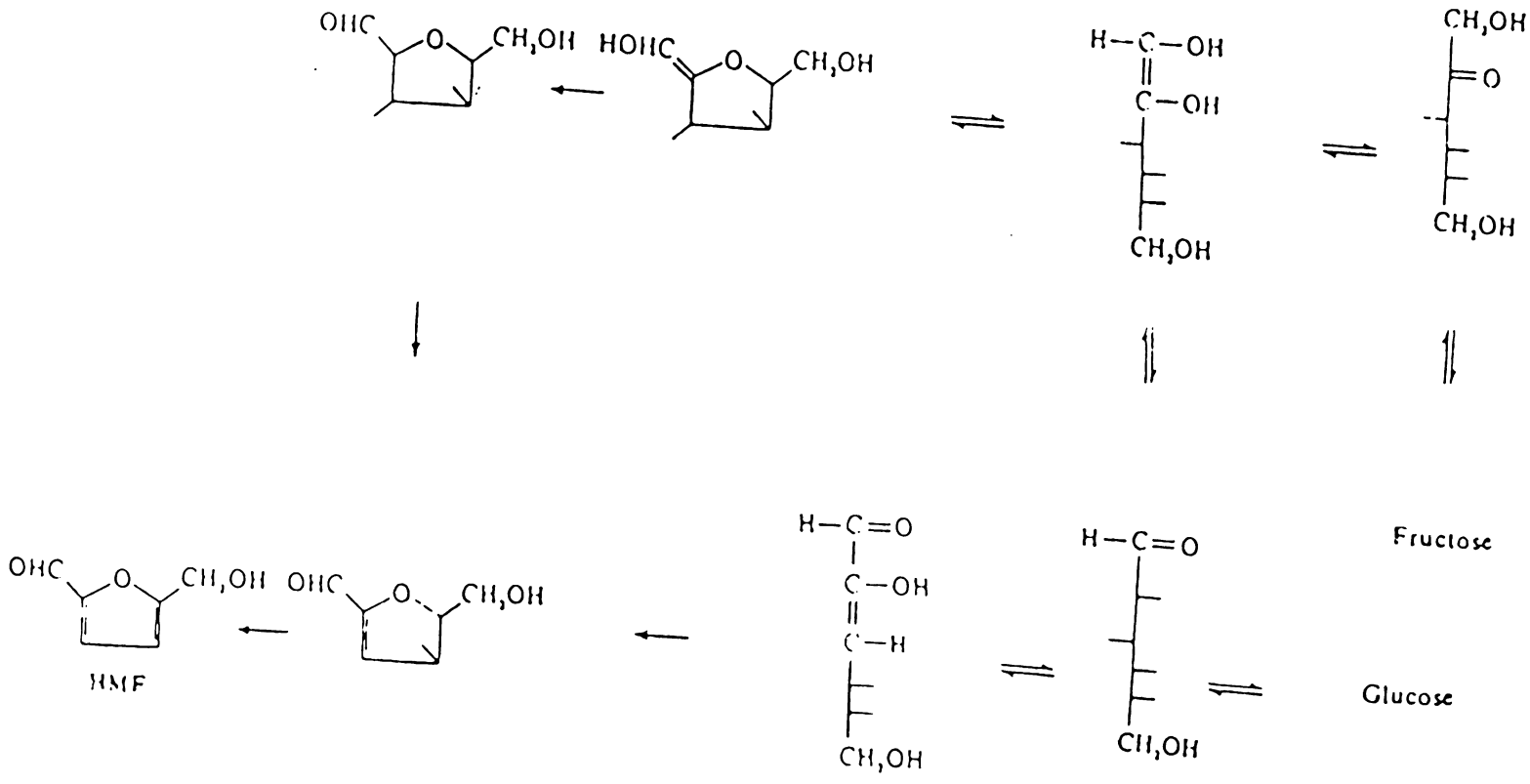
The foramtion of a cyclic precursor to HMF may be the rate determining step in the dehydration reaction. It was shown in Scheme 1.

C. Anet and Moye mechansim:

The formation of 1,2-enediol may be the rate determining step in the dehydration reaction (H. Harry Szmant: 1981). It was shown in Scheme 2.

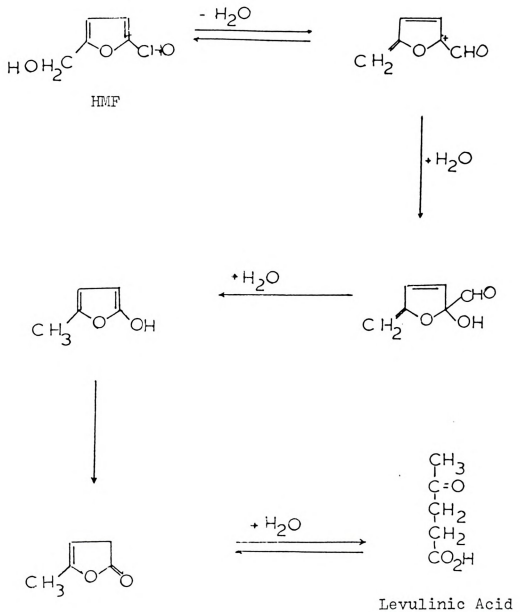


Scheme 1. Mechanism of dehydration of glucose and fructose



Scheme 2. Mechanism of dehydration of glucose and fructose

DEHYDRATION and HYDROLYSIS of 5-Hydroxymethyl-2-furaldehyde



Scheme 3. Mechanism of dehydration and hydrolysis HMF

LITERATURE REVIEW

A. SUGAR DEHYDRATION:

I. EARLY WORK (1895 - 1966)

Dull [38] discovered 5-hydroxymethyl-2-furaldehyde using the oxalic acid to dehydrate Inulin in the aqueous solution. Bonner et al [16] reported that HMF was obtained in a 71 mole % yield (based on the fructose portion) by using iodine as a catalyst in N,N-dimethylformamide to dehydrate sucrose. Wiggins [17] used the oxalic acid to study different carbohydrate sources including glucose, fructose, lactose, starch, and cellulose from wood pulp to dehydrate into levulinic acid. The yield was usually less than 25 % at the atmospheric pressure. Mckibbin [18] used autoclaves to increase reaction temperature to 160 - 200 ^{0}C, and then the yield increased. It was shown that a higher temperature would result in a higher yield of levulinic acid. Moye used mineral acid to study the dehydration of various ketohexose in the nonaqueous slovent for five seconds at the solvent boiling point. A high yield of HMF in excess of 80% was obtained.

II. HOMOGENEOUS INORGANIC ACID AS CATALYST

(1). Dilute Sulfuric Acid

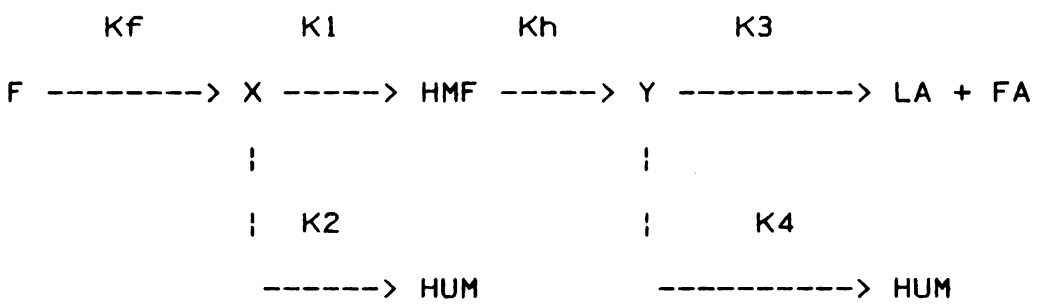
EL. S. Amin[8] has shown that the solution of D-fructose (10.0g) in 500ml of 10% sulfuric acid was heated for 35 hr. The nonvolatile products were shown to be brown black water-soluble products (11.4%) and water-insoluble products (69 %), the rests of the products (19.6%) were volatile materials which contained 5.6% acetone and 9% carbon dioxide.

(2). Hydrochloric Acid

The dehydration of D-fructose (0.25-1.0 M) to HMF and the dehydration of HMF (0.25-1.0 M) to LA and Formic acid(FA) in 0.5-2.0 M HCl at 95 ^{0}C has been studied by B. F. M. Kuster et al[19] . They indicated that more acidic conditions were needed for the formation of LA than that of HMF. The decrease of water concentration, equivalent to the increase of the acidity of the solution, highly increased the conversion rate of D-fructose, but slightly decreased the conversion rate of HMF. The value of PH apparently affected the reaction type. No HMF would be formed, when the PH value of the solution was greater than 3.9. No levulinic acid would be formed, when the PH value of the solution was greater than 2.7. D-glucose appeared to indicate the occurence of isomerization while the PH value of the solution was greater than 4.5. Weak-acid anion would lower the yield of HMF and enhence the isomerization to glucose. The first order conversion of D-fructose and HMF

is fit to the experi-mental data. The order of the formation rate of humin was 1.3 for the intermediate between D-fructose and HMF; and 1.7 for the intermediate between HMF and LA.

A kinetic model was proposed as follows:



F: fructose; HMF: 5-hydroxymethyl-2-furaldehyde;
HUM: humin; LA: levulinic acid
FA: formic acid; X,Y: intermediates
Kf, Kh, K1, K2, K3, and K4 : rate constants

$$d(F)/dt = -Kf*(F)$$

$$d(X)/dt = Kf*(F)-K1*(X)-K2*(X)^{1.3}$$

$$d(HMF)/dt = K1*(X)-Kh*(HMF)$$

$$d(Y)/dt = Kh*(HMF)-K3*(Y)-K4*(Y)^{1.7}$$

$$d(LA)/dt = K3*(Y)$$

$$2.1 = Kx = Kf^{-0.3} * K1^{1.3} / K2$$

$$1.7 = Ky = Kh^{-0.7} * K3^{1.7} / K4$$

III. STRONGLY ACIDIC ION-EXCHANGE RESIN AS CATALYST

(1). Water-Resin Biphase System

H. F. Rase[15] obtained HMF and LA from sucrose by using highly acidic ion-exchange resins as catalysts. Four commercial resins (Dowex MSC-1H, Amberlyst 15, Amberlyst XN-1010, and Amberlyst XN-1005) were used. The former three resins achieved the selectivity of 83 % LA for 24 hr reaction time at 100 ^{0}C, but the yield percentage of levulinic acid was less than 25 %. They indicated that the resin pore size had a strong effect on the selectivity. It was shown that HMF was favored by a larger pore, but LA by a smaller pore.

(2). Solvent-Resin Biphase System

Nakamura [20] used two types of the strongly acidic ion-exchange resins with a low divinylbenzene (DVB) content as the catalyst and Dimethyl sulfoxide (DMSO) as the solvent. One was Porous type: Diaion PK-208, PK-216, and PK-228. The other was Gel type: Amberlite IR-118, IR-120, and Lewatit SC-108. A continuous dehydration of D-fructose was carried out under 60 ^{0}C. A 90 mole% yield of HMF was obtained (basis on D-fructose) for 8.3 hr reaction time at 80 ^{0}C with Diaion PK-216.

The rate of HMF formation was proposed as follows:

$$d(HMF)/dt = k * [(F)' - (HMF)]$$

(F)': the initial concentration of D-fructose

(HMF) : the concentration of HMF

k : the rate constant

The rate constant k was reversely proportional to DVB content in the resin used. The rate constant of the porous resin was greater than that of the gel-type, when the DVB content in resins was the same.

(3). Water-Solvent-Resin Triphase System

Luc Rigal et al[21, 22] explored new ways for the synthesis of HMF which could lead to improve yields by ion-exchange resins as catalysts with an extractive sovlent (MIBK) in a triphasic system. The ratio of the extractive solvent to water was 9. The reaction temperature was fixed at the boiling point of the water-methyl isobutyl ketone azeotrope (88 ^{0}C). The macroporous strong acid resins (Lawatit SPC 108, SPC 118, Nafion-H, and Spherosil S) gave the high yield and high selectivity of HMF for 15 hr reaction time, but no reaction in the presence of weakly acidic ion-exchange resins (e.g. Duolite CC3, Amberlite IRC 50). An increase in the average diameter of the pores in the resins allowed higher yield of HMF than of LA. In Table 2, the conversion rate of fructose with MIBK as an extractive solvent was three-fold greater than taht without MIBK. Some solvents (MIBK, dichlor-ethylether, and benzonitrile) could promote the reaction to obtain high

yield of HMF. Some solvents (alkane, diethyl ketone, t-butyl methyl ether) didn't give high yields of HMF due to their lack of affinity toward the ion exchange resins, or due to the insolubility of HMF (a polar compound) in these non-polar solvents with the weak dielectric constants. The conversion rate of fructose was an increasing fuction of the amount of MIBK introduced. A decrease in the ratio of water to solvent gave rise to an increased conversion rate. It was a strong evidence of solvent factor in this dehydration reaction.

Table 2. Effect of a solvent (MIBK) (Luc Rigal:1981)

concentration of D-fructose (g/dm^3)	222	222
water (cm^3)	20	100
solvent MIBK (cm^3)	180	none
HMF (%)	63	14

IV. LEWIS ACID AS CATALYST

A 95 - 97% conversion of fructose to HMF was reported by H. Szmant[23] by using 25 mole% (based on fructose) boron trifluoride etherate catalyst ($BF_3 \cdot Et_2O$), and dimethyl sulphoxide (DMSO) as a solvent for reaction times of 30 minutes at 100 ^0C in an inert gas (N_2) atmosphere. They indicated that the yield of HMF was a function of solvents,

reaction time, the ratio of catalysts to sugars, reaction temperatures, and starting materials. The yield of HMF increased very sharply to a maximum point as the reaction time increased, but then decreased sharply in all solvents except in DMSO. It implied that the DMSO would provide more stable reaction medium for sugar dehydration. Meanwhile, they indicated that the higher temperature would result in the higher yield of HMF.

V. LITERATURE SUMMARY

Van Einenstein (1909) dehydrated fructose using oxalic acid as a catalyst in the aqueous solution for 3-4 hr at 145 ^{0}C. HMF yield of 22-29 % was obtained. Haworth (1944) dehydrated sucrose using the same acid in the aqueous solution for 2-3 hr at 145 ^{0}C. Only HMF yield of 27 % (based on 12 carbons) was obtained and glucose was completely recovered from sucrose. Stone (1950) dehydrated glucose using phosphoric acid as a catalyst in the aqueous solution for 10 minutes at 190 ^{0}C. A low yield (15.5 %) of HMF was obtained. Rice (1958) dehydrated fructose using phosphoric acid in a water-ketone biphasic solvent up to 48 hrs at 200 ^{0}C. A high yield (65-85%) of HMF was obtained. Moye (1966) dehydrated ketohexoses using mineral acid in nonaqueous solvents for 5 seconds at the solvent boiling point. A high yield of HMF in excess of 80 % was obtained. Kuster (1977) dehydrated fructose using hydrocholoric acid in the aqueous solution for 24 hr at 95 ^{0}C. A high yield

(65-80 mole %) of levulinic acid was obtained. Szmant (1981) dehydrated fructose using boron trifluoride etherate as a catalyst in the nonaqueous solvent about one hour at 100 ^{0}C. A high yield (78-97 %) of HMF was obtained.

Rase (1975) dehydrated sucrose using Amerlyst ion-exchange resins and Dowex resins in the aqueous solution for 24 hr at 100 ^{0}C. A low yield (less than 25 %) of levulinic acid was obtained. Nakamura (1980) dehydrated fructose using Diaion ion exchange resins in DMSO solvent for 8.3 hr at 80 ^{0}C. A high yield (90 %) of HMF was obtained. Rigal (1981) dehydrated fructose using Lewatit, Amberlite, and super-acid ion exchange resins in a water-MIBK biphasic solvent for 4 hr at 88 ^{0}C. A high yield (about 50 %) of HMF was obtained.

Table 3. Literature summary of sugar dehydration

(1909 to 1981)

Year	material	catalyst	solvents	temp. (^{0}C)	time	product	ref.
1909	fructose	oxalic acid	water	145	3-4hr	29%HMF	24
1944	sucrose	oxalic acid	water	145	2-3hr	27%HMF	13
1945	sucrose	PH=2-3	water	145	3-4hr	22%HMF	25
1950	glucose	H_3PO4	water	190	10min	15.5%HMF	26

(continuous)

Year	material	catalyst	solvents	temp.	time	product	ref.
1958	fructose	H_3PO_4	Ketone/water =4:1	200	48hr	65-85%HMF	27
1962	glucose	H_3PO_4 + NH_3	Water/dioxane 1:1	200	37min	23%HMF	28
		H_3PO_4 +$N(CH_3)_3$	1:1	200	37min	30%HMF	28
		H_3PO_4 +pyridine	1:1	200	37min	44%HMF	28
1966	fructose	H_2SO_4	2-methyl ethanol	126	5sec	75%HMF	29
			tetrahydro-furfuralalcohol	78	5sec	74%HMF	29
		HCl	methyl carbinol	193	5sec	80%HMF	29
		I_2	methyl carbinol	193	5sec	80%HMF	29
1975	sucrose	Dowex Amberlyst -15	water	100	24hr	24%LA	15
		Amberlyst XN-1010	water	100	24hr	23%LA	15
		Amberlyst XN-1005	water	100	24hr	15%LA	15
			water	100	24hr	9%LA	15

(continuous)

Year	material	catalyst	solvents	temp.	time	product	ref.
1977	fructose	HCl	water	95	24hr	65-80%LA	19
1980	fructose	Diaion	DMSO	80	8.3hr	90%HMF	20
1981	fructose	Lewatit SC-102	MIBK/water 9:1	88	4hr	47%HMF	21
		Amberlite IR-118	9:1	88	4hr	58%HMF	21
		Duolite C-26	9:1	88	4hr	54%HMF	21
		Amberlite A-200C	9:1	88	4hr	42%HMF	21
		Amberlyst A-15	9:1	88	4hr	30%HMF	21
		Lewatit SPC -118	9:1	88	24hr	51%HMF	21
		Lewatit SPC -108	9:1	84	24hr	62%HMF	21
		Spherosil S	9:1	88	24hr	53%HMF	21
		Nafion-501H	9:1	88	15hr	50%HMF	21
1981	fructose	$BF_3.Et_2O$	Carbitol	100	0.5hr	40%HMF	23
			Mecellosolve	100	1.0hr	78%HMF	23
			Cellosolve	100	2.0hr	63.5%HMF	23
			DMF	100	1.5hr	89.2%HMF	23
			DMSO	100	0.75hr	98.8%HMF	23

B. LEVULINIC ACID CONVERSION:

Levulinic acid, which is a bifunctional compound, has both keto and carboxyl groups. It is a potential intermediate in producing pharmaceuticals, pesticides, dye and plasticizes. Levulinic acid can be catalytically converted to alcohols or ketones. The related researches for levulinic acid conversion are reviewed as follows:

I. METAL AS CATALYST

(1). Hydrogenation

Reid H. Leonard[2] indicated that the catalytic hydrogenation of levulinic acid over Ni and Cu-Cr above 200 C would yield the substantial amount of 1,4-pentanediol, and the small amount of alpha-methyltetrahydrofuran and 1-pentanol. The reaction scheme is shown as follows:

$$CH_3COC_2H_4COOH \xrightarrow[Ni]{H_2} \text{gamma-valeralactone} \xrightarrow[Cu\text{-}Cr]{2H_2} \text{1,4 pentanediol}$$

$(C_5H_8O_3)$ $(C_5H_8O_2)$ $(C_5H_{12}O_2)$

$+$

H_2O

(2). decarboxylation

Wilhelm F. Maier[30] investigated decarboxylation of a variety of carboxylic acids in the gas phase over Ni/Al_2O_3 + H_2 between 150 ^0C and 280 ^0C and Pd/SiO_2 + H_2 at 330 ^0C. The over-all reaction was considered as:

$$RCOOH \xrightarrow{\text{catalyst}} RH + CO_2$$

They found that the heptanoic acid was completely unreacted when N_2 instead of H_2 was used as a carried gas , even though no hydrogen was needed in the over-all stoichiometry. It proved that a catalytic site might be a metal/H complex instead of metal itself. The reaction mechanism is shown as follows:

$$2Pd + H_2 \rightleftharpoons 2\ Pd\text{-}H$$

$$RCOOH' + Pd\text{-}H \longrightarrow RCOOH'\text{-}Pd\text{-}H$$

$$RCOOH'\text{-}Pd\text{-}H \rightleftharpoons RH + Pd\text{-}H' + CO_2$$

They showed that levulinic acid was completely decomposed not to 2-Butanone but to gamma-valerolactone by above reaction scheme in the same conditions. This implies that hydrogenation is more active than decarboxylation of levulinic acid over metal catalysts.

(3). Hydrogenolysis or Hydrogenation by electrocatalysis

Toshiro Chiba et al[31] indicated that the Raney Nickel as a good catalytic electrode brought about the hydrogenation of levulinic acid to gamma-valerolactone because of a large surface area and a high hydrogen-adsorption activity. The reaction mechansim for levulinic acid is shown as follows:

$$H_2O + 2\ Ra\text{-}Ni \longrightarrow 2\ Ra\text{-}Ni\text{-}H + 1/2\ O_2$$

$$CH_3COC_2H_4COOH + Ra\text{-}Ni\text{-}H \Longleftrightarrow CH_3COC_2H_4COOH\text{-}Ra\text{-}Ni\text{-}H$$

$$CH_3COC_2H_4COOH\text{-}Ra\text{-}Ni\text{-}H \Longleftrightarrow C_5H_8O_2 + H_2O + Ra\text{-}Ni$$

(gamma-valerolactone)

(73 % yield)

II. CONDUCTIVE METAL OXIDE AS CATALYST

Photocatalysis

H. L. Chum[32] showed that the photocatalytic decarboxylation of levulinic acid in slurries composed of n-TiO_2 /Pt led to the major products: methyl ethyl ketone and carbon dioxide. The secondary products such as acetaldehyde, acetone, acetic acid, and propionic acid might be produced by cleavage and oxidation of the relevant C-C bonds either of levulinic acid or of methyl ethyl ketone. The reaction scheme is shown as follows:

$$CH_3COC_2H_4COOH \xrightarrow[n\text{-}TiO_2/Pt]{h\nu} CH_3COC_2H_5 + CO_2$$

The mole yield of CO_2 (based on levulinic acid) is quite low (about 0.4 to 1.4%). How to make these reactions occur at much higher rate and yield is important but not well-reported yet.

III. SOLID ACID AS CATALYST

(1). dehydration and decarboxylation

The results by C. D. Chang[1] for the conversion of acetic acid and acetone into hydrocarbons over ZSM-5 (famous Mobil catalyst) are shown below. The dehydration of acetone at 399 ^{0}C, LHSV of 8.0 hr^{-1} led to 95.3 % conversion and yielded 93.9 % hydrocarbons and 6.1 % CO + CO_2. The dehydration of acetic acid at 371 ^{0}C, LHSV of 1.0 hr^{-1} led to 29.9 % conversion and yielded 57.6 % hydrocarbons, 41.2 % CO_2 and 1 % CO and 0.1 % acetone. It showed that the deoxygenation of acetone and acetic acid occured via dehydration and decarboxylation. Levulinic acid with both keto and carboxylic group seems convertible to hydrocarbons by zeolite under certain favorable reaction conditions.

In general,

reactivity of functional group into hydrocarbons over ZSM-5:

alcohol > aldehyde > ketone > acid

(2). decarboxylation

Masayuki Otake[33] investigated the gaseous decomposition of primary, secondary, and tertial carboxylic acids at 200-300 OC over heteropoly acids. The main products are carbon monoxide and olefins; ethylene from propionic acid(PRAC), propene from isobutyric acid(IBAC), butene from pivaric acid (trimethyl-acetic acid, TMAA). The conversions were above 90 %. But both butric and valeric acid were inactive on this catalyst below 300 ^{0}C. Otake did not study levulinic acid.

The reaction scheme is shown as follows:

$$RC(H)(R')-COOH \xrightarrow{\text{solid acid}} RC(R')=CR' + CO + H_2O$$

catalytic activity for decomposition of carboxylic acid

$H_3PO_4 > H_3[PW_{12}O_{40}]$ or $H_4[SiW_{12}O_{40}] > SiO_2\text{-}Al_2O_3 >> SiO_2$ or Al_2O_3

reactivity of carboxylic acid

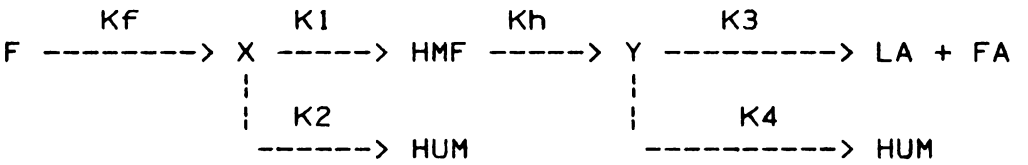
tertial > secondary > primary

From the above conclusions, it would logical that levulinic acid, primary carboxylic acid, could be less convertible to olefins by heteropoly acid even at high temperatures.

KINETIC MODEL OF FRUCTOSE DEHYDRATION

(A). Homogeneous Model

The following model and examples were presented by Ben F. M. Kuster (1976).



F: fructose; HMF: 5-hydroxymethyl-2-furaldehyde;

HUM: humin; LA: levulinic acid

FA: formic acid; X,Y: intermediates

Kf, Kh, K1, K2, K3, and K4 : rate constants

A typical example was the dehydration of D-fructose (0.25-1.0 M) to HMF and the dehydration of HMF (0.25-1.0 M) to LA and FA in 0.5-2.0 M HCl. The first order conversion of D-fructose and HMF was in an agreement with the experimental results. So, the differential equations could be derived:

$$d(F)/dt = -Kf*(F) \qquad \text{----------(1)}$$

$$d(X)/dt = Kf*(F)-K1*(X)-K2*(X)^{Nx} \qquad \text{----------(2)}$$

$$d(HMF)/dt = K1*(X)-Kh*(HMF) \qquad \text{----------(3)}$$

$$d(Y)/dt = Kh*(HMF)-K3*(Y)-K4*(Y)^{Ny} \qquad \text{----------(4)}$$

$$d(LA)/dt = K3*(Y) \qquad \text{----------(5)}$$

Because the concentration of X and Y were very low, the steady-state concept could be applied. i.e. d(X)/dt = 0 ; d(Y)/dt = 0

So, $Kf*(F) = K1*(X) + K2*(X)^{Nx}$ ----------(6)

$Kh*(HMF) = K3*(Y) + K4*(Y)^{Ny}$ ----------(7)

Let Sx : the fraction of D-fructose reacting to HMF

Sy : the fraction of HMF reacting to LA

$Sx = -d(HMF)/d(F) = K1*(X)/[Kf*(F)]$ ----------(8)

$Sy = -d(LA)/d(HMF) = K3*(Y)/[Kh*(HMF)]$ ----------(9)

Substituted (8),(9) into (6),(7)

$Sx^{Nx}/[1-Sx] = Kx*(F)^{[1-Nx]}$ ----------(11)

$Sy^{Ny}/[1-Sy] = Ky*(HMF)^{[1-Ny]}$ ----------(12)

where $Kx = Kf^{[1-Nx]}*K1^{Nx}/K2$

$Ky = Kh^{[1-Ny]}*K3^{Ny}/K4$

The differential equations were fully determined by the model parameters:

Kf, Kx, Kh, Ky, Nx, and Ny.

First step, values for Kf and Kh would be easily calculated from the conversion data for D-fructose and HMF. Next step, Ky and Ny were calculated from LA data for the reaction starting with HMF. Several combinations of Ky and Ny could be used equally well to fit the experimental data. However, only for Ny = 1.7, Ky had an uniform constant

value of 1.7 for all experiments. So, Ky = 1.7 and Ny = 1.7 were chosen. Thereafter, Kx, Nx, Kh, and Kf were calculated from HMF and LA data for the reaction starting with D-fructose, using the values of Ky and Ny already obtained. Again, there were several combinations of Kx and Nx which were able to be used equally well to fit the experimental data and applied the same values of Kh and Kf obtained from first step. When Ky and Ny were fixed at 1.7, only for Nx = 1.3, Kx had an uniform constant value of 2.1 for all data sets. Kx = 2.1 and Nx = 1.3 were picked up. Therefore,

$$d(F)/dt = -Kf*(F)$$

$$d(X)/dt = Kf*(F)-K1*(X)-K2*(X)^{1.3}$$

$$d(HMF)/dt = K1*(X)-Kh*(HMF)$$

$$d(Y)/dt = Kh*(HMF)-K3*(Y)-K4*(Y)^{1.7}$$

$$d(LA)/dt = K3*(Y)$$

$$2.1 = Kx = Kf^{-0.3} * K1^{1.3} / K2$$

$$1.7 = Ky = Kh^{-0.7} * K3^{1.7} / K4$$

(B). Heterogeneous Model

The reaction scheme : F ---------> HMF

The rate depends,inside the ion exchanger, on diffusion and adsorption phenomena.

Diffusion: $Na = Kg * [(Fo) - (Fi)]$ ----------(1)

Na : molar flux of fructose

(Fo) : concentration of fructose inside catalyst

(Fi) : concentration of fructose outside catalyst

Kg : diffusivity

Adsorption and Surface Reaction: for rate-controlling concept

$$Fi \underset{K2}{\overset{K1}{<=====>}} X \qquad r.d.s. \qquad Ri = K1*(Fi) - K2*(X) \quad ---(2)$$

$$X + S <=====> XS \qquad K3 = (XS)/(X)/(S) \quad -----(3)$$

$$XS <======> HMFS \qquad K4 = (HMFS)/(XS) \quad ----(4)$$

$$HMFS <======> HMF + S \qquad K5 = (HMF)*(S)/(HMFS) \quad --(5)$$

$(X) = (HMF)/[K3*K4*K5]$

S: active sites of catalysts

X, XS, and HMFS : intermediates

HMF : 5-hydroxymethyl-2-furaldehyde

Ro : the global rate of fructose converted

For steady state: Na = Ri = Ro ;

$$Na = Kg * [(Fo)-(Fi)] = Ri = K1*(Fi) - K2*(X)$$

$$Fi = Kg/[K1+Kg]*(Fo) + K2/[K1+Kg]/[K3*K4*K5]*(HMF)$$

$$Ro = Na = Kg*[(Fo) - (Fi)]$$

$$= \{ Kg/[Kg+K1] \} * \{ K1*(Fo) - K2/[K3*K4*K5]*(HMF) \}$$

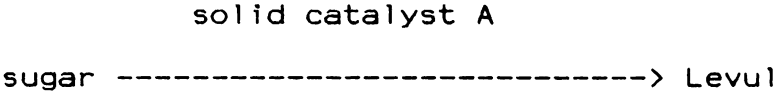
It is in a good agreement with the Nakamura equation :

$$R = d(HMF)/dt = -d(F)/dt = K * [(Fo) - (HMF)]$$

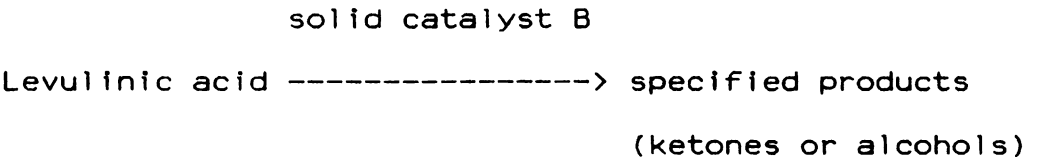
OBJECTIVES AND RESEARCH PLAN

The long term goal of this research is to develop a continuous process for the catalytic conversion of sugars to chemicals such as ketones or alcohols by using a solid catalyst. This process would be an alternative to fermentation of sugars. The advantages of our concept relative to fermentation are: (1) high carbon conversion (2) short reaction time (3) no dilution required (4) ease of catalyst separation and recovery and (5) high feasibility for the continuous process. In this new process, there are two important reaction schemes: (1) catalytic dehydration of sugars into levulinic acid, and (2) catalytic conversion of levulinic acid into alcohols or ketones. These reaction schemes are illustrated as follows:

Reaction scheme 1: Dehydration:



Reaction scheme 2: Decarboxylation / Hydrogenation:



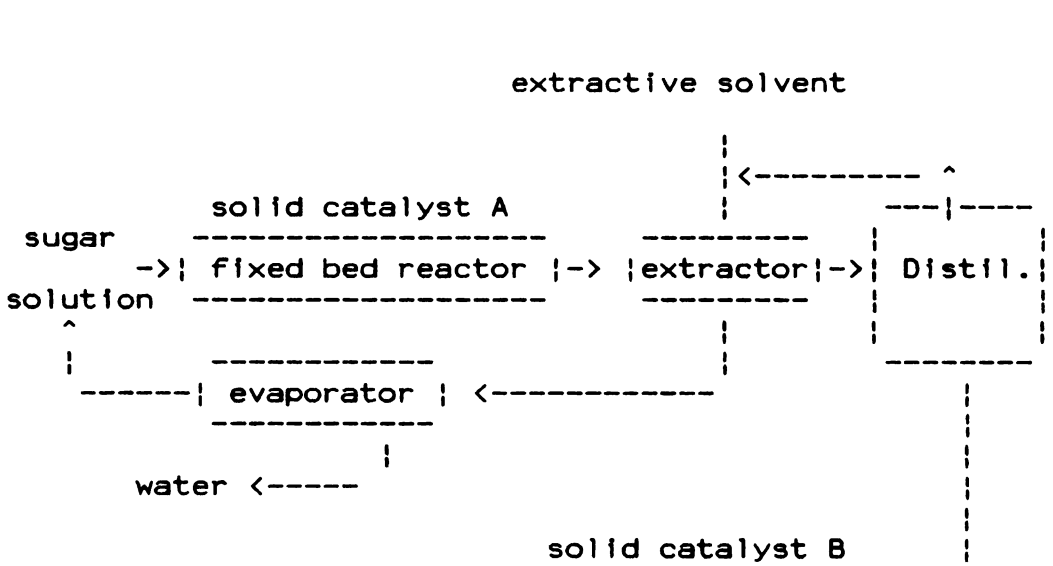


Figure 1. Schematic diagram of research process

The immediate goal is to explore the dehydration of sugars into levulinic acid using solid acid catalysts. This work is significant because previous studies (acid-catalyzed dehydration of sugars) have not produced the high yield and high selectivity of levulinic acid. The first-stage research is: (a) to design and develop specifications of solid acidic catalysts for preliminary experiments, and (b) to set up a small-scale batch experimental facility to conduct preliminary sugar dehydration over solid acid catalysts.

Two laboratory studies are conducted:

Study 1: to determine if one step catalytic dehydration of sugars to gas phase hydrocarbons is possible by using solid acids.

sugar: aqueous sucrose solution
solid acids: NaX, ZSM-5, and 12-Tungstosilicic acid

Study 2: to determine the nature and yield of the dehydration products in the liquid phase by using solid acid.

sugar: fructose
solid acids: LZY zeolite and 12-Tungstosilicic acid

EXPERIMENT

STUDY 1:

I. DESIGN OF THE APPARATUS

The reactor was a 500ml three-neck flask. One of its necks was connected by a distilling adapter which was extended to a 400 ml Liebieg condenser. The other necks were connected by reducing adapters which were connected by flow adapters. One of these two was extended to a nitrogen gas cylinder. The other was reserved to connect a manometer gauge to detect the reaction pressure. When the reaction occured, the vapor products would pass by a vaccum-type distillation adapter and go through the condenser to a 50 ml flask liquid collector. The condensable vapor would be condensed in the liquid collector. The uncondensable gas would be pushed into a 500 ml gas-collected flask by draining water out. The heat source was a Thermolyne Hot Plate. The temperature was measured by a -10 ^{0}C to 260 ^{0}C thermometer. A schematic diagram of the apparatus is shown in Fig 2.

A. nitrogen cylinder
B. thermometer
C. 500 ml three-neck flask
D. hot plate
E. condenser
F. liquid collector
G. gas collector
H. suction pump
J. water vessel
K. water vessel

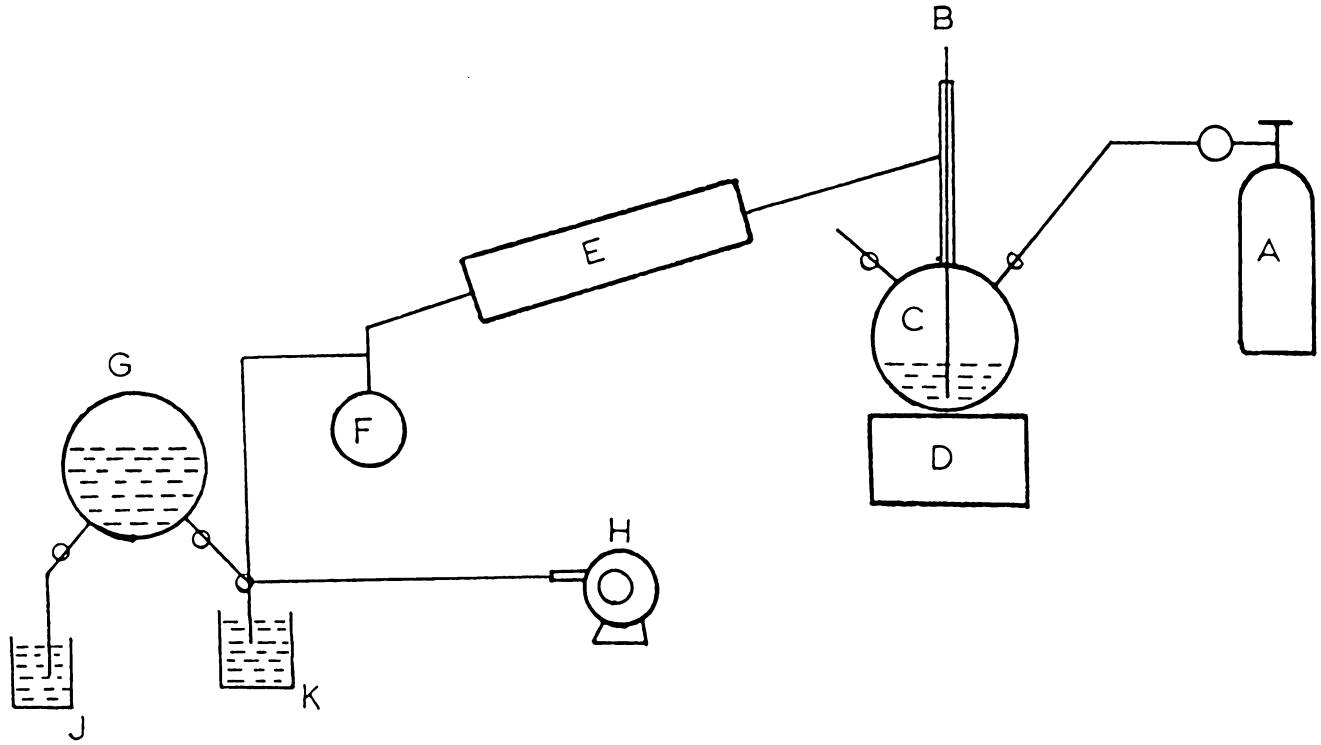


Figure 2. Schematic diagram of experimental apparatus for study 1

II. MATERIAL PREPARATION

A. Catalyst Preparation:

Three types of strong acid catalysts were used:

(1) Heteropoly acid: $H_4[SiW_{12}O_{40}]\ 7H_2O$

(2) Zeolite: ZSM-5 and NaX

(3) Inorganic acid: H_2SO_4

The 12-Tungstosilicic acid was prepared by the following procedures (Jolly, Willaiam L.: 1970):

$$12\ WO_4^{-2} + SiO_3^{-2} + 26\ H^{+} \longrightarrow H_4[SiW_{12}O_{40}]\ 7H_2O + 4\ H_2O$$

1. dissolve 50g sodium tungstate(+6) 2-hydrate in 100 ml H_2O
2. add 2.7 ml sodium silcate solution (40 ^{0}Be')
3. briskly stir and heat at boiling while adding 30 ml concentrated HCl drop by drop
4. cool, filte, and add 20 ml concentrated HCl
5. shake the solution with 35 ml diethyl ether (If no three phase, add more little ether.)
6. collect the bottom layer and add 12 ml concentrated HCl and 38 ml H_2O with 10 ml ether.
7. shake and collect the bottom phase into dish and stand in a drafty hood for two days.
8. dry the remaining crystal at 70 ^{0}C for 2 hrs.
9. yield 32g crystal avoiding contacting with anything metallic.

The zeolites can be purchased from Mobil Company.

B. Reagent Preparation:

The amounts of reagent for each run were weighed on a Cahn eletrobalance and described as follows:

RUN #001: 20.0 g sucrose dissolved in 30.0 ml water added with 0.5 g NaX zeolite, PH = 8.0

RUN #002: 20.0 g sucrose dissolved in 30.0 ml water added with 0.5 g ZSM-5, PH = 7.0

RUN #003: 20.0 g sucrose dissolved in 30.0 ml, 0.05 M H_2SO_4, PH = 1.0

RUN #004: 20.0 g sucrose dissolved in 30.0 ml water added with 3 ml, 98.8% H_2SO_4 and 1.0 g NaX zeolite, PH = 4.0

RUN #005: 20.0 g sucrose dissolved in 30.0 ml, 0.015 M H_2SO_4 added with 0.5 g $H_4[SiW_{12}O_{40}]7H_2O$, PH = 1.3

III. EXPERIMENTAL PROCEDURE

The aqueous sucrose solution was prepared by the specified acidic medium, and the PH value of the aqueous solution was indicated by PH paper, before the experiment run. After the apparatus was set up, water pump was used to suck the air out for 5 min. An inert atmosphere (99.9% nitrogen gas) was maintained throughout the reaction. The reactor was heated from room temperature to 95^{0}C. The gas was collected in 500 ml gas-collect flask. Analyses for gaseous products were carried out using Varian-3700 Gas Chromatography. All reactions had the change values of PH which were indicated by PH paper, but some turned clear liquid to yellow.

IV. ANALYTIC EQUIPMENT AND TECHNIQUES

Varian 3700 Gas Chromatography via
Hewlett Packard 3390A Reporting Integrator

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purpose: qualitative and quantitative determination for the gas products of the sugar dehydration.

G.C. specifications:

column: amorphous silica gel, 4m x 1/4 in

carrier gas: helium, 30 c.c./min

inject temperature: 110 ^{0}C

detector temperature: 110 ^{0}C

oven temperature: 41 ^{0}C (isothermal)

detector type: Thermal Conductivity Detector

gas volume injection: 0.5 ml

attenuation: 4

Operating Procedure:

1. turn on the helium gas.
2. adjust flowrate at 30 c.c./min for both the left (reference) and right column.
3. turn on the main power, and wait for instrument warm-up and stabilty for 1 hr to 2 hr
4. set the MODE to TCD
5. turn on the detector power
6. adjust detector output level for zeroing baseline
7. inject the 0.5 ml gas sample.

The standard calibration for N_2 and CO_2 is shown in Figure 4. One of the experimental results in study 1, Run #001, is shown in Figure 5.

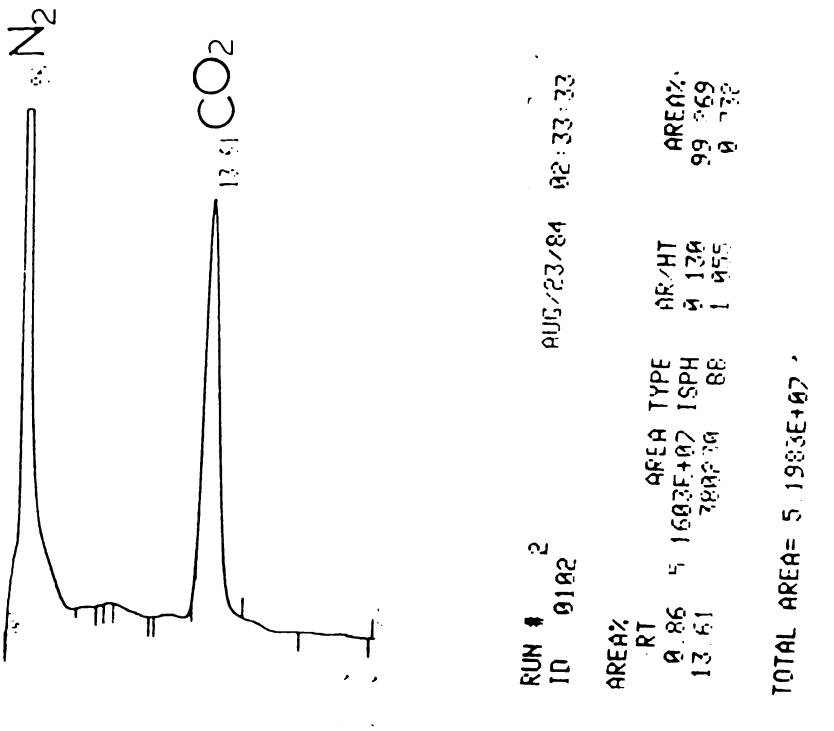


Figure 4. Gas chromatography of standard N_2 and CO_2

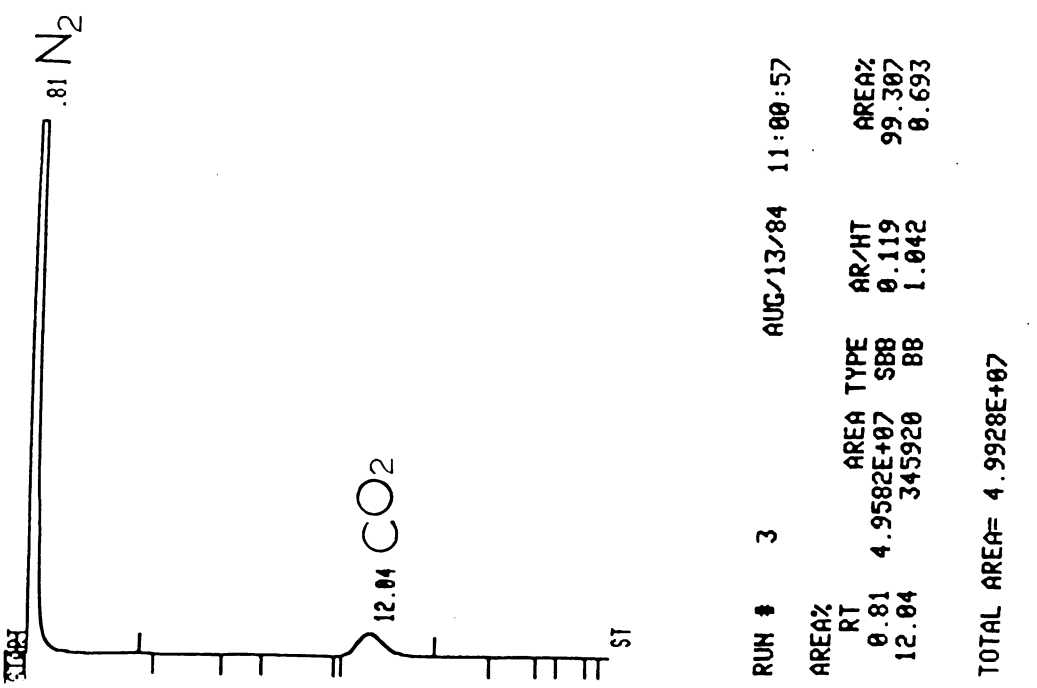


Figure 5. Gas chromatography of Run # 001

V. EXPERIMENTAL RESULTS

Table 4: A summary of results for study 1

run no.	solvent (gram)	catal. (gram)	temp. (^{0}C)	react. time	PH	gas prod. vol,yield	liquid(PH) color
#001	water 30.0	NaX 0.5	95	0.5hr	8.0	CO_2 3.4ml yield=0.24%	PH=6.0 pale yellow
#002	water 30.0	ZSM-5 0.5	95	0.5hr	7.0	CO_2 3.0ml yield=0.21%	PH=6.0 clear
#003	water (30.0g, 0.05M)	H_2SO_4	95	0.5hr	1.0	CO_2 3.5ml yield=0.25%	PH=1.5 yellow
#004	water 30.0	NaX 1.0 H_2SO_4 (98.8%, 3g)	95	0.5hr	4.0	CO_2 4.3ml yield=0.30%	PH=4.0 yellow
#005	water (30.0g, 0.015M)	H_2SO_4 HPA 0.5 g	95	0.5hr	1.3	CO_2 4.0ml yield=0.28%	PH=1.6 brown

note: 20.0 gram sucrose is used as sugar for each run.
HPA: heteropoly acid, $H_4[SiW_{12}O_{40}]7H_2O$
NaX: X type zeolite (Faujasite), $Na_{56}[(AlO_2)_{56}(SiO_2)_{106}]\ 264H_2O$
ZSM-5: zeolite, n < 27, typically about 3
$Na_nAl_nSi_{96-n}O\ 16H_2O$

STUDY 2:

I. DESIGN OF THE APPARATUS

The batch reactor was a 200 mm long glass test tube with an inner diameter of 25 mm. The reactor was dipped into a light paraffin oil batch which was a 4000 ml beaker equipped with a 0 ^{0}C to 150 ^{0}C thermostat. The reactor was plugged by a #3 rubber stopper which contained with two 3mm-inner diameter tubes for nitrogen purging. The inlet tube was connected by a rubber tube to a nitrogen cylinder tank, while the outlet tube was extended to a water pump and an oil vessel. A schematic diagram of the apparatus is shown in Fig 3.

A. nitrogen cylinder
B. thermostat
C. oil bath
D. 20.0 cm x 2.5 cm test tube
E. suction pump
F. water vessel

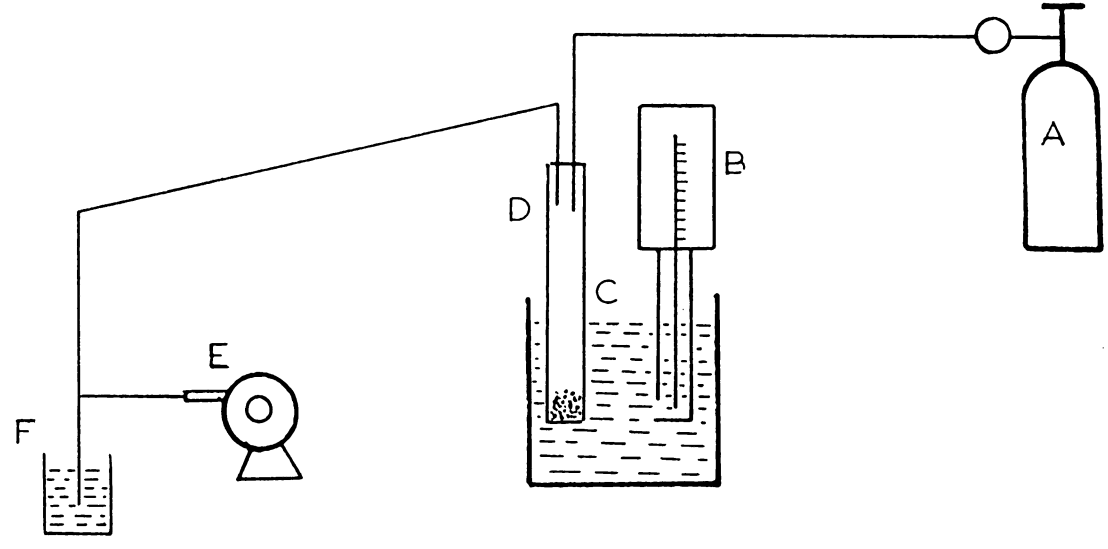


Figure 3. Schematic diagram of experimental apparatus for study 2

II. MATERIAL PREPARATION

A. Catalyst Preparation:

Two types of strong solid acid catalysts were used:

(1) Heteropoly acid: HPA; $H_4[SiW_{12}O_{40}]\ 7H_2O$

(2) Zeolite: LZY; Linde Zeolite Y type (Faujasite),

$$Me_{s/n}[(AlO_2)_t(SiO_2)_z]mH_2O \text{ with } z/t > 2$$

The preparation of catalysts was the same as study 1.

B. Reagent Preparation:

The amounts of reagent for each run were weighed on a Cahn eletrobalance and described as follows:

RUN #006, RUN #007, and RUN #008: 1.000 g fructose

RUN #009: 1.000 g fructose added with 1.000 g HPA

RUN #010: 1.000 g fructose dissolved in 2.50 ml water added with

RUN #011, RUN #012, RUN #013, RUN #014, RUN #015, RUN #016, and

RUN #017: 1.000 g fructose added with 1.000 g LZY zeolite

LZY zeolite

III. EXPERIMENTAL PROCEDURE

Fructose, LZY zeolite, and heteropoly acid were weighed on a Cahn eletrobalance. To purge air out and to maintain an inert atmosphere were the same procedures as the Study 1 did. A steady state temperature was obtained in the oil bath, before the apparatus was set up. The reaction proceeded for a desired period of time. After the end of reaction, the solid residues along with the catalyst were added with 5.0 ml deionized, distillated water and briskly stirred until the solid residues were completely dissolved to be a dirty solution. A clean solution was obtained by filtrating the dirty solution out of the solid catalyst. A small amounts of clean solution were diluted to a suitable concentration for each HPLC operating requirement.

The determination of fructose in the aqueous solution was made by HPLC with the LDC 1107 refractometer detector. The determination of both HMF and levulinic acid in the aqueous solution was made by HPLC with the SF 770 UV detector at 220 nm wavelength, which was chosen from the UV spectrum on Perkin-Elmer Lambda 3 UV/VIS spectophotometer for the standard solution of fructose, HMF, and LA. The chromatogram and chromatographic data were automatically acquired and analized on IBM-9000 microcomputer system.

IV. ANALYTIC EQUIPMENT AND TECHNIQUES

A. Perkin-Elmer Lambda 3 Spectrophotometer via Perkin-Elmer R-100A Chart Recorder

****

purpose: determination of bestabsorbance wavelength for fructose, LA and HMF

principle: double-beam, UV-Visible spectrophotometer with a microcomputer control, which programs changes Tungsten-bromine lamp for visible light and Deuterium lamp for UV light.

detector: side-window photomultiplier

operating procedure:

1. turn on the main power and turn on the record power
2. turn on the UV or VIS power
3. allow at least 30 minutes for instrument warm-up
4. select MODE button to select reading mode (usuallly ABS, ABS means Absorbance.)
   select the desired SCAN SPEED (usually 60 nm/min)
5. press SAFE MEM until a " C " appears in the display
6. place solvent blank in both the reference and the sample cuvettes
7. press RUN for correction of difference in cuvettes
8. choose the wavelength limit

a. press " Lambda LIM " button, and enter the maximum wavelength limit you want

b. press " Lambda LIM " button, and enter the minimum wavelength limit you want

9. choose the full scale limit

a. press " ORD LIM " button, and enter the maximum ordinate limit you want

b. press " ORD LIM " button, and enter the minimum ordinate limit you want

10. press " AUTO ZERO " button

11. select the chart speed (usually 60 mm/min)

12. adjust the pen position by pressing " PEN LIFT "

a. LEFT or RIGHT

press " L/R " for coarse adjustment

press " ZERO ADJUST " button and Thumbwheel for fine adjustment

b. FORWARD or BACKWARD

turn the thumbwheel for adjustment

13. place the sample in " SAMPLE " cuvette

14. press " RUN "

Routine operation:

1. clean the sample cuvette and place the another sample into it

2. press " RUN "

Shut-down

1. clean the cuvettes and put them back

2. turn off the UV or VIS light

3. turn off the Record power

4. turn off the main power

B. HPLC on BIORAD 42A and 87 P in series via
LDC Model 1107 differential refractometer

****

detector principle: monitoring the quantitative difference in the refractive index between two liquids

HPLC specifications:

column: Aminex HPX-42A and HPX-87P Heavy Metal in series, 300 x 7.8 mm for each

mobil phase: deionized, distillated water (HPLC water)

flowrate: 0.6 ml/min

temperature: 85 ^{0}C (isothermal)

pressure: 450 to 600 psi (less than 1000 psi, sensitive to temperature of column)

inject volume: 30 ul to 50 ul

suitable standard quantities: less than 0.5 mg

Detector specifications:

attenuation: 2.0

trasmittance: 0.5

Operating Procedure:

1. fill the eluant reservoir with degassed HPLC water

2. check the Haake water level

3. turn on the Haake column jacket circulator

4. turn on the Haake column jacket heater
5. check whether a steady state temperature is 85 ^{0}C after 30 minutes
6. switch on the refractometer and allow at least 1 hr for instrument warm-up
7. set the Refractometer range at 2 and the transmittance to 0.5 via the fine adjustment.
8. turn on the HPLC pump (already set at 23 flowrate about 0.6 ml/min)
9. allow 30 min to 1 hr to achieve stable baseline

Routine Operation:

1. open the data file on channel #2 with the method file: SUGARCOL for CAP of IBM 9000 system
2. neutralize the sample to be PH = 5.0 - 7.2
3. weigh the equal volume of 1.0 mg/ml Inositol as the internal standard
4. flush the sample loop with 50 ul HPLC water
5. inject 30 - 50 ul sample
6. pull the manual inject bar from right to left
7. switch channel #2 from ready to run
8. End of Run, pull the manual inject bar from left to right

Shut-down:

1. flush the sample loop with 50 ul HPLC water
2. turn off the HPLC pump, the Haake circculator, and the Haake Heater

3. switch off the refractometer

The standard calibration for fructose and inositol is shown in Figure 6. The standard calibration for glucose and inositol is shown in Figure 7. The standard calibration for sucrose and inositol is shown in Figure 8. One of experimental serults, Run #017, is shown in Figure 9.

Note

Typical sugar retention time on this HPLC is shown as follows:

trimer ---------- 18 min

dimer ---------- 21 min

sucrose ---------- 23 min

glucose --------- 25 min

xylose ---------- 27 min

mannose ---------- 29 min

fructose --------- 30 min

inositol --------- 36 min

C. HPLC Spectra-Physics SP 8000 via
Schoeffel SF 770 Spectroflow Monitor

****

purpose: qualitative and quantitative determination of levulinic acid, HMF

principles: SP-8000 is microprocessor controlled high performance liquid phase chromatograph, which programs runs of parameter sets, temperature and mobil phase program.

HPLC specifications:

column: Zorbax ODS (Octadecyl Sulfate)

mobil phase: A: 0.13 % Heptafluoro-Butyric acid (HFBA)

B: 0.13 % HFBA + 80 % (v/v) acetonitrile

programming:

Time	A %	B %
0.0	100.0	0.0
15.0	70.0	30.0
20.0	70.0	30.0
25.0	100.0	0.0

temperature: room temperature (isothermal)

pressure: above 1000 psi

(retention time sensitive to press.)

flowrate: 0.5 ml/min

inject volume: 30 to 50 ul

suitable standard quantity: less than 0.5 mg

UV detector specifications:

absorbancy: 0.4

wavelength: 220 nm

Operating Procedure:

start-up:

1. check solvent A, B level (reservoir A, B should be at least half full)
2. connect channel #4 box to IBM 9000 system
3. turn on the main power
4. turn on the UV/VIS detector power and allow 30 sec in START position, before switching in ON position
5. turn on the helium gas for degass solvents at 2 - 5 psi

6. sparge briskly the solvent for 5 min, then adjust to less than 10.0 ml/min
7. set UV/VIS absorbancy at 0.4
8. set UV/VIS wavelength at 220 nm
9. type M: and press RETURN (create the mobil phase no. 1)
10. type AB and press RETURN (select solvent A and B)
11. type 100 and press RETURN
12. type 15 and press RETURN
13. type 70 and press RETURN
14. type 20 and press RETURN
15. type 70 and press RETURN
16. type 25 and press RETURN
17. type 100 and press RETURN
18. type EX and press RETURN
19. type MI1 and press RETURN
20. type F:0.5 and press RETURN
21. type QG and press RETURN
22. waiting until the constant flowrate and ready light on
23. type GB and press RETURN to check the baseline
    type GX and press RETURN to end the baseline

Routine Operation:

24. open the data file on channel #4 with the method: SUGAR for CAP of IBM 9000 system
25 filte the 70 ul sample solution by micropore filter (0.45 um)
26. type "SO" and press RETURN
27. flush the sample loop with HFBA

28. type "SK" and press RETURN
29. type "SO" and press RETURN
30. inject 30 to 50 ul sample
31. type "SK" and press RETURN
32. waiting for "pump marker " light to come on, then manually lower injection handle
33. end of run , type EX,and press RETURN
34. pull the injection handle bar back after hearing two clicks

Shut-down

35. type "SO ", and press RETURN
36. flush the sample loop with HPLC water
37. type "SK", and press RETURN
38. type F:0.0, and press RETURN
39. Turn off the main power and the detector power
40. Turn off the helium gas

The standard calibration for levulinic acid and HMF is shown in Figure 10. One of experimental results, Run #017, is shown in Figure 11.

D. IBM Instrument's Chromatography Application Program on the microcomputer 9000 system

****

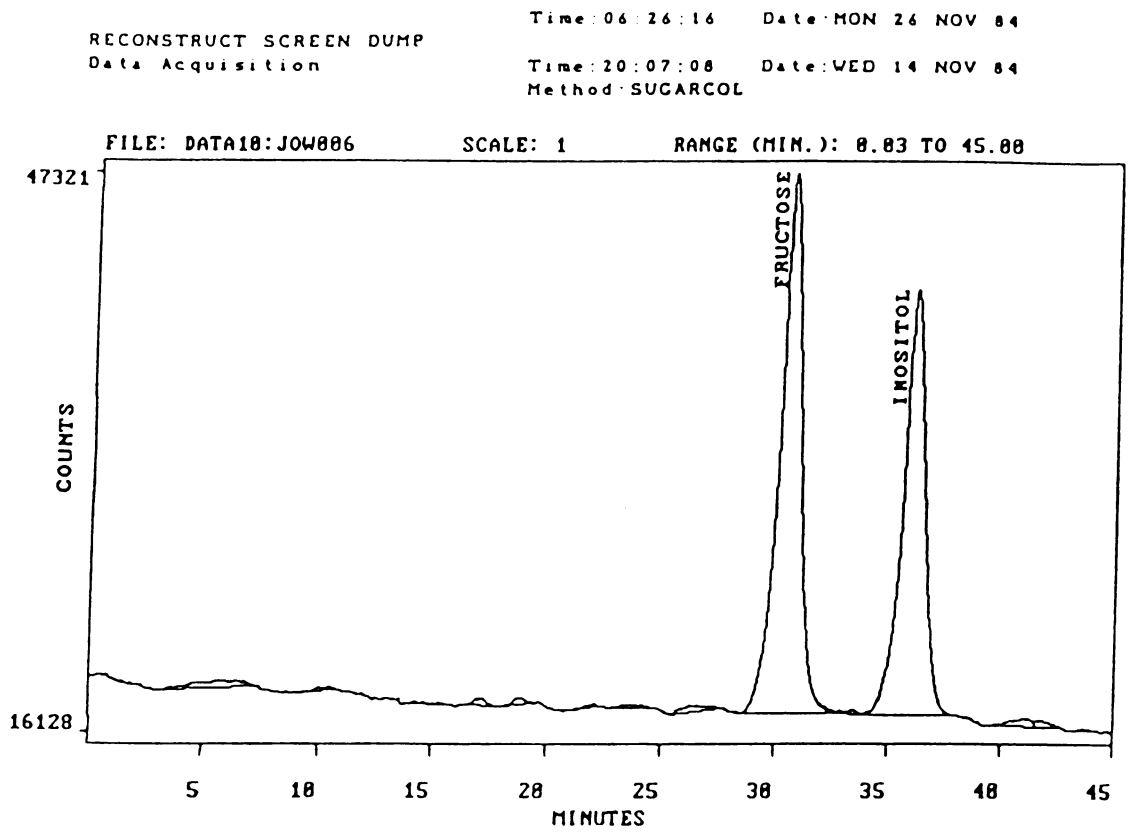
purpose: acquiring, storing, and analyzing chromatographic data automatically

Operating Procedure:

1. turn on the Disk Drive Power
2. insert Operating System Diskette, press Ctrl/Alt & Del
3. insert CAP diskette, type CAPMC 1 and press RETURN
4. insert the Data File diskette and press RETURN (into Chromatography mode)
5. press softkey EDIT (into edit channel)
6. create a method file

   for noncalibration, fill the pages 1, 2, 3, 4, and 7 out

   for calibration, fill the pages 5, 6 and Conc. Table out
7. press pad on the screen EXIT
8. press softkey READY
9. choose the channel number
10. fill the data file name and the specifications out
11. press pad on the screen EXIT
12. the channel will be automatically ready to acquire and storethe chromatographic data



Inverse Response Factor: Fructose 1.92 x E-7
(mg/area) Inositol 1.62 x E-7

Figure 6. Chromatography of standard Fructose and Inositol

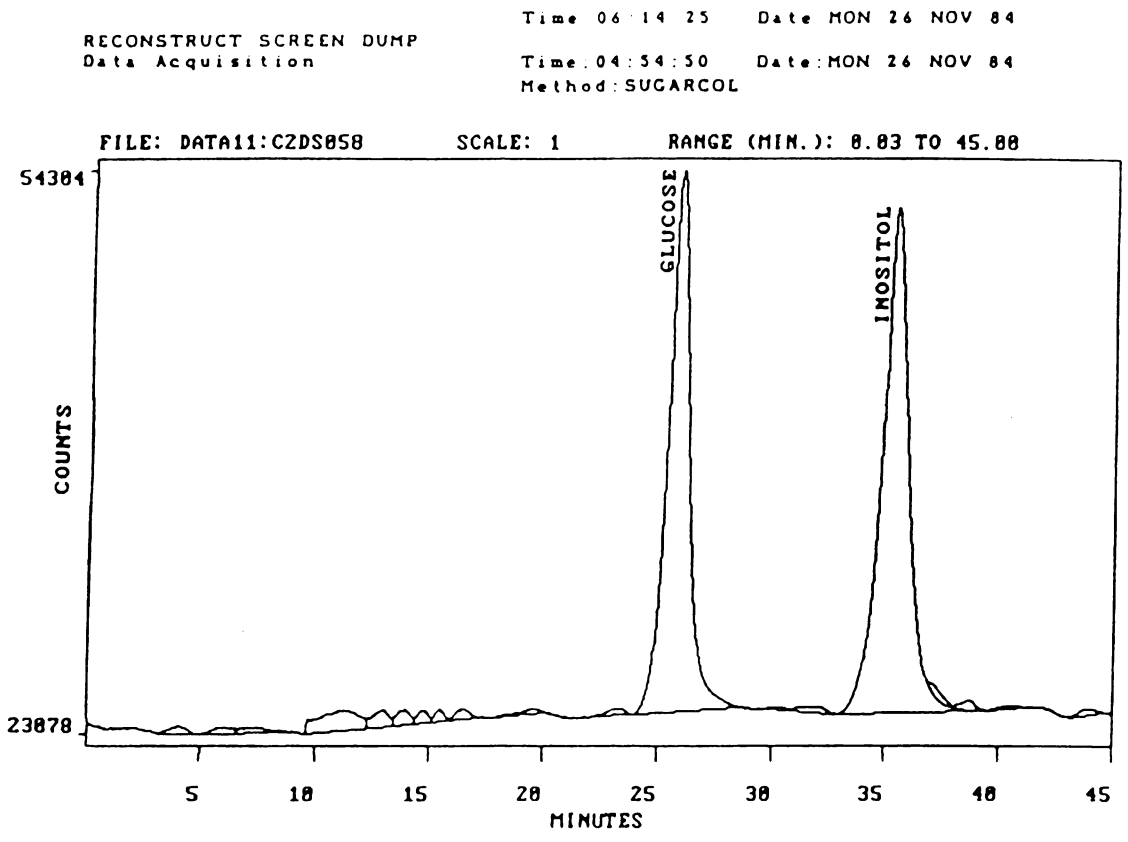


Figure 7. Chromatography of standard Glucose and Inositol

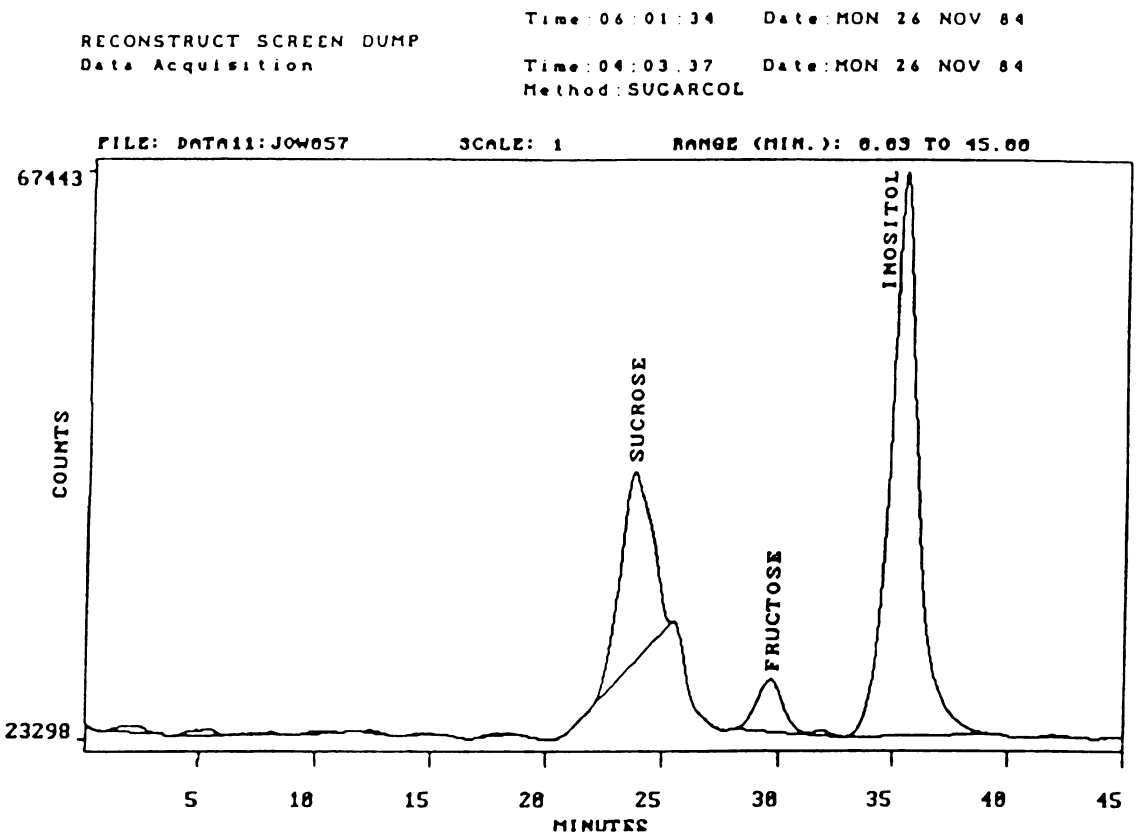


Figure 8. Chromatography of standard Sucrose and Inositol

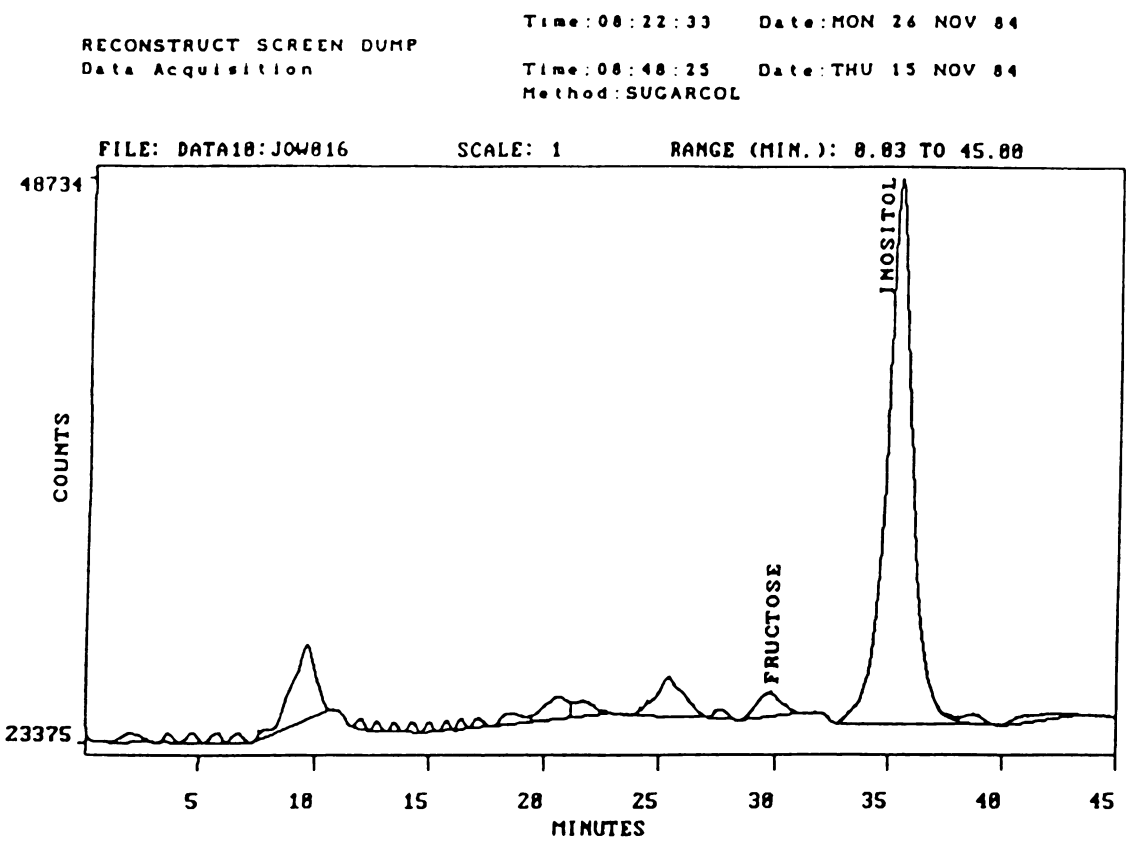


Figure 9. Chromatography of Run #017

Table 5. Area percent report from IBM 9000 system

Run #017

```
Channel #.....REINT     Time:06:47:43    Date:MON 26 NOV 84
Sample name.....FRUCTOSE+LZY,140°C,15hr
Data file.....DATA10:JOW016
Method name.....SUGARCOL

Author.....JINDER JOW
Instrument.....HPLC SUGAR REFRACTOMETER
Column.....BIORAD 42A and 87F IN SERIES
Notes.....INOSITOL STD;INJ: 50ul;300-500ug;PH=5-7
          INITIAL FRUCTOSE:.4mg; INOSITOL:..294mg

Run time.....45.00 min.      Delay time...0.00 min.
Acq. time .....08:48:25      Acq. date....THU 15 NOV 84
Start PW.....20.00 sec.      End PW.....20.00 sec.
Slope sens.....3.00 uv/sec.

Area reject....50000
# peaks found..23
```

AREA PERCENT REPORT

Peak	R.T.(min)	R/S	Peak name	Area %	Area	Peak Ht.	BL
1	9.614		X1 (9.6 min)	10.058	246888	251	BB
2	20.611		X2 (20.6 min)	2.955	72530	577	VV
3	25.393		X3 (GLUCOSE)	6.174	151537	2015	BV
4	29.796		FRUCTOSE	3.418	83889	646	BB
5	35.258		INOSITOL	77.395	1899698	24520	BE
TOTALS				100.000	2454542		

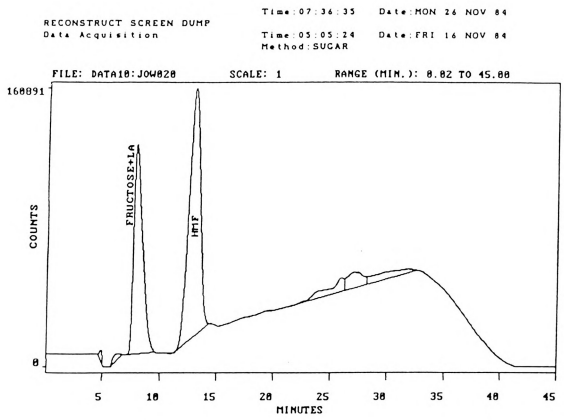


Figure 10. Chromatography of standard Fructose, LA, and HMF

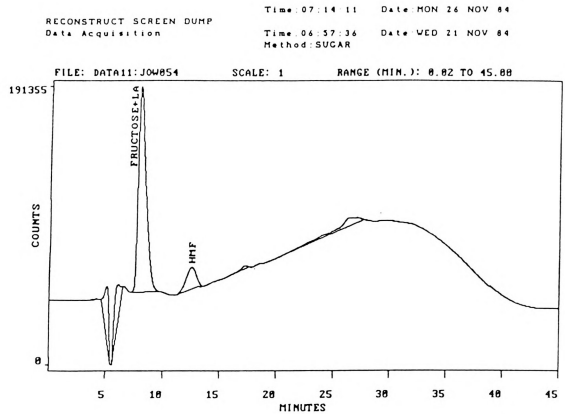


Figure 11. Chromatography of Run #017

V. EXPERIMENTAL RESULTS

Table 6: A summary of results for study 2

run no	reaction condition: cata.	solvent	temp. (^{0}C)	time (hr)	F conv.	component distribution: F %	LA %	HMF %	X %
#006	none	none	95	1.0	0.0	100.0	0.0	0.0	0.0
#007	none	none	120	1.0	25.4	74.6	5.3	0.0	20.1
#008	none	none	140	1.0	32.2	67.8	32.0	0.0	0.2
#009	HPA	none	95	1.0	60.9	39.1	47.0	0.0	13.9
#010	LZY	water	95	1.0	9.9	90.1	5.3	0.0	4.6
#011	LZY	none	95	1.0	36.3	63.7	35.4	0.0	0.9
#012	LZY	none	120	1.0	42.2	57.8	39.2	0.0	3.0
#013	LZY	none	140	0.5	47.3	52.7	16.8	0.0	30.5
#014	LZY	none	140	1.0	55.3	44.7	25.1	0.0	30.2
#015	LZY	none	140	2.0	70.3	29.7	33.5	1.2	35.6
#016	LZY	none	140	5.0	87.4	12.6	66.8	2.0	18.6
#017	LZY	none	140	15.0	96.0	4.0	43.2	4.4	48.4

Note: F conv. is the conversion percentage of Fructose.
F % is the component percentage of Fructose.
LA % is the yield percentage of Levulinic acid.
HMF % is the yield percentage of HMF
X % is the yield percentage of unidentified products.
All percentages are based on the initial fructose of 1.0 gram.
The ratio of catalyst to fructose is 1.0.
Water as a solvent is added 2.5 ml in run #010.
HPA: heteropoly acid, $H_4[SiW_{12}O_{40}]\ 7H_2O$
LZY: Linde Zeolite Y type (Faujasite),
$Me_{s/n}[(AlO_2)_t(SiO_2)_z]\ mH_2O$ with $z/t > 2$

Table 7: Reaction time effect for study 2 at 140 C with LZY

run no	catalyst	solvent	temp. (°C)	time (hr)	F %	LA %	HMF %
#013	LZY	none	140	0.5	47.3	16.8	0.0
#014	LZY	none	140	1.0	55.3	25.1	0.0
#015	LZY	none	140	2.0	70.3	33.5	1.2
#016	LZY	none	140	5.0	87.4	66.8	2.0
#017	LZY	none	140	15.0	96.0	43.2	4.4

Note: F % is the conversion percentage of Fructose.

LA % is the yield percentage of Levulinic acid.

HMF % is the yield percentage of 5-hydroxymethyl-2-furaldehyde.

The ratio of catalyst to fructose is 1.0.

All percentages are based on the initial fructose of 1.0 gram.

HPA: heteropoly acid

LZY: Linde Zeolite Y type (Faujasite),

Table 8: Temperature effect for study 2 for 1 hr with LZY

run no	catalyst	solvent	temp. (°C)	time (hr)	F %	LA %	HMF %
#011	LZY	none	95	1.0	36.3	35.4	0.0
#012	LZY	none	120	1.0	42.2	39.2	0.0
#014	LZY	none	140	1.0	55.3	25.1	0.0

Note: F % is the conversion percentage of Fructose.

LA % is the yield percentage of Levulinic acid.

HMF % is the yield percentage of 5-hydroxymethyl-2-furaldehyde.

The ratio of catalyst to fructose is 1.0.

All percentages are based on the initial fructose of 1.0 gram.

LZY: Linde Zeolite Y type (Faujasite),

Table 9: Temperature effect for study 2 for 1 hr without LZY

run no	catalyst	solvent	temp. (°C)	time (hr)	F %	LA %	HMF %
#006	none	none	95	1.0	0.0	0.0	0.0
#007	none	none	120	1.0	25.4	5.3	0.0
#008	none	none	140	1.0	32.2	32.0	0.0

Note: F % is the conversion percentage of Fructose.

LA % is the yield percentage of Levulinic acid.

HMF % is the yield percentage of 5-hydroxymethyl-2-furaldehyde.

The ratio of catalyst to fructose is 1.0.

All percentages are based on the initial fructose of 1.0 gram.

Table 10: Catalyst effect for study 2 for 1 hr at 95 °C

run no	catalyst	solvent	temp. (°C)	time (hr)	F %	LA %	HMF %
#006	none	none	95	1.0	0.0	0.0	0.0
#011	LZY	none	95	1.0	36.3	35.4	0.0
#009	HPA	none	95	1.0	60.9	47.0	0.0

Note: F % is the conversion percentage of Fructose.

LA % is the yield percentage of Levulinic acid.

HMF % is the yield percentage of 5-hydroxymethyl-2-furaldehyde.

The ratio of catalyst to fructose is 1.0.

All percentages are based on the initial fructose of 1.0 gram.

HPA: heteropoly acid

LZY: Linde Zeolite Y type (Faujasite)

Table 11: Water effect for study 2 for 1 hr at 95 °C with LZY

run no	catalyst	solvent	temp. (°C)	time (hr)	F %	LA %	HMF %
#010	LZY	water	95	1.0	9.9	5.3	0.0
#011	LZY	none	95	1.0	36.3	35.4	0.0

Note: F % is the conversion percentage of Fructose.

LA % is the yield percentage of Levulinic acid.

HMF % is the yield percentage of 5-hydroxymethyl-2-furaldehyde.

The ratio of catalyst to fructose is 1.0.

Water as a solvent is added 2.5 ml in run #010.

All percentages are based on the initial fructose of 1.0 gram.

LZY: Linde Zeolite Y type (Faujasite),

Table 12: Isomerization of fructose for study 2

reaction condition					yield percentage
run no	catalyst	solvent	temp. (°C)	time (hr)	Glucose (25.39 min) %
#006	none	none	95	1.0	0.0
#007	none	none	120	1.0	4.3
#008	none	none	140	1.0	4.8
#009	HPA	none	95	1.0	0.0
#010	LZY	water	95	1.0	9.8
#011	LZY	none	95	1.0	3.3
#012	LZY	none	120	1.0	8.3
#013	LZY	none	140	0.5	2.3
#014	LZY	none	140	1.0	11.3
#015	LZY	none	140	2.0	7.0
#016	LZY	none	140	5.0	6.8
#017	LZY	none	140	15.0	5.9

Note: The ratio of catalyst to fructose is 1.0.

Water as a solvent is added 2.5 ml in run #010.

All percentages are based on the initial fructose of 1.0 gram.

HPA: heteropoly acid

LZY: Linde Zeolite Y type (Faujasite)

Table 13: Mass balance of run #017 for different reject area

retention time (min)	(1) mg	%	(2) mg	%
LA	0.1732	43.3	0.1732	43.3
HMF	0.0176	4.4	0.0176	4.4
2.01	-----		0.003	0.8
3.63	-----		0.002	0.5
4.71	-----		0.002	0.5
5.76	-----		0.002	0.5
6.70	-----		0.002	0.5
9.61	0.038	9.5	0.038	9.5
11.98	-----		0.001	0.3
12.7	-----		0.001	0.3
13.4	-----		0.001	0.3
14.2	-----		0.002	0.5
14.96	-----		0.001	0.3
15.72	-----		0.001	0.3
16.72	-----		0.002	0.5
17.16	-----		0.002	0.5
18.4	-----		0.005	1.3
20.6	0.011	2.8	0.011	2.8
21.7	-----		0.007	1.8
glucose	0.023	5.8	0.023	5.8
fructose	0.016	4.0	0.016	4.0
38.7	-----		0.003	0.8
42.5	-----		0.006	1.5
total amount (mg)	0.279		0.324	
%	70 %		81 %	

Note:

Compounds except HMF and LA were determined by HPLC Refractometer by two different reject area: (1) reject area on HPLC with the refractometer was set 50,000 and(2) reject area on HPLC with the refractometer was set 5,000. HMF and LA in both (1) and (2) were determined by HPLC with the UV detector whose reject area was set 10,000. Total amounts of initial Fructose in these sample of run #017 are 0.4 mg.

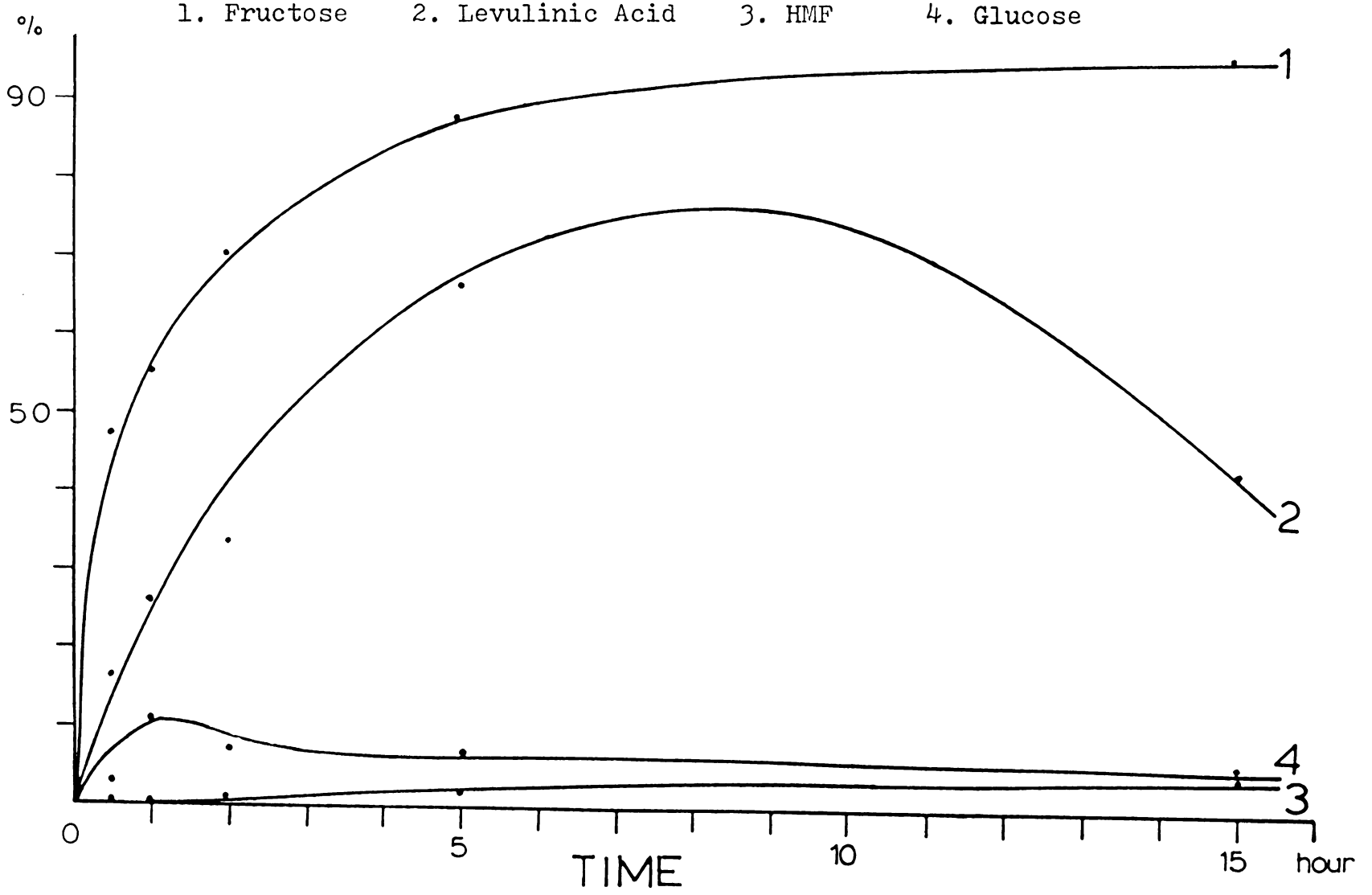


Figure 12. Conversion percentage of Fructose and Yield percentage of Levulinic Acid Glucose, and HMF vs reaction time at 140 C with LZY zeolite

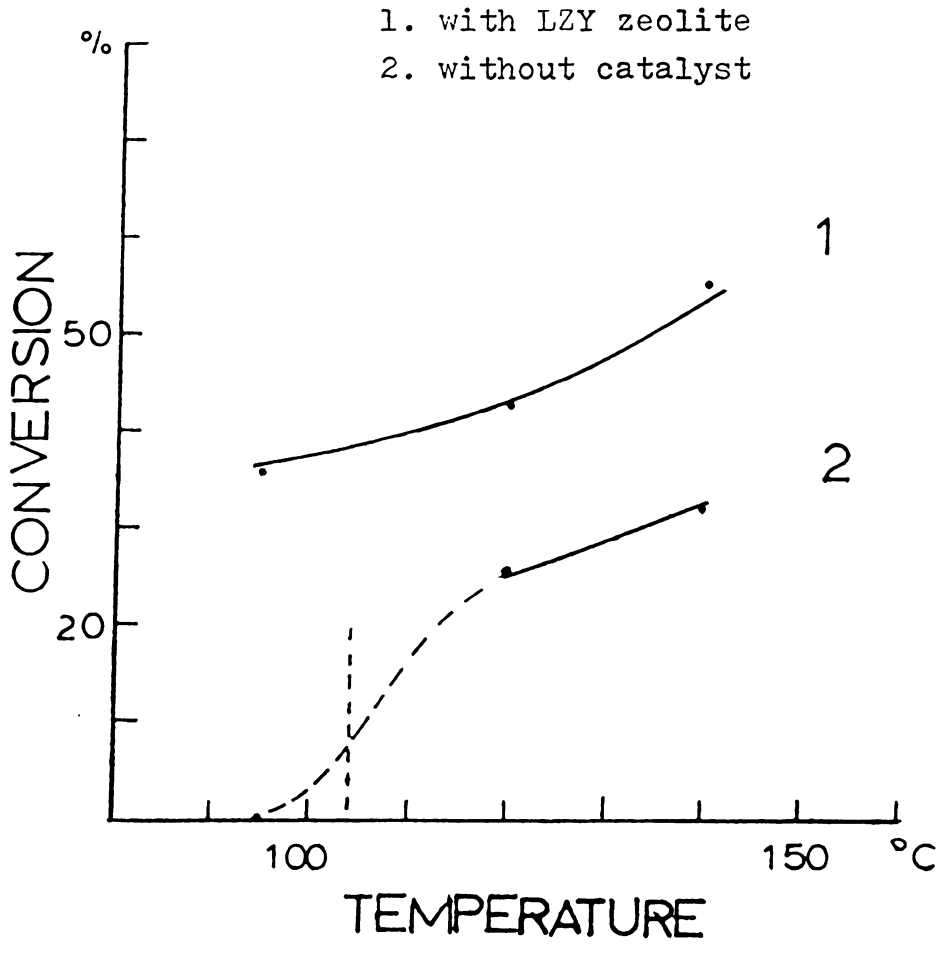


Figure 13. Conversion percentage of Fructose with and without LZY zeolite vs temperature for 1 hr reaction time

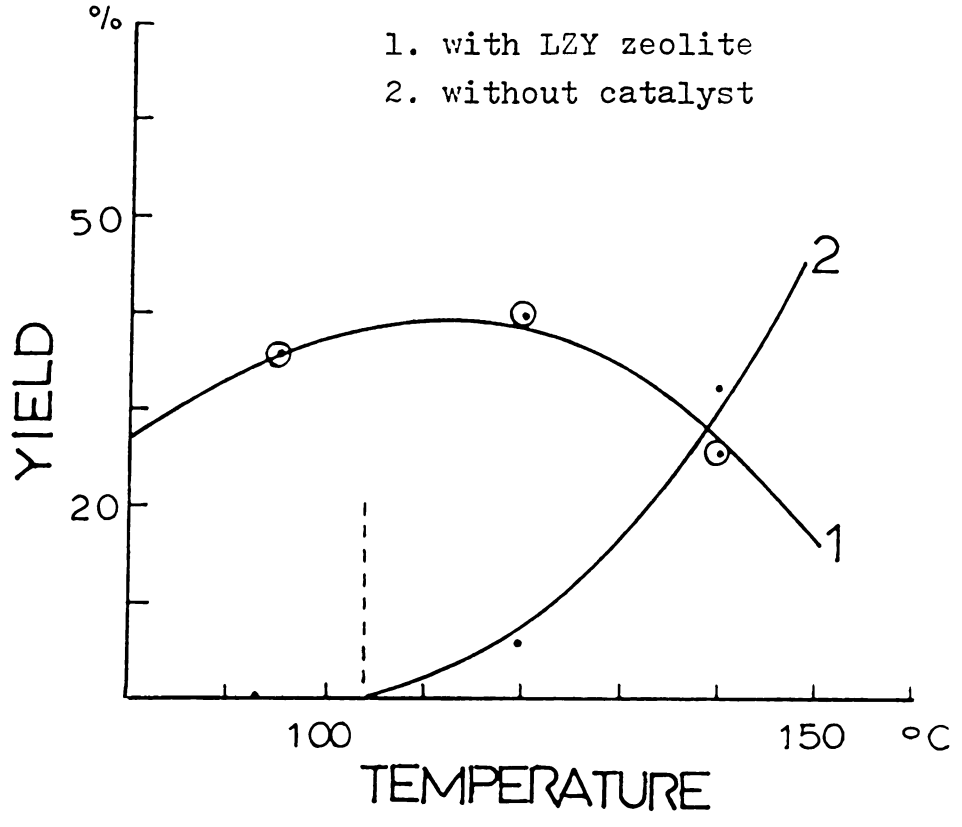


Figure 14. Yield percentage of Levulinic Acid with and without LZY zeolite vs temperature for 1 hr reaction time

DISCUSSION OF EXPERIMENTAL RESULTS

I. An evidence of the dehydration reaction of sugars over zeolites and heteropoly acids

For study 1, only carbon dioxide was obtained in the gas phase, even though we modified the acidic aqueous sucrose solution with a NaX zeolite for Run #004 or a heteropoly acid for Run #005. The experimental results in study 1 showed that the value of PH and the color of the aqueous sucrose solution were due to the decomposition of sucrose. From the literature reviews, it was observed that the solution of sugars heated under the acidic medium would produce a yellow, followed by a brown, and finally a black viscous product. A. M. Taher[35] had clearly reported that the yellow color was due to the formation of gamma-unsaturated, dicarbonyl compounds for the dehydration of sugars (such as HMF for hexose and 2-Furaldehyde for pentose). It could be explained that the clear aqueous sucrose solution turned out to be yellow and viscous. It might be explained that a change in PH was due to the formation of soluble acidic products (such as levulinic acid and formic acid).

II. Parameters of the dehydration of fructose over solid acid catalysts

The parameters in the dehydration of sugars are:(1) characteristics of catalysts, (2) types of sugars, (3) the ratio of catalyst to sugar, (4) temperature, (5) pressure, (6) reaction time, (7) solvent effect, and (8) an air or an inert atmosphere. This experiment was designed and run in twelve different conditions to explore the behavior of the following parameters: catalyst effect, temperature effect, reaction effect, and water as a solvent. The other reaction parameters were fixed: an inert (nitrogen gas) atmosphere, the ratio of catalyst to sugar = 1, atmospheric pressure, and fructose as the sugar.

1. Temperature effect and catalyst effect:

In Figure 13, it was shown that the conversion of frucose with LZY zeolite was higher than that without a catalyst, and both were proportional to temperature. But there was a drastic difference below the melting point of fructose. Fructose conversion of 36 % was obtained for the former, but zero for the latter at 95 ^{0}C.

In Figure 14, it was indicated that the formation of levulinic acid without a catalyst was proportional to temperature. But the formation of levulinic acid with LZY

zeolite, which was a concave curve, would pass a maximum about 110 ^{0}C - 120 ^{0}C. Two reasons for this are: (1) the formation of dehydrated products (such as Humin) parallel to levulinic acid would be much enhanced over a certain temperature (e.g. 110 ^{0}C - 120 ^{0}C), and (2) the further conversion of levulinic acid might be much significant over a certain temperature. Meanwhile, it was also showed that a drastic yield of levulinic acid occured below the melting point of fructose using LZY zeolite in this case.

As can be seen in Table 9, the conversion of fructose with heteropoly acid was higher than that with LZY zeolite. The yield of levulinic acid from fructose with heteropoly acid was higher than the yield of levulinic acid from fructose with LZY zeolite. But the selectivity of levulinic acid with heteropoly acid was less than that with LZY zeolite. This could be explained by the two reasons mentioned in the above paragraph. It is implied that the more acidic catalyst enhances much more the side reaction than the formation of levulinic acid, since the acidity of heteropoly acid is higher than that of LZY zeolite.

2. Reaction time effect:

The conversion of fructose and the yield of HMF would be proportional to the reaction time, but the yield of HMF was only observed for reaction times of 2 hours or greater at 140 ^{0}C. The reaction time affected the yield of levulinic acid in the same way as the temperature did.

3.Water as a solvent:

It was apparently shown that water would reduce the conversion of fructose and the yield of levulinic acid. Two reasons for this are: (1) water would reduce the acidity of the reaction medium which caused low reactivity, and (2) the fructose had high affinity toward water rather than toward the surface of the catalyst. The latter reason could apply to the dehydration of fructose using a strongly acidic ion-exchange resin[21, 22] in literatures.

The same tendency in the homogeneous catalyst systems was reported by B. F. M. Kuster [19]. Generally, sugars has insolubility in organic solvents but high solubility in water. There are some good nonaqueous solvents [37] reported for sugars, which are pyridine, N,N-dimethyl-foramide, sulpholane, dimethylsulphoxide (DMSO), morpholine, r-butyrolactone, furfuryl alcohol, tetrahydrofurfuryl alcohol, monoallyl ethers of ethylene glycol, 2-methoxy ethanol, methyl carbionol, and dimethyl formamide (DMF). But only DMSO as a solvent provided the stable yield of HMF in the dehydration of sugars. This phenomena has been proven by Nakamura[20], Rigal[21, 22], and Szmant [23], who use ion-exchange resins and boron trifluoroide etherate as catalysts, separately. It seems that the solvent for sugar dehydration will reduce the reactivity of the acidic catalyst.

III. Significant discoveries

The high yield of levulinic acid was obtained by using LZY zeolite as a catalyst and fructose as a sugar at the moderate temperatures. Specially, there was a drastic difference for both the conversion rate of fructose and the yield rate of levulinic acid below the melting point of frucotse with LZY zeolite.

The isomerization of fructose to glucose occured in this nonsolvent dehydration reaction. There were three different kinetic models used in the isomerization reaction of hexose , which were either an enolate-ion mechanism or a hydroxyl-ion dependent mechanism. The results might be a good explanation for the enolate-ion mechanism in the isomerization of hexose due to the lack of the hydroxyl ion in the reaction.

The conversion of fructose in this nonsolvent system was not fit to the first order conversion which was obtained in the solvent system. The order of the conversion rate of fructose in this nonsolvent system of our work was higher than that of the solvent system reported in the literature using either an inorganic acid or a strongly acidic ion-exchange resin as a catalyst. For example, the conversion of fructose was carried out at 140 ^{0}C with LZY zeolite under an inert atmosphere.

Kinetic model: F --------> products

$d[F]/dt = -K \times [F]^n$

$\{[F]^{1-n} - [Fo]^{1-n}\}/[Fo]^{1-n}$

$= \{(n-1)/[Fo]^{1-n}\} \times K \times t$

Let $B = (n-1)/[Fo]^{1-n}$;

$C = [F] / [Fo]$; $[Fo] = 1.0 / 180.0$

$C^{1-n} - 1.0 = B \times t$

No.	t (hr)	C (%)	for $C^{1-n} = B \times t + A$
1	0.0	1.0	r = 0.9832
2	0.5	0.527	A = 1.000705
3	1.0	0.447	B = 0.07092
4	2.0	0.297	n = 2.648
5	5.0	0.126	
6	15.0	0.04	so, K = 0.06226 $mole^{-1.65}$ / sec

HMF did not exhibit the behavior of a reaction intermediate in our work, but levulinic acid did. Also, isomerization of hexose occured during the reaction. There might be another reaction scheme than that discussed in the literature reviews to explain the formation of levulinic acid and the isomerization in this nonsolvent system of our work using solid acid catalysts.

A variation of reaction scheme is proposed as follows:

F: fructose, X: intermediate, G: glucose, Y: intermediate

HMF: 5-hydroxymethyl-2-furaldehyde, LA : levulinic acid

Z1, Z2, and Z3 : either insoluble products or unidentified products

(2) and (5) are more favorable reactions than (3) in this nonsolvent system. (7), (6), and (3) will be promoted after increasing either temperature or reaction time. But (4) seems to be prohibited in this non-solvent system.

IV. Material Loss and Uncertainties in Data

It was seen that there was still 20 % weight loss for Run #017, even though all the trace unknown products were taken into account in Table 11. Two facts could be explained for this: (1) there were brown to black undetermined insoluble residues (such as Humin, carbon, and copolymer of fructose and HMF) deposited upon catalyst, filtrating out of the yellow solution and (2) some soluble dehydrated products might be unable to be determined by these two HPLC's.

The amount of levulinic acid and HMF was calculated by the area percentage method, but the amount of glucose was calculated by the internal standard method. Material balances did not close for Runs #008, #010, #011, and #012, since the mass of products including glucose exceeded the mass of reactant. Two possible reasons for this are: (1) the isomerization of fructose to glucose was overestimated due to the overestimated conversion factor of glucose to the internal standard and (2) the yield of levulinic acid was overmeasured due to the incorrect sample concentration.

CONCLUSIONS

Sugars are major products in the saccharification of lignocellusic materials. The efficient conversion of sugars to high-value products is a very important step in the biomass-to-chemicals concept. A major question is : what is the "best" use of sugars in production of fuels and chemicals. Today, fermentation is used to convert sugars to alcohol. There are four disadvantages of fermentation all adversely affecting economics: (1) long reaction time, (2) high energy requirements to separate the dilute product water system, (3) low carbon conversion, and (4) batch processing because of inability to control all reactions.

In past years, related research work has been done on the catalytic dehydration, in place of fermentation, of sugars to chemicals (such as levulinic acid and HMF) using either an homogeneous acid or an ion-exchange resin as a catalyst. Some significant improvements relative to fermentation have made: (1) high carbon conversion, (2) lower reaction time, (3) no dilute medium required, (4) high yield and selectivity of the intermediate dehydrated product (HMF), and (5) availability of continuous process development. But the rate of levulinic acid, the final dehydrated product, was quite low in these researches. Our

research has positively shown that the high yield of levulinic acid was obtained by using an LZY zeolite for a short reaction time at moderate temperatures. Especially, there was a drastic difference in the conversion rate of fructose and the yield rate of levulinic acid below the melting point of fructose with and without LZY catalyst. The conversion and yield rates were zero without catalyst below the melting point of fructose. The subsequent catalytic hydrogenation of levulinic acid to alcohol may be feasible due to the high reactive nature of the carboxyl and keto groups. The modification of the solid catalyst to catalyze the levulinic acid to alcohol reaction in a hydrogen atmosphere is an interesting topics for further research.

The influence of water as a solvent highly decreased both the conversion rate of fructose and the yield of levulinic acid. The same tendency was reported by B. F. M. Kuster[19]. Generally, sugars has insolubility in organic solvents but high solubility in water. There are some good nonaqueous solvents reported for sugars. But only DMSO as a solvent for the dehydration of sugars provided the stable yield of HMF. This phennomenon was proven by Nakamura[20], Rigal[21, 22], and and Szmant[23], who used ion-exchange resins and boron trifluoroide etherate as catalysts, separately. It seems that the solvent for sugar dehydration will reduce the reactivity of the acidic catalyst.

HMF did not exhibit the behavior of a reaction intermediate in our work, but levulinic acid did. Also, isomerization of hexose occured during the reaction. There might be another reaction scheme than that discussed in the literature reviews to explain the formation of levulinic acid and the isomerization in this nonsolvent system using solid acid catalysts.

The order of the catalytic conversion rate of fructose was about 2.65 and the rate constant was 0.0623 mole$^{-1.65}$/sec at 140 ^{0}C with LZY. The order of the conversion rate of fructose in this nonsolvent system of our work was higher than that of the solvent system reported in the literatures using either an inorganic acids or strongly acidic ion-exchange resin catalysts.

The increase of temperature, reaction time, and acidity of the catalyst highly enhances the formation rate of side reaction products such as humin and carbon over the formation rate of levulinic acid. But the yield of levulinic acid may be optimized with either temperature or reaction time. This implies that at the maximum yield of levulinic acid, there is a minimum of side products such as humin and carbon. Further work on the optimization of these parameters is required for process development.

RECOMMENDATIONS

This research has confirmed the feasibility and advantages of the dehydration of fructose using solid acid catalystse. Further work is suggested as follows in order to fully develop the continuous catalytic dehydration of sugars into chemicals.

(1). chemical engineering feasible study:

- (a). process flow design and synthesis
- (b). material and energy balance
- (c). economic analysis

(2). best catalyst selection:

- (a). different types of solid acid catalysts (specially, zeolites and heterolpoy acids)
- (b). acidity effect for the same type of catalyst
- (c). pore effect for the same type of catalyst

(3). examination of various sugars for this system

- (a). Hexose: glucose, mannose, and galactose
- (b). Pentose: xylose and arabinose
- (c). Dimer: sucrose and maltose

(4). examination of starch, hemicellulose and cellulose

(5). kinetic investigation to evulate rate constant and rate expression

(a). reaction time effect for a wild range of temperature

(b). effect of pressure at a different temperature

(c). the different ratio of catalyst to sugar

(d). the difference between an air and an inert atmosphere

(6). derivation and verification of reaction scheme and kinetic model

(7). determination of insoluble products in the reaction

(8). determination of moles of water produced to indicate the degree of dehydration

(9). examination of various solvent effects

(10). modification of solid acid catalysts and reaction medium to further convert levulinic acid to alcohols or ketones

(a). Hydrogen as a carrier gas and reactant to proceed hydrogenation over metal catalyst

(b). High temperature decarboxylation over solid acids

The equipment which is required to execute this research is listed as follows:

(1). HPLC to determine the liquid products

(2). good separating ability of packed column for HPLC

(3). TCD G.C. to determine the gas products (such as water, carbon dioxide, etc.)

(4). Thermogravimeter to determine the insoluble products

(5). PH meter to determine the acidity of reaction

(6). Automated data acquisition system

APPENDIX

Calculations and procedures for experimental results are presented as follows:

1. Calculation of the response factor for both standard fructose and inositol on HPLC via LDC 1107 refractometer.
2. Calculation for conversion of fructose and yield of glucose on HPLC via LDC 1107 refractometer.
3. Calculation of the response factor for standard fructose, levulinic acid, and HMF on HPLC SP-8000 via SF 770 UV detector.
4. Calculation for yield of levulinic acid and HMF on HPLC SP-8000 via SF 770 UV detector.
5. Reintegration of Run #017 on HPLC via LDC 1107 refractometer set reject area: 5000
6. Properties of Catalyst

Note: All data files are storedd in CAP of IBM 9000 microcomputer system, MSU-DOE Plant Research Laboratory, Michigan State University

1. Calculation of the response factor for both standard fructose and inositol on HPLC via LDC 1107 Refractometer

reject area: 50,000 set in the method files (SUGAR) of CAP of IBM 9000 microcomputer system

CALCULATION OF RESPONSE FACTOR FOR FRUCTOSE AND INOSITOL

	FRUCTOSE			INOSITOL			
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
files DATA10:	amount (mg)	area amount/area		amount (mg)	area amount/area		
JOW006	0.373	1935885	1.93E-7	0.252	1585003	1.59E-7	0.824
JOW019	0.403	2080774	1.94E-7	0.250	1525430	1.64E-7	0.845
JOW020	0.050	263155	1.90E-7				

These standard runs were designed to calculate the response factors of fructose and inositol.

(1) and (4) are known from the preparation.

(2) and (5) are obtained from chromatographic data for each run.

Rf: the response factor of fructose

Ri: the response factor of inositol

(3)=(1)/(2) : the inverse response factor of fructose.

(6)=(4)/(5) : the inverse response factor of inositol.

(7)=(6)/(3) : Rc; the conversion factor for Rf to Ri.

For area percentage method, we average the inverse response factor for fructose, and inositol.

Rf^{-1} = 1.92E-7 and Ri^{-1}=1.62E-7

They will be used in next part to calculate our experimental data.

For the internal standard method, we average the conversion factor (Rc = 0.835), which is used to compare with area percentage method and calculate for unknown products.

2. Calculation for the conversion of fructose and yield of glucose on HPLC via LDC 1107 Refractometer

reject area: 50000 set in the method file (SUGAR) of CAP of IBM-9000 system.

AREA PERCENTAGE METHOD FOR CONVERSION OF FRUCTOSE

		(8)	(9)	(10)
Run No.	Data file	area	amount(mg)	conversion (%)
#006	DATA10:JOW007	2081292	0.400	0.0
#007	DATA10:JOW009	1553331	0.298	25.4
#008	DATA10:JOW010	1411958	0.271	32.2
#009	DATA10:JOW008	814896	0.159	60.9
#010	DATA10:JOW012	1876441	0.360	9.9
#011	DATA10:JOW018	1326204	0.255	36.3
#012	DATA11:JOW028	1203029	0.231	42.2
#013	DATA11:JOW053	1171950	0.189	47.3
#014	DATA10:JOW017	931131	0.179	55.3
#015	DATA11:JOW055	618335	0.119	70.3
#016	DATA10:JOW015	263156	0.051	87.4
#017	DATA10:JOW016	83889	0.016	96.0

(8) is obtained from the chromatographic data.

(9) = (8) × Rf^{-1}

(10) = [0.400 - (9)]/ 0.400 × 100 %

INTERNAL STANDARD CALCULATION FOR CONVERSION OF FRUCTOSE

		¦FRUCTOSE¦	INOSITOL	¦	FRUCTOSE
Run No.	Data file	area (8)	area (11)	amount (12)(mg)	amount (13)(mg)	conversion (14) %
#006	DATA10:JOW007	2081292	1685997	0.267	0.392	2.0
#007	DATA10:JOW009	1553331	1748548	0.273	0.291	27.3
#008	DATA10:JOW010	1411958	1684892	0.264	0.263	34.3
#009	DATA10:JOW008	814896	none	none	none	none
#010	DATA10:JOW012	1876441	1573563	0.248	0.354	11.5
#011	DATA10:JOW018	1326204	1325509	0.21	0.252	37.0
#012	DATA11:JOW028	1203029	none	none	none	none
#013	DATA11:JOW053	1171950	none	none	none	none
#014	DATA10:JOW017	931131	1753830	0.276	0.174	56.5
#015	DATA11:JOW055	618335	none	none	none	none
#016	DATA10:JOW015	263156	1601295	0.259	0.51	87.3
#017	DATA10:JOW016	83889	1899698	0.294	0.015	96.3

(8) and (11) are obtained from the chromatographic data.

(12) is known by preparation.

Rc: conversion factor of fructose to inositol

(13) = (8) × (12) / (11) / Rc : amount of fructose

(14) = [0.400 - (12)] / 0.400 × 100 % ;

conversion % of fructose

INTERNAL STANDARD CALCULATION FOR YIELD % OF GLUCOSE

Run No.	Data file	area	area	amount (mg)	%
		inositol	X3 (glucose)		
		(11)	(15)	(16)	(17)
#006	DATA10:JOW007	1685997	none	none	none
#007	DATA10:JOW009	1748548	110983	0.017	4.3
#008	DATA10:JOW010	1684892	123724	0.019	4.8
#010	DATA10:JOW012	1573563	246086	0.039	9.8
#011	DATA10:JOW018	1325509	84980	0.013	3.3
#014	DATA10:JOW017	1753830	285476	0.045	11.3
#016	DATA10:JOW015	1601295	166351	0.027	6.8
#017	DATA10:JOW016	1899698	151537	0.023	5.9

(11) and (15) are obtained from the chromatographic data.

(12) is the same as the above case.

Rc: conversion factor of glucose to inositol; assumed 1.

(16) = (12) x (15) / (11) / Rc ; the amount of glucose

(17) = (16) / 0.400 x 100 % ; yield % of glucose

0.400 mg: total amount of initial fructose in these samples

AREA PERCENT METHOD FOR YIELD CALCULATION OF UNKNOWN PRODUCT

Run No.	Data file	area	amount (mg)	%
		X3 (glucose)		
		(18)	(19)	(20)
#009	DATA10:JOW008	none		
#012	DATA11:JOW028	216688	0.035	8.8
#013	DATA11:JOW053	57802	0.009	2.3
#015	DATA11:JOW055	186147	0.028	7.0

(19) = (18) x Ri^{-1} ; amount of glucose

(20) = (19) / 0.400 x 100 % ; yield % of glucose

0.400 mg: total amount of initial fructose in these samples

3. Calculation of the response factor for standard fructose, levulinic acid, and HMF on HPLC SP-8000 via SF 770 UV detector

reject area: 10,000 set in the method file (SUGARCOL) of CAP IBM 9000 microcomputer system

CALCULATION FOR THE RESPONSE FACTOR OF STANDARD FRUCTOSE

Data file	amount (mg)	area	amount/area
	(21)	(22)	(23)
DATA10:ZEPM026	0.05	9154698	5.461E-9
DATA10:ZEPM027	0.05	8704727	5.744E-9
DATA10:JOWW021	0.05	7903008	6.327E-9

(23) = (21) / (22);the inverse response factor of fructose

(23) : $Rf1^{-1}$

For the area percentage method, the inverse response factor of fructose is the average of summation of (23).

That is $Rf1^{-1}$ =5.844E-9.

CALCULATION OF RESPONSE FACTOR FOR STANDARD LEVULINIC ACID

data file	amount (mg)	area	amount/area
	(24)	(25)	(26)
DATA10:ZEPM025	0.05	12905872	3.874E-9
DATA10:JOW001	0.05	12005791	4.164E-9

(26) = (24) / (25); the inverse response factor of levulinic acid ; $R1^{-1}$

For the area percentage method, the inverse response factor of levulinic acid is the average of summation of (26).

That is RI^{-1} = 4.019E-9.

CALCULATION OF THE RESPONSE FACTOR FOR STANDARD HMF

data file	amount (mg)	area	amount/area
	(27)	(28)	(29)
DATA10:ZEPM025	0.005	8558126	5.842E-10
DATA10:ZEPM027	0.005	8132644	6.148E-10
DATA10:ZEPM028	0.005	8767719	5.703E-10
DATA10:JOW003	0.003	5114199	5.866E-10
DATA10:JOW004	0.001	1605398	6.229E-10
DATA10:JOW043	0.005	8856750	5.645E-10

(29) = (27) / (28): the inverse response factor of HMF;Rh— 1

For the area percentage method, the inverse response factor of HMF is the average of summation of (29).

That is Rh^{-1} = 6.042E-10.

4. Calculation for yield of levulinic acid and HMF

on HPLC via LDC 1107 Refractometer.

area reject: 10,000 set in the method file (SUGARCOL) of

CAP of IBM 9000 microcomputer system

CALCULATION FOR YIELD OF LEVULINIC ACID AND HMF

		(30)	(31)	(32)	(33)	(34)	(35)	(36)
			Levulinic Acid			HMF		
Run No.	Data file DATA11	Total area	area	amount (mg)	yield (%)	area	amount (mg)	yield (%)
#006	JOW050	15242128	0	0.0	0.0	0	0.0	0.0
#007	JOW056	7030498	656579	0.0027	5.3	0	0.0	0.0
#008	JOW045	9834814	4038398	0.0162	32.5	0	0.0	0.0
#009	JOW044	9209231	5851160	0.0235	47.0	0	0.0	0.0
#010	JOW047	8365761	665725	0.0027	5.4	0	0.0	0.0
#011	JOW048	9857799	4403608	0.0177	35.4	0	0.0	0.0
#012	JOW046	9824472	4883616	0.0196	39.2	0	0.0	0.0
#013	JOW052	7544762	2090570	0.0084	16.8	0	0.0	0.0
#014	JOW031	6950958	3122329	0.0125	25.1	0	0.0	0.0
#015	JOW054	6721986	4176696	0.0168	33.5	990361	0.0006	1.2
#016	JOW029	9401160	8310321	0.033	66.8	1711646	0.001	2.0
#017	JOW027	5722627	5380403	0.0216	43.2	3672184	0.0022	4.4

(30) and (34) are obtained from the chromatographic data.

(10) is given from part two ; conversion % of fructose

(31) = (30) - [1.0 - (10)] x 0.05 / $Rf1^{-1}$;

subtotal area of LA

(32) = $R1^{-1}$ x (31); the amount of LA

(35)= (34) x Rh^{-1} ; the amount of HMF

(33) = [0.05 - (32)] / 0.05 ; the yield % of LA

(36) = [0.05 - (35)] / 0.05 ; the yield % of HMF

0.05mg: total amount of initial fructose in these samples

5. Reintegration of Run #017

on HPLC via LDC 1107 Refractometer

area reject: 5,000 set in the method file (SUGAR) of CAP of IBM 9000 microcomputer system

Retention time (min)	area	amount	yield (%)	
(37)	(38)	(39)	(40)	
2.01	22492	0.003	0.8	
3.63	10284	0.002	0.5	
4.71	15312	0.002	0.5	
5.76	15634	0.002	0.5	
6.70	15432	0.002	0.5	
9.61	246888	0.038	9.5	X1
11.98	8596	0.001	0.3	
12.7	8828	0.001	0.3	
13.4	9356	0.001	0.3	
14.2	9946	0.002	0.5	
14.96	9542	0.001	0.3	
15.72	8508	0.001	0.3	
16.72	9754	0.002	0.5	
17.16	13303	0.002	0.5	
18.4	32698	0.005	1.3	
20.6	72530	0.011	2.8	X2
21.7	42339	0.007	1.8	
25.39	151537	0.023	5.8	glucose (X3)
27.57	14937	0.002	0.5	
29.8	83889	0.016	4.0	fructose
38.7	22265	0.003	0.8	
42.5	39541	0.006	1.5	

(37) and (38) are obtained from the chromatographic data.

(39) = (38) x Ri^{-1} ; amount of each compound

(40)=[0.05 - (39)]/0.05 ; yield percentage of each compound

0.05 mg: total amount of initial fructose in these samples

6. Properties of Catalyst

A. Heteropoly acid

General formula: $H_q [X_x M_m O_y]$ (usually x < m)

X: center atoms (hetroatoms) ; P, Si, Te, As, Mn

M: coordinated atoms (polyatoms) ; Mo, W, V, Nb

x:m = 1:12, 1:11, 1:10, 1:9, and 1:6

H replaced by the metal ion called salt of heteropoly acids

General properties:

1. high molecular weight electrolytes over 4000.
2. significantly soluble in water and organic solvents.
3. strong acid and protons have the same dissociation constant.
4. strong oxidizing agents which change to blue color upon reduction
5. free acids as well as salts contain many molecules of water of crystallization.
6. decomposed by strong base.
7. heteropoly acids show brilliant colorations.

B. Zeolite:

General formula: $M_{x/n}[(AlO_2)_x(SiO_2)_y]\ w\ H\ O$

n : the charge of the cation

w : numbers of hydration of water on the structure

y/x : from zero to infinite

General properties:

1. reversible dehydration: dehydration of Bronsted acid to Lewis acid
2. ion exchange property.
3. molecular seiving catalyst.
4. high selectivity of reactant, product and restricted transition state.
5. high stability (i.e. high Si/Al,high stability ,low acidity)
6. highly crystalline and high surface area

REFERENCES

1. Chang, Clarence D. and Silvestri, Anthony J., Journal of Catalysis, 47, 249, (1977)
2. Leonard, Reid H., Ind. Eng. Chem.,48 (8), 1331, (1956)
3. Harris, John F. and Feather, Milton S., Advan. Carbohydr. Chem. Biochem., 28, 161, (1973)
4. McKibbins, S. W., Ph. D. Thesis, Univ. of Wisconsin (1958)
5. Speck, J. C., Jr., Advan. Carbohydr. Chem. 13, 63, (1958)
6. Feather, M. S., Carbohydr. Res., 7, 86, (1968)
7. Shaw, Philip E., Carbohydr. Res., 5, 266, (1967)
8. Amin, EL S., Carbohydr. Res., 4, 96, (1967)
9. Heyns, K., Carbohydr. Res. 6, 436, (1968)
10. Krol, B., Acta Aliment. Pol., 4, 287, (1978)
11. Bonner, T. G., J. Chem. Soc., 1960, 787, (1960)
12. Anet, E. F. L. J., Advan. Carbohydr. Chem., 19, 181, (1964)
13. Haworth, W. N. and Jones, W. G. M., J. Chem. Sco., 1944, 667, (1964)
14. Harris, D. W. and Feather, M. S., J. Org. Chem., 39, 724, (1974)
15. Rase, Howard F., Ind. Eng. Chem. Prod. Res. Dev. 14, 40, (1975)

16. Bonner, T. G., Bowrne, E. J. and Ruszkieuier, M., J. Chem. Soc., 1944, 667, (1944)
17. Wiggins, L. F., Advan. Carbohydr. Chem., 4, 293, (1949)
18. McKibbin, S.;Harris, J.; Saeman, J. and Neil, W., Forest Product J., Jan. 1962, 17, (1962)
19. Kuster, Ben F. M. and Feather, L. M., Carbohydr. Res., 54, 159, (1977)
20. Nakamura,Yoshio, and Morikawa, Shunichi, Bull. Chem. Soc. Jpn, 53, 3705, (1980)
21. Rigal, Luc, J. Chem. Tech. Biotechnol., 31, 489, (1981)
22. Rigal, Luc, Ind. Eng. Chem. Prod. Res. Dev., 20, 719, (1981)
23. Szmant,H. H. and Chundury, D. D., J. Chem. Tech. Biotechnol., 31, 135, (1981)
24. Van Einenstein, W. A. and Blanksma, J., J. Chem. Weeklad, 6, 717, (1909)
25. Wiggin, L. F. and Montgomery, R., J. Soc. Chem. Ind. Lond.,66, 31, (1945)
26. Stone, J. E. and Blundell, M. J., Can., J. Res., 28, 676, (1950)
27. Rice, F. A. H., J. Org. Chem., 23, 465, (1958)
28. Mednick, M. L., J. Org. Chem., 27, 398, (1962)
29. Moye, C. F. and Goldsck, R. F., J. Appl. Chem., 16, 207, (1966)
30. Maier, W. F.; Roth, W.; Thies I. and Schleyer P. R., Chem. Ber., 115, 808, (1982)

31. Chiba, T.; Okimoto, M. and Nagai, H.,Bull. Chem. Soc. Jpn.,56, 719, (1983)

32. Chum, H. L.; Ratcliff M.; Posey F. L.; Turner J. A. and Nozek, A. J., J. Phys. Chem., 87, 3089, (1983)

33. Otake, Masaayaki and Onoda, Takeru, J. Catalysis, 38, 494, (1975)

34. Jolly, William L., " the systhesis and charaterization of Inorganic Compounds", 32, 460, (1970)

35. Taher, A. M. and Cutes, D. M., Carbohydrate Research, 34, 249, (1974)

36. Kooyman, C.; Vellenga, K. and Dewilt, H. G. J., Carbohydrate Research, 54, 33, (1977)

37. Moye, C. J., and Smythe, B. M., Carbohydrate Research, 1, 284, (1965)

38. Dull, G. Chem. Ztg., 19, 1003, (1895)