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Title: Reactions of Glucose in H-Y Zeolite Catalysts

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Gregory L. Rorrer

Y-Zeolite catalysts have the potential to promote the shape-selective conversion of glucose to oxygenated hydrocarbons at fairly low temperature (100 to 130°C). Reaction of glucose solution with H-Y Zeolite catalyst powder was carried out in a well-mixed batch reactor. This reaction was studied as a function of reaction time (0 to 24 hours), temperature (100 to 130°C), catalyst loading (10:1 to 1:1 glucose:Y-Zeolite), and initial glucose concentration (12% to 58% g glucose/g solution). Unreacted glucose and reaction products were analyzed by HPLC.

The dehydration of glucose solution by H-Y Zeolite catalyst powder resulted in 90% conversion at 2:1 glucose: H-Y Zeolite and 130°C. At these conditions, maximum levulinic acid and formic acid yields were 15% and 30% respectively.

A pseudo first-order process was used to estimate the apparent rate constant for glucose conversion at various temperatures. From the Arrhenius equation, the apparent activation energy was estimated as 22.06 kCal/mole for glucose solution initially at 12% weight.

Based on the product distribution data, a reaction model for glucose dehydration to HMF, levulinic acid, and formic acid in Y-Zeolite catalysts was proposed.

Reactions of Glucose in H-Y Zeolite Catalysts

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Assistant Professor of Chemical Engineering in charge of major

Redacted for Privacy

Head of Chemical Engineering Department

Redacted for Privacy

Dean of Graduate School

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REACTIONS of GLUCOSE in H-Y ZEOLITE CATALYSTS

Chapter 1

INTRODUCTION

Presently, the most common process used for converting glucose and other sugars to valuable organic chemicals such as organic acids and alcohols is fermentation. However, bio-processes for sugar conversion have inherent limitations including long residence times, low yield, and narrow range of temperature and pH. Also, significant amounts of carbon in the carbohydrate feed are lost to carbon dioxide. Most fermentation processes for converting sugar cannot compete with petrochemical-based processes for production of commodity organic chemicals.

It is well known that catalysts generally improve reaction rates under a boarder range of process conditions. Previous work has established that the acid-catalyzed dehydration of sugars such as (D)-fructose, (D)-glucose or other monosaccharides can yield 5-hydroxymethylfurfural (HMF), 4-oxopentanoic acid (levulinic acid) and formic acid. Especially, levulinic acid is a useful organic intermediate which can be converted to several chemicals and fuels (Leonard, 1956). Unfortunately, no studies have shown high product yield and catalyst reuse. Furthermore, most experiments were conducted only on lab scale, not a process scale.

Solid-liquid dehydration systems using the catalyst as the solid phase can solve problems related to the reuse of the catalyst and the conversion and separation of products. The concept of dehydration on strongly acidic particles such as ion-exchange resins leads to the idea that other types of solid-acid catalysts could also dehydrate sugars and yield the same products. Solid-acid zeolite catalysts are promising candidates.

Zeolite catalysts can improve the yield and selectivity of chemical reactions. With molecular sized channels, the zeolite allows only molecules of certain sizes and shapes access to catalytic sites.

Glucose is an inexpensive, abundant, and renewable raw material for organic chemicals production. The dehydration of glucose in H-Y zeolite catalysts is largely unexplored.

Solid acid Y-zeolite catalysts, which act as both an acid catalyst and a molecular sieve, could potentially promote a high yield and selectivity of oxygenated hydrocarbons. Solid acid Y-zeolites may in particular promote the shape-selective dehydration of sugars to levulinic acid and formic acid.

Y-zeolites have highly a ordered porous structure. The specific pore and cage arrangement shown in Figure 1.1 has cubic symmetry and can accommodate the glucose molecule for selective molecular arrangement.

Y-ZEOLITE Molecular Structure

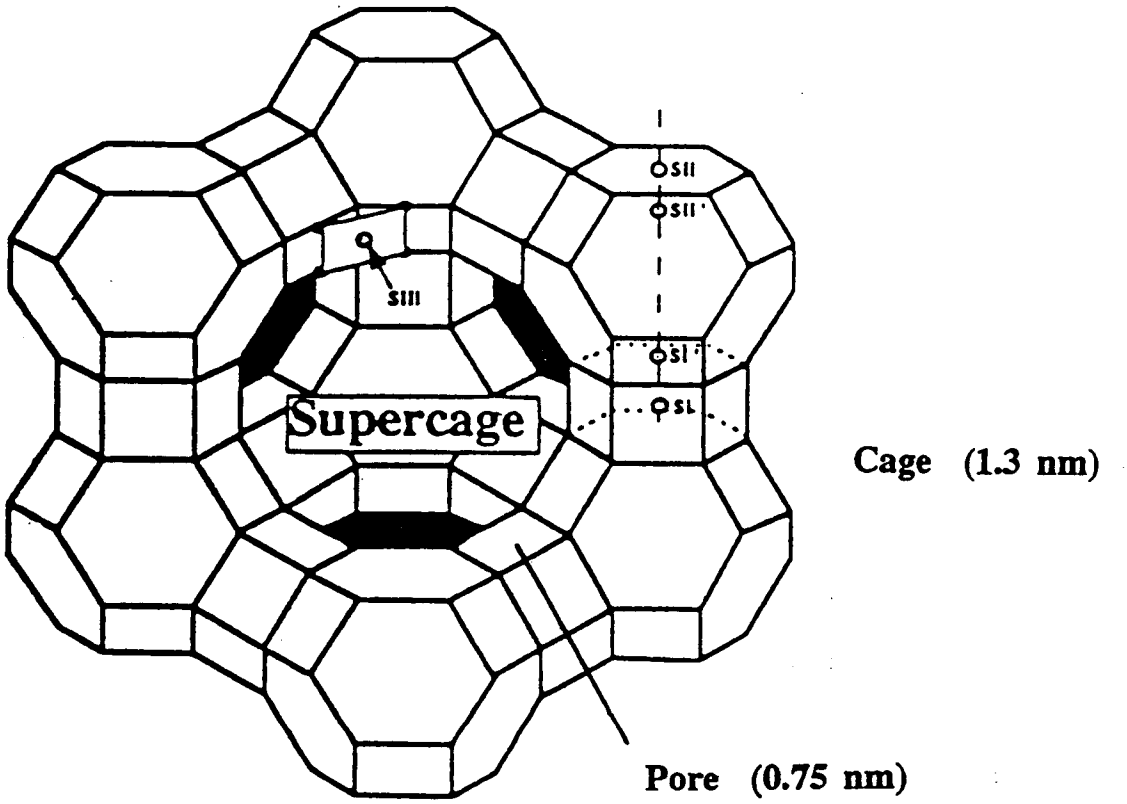


Figure 1.1 Cage-pore structure of Y-zeolite catalyst.

The proposed mechanism of the shape selective reaction of (D)-glucose in a Y-zeolite catalyst is the following. First, The glucose ring is cleaved by Bronsted-acid sites anchored on surface of the H-Y zeolite. The resulting linear 1,2 enediol passes through 0.75 nm pores of Y-zeolite matrix and into a 1.3 nm cage. Inside the cage, HMF is formed. In the cage, HMF is rehydrated to the smaller, linear molecules levulinic acid and formic acid. Unlike HMF, these molecules can thread through the pores and diffuse out into liquid phase.

In this study, the dehydration of (D)-glucose by H-Y zeolite powder was conducted in a well-mixed batch reactor at low reaction temperature (100°C to 130°C). Water was used as the reaction solvent. The reaction products were analyzed by high performance liquid chromatography.

If industrially significant oxygenated hydrocarbons could be produced by shape-selective conversion of glucose in Y-zeolite catalysts, then this research could lead to new technologies for production of those organic chemicals.

Research Goals and Objective

This thesis has two major goals. The first goal is to investigate the feasibility of dehydrating glucose to oxygenated hydrocarbons by Y-zeolite catalysts at low temperatures (100°C to 130°C). The second goal is to characterize the reaction chemistry and rate processes involved in the diffusion and reaction of (D)-glucose in solid acid Y-zeolite catalysts.

The specific objectives of this thesis are to:

1. Perform well-mixed batch reactor experiments with (D)-glucose solution in water and H-Y zeolite catalyst.
2. Identify and quantify target reaction products such as levulinic acid, formic acid and HMF.
3. Measure glucose conversion and product formation rates as a function of process parameters including temperature, sugar concentration, catalyst loading ratio and mixing intensity.
4. Investigate the effect of process parameters on product yield and selectivity.
5. Propose a reaction mechanism.
6. Estimate the activation energy for glucose conversion based on a pseudo first order process.

Chapter 2

LITERATURE REVIEW

Presently, there are a large number of research projects relating to various methods and technologies of carbohydrate conversion to other organic compounds such as acids or alcohols. Each project seems to focus on how to produce those compounds economically and efficiently. As mentioned in Chapter 1, catalytic reaction processes have some potential benefits over fermentation processes.

Most catalytic reaction processes are concerned with the dehydration of sugars with acid catalysts or proton donator catalysts. Many previous studies explored the reaction of sugars with aqueous acids. They reported that dilute mineral acid catalysts irreversibly dehydrate glucose or fructose to HMF, levulinic acid and formic acid. For example, Shaw et.al. (1967) reacted 240 g of glucose in 440 mL of water at 100°C and pH 1 to 3.5, and other investigators considered reactions of glucose and fructose higher temperature from 200°C to 350°C with 0.8 N to 1.6 N HCl (Kullury et al.,1988; Nelson et al.,1988). A maximum HMF yield of 0.5 g mole/L was obtained from the reaction of 1 g mole/L glucose solution with $AlCl_3$ at 367°C (Dadgar and Fouth, 1983).

The mineral acid concentration acidity influenced the dehydration of fructose but not the rehydration of HMF to

levulinic acid and formic acid. The reaction of 1 M D-fructose and 1 M HCl at 95°C yielded a maximum levulinic acid concentration of 0.65 M after 24 hours and a maximum HMF concentration of 0.25 M after 2 hours. The selectivity of levulinic acid with respect to maximum HMF was 1.12 (Kuster et al., 1977, I-IV). A selectivity of 1 was obtained from the reaction of 33.3 mM glucose with diluted acid at pH 2.0 at 190°C after 100 min. Carbon formation, 0.1 mole carbon/mole glucose, also occurred at the same conditions after 75 min (Baugh and McCarty, 1988).

Fructose can also be dehydrated to HMF and levulinic acid by dilute mineral acids (1 to 5 mM) in super critical water at 200°C to 385°C and 34.5 MPa. A maximum HMF yield of 0.66 mole/mole fructose was obtained from the reaction of 0.05 M fructose and 2 mM H_2SO_4 at 250°C and 34.5 MPa (Antal et al., 1987, 1988).

Kinetic models and rate equations for fructose dehydration are reported at 95°C with 0.5 to 2 M HCl. A kinetic model was also developed for the rehydration of HMF to levulinic acid and formic acid at 170 to 230°C with pH 1 to 4 (Kuster et al.,1977 I-IV; Baugh and McCarty, 1988).

Although aqueous acid catalyzed dehydration of sugars have been studied significantly, this process has many disadvantages including difficult separation of acid catalyst from the products, low selectivity of desired products, and formation of humin byproducts.

Recent studies considered commercial acidic ion-exchange resins for dehydration of sugars in water or polar solvents. The heterogeneous dehydration of 0.52 mole/L sucrose on Dowex MSC-1 H ion-exchange resins yielded HMF of 0.125 mole/L after 2 hours, levulinic acid of 0.25 mole/L after 24 hours, and maximum selectivity of 0.5 mole of levulinic acid/mole of soluble products. These studies also suggested that the selectivity increased with decreasing pore diameter (Schraufnagel and Rase, 1975). The dehydration of fructose with ion-exchange resins was confirmed by 1.2 M fructose with Lewalitt SPC 118 resins at 88°C, which yielded 0.66 mole HMF per mole of consumed fructose (Rigal et al.,1981). This process is attractive because the small pore size of the resin improves selectivity of levulinic acid. Additionally, the resin is a reusable solid catalyst. However, yields of levulinic acid are fairly low and the resins cannot tolerate higher temperature required for rapid reaction rates. In other studies, solvents such as methyl isobutyl ketone were used to improve the levulinic acid and HMF yields (Mercadier et al.,1981). The reaction of 222 g/dm^3 fructose solution with SPC 108 resins obtained a 0.13 mole Levulinic acid and 0.66 mole HMF. The maximum selectivity of levulinic acid to HMF was 0.2.

Other studies considered novel acid catalysts that gave same the products and higher yield (Szmant and Chundury, 1981). Dehydration of 0.05 moles of fructose dehydration by

0.0125 moles of boron trifluoride etherate catalyst, BF_3Et_2O, at 1 atm and 373 K resulted in 0.98 mole HMF/mole fructose. A 0.42 HMF yield was obtained from 0.05 moles of glucose at the same conditions. These results suggested that the reaction activity of fructose was higher than glucose.

Several previous studies used solid-acid catalysts for sugar dehydration to other hydrocarbons. Dehydration of glucose to gasoline-range hydrocarbons over H-ZSM5 zeolite catalyst in a water/methanol mixture at temperature ranging 300°C to 650°C in fluidized bed reactor is reported and patented (Chen et al., 1985, 1986; U.S. patent # 4503278). However, the overall yield of aliphatic and aromatic hydrocarbons was only 20% based on carbon retention. Product selectivity was low and there were many by-products such as carbon monoxide, coke and water. These results were recently confirmed in a fixed-bed microreactor with H-ZSM5, Zn-ZSM5, and Mn-ZSM5 zeolite catalysts (Haniff and Dao, 1988; Dao et al.,1988). They also observed that significant thermal polymerization occurred at 400°C and caused low product yield.

The dehydration of glucose on ZSM5 zeolite catalysts did not express the molecular-sieve capability of zeolite. That was the reason product yield and selectivity were low. The 0.5 nm ZSM5 zeolite pore diameter was not large enough to accommodate a large glucose molecule (0.9 nm) for selective molecular rearrangement. Also the temperature

range (300°C to 650°C) promoted the polymerization of glucose and products.

To improve those disadvantages, one experiment gave the result that dehydration of molten (D)-fructose could also occur on LZY-zeolite powder catalyst which has highly ordered, open porous structure larger than ZSM5 (Jow et al.,1987). The reaction was investigated in a sealed test tube at 140°C with 1:1, catalyst:(D)-fructose by weight. The results presented yields of 43.2% weight levulinic acid and 4.4% weight HMF with respect to weight initial fructose. The selectivity was 10.7 mole levulinic acid/mole HMF. This incomplete work established the feasibility of sugar dehydration by Y-zeolites to produce high yields of levulinic acid. However, the reaction technique was not sufficient to operate in large scale process.

In summary, previous work has established the feasibility of dehydration of glucose and fructose using various kinds of acid catalysts. Unfortunately, most of these studies have not had successes in terms of yield and selectivity of products. Those experiments faced problems related to an impractical or complicated process system, difficult product separation from the catalyst, and catalyst reuse.

Other sugars can possibly be dehydrated and produced with high product yield and selectivity by Y-zeolite catalyst. Glucose is considered as the primary product of lignocellulose hydrolysis and is an economical raw material

for chemical manufacture. The direct conversion of (D)-glucose using Bronsted-acid Y-zeolite catalyst in a solid-liquid system to yield levulinic acid, formic acid and other useful compounds could be feasible. Future experiments need to be concerned about studying these reactions in practical systems such as well-mixed batch or mixed flow reactors in order to enhance the rate of reaction and mass transfer. Furthermore, in this heterogeneous reaction system, the catalyst is easily separated from reaction products which improves the technical feasibility of the proposed process relative to aqueous mineral acids.

Chapter 3

EXPERIMENTAL METHODS

3.1. Materials

(D)-glucose in crystalline form was obtained from Sigma Chemical Company. (D)-glucose has molecular weight of 180.16, melting point of 146 to 150°C, and mean molecular size of 0.9 nm.

H-Y zeolite (Faujasite) catalyst powder was obtained from the PQ Corporation (VALFOR CP 300-35). The Y-zeolite is alumino silicate crystal and has a surface area of 700 m^2/g, a unit cell size of 2.435 nm and a silica/alumina molar ratio of 6.5. The H-Y zeolite catalyst powder size is mostly smaller than 38 microns (71% weight) as determined by a 15 hour sieving of 30 g H-Y zeolite powder with six sieve tray sizes ranging from 38 to 106 microns on a sieve shaker. The size distribution of H-Y zeolite powder is shown in Figure 3.1. The H-Y zeolite catalyst has Bronsted acid sites exchanged for sodium sites in the crystalline matrix. The pore matrix of Y-zeolite consists of 0.75 nm channels connected to 1.3 nm cages arranged in cubic symmetry. The number and acid strength of active sites on H-Y zeolite are 10^{21} sites/g and $3x10^{-4}$ % of H_2SO_4 for dehydration processes (Jacobs P.A., 1977).

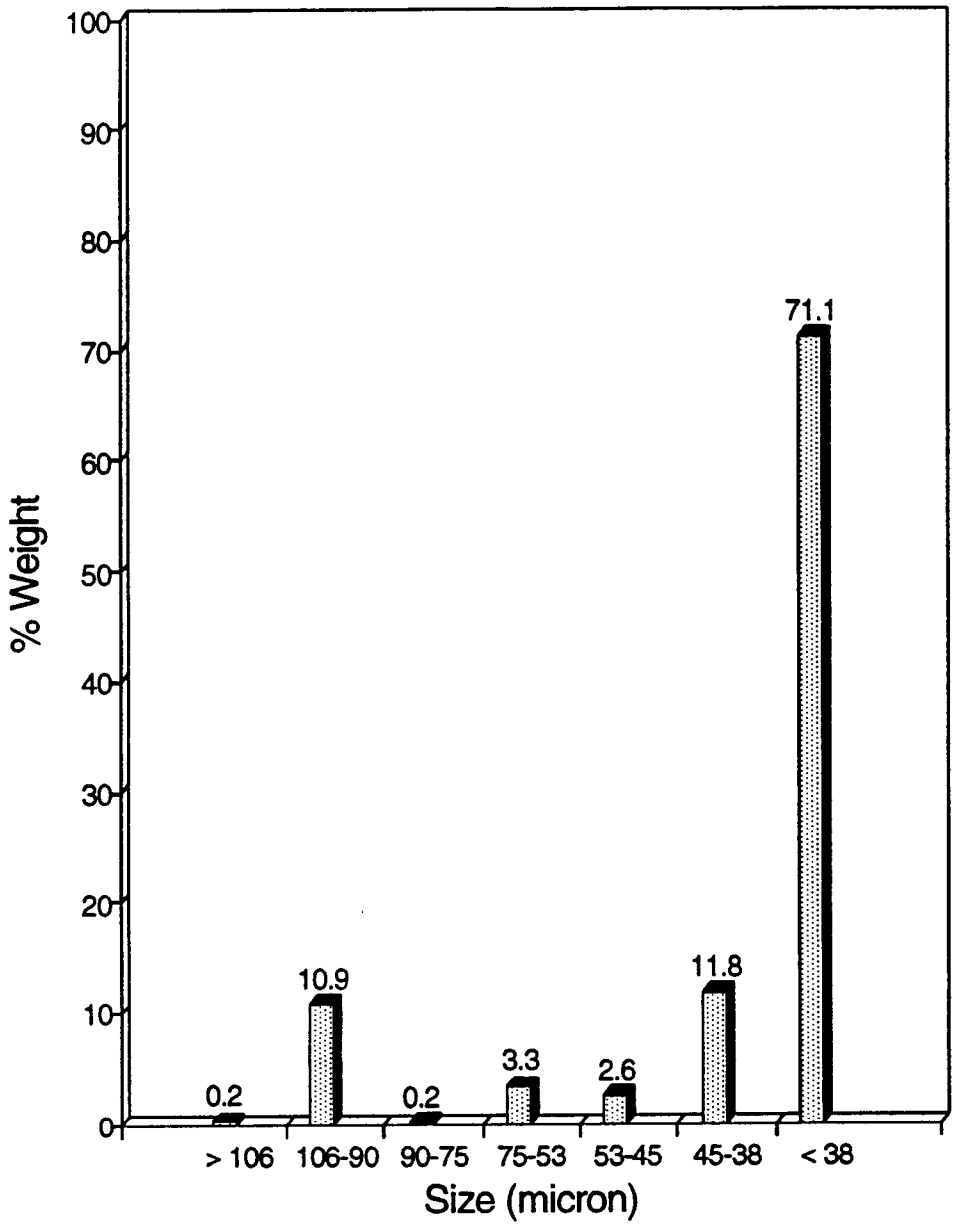


Figure 3.1 H-Y zeolite catalyst powder (VALFOR CP 300-35) size distribution.

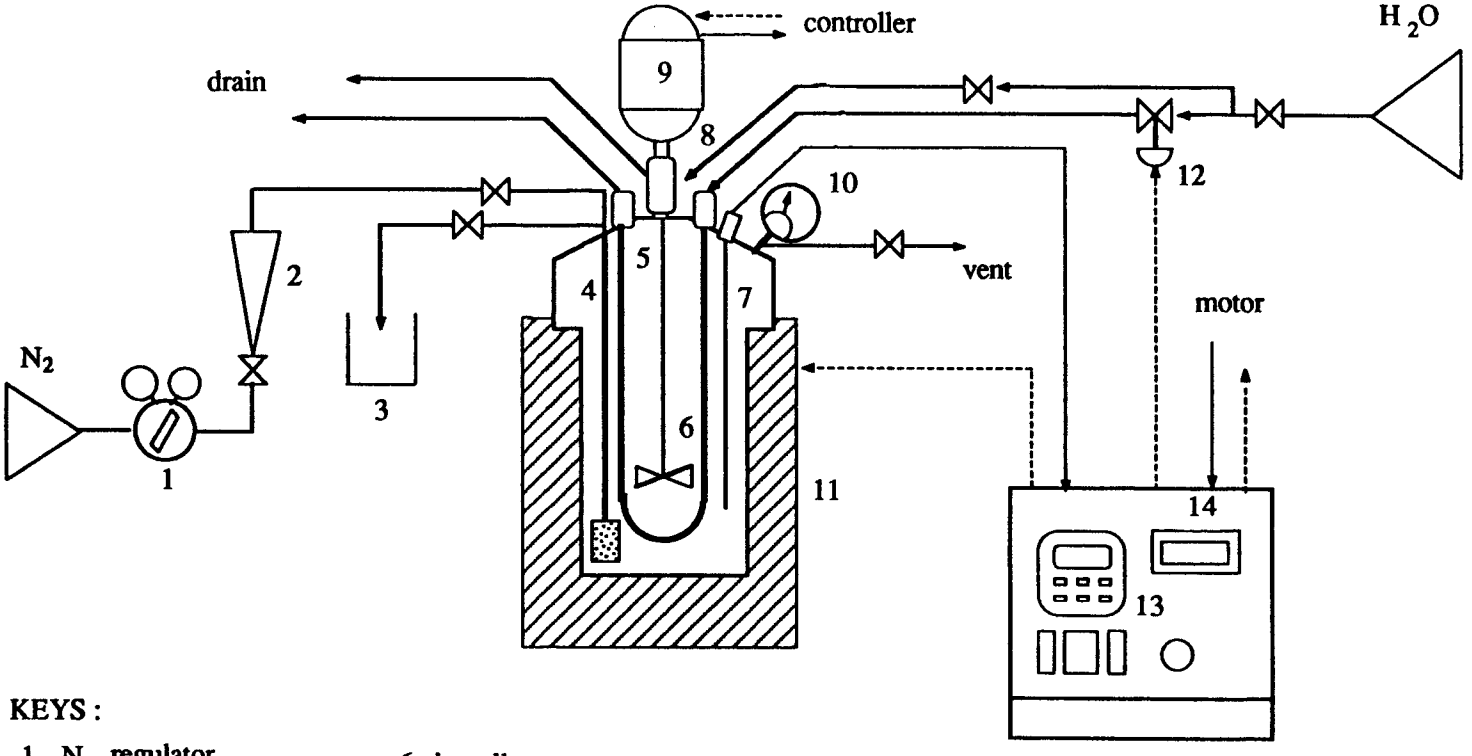
3.2. Batch reactor

A 300 mL, well-mixed Parr reactor was used for reaction studies. The reactor is equipped with a PID temperature controller and a mixer with tachometer. The reactor vessel is constructed of T-316 stainless steel and is rated at 2000 psig maximum pressure and 400°C maximum temperature. The reactor head plate is assembled with a gas inlet, sampling outlet, pressure relief, type-J thermocouple, leak-proof impeller and heat exchanger with taps and solenoid valve for cooling water. The control unit contains the PID controller, impeller speed controller, and tachometer. The PID controller controls the heating jacket surrounding the reactor and the solenoid valve for regulating cooling water flow through the heat exchanger. The fully instrumented reactor is illustrated in Figure 3.2.

3.3. Reaction procedures

(D)-glucose was dissolved in deionized distilled water. The total weight of the glucose and the water was 170 g. A known weight of H-Y zeolite powder and (D)-glucose solution were charged into the 300 mL reactor. The reactor head plate was mounted on to the vessel and sealed. The sealed reactor was purged with N_2 at 30 to 60 psig overlay to pressurize the liquid for sampling. The reactor was then heated to the desired set-point temperature and stirred at

BATCH REACTOR SCHEMATIC



KEYS :

1. N_2 regulator
2. N_2 flowmeter
3. sample vial
4. sample dip tube & 10 micron filter
5. internal cooling loop
6. impeller
7. thermocouple
8. impeller shaft cooling sleeve
9. impeller motor
10. pressure guarge
11. heating jacket
12. solenoid valve
13. PID temperature controller
14. tachometer

Signal Line
A/C Line
Tubing

Figure 3.2 Well-mixed batch reactor system.

Table 3.1 Experimental reaction process parameters.

Parameter	Investigated range
temperature (°C)	100°C to 130°C
initial glucose concentration (g glucose per g solution)	0.12 and 0.58
initial glucose wt.: H-Y zeolite wt.	1:1 to 10:1
mixing speed (rpm)	150 to 1200
maximum reaction time (hours)	10 to 24
internal standard:	
butyric acid (mg/mL)	4 to 6
myo-inositol (mg/mL)	20 to 30

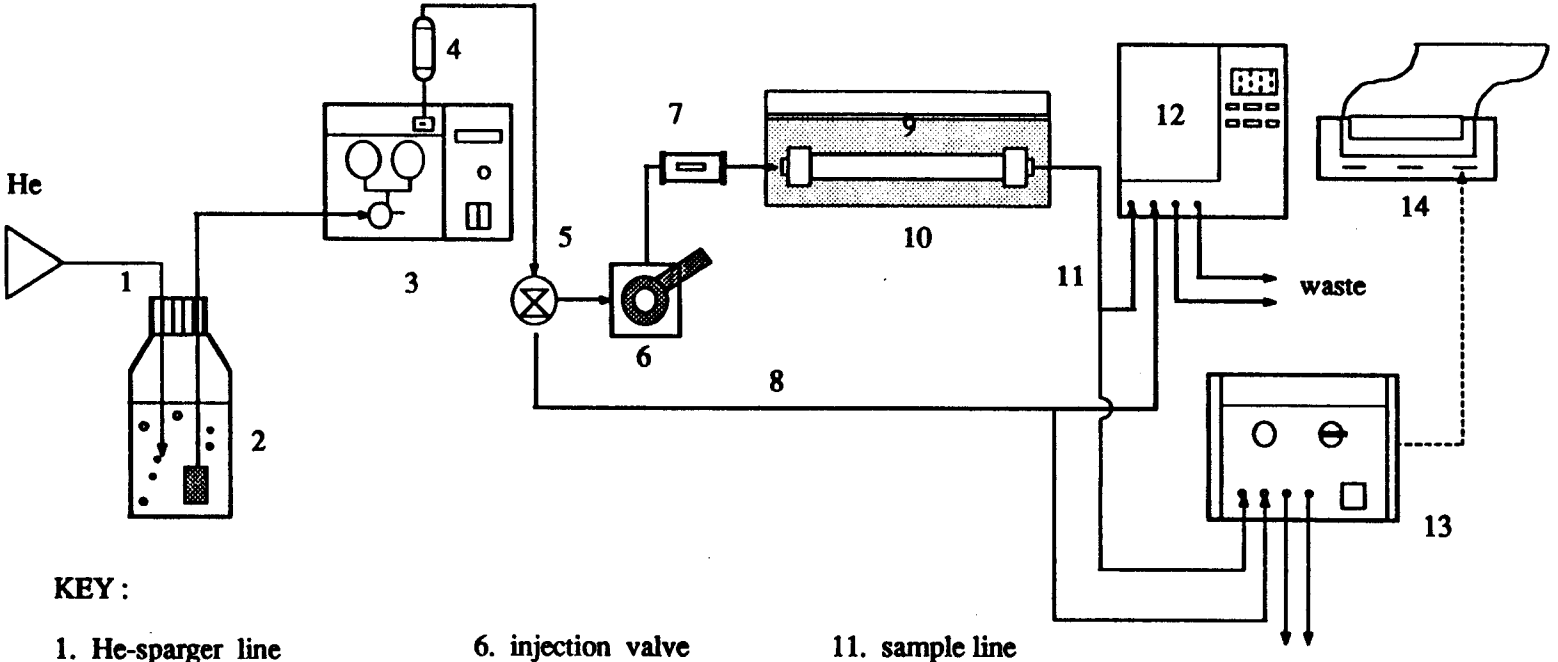
the desired speed by the impeller. The liquid phase was sampled at desired time intervals: 1 hour intervals for the first 10 hours, 2 hour intervals from 10 hours to 16 hours and a final sample was taken at 24 hours. About 0.5 mL of the liquid phase was sampled at each time. The experimental process parameters are shown in Table 3.1.

The liquid phase reaction samples were prepared for analysis. Each sample from the reactor was weighed to precision of 0.1 mg. To this sample, 6 mL of a solution containing a known amount of butyric acid (internal standard for organic acid analysis) and a known amount of myo-inositol (internal standard for sugar analysis) were added and mixed throughly. This diluted sample containing the chromatography standards was then filtered with 0.45 μm membrane filter and stored in a dark freezer.

3.4. High performance liquid chromatography

The reaction mixture components and compositions were analyzed by High Performance Liquid Chromatography, HPLC. The HPLC system consists of a Waters 501 isocratic solvent pump, an Eldex column oven, a 20 μL Rheodyne 725 zero dead-volume injector valve, an Altex 156 refractive index (RI) detector a Waters 484 variable wavelength UV/VIS detector. Each detector was interfaced to a Beckman 427 integrator and IBM PC/XT computer for on-line data acquisition. The HPLC system is schematically shown in Figure 3.3.

HPLC SCHEMATIC



KEY :

1. He-sparger line
2. solvent bottle
3. 2-stage solvent pump
4. in-line filter
5. prime/purge valve
6. injection valve
7. guard column
8. solvent reference line
9. column
10. column oven
11. sample line
12. UV/VIS detector
13. RI detector
14. data acquisition system

Figure 3.3 High Performance Liquid Chromatography.

Unreacted sugars and oxygenated hydrocarbons are analyzed separately. Sugars were separated on a BIO-RAD HPX 87-P HPLC column at 85°C. The mobile phase was degassed HPLC grade water at 0.6 mL/min. The effluent sugars were determined by an RI detector.

Organic acids were separated on a BIO-RAD HPX 87-H HPLC column at 65°C. The mobile phase was degassed 0.005 M H_2SO_4 solution at 0.6 mL/min. The UV/VIS detector was used to monitor the effluent compounds. Most analyses were conducted at 210 nm or 270 nm. The optimum wavelengths (λ_{max}) of HMF, levulinic acid, and formic acid are 284, 270, and 205 respectively. The extinction coefficient (ϵ) at the optimum wave length for HMF, levulinic acid, and formic acid are 17783, 25.12, and 44.67 respectively.

The HPLC was calibrated prior to reaction sample analysis. Briefly, various concentrations of standard compounds were mixed with the internal standard. Butyric acid was the internal standard for organic acid analysis and myo-inositol was the internal standard for sugar analysis. The standard solution was analyzed by HPLC with a suitable column and detector. The chromatogram peak area of the interested component was determined and the response factor, R_F, (μV.sec/μg) was obtained by a least-squares fit of concentration versus peak area data for each component.

Representative HPLC chromatograms of standard sugar and oxygenated hydrocarbon solutions are given in Figure 3.4 to 3.6. An HPLC chromatogram of a standard sugar mix

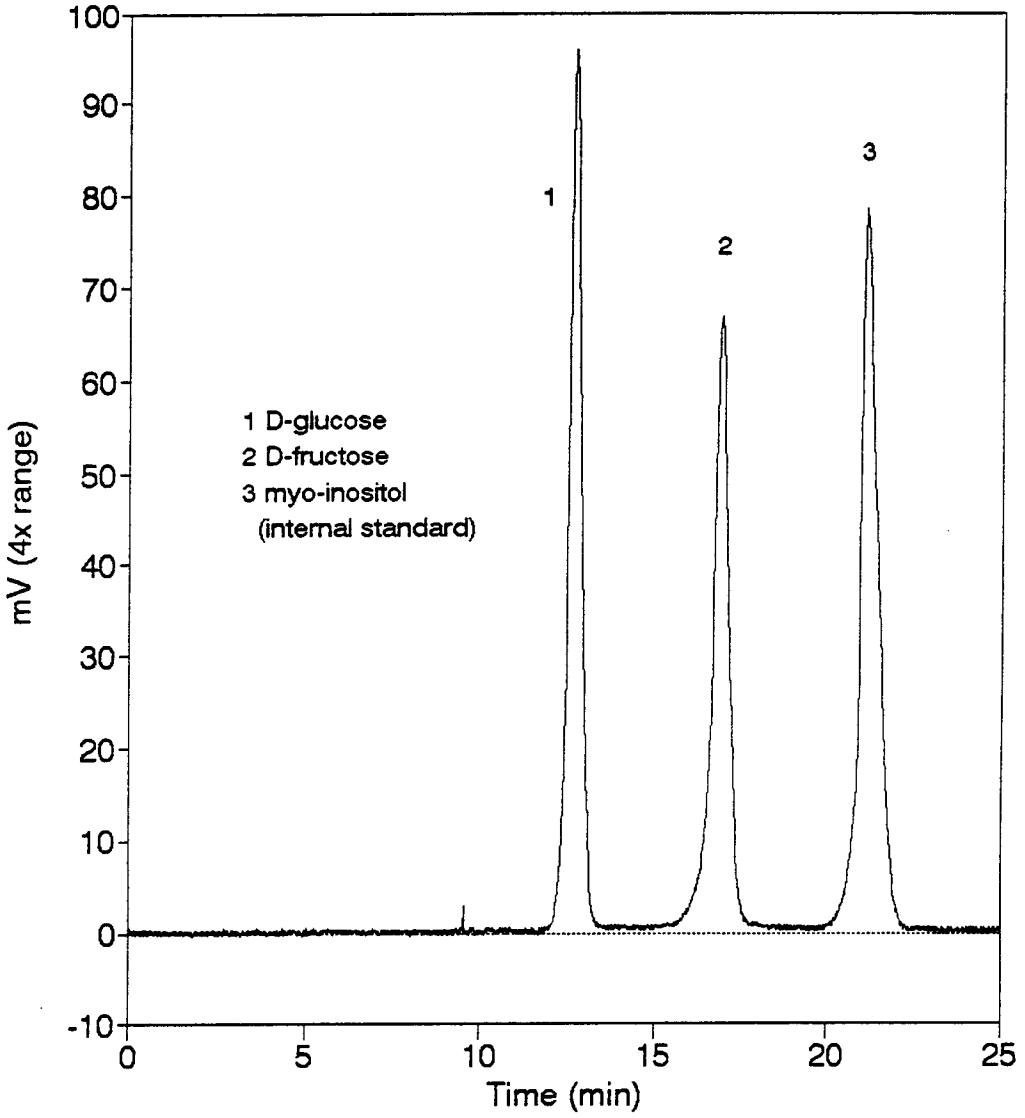


Figure 3.4 HPLC chromatogram of standard sugars using HPX 87-P column and RI detector.

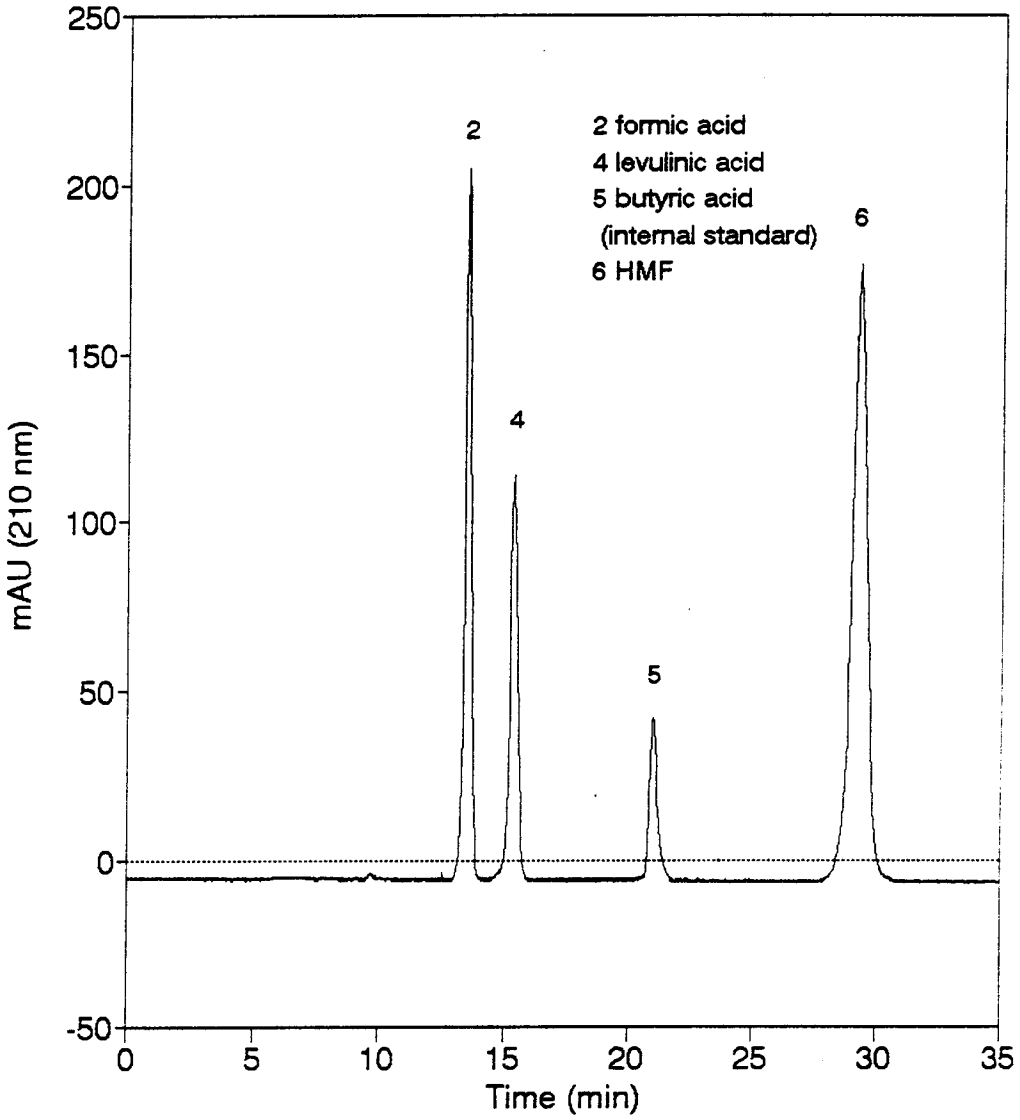


Figure 3.5 HPLC chromatogram of standard oxygenated hydrocarbons using HPX 87-H column and UV/VIS detector at 210 nm.

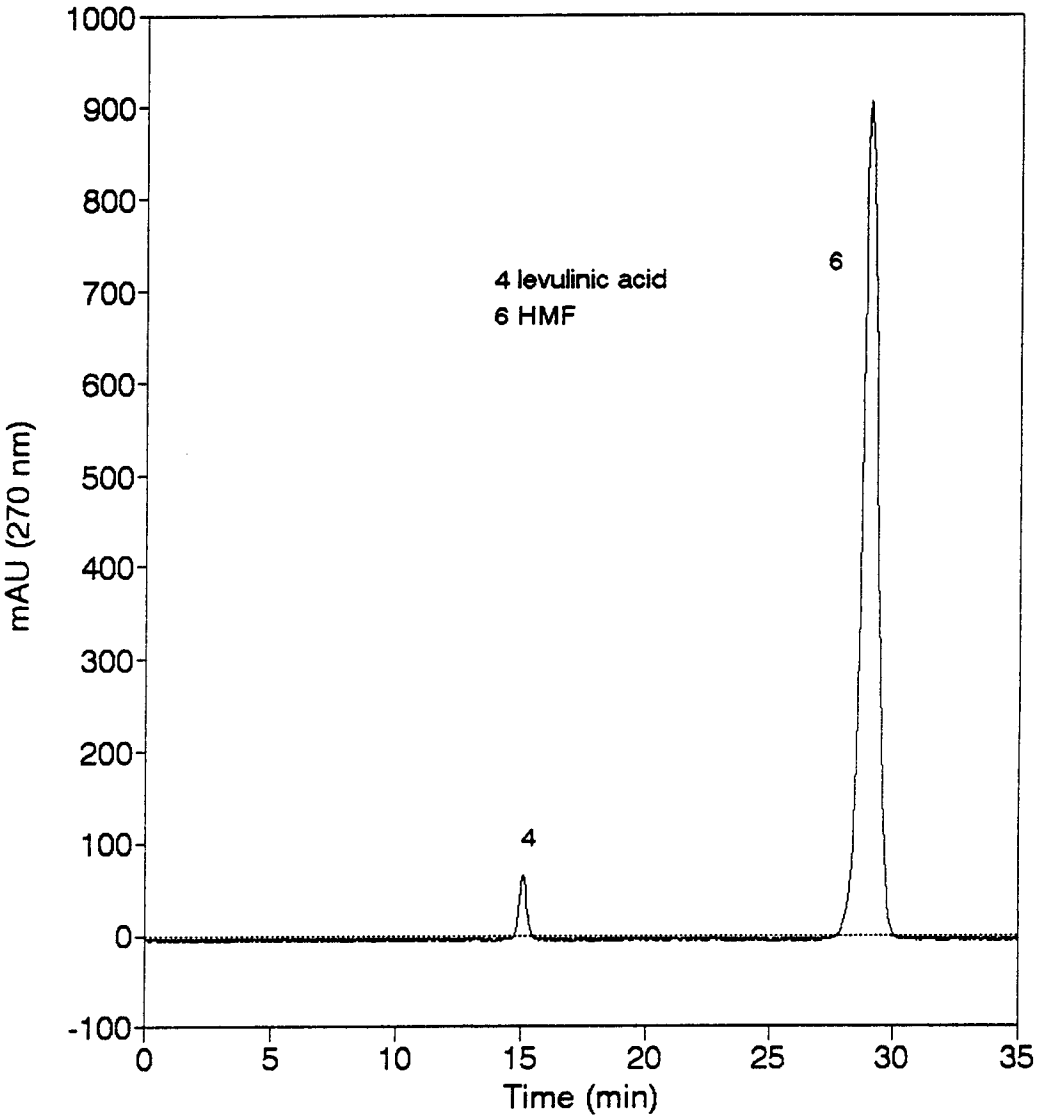


Figure 3.6 HPLC chromatogram of standard oxygenated hydrocarbons using HPX 87-H column and UV/VIS detector at 270 nm.

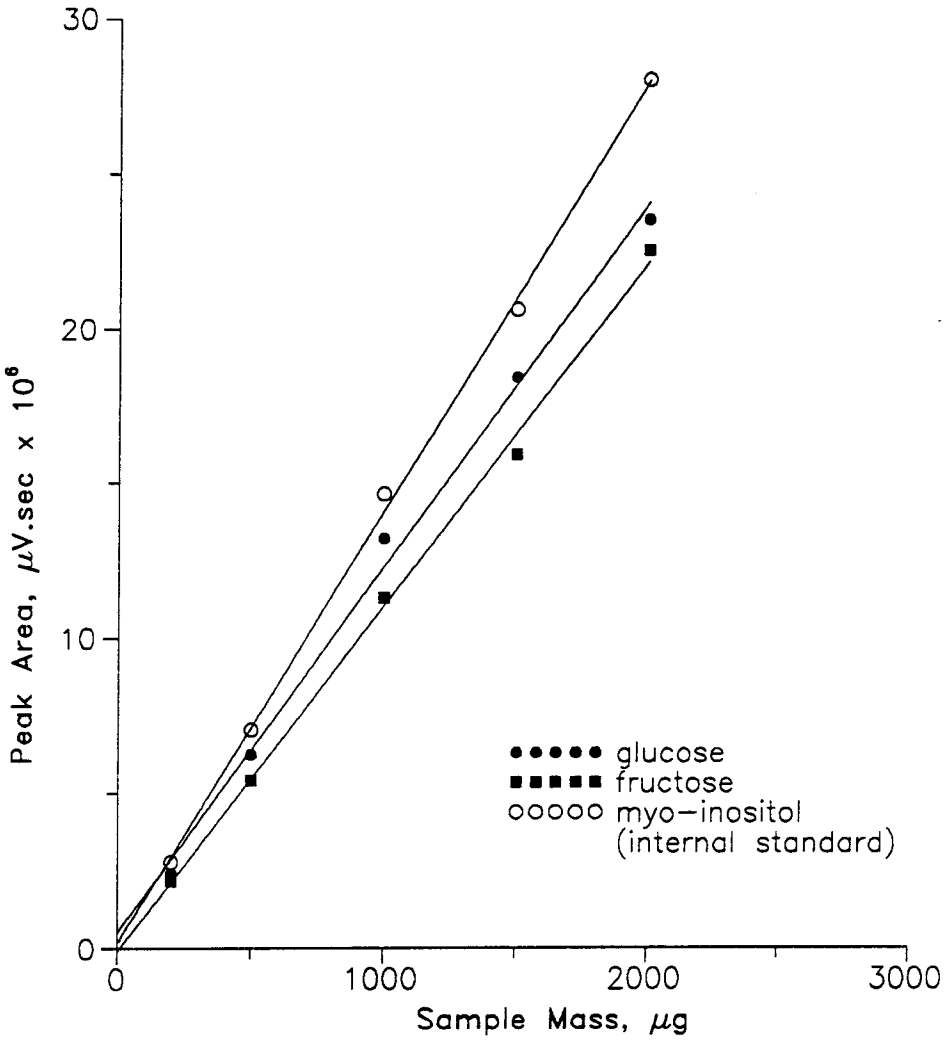


Figure 3.7 HPLC calibration of HPX 87-P column with RI detector at 4x range.

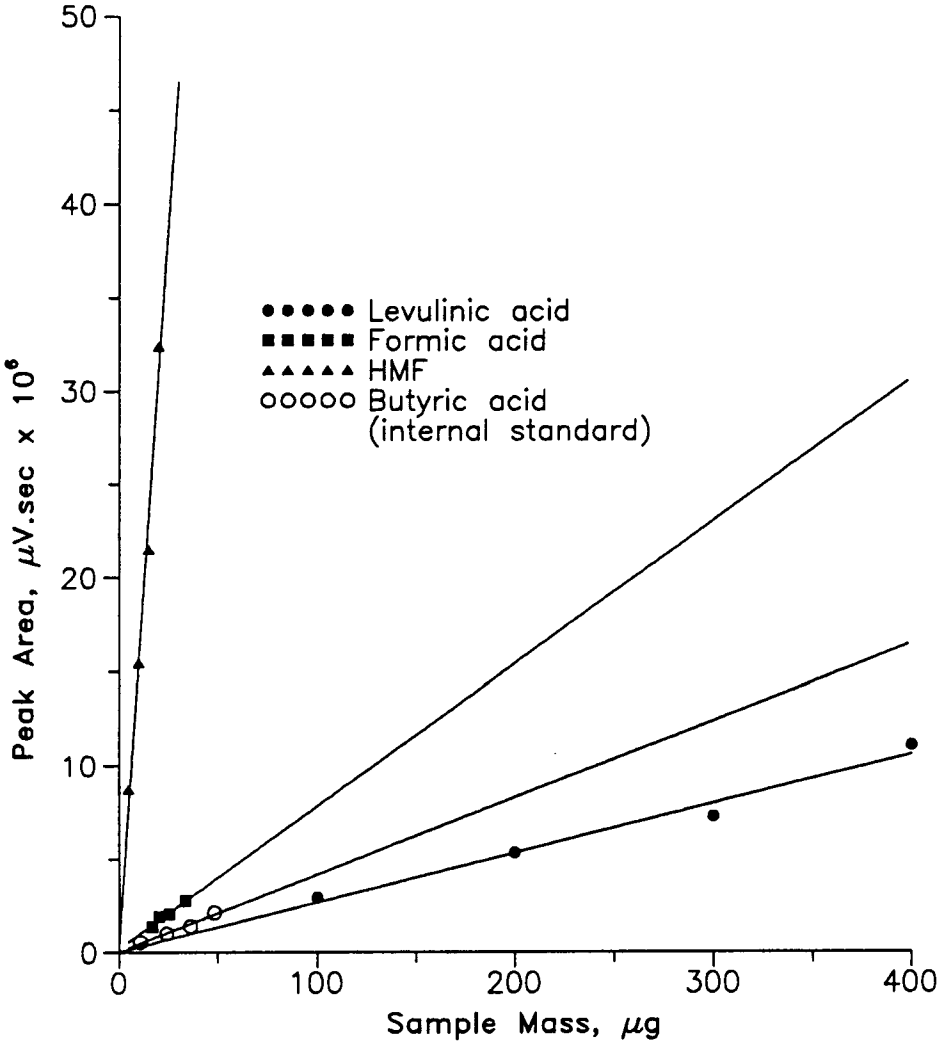


Figure 3.8 HPLC calibration of HPX 87-H with UV/VIS detector at 210 nm.

Table 3.2 HPLC response factors of sugars.

Sugar analysis

Column: BIO-RAD HPX 87-P

Temperature: 85°C

Eluant: HPLC grade water

Eluant flowrate: 0.6 mL/min

RI detector range: 4x

Component	Response factor, R_F (μV.sec/μg)
(D)-glucose	12092.59 ± 242.75
(D)-fructose	11029.00 ± 151.91
myo-inositol	13981.23 ± 134.97

Table 3.3 HPLC response factors, R_F of oxygenated hydrocarbons.

Oxygenated hydrocarbons analysis

Column: BIO RAD HPX 87-H

Temperature: 65°C

Eluant: 0.005 M H_2SO_4

Eluant flowrate: 0.6 mL/min

UV/VIS detector wavelength: 210 nm

Component	Response factor, R_F (μV.sec/μg)
levulinic acid	26322.91 ± 976.52
formic acid	83391.51 ± 2828.78
α-angelicalactone	45706.22 ± 2795.59
HMF	1547573.08 ± 56377.46
butyric acid	44722.31 ± 1693.49

(20 μL of 10.01 mg/mL glucose, 10.01 mg/mL fructose, and 10.50 mg/mL myo-inositol internal as standard) is presented in Figure 3.4. An HPLC chromatogram of a standard oxygenated hydrocarbons mix (20 μL of 0.05 mg/mL HMF, 10.02 mg/mL levulinic acid, 5.03 mg/mL formic acid, and 5.12 mg/mL butyric acid as internal standard) at 210 nm is presented Figure 3.5. For comparison, an HPLC chromatogram of the same oxygenated hydrocarbon standards at 270 nm is presented in Figure 3.6.

Analyses at 210 nm and 270 nm are significantly different. At 210 nm, all oxygenated hydrocarbons were detected satisfactorily. The response of levulinic acid relative to HMF at 210 nm is very low. The ratio of response, when compensated per unit mass of each component, was 58.79 HMF/levulinic acid. At 270 nm, formic acid and butyric acid were not detected, but levulinic acid and HMF were detected. However, the ratio of response at 270 was 319.56 HMF/levulinic acid.

All HPLC calibration data for both sugars and organic acid analyses are shown in Appendix C. Table 3.2 summarizes the response factor of each component. Figure 3.7 and 3.8 show the calibration curves.

3.5. Reaction sample analysis

After thawing reaction sample solution, 20 μL of the prepared sample was injected into the HPLC and analyzed.

Sugars and oxygenated hydrocarbons were analyzed separately as detailed in section 3.4. Peak area data from the integrator and the computer were used to estimated the amount of organic acids and sugars in the reaction sample, based on the response factors given in Tables 3.2, and 3.3. Equations (D-1), (D-2), (D-3), (D-4), (D-5) and (D-15) in Appendix D were used to calculate the conversion of glucose and the product yields. Representative HPLC chromatograms of the liquid reaction sample are given in Figures 3.9 to 3.11. Figure 3.9 shows the HPLC chromatogram of sugars in the reaction sample obtained after 10 hours under the following reaction conditions: 0.12 g glucose/g solution and 2:1 glucose:H-Y zeolite at 130°C and 300 rpm.

Figure 3.10 shows the HPLC chromatogram at 210 nm for oxygenated hydrocarbons for the reaction sample given in Figure 3.10. Chromatogram peaks, detected and quantified at 210 nm, were levulinic acid, formic acid, HMF, and butyric acid. Five small additional peaks were not identified. All peaks were clearly detected except levulinic acid, which showed a low response at 210 nm. Levulinic acid was assumed to have a higher response at the optimum wavelength of 270 nm. The chromatogram at 270 nm is shown in Figure 3.11. It was found that although the levulinic acid gave a slightly high response at 270 nm relative to 210 nm, the response was still very low. Formic acid and HMF also gave the higher response at 270 nm relative to 210 nm. Unfortunately, butyric acid, the internal standard, was not detected at

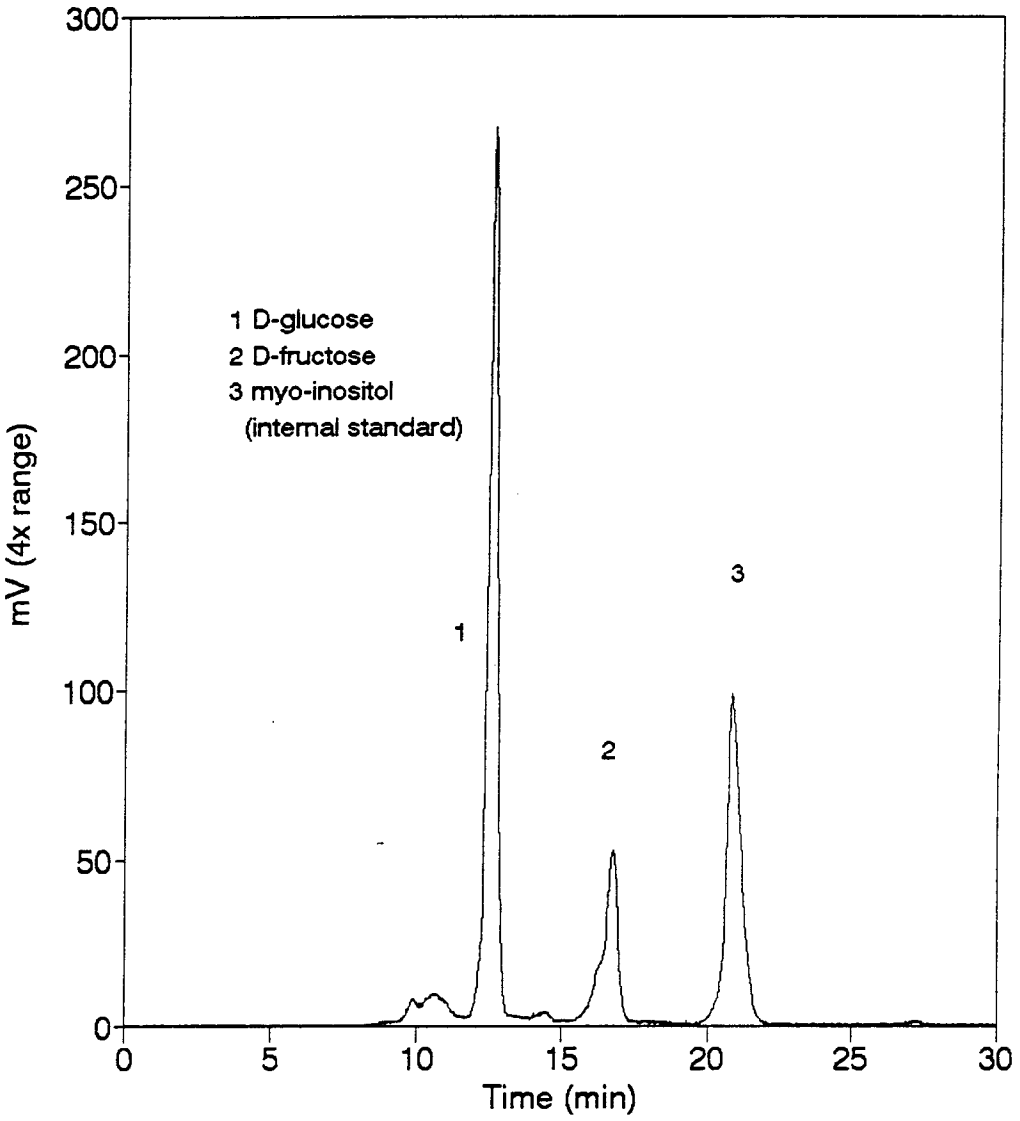


Figure 3.9 Sample HPLC chromatogram of sugar analysis of reaction sample using HPX 87-P column and RI detector.

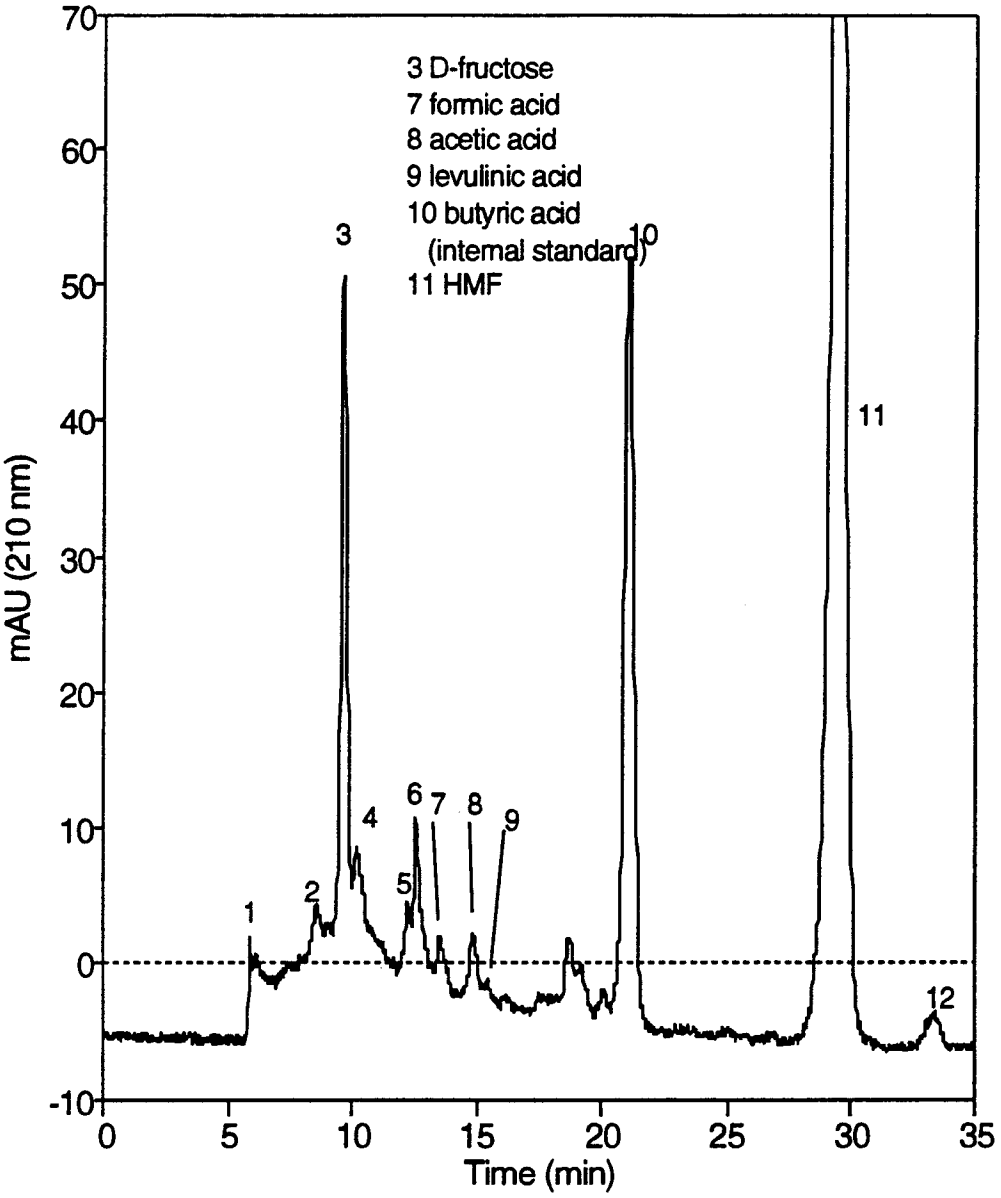


Figure 3.10 Sample HPLC chromatogram of oxygenated hydrocarbon analysis of reaction sample using HPX 87-P column and UV/VIS detector at 210 nm.

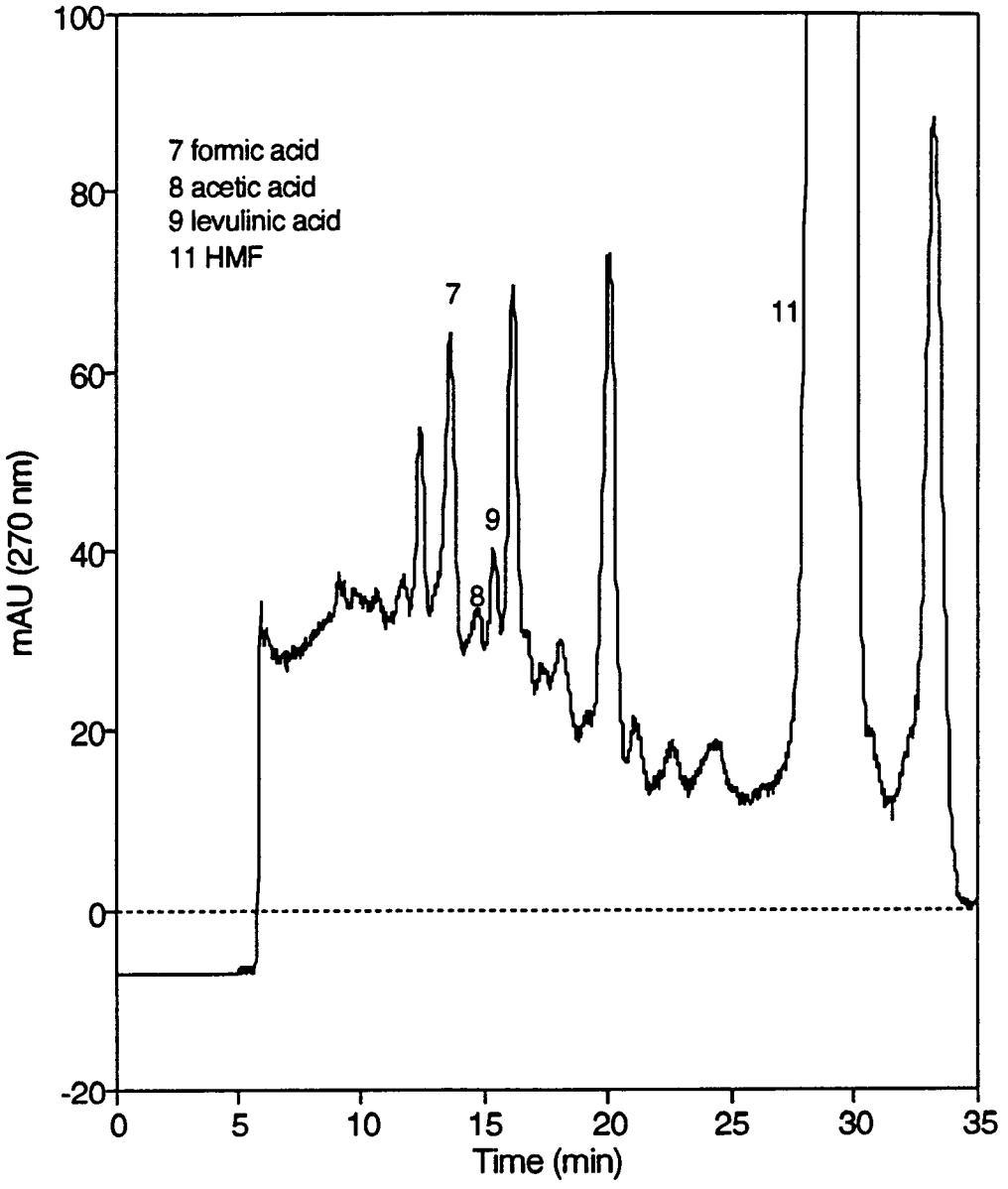


Figure 3.11 Sample HPLC chromatogram of oxygenated hydrocarbon analysis of reaction sample using HPX 87-P column and UV/VIS detector at 270 nm.

Table 3.4 HPLC chromatogram peak of oxygenated hydrocarbon analysis summary.

Peak #	Component	Retention time (min)	λ_{max} (nm)
1		6.6	190
2		8.6	190
3	D-fructose	9.6	na
4		10.1	200
5		12.3	280
6		12.8	280
7	Formic acid	13.5	205
8	Acetic acid	14.7	na
9	Levulinic acid	15.3	270
10	Butyric acid	21.0	208
11	HMF	29.3	284
12		33.1	280

Note : Peaks with blank name are unidentified components and maximum UV wavelength are determined from the detection of the same sample with various UV/VIS detector wavelengths. (na = not available)

270 nm. Also several of the unknown peaks detected at 210 nm were not detected at 270 nm.

3.6. Total acid content, pH, and density estimation

At the end of reaction, the reactor contents were vacuum filtered. The filtrate was a clear yellow to dark brown solution, depending on the reaction conditions. The insoluble fraction contained a dark brown solid residue dispersed on the catalyst powder. The acid content, pH, and density of the filtrate were determined by standard methods. The acid content of reaction mixture was measured by titration with 0.1 N NaOH. The acid content was calculated by equations (D-10) and (D-11) in Appendix D. A Corning pH meter with combination electrode measured the pH of the reaction mixture. The density of the liquid reaction mixture was determined by weight on volume.

3.7. Insoluble residue analysis

A vacuum desiccator was used for drying the insoluble reaction products and catalyst. The solid phase from filtering was dried in a vacuum desiccator for approximately 20 days or until the weight was constant. The insoluble solid residue on the catalyst was determined by washing, refiltering and drying of a small portion (about 1 g) of dried solid phase. The amount of insoluble residue on

catalyst was estimated using equations (D-12), (D-12), (D-13) and (D-14) of Appendix D.

The results in the next chapter were obtained from one experiment for each parameter study. Conversion and product yields include the error caused by the deviation of response factor estimation. The percent deviation of quantity for each component are the following:

Component	% Error
Glucose	± 1.01
Fructose	± 0.35
Levulinic acid	± 0.61
Formic acid	± 0.44
HMF	± 0.48

Chapter 4

EXPERIMENTAL RESULTS

The reaction of (D)-glucose solution with H-Y zeolite catalyst powder was conducted in a 300 mL well-mixed batch reactor. The results are splitted into two sections according to the (D)-glucose concentration introduced to the reaction. Each section includes parameter studies affecting the glucose conversion, product yield (formic acid, levulinic acid, and HMF), acid content, pH, and insoluble residue.

4.1. Low (D)-glucose concentration reaction

An initial glucose concentration of 0.12 g glucose per g solution (20 g glucose in 150 g distilled water) was introduced into reactor at various temperatures (110°C to 130°C) and H-Y zeolite powder loadings (10:1 to 1:1 glucose:H-Y zeolite by weight) at a constant mixing speed of 300 rpm. Mixing speeds of 300 rpm and higher did not significantly affect the reaction rate, implying that the external mass transfer resistances were minimized. Section 4.2.2. details experiments conducted at different mixing speeds.

4.1.1. Temperature influence

The reaction was studied at temperatures ranging from 110°C to 130°C. The H-Y zeolite catalyst loading was kept at a constant 2 g glucose per 1 g catalyst. Tabular conversion and product yield versus time data at these temperature are given in Tables E-7, E-9, E-10, and E-13 of Appendix E.

The glucose conversion versus time profiles are presented as Figure 4.1 at temperature of 110°C to 130°C. The maximum glucose conversion and glucose conversion rate increased as the reaction temperature increased. After a 24 hour reaction time, the maximum glucose conversions are 34% at reaction temperature 110°C, 62% at reaction temperature 120°C, and 83% at reaction temperature 130°C.

A control reaction with no catalyst showed that the decomposition of glucose still occurred at 130°C, but not at 110°C. In other words, higher temperature caused more glucose decomposition. However, compared to the conversion with H-Y zeolite, the decomposition was still fairly low.

Product yield profiles are shown in Figures 4.2, 4.3, 4.4, and 4.5 for formic acid, levulinic acid, HMF and fructose respectively. The product yield versus reaction time profiles increased as temperature increased, and formic acid yields are higher than levulinic acid and HMF yields. After 24 hour reaction time, the yields are given as:

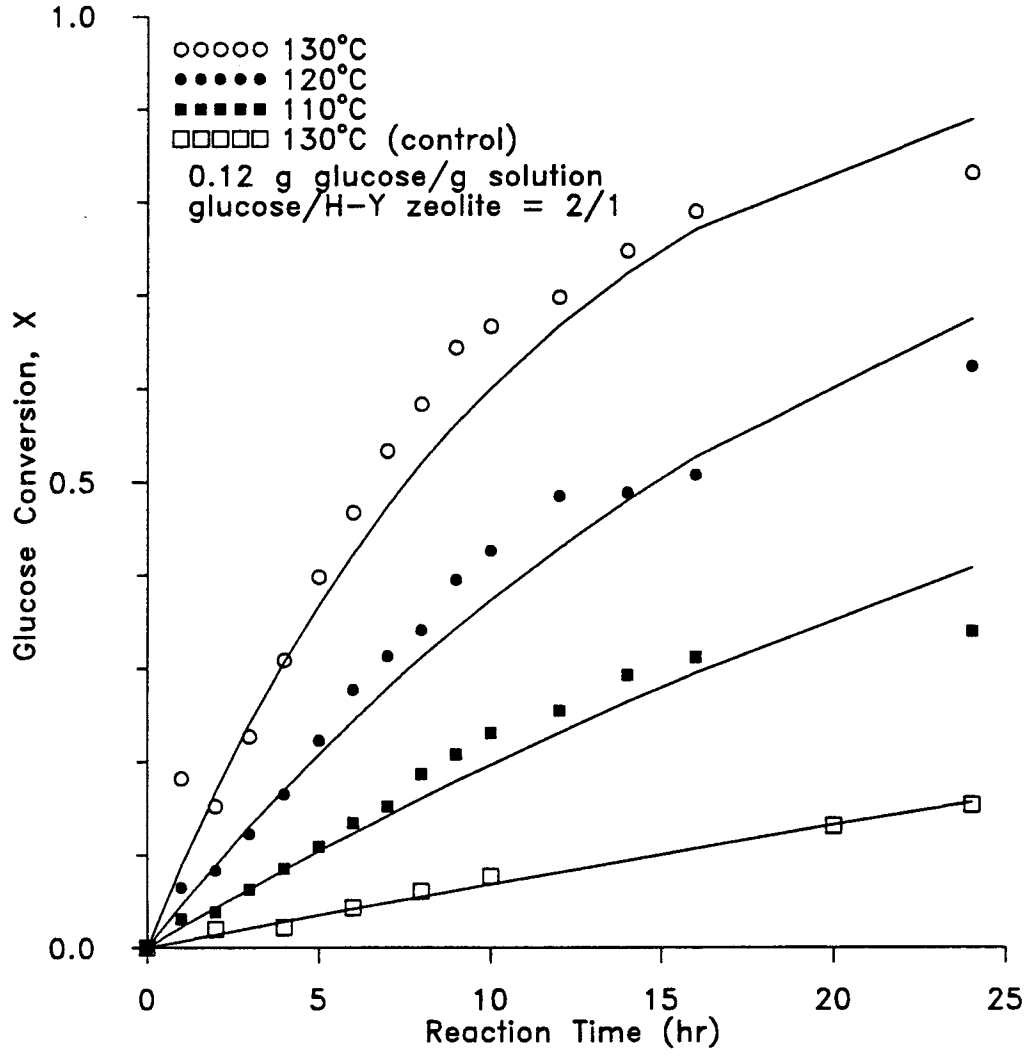


Figure 4.1 (D)-glucose conversion versus reaction time for 0.12 g glucose/g solution and 2:1 catalyst loading at 300 rpm from 110°C to 130°C.

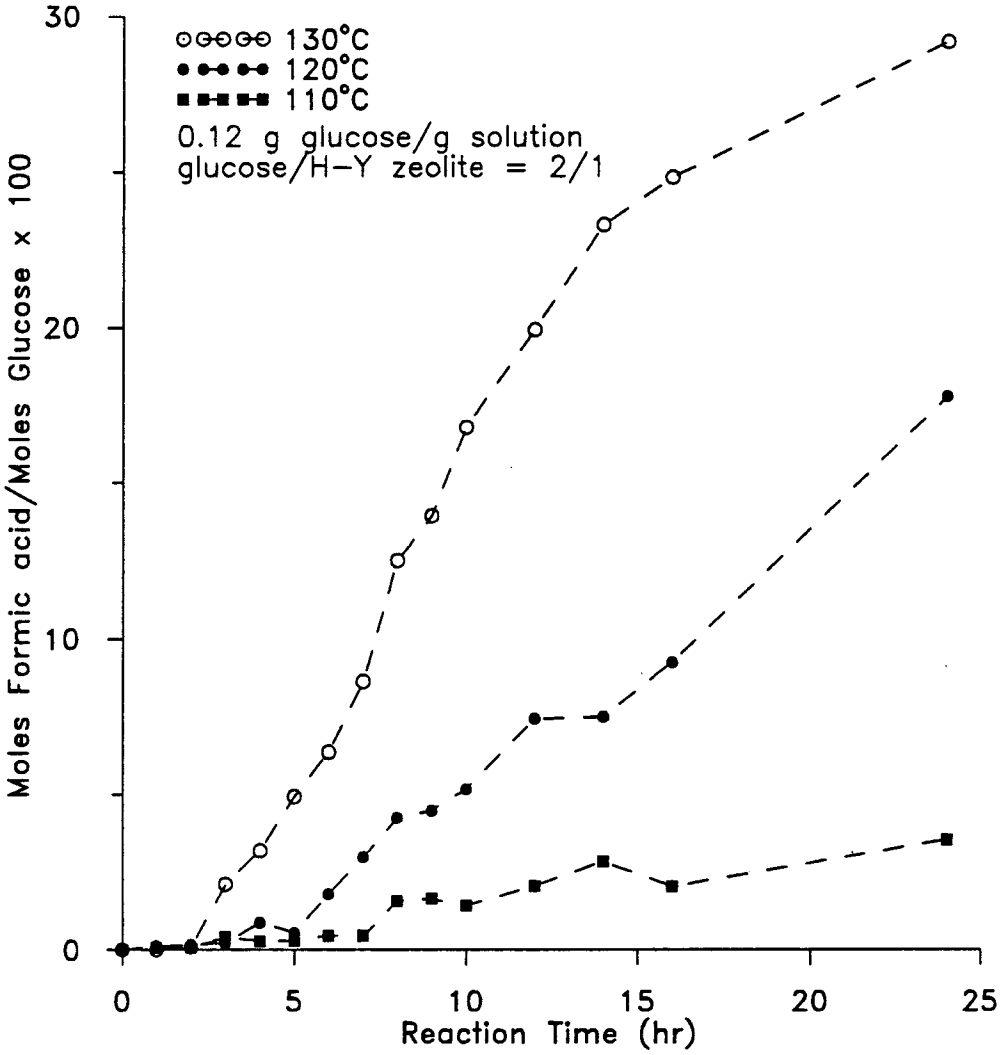


Figure 4.2 Formic acid yield versus reaction time for 0.12 g glucose/g solution and 2:1 catalyst loading at 300 rpm from 110°C to 130°C.

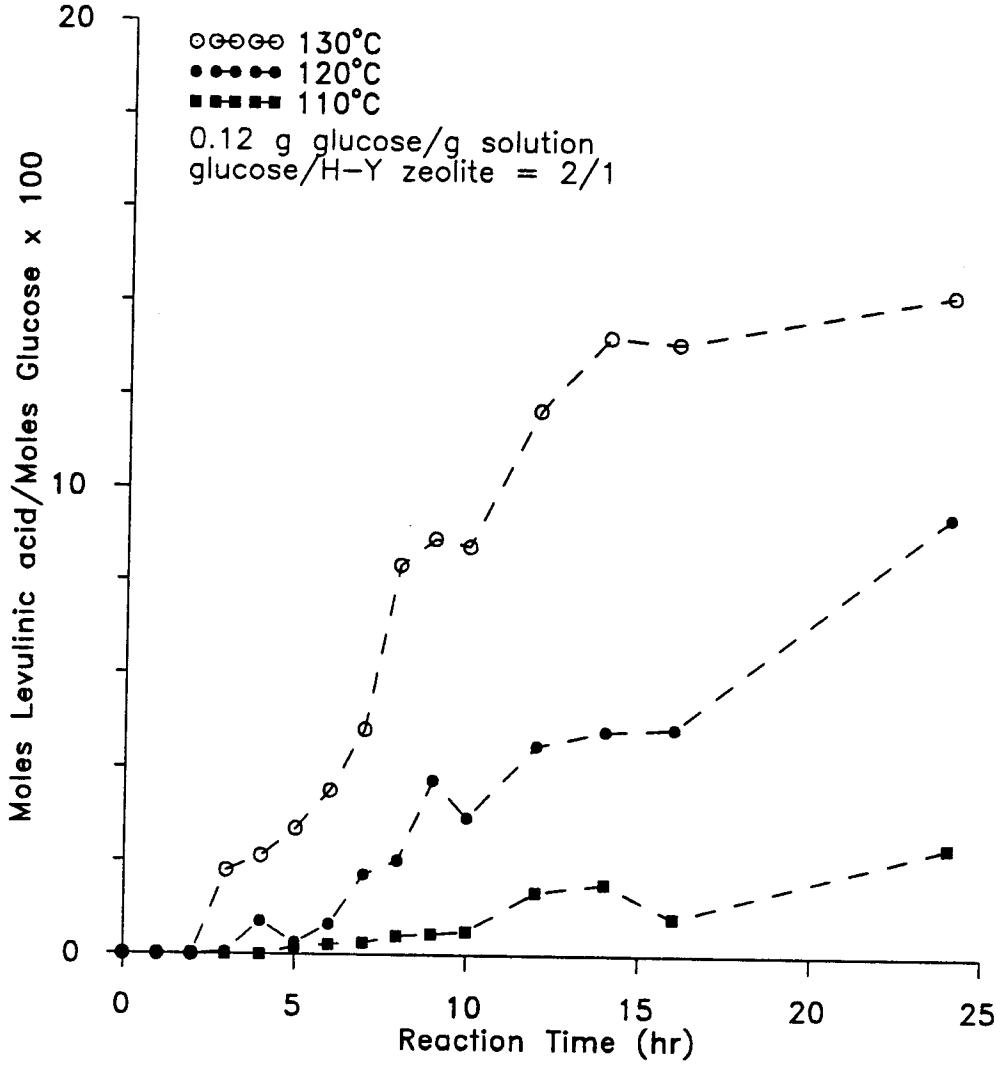


Figure 4.3 Levulinic acid yield versus reaction time for 0.12 g glucose/g solution and 2:1 catalyst loading at 300 rpm from 110°C to 130°C.

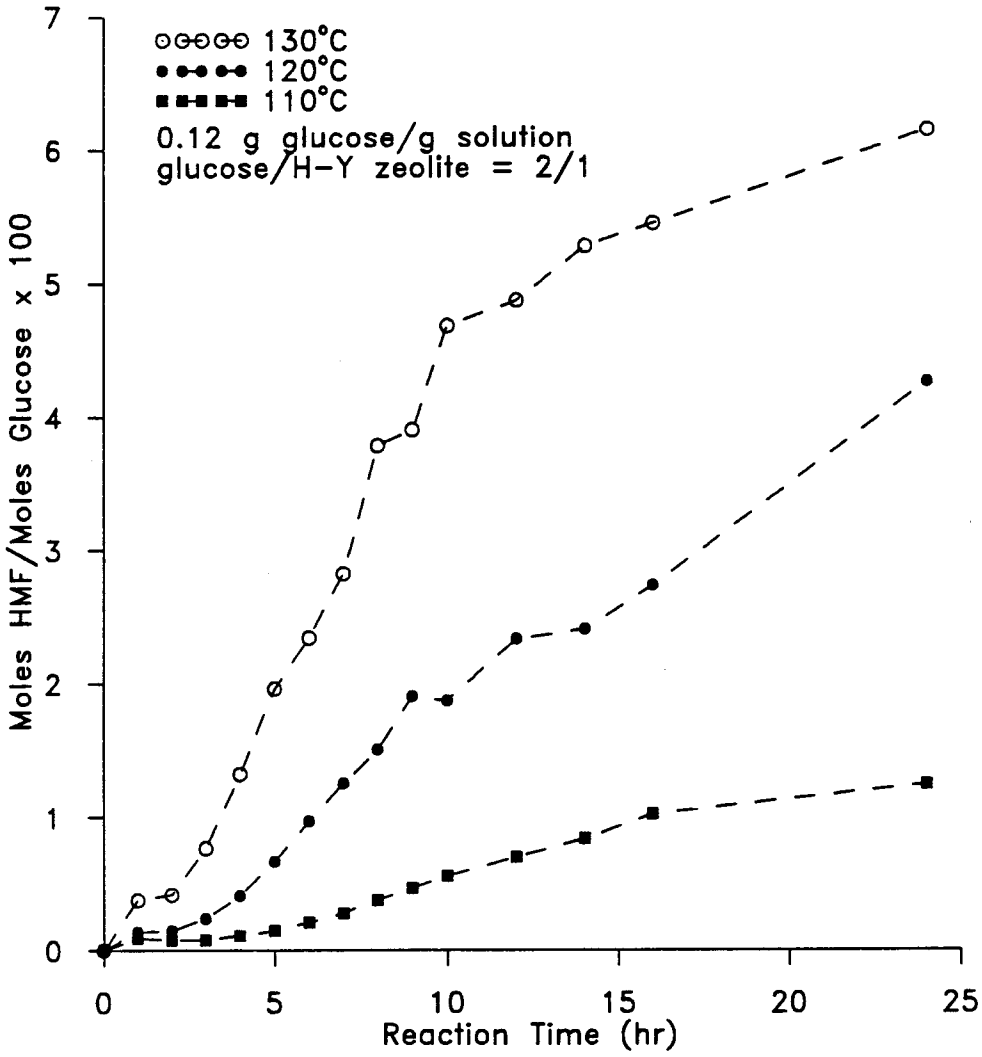


Figure 4.4 HMF yield versus reaction time for 0.12 g glucose/g solution and 2:1 catalyst loading at 300 rpm from 110°C to 130°C.

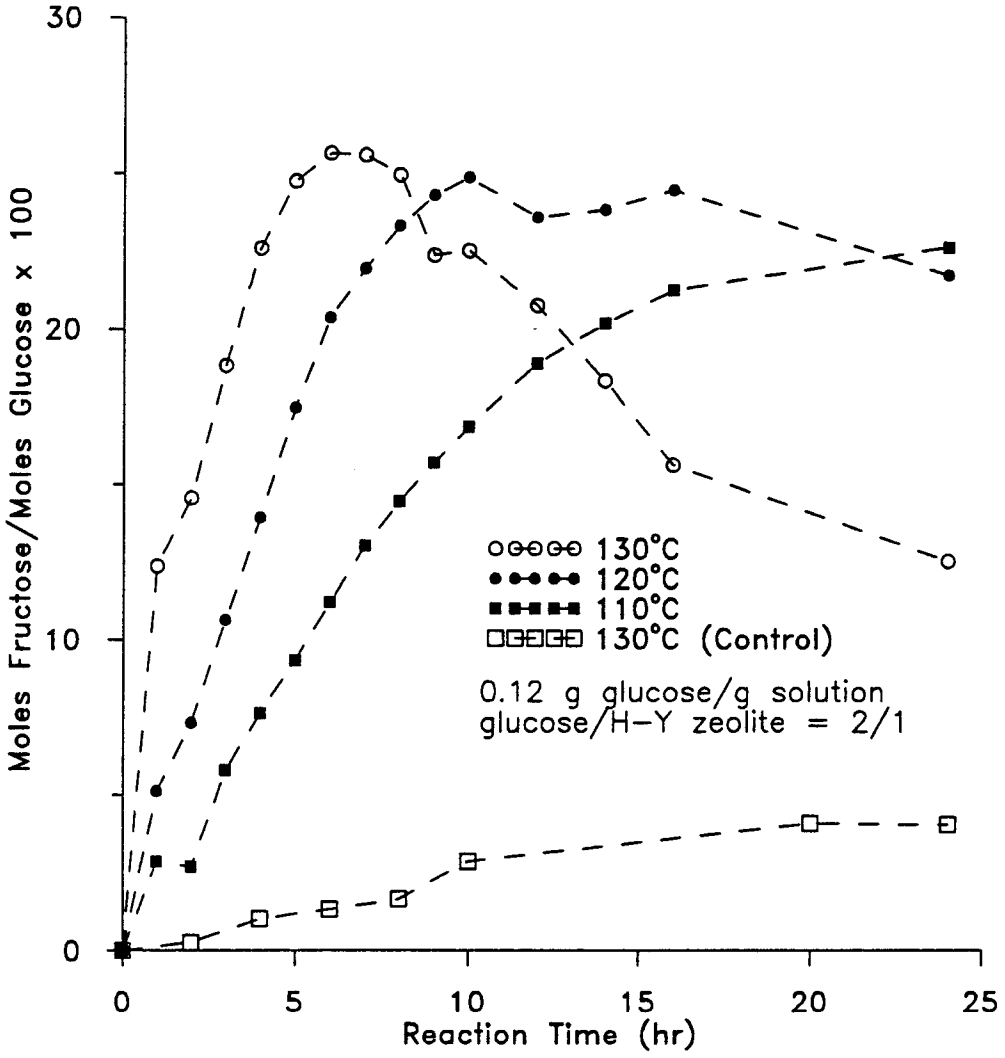


Figure 4.5 (D)-fructose yield versus reaction time for 0.12 g glucose/g solution and 2:1 catalyst loading at 300 rpm from 110°C to 130°C.

temperature	formic acid	levulinic acid	HMF
110°C	3.55%	2.34%	1.24%
120°C	17.74%	9.41%	4.26%
130°C	29.16%	14.17%	6.16%

Isomerized sugar formation needs to be described separately from acid-catalyzed dehydration products. Fructose was produced by the Y-zeolite catalyzed isomerization of glucose. As shown in Figure 4.5, the maximum fructose yield increased as the temperature increased. However, in all cases, after the maximum fructose yield was achieved, the fructose yield decreased, indicating fructose was being reacted. At 110°C the maximum fructose yield was 22.63% after 24 hours. At 120°C, the maximum fructose yield was 24.84% after 10 hours and 21.73% after 24 hours. At 130°C, the maximum fructose yield was 25.63% after 6 hours and 12.51% after 24 hours. The control experiment at 130°C yielded the maximum fructose of 4.04% after 24 hours.

Acid content, pH, and insoluble residue on catalyst were measured after 24 hours as shown in Figures 4.6, 4.7, and 4.8 respectively. Figure 4.6 shows the acid content estimated by titration and acid yield summation from HPLC. The acid content increased with increasing reaction temperature. Analogously, the insoluble residue on catalyst increased with increasing temperature. The pH decreased with increasing temperature.

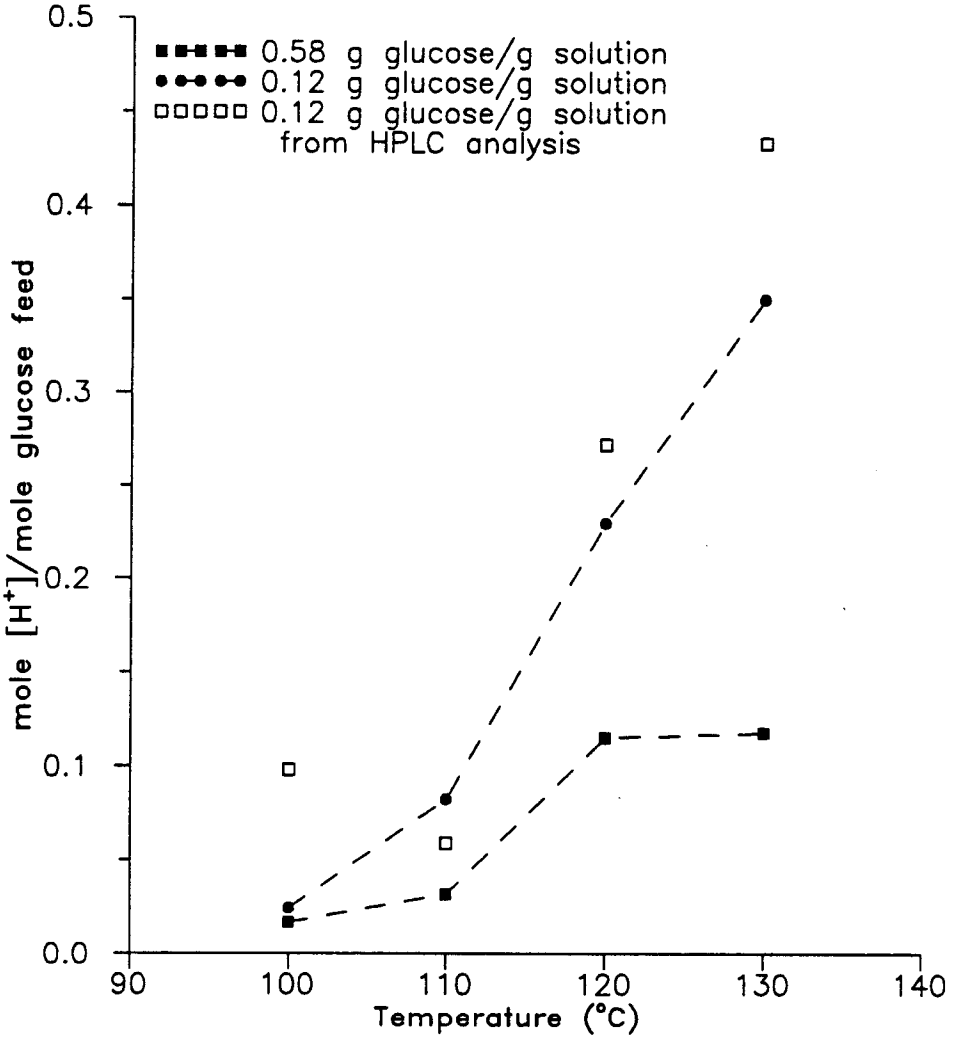


Figure 4.6 Acid content in reaction mixture for 0.12 and 0.58 g glucose/g solution.
Reaction conditions: 0.12 g glucose/g solution and 2:1 catalyst loading for 24 hour reaction, 0.58 g glucose/g solution and 10:1 catalyst loading for 10 hour reaction at 300 rpm from 100°C to 130°C.

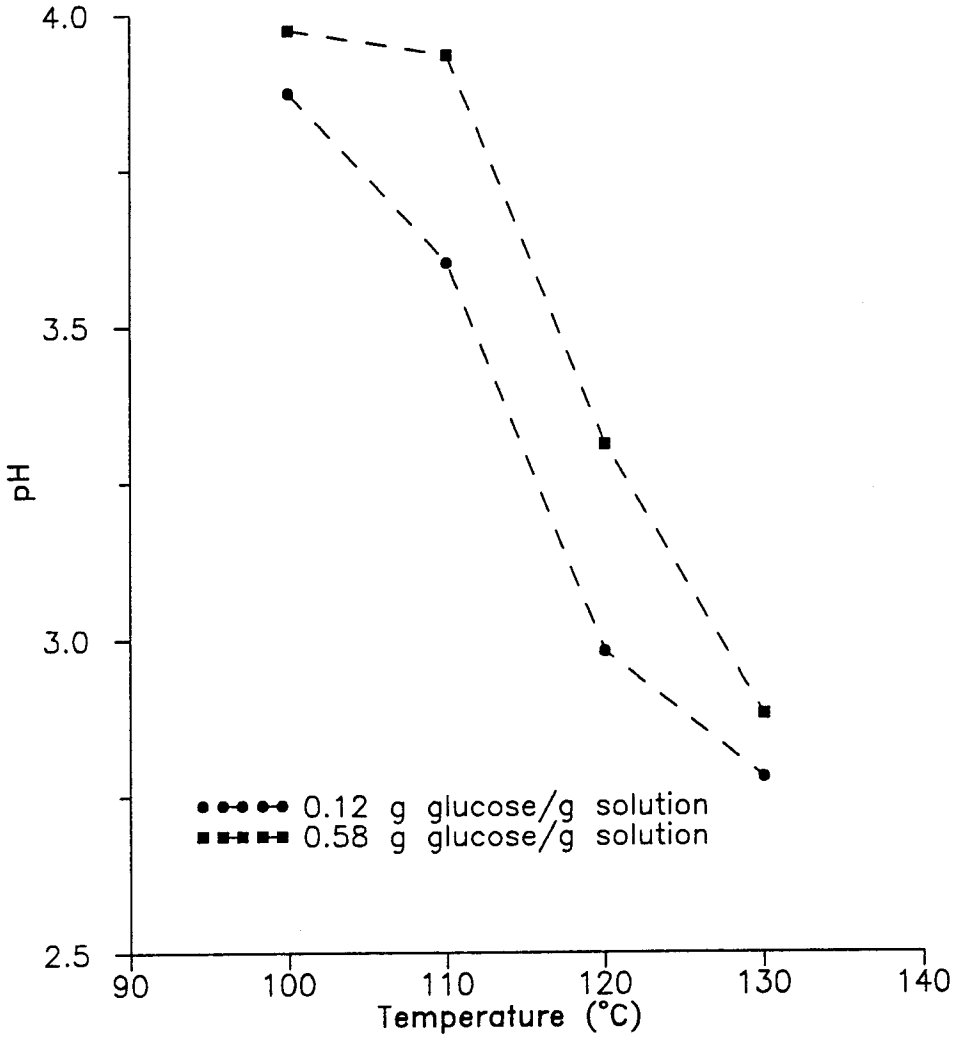


Figure 4.7 pH of reaction mixture for 0.12 and 0.58 g glucose/g solution. Reaction conditions: 0.12 g glucose/g solution and 2:1 catalyst loading for 24 hour reaction, 0.58 g glucose/g solution and 10:1 catalyst loading for 10 hour reaction at 300 rpm from 100°C to 130°C.

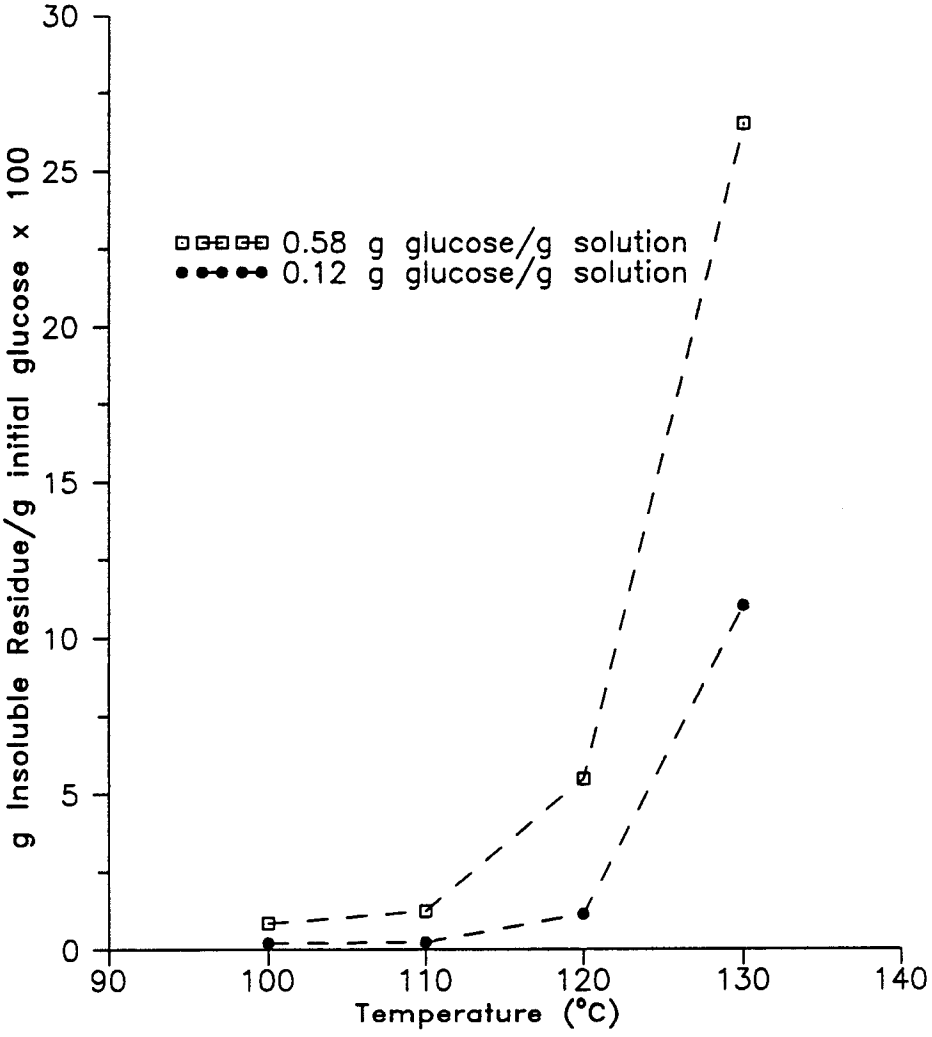


Figure 4.8 Insoluble residue on catalyst from reaction of 0.12 and 0.58 g glucose/g solution. Reaction conditions: 0.12 g glucose/g solution and 2:1 catalyst loading for 24 hour reaction, 0.58 g glucose/g solution and 10:1 catalyst loading for 10 hour reaction at 300 rpm from 100°C to 130°C.

4.1.2. H-Y zeolite loading influence

The H-Y zeolite catalyst loading, defined as glucose weight per H-Y zeolite powder weight was varied from 10:1 to 1:1. The reaction conditions were maintained at 130°C and 300 rpm mixing speed. Glucose conversion and product yield data at 10:1, 5:1, 2:1, and 1:1 catalyst loadings are given in Tables E-7, E-11, E-12, and E-14 of Appendix E.

Figure 4.9 shows the influence of catalyst loading on the glucose conversion versus time profiles. Decreasing glucose per H-Y zeolite increased the glucose conversion rate and the maximum glucose conversion. After a 24 hour reaction time, the maximum conversion are 67%, 73%, 83%, and 92% at 10:1, 5:1, 2:1, and 1:1 catalyst loadings respectively.

Formic acid yields shown in Figure 4.10 increased with decreasing catalyst loading, except at 1:1 catalyst loading At a catalyst loading of 1:1, the maximum formic acid yield was 28.01%, which is lower than the reaction at 2:1 catalyst loading. The maximum formic acid yield at 2:1 catalyst loading was 29.82%. For other catalyst loading, the maximum formic acid yields were 26.03 at 5:1 and 22.63% at 10:1 after 24 hours.

Levulinic acid yield profiles presented in Figure 4.11 show that a catalyst loading of 2:1 has a higher yield than the catalyst loading of 1:1. After 24 hours, the levulinic acid yield at a 1:1 catalyst loading is 13.39% while a 2:1

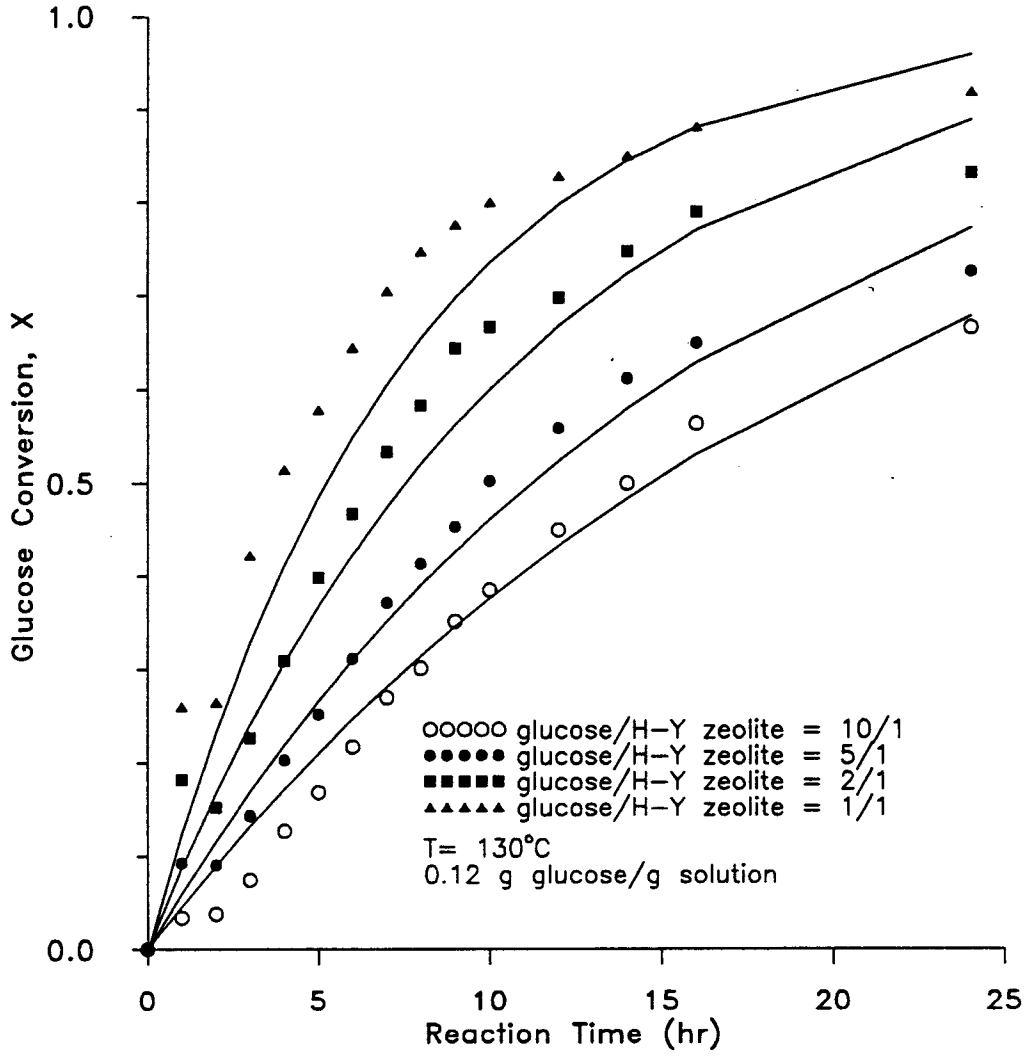


Figure 4.9 (D)-glucose conversion versus reaction time for 0.12 g glucose/g solution at 130°C and 300 rpm from 1:1 to 10:1 catalyst loadings.

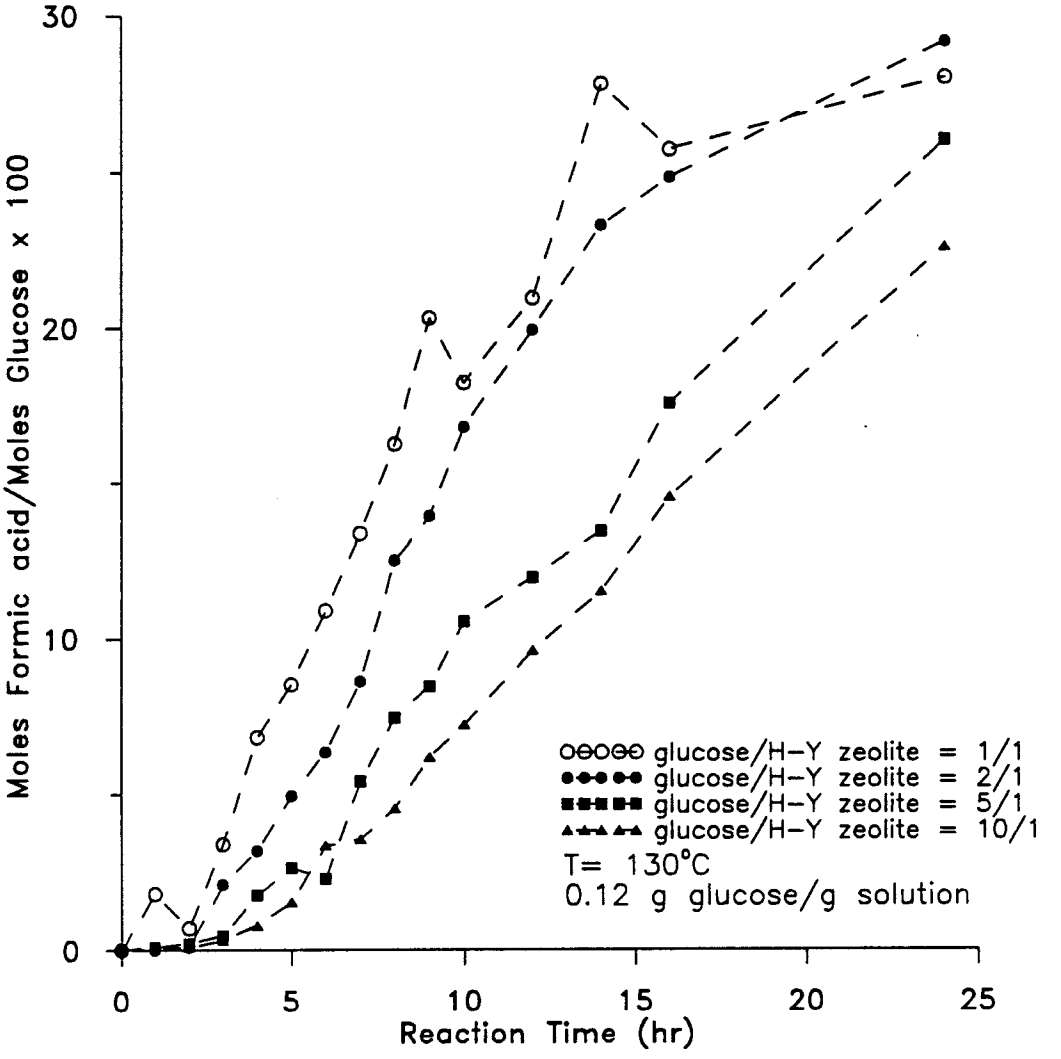


Figure 4.10 Formic acid yield versus reaction time for 0.12 g glucose/g solution at 130°C and 300 rpm from 1:1 to 10:1 catalyst loadings.

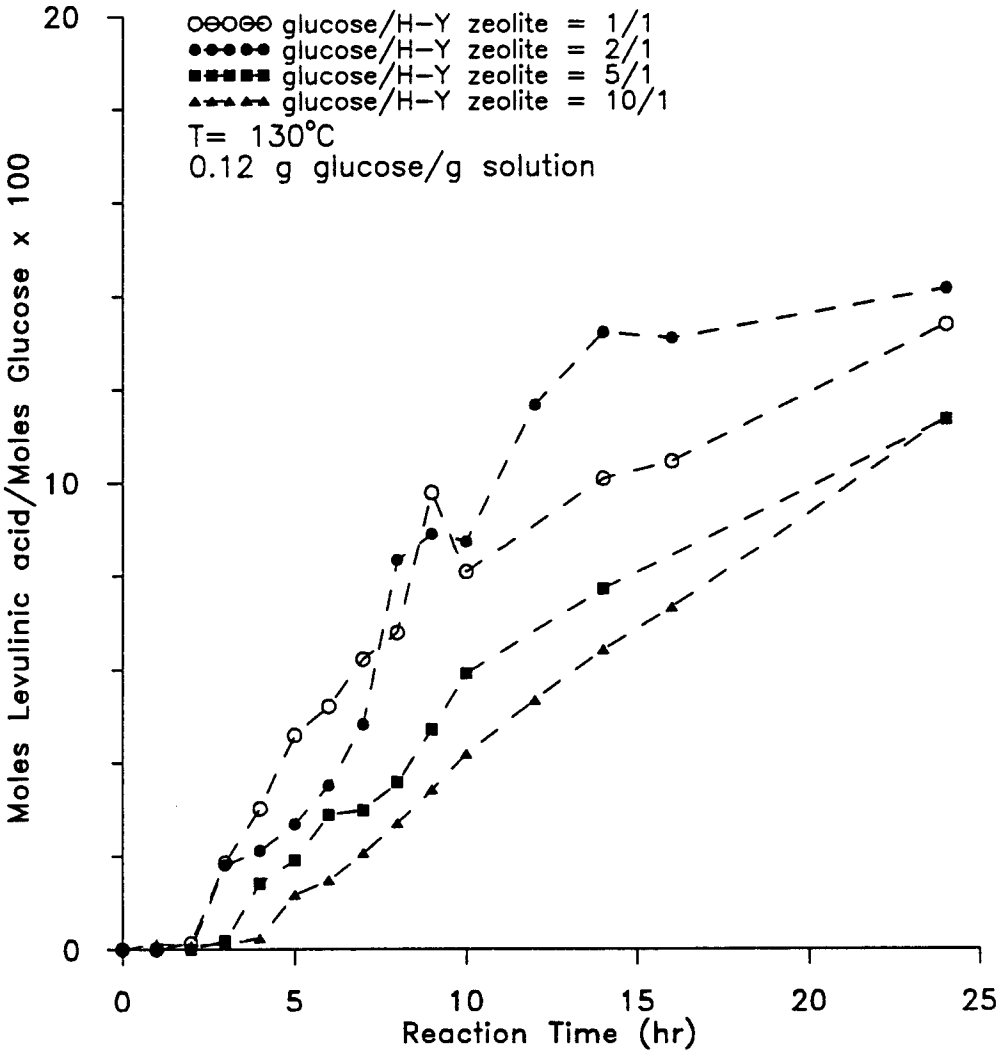


Figure 4.11 Levulinic acid yield versus reaction time for 0.12 g glucose/g solution at 130°C and 300 rpm from 1:1 to 10:1 catalyst loadings.

loading gives a higher value of 14.17%. The levulinic acid yields at catalyst loadings of 10:1 and 5:1 gave the same value of about 11.3% after 24 hour reaction time.

The effect of catalyst loading on HMF yield is shown in Figure 4.12 In the first ten hours of the reaction, the HMF production rate increased with decreasing ratio of glucose per H-Y zeolite. However, after 10 hours, the HMF yield leveled off to different values depending on the catalyst loading:

catalyst loading	HMF yield
10:1	6.74%
5:1	6.03%
2:1	6.15%
1:1	4.15%

It appears that the highest catalyst loading gave the highest HMF yield. This indicates that at low catalyst loadings, more HMF is reacted. This trend is expected, since HMF is a reaction intermediate for organic acids production.

As shown in Figure 4.13, the maximum fructose yield increased as the catalyst loading decreased. However, in all cases, after the maximum fructose yield was achieved, the fructose yield decreased. At 10:1 catalyst loading, the maximum fructose yield was 22.73% after 14 hours and 19.58% after 24 hours. At a 5:1 catalyst loading, the maximum fructose yield was 24.15% after 9 hours and 17.22% after 24 hours. At a 2:1 catalyst loading, the maximum fructose

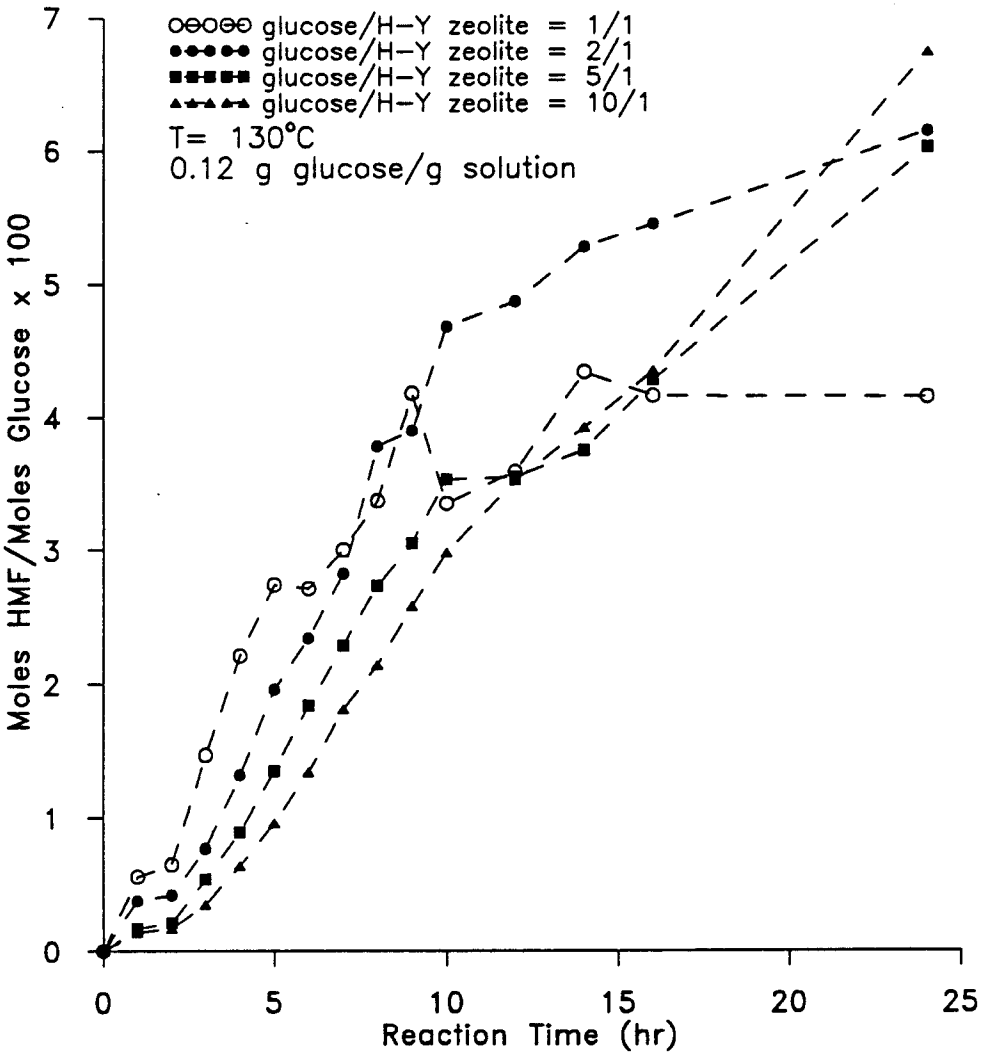


Figure 4.12 HMF yield versus reaction time for 0.12 g glucose/g solution at 130°C and 300 rpm from 1:1 to 10:1 catalyst loadings.

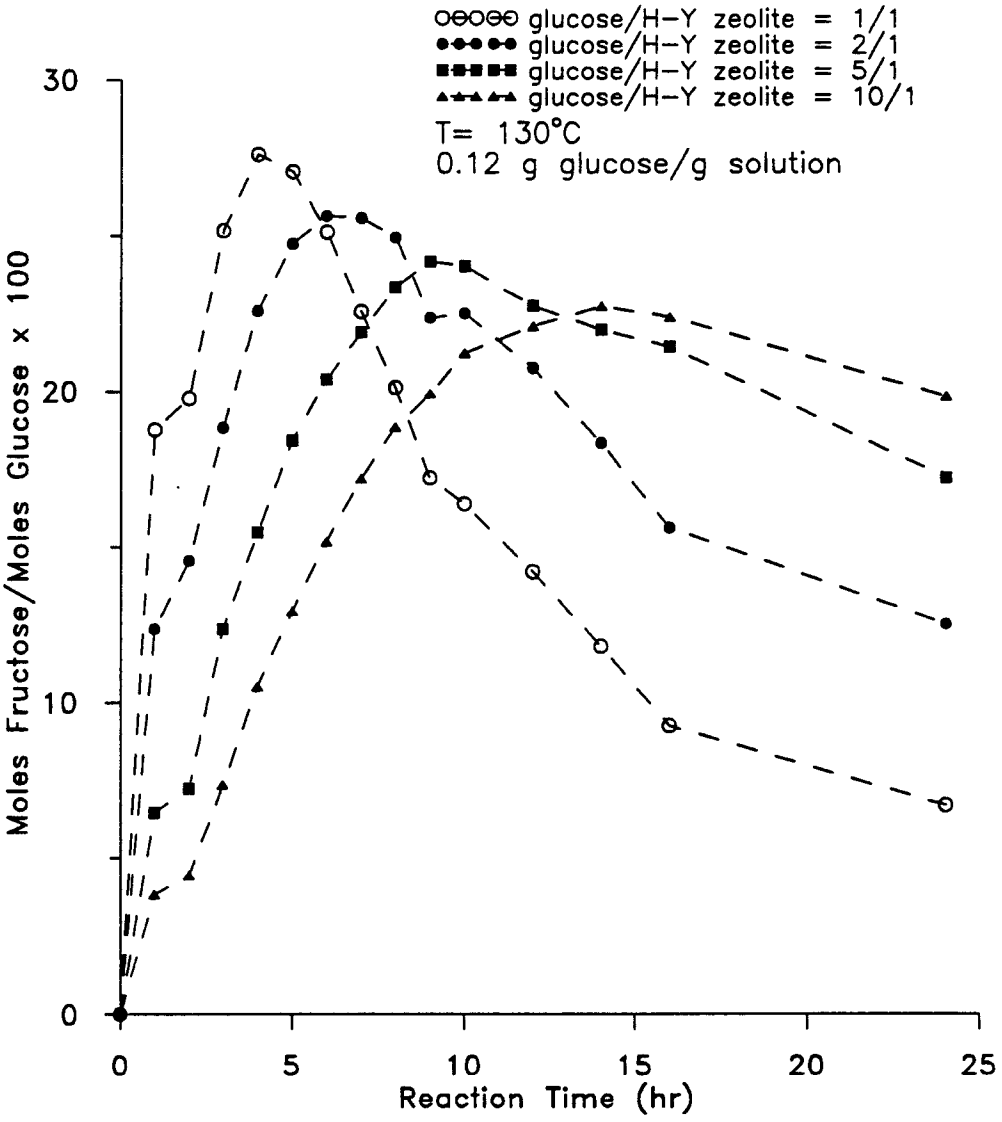


Figure 4.13 (D)-fructose yield versus reaction time for 0.12 g glucose/g solution at 130°C and 300 rpm from 1:1 to 10:1 catalyst loadings.

yield was 25.63% after 6 hours and 12.51% after 24 hours. At a 1:1 catalyst loading, the maximum fructose yield was 27.60% after 4 hours and 6.70% after 24 hours.

The effect of catalyst loading on the acid content, pH of the reaction mixture, and the insoluble residue on the catalyst after 24 hour reaction time are shown in Figures 4.14, 4.15, and 4.16 respectively after 24 hours. The acid content was compared for both estimation. As the catalyst loading decreased, both acid content and insoluble residue on catalyst increased.

Material balance data for low (D)-glucose concentration reactions are given in Table 4.1. As the reaction temperature increased or catalyst loading decreased, the amount of unknown products increased.

The selectivity of formic acid and levulinic acid with respect to HMF increased slightly at higher temperatures or lower H-Y zeolite loadings. The range of selectivity is from 2.8 to 6.7 for formic acid and from 1.7 to 3.2 for levulinic acid. Selectivity data are shown in Table 4.2. This selectivity data shows that more (D)-glucose is converted to formic acid and levulinic acid than to HMF.

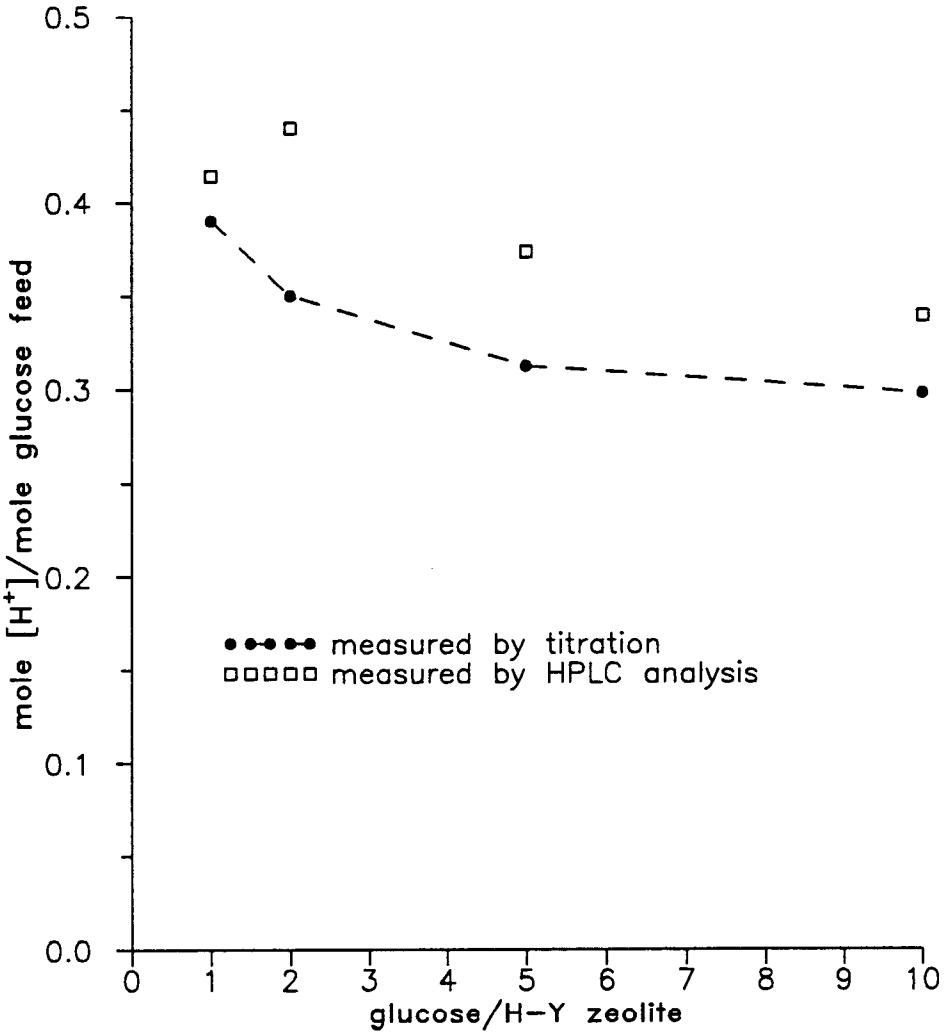


Figure 4.14 Acid content in reaction mixture for 0.12 g glucose/g solution at 130°C and 300 rpm after 24 hours from 1:1 to 10:1 catalyst loadings.

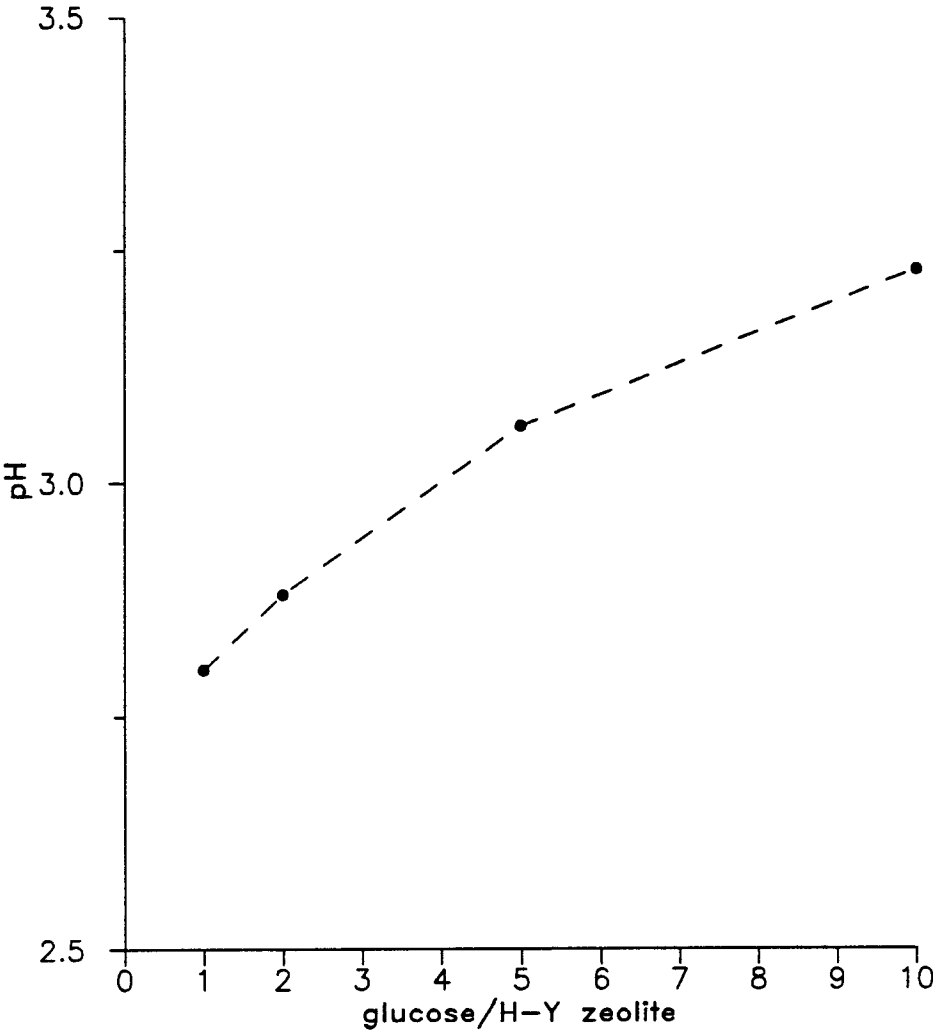


Figure 4.15 pH of reaction mixture for 0.12 g glucose/g solution at 130°C and 300 rpm after 24 hours from 1:1 to 10:1 catalyst loadings.

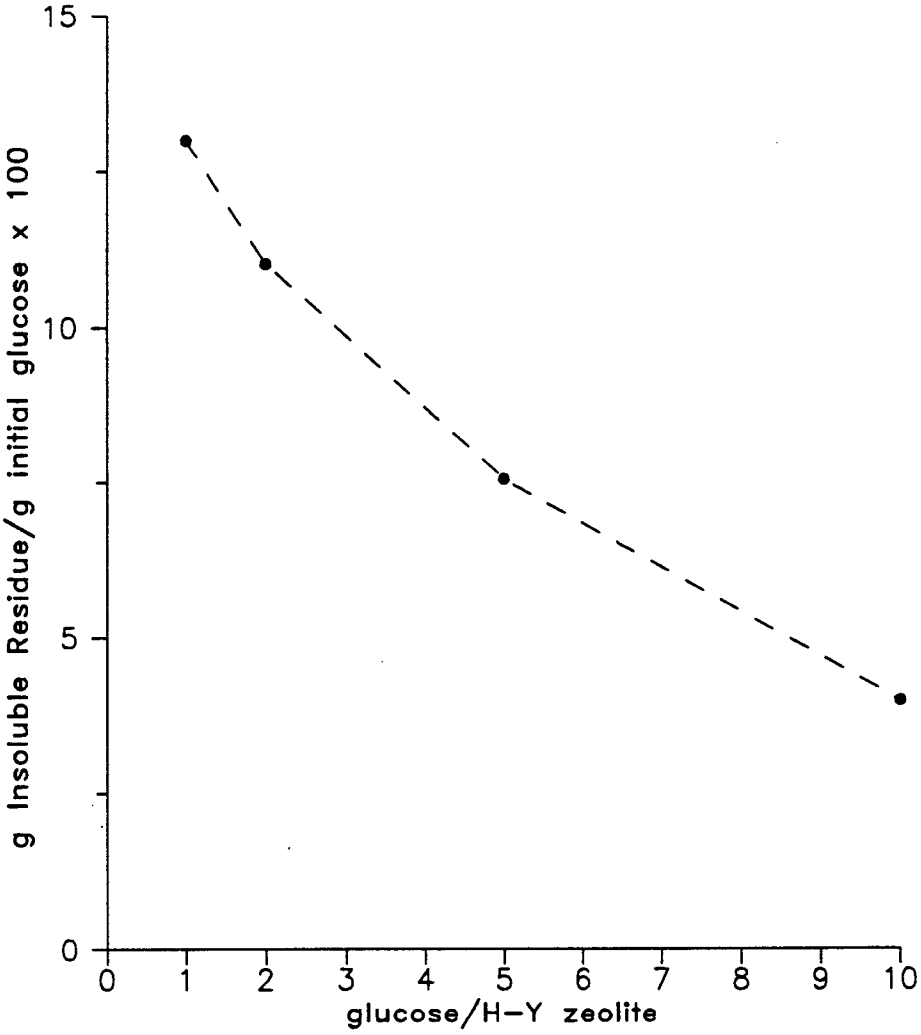


Figure 4.16 Insoluble residue on catalyst from reaction of 0.12 g glucose/g solution at 130°C and 300 rpm after 24 hours from 1:1 to 10:1 catalyst loadings.

Table 4.1 Material balance summary of low (D)-glucose concentration reaction.

Temperature influence

0.12 g (D)-glucose/g solution

2:1 glucose:H-Y zeolite

300 rpm mixing speed

24 hours reaction time

	Temperature		
	110°C	120°C	130°C
(D)-glucose, g	20.00	20.00	20.00
Total reactant, g	20.00	20.00	20.00
unreacted glucose, g	13.39	7.61	3.39
formic acid, g	0.18	0.91	1.49
levulinic acid, g	0.30	1.21	1.83
HMF, g	0.17	0.59	0.86
α-angelicalactone, g	0.00	0.00	0.97
(D)-fructose, g	4.52	4.35	2.50
insoluble residue, g	0.05	0.23	2.20
Total known products, g	18.61	14.90	13.24
unknown products, g	1.39	5.10	6.76

Table 4.1 (continued) Material balance summary of low (D)-glucose concentration reaction.

H-Y zeolite loading influence

0.12 g (D)-glucose/g solution

130°C reaction temperature

300 rpm mixing speed

24 hours reaction time

	g glucose:g H-Y zeolite			
	1:1	2:1	5:1	10:1
(D)-glucose, g	20.00	20.00	20.00	20.00
Total reactant, g	20.00	20.00	20.00	20.00
unreacted glucose, g	1.63	3.39	5.60	6.78
formic acid, g	1.43	1.49	1.33	1.16
levulinic acid, g	1.73	1.83	1.47	1.47
HMF, g	0.58	0.86	0.85	0.94
α-angelicalactone, g	0.00	0.97	1.75	0.78
(D)-fructose, g	1.34	2.50	3.45	3.98
insoluble residue, g	2.60	2.20	1.51	0.80
Total known products, g	9.31	13.24	15.96	15.91
unknown product, g	10.69	6.76	4.04	4.09

Table 4.2 Selectivity of formic acid and levulinic acid with respect to HMF at low (D)-glucose concentration reaction.

0.12 g (D)-glucose/g solution

300 rpm mixing speed

24 hours reaction time

Temperature (°C)	g glucose: g H-Y zeolite	selectivity (mole/mole HMF) formic acid	levulinic acid
110	2:1	2.8	1.9
120	2:1	4.2	2.2
130	2:1	4.7	2.3
130	1:1	6.7	3.2
130	5:1	4.3	1.9
130	10:1	3.4	1.7

4.2. High (D)-glucose concentration reaction

An initial glucose concentration of 0.58 g glucose per g solution (100 g glucose in 70 g distilled water) was introduced into reactor at a constant H-Y zeolite powder loading of 10:1 catalyst loading at various temperatures (100°C to 130°C) and mixing speeds (150 to 1200 rpm). Since oxygenated hydrocarbons analysis for this high concentration reaction was complicated by several by-products, the levulinic acid yield, formic acid yield, material balance, and selectivity data were not presented because of analysis uncertainty.

4.2.1. Temperature Influence

The reaction was studied at temperature ranging from 100°C to 130°. The mixing speed was kept constant at 300 rpm. Tabular conversion and product yield versus time data at these temperatures are provided in Tables E-1, E-2, E-3, E-6, and E-8 of Appendix E.

The glucose conversion versus time profiles are presented as Figure 4.17 at temperatures of 100°C to 130°C. The maximum glucose conversion and glucose conversion rate increased as the reaction temperature increased. After a 10 hour reaction time, the maximum glucose conversions were 16% at a reaction temperature of 100°C, 29% at a reaction temperature of 110°C, 46% at a reaction temperature of 120°C,

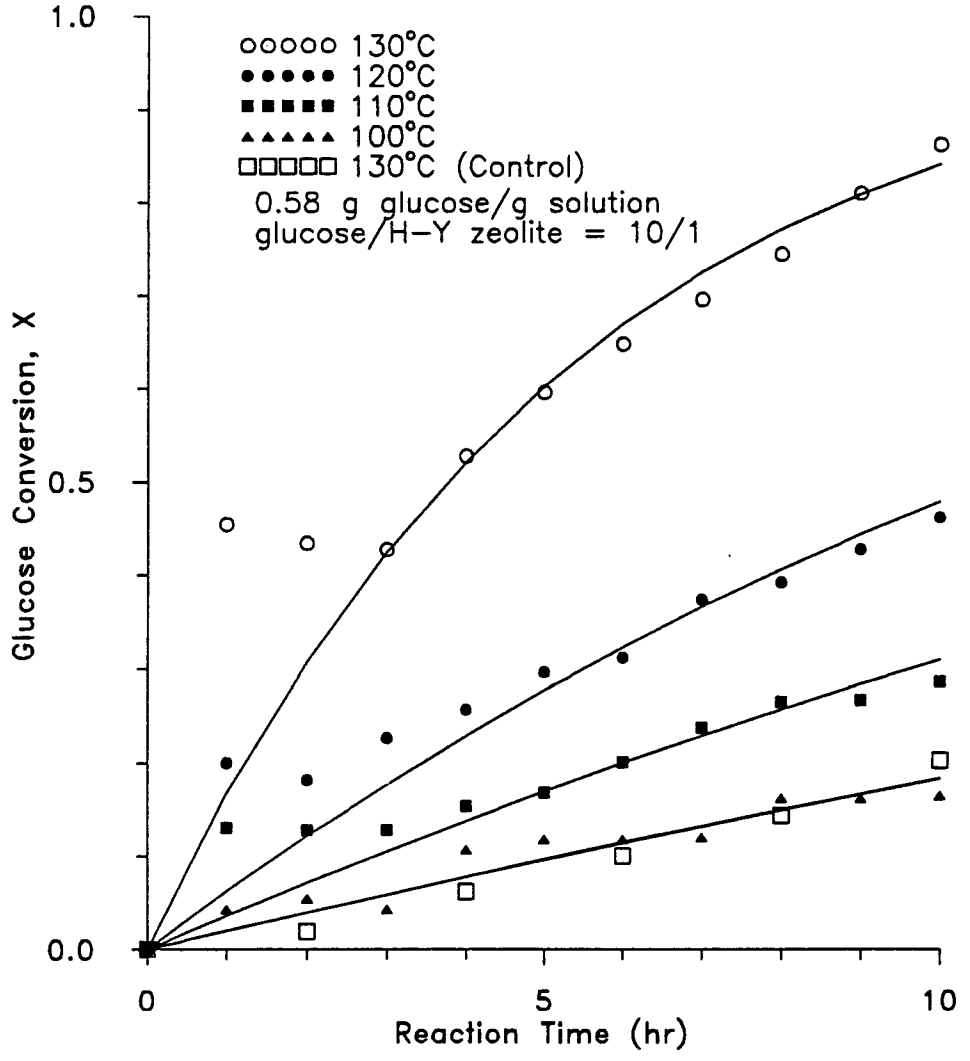


Figure 4.17 (D)-glucose conversion versus reaction time for 0.58 g glucose/g solution and 10:1 catalyst loading at 300 rpm from 100°C to 130°C.

and 86% at a reaction temperature of 130°C.

A control reaction with no catalyst shows that the decomposition of glucose occurred at 130°C. In other words, higher temperature caused more glucose decomposition. However, compared to the conversion with H-Y zeolite, the decomposition was still fairly low. However, more decomposition occurred for the concentrated than for the low concentration.

Product yield profiles are shown in Figure 4.18 and 4.19 for HMF and fructose respectively. The product yield versus reaction time profiles increased as temperature increased. The HMF yields are lower than fructose yields. After 10 hour reaction time, the yields are given below:

temperature	HMF yield
100°C	0.19%
110°C	0.30%
120°C	0.57%
130°C	2.93%

Fructose is described separately from acid-catalyzed dehydration products. As shown in Figure 4.19, the maximum fructose yield increased as the temperature increased. However, at 130°C, after the maximum fructose yield was achieved, the fructose yield decreased. At 100°C, 110°C, and 120°C, the maximum fructose yields were 13.32%, 17.96%, and 18.90% respectively after 10 hours. At 130°C, the maximum fructose yield was 19.54% after 4 hours and 6.32 after 10 hours.

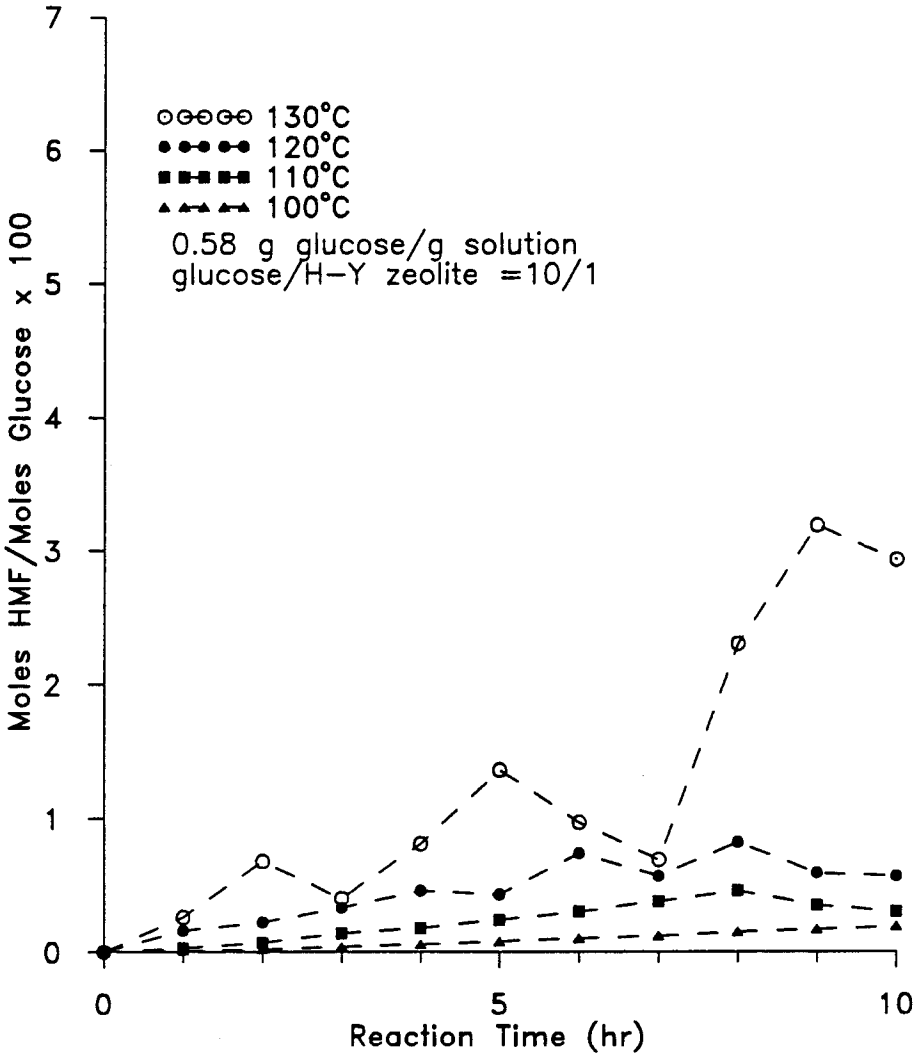


Figure 4.18 HMF yield versus reaction time for 0.58 g glucose/g solution and 10:1 catalyst loading at 300 rpm from 100°C to 130°C.

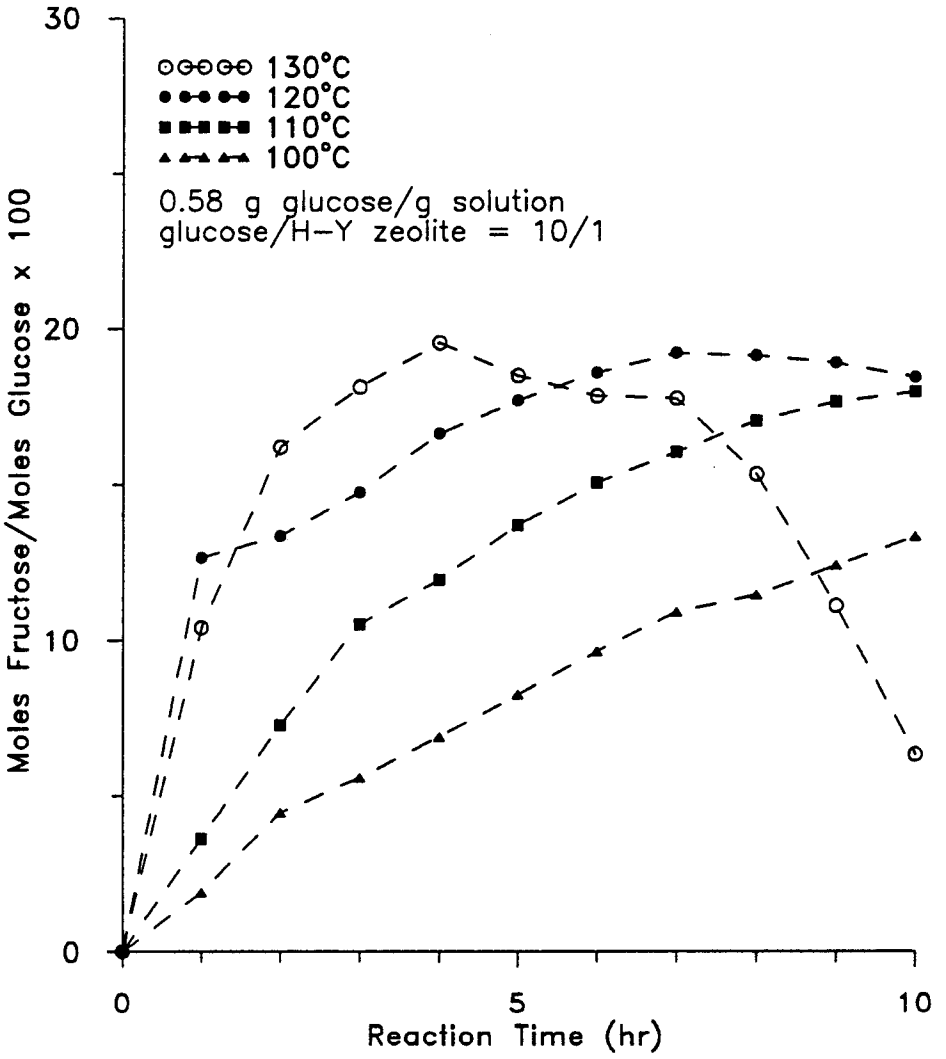


Figure 4.19 (D)-fructose yield versus reaction time for 0.58 g glucose/g solution and 10:1 catalyst loading at 300 rpm from 100°C to 130°C.

Acid content, pH, and insoluble residue on catalyst were measured after 10 hours as shown in Figures 4.6, 4.7, and 4.8 respectively. The acid content increased with increasing reaction temperature. Analogously, the insoluble residue on catalyst increased with increasing temperature. The pH decreased with increasing temperature. Acid content and insoluble residue are higher and pH is lower than acid content, insoluble residue, and pH obtained from the low concentration reaction.

4.2.2. Mixing Influence

Reactions were studied with impeller speeds varying from 150 to 1200 rpm at a reaction temperature of 130°C. Tabular glucose conversion and product yield data are summarized in Tables E-2, E-4, and E-5 of Appendix E.

Glucose conversion versus reaction time profiles shown in Figure 4.20 for each mixing speed were not significantly different. At 150 rpm, conversion was slightly lower than the others. The largest difference of conversion at 10 hours was about 1%. However, the profiles are almost the same for all mixing speeds. Based on this data, it was assumed that mixing speeds of 300 rpm or higher were sufficient to minimize external mass transfer resistances.

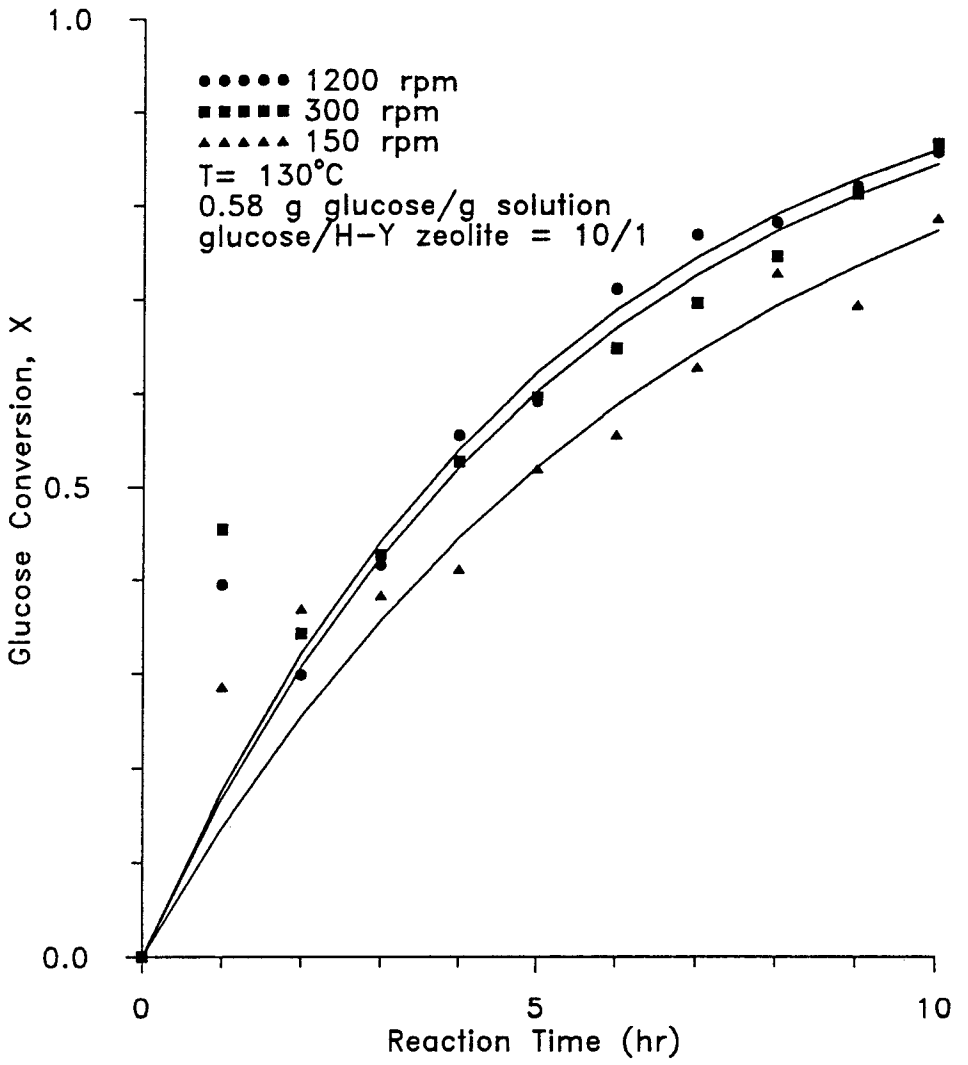


Figure 4.20 (D)-glucose conversion versus reaction time for 0.58 g glucose/g solution and 10:1 catalyst loading at 130°C from 150 rpm to 1200 rpm.

Product yield profiles for HMF and fructose shown in Figure 4.21 and 4.22 also confirm the results of the mixing effect. The yield profiles almost superimpose each other except for some point at about 9 to 10 hours of reaction time.

Acid content, pH, and insoluble residue on catalyst after 10 hours reaction also were not significantly affected by mixing speed.

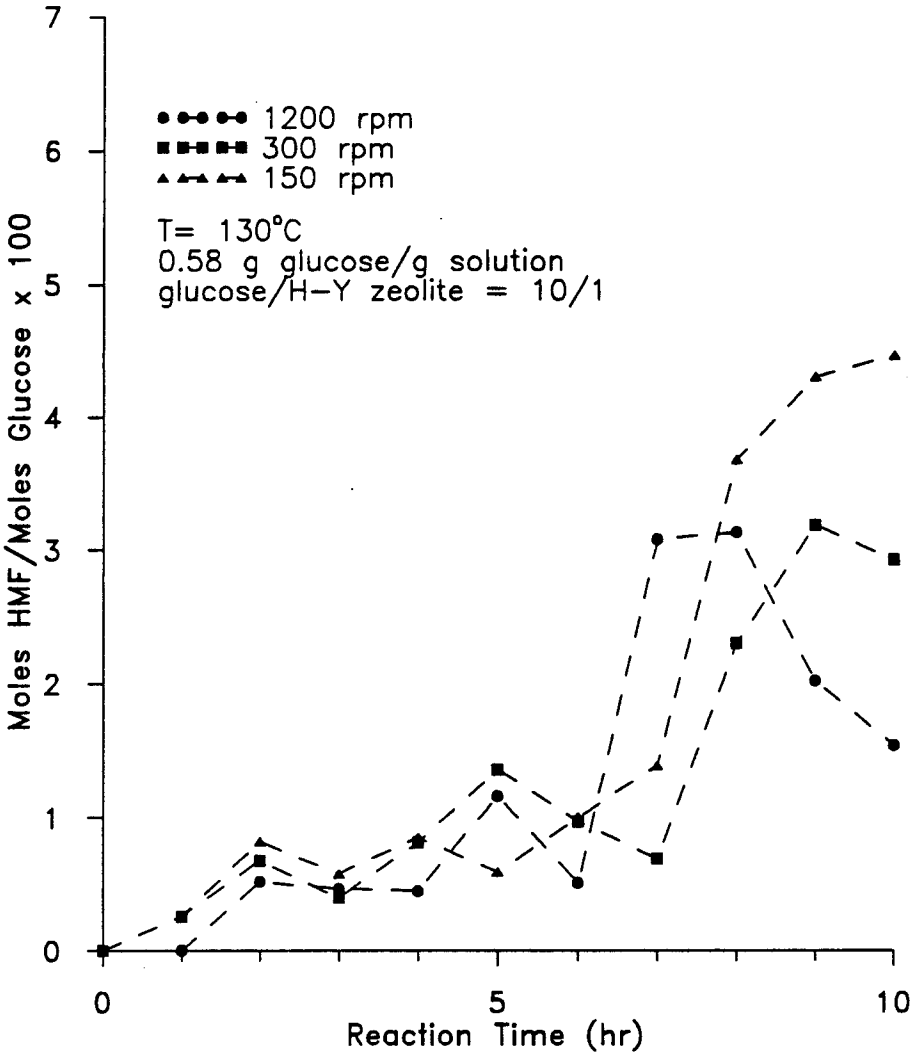


Figure 4.21 HMF yield versus reaction time for 0.58 g glucose/g solution and 10:1 catalyst loading at 130°C from 150 rpm to 1200 rpm.

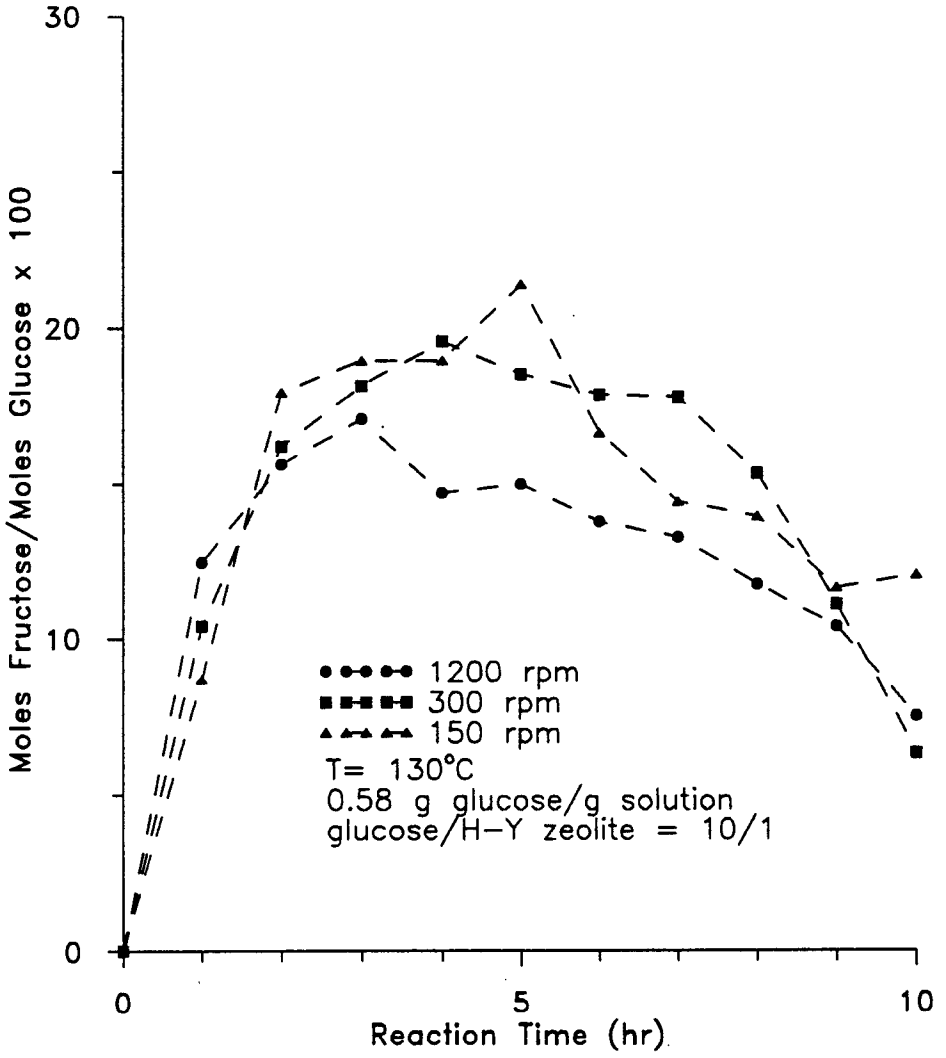


Figure 4.22 (D)-fructose yield versus reaction time for 0.58 g glucose/g solution and 10:1 catalyst loading at 130°C from 150 rpm to 1200 rpm.

4.3. Apparent rate constant and activation energy

The apparent rate constant (k_{app}) and activation energy (E) were estimated in order to empirically correlate glucose conversion versus time data with process parameters. This estimation involved no specific reaction kinetic model and was based only on the condition that the reaction of (D)-glucose was a pseudo first-order process. The pseudo first-order rate equation assumed under minimal mass transfer resistances is

$$X = 1 - \exp(-k_{app}.t) \qquad (4\text{-}1)$$

where X is conversion of (D)-glucose and t is reaction time. The apparent rate constant, k_{app}, for each process parameter was estimated by least-squares fit of the following equation

$$\ln \frac{1}{1 - X} = k_{app}.t \qquad (4\text{-}2)$$

where ln(1/1-X) is the dependent variable and t is the independent variable. Least-squares slope of this line is k_{app}.

The apparent activation energy was estimated using the Arrhenius equation, given by

$$k_{app} = k_0.\exp(-E/RT) \qquad (4\text{-}3)$$

where k_{app} is the apparent rate constant at absolute temperature, k_0 is the Arrhenius constant, E is the apparent activation energy, and R is the gas constant. The natural logarithm of both sides of equation (4-3) yields a linear relationship

$$\ln(k_{app}) = \ln(k_0) - E/RT \qquad (4\text{-}4)$$

A least-squares fit of $\ln(k_{app})$ and 1/T obtained -E/R as the slope and $\ln(k_0)$ as the intercept.

Apparent rate constants for glucose conversion versus time data for both low and high glucose concentration reactions are shown in Tables 4.3 and 4.4 respectively. The least-squares lines for each process parameter based on equation (4-2) are given in Figures 4.23 and 4.24 for low glucose concentration reactions, and in Figures 4.25 and 4.26 for high glucose concentration reactions. The apparent rate constant is higher when the temperature is increased or catalyst loading is decreased. The apparent rate constants of high glucose concentration reactions are not significantly different from of low glucose concentration reaction determined by statistical testing of interaction between conversion of each temperature.

Apparent activation energy estimation for both cases are not statistically different: 22.06 ± 0.45 kCal/mole for low concentration reactions and 21.36 ± 2.65 kCal/mole for high concentration reactions. The value of k_0 at high concentration reaction is 6.04×10^{10} hr^{-1} and at low concentration reaction is 8.58×10^{10} hr^{-1}. The Arrhenius plots for both cases are shown in Figure 4.27.

As shown in Figure 4.28, the apparent rate constant increased nearly linearly with H-Y zeolite:glucose catalyst loading.

From the literature review, the activation energy for

dehydration of 5 g glucose in 100 mL water with 0.4% to 1.6% sulfuric acid from 170°C to 190°C was 32.7 kCal/mole and k_0 was 1.12×10^{16} C_{acid} hr^{-1} (Saeman, 1945) where C_{acid} is the percent weight of acid. This activation energy was confirmed by McKibbins (1958). Baugh and McCarty (1988) also found that the glucose decomposition activation energy was 28.9 kCal/mole, and k_0 that was a function of pH. In summary, the apparent activation energy for the reaction of glucose with H-Y zeolite is lower than the activation energy for similar reactions with aqueous acids.

Since the number of active sites on H-Y zeolite catalyst is known (10^{21} sites/g, Saeman,1945), an equivalent aqueous acid concentration for 10 g catalyst loading was estimated as 0.097 N. The rate constant for glucose decomposition by aqueous acid, k_{pre} (Baugh and McCarty, 1988), is estimated from:

$$k_{pre} = [4.9 \times 10^{11} + 1.5 \times 10^{13}(10^{-pH}) + 4.7 \times 10^{22}(10^{pH-14})] \exp(-28900/RT) \qquad (4\text{-}5)$$

The glucose conversion assuming reaction with equivalent aqueous acid versus time at 130°C with 2:1 catalyst loading was estimated and compared to the actual conversion obtained from the experiment (Figure 4.29). Since equation (4-5) was applied to a higher reaction temperature and a different reaction system, the predicted glucose conversion based on the equivalent mineral acid concentration did not exactly reproduce the experimental results.

Table 4.3 Apparent rate constants and activation energy of low (D)-glucose concentration reaction.

0.12 g (D)-glucose/g solution

300 rpm mixing speed

24 hours reaction time

Reaction Temp. (°C)	g glucose: g H-Y zeolite	k_{app} (hr^{-1})
110	2.0	0.0218 ± 0.0010
120	2.0	0.0466 ± 0.0016
130	2.0	0.0917 ± 0.0039
130	5.0	0.0617 ± 0.0017
130	1.0	0.1327 ± 0.0068
130	10.0	0.0472 ± 0.0010
130 (control)	0.0	0.0070 ± 0.0002

Activation Energy (E) and Arrhenius constant (k_0)

E (kCal/mole): 22.06 ± 0.45

k_0 (hr^{-1}): 8.58×10^{10}

r^2 : 0.99

Table 4.4 Apparent rate constants and activation energy of high (D)-glucose concentration reaction.

0.58 g (D)-glucose/g solution

10:1 glucose:H-Y zeolite

10 hours reaction time

Reaction Temp. (°C)	Mixing Speed (rpm)	k_{app} (hr^{-1})
100	300	0.0203 ± 0.0010
110	300	0.0372 ± 0.0021
120	300	0.0650 ± 0.0032
130	150	0.1473 ± 0.0054
130	1200	0.1943 ± 0.0057
130	300	0.1842 ± 0.0077
130 (control)	300	0.0202 ± 0.0012

Activation Energy (E) and Arrhenius constant (k_0)

E (kCal/mole): 21.36 ± 2.65

k_0 (hr^{-1}): 6.04×10^{10}

r^2 : 0.97

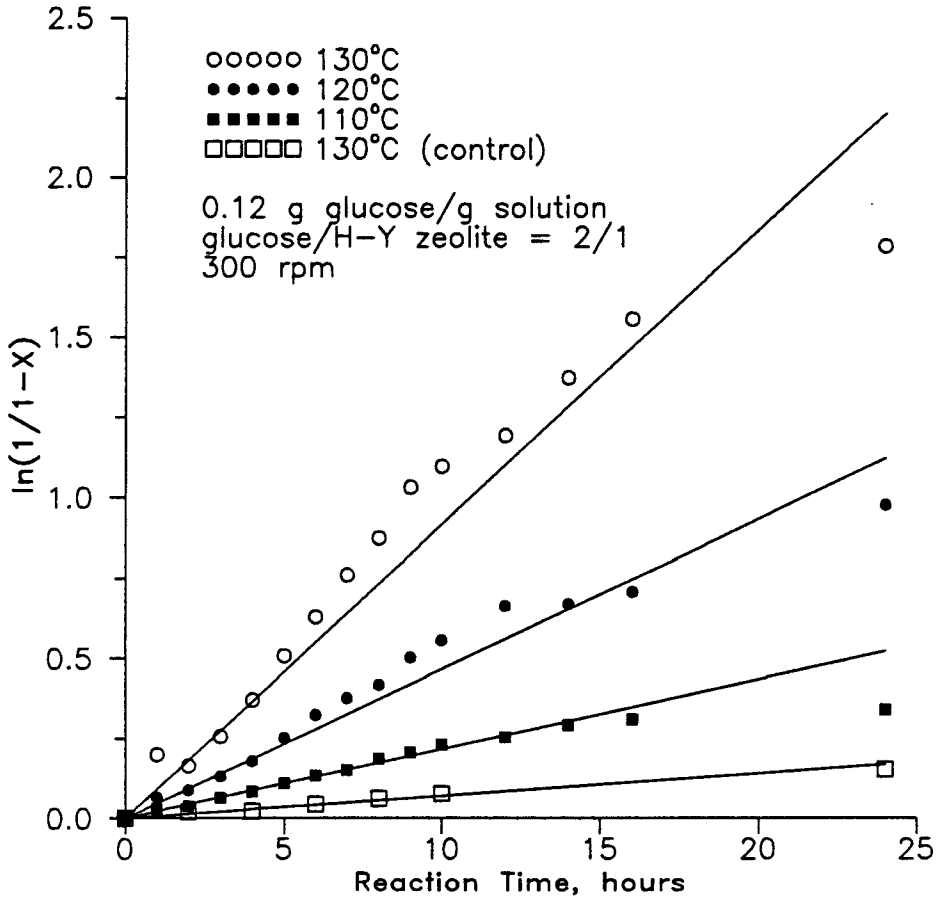


Figure 4.23 Least-squares rate constant estimate for 0.12 g glucose/g solution and 2:1 catalyst loading at 300 rpm from 110°C to 130°C.

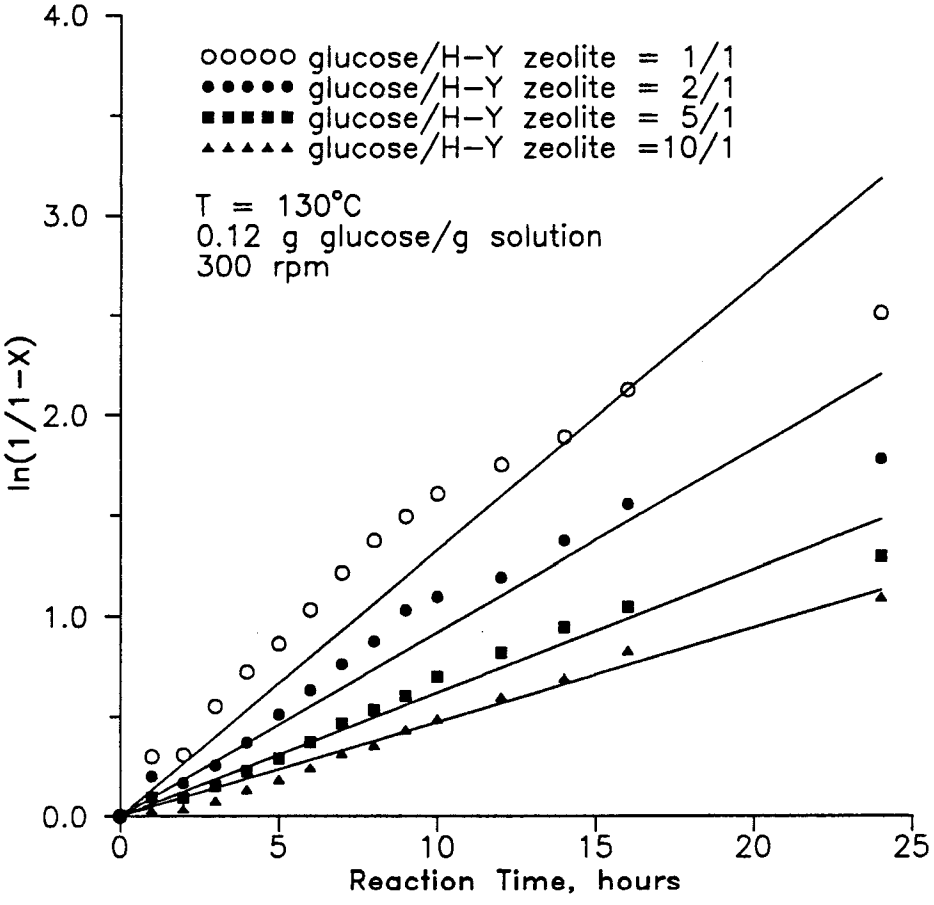


Figure 4.24 Least-squares rate constant estimate for 0.12 g glucose/g solution at 130°C and 300 rpm from 1:1 to 10:1 catalyst loadings.

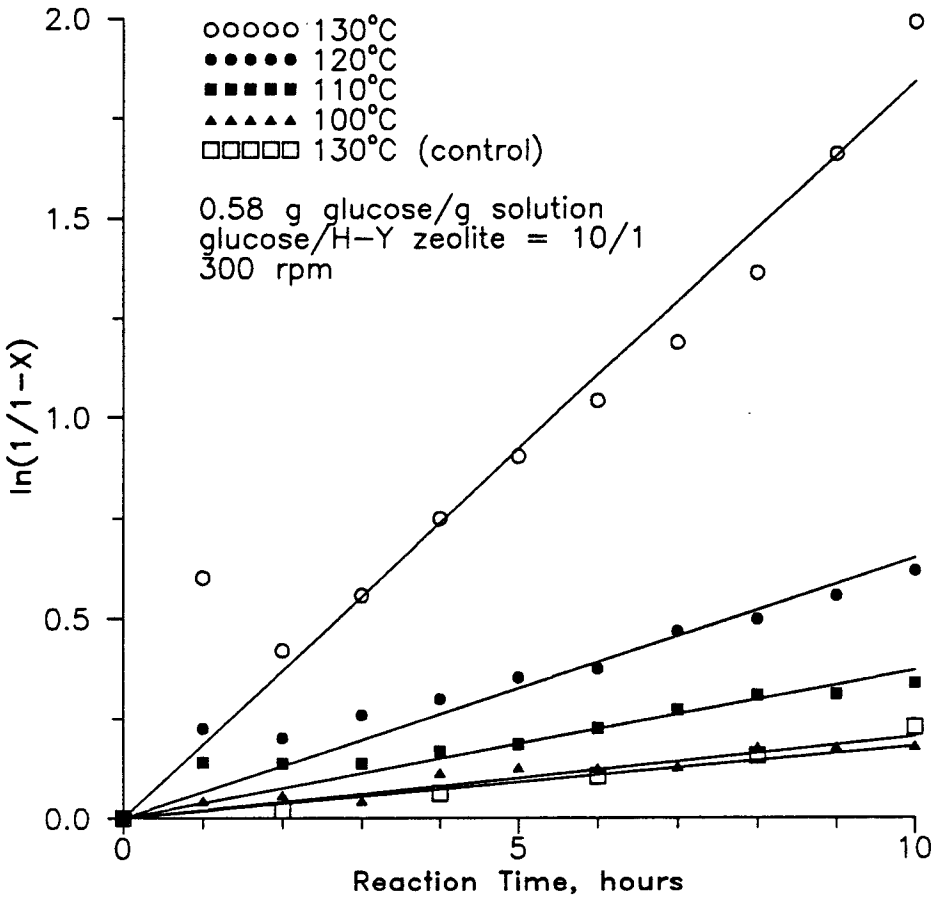


Figure 4.25 Least-squares rate constant estimate for 0.58 g glucose/g solution and 10:1 catalyst loading at 300 rpm from 100°C to 130°C.

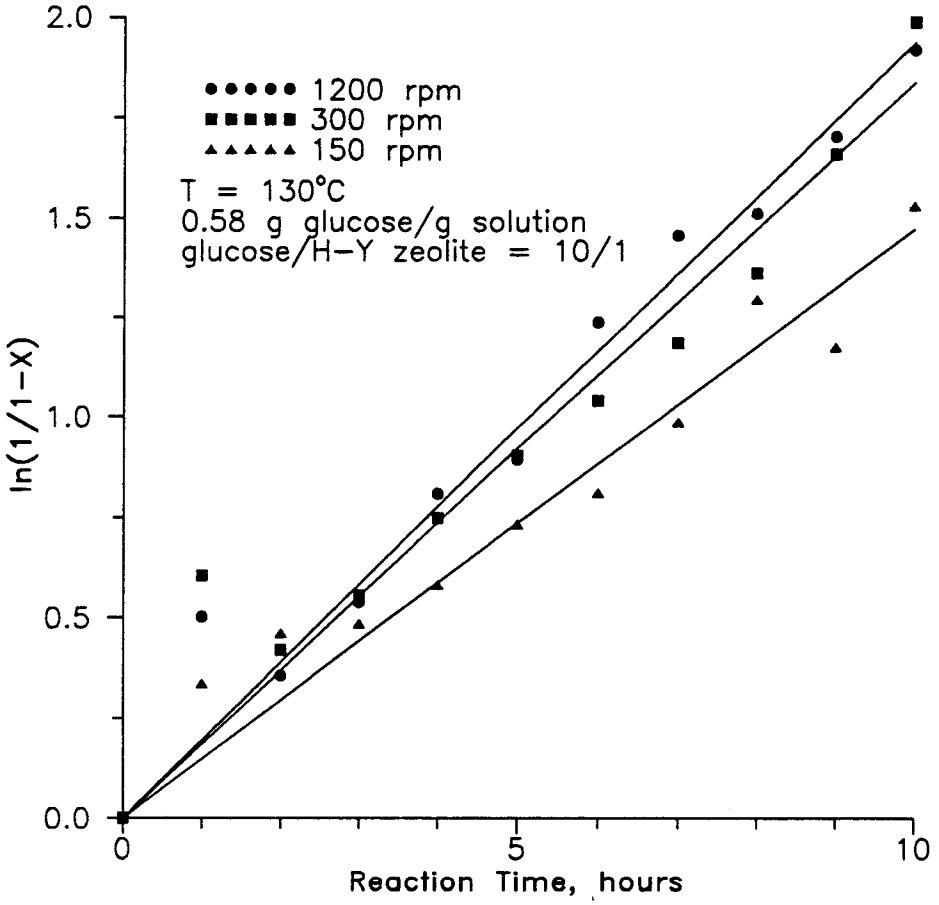


Figure 4.26 Least-squares rate constant estimate for 0.58 g glucose/g solution and 10:1 catalyst loading at 130°C from 150 rpm to 1200 rpm.

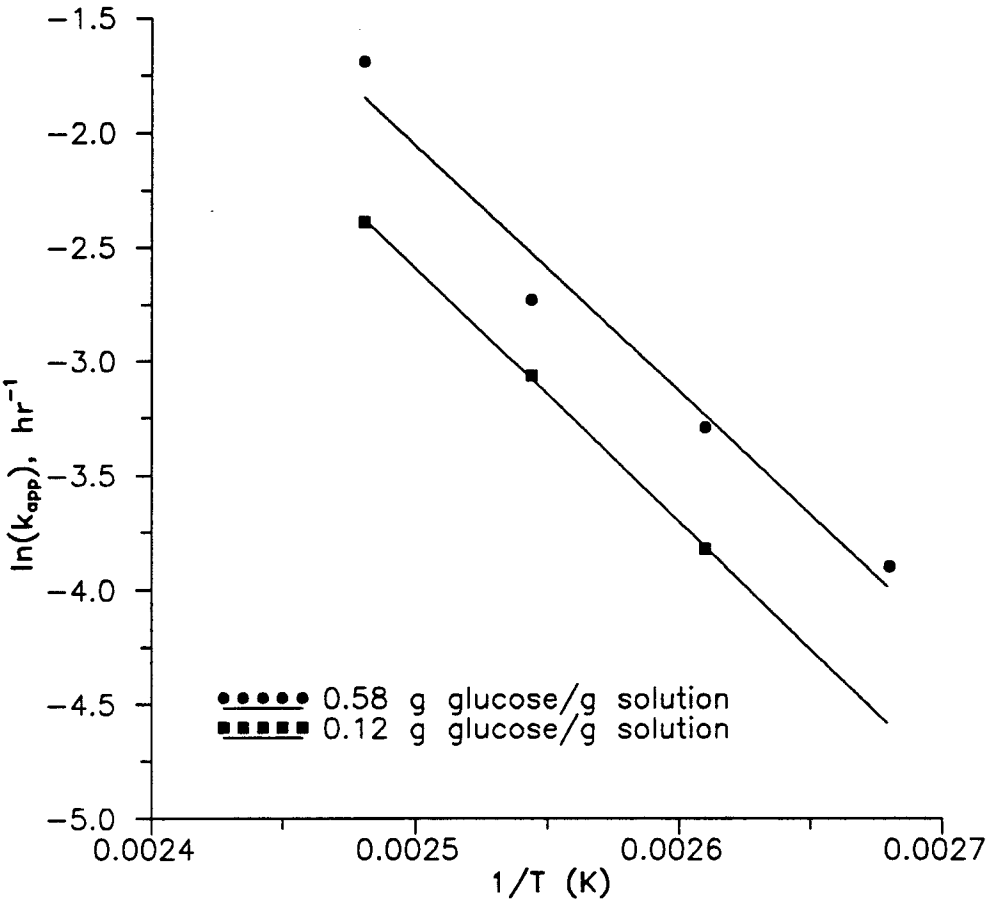


Figure 4.27 Arrhenius plot for 0.12 and 0.58 g glucose/g solution reaction with 2:1 and 10:1 catalyst loading respectively at 300 rpm from 100°C to 130°C.

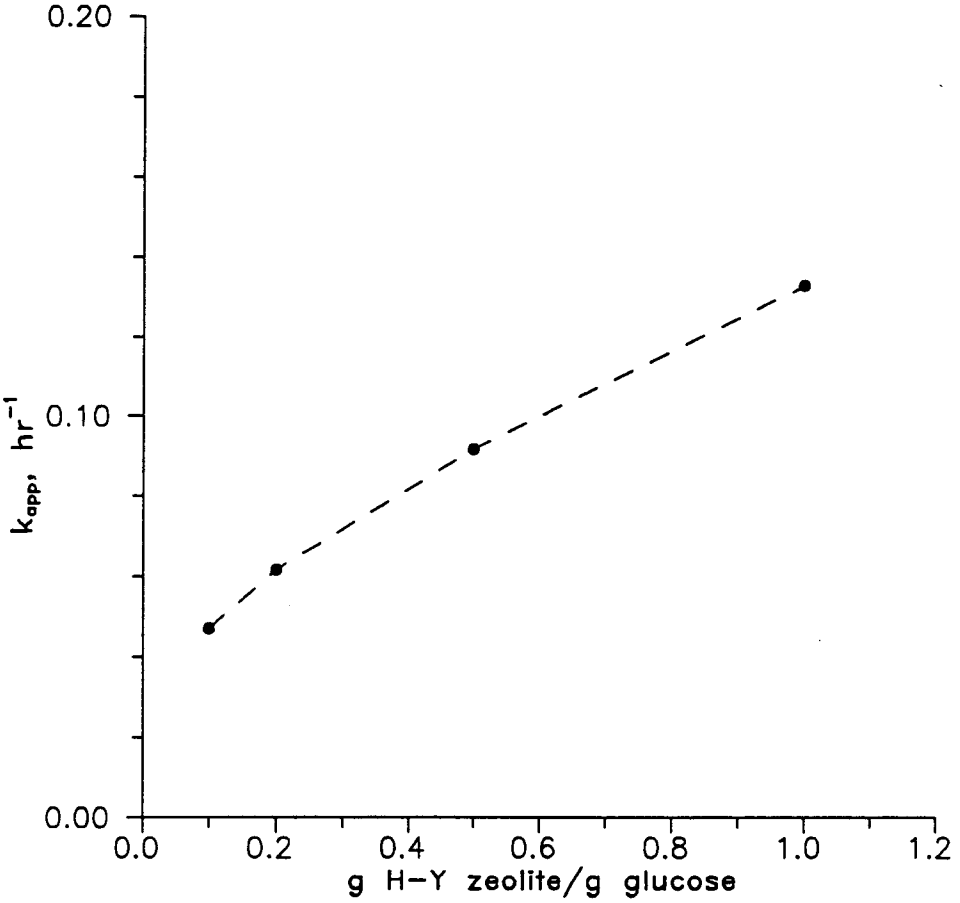


Figure 4.28 k_{app} versus catalyst loading at 130°C and 300 rpm.

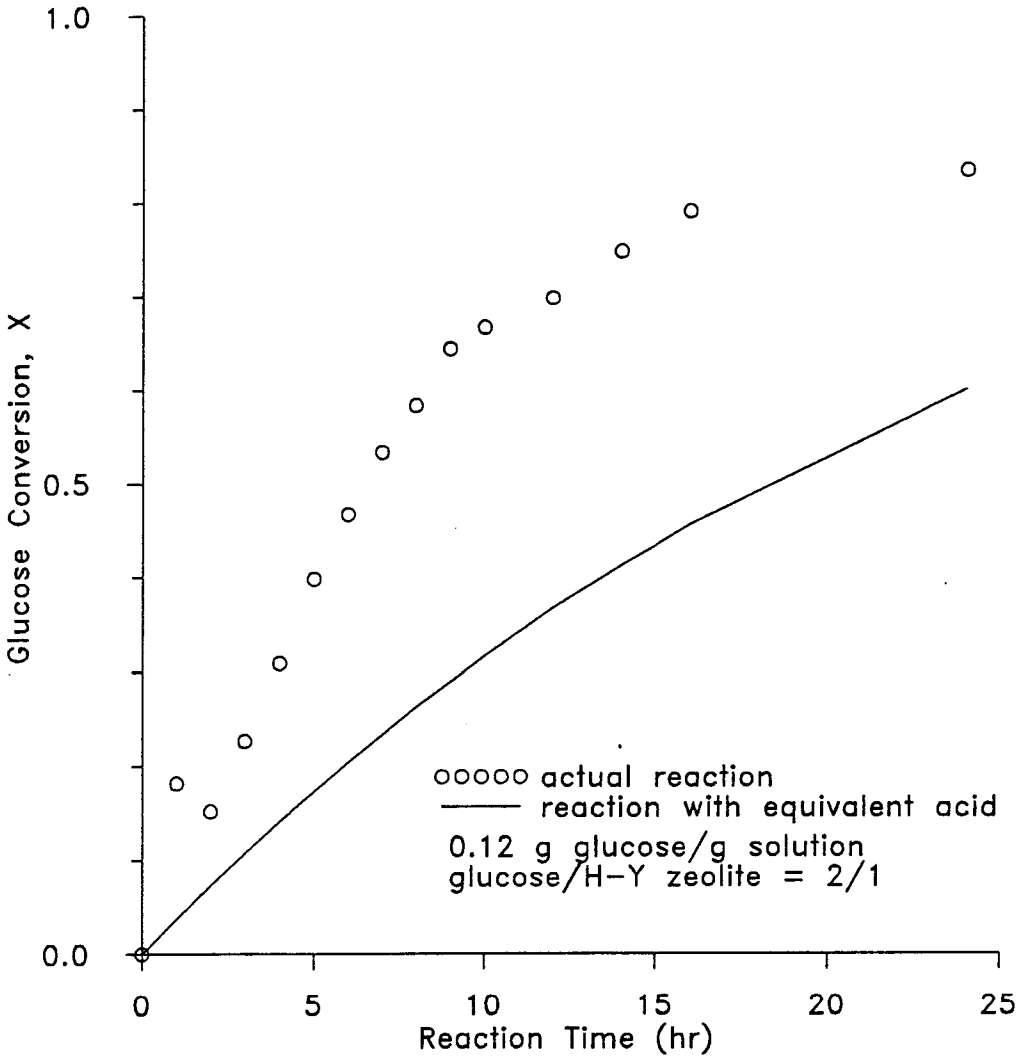


Figure 4.29 Comparison of experimental glucose conversion and predicted conversion based on equivalent aqueous acid catalyst.
Reaction condition: 0.12 g glucose/g solution with 2:1 catalyst loading at 130°C.

Chapter 5

DISCUSSION and PROPOSED REACTION PROCESSES

The reactions of glucose in the H-Y zeolite catalyst depended on several process parameters. Four process parameters, including catalyst loading, temperature, mixing speed, and initial glucose concentration were investigated. Increasing the catalyst loading nearly linearly increased the glucose conversion rate, which implies that Y-zeolite catalyst can catalyze the reactions with glucose. Furthermore, control experiments conducted at the same process parameters but without catalyst added showed minor decomposition of glucose but no formation of organic acid products. In other words, the dehydration of glucose to organic acids did not occur unless H-Y zeolite catalyst was present.

The dependence of glucose conversion rate on temperature yielded a high activation energy of about 22 kCal/mole. Also, mixing speeds higher than 300 rpm did not significantly affect the reaction rate. These results point to reaction limited processes rather than mass transfer limited processes.

Product yield versus time profiles for formic acid, levulinic acid, HMF, and fructose are compared in Figure 5.1. Fructose was produced by acid-catalyzed isomerization of glucose on the surface of the catalyst particle. Both glucose and fructose were converted almost completely to

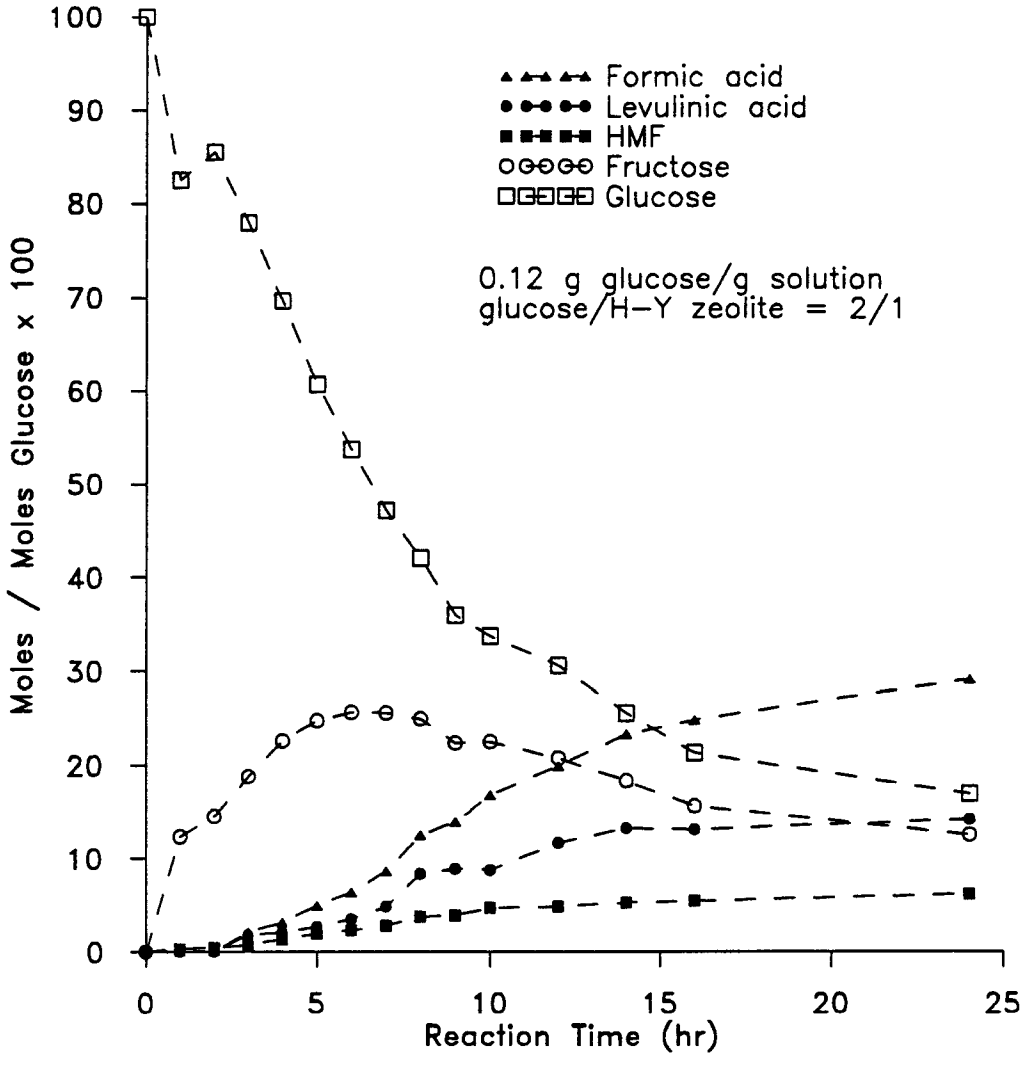


Figure 5.1 Product distribution of low (D)-glucose concentration reaction at 130°C and 2:1 catalyst loading.

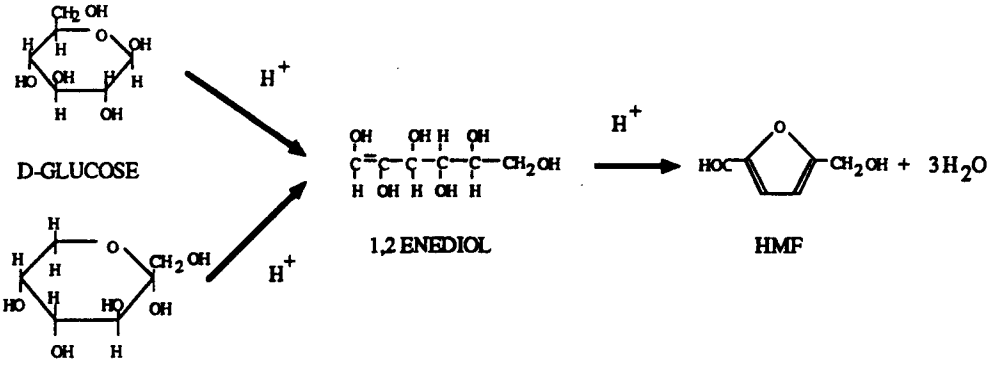
other products. The yield profile of HMF was lower than levulinic acid and formic acid yield profiles. This result implies that HMF, as an intermediate, continued to react to formic acid, levulinic acid, and other products such as insoluble residue. The difference between levulinic acid and formic acid yields might due to the molecular size and weight. Since formic acid molecule is smaller, formic acid competitively diffuses through the pores of catalyst to the aqueous phase better than levulinic acid. Selectivities of levulinic acid and formic acid with respect to HMF, which are about 2 and 4, may support the shape-selective mechanism presented in Chapter 1 and the different yields of both acid. The insoluble residue retained on catalyst also suggests that coke is deposited on the particle surface and perhaps inside the catalyst pore structure by carbonization of reactants and products.

Reaction processes which described glucose conversion and product formation were identified as the dehydration of glucose and fructose, the rehydration of HMF to levulinic acid and formic acid, the isomerization of glucose to fructose, and the carbonization of HMF and other products to insoluble residue. These reaction processes are schematically illustrated in Figure 5.2.

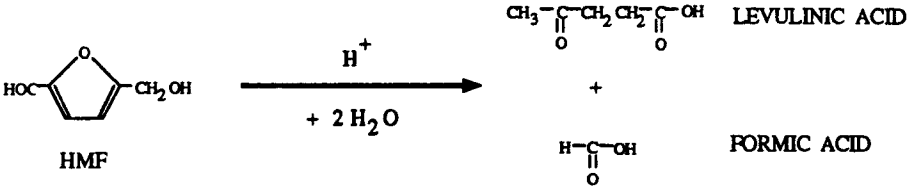
The individual reaction processes shown in Figure 5.2 were assembled into a reaction scheme in order to explain the experimental results, including shape-selective dehydration reactions as concluded above processes,

REACTION PROCESSES

(1) Dehydration



(2) Partial Rehydration



(3) Isomerization

(4) Carbonization

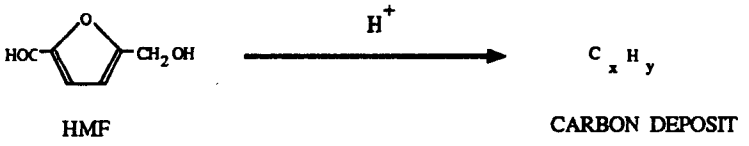


Figure 5.2 Reaction processes.

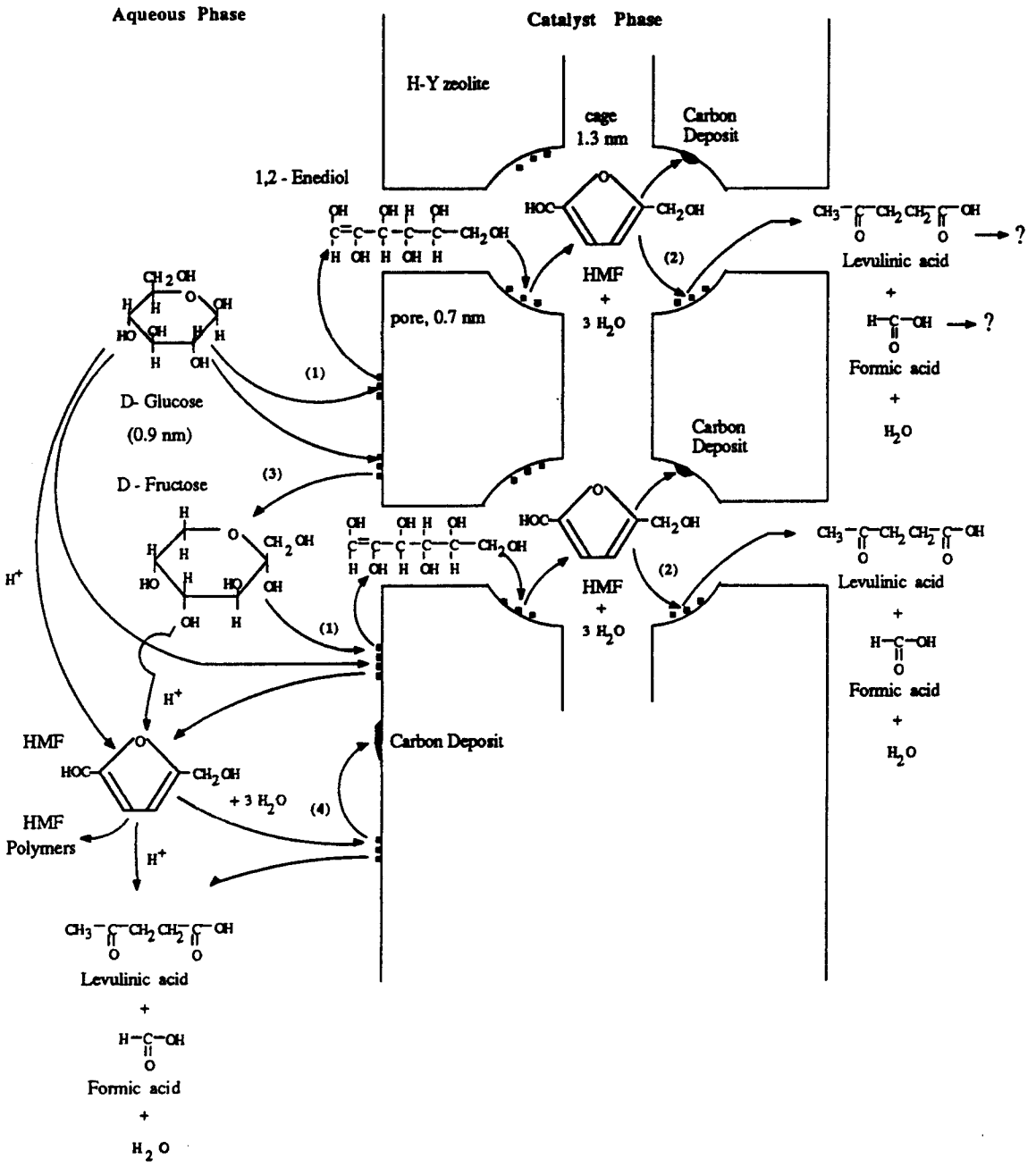


Figure 5.3 Scheme of diffusion and reaction of glucose in the H-Y zeolite catalyst.

and the formation of products.

In Figure 5.3, there are three main reaction zones: reaction on the outer surface of the catalyst, shape-selective reactions within the catalyst, and reactions in the bulk phase. On the outer surface of the catalyst, the glucose molecule adsorbs onto the Bronsted acid sites, which catalyze isomerization of glucose to fructose and cleavage of the glucose ring to an unstable 1,2 enediol intermediate. The 1,2 enediol either dehydrates to HMF on the catalyst outer surface or within the Y-zeolite porous matrix. Fructose also reacts analogously to glucose and yields an unstable 1,2 enediol. HMF can be rehydrated by the active site on the surface to yield levulinic acid and formic acid. For shape-selective reaction processes in the porous matrix of Y-zeolite catalyst, the 1,2 enediol from cleavage of glucose on the catalyst surface diffuses through the pores of the Y-zeolite and reacts with an active site in a cage. HMF is formed in the cage, which is subsequently rehydrated to levulinic acid and formic acid or is carbonized to a coke deposit in the pores of catalyst. HMF is trapped in the cage, but the linear organic acid molecules can diffuse out, which improves selectivity of these products relative to HMF.

The unknown products as indicated in the mass balances and unidentified peaks in the HPLC chromatograms may suggest unexplained processes such as derivation of HMF, formic acid, or levulinic acid.

Chapter 6

CONCLUSIONS and RECOMMENDATIONS

Heterogeneous acid-catalyzed dehydration of (D)-glucose can feasibly be accomplished as solid-liquid system in a batch reactor. Specifically, glucose solution in water and H-Y zeolite powder react and yield organic acids in a well-mixed batch reactor with controlled temperature, pressure and mixing impeller speed. HPLC, used to analyze reaction mixture, gave excellent results in terms of separation and response of target compounds except for levulinic acid, which gave a low detector response.

The experimental results imply that the dehydration of (D)-glucose in H-Y zeolite catalysts can react glucose to 90% conversion at 130°C and high catalyst loading (1:1 glucose:H-Y zeolite). Maximum levulinic acid and formic acid yields were 15% and 30% respectively. Yields of HMF, an intermediate in the dehydration of glucose to organic acids, were about 7%. The reaction also yielded several unknown compounds as evidenced by HPLC analysis.

Glucose conversion and product yield increased with increasing reaction time and tended to be higher when temperature were increased or catalyst loading were decreased. Furthermore, reaction experiments conducted at mixing speeds ranging from 150 to 1200 rpm implied that external mass transfer resistances were minimized at impeller speeds of 300

rpm or higher. Reactions with glucose solution containing 12% glucose also yielded a simpler product distribution relative to high concentration solution containing 58% glucose.

A pseudo first-order process was used to correlate the glucose conversion versus time data. An apparent rate constant obtained from this estimation was evaluated as a function of process parameters including temperature and catalyst loading. The apparent rate constant increased with increasing temperature. The apparent rate constant also increased linearly with increasing catalyst/glucose ratio, which implies that the reaction occurs primarily on the catalyst surface. The apparent activation energy was estimated according to the Arrhenius equation and activation energies for this process are 22.06 kCal/mole and 21.36 kCal/mole at initial glucose concentrations of 12% and 58% weight respectively.

A reaction model was proposed based on the product distribution data. This model represents a complicated system that includes several coupled reactions including dehydration, rehydration, isomerization, and carbonization.

Since the mass balance data suggests that the amount of unknown products increased with increasing glucose conversion, the reaction model and proposed shape selective reaction processes are still open-end questions.

Recommendations

This study focused only on limited range of process parameters and did not uncover all the possible reaction processes. Future work needs to consider:

1. The effect of temperature at temperature higher than 130°C.
2. The effect of initial glucose concentration, especially in the range of 1% to 10% concentration.
3. Reaction with other sugars such as fructose, sucrose, and xylose which might yield different products and product formation rates.
4. Reaction with other types of catalysts such as pillared clays, which have pore sizes large enough to a) the accommodate the whole glucose molecule and b) effect product selectivity by competitive diffusion out of the pores.
5. Reaction and diffusion process models which describe the reaction chemistry and predict product formation rates.

Chapter 7

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APPENDIXES

Appendix A

Experimental Procedures

Reactants Preparation

Sugar Solution

1. Weigh sugar as desired.
2. Weigh distilled water as desired in beaker.
3. Place beaker with distilled water on hot plate.
4. Put magnetic stirrer bar in beaker, operate it properly.
5. Put sugar in distilled water, add small amount for each time, wait until most of sugar dissolved for next time.
6. Warm this solution if necessary, to dissolve all sugar.
7. Keep sugar solution in refrigerator.

Catalyst

1. Divide Y-zeolite powder from container and put into small container such as beaker.
2. Keep it in vacuum desiccator.
3. Weigh as desired when using.
4. Keep the rest in vacuum desiccator.

HPLC Eluant (0.005 M sulfuric acid)

1. Degas HPLC grade water about 1 liter by heating and stirring about 1-1.5 hr, allow to cool down.
2. Put degassed water into 1 liter volumetric flask about 100 mL.
3. Measure 0.275 mL sulfuric acid, put into volumetric flask.
4. Add degassed water to obtain the desired volume.
5. Before using, degas with He again in solvent bottle.

Reactor Operations

Loading

1. Check all valves on the reactor head closed.
2. Remove split rings and reactor head.
3. Clean and wipe dry inside of the bomb.
4. Load solution and catalyst into the bomb.
5. close reactor head.
6. Put on and tight the split rings.
7. Place reactor on the clamp.
8. Elevate heating jacket to the position.
9. Connect stirrer hub.

Start-Up

1. Turn on the controller, Press reset button at the back.
2. Key in temperature set point.
3. Turn on motor switch.
4. Set stirrer speed as desired, displayed by tachometer.
5. Open water inlet valves for cooling sleeve and cooling loop (at solenoid valve).
6. Open N_2 cylinder head valve and regulator, set pressure.
7. Open gas inlet valve at reactor,adjust as desired pressure.
8. Turn on heater switch, set to "HIGH" position.
9. Adjust pressure, temperature and speed if necessary.

note: Start up should not take more than 10 min.

Sampling

1. Close gas inlet valve.
2. Open sample outlet valve.
3. Flush line about 2 mL, Close valve.
4. Place sample vial at the end of sample outlet tube.
5. Open sample outlet valve again.
6. Take and weigh sample as desired.
7. Close sample outlet valve when obtained.
8. Open gas inlet valve, adjust pressure.

Sample Preparation

1. Dilute sample taken as desired.
2. Add internal standard solution.
3. Stir if necessary.
4. Place 0.45 micron filter membrane in cartridge.
5. Withdraw mixed sample with 10 mL syringe.
6. Place filter cartridge from 4. at the end of syringe.
7. Press syringe to filter mixed sample into clean vial.
8. Keep filtered sample in freezer.
9. Discard used filter membrane.
10. Clean filter cartridge and syringe, rinse w/ HPLC grade water.

Shut down

1. Turn off heater switch.
2. Set temperature on controller to room temperature.
3. Allow reactor to cool down.
4. Close gas inlet valve, open gas release valve.
5. Adjust stirrer speed to zero, turn off its switch.
6. Open split rings and reactor head.
7. Prepare suction filter set.
8. Filter mixture in reactor.
9. Put filtrate in bottle, label and keep in freezer.
10. Weigh filtered cake, keep in vacuum desiccator.

Cleaning

1. Clean bomb and reactor head.
2. Fill bomb with distilled water.
3. Close reactor head and gas release valve.
4. Open gas inlet valve to pressure reactor.
5. Close gas inlet valve.
6. Open sample outlet tube to flush sampling line.
7. Close sample outlet valve, remove reactor head.
8. Wipe bomb and reactor head dry.
9. Close gas cylinder valve.
10. Open gas inlet valve to release gas in line and dry sampling line.
11. Close reactor, place split rings, do not tight.
12. Place reactor on clamp.

Residue Estimation Procedures

1. Weigh dried mixture cake from reaction.
2. Determine weight on the last period.
3. Keep drying in vacuum desiccator until weight not change.
4. Calculate final cake weight.
5. Divide cake about 1 g portion.
6. Weigh no.1 filter paper.
7. Prepare suction filter set.
8. Dissolve and stir cake portion in hot distilled water.
9. After 15 min., filter mixture.
10. Dry washed cake in vacuum desiccator.
11. Keep drying until weight not change.
12. Calculate weight loss after washing.
13. Calculate weight loss for whole cake.
14. Determine weight gain from cake weight suppose to be washed and catalyst charged weight.
15. Calculate % weight gain or % residue on catalyst.

HPLC Operations

Start up

1. Open He-gas cylinder valve and regulator.
2. Degas eluant in solvent bottle using He sparging, use flow meter to control He flow rate.
3. Check system, place waste reservoirs.
4. Turn on pump, column oven, detector and integrator.
5. Connect eluant delivery tube, prime pump.
6. Set column oven temperature to desired point.
7. Set eluant flow rate to 0.1 mL/min.
8. Adjust the 3-way valve to allow eluant flow through both sample and reference cell of the detector.
9. When column temperature reach set point, adjust flow rate as required.
10. Close 3-way valve to allow eluant flow through only sample cell.
11. Set detector and integrator parameters as desired (see Integrator Setting and HPLC analytical conditions).
12. Allow the set system to warm up about 1 hr.
13. Check steady of base line and PT value from integrator.

Sample Injection

1. Defroze sample at ambient temperature (if necessary).
2. Flush injection port of injection valve at "LOAD" position using HPLC grade water filled in micro syringe several times.
3. Check PT value within acceptable range (not exceed 200).
4. Withdraw sample with micro syringe, avoid bubble.
5. Place syringe's needle into injection port.
6. Switch injection valve's lever to "INJECT" position.
7. Start integrator and other data acquisition system.
8. Remove syringe, wash and keep in proper place.

Shut Down

1. Set column oven temperature to 25°C, open the oven cover.
2. Set eluant flow rate to 0.1 mL/min.
3. Turn off integrator and detector.
4. Allow the column to cool down to ambient temperature.
5. Turn off pump and oven controller.
6. Close He-cylinder valve, regulator and flow meter.
7. Disconnect eluant delivery tube, close all open-end tubes with plastic cap.
8. Close all valves on the solvent bottle lid.

Pump Priming

1. Insert hypo needle into tube leading from draw-off valve.
2. Open the draw-off valve.
3. With draw eluant, close valve and dispose eluant from syringe.
4. Do 3. until eluant remains fully in syringe.
5. Start pump at 0.1 mL/min flow rate.
6. Press plunger, allow 2 ml of eluant get into the pump.
7. Close the draw-off valve.
8. Remove syringe and tube leading, clean them.

Integrator Setting (Beckman 427)

1. Turn on integrator, input date and time.
2. Press CHT SP, set chart speed (Default value, 0.25 cm/min).
3. Press ATTN, set attenuation.
4. Press DIALOG, set run time, skip file name by ENTER, set TT=(run time required,min), enter, input TF=ER, enter, input TV=1, enter and set METHOD NUMBER (MN) = 0.
5. Check peak threshold by PT EVAL, value should not exceed 200.
6. Begin operation by press INJ A and finish by same button.

NOTE: All instrument instruction manuals should be studied before beginning operation.

HPLC Column Switching

1. Remove column from oven and cartridge holder with guard column.
2. Put cap screws at the end of column and cartridge holder, keep in their boxes according to the storage instruction.
3. Replace new eluant, if required, in the solvent bottle.
4. Degas new eluant by sparging He.
5. Start the pump as sec. A with new eluant.
6. Flush line up to injection valve outlet with 5.0 mL/min flow rate, flush about 50 mL.
7. Place new column in the oven, connect the column outlet to detector, DO NOT connect the inlet now.
8. Reduce flow rate to 0.1 mL/min, connect new cartridge holder with guard column suited the new column next to injection valve.
9. Flush guard column about 10 mL with 0.7-1.0 mL/min flow rate.
10. reduce flow rate to 0.1 ml/min, connect cartridge holder outlet to the column inlet.
11. Flush column and detector with new eluant at 0.1-0.2 mL/min flow rate about 50 mL.
12. Shut down as shut down procedures.

Shut-Down (Long term)

1. Shut down as usual first.
2. Remove column from oven and cartridge holder with guard column.
3. Put cap screws at the end of column and cartridge holder, keep in their boxes according to the storage instruction.
4. If current eluant is water, skip to , if not do 5.
5. Connect injection valve outlet to detector inlet with flexible tube.
6. Replace eluant in the solvent bottle with HPLC grade water.
7. Degas HPLC grade water by sparging He.
5. Start the pump as sec. A with HPLC grade water.
6. Flush pump, injection valve through both cell of detector with 5.0 mL/min flow rate about 50 mL.
7. Turn off pump, close He-cylinder valve, regulator and flow meter, disconnect eluant delivery tube and flexible tube.
8. Close all open-end tubes with plastic cap.
9. Close all valves on the solvent bottle lid.
10. Empty solvent bottle.

HPLC Analytical Conditions

Acid Analysis

Purpose : Oxygenated hydrocarbon product analysis
Column : BIO-RAD HPX 87-H
Temperature : 65°C
Eluant : 0.005 M H_2SO_4
Flow rate : 0.6 mL/min
Standard Solution : Butyric Acid
Standard Solution Retention Time : 20.9-21.0 min
Detector : Water 484 UV/VIS detector
Detector Default Setting:
    Wave length : 210 nm
    Sensitivity : 2.0 AUFS
    Filter : 1.0
Sample loop : 20 micro liters

Carbohydrate Analysis

Purpose : Reactant (sugar) analysis
Column : BIO-RAD HPX 87-P
Temperature : 85°C
Eluant : HPLC Grade Water
Flow rate : 0.6 mL/min
Standard Solution : myo-Inositol
Standard Solution Retention Time : 20.9-21.0 min
Detector : Altex 156 Refractive Index detector
Detector Default Setting:
    RI Range : 4x
Sample loop : 20 micro liters

Note: Standard retention time is presented by this analysis conditions only.

Acid Content Determination

1. Set micro burette.
2. Prepare 0.1 N NaOH and phenolpthaline.
3. Fill burette with 0.1 N NaOH, avoid any bubble.
4. Weigh sample about 0.1-0.2 g, dilute with 30 mL distilled water in 150 mL conical flask.
5. Add phenolpthaline about 2-3 drops to the sample.
6. Titrate sample with 0.1 N NaOH, until sample solution is clear pink.
7. Obtain volume of used NaOH, determine amount of acid.
8. Calculate Normality of sample and Ratio of acid and amount of reactant used.
9. Measure pH using pH meter, calibrate with pH 4 buffer solution.

Appendix B

Temperature Controller Response

Controller Specification

Model : LFE 4842

Type : PID

Unit : °C

Time : hr, min

Cycle Time : 15 sec

Proportional Band : 1% or 6°C

Operating Range : 0 to 400°C

Input Thermocouple : type J

Readout Resolution : 1°C

Set Point Resolution : 1°C

Control Output 1 : 15 amp

Control Output 2 : 0.15 amp

Note : Output 1 drives the heater. Output 2 activates solenoid valve for cooling loop.

Condition

Medium : 200 mL distilled water

Mixing Speed : 170 rpm

Pressure : 30 psi

Heater Setting : HIGH

Set Point Temperature (SP): 80, 100, 120 and 140°C

Reset set point time : after 10 min.

Observation Data

Table B-1 Temperature controller calibration data

Time (min)	Avg. Temp (°C)			
	SP=80°C	SP=100°C	SP=120°C	SP=140°C
0	30.0	30.0	30.0	30.0
2	30.0	30.0	30.0	30.0
4	30.0	30.0	30.0	30.0
6	30.0	30.0	30.0	30.0
8	30.0	30.0	30.0	30.0
10 *	30.0	30.0	30.0	30.0
12	30.0	30.0	30.0	30.0
14	37.0	36.0	37.0	38.0
16	53.5	53.5	52.5	53.0
18	82.0	82.0	83.0	82.5
20	82.0	94.5	91.5	92.5
22	81.5	101.0	100.5	101.5
24	80.5	100.0	109.0	108.0
26	80.0	100.0	118.5	114.0
28	80.0	99.5	121.0	120.5
30	81.0	99.5	120.0	132.0
32	80.0	100.5	120.5	140.0
34	80.0	100.0	119.0	140.0
36	79.5	100.0	119.5	140.0
38	80.0	100.0	120.0	139.5
40	80.0	100.5	120.0	139.0
42	81.0	100.0	120.0	140.0
44	81.0	100.0	120.0	140.0
46	80.0	100.5	120.0	140.0
48	80.0	100.0	120.0	140.0
50	80.0	100.0	120.0	140.0

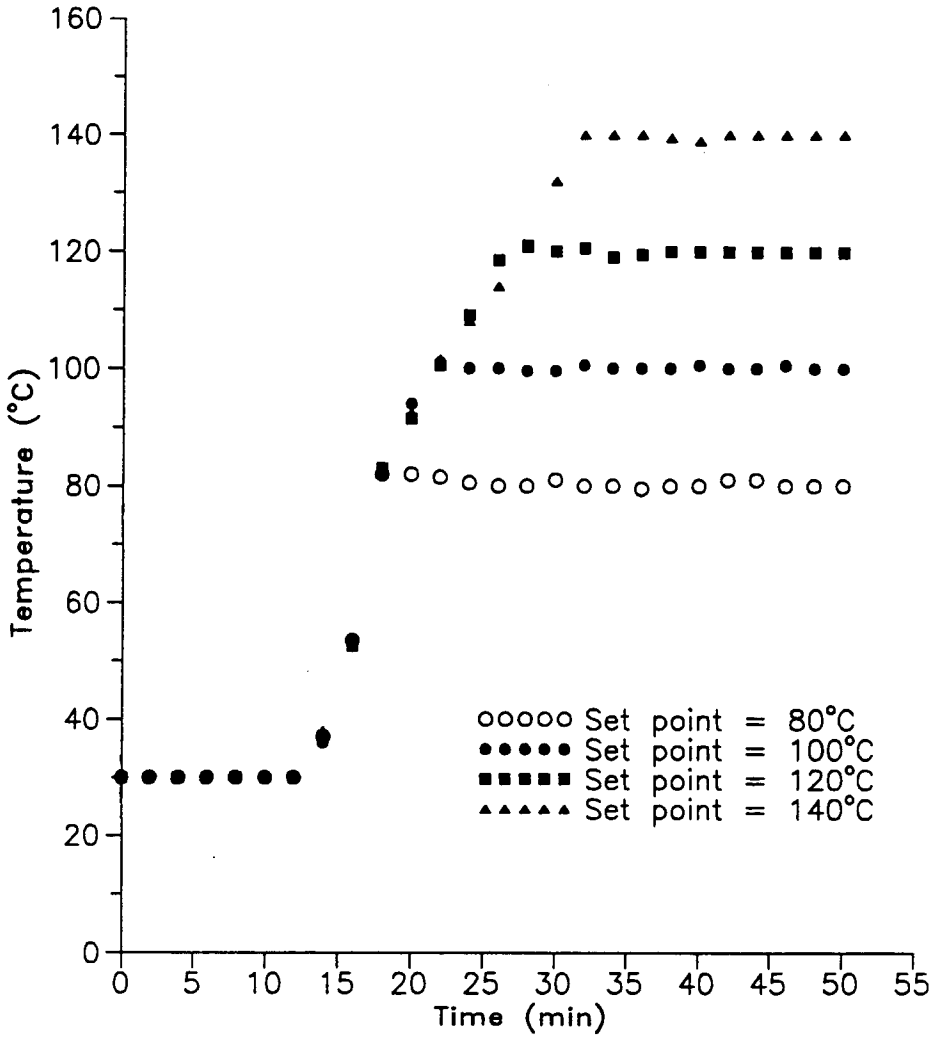

Figure B-1 Temperature response versus time of controller.

Appendix C
HPLC Calibration

Sugar analysis

Column: BIO RAD HPX 87-P

Temperature: 85°C

Eluant: HPLC grade water

Eluant flowrate: 0.6 mL/min

RI detector range: 4x

Sample loop: 20 μL

Glucose

Table C-1 HPLC calibration data of D-glucose.

Concentration (mg/mL)	Mass in Sample loop (μg)	Chromatogram Retention Time (min)	Chromatogram Peak Area (μV.sec)
10.01	200.26	12.72	2428277.00
25.03	500.66	12.72	6253010.50
50.07	1001.32	12.78	13181573.00
75.10	1501.98	12.83	18368171.50
100.13	2002.64	12.88	23476238.50

Response Factor, R_F (μV.sec/μg): 12092.59

Standard error of R_F: 242.75

r^2: 0.99

Fructose

Table C-2 HPLC calibration data of D-fructose.

Concentration (mg/mL)	Mass in Sample loop (μg)	Chromatogram Retention Time (min)	Chromatogram Peak Area (μV.sec)
10.01	200.12	16.94	2202486.50
25.02	500.30	16.91	5418955.50
50.04	1000.60	16.91	11262475.50
75.05	1500.90	16.94	15875779.50
100.06	2001.20	16.96	22491200.00

Response Factor, R_F (μV.sec/μg): 11029.00
Standard error of R_F: 151.91
r^2: 0.99

myo-Inositol

Table C-3 HPLC calibration data of myo-inositol.

Concentration (mg/mL)	Mass in Sample loop (μg)	Chromatogram Retention Time (min)	Chromatogram Peak Area (μV.sec)
10.50	200.16	21.10	2802859.00
25.02	500.42	20.81	7046869.00
50.04	1000.84	20.46	14615584.50
75.06	1501.26	20.30	20590050.50
100.08	2001.68	20.16	27961182.50

Response Factor, R_F (μV.sec/μg): 13981.59
Standard error of R_F: 134.97
r^2: 0.99

Oxygenated hydrocarbon analysis

Column: BIO RAD HPX 87-H

Temperature: 65°C

Eluant: 0.005 M H_2SO_4

Eluant flowrate: 0.6 mL/min

UV/VIS detector wavelength: 210 nm

Sample loop: 20 μL

Levulinic acid

Table C-4 HPLC calibration data of levulinic acid.

Concentration (mg/mL)	Mass in Sample loop (μg)	Chromatogram Retention Time (min)	Chromatogram Peak Area (μV.sec)
5.01	100.15	15.46	3861458.50
5.08	101.67	15.49	2508583.50
5.01	100.15	15.53	2479639.50
5.08	101.67	15.54	2855127.50
10.02	200.30	15.48	4855697.00
10.02	200.30	15.52	5812912.00
10.17	203.34	15.52	4717899.00
10.17	203.34	15.50	5879250.00
15.02	300.45	15.49	7174888.00
15.25	305.01	15.50	6987487.00
15.02	300.45	15.52	7300928.00
15.25	305.01	15.48	7523587.00
20.03	400.60	15.47	9420472.00
20.33	400.68	15.46	9895582.00
20.33	400.68	15.46	11358495.50
20.03	400.60	15.50	13745538.50

Response Factor , R_F (μV.sec/μg): 26322.91

Standard error of R_F: 976.01

r^2: 0.89

Formic acid

Table C-5 HPLC calibration data of formic acid.

Concentration (mg/mL)	Mass in Sample loop (μg)	Chromatogram Retention Time (min)	Chromatogram Peak Area (μV.sec)
0.85	16.94	13.53	1371541.50
1.02	20.32	13.50	1915729.00
1.27	25.40	13.50	2037373.00
1.69	33.86	13.53	2772040.00

Response Factor, R_F (μV.sec/μg): 83391.51
Standard error of R_F: 2828.78
r^2: 0.94

α-Angelicalactone

Table C-6 HPLC calibration of α-angelicalactone.

Concentration (mg/mL)	Mass in Sample loop (μg)	Chromatogram Retention Time (min)	Chromatogram Peak Area (μV.sec)
0.50	9.98	17.47	418863.50
0.60	11.98	17.49	479636.00
0.75	14.98	17.50	625615.00
1.00	19.96	17.48	1016158.00

Response Factor, R_F (μV.sec/μg): 45706.22
Standard error of R_F: 2795.59
r^2: 0.91

HMF

Table C-7 HPLC calibration data of HMF.

Concentration (mg/mL)	Mass in Sample loop (μg)	Chromatogram Retention Time (min)	Chromatogram Peak Area (μV.sec)
0.25	5.05	29.31	11362338.00
0.25	5.05	29.30	7500733.00
0.25	5.05	29.33	7424180.00
0.25	5.05	29.34	8577825.50
0.51	10.10	29.28	12969425.00
0.51	10.10	29.28	17243959.50
0.50	10.04	29.29	14067102.00
0.50	10.04	29.32	17545501.50
0.76	15.15	29.28	21210713.00
0.75	15.06	29.28	20770564.50
0.76	15.15	29.23	21672842.00
0.75	15.06	29.28	22428863.00
1.01	20.20	29.29	27766873.00
1.00	20.08	29.28	29323139.50
1.00	20.08	29.26	32026006.50
1.01	20.20	29.23	40435824.50

Response Factor, R_F (μV.sec/μg): 1547573.08

Standard error of R_F: 56377.46

r^2: 0.89

Butyric aid

Table C-8 HPLC calibration data of butyric acid.

Concentration (mg/mL)	Mass in Sample loop (μg)	Chromatogram Retention Time (min)	Chromatogram Peak Area (μV.sec)
0.60	12.09	21.04	747806.00
0.54	10.78	21.09	454288.00
0.60	12.09	20.99	481832.00
0.54	10.78	21.04	518809.50
1.21	24.18	21.02	936081.00
1.21	24.18	21.07	1143925.00
1.08	21.56	21.04	868374.00
1.08	21.56	21.02	1080649.00
1.81	36.27	21.02	1418645.50
1.62	32.34	21.07	1316061.00
1.81	36.27	20.96	1436822.00
1.62	32.34	21.02	1427084.50
2.42	48.36	21.02	1878545.50
2.16	43.12	21.04	1859955.00
2.16	43.12	21.02	2048393.50
2.42	48.36	21.02	2785723.00

Response Factor, R_F (μV.sec/μg): 44722.31

Standard error of R_F: 1693.49

r^2: 0.89

Appendix D

Calculation Example

(1) Component Weight in Sample

$$M_1 = \frac{A_1}{A_s} \times \frac{R_{Fs}}{R_{F1}} \times M_s \qquad \text{(D-1)}$$

(2) Weight and % Weight in Reactor

$$\%Wt_1 = \frac{M_1}{1000 \times S} \times 100 \qquad \text{(D-2)}$$

$$Wt_1 = \frac{M_1}{1000 \times S} \times M_T \qquad \text{(D-3)}$$

(3) Conversion

If component 1 is glucose, conversion can be obtained by

$$X = \frac{Wt_i - Wt_1}{Wt_i} \qquad \text{(D-4)}$$

(4) Yield

$$Y_1 = \frac{M_1 \times M_T}{1000 \times S \times MW_1} \times \frac{MW_g}{M_g} \times 100 \qquad \text{(D-5)}$$

(5) Reaction Rate Constant

$$X = 1 - \exp(-k_{app}\, t) \qquad \text{(D-6)}$$

$$\ln \frac{1}{1-X} = k_{app}\, t \qquad \text{(D-7)}$$

Least square fit between ln (1/1-X) and t to find coefficient of t as k_{app}

(6) Activation Energy

$$k_{app} = k_0 \, e^{-E/RT} \qquad \text{(D-8)}$$

or $$\ln k_{app} = \ln k_0 - E/RT \qquad \text{(D-9)}$$

Least square fit between ln k_{app} v.s. 1/T to find coefficient of 1/T as -E/R and intercept as ln k_0

(7) Acid Content

$$N = \frac{N_{NaOH} \times V}{S_t} \times \rho_s \qquad \text{(D-10)}$$

$$N_R = \frac{N \times M_T \times MW_g}{1000 \times \rho_s \times M_g} \qquad \text{(D-11)}$$

(8) Insoluble Residue

$$C_R = \frac{CWt_a \times TCWt_b}{CWt_b \times CWt} \qquad \text{(D-12)}$$

$$S_R = C_R \times CWt \qquad \text{(D-13)}$$

$$\%S_R = \frac{S_R}{M_g} \times 100 \qquad \text{(D-14)}$$

(9) Selectivity

$$S_1 = \frac{Y_1}{Y_{HMF}} \qquad \text{(D-15)}$$

Appendix E

Reaction Analysis Data

Reaction Run # 11 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.58 Total mass : 170.06 g

(D)-glucose : 100.00 g Water weight : 70.06 g

g glucose/g H-Y zeolite : 10.0 H-Y zeolite : 10.0122 g

Reaction temperature : 100°C Mixing speed : 300 rpm

Total reaction time : 10 hr Pressure : 30 psi

Internal Standard : butyric acid, 15.15 mg

myo-inositol, 40.012 mg

Table E-1 Reaction run# 11, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
1	4.30	1.89	0.01	0.01	0.00	0.00
2	5.53	4.46	0.02	0.00	0.00	0.00
3	4.31	5.58	0.04	0.00	0.00	0.00
4	10.70	6.89	0.06	0.14	0.00	0.01
5	11.83	8.25	0.08	0.08	0.00	0.00
6	17.75	9.63	0.10	0.19	0.00	0.01
7	11.95	10.89	0.12	0.24	0.00	0.01
8	16.16	11.44	0.15	0.32	0.01	0.01
9	16.21	13.17	0.17	0.40	0.01	0.02
10	16.47	14.15	0.19	0.49	0.01	0.02

Reaction Run # 13 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.58 Total mass : 170.06 g

(D)-glucose weight : 100.00 g Water weight : 70.06 g

g glucose/g H-Y zeolite : 10.0 H-Y zeolite : 10.0123 g

Reaction temperature : 130°C Mixing speed : 300 rpm

Total reaction time : 10 hr Pressure : 30-60 psi

Internal Standard : butyric acid, 13.614 mg

myo-inositol, 80.032 mg

Table E-2 · Reaction run# 13, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
1	45.37	10.39	0.26	0.70	0.00	0.05
2	34.28	16.19	0.68	2.16	0.05	0.22
3	42.73	18.12	0.40	4.70	1.83	0.90
4	52.66	19.54	0.81	9.01	3.64	2.65
5	59.47	18.49	1.36	16.61	6.49	4.21
6	64.67	17.83	0.97	12.83	6.26	3.98
7	69.49	17.75	0.69	9.05	6.21	2.94
8	74.37	15.32	2.30	27.96	13.36	6.89
9	81.00	11.10	3.19	11.34	3.82	1.73
10	86.34	6.32	2.93	11.50	2.78	3.81

Reaction Run # 14 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.58 Total mass : 170.08 g

(D)-glucose weight : 100.00 g Water weight : 70.08 g

g glucose/g H-Y zeolite : 10.0 H-Y zeolite : 10.0103 g

Reaction temperature : 110°C Mixing speed : 300 rpm

Total reaction time : 10 hr Pressure : 30-50 psi

Internal Standard : butyric acid, 13.614 mg

myo-inositol, 80.032 mg

Table E-3 Reaction run# 14, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
1	13.08	3.62	0.03	0.05	0.00	0.00
2	12.78	7.27	0.07	0.08	0.01	0.00
3	12.83	10.51	0.14	0.22	0.01	0.02
4	15.41	11.93	0.18	0.32	0.01	0.02
5	16.82	13.69	0.24	1.46	0.27	0.14
6	20.10	15.06	0.30	1.88	0.34	0.20
7	23.76	16.03	0.38	2.47	0.42	0.24
8	26.45	17.04	0.46	3.30	0.55	0.35
9	26.69	17.64	0.35	2.89	0.00	0.40
10	28.74	17.96	0.30	2.62	0.00	0.38

Reaction Run # 16 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.58 Total mass : 170.06 g

(D)-glucose weight : 100.00 g Water weight : 70.06 g

g glucose/g H-Y zeolite : 10.0 H-Y zeolite : 10.0019 g

Reaction temperature : 130°C Mixing speed : 1200 rpm

Total reaction time : 10 hr Pressure : 30-60 psi

Internal Standard : butyric acid, 13.614 mg

myo-inositol, 80.016 mg

Table E-4 Reaction run# 16, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
1	39.48	12.43	0.30	2.78	0.00	0.52
2	28.92	15.62	0.52	1.48	0.00	0.14
3	41.59	17.07	0.47	5.45	0.00	1.03
4	55.47	14.68	0.45	5.38	0.00	2.18
5	59.07	14.97	1.16	14.85	0.00	4.41
6	71.00	13.74	0.51	7.32	0.00	3.21
7	76.70	13.24	3.08	10.13	0.00	1.79
8	77.96	11.73	3.13	10.96	0.00	1.73
9	81.82	10.37	2.02	26.34	0.00	6.01
10	85.38	7.51	1.54	21.05	0.00	5.47

Reaction Run # 17 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.58 Total mass : 170.43 g
(D)-glucose weight : 100.00 g Water weight : 70.43 g
g glucose/g H-Y zeolite : 10.0 H-Y zeolite : 10.0077 g
Reaction temperature : 130°C Mixing speed : 150 rpm
Total reaction time : 10 hr Pressure : 30-60 psi
Internal Standard : butyric acid, 13.614 mg
myo-inositol, 80.016 mg

Table E-5 Reaction run# 17, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
1	28.57	8.68	0.26	2.87	0.00	0.00
2	36.91	17.90	0.82	0.27	0.00	0.01
3	38.34	18.94	0.58	0.49	0.00	0.12
4	44.13	18.93	0.85	0.83	0.00	0.19
5	51.90	21.38	0.59	0.68	0.00	0.18
6	55.50	16.62	1.00	1.23	0.00	0.34
7	62.71	14.40	1.39	1.63	0.00	0.45
8	72.59	13.93	3.68	1.11	0.00	0.15
9	69.15	11.62	4.30	1.32	0.00	0.15
10	78.37	12.02	4.46	1.48	0.00	0.14

Reaction Run # 19 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.58 Total mass : 170.00 g

(D)-glucose weight : 100.00 g Water weight : 70.00 g

g glucose/g H-Y zeolite : 0.0 H-Y zeolite : 0.00 g

Reaction temperature : 130°C Mixing speed : 150 rpm

Total reaction time : 10 hr Pressure : 30-60 psi

Internal Standard : butyric acid, 13.614 mg

myo-inositol, 80.016 mg

Table E-6 Reaction run# 19, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.000	0.00	0.00	0.00	0.00
2	1.91	0.001	0.00	0.00	0.00	0.00
4	6.15	0.002	0.00	0.00	0.00	0.00
6	10.04	0.003	0.00	0.00	0.00	0.00
8	14.43	0.004	0.00	0.00	0.00	0.00
10	20.29	0.004	0.00	0.00	0.00	0.00

Reaction Run # 20 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.12 Total mass : 170.05 g

(D)-glucose weight : 20.00 g Water weight : 150.05 g

g glucose/g H-Y zeolite : 2.0 H-Y zeolite : 10.0021 g

Reaction temperature : 130°C Mixing speed : 300 rpm

Total reaction time : 24 Pressure : 30-60 psi

Internal Standard : butyric acid, 18.15 mg

myo-inositol, 90.072 mg

Table E-7 Reaction run# 20, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
1	18.19	12.35	0.38	0.00	0.00	0.00
2	15.21	14.54	0.42	0.09	0.00	0.09
3	22.69	18.82	0.77	2.10	1.79	0.65
4	30.90	22.58	1.32	3.19	2.10	1.07
5	39.84	24.73	1.96	4.93	2.69	1.40
6	46.70	25.63	2.34	6.36	3.51	1.98
7	53.27	25.57	2.82	8.61	4.82	2.76
8	58.31	24.93	3.78	12.47	8.32	4.21
9	64.33	22.35	3.90	13.90	8.89	4.85
10	66.57	22.50	4.68	16.76	8.73	5.03
12	69.65	20.74	4.87	19.91	11.65	7.18
14	74.65	18.33	5.28	23.27	13.22	8.76
16	78.87	15.61	5.45	24.81	13.09	8.23
24	83.17	12.51	6.15	29.16	14.17	8.90

Reaction Run # 21 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.158 Total mass : 170.00 g

(D)-glucose weight : 100.00 g Water weight : 70.00 g

g glucose/g H-Y zeolite : 10.0 H-Y zeolite : 10.0039 g

Reaction temperature : 120°C Mixing speed : 300 rpm

Total reaction time : 10 hr Pressure : 30-60 psi

Internal Standard : butyric acid, 18.150 mg

myo-inositol, 90.072 mg

Table E-8 Reaction run# 21, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
1	20.06	12.65	0.16	0.30	0.00	0.00
2	18.18	13.34	0.22	1.01	0.00	0.01
3	22.66	14.75	0.33	0.79	0.00	0.10
4	25.67	16.62	0.46	1.31	0.00	0.08
5	29.60	17.68	0.43	3.40	0.00	0.10
6	31.16	18.59	0.74	5.82	0.00	1.35
7	37.35	19.21	0.57	5.83	0.00	0.88
8	39.23	19.13	0.82	8.37	0.00	2.62
9	42.72	18.90	0.59	8.26	0.00	1.33
10	46.08	18.44	0.57	7.41	0.00	2.45

Reaction Run # 24 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.12 Total mass : 170.23 g

(D)-glucose weight: 20.00 g Water weight: 150.23 g

g glucose/g H-Y zeolite : 2.0 H-Y zeolite : 10.0115 g

Reaction temperature : 120°C Mixing speed : 300 rpm

Total reaction time : 24 hr Pressure : 30-60 psi

Internal Standard : butyric acid, 18.15 mg

myo-inositol, 90.072 mg

Table E-9 Reaction run# 24,conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
1	6.51	5.13	0.14	0.12	0.00	0.00
2	8.30	7.32	0.15	0.17	0.00	0.00
3	12.27	10.62	0.24	0.21	0.05	0.00
4	16.46	13.91	0.41	0.87	0.72	0.00
5	22.33	17.46	0.67	0.54	0.26	0.00
6	27.67	20.36	0.97	1.78	0.66	0.00
7	31.33	21.94	1.25	2.97	1.71	0.00
8	35.14	23.30	1.50	4.25	2.02	0.00
9	39.48	24.28	1.90	4.49	3.78	0.00
10	42.63	24.84	1.87	5.17	2.92	0.00
12	48.54	23.57	2.33	7.42	4.47	0.00
14	48.81	23.81	2.40	7.47	4.79	0.00
16	50.72	24.44	2.73	9.22	4.85	0.00
24	62.31	21.73	4.26	17.74	9.41	0.00

Reaction Run # 25 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.12 Total mass : 170.27 g

(D)-glucose weight : 20.00 g Water weight : 150.27 g

g glucose/g H-Y zeolite : 2.0 H-Y zeolite : 10.0085 g

Reaction temperature : 110°C Mixing speed : 300 rpm

Total reaction time : 24 hr Pressure : 30-60 psi

Internal Standard : butyric acid, 18.15 mg

myo-inositol, 90.072 mg

Table E-10 Reaction run# 25, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
1	3.06	2.86	0.09	0.07	0.00	0.00
2	3.84	2.69	0.08	0.69	0.00	0.00
3	6.25	5.80	0.08	0.41	0.00	0.00
4	8.51	7.62	0.11	0.28	0.00	0.00
5	10.89	9.32	0.15	0.30	0.17	0.00
6	13.42	11.19	0.21	0.46	0.22	0.00
7	15.17	13.01	0.28	0.45	0.25	0.00
8	18.72	14.43	0.38	1.56	0.41	0.00
9	20.80	15.68	0.47	1.63	0.45	0.00
10	23.11	16.85	0.56	1.42	0.50	0.00
12	25.51	18.89	0.70	2.04	1.34	0.00
14	29.22	20.17	0.84	2.84	1.52	0.00
16	31.09	21.23	1.02	2.03	0.80	0.00
24	33.86	22.63	1.24	3.55	2.34	0.00

Reaction Run # 26 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.12 Total mass : 170.37 g

(D)-glucose weight : 20.00 g Water weight : 150.37 g

g glucose/g H-Y zeolite : 10.0 H-Y zeolite : 2.01 g

Reaction temperature : 130°C Mixing speed : 300 rpm

Total reaction time : 24 hr Pressure : 30-60 psi

Internal Standard : butyric acid, 18.15 mg

myo-inositol, 90.072 mg

Table E-11 Reaction run# 26, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
1	3.37	3.84	0.14	0.11	0.12	0.06
2	3.80	4.45	0.17	0.08	0.09	0.05
3	7.51	7.35	0.35	0.32	0.12	0.05
4	12.73	10.50	0.64	0.79	0.24	0.08
5	16.80	12.93	0.96	1.53	1.16	0.49
6	21.66	15.16	1.34	3.34	1.47	0.70
7	26.97	17.20	1.81	3.56	2.05	1.01
8	30.11	18.84	2.14	4.54	3.69	1.43
9	35.12	19.92	2.58	6.19	3.41	2.00
10	38.53	21.21	2.98	7.22	4.18	2.43
12	44.88	22.08	3.52	9.59	5.35	3.52
14	49.87	22.73	3.92	11.49	6.42	4.29
16	56.29	22.39	4.35	14.52	7.31	5.49
24	66.58	19.85	6.74	22.63	11.38	7.11

Reaction Run # 28 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.12 Total mass : 170.43 g

(D)-glucose weight : 20.00 g Water weight : 150.43 g

g glucose/g H-Y zeolite : 5.0 H-Y zeolite : 4.0008 g

Reaction temperature : 130°C Mixing speed : 300 rpm

Total reaction time : 24 hr Pressure : 30-60 psi

Internal Standard : butyric acid, 18.075 mg

myo-inositol, 90.072 mg

Table E-12 Reaction run# 28, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
1	9.27	6.46	0.17	0.08	0.00	0.00
2	9.09	7.23	0.21	0.21	0.00	0.00
3	14.25	12.35	0.54	0.46	0.19	0.00
4	20.29	15.45	0.89	1.75	1.41	0.00
5	25.19	18.43	1.35	2.64	1.91	0.00
6	31.14	20.37	1.84	2.29	2.89	0.54
7	37.10	21.90	2.29	5.40	2.98	1.84
8	41.33	23.33	2.73	7.46	3.58	2.45
9	45.30	24.15	3.05	8.46	4.70	3.03
10	50.21	24.01	3.53	10.52	5.90	3.76
12	55.82	22.74	3.55	11.93	0.00	4.63
14	61.06	21.97	3.75	13.43	7.70	5.36
16	64.87	21.42	4.28	17.52	0.00	6.74
24	72.64	17.22	6.03	26.03	11.34	16.07

Reaction Run # 32 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.12 Total mass : 170.13 g

(D)-glucose weight : 20.00 Water weight : 150.13 g

g glucose/g H-Y zeolite : 0.0 H-Y zeolite : 0.00 g

Reaction temperature : 130°C Mixing speed : 300 rpm

Total reaction time : 24 hr Pressure : 30-60 psi

Internal Standard : butyric acid, 18.075 mg

myo-inositol, 90.072 mg

Table E-13 Reaction run# 32, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
2	2.01	0.26	0.00	0.00	0.00	0.00
4	2.18	1.02	0.00	0.00	0.00	0.00
6	4.31	1.32	0.00	0.00	0.00	0.00
8	6.10	1.65	0.00	0.00	0.00	0.00
10	7.74	2.87	0.00	0.00	0.00	0.00
20	13.06	4.09	0.00	0.00	0.00	0.00
24	15.26	4.04	0.00	0.00	0.00	0.00

Reaction Run # 33 Analysis

Reaction Parameters

g (D)-glucose/g solution : 0.12 Total mass : 170.04 g

(D)-glucose weight : 20.00 g Water weight : 150.04 g

g glucose/g H-Y zeolite : 1.0 H-Y zeolite : 20.0116 g

Reaction temperature : 130°C Mixing speed : 300 rpm

Total reaction time : 24 hr Pressure : 30-60 psi

Internal Standard : butyric acid, 18.075 mg

myo-inositol, 90.072 mg

Table E-14 Reaction run# 33, conversion and product yield.

Time (hr)	% glucose Conver.	mol/mol glucose x 100 Fructose	HMF	Formic acid	Levulinic acid	Angelica lactone
0	0.00	0.00	0.00	0.00	0.00	0.00
1	25.99	18.76	0.56	1.18	0.00	0.00
2	26.50	19.77	0.65	0.70	0.13	0.00
3	42.24	25.16	1.47	3.39	1.86	0.00
4	51.35	27.60	2.21	6.84	3.03	0.00
5	57.80	27.05	2.75	8.52	4.59	0.00
6	64.63	25.11	2.71	10.87	5.21	0.00
7	70.35	22.56	3.00	13.35	6.22	0.00
8	74.67	20.12	3.37	16.22	6.78	0.00
9	77.53	17.22	4.18	20.30	9.77	0.00
10	79.93	16.37	3.35	18.19	8.08	0.00
12	82.65	14.19	3.59	20.94	0.00	0.00
14	84.90	11.79	4.34	27.78	10.38	0.00
16	88.04	9.24	4.16	25.69	10.44	0.00
24	91.88	6.70	4.15	28.01	13.39	0.00

Appendix F
Reaction Product Summary

0.58 g glucose/g solution reaction

Table F-1 High (D)-glucose concentration reaction product.

Run#	#11	#13	#14	#16	#17	#21
temperature (°C)	100	130	110	130	130	120
mixing speed (rpm)	300	300	300	1200	150	300
glucose (g)	100.00	100.00	100.00	100.00	100.00	100.00
H-Y zeolite (g)	10.012	10.012	10.010	10.002	10.008	10.004
Cat. loading	10:1	10:1	10:1	10:1	10:1	10:1
Reaction time (hr)	10	10	10	10	10	10
density (g/mL)	1.266	1.208	1.243	1.046	1.129	1.064
avg. acid (N)	0.069	0.464	0.128	0.400	0.405	0.399
mol H^+/mol glucose	0.017	0.118	0.032	0.117	0.110	0.115
pH	3.97	2.85	3.93	2.85	2.68	3.31
solid residue (g)	1.25	26.50	1.24	18.27	17.10	0.48
% solid residue	0.83	26.50	1.24	18.27	17.10	0.48

0.12 g glucose/g solution reaction

Table F-2 Low (D)-glucose concentration reaction product.

Run#	#20	#24	#25	#26
temperature (°C)	130	120	110	130
mixing speed (rpm)	300	300	300	300
glucose (g)	20.00	20.00	20.00	20.00
zeolite (g)	10.002	10.014	10.009	2.010
Cat. loading	2:1	2:1	2:1	10:1
Reaction time (hr)	24	24	24	24
density (g/mL)	1.015	1.036	1.041	1.027
avg. acid (N)	0.232	0.155	0.056	0.199
mol H^+/mol glucose	0.349	0.229	0.082	0.297
pH	2.78	2.98	3.60	3.23
solid residue (g)	2.20	0.23	0.05	0.79
% solid residue	11.02	1.134	0.25	3.99

Table F-2 (continued) Low (D)-glucose concentration reaction product.

Run#	#28	#29	#33
temperature (°C)	130	100	130
mixing speed (rpm)	300	300	300
glucose (g)	20.00	20.00	20.00
zeolite (g)	4.001	10.011	20.012
Cat. loading	5:1	2:1	1:1
Reaction time (hr)	24	24	24
density (g/mL)	1.027	1.037	1.011
avg. acid (N)	0.208	0.016	0.257
mol H^+/mol glucose	0.312	0.024	0.390
pH	3.06	3.87	2.78
solid residue (g)	1.51	0.04	2.59
% solid residue	7.543	0.20	12.98

Appendix G

Material Balance

Material Balance

Reaction Run # 11

Reaction Conditions
H-Y-zeolite Powder : 10.0122 g
Temperature 100 C Mixing Speed 300 rpm
Pressure 30 psi Sampling Perieod 1 hr.
Reaction Time: 10 hr

Table G-1. Reaction run# 11, material balance.

Reactant:	
Glucose fed into reactor (g)	100.0000
TOTAL REACTANT	100.0000
Distilled water (g)	70.06
Total Mass Input (g)	170.06
Products:	
Unreacted glucose : Wt (g)	78.7197
D-fructose : Wt (g)	16.0480
HMF : Wt (g)	0.1380
Formic acid : Wt (g)	0.4469
Levulinic acid : Wt (g)	0.1475
Angelicalactone : Wt (g)	0.0941
Insoluble Residue (g)	1.2510
TOTAL PRODUCTS:	96.8452

Material Balance

Reaction Run # 13

Reaction Conditions
H-Y-zeolite Powder : 10.0123 g
Temperature 130 C Mixing Speed 300 rpm
Pressure 30 psi Sampling Perieod 1 hr.
Reaction Time: 10 hr

Table G-2. Reaction run# 13, material balance.

Reactant:	
Glucose fed into reactor (g)	100.0000
TOTAL REACTANT	100.0000
Distilled water (g)	70.06
Total Mass Input (g)	170.06
Products:	
Unreacted glucose : Wt (g)	13.6641
D-fructose : Wt (g)	6.3240
HMF : Wt (g)	2.0502
Formic acid : Wt (g)	2.9413
Levulinic acid : Wt (g)	1.8003
Angelicalactone : Wt (g)	2.0730
Insoluble Residue (g)	26.4960
TOTAL PRODUCTS:	55.3489

Material Balance

Reaction Run # 14

Reaction Conditions
H-Y-zeolite Powder : 10.0103 g
Temperature 110 C Mixing Speed 300 rpm
Pressure 30 psi Sampling Perieod 1 hr.
Reaction Time: 10 hr

Table G-3. Reaction run# 14, material balance.

Reactant:	
Glucose fed into reactor (g)	100.0000
TOTAL REACTANT	100.0000
Distilled water (g)	70.08
Total Mass Input (g)	170.08
Products:	
Unreacted glucose : Wt (g)	71.2570
D-Fructose : Wt (g)	17.9690
HMF : Wt (g)	0.2105
Formic acid : Wt (g)	0.6689
Levulinic acid : Wt (g)	0.3551
Angelicalactone : Wt (g)	0.2069
Insoluble Residue (g)	1.2390
TOTAL PRODUCTS:	91.9064

Material Balance

Reaction Run # 16

Reaction Conditions
H-Y-zeolite Powder : 10.0019 g
Temperature 130 C Mixing Speed 1200 rpm
Pressure 30 psi Sampling Perieod 1 hr.
Reaction Time: 10 hr

Table G-4. Reaction run# 16, material balance.

Reactant:	
Glucose fed into reactor (g)	100.0000
TOTAL REACTANT	100.0000
Distilled water (g)	70.06
Total Mass Input (g)	170.06
Products:	
Unreacted glucose : Wt (g)	14.6203
D-fructose : Wt (g)	7.5140
HMF : Wt (g)	1.0816
Formic acid : Wt (g)	5.3810
Levulinic acid : Wt (g)	0.0000
Angelicalactone : Wt (g)	2.9810
Insoluble Residue (g)	18.2740
TOTAL PRODUCTS:	49.8519

Material Balance

Reaction Run # 17

Reaction Conditions
H-Y-zeolite Powder : 10.0077 g
Temperature 130 C Mixing Speed 150 rpm
Pressure 30 psi Sampling Perieod 1 hr.
Reaction Time: 10 hr

Table G-5. Reaction run# 17, material balance.

Reactant:	
Glucose fed into reactor (g)	100.0000
TOTAL REACTANT	100.0000
Distilled water (g)	70.13
Total Mass Input (g)	170.43
Products:	
Unreacted glucose : Wt (g)	21.6263
D-fructose : Wt (g)	12.0190
HMF : Wt (g)	3.1275
Formic acid : Wt (g)	0.3782
Levulinic acid : Wt (g)	0.0000
Angelicalactone : Wt (g)	0.0801
Insoluble Residue (g)	17.0980
TOTAL PRODUCTS:	54.3291

Material Balance

Reaction Run # 20

Reaction Conditions
H-Y-zeolite Powder : 10.0021 g
Temperature 130 C Mixing Speed 300 rpm
Pressure 30-60 psi Sampling Perieod 1 hr.
Reaction Time: 24 hr

Table G-6. Reaction run# 20, material balance.

Reactant:	
Glucose fed into reactor (g)	20.0000
TOTAL REACTANT	20.0000
Distilled water (g)	150.05
Total Mass Input (g)	170.05
Products:	
Unreacted glucose : Wt (g)	3.3937
D-fructose : Wt (g)	2.5000
HMF : Wt (g)	0.8622
Formic acid : Wt (g)	1.4900
Levulinic acid : Wt (g)	1.8297
Angelicalactone : Wt (g)	0.9694
Insoluble Residue (g)	2.2040
TOTAL PRODUCTS:	13.2488

Material Balance

Reaction Run # 21

Reaction Conditions
H-Y-zeolite Powder : 10.0039 g
Temperature 120 C Mixing Speed 300 rpm
Pressure 30 psi Sampling Perieod 1 hr.
Reaction Time: 10 hr

Table G-7. Reaction run# 21, material balance.

Reactant:	
Glucose fed into reactor (g)	100.00
TOTAL REACTANT	100.00
Distilled water (g)	70.00
Total Mass Input (g)	170.00
Products:	
Unreacted glucose : Wt (g)	53.4594
D-fructose : Wt (g)	18.9040
HMF : Wt (g)	0.3970
Formic acid : Wt (g)	1.8932
Levulinic acid : Wt (g)	0.0000
Angelicalactone : Wt (g)	1.2253
Insoluble Residue (g)	0.4850
TOTAL PRODUCTS:	76.3639

Material Balance

Reaction Run # 24

Reaction Conditions
H-Y-zeolite Powder : 10.0115 g
Temperature 120 C Mixing Speed 300 rpm
Pressure 30-60 psi Sampling Perieod 1 hr.
Reaction Time: 24 hr

Table G-8 Reaction run# 24, material balance.

Reactant:	
Glucose fed into reactor (g)	20.0000
TOTAL REACTANT	20.0000
Distilled water (g)	150.23
Total Mass Input (g)	170.23
Products:	
Unreacted glucose : Wt (g)	7.6077
D-fructose : Wt (g)	4.3500
HMF : Wt (g)	0.5971
Formic acid : Wt (g)	0.9067
Levulinic acid : Wt (g)	1.2152
Angelicalactone : Wt (g)	0.0000
Insoluble Residue (g)	0.2270
TOTAL PRODUCTS:	14.9037

Material Balance

Reaction Run # 25

Reaction Conditions
H-Y-zeolite Powder : 10.0085 g
Temperature 110 C Mixing Speed 300 rpm
Pressure 30-60 psi Sampling Perieod 1 hr.
Reaction Time: 24 hr

Table G-9. Reaction run# 25, material balance.

Reactant:	
Glucose fed into reactor (g)	20.0000
TOTAL REACTANT	20.0000
Distilled water (g)	150.27
Total Mass Input (g)	170.27
Products:	
Unreacted glucose : Wt (g)	13.3871
D-fructose : Wt (g)	4.5220
HMF : Wt (g)	0.1743
Formic acid : Wt (g)	0.1815
Levulinic acid : Wt (g)	0.3026
Angelicalactone : Wt (g)	0.0000
Insoluble Residue (g)	0.0470
TOTAL PRODUCTS:	18.6146

Material Balance

Reaction Run # 26

Reaction Conditions
H-Y-zeolite Powder : 2.01 g
Temperature 130 C Mixing Speed 300 rpm
Pressure 30-60 psi Sampling Perieod 1 hr.
Reaction Time: 24 hr

Table G-10. reaction run# 26, material balance.

Reactant:	
Glucose fed into reactor (g)	20.0000
TOTAL REACTANT	20.0000
Distilled water (g)	150.37
Total Mass Input (g)	170.37
Products:	
Unreacted glucose : Wt (g)	6.7763
D-fructose : Wt (g)	3.9800
HMF : Wt (g)	0.9456
Formic acid : Wt (g)	1.1591
Levulinic acid : Wt (g)	1.4721
Angelicalactone : Wt (g)	0.7761
Insoluble Residue (g)	0.7980
TOTAL PRODUCTS:	15.9071

Material Balance

Reaction Run # 28

Reaction Conditions
H-Y-zeolite Powder : 4.0008 g
Temperature 130 C Mixing Speed 300 rpm
Pressure 30-60 psi Sampling Perieod 1 hr.
Reaction Time: 24 hr

Table G-11. Reaction run# 28, material balance.

Reactant:	
Glucose fed into reactor (g)	20.0000
TOTAL REACTANT	20.0000
Distilled water (g)	150.43
Total Mass Input (g)	170.43
Products:	
Unreacted glucose : Wt (g)	5.6004
D-fructose : Wt (g)	3.4500
HMF : Wt (g)	0.8464
Formic acid : Wt (g)	1.3333
Levulinic acid : Wt (g)	1.4681
Angelicalactone : Wt (g)	1.7546
Insoluble Residue (g)	1.5090
TOTAL PRODUCTS:	15.9618

Material Balance

Reaction Run # 33

Reaction Conditions
H-Y-zeolite Powder : 20.0116 g
Temperature 130 C Mixing Speed 300 rpm
Pressure 30-60 psi Sampling Perieod 1 hr.
Reaction Time: 24 hr

Table G-12. Reaction run# 33, material balance.

Reactant:	
Glucose fed into reactor (g)	20.0000
TOTAL REACTANT	20.0000
Distilled water (g)	150.04
Total Mass Input (g)	170.04
Products:	
Unreacted glucose : Wt (g)	1.6332
D-fructose : Wt (g)	1.3400
HMF : Wt (g)	0.5814
Formic acid : Wt (g)	1.4314
Levulinic acid : Wt (g)	1.7289
Angelicalactone : Wt (g)	0.0000
Insoluble Residue (g)	2.5970
TOTAL PRODUCTS:	9.3119

Appendix H

HPLC Peak Isolation

A representative chromatogram of the reaction products is shown in Figure 3.10 that contain complicated isolation. The product distribution was complicated, and not all peaks were fully isolated. The identified an unidentified compound retention times are given in Table H-3. At the standard analysis conditions, some peaks from the reaction samples matched with the standard compounds and were easily identified and determined but some were not. Therefore, the peak area results from the integrator need to be confirmed and major peak identification is priority.

HPLC Evaluation

The interested components, formic acid and levulinic acid, gave small response with these analysis parameters. As a result, it was difficult to determine the composition of these components accurately. To investigate this problem, a standard solution of levulinic acid and formic acid were added to the reaction sample to confirm the calibration of those peaks. From Table H-1 and H-2, they show that the retention times of both components from the original reaction sample and modified samples are almost the same. The peak areas, which account for the composition of both acids, had an error of about 5% from the actual amount of the standard solutions added.

Chromatogram peak isolation

To identify some of the peaks in product distribution profile, the same standard-adding technique was introduced to point out the known components. The known peaks which were identified are levulinic acid, formic acid, HMF, and butyric acid as the internal standard. The other identified peaks are D-fructose with retention time (RT), 9.6 min, acetic acid with RT of 14.7 min, and α-angelicalactone with RT of 17.4 min. Although D-fructose shows a significant peak, it is preferred to beseparated accurately with carbohydrate column, HPX 87-P, and refractive index detector. Acetic acid and α-angelicalactone have the problem: retention time is not repeatable for all samples. In some samples, the retention time exceeds ± 0.25 min of standard retention time. Therefore, these two compounds are not estimated compositions.

Some compounds were also checked and gave negative results. Acetone, succinic acid, and anhydrous-β-D-glucose have retention time of 21.4, 11.3 and 11.9 min respectively.

After the UV/VIS detector was changed to 270 nm, the chromatogram presented a new profile which boosted some peaks. Figure 3.10 shows a new profile at this wavelength, levulinic acid and formic acid peaks were clearer. Actually, the response ratio of levulinic acid relative to HMF at 270 nm is lower than at 210 nm and butyric acid peak can not be detected. Therefore at 270 nm, The composition of those compounds could not be estimated by the internal standard method.

HPLC Evaluation data

Column : HPX-87-H Temperature : 65°C

Eluant : 0.005 M H_2SO_4 Flowrate : 0.6 mL/min

Detector : UV/VIS with wavelength 210 nm

Sample weight : 0.0554 g

Internal standard : butyric acid, 2.0649 mg

Formic acid

formic acid standard solution : 1.524 mg in 0.3 mL

Table H-1 HPLC evaluation of formic acid.

Sample Status	Peak area (μV.sec) butyric acid	formic acid	Formic acid wt. in sample	RT
original	1640038.0	264875.5	0.178	13.58
added	1668836.5	2444717.0	1.622	13.52

Formic acid adding : from HPLC, 1.444 mg

: from actual adding, 1.524 mg

% error of evaluation : 5.285 %

Levulinic acid

levulinic acid standard solution : 3.013 mg in 0.3 mL

Table H-2 HPLC evaluation of levulinic acid.

Sample Status	Peak area (μV.sec) butyric acid	levulinic acid	Levulinic acid wt. in sample	RT
original	1640038.0	118014.5	0.252	15.41
added	1731493.5	1659469.5	3.362	15.39

Levulinic acid adding : from HPLC, 3.110 mg

: from actual adding, 3.013 mg

% error of evaluation : 3.209 %

Table H-3 Standard Compound Retention time.

Compound	Retention Time, RT (min)
D-fructose	9.6
succinic acid	11.3
anhydrous-ß-D-glucose	11.9
formic acid	13.5
acetic acid	14.7
levulinic acid	15.3
α-angelicalactone	17.4
butyric acid	21.0
acetone	21.4
HMF	29.3