Kinetics of Glucose Decomposition during Dilute Acid Hydrolysis of Lignocellulosic Biomass

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Introduction

- **Recent advancement on dilute acid hydrolysis of biomass:**
  1. development of various reactor configurations;
  2. development in kinetic investigation, especially from exploration of a broader range of reaction conditions

- **Extremely low concentration of acid (e.g. 0.05-0.2 wt% sulfuric acid) and high temperature (e.g. 200 - 230oC) is a range of reaction conditions to effectively hydrolyze biomass. But the kinetic data are not currently available**

- **Objectives of this study:**
  1. investigate glucose decomposition kinetics
  2. provide kinetic parameters for mathematical calculation
  3. explain the discrepancy of glucose yield predicted by conventional hydrolysis kinetics for percolation reactors

Decomposition Profile and Products
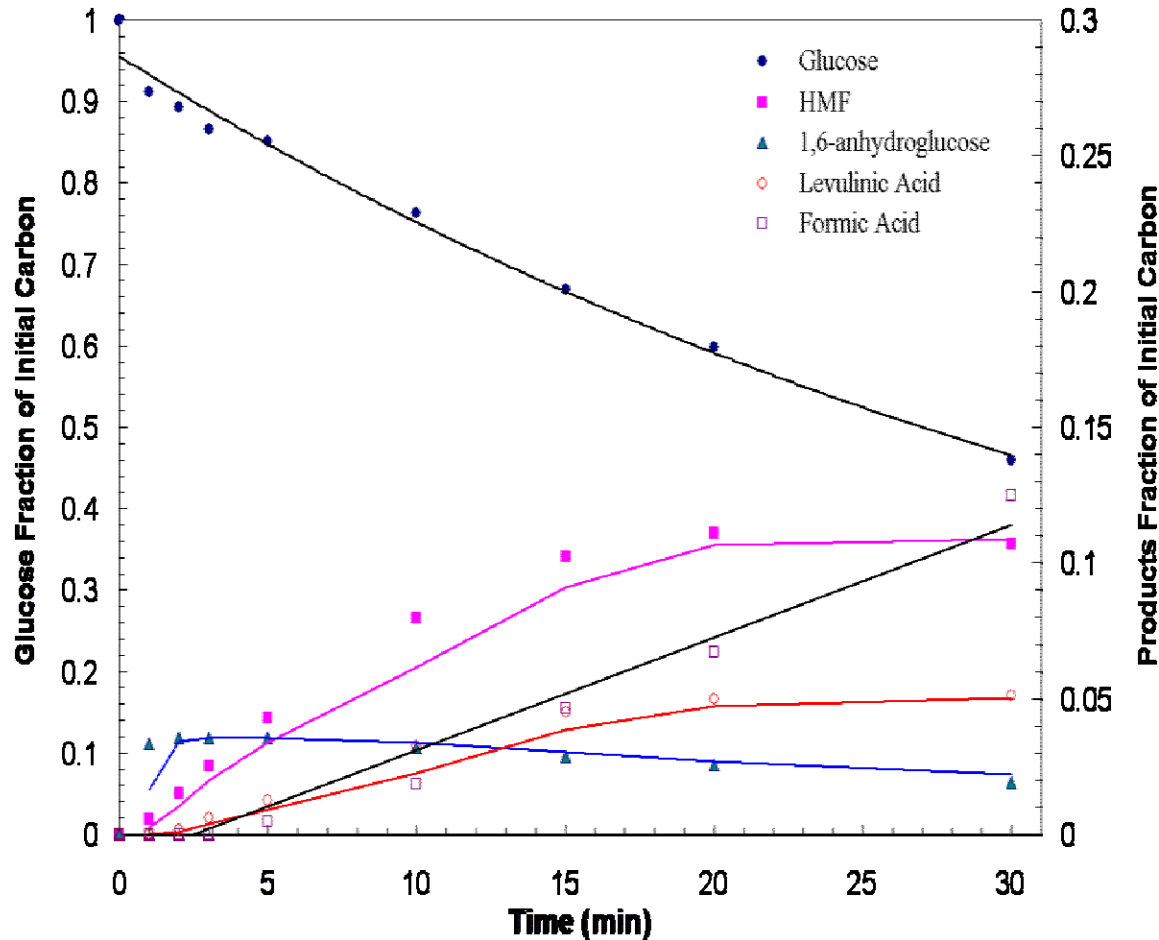
- **Experiments conducted under various pH and temperature conditions**

- **First order kinetics is applicable**

- **Trend line does not trace back to origin**

- **Other Products include:**
  - **Fructose**
  - **Cellubiose**
  - **Acetic Acid**
  - **Humic Solid (Solid Precipitate)**
  - **Gaseous Products**

Profile of glucose decomposition and formation of decomposition products (0.125 M Glucose, 200 oC, pH 1.8, and glass ampoule reactor)

pH vs. Decomposition Rate
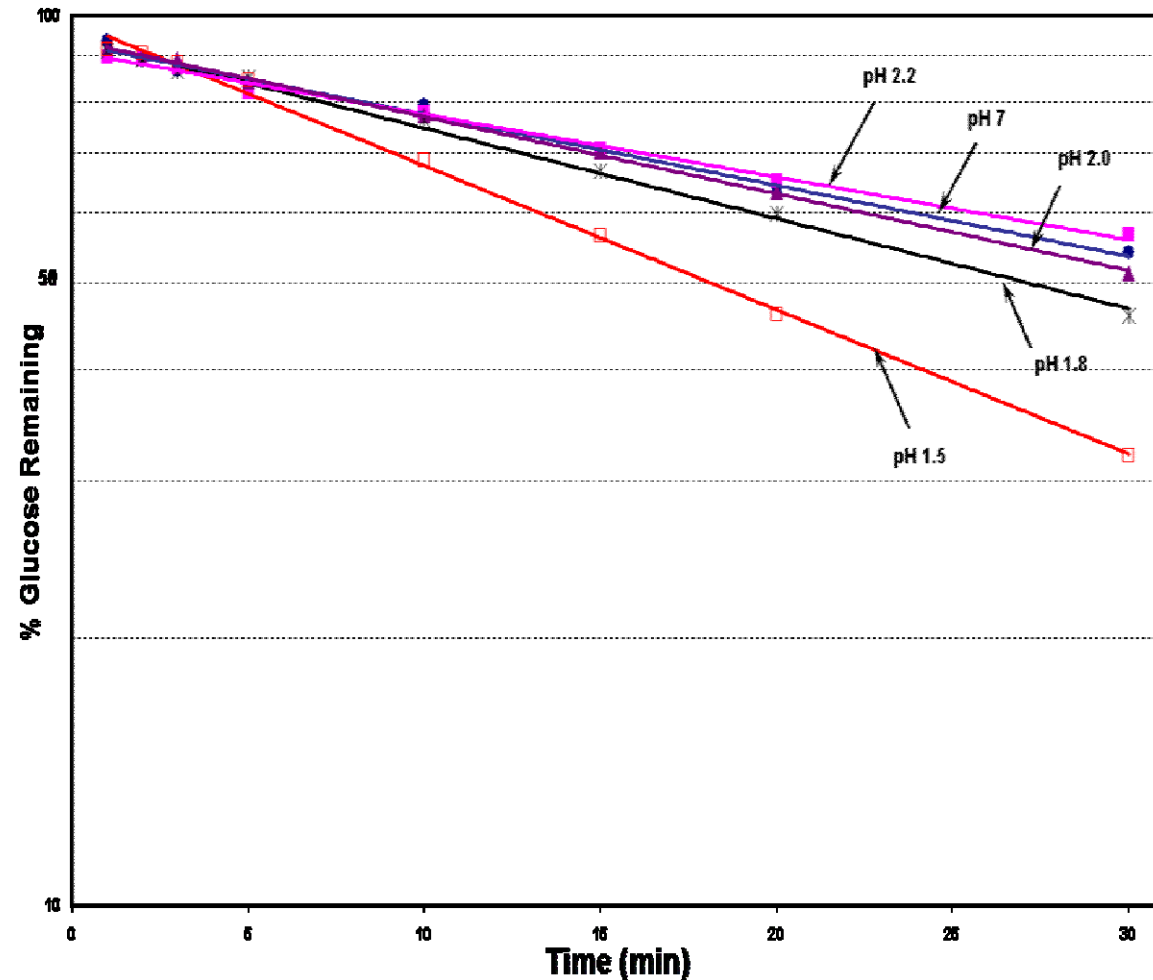
■ **Reaction rate under pH2.2 is almost identical as pH 7 and rate constant does not change much within pH 2.2-7**

■ **Conventional kinetic theory cannot explain the observations**

■ **Solvent factor are the dominant effect within pH2.2-7, and both acid factor and base factor play secondary role.**

Profiles and trend lines of glucose decomposition under different pH medium and 200ºC temperature conditions.

Kinetic Model and Parameters

■ **Arrhenius equation and acid-base catalysis general rules can be applied to glucose decomposition:**

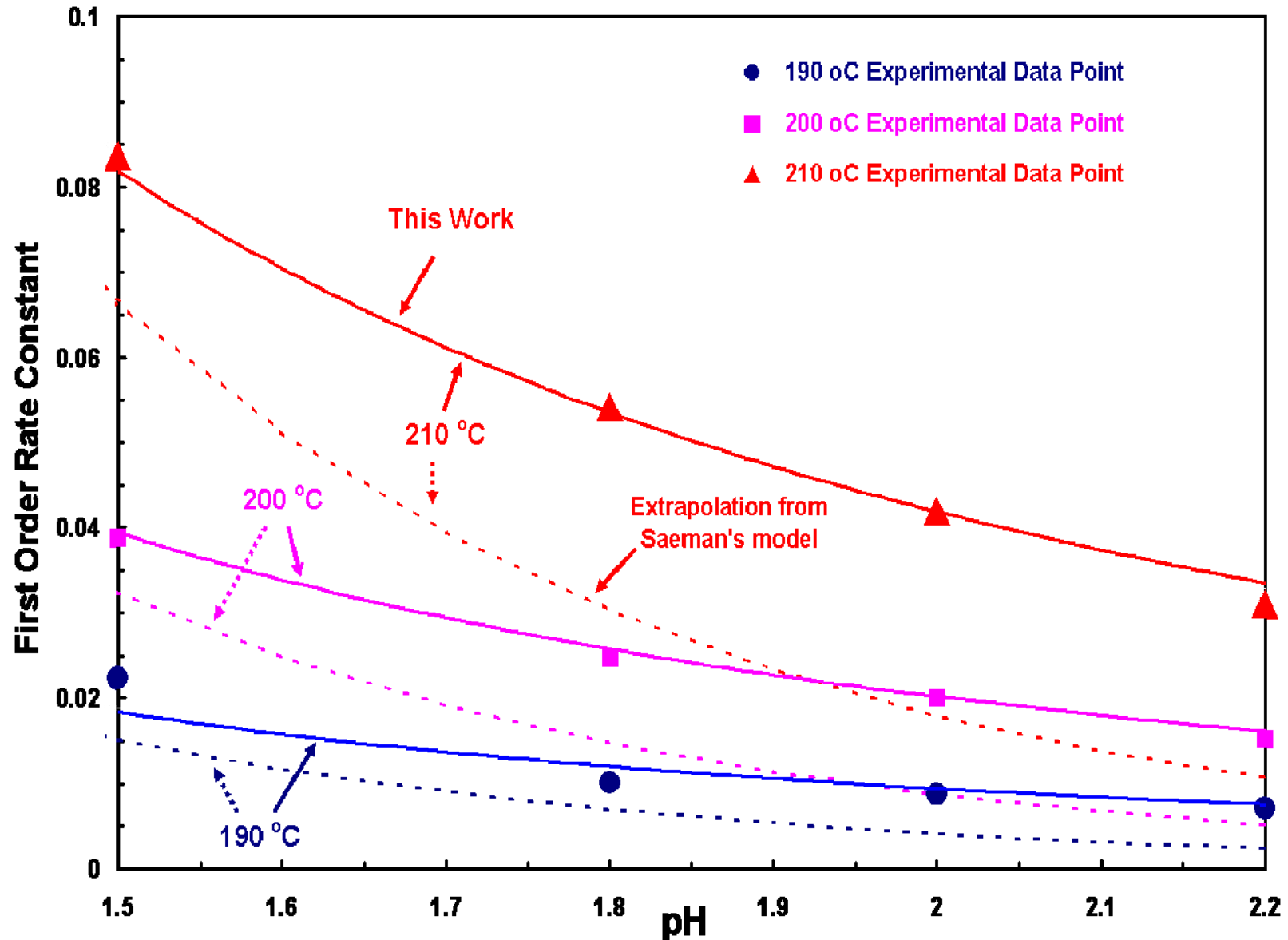$$K_v = [K_{H_2O} + K_{H^+} (H^+) + K_{OH^-} (OH^-)] \exp[-E/(RT)] \quad (1)$$

■ **Use SAS regression and ignore the OH- item under acidic condition:**

$$k^{Glu} = [2.132 \times 10^{13} + 2.148 \times 10^{15} \times (10^{-pH})] \times \exp[-139000/(RT)] \quad (2)$$

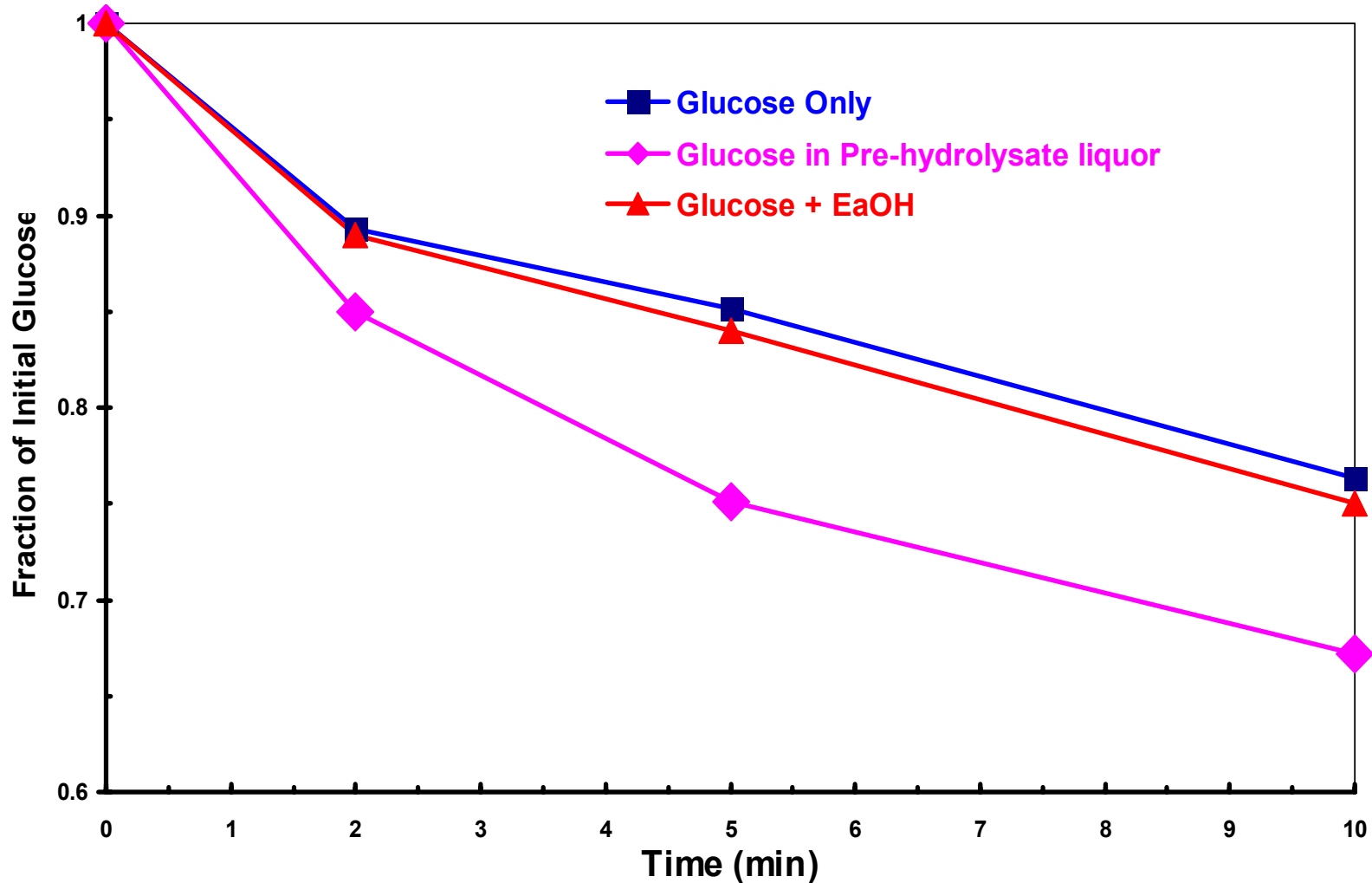❑ **This kinetic model can accurately predict the first order rate constant under acidic conditions, especially in the range of extremely low acid (ELA) concentration (e.g. 1.5-2.2 of pH)**

❑ **Conventional kinetic model cannot predict the rate constant under ELA conditions due to its ignorance of solvent factor.**

Comparison of Modeling Results

Legend:
- ● 190 oC Experimental Data Point
- ■ 200 oC Experimental Data Point
- ▲ 210 oC Experimental Data Point

This Work

210 °C

200 °C

190 °C

Extrapolation from Saeman's model

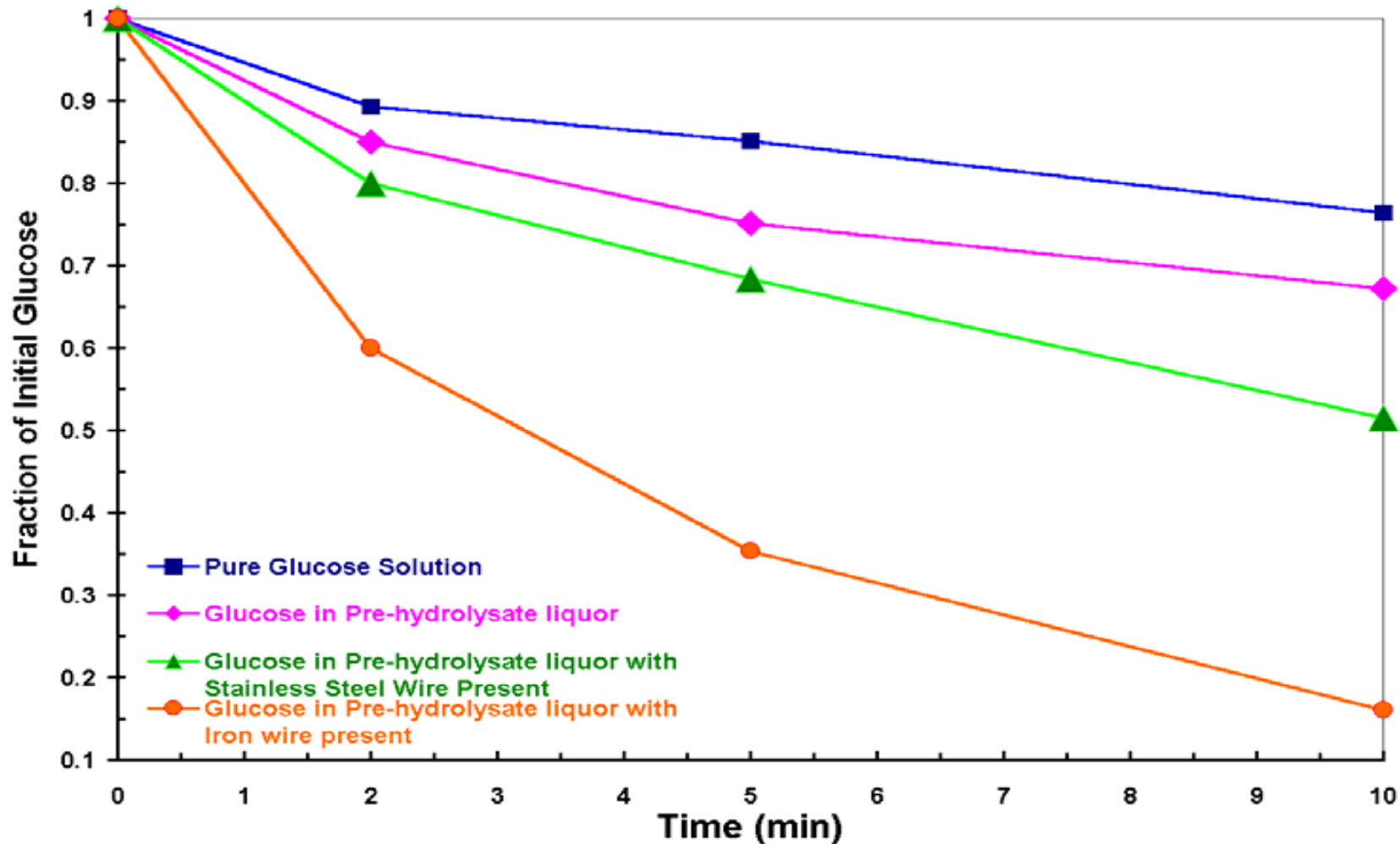Y-axis: First Order Rate Constant

X-axis: pH

Medium Effect on Glucose Degradation

Glucose decomposition under different medium and condition of pH=2.0 and temperature=200°C. Pre-hydrolysate liquor contains acid soluble lignin.

Metal Effect on Glucose Degradation

Glucose decomposition in presence of different metals and under pH=2.0 and temperature=200ºC. This study simulates the actual glucose decomposition under acid hydrolysis process

Observations of above Medium Effects

■ **Glucose decomposition rate may change dramatically in the medium of actual acid hydrolysis process**

■ **Glucose undergoes faster dissapearance in prehydrolyzed liquor than in pure acidic medium because of possible lignin-glucose re-combination:**

Glucose/Oligomer + *ASL* $\rightarrow$ *ASL-Glucose or ASL-Oligomer*

■ **Metal presence in prehydrolyzed medium will further affect the rate of glucose disappearance:**
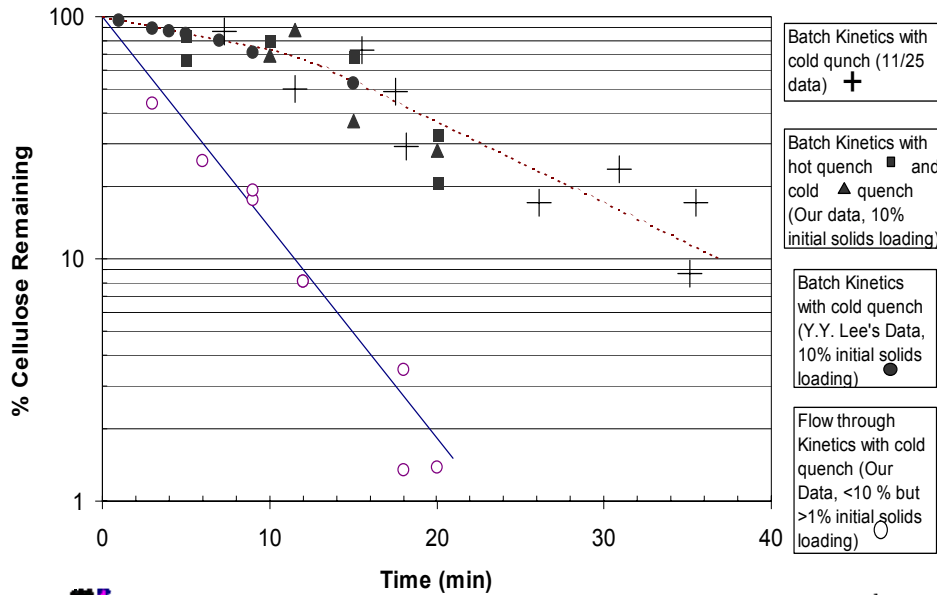
- **Copper (Gu) has very little effect**

- **Stainless Steal (S.S.) has large effect on glucose and disappearance rate is obviously fasten**
  * The S.S. cap on a Hastelloy bomb reactor can cause 30% more degradation than glass ampoule reactor

- **Iron (Fe) has strongest impact on glucose decomposition.**

Additional Proof for Lignin recombination

UP: Comparison between batch and flow-through reactor (R. Torget, 1998). Pretreated yellow poplar (with lignin and xylan free) hydrolysis kinetics at 225 oC, pH 2.2.

Down: Comparison between batch and flow-through reactor (This work). Hydrolysis Kinetics at 205oC, pH 2.2 with a-cellulose (no lignin content)..
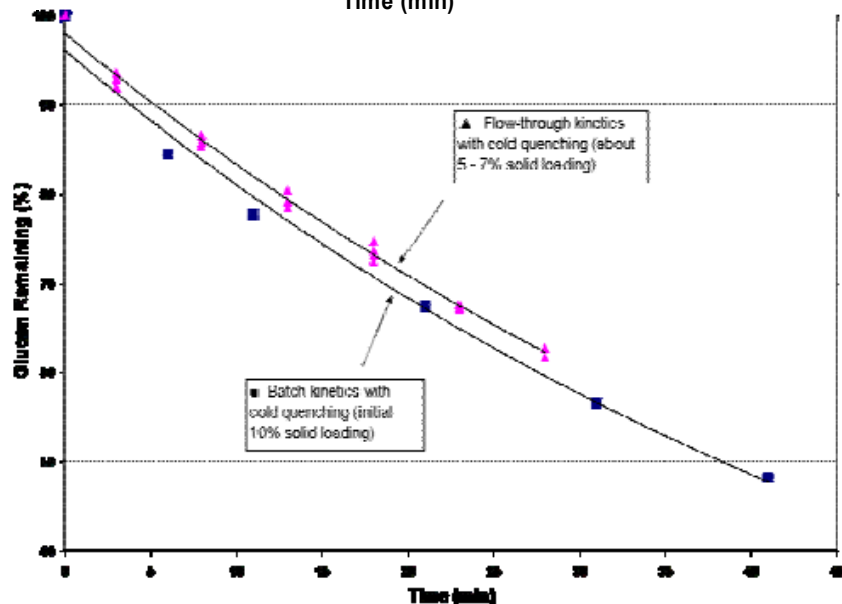
■ **Hydrolysis rates are identical for batch and flow-through reactors with no lignin but 2-3 times different when acid-soluble lignin (ASL) presence.**

■ **ASL may slow down the hydrolysis rate due to the recombination with cellulose or oligomers at reducing end.**

Conclusions (I)

■ For acid concentration less than 0.1% (pH>2.0) and at temperatures above 200°C, the rate of glucose decomposition is relatively constant.

■ The kinetic pattern for glucose decomposition are affected by pH, temperature and reaction medium. Acid-base catalysis general rules are applicable and the general mathematical model is obtained to predict the glucose degradation under acidic conditions

■ Glucose decomposition is faster in mediums containing pre-hydrolysate liquor, but slower if the presence of ethanol in this liquor.

Conclusions (II)

■ Glucose in lignocellulosic hydrolysates with lignin also decomposes faster than glucose in α-cellulose hydrolyzates

■ Above findings plus the fact that ethanol has higher affinity with lignin than glucose collectively indicate that glucose reacts with ASL.

■ Further proof is the comparison of biomass hydrolysis rate between batch and flow-through reactors with or without presence of lignin. Flow-through mode can improve hydrolysis rate by prompt removal of lignin-contained hydrolysate, but will not affect the hydrolysis rate where non lignin is presented.

Acknowledgments