

Kinetics of Glucose Decomposition during Dilute Acid Hydrolysis of Lignocellulosic Biomass

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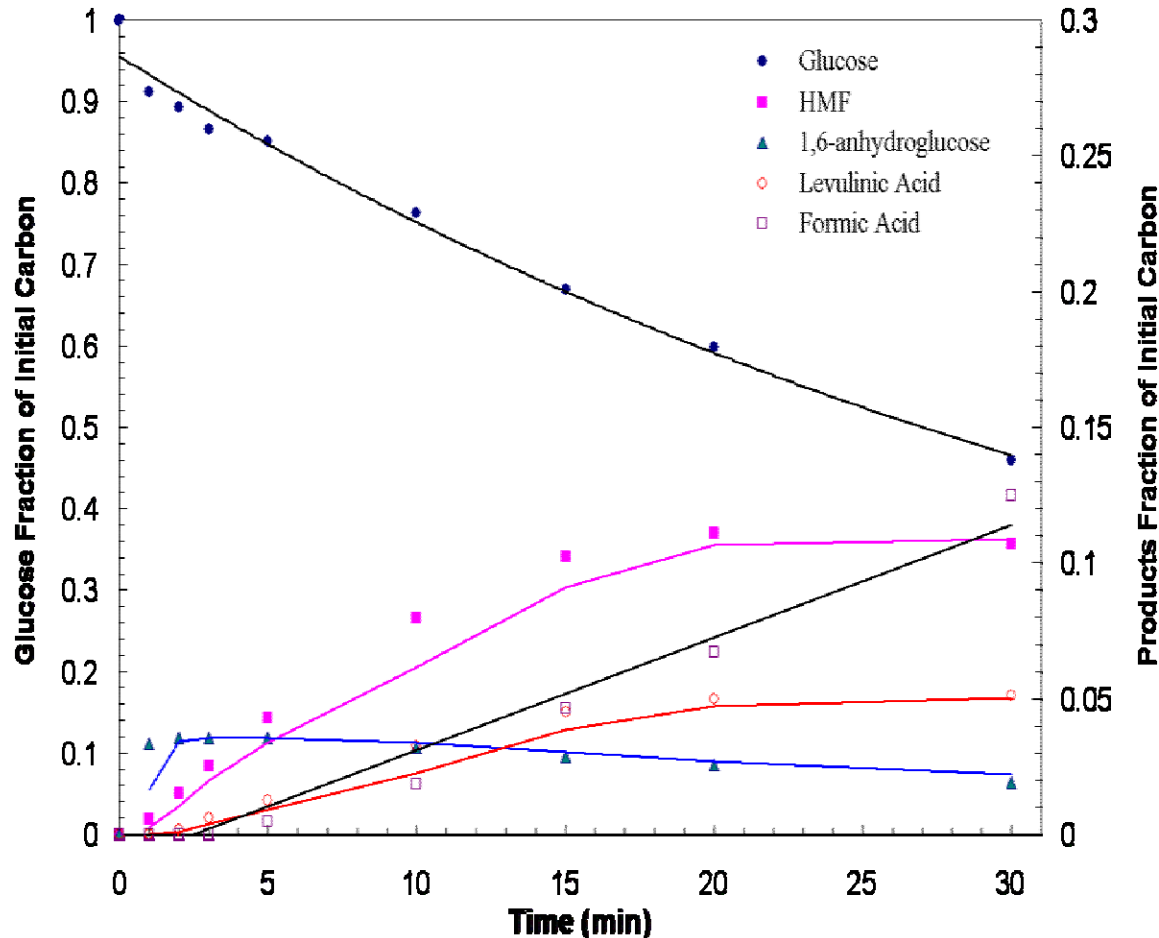
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Introduction

- **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

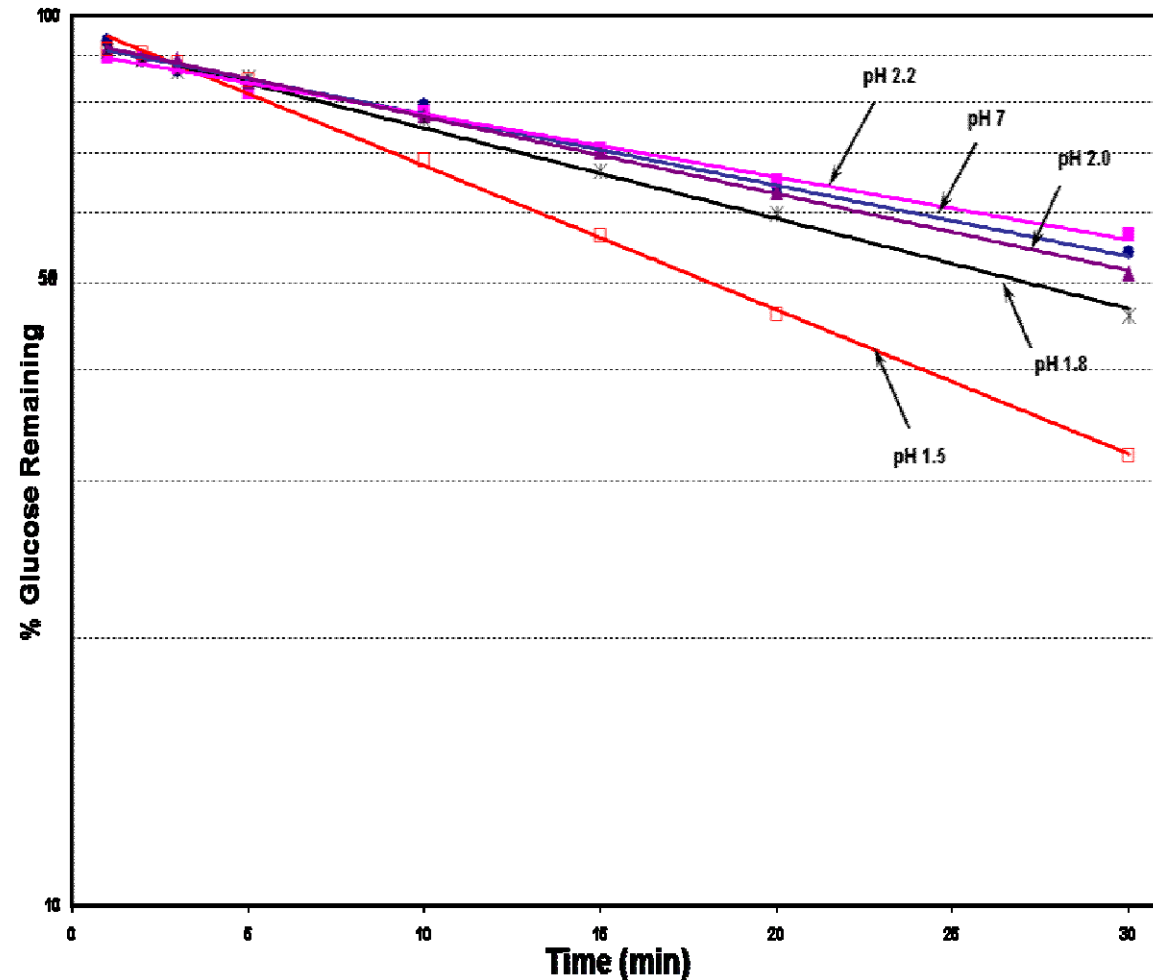
Decomposition Profile and Products



- 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 pH 2.2 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 factors are the dominant effect within pH 2.2-7, and both acid factor and base factor play secondary roles.

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

Kinetic Model and Parameters

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

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

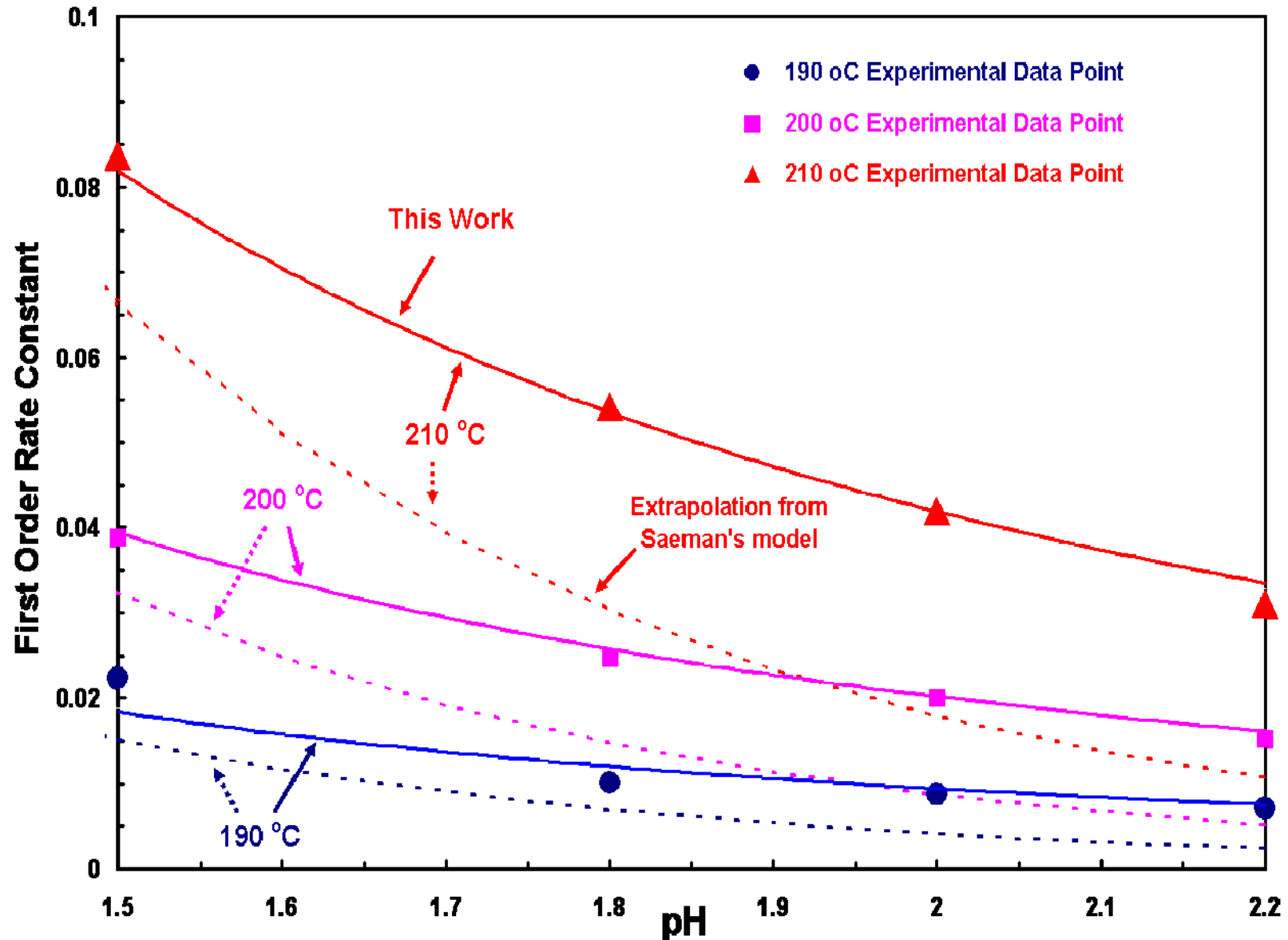
■ Use SAS regression and ignore the OH- item under acidic condition:

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

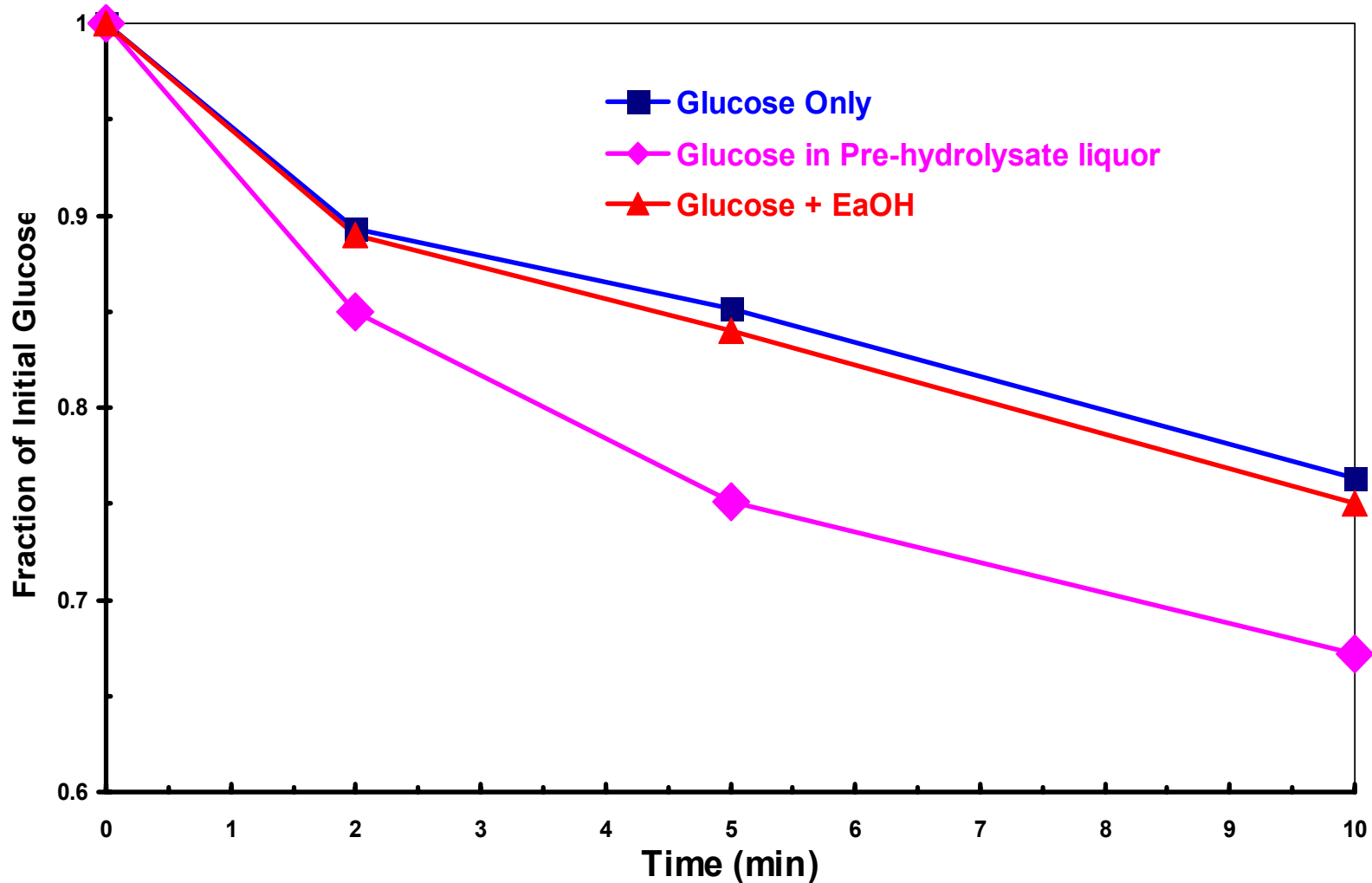
□ This kinetic model can accurately predict the first order rate constant under acidic conditions, especially in the range of extremely low acid (ELA) concentration (e.g. 1.5-2.2 of pH)

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

Comparison of Modeling Results

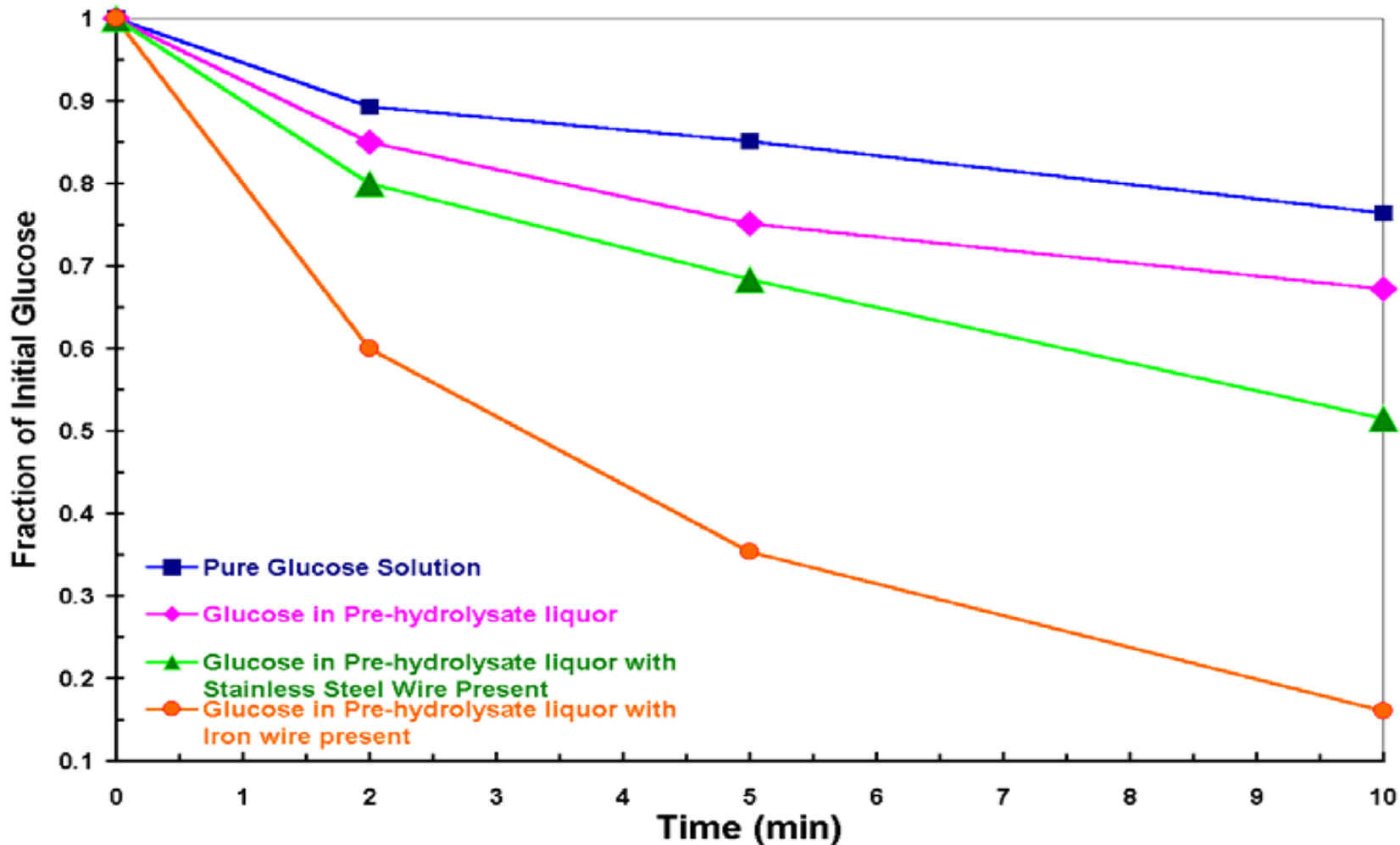


Medium Effect on Glucose Degradation



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=200°C. 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 disappearance in prehydrolyzed liquor than in pure acidic medium because of possible lignin-glucose re-combination:



■ Metal presence in prehydrolyzed medium will further affect the rate of glucose disappearance:

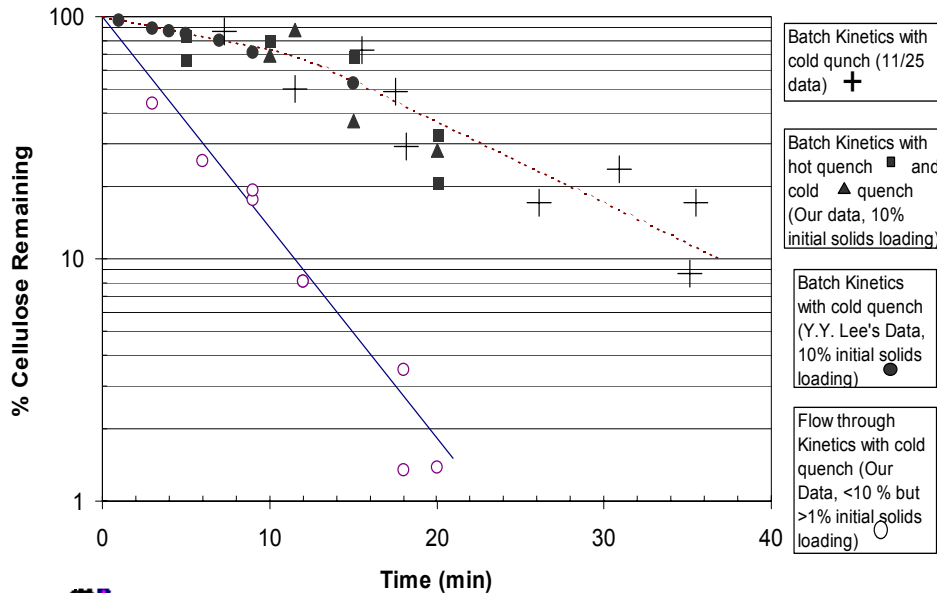
- Copper (Cu) has very little effect

- Stainless Steel (S.S.) has large effect on glucose and disappearance rate is obviously faster

* The S.S. cap on a Hastelloy bomb reactor can cause 30% more degradation than glass ampoule reactor

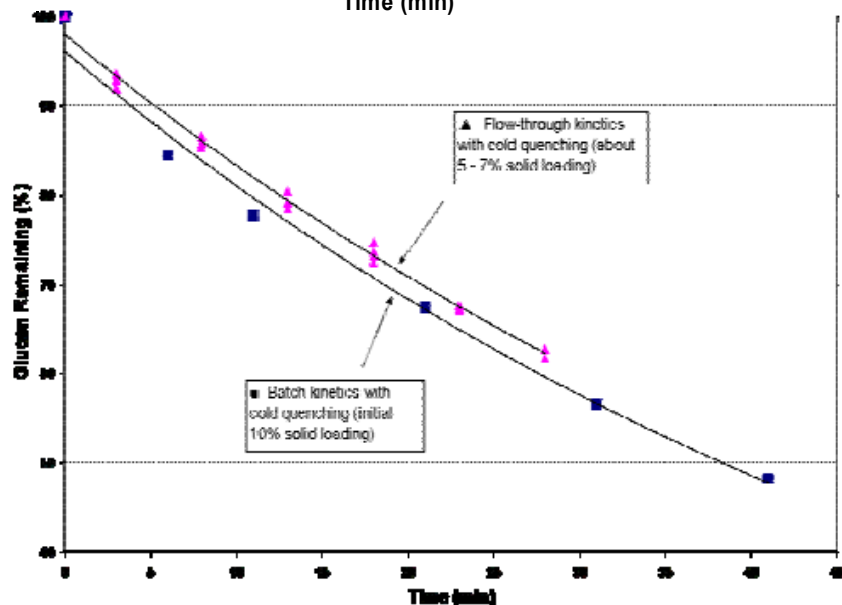
- Iron (Fe) has strongest impact on glucose decomposition.

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% ($\text{pH} > 2.0$) 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 hydrolysates**
- **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

We gratefully acknowledge the Financial support provided by:

- DOE (DE-FC36-01GO11072)**
- NREL (Subcontract-ACO-1-31003-01).**