ANNOUNCEMENT

PART I: STI PRODUCT DESCRIPTION

(To be completed by Recipient/Contractor)

A. STI Product Identifiers

1. REPORT/PRODUCT NUMBER(s)

None

2. DOE AWARD/CONTRACT NUMBER(s)

DE-FC36-01GO11072

3. OTHER IDENTIFYING NUMBER(s)

B. Recipient/Contractor

Auburn University, Auburn, AL

H. Sponsoring DOE Program Office

DOE/EERE

Golden Field Office

I. Subject Categories (list primary one first)

*Lignocellulosic Cellulosic Biomass, Agricultural
Residues, Dilute-Acid Hydrolysis, Kinetic Models,
Solvent Effects, Decomposition of glucose*

J. Description/Abstract

The overall objective of this research is to delineate the process of the dilute-acid hydrolysis of biomass and seek better understanding of the reactions involving dilute-acid treatment of lignocellulosic biomass. Specifically the scope of the work entails the following two primary technical elements:

- ☐ Verification of the heterogeneous nature of the reaction mechanism in dilute-acid hydrolysis of cellulosic component of the biomass.
- ☐ Experimental investigation to identify the overall reaction pattern and the kinetic constants associated with dilute-acid hydrolysis of the cellulosic component of the agricultural residues.

The major findings of this work are summarized as follows.

Heterogeneous Aspects of Acid Hydrolysis of α -Cellulose:

Hydrolysis of α -cellulose by H_2SO_4 is a heterogeneous reaction. As such the reaction is influenced by physical factors. The hydrolysis reaction is therefore controlled not only by the reaction conditions (acid concentration and temperature) but also by the physical state of the cellulose. As evidence of this, the reaction rates measured at the high-temperature region (above $200^\circ C$) exhibited a sudden change in apparent activation energy at a certain temperature, deviating from Arrhenius law. Furthermore, α -cellulose, once it was dissolved into concentrated H_2SO_4 and reprecipitated, showed a reaction rate two orders of magnitude higher than that of untreated cellulose, about the same magnitude as cornstarch. The α -cellulose when treated with a varying level of H_2SO_4 underwent an abrupt change in physical structure (fibrous form to gelatinous form) at about 65% H_2SO_4 . The sudden shift of physical structure and reaction pattern in response to acid concentration and temperature indicates that the main factor causing the change in cellulose structure is disruption of hydrogen bonding. Finding effective means of disrupting hydrogen bonding before or during the hydrolysis reaction may lead to a novel biomass saccharification process.

A Comprehensive Kinetic Model for Dilute-Acid Hydrolysis of Cellulose

Acid-catalyzed hydrolysis is controlled not only by temperature and acid concentration but also by the physical state of the cellulose. Under low temperature and acid condition the cellulose structure stays in stable crystalline form. Therefore, the prevailing reaction mode is endwise hydrolysis. Glucose then becomes the main

sugar product. However, when temperature and/or acid concentration is raised to a certain level, the cellulose structure becomes unstable by breakage of hydrogen bonding, the primary force that holds the cellulose structure. Once the crystalline structure of the cellulose is disrupted, acid molecules can penetrate into the inner layers of the cellulose chains. In support of this hypothesis, we have experimentally verified that a substantial amount of oligomers is formed as reaction intermediates under extremely low-acid and high-temperature conditions. We also found that the breakage of hydrogen bonds occurs rather abruptly in response to temperature. One such condition is 210°C, 0.07% H₂SO₄. Glucose, once it is formed in the hydrolysate, interacts with acid-soluble lignin, forming a lignin-carbohydrate complex. This occurs concurrently with other reactions involving glucose such as decomposition and reversion. On the basis of these findings, a comprehensive kinetic model is proposed. This model is in full compliance with our recent experimental data obtained under a broad range of reaction conditions.

Effect of Ethyl Alcohol on Dilute Acid Hydrolysis of Cellulosic Component in Biomass

The effect of ethanol on dilute acid hydrolysis of cellulosic component of biomass was investigated. The yields of glucose are improved by addition of low-level ethanol into the dilute sulfuric acid solution especially when the hydrolysis is conducted in a flow-through reactor. Ethanol increases the rate of cellulose hydrolysis and suppresses glucose-lignin interaction thus rendering high glucose yield. The reaction between acid solubilized lignin and glucose is believed to be an additional pathway existing in sugar decomposition pattern. Ethanol is the main product of the biomass to fuel conversion process. As such it does not have to be separated from the hydrolyzate. The idea of ethanol addition may prove itself to be a viable process option in dilute acid hydrolysis of biomass.

Kinetics of Glucose Decomposition during Dilute Acid Hydrolysis of Lignocellulosic Biomass

Recent research work in house and at NREL has demonstrated that extremely low concentration of acid (e.g. 0.05-0.2 wt% sulfuric acid) and high temperature (e.g. 200 - 230°C) is a range of reaction conditions that can be effectively applied for hydrolysis of the cellulosic component of biomass. These conditions are far apart from those of the conventional dilute-acid hydrolysis processes, and the kinetic data for glucose decomposition are not currently available. In this study, kinetics of glucose decomposition was experimentally investigated covering experimental conditions of 1.5-2.2 pH and 180 – 230°C using glass ampoule reactors. The primary factors controlling glucose decomposition is the reaction medium, acid concentration, and temperature. Based on the experimental data, a kinetic model was developed and the best-fit kinetic parameters were determined. However, consistent discrepancy was found in the rate of glucose disappearance between the model based on pure glucose data and those observed during the actual process of lignocellulosic biomass hydrolysis. This was taken as an indication that glucose recombines with acid-soluble lignin during the hydrolysis process, and it was incorporated accordingly into the overall model of glucose decomposition.

C. STI Product Title

Fundamental Study on Kinetics and Transport Phenomena in Low-Water Dilute-Acid Total Hydrolysis of Cellulosic Biomass (Year 2)

D. Author(s)

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E. STI Product Issue Date/Date of Publication

03/24/2004 (mm/dd/yyyy)

F. STI Product Type (Select only one)

- X 1. TECHNICAL REPORT
X Final ☐ Other (specify) _____
2. CONFERENCE PAPER/PROCEEDINGS
Conference Information (title, location, dates)

3. JOURNAL ARTICLE
a. TYPE: ☐ Announcement Citation Only
☐ Preprint ☐ Postprint
b. JOURNAL NAME

c. VOLUME _____ d. ISSUE _____
e. SERIAL IDENTIFIER (e.g. ISSN or CODEN)

☐ OTHER, SPECIFY

G. STI Product Reporting Period (mm/dd/yyyy)

10/01/2001 Thru 12/31/2003

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- ☐ 7. OFFICE OF NUCLEAR ENERGY APPLIED TECHNOLOGY

L. Recipient/Contractor Point of Contact Contact

for additional information (contact or organization name to be included in published citations and who would receive any external questions about the content of the STI Product or the research contained therein)

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ANNOUNCEMENT

PART II: STI PRODUCT MEDIA/FORMAT and LOCATION/TRANSMISSION

(To be completed by Recipient/Contractor)

A. Media/Format Information:

1. MEDIUM OF STI PRODUCT IS:
☒ Electronic Document ☐ Computer medium
☐ Audiovisual material ☒ Paper ☐ No full-text
2. SIZE OF STI PRODUCT 130 pages
3. SPECIFY FILE FORMAT OF ELECTRONIC
DOCUMENT BEING TRANSMITTED, INDICATE:
☐ SGML ☐ HTML ☐ XML ☒ PDF Normal ☐ PDF Image
☐ WP-Indicate Version (5.0 or greater) _____
Platform/operating system _____
- ☐ MS-Indicate Version (5.0 or greater) _____
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- ☐ Postscript _____
4. IF COMPUTER MEDIUM OR AUDIOVISUAL
 - a. Quantity/type (*specify*) _____
 - b. Machine compatibility (*specify*) _____
 - c. Other information about product format a user
needs to know: _____

B. Transmission Information:

STI PRODUCT IS BEING TRANSMITTED:

- ☐ 1. Electronic via Elink
- ☒ 2. Via mail or shipment to address indicated
in award document (*Paper products,
CD-ROM, diskettes, videocassettes, et.*)
Bound Report and CD-ROM
- ☐ 2a. Information product file name
(*of transmitted electronic format*)
Final Report- DE-FC36-01GO11072

PART III: STI PRODUCT REVIEW/RELEASE INFORMATION

(To be completed by DOE)

A. STI Product Reporting Requirement Review:

- ☒ 1. THIS DELIVERABLE COMPLETES ALL
REQUIRED DELIVERABLES FOR THIS AWARD
- ☐ 2. THIS DELIVERABLE FULFILLS A
TECHNICAL REPORTING REQUIREMENT,
BUT SHOULD NOT BE DISSEMINATED
BEYOND DOE.

B. DOE Releasing Official

- ☐ 1. I VERIFY THAT ALL NECESSARY
REVIEWS HAVE BEEN COMPLETED AS
DESCRIBED IN DOE G 241.1-1A, PART II,
SECTION 3.0 AND THAT THE STI
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Released by (*name*) _____

Date _____
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Describing the data fields: Descriptions of the various DOE F 241.3 data fields, STI Products, format, etc., can be found in ATTACHMENT 3 and other sections of the DOE G 241.1-1A, Guide to the Management of Scientific and Technical Information. Available online at <http://www.osti.gov/stip/>

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RECORD STATUS - This is a required field. The record status identifies the announcement record or the STI Product as new, or revised. If the record status is not provided, the record is considered "New."

Part I: STI PRODUCT DESCRIPTION (To be completed by Recipient/Contractor)

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1. **Report/Product Number(s).** This is a required field. The unique primary report or product number assigned to the STI product. If a report number is not provided, the word "NONE" should be entered.

Following are examples of report number formats for multiple volumes, parts, or revisions:

DOE/ID/13734-2

DOE/NE/01834--1-Pt. 1

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Example: University of Tennessee, Knoxville, TN

C. STI PRODUCT TITLE - This is a required field. Provide the title exactly as given on the product itself, including part, volume, edition, and similar information.

D. AUTHOR(s) - This is a required field. Provide the name of the author (last name first) of the STI product. More than one author may be provided; separate multiple entries with a semicolon and a space. If an author does not exist, the word "None" should be entered.

Examples: Jones, T.M.; Markay, Arthur R. III
Fields, J.M., ed.

Author(s) E-mail Address(es). Provide the e-mail address for each author. Multiples may be provided; they should be listed in the same order as the authors and should be separated by a semicolon and a space.

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F. STI PRODUCT TYPE - This is a required field. It should agree with the reporting requirement identifier in the reporting requirements checklist; federal assistance reporting checklist; or in the statement of work if the product is a required deliverable that warrants accountability.

1. **Technical Report.** Identify the type of technical report provided.
2. **Conference Paper.** Provide all available conference information. An agenda alone is not sufficient for announcement.
3. **Journal Article.** Provide all available Journal Article information.

G. STI PRODUCT REPORTING PERIOD. Specify the beginning and ending dates of the period covered by the STI product.

H. SPONSORING DOE PROGRAM OFFICE - Enter the name or acronym of the DOE Program Office (e.g., Office of Science or SC) providing the funding for the work described in the STI product. For projects funded by more than one Program Office, indicate all sources of the DOE funding in descending order of dollar amount of funding appropriated. Separate multiple program offices with a semicolon and a space. If no sponsoring DOE Program Office is provided, "DOE" will be the sponsor.

I. SUBJECT CATEGORIES - Select one or more categories from the list provided. List the primary one first. A list of subject categories is available at (<http://www.osti.gov/elink/>).

Keywords. Provide terms which describe the content of the publication. More than one term may be entered; separate multiple terms with a semicolon and a space.

J. DESCRIPTION/ABSTRACT - Provide a clear, concise, and publicly releasable English language summary of the information content of the STI product. The abstract length should be no more than 5,000 characters. If you are utilizing paper media, you may provide via attachment.

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L. RECIPIENT/CONTRACTOR POINT OF CONTACT. Provide the organization or individual(s) name with corresponding contact information who will be included in the published citation as the point of contact and will respond to external questions about the content of the STI product.

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1. **Medium.** This is a required field. Select one of the medium options provided. Note: When announcement record only is submitted, select "No full-text."

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2. Indicated if the STI product is not suitable for dissemination beyond DOE based on report type or content, it is being submitted because it fulfills a technical information reporting requirement.

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