

## **R&D ADVANCES IN CATALYSIS FOR BIOCHEMICALS**

A technical investigation  
commissioned by the members of the  
Catalytic Advances Program (CAP)

Client Private  
December 2012



### The Catalytic Advances Program (CAP)

The **Catalytic Advances Program (CAP)** is an information resource for research and development organizations in the petroleum, chemical, and polymer industries. By the direction of the member companies (through balloting and other interactive means), the program delivers a range of timely and insightful information and analyses which are accessible exclusively to members and protected by confidentiality agreements. The objective is to provide a technical update on commercially viable advances in catalysis as well as benchmark commercial advances in catalysis and process technology.

Members receive three in-depth **CAP Technical Reports** which are written and peer reviewed by leading scientists and experienced industry professionals in areas selected by the membership (via ballot); weekly *CAP Communications* (delivered via e-mail) which provide the latest updates on technical breakthroughs, commercial events and exclusive development opportunities; and attendance at the **CAP Annual Meeting**.

The **Catalytic Advances Program (CAP)** is available on a membership basis from The Catalyst Group Resources (TCGR). For further details, please contact Matthew A. Colquitt at [Matthew.A.Colquitt@catalystgrp.com](mailto:Matthew.A.Colquitt@catalystgrp.com) or +1.215.628.4447 (x1130).



P.O. Box 680  
Spring House, PA 19477 U.S.A  
ph: +1.215.628.4447  
fax: +1.215.628.2267  
website: [www.catalystgrp.com](http://www.catalystgrp.com)

## CONTENTS

<b>EXECUTIVE SUMMARY .....</b>	<b>xiii</b>
<b>1. INTRODUCTION .....</b>	<b>1</b>
<b>2. FEEDSTOCKS TO INTERMEDIATES .....</b>	<b>5</b>
2.1 INTRODUCTION.....	5
2.1.1 Technological Achievements .....	7
2.1.2 Pretreatment and Characterization .....	9
2.1.2.1 Physical techniques .....	9
2.1.2.1.1 Microwave irradiation .....	9
2.1.2.1.2 Ultrasonic treatment .....	10
2.1.2.2 Chemical methods .....	10
2.1.2.2.1 Acid and alkali pretreatment .....	10
2.1.2.2.2 Chemical agent pretreatment.....	11
2.1.2.2.3 Ionic liquid (IL) pretreatment.....	11
2.1.3 Homogeneous vs. Heterogeneous Catalysis.....	11
2.1.3.1 Solid-solid interactions.....	13
2.2 CATALYTIC BREAKDOWN OF FEEDSTOCKS .....	15
2.2.1 Hydrolysis by Homogeneous Catalysts.....	15
2.2.2 Hydrolysis by Heterogeneous Catalysts.....	17
2.2.2.1 Acid zeolites .....	17
2.2.2.1.1 Loading of super acids .....	18
2.2.2.1.2 Composite zeolites .....	18
2.2.2.2 Metal oxides .....	19
2.2.2.3 Cation-exchange resins.....	19
2.2.2.4 Supported solid acid catalysts .....	21
2.2.2.4.1 Supported metal oxide acid catalysts .....	21
2.2.2.4.2 Supported carbonaceous solid acid catalysts.....	21
2.2.2.5 Heteropoly compounds.....	22
2.2.2.6. Comparison of solid acid catalyst activities .....	23
2.2.3 Hydrogenation/Hydrogenolysis.....	25
2.2.3.1 C-O and C=O bond activation.....	25

2.2.3.1.1	Activation on metal surfaces .....	25
2.2.3.1.2	Activation on metal sulphides .....	27
2.2.4	Catalytic Fast Pyrolysis .....	28
2.2.5	Catalytic Conversion in Ionic Liquids .....	32
2.2.5.1	Cellulose solubilisation in ILs .....	32
2.2.5.2	Effect of the anion on the cellulose dissolution .....	34
2.2.5.3	Effect of the cation on the dissolution .....	34
2.2.5.4	Mechanism of solubilization.....	35
2.2.6	Combined Transformations .....	36
2.2.6.1	Simultaneous saccharification and fermentation .....	36
2.2.6.2	Catalytic hydrothermal gasification of biomass .....	37
2.2.7	Other Catalytic Feedstock Processing Methods .....	37
2.2.7.1	Catalytic lignin transformations .....	37
2.2.7.1.1	Catalytic cracking and hydrolysis.....	38
2.2.7.1.2	Hydrolysis and hydrogenation.....	38
2.2.7.1.3	Oxidation .....	39
2.2.7.2	Oleochemical transformations .....	40
2.2.7.3	Glycerol conversions .....	41
2.3	TECHNICAL HURDLES .....	43
2.3.1	High-temperature Conversions .....	44
2.3.2	Low-temperature Conversions.....	44
2.4	CONCLUSIONS AND RECOMMENDATIONS .....	46
2.5	REFERENCES .....	48
<b>3.</b>	<b>INTERMEDIATES TO BIOCHEMICALS.....</b>	<b>55</b>
3.1	INTRODUCTION .....	55
3.1.1	Platforms and Intermediates .....	55
3.2	CATALYSIS AND ENGINEERING FOR BIOCHEMICALS PRODUCTION .....	57
3.2.1	C <sub>1</sub> Containing Compounds .....	60
3.2.2	C <sub>2</sub> Containing Compounds .....	61
3.2.3	C <sub>3</sub> Containing Compounds .....	62
3.2.4	C <sub>4</sub> Containing Compounds .....	63
3.2.5	C <sub>5</sub> Containing Compounds .....	64
3.2.6	C <sub>6</sub> Containing Compounds .....	67
3.2.7	Others.....	68

3.3 TECHNICAL HURDLES .....	70
3.4 CONCLUSIONS AND RECOMMENDATIONS .....	71
3.5 REFERENCES .....	73
<b>4.0 INDEX .....</b>	<b>77</b>

## FIGURES

Figure 2.1	General composition of lignocellulosic biomass feedstocks.....	5
Figure 2.2	Simplified cellulose structure: (A) cellulose polymer; and (B) inter and intra H-bonds present in cellulose chains .....	6
Figure 2.3	Top applicants of patents in the field of biomass conversion .....	8
Figure 2.4	Products yields in the hydrolysis of crystalline cellulose in water using different acid catalysts.....	14
Figure 2.5	Proposed mechanism for cellulose hydrolysis .....	16
Figure 2.6	Consecutive reaction steps during the cellulose hydrolysis in dilute acid medium .....	16
Figure 2.7	Combination of cellulose conversion and product separation by cation-exchange resin .....	20
Figure 2.8	Preparation of sulfonated amorphous carbon from glucose and lignin by different synthesis pathways .....	22
Figure 2.9	Hydrogenolysis of diaryl ethers using Ni(COD) <sub>2</sub> and SIPr-HCl as an NHC ligand.....	26
Figure 2.10	Hydrogenation pathway of propanal on MoS <sub>2</sub> .....	28
Figure 2.11	Overall reaction chemistry for the catalytic fast pyrolysis of cellulose. ....	29
Figure 2.12	Single pass yields for catalytic fast pyrolysis of pine wood with propylene as a co-feed. The yield based on total carbon fed to the reactor. ....	30
Figure 2.13	Reaction network of furan conversion into aromatics over ZSM-5 at 600°C. ....	31
Figure 2.14	Possible insertion of an imidazolium chloride in the cellulose matrix.....	35
Figure 2.15	Variation in C-O hydrogenolysis activity ( <i>k</i> <sub>1</sub> ) for M-Mo/Al <sub>2</sub> O <sub>3</sub> catalysts as a function of periodic table position of M.....	39
Figure 2.16	Homo-metathesis reaction of methyl oleate.....	40
Figure 2.17	Cross-metathesis of methyl oleate.....	40
Figure 2.18	Possible reaction network of glycerol APR.. ....	43
Figure 3.1	Feedstocks, platforms, processes, and products - simplified chart .....	55
Figure 3.2	Feedstocks, platforms, processes, and products - detailed chart .....	56
Figure 3.3	Cellulosic mass fractionations and potential products .....	66

Figure 3.4	Recently developed process eliminating need for simultaneous conversion of cellulose and xylose without separation steps .....	66
Figure 3.5	Different routes and various catalytic path ways .....	67
Figure 3.6	Reaction chemistry for the Catalytic Fast Pyrolysis of cellulose into aromatics and olefins .....	69

## TABLES

Table 2.1	Biorefinery demonstration projects: plant capacity, planned or under construction .....	7
Table 2.2	Hydrogenation of cellobiose in BMImC1 .....	13
Table 2.3	Comparison of catalytic properties and activities of solid acid catalysts for cellulose hydrolysis to glucose .....	24
Table 2.4	Simulated surface coverages and rate of methanol formation as a function of temperature. ....	26
Table 2.5	Principal solvent used to dissolve cellulose.....	32
Table 2.6	Examples of solubility of different bio-products in ILs and organic solvents .....	33
Table 3.1	NREL and PNNL Top 12 Bio-Chemicals .....	57
Table 3.2	U.S. DOE Funded Pilot and Demonstration Plants for Biochemicals.....	58
Table 3.3	Overview of companies, products, and status of biomass-derived chemical building blocks.....	59