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DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

2.5.4.407.Cascade reactions with Technische Universität München (TUM) and University of Toronto (U of T)

March 24, 2015

Conversion R&D

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Problem Statement

How can liquid transportation fuel from biomass be economically competitive?

Feedstock → **Conversion** → Distribution

- Parameters identified by TEA (Jones, et. al. 2013) as cost drivers:

Parameter	Contribution to TEA
Pressure	▪ Reactor, heat exchanger (CAPEX); compressor (OPEX)
Catalyst	▪ Reactor (CAPEX); Material (OPEX)
Carbon yield	▪ Denominator in calculating MFSP! $\frac{\$}{gge} = \frac{CAPEX+OPEX}{YIELD}$

How can yield be improved?

Alternative pathway: **converting small oxygenated compounds (typically lost as gas) into fuel**

Goal Statement

- Develop an **alternative pathway** utilizing **lower H_2 pressures** to reduce O content
  - Current operating pressure: 2000 psig (135 bar)
  - Hydrogenation: occurs at 730 psig (50 bar)
- **Recover small oxygenates** typically lost as non-condensable gas **through alkylation** to improve C efficiency.
  - TUM reported alkylation of phenols at low H_2 pressure
- Generate scientific knowledge that may **inform current or proposed upgrading pathways (industrial interest in alkylation).**
  - Graded approach starting with model compounds to more complicated feed (bio-oil fractions) to whole bio-oil.

The data generated in this project aims to contribute to the knowledge that will enable the US to develop a healthy bio-economy.

Quad Chart Overview

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Timeline

- Awarded: Dec. 2010
- Rescope start: January 2014
- Proposed end: March 2015

Barriers

- Tt-F (Deconstruction of Biomass to Form Bio-oil Intermediates)
- Tt-H (Bio-oil Stabilization)
- Tt-J (Catalytic Upgrading to Fuels and Chemicals)
- Tt-L (Knowledge Gaps in Chemical Processes)

Budget

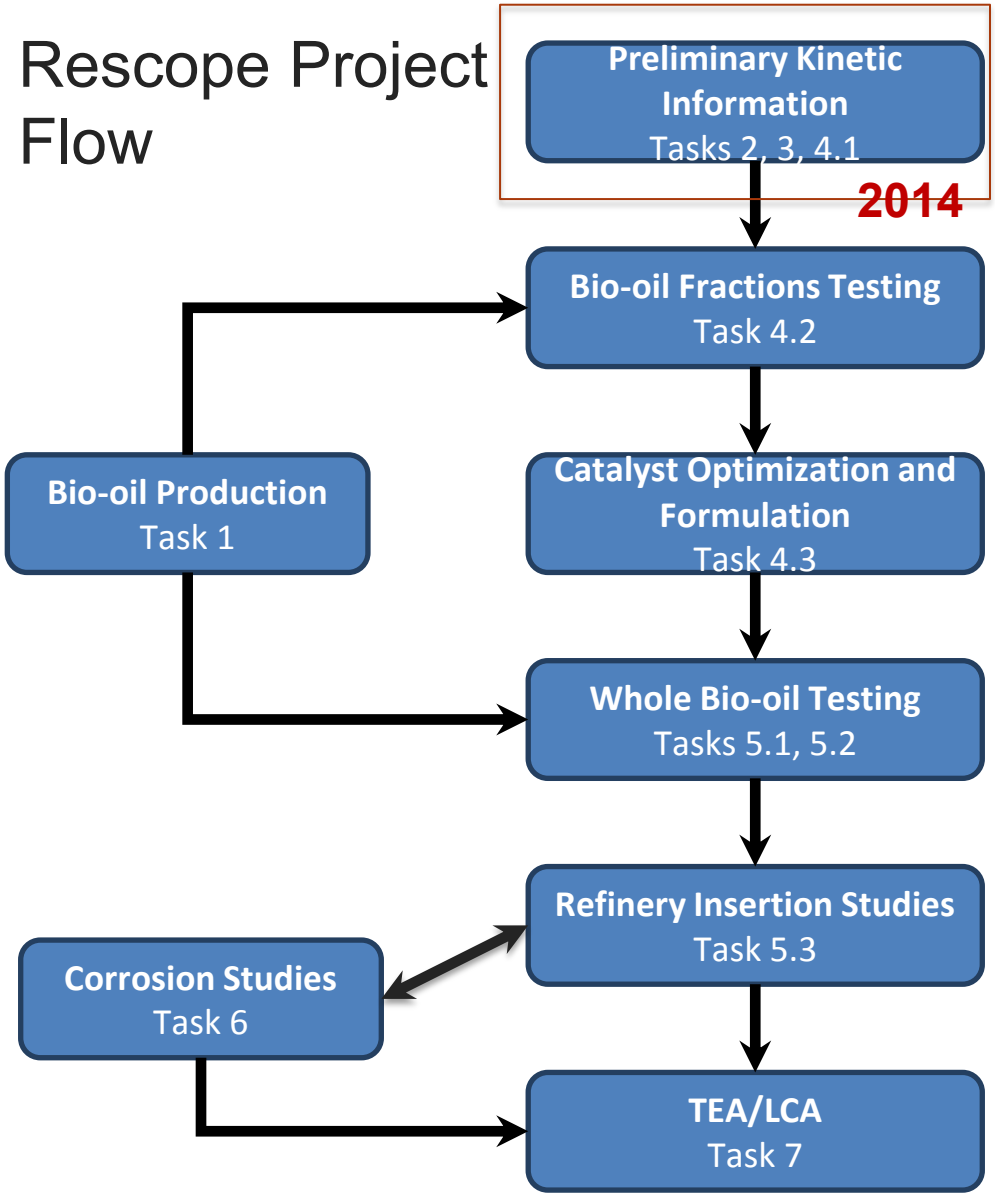
	Total Costs FY 10 - 12	Costs FY 13	Costs FY 14	Total planned funding (FY 15 – end)
DOE Funded	$ 599,955	$25,195	$330,737	$180,115
Cost Share (Comp.)	$ 10, 645 (UOP)	0	$ 64,504	

Partners

- **Partners**
  - Technische Universität München (TUM)
  - University of Toronto (U of T)
- Institute for Integrated Catalysis (PNNL)

1 - Project Overview

- Rescope Project Flow



- Graded approach, i.e. **increasing complexity of feed**
- Complete evaluation of proposed alternative route

- Commercial partners changed research priorities but still interested in preliminary kinetic information, particularly alkylation
- Leveraged university partners expertise
  - TUM – alkylation, catalysis and fundamental science
  - U of T – kinetic modeling and catalysis

Knowledge from preliminary kinetic studies can leverage:

- **Catalyst development**
- **Process development**

2 – Technical Approach

Conduct kinetic studies (less than 10% conversion) of individual reactions at low P (<50 bars) and low T (<250°C) in batch reactor

Selective hydrogenation of small oxygenates

- Conversion of acetic acid and furfural to alcohol
- **Product:** ethanol, furfuryl alcohol
- Requires metal catalyst

Alkylation

- Reaction between alcohol and catechol
- **Product:** alkylated aromatic
- Requires acid catalyst

Aromatic ring hydrogenation

- Conversion of alkylated aromatic to napthenic alcohol
- **Product:** alkylated cyclohexanol compounds
- Requires metal catalyst

Dehydration of naphthenic alcohol

- Removal of oxygen
- **Product:** deoxygenated alkylated compound
- Requires acid catalyst

TARGET: Cascade reaction in one pot

Potential challenges:

- **Reproducibility of data**: preliminary experiments confirm repeatability of data between laboratories and compared to literature data
- **Undesired reaction kinetics:** fundamental understanding of the reactions

Critical success factor:

$$k_{\text{selective hydrogenation}} > k_{\text{alkylation}} > k_{\text{aromatic ring hydrogenation}} > k_{\text{dehydration}}$$

2 – Management Approach

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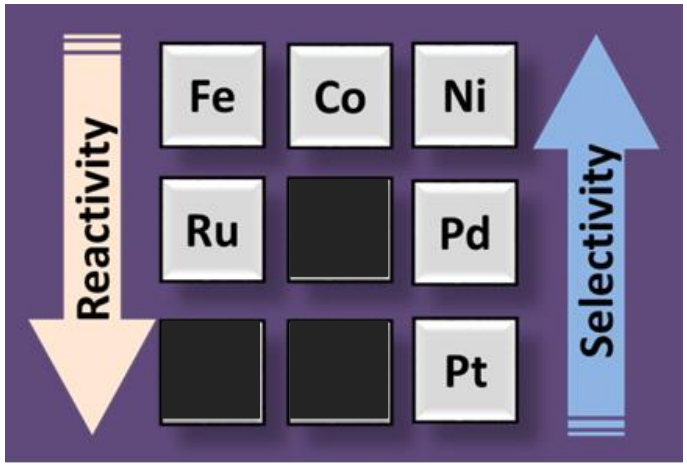
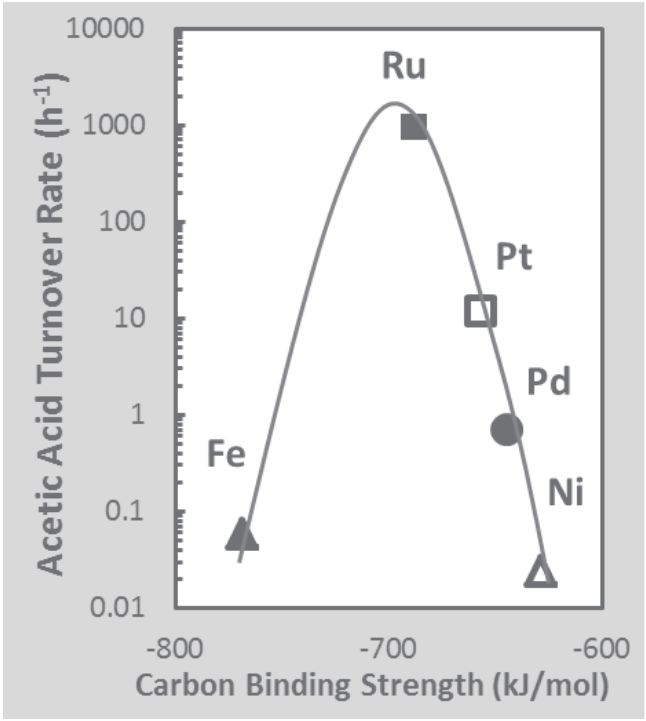
- **Approach structure:**
  - Project Management Plan **(PMP)**
    - U of T Scope – selective hydrogenation of acetic acid and furfural
    - TUM Scope – alkylation, aromatic hydrogenation, dehydration and one-pot experiments
  - Annual Operating Plan **(AOP)**
  - **Quarterly** reporting to BETO
    - Quarterly reports from partners
- **Potential challenges:**
  - **International collaboration**: scheduled webinar presentations, frequent communications through e-mails or phone
- **Critical success factor:**
  - Deliver milestones

3 – Selective Hydrogenation of Small Oxygenates (Acetic Acid)

- **Objective:** Hydrogenate small oxygenates
  - acetic acid and furfural – representative small oxygenates present in bio-oil
- **Relevance:** Increase C efficiency
- **Accomplishment:**
  - Identified trends: **periodic reactivity** and **selectivity** trends; **activity** and **carbon binding strength** trends
    - **Informs catalyst selection**





3 – Selective Hydrogenation of Small Oxygenates (Acetic Acid)

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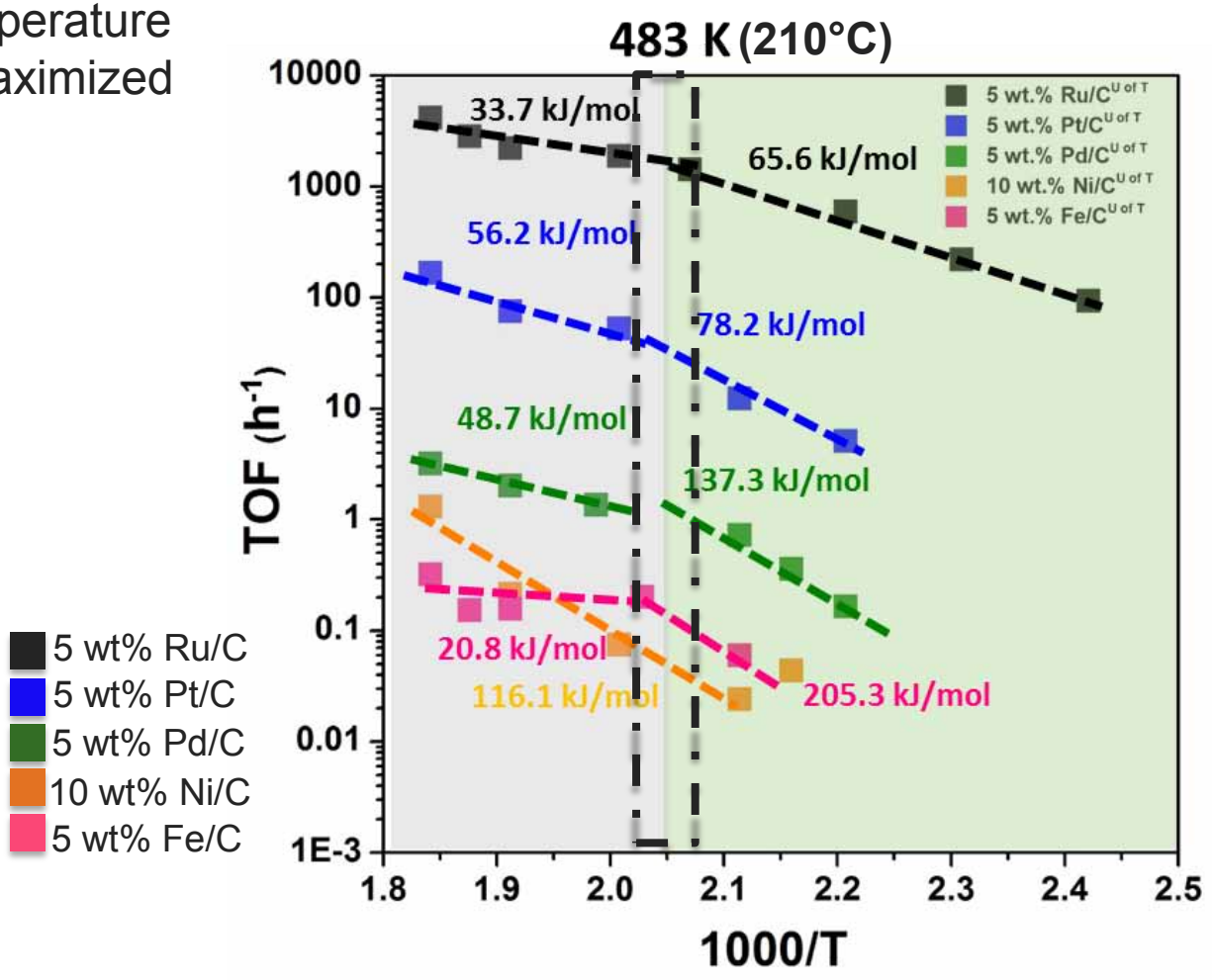
- **Accomplishment:**
  - Identified a **threshold temperature** relationship with **activation energy**
    - Informs temperature range for maximized conversion



3 – Selective Hydrogenation of Small Oxygenates (Acetic Acid)

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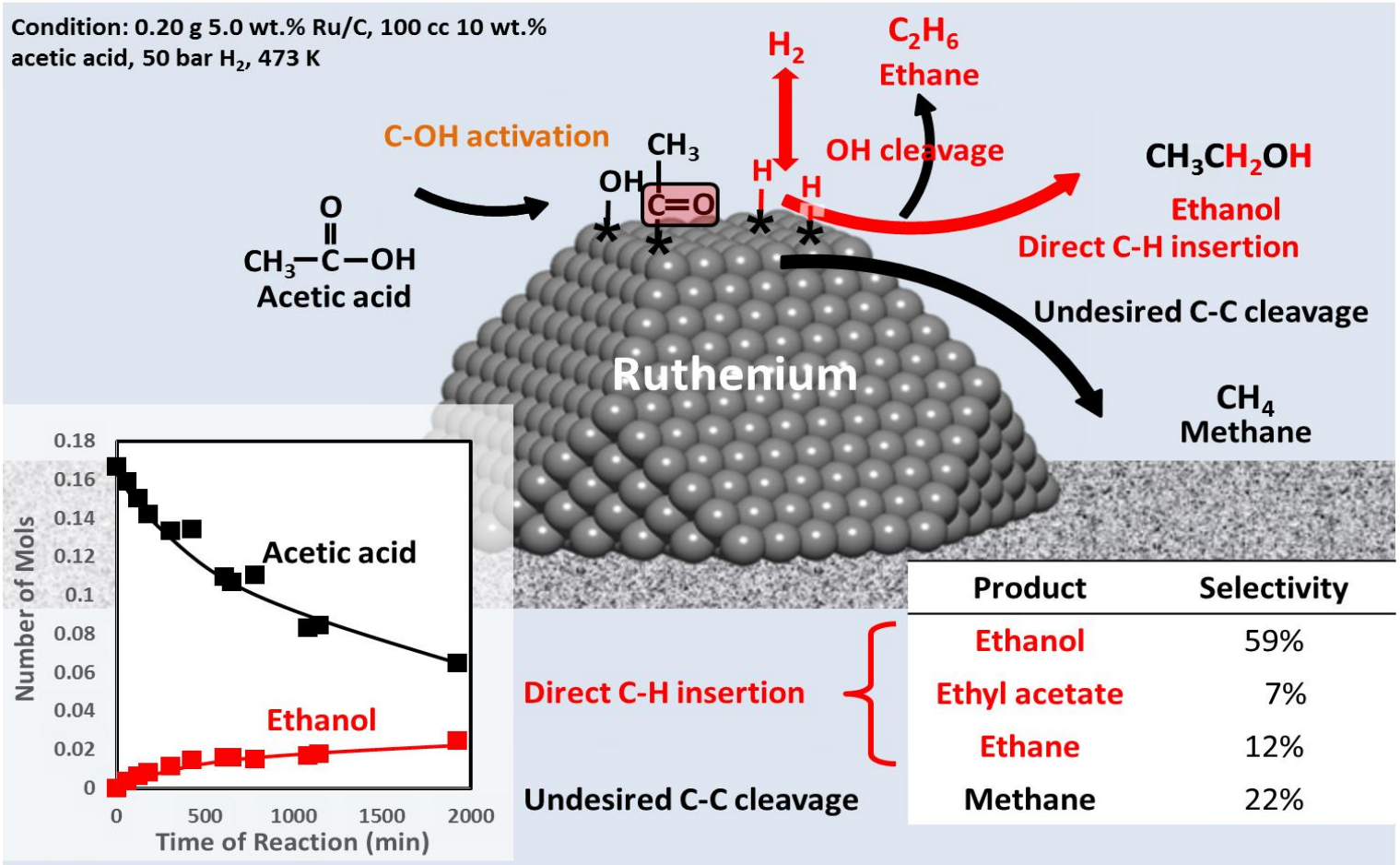
- **Accomplishment:** Establishment of a **reaction pathway**
  - **Identification of intermediate steps that need to be optimized to get the desired product**



Product	Selectivity
Ethanol	59%
Ethyl acetate	7%
Ethane	12%
Methane	22%

[1] H. Olcay, L. Xu, Y. Xu, G.W. Huber, Aqueous-Phase Hydrogenation of Acetic Acid over Transition Metal Catalysts, CHEM. CAT. CHEM., 2 (2010) 1420-1424.
[2] Y. Nakagawa, K. Takada, M. Tamura, K. Tomishige, Total Hydrogenation of Furfural and 5-Hydroxymethylfurfural over Supported Pd–Ir Alloy Catalyst, ACS Catalysis, 4 (2014) 2718-2726.
[3] Y. Yang, Z. Du, Y. Huang, F. Lu, F. Wang, J. Gao, J. Xu, Conversion of furfural into cyclopentanone over Ni-Cu bimetallic catalysts, Green Chemistry, 15 (2013) 1932-1940.

3 – Selective Hydrogenation of Small Oxygenates (Furfural)

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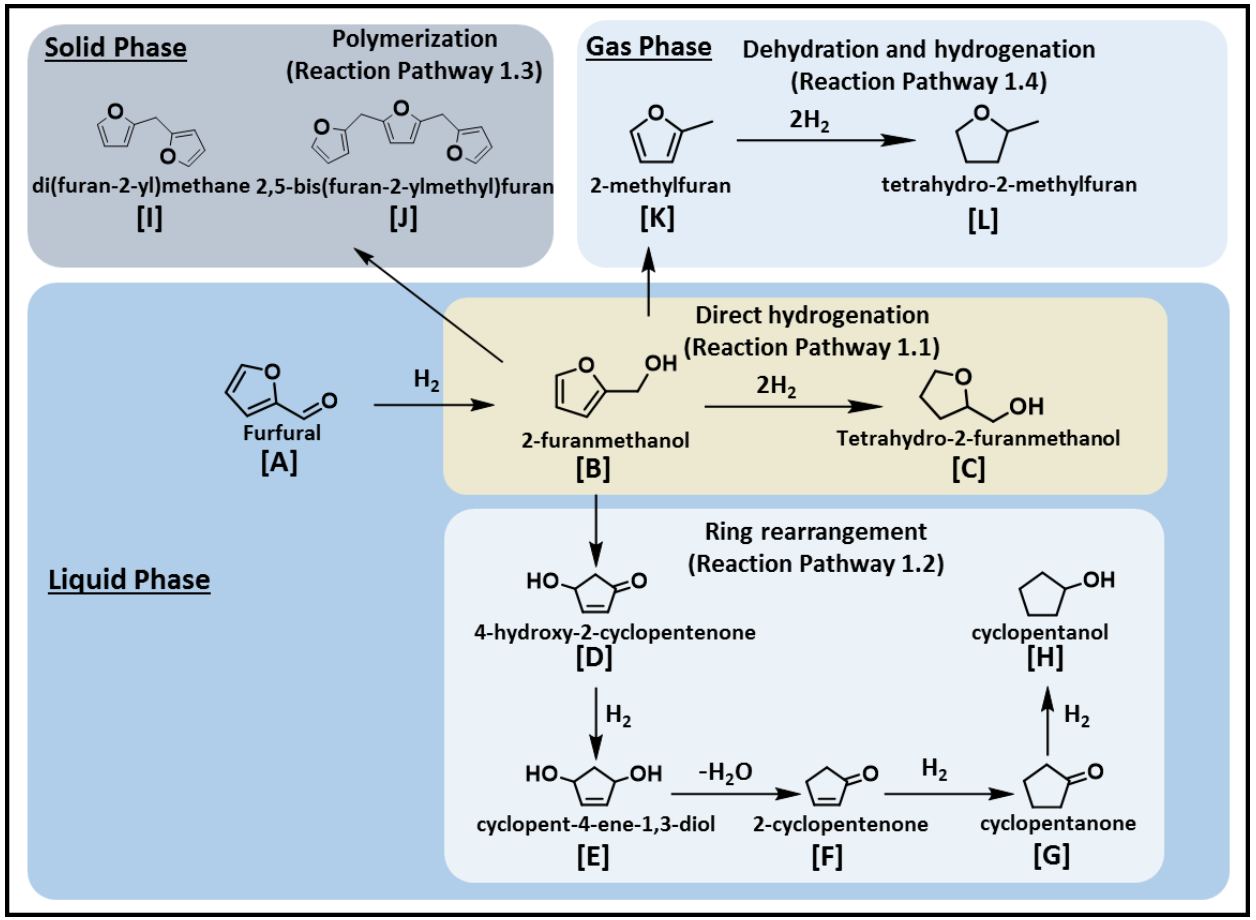
- **Accomplishment:** Establishment of a **reaction pathway** (also for acetic acid, see additional slides)



Is there **potential for controlled molecular mass enhancement** (C_5 → C_{10}/diesel size)?

3 – Alkylation

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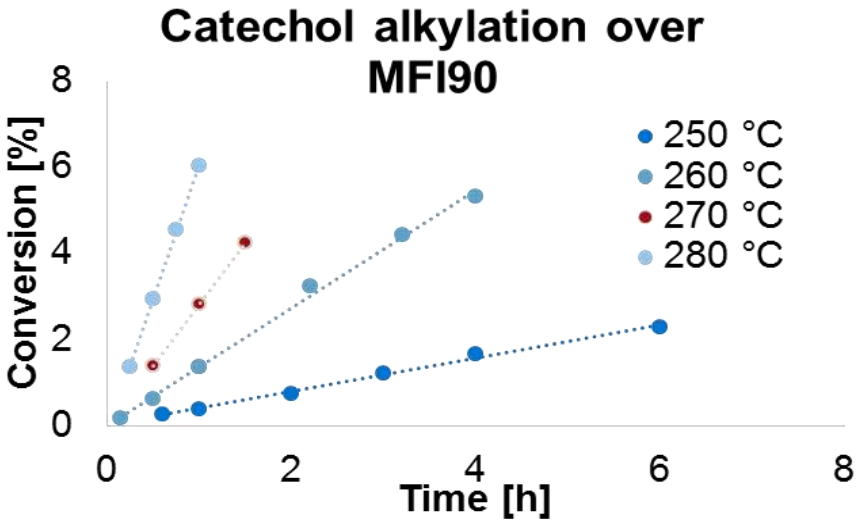
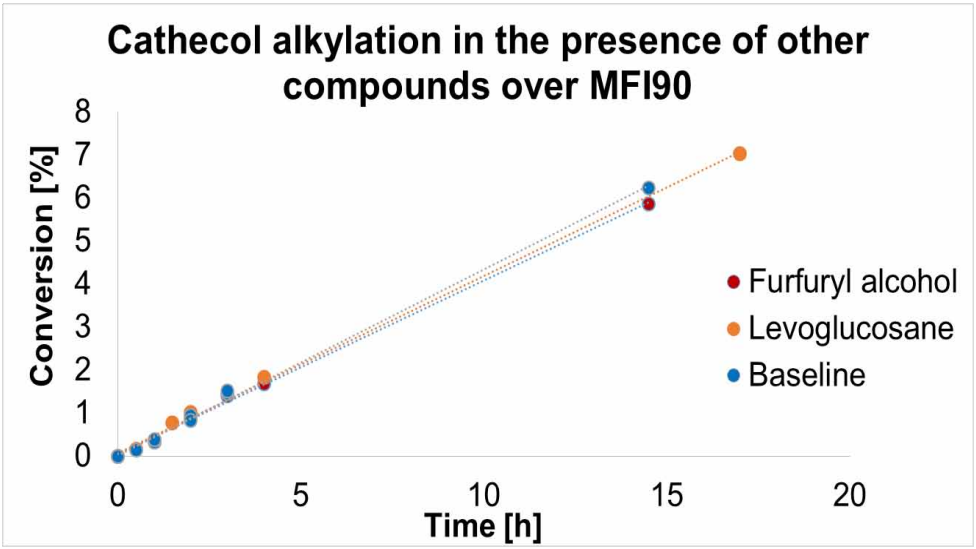
- **Objective:** React alcohol with aromatic compounds
  - ethanol and catechol – product of acetic acid and most abundant single aromatic compound
- **Relevance:** Improve C efficiency
- **Accomplishment:**
  - Showed that addition of **levoglucosan** and **furfuryl alcohol did not affect alkylation** in 17 hours





0.5 g catalyst, 1g catechol, 20 ml ethanol, 80 ml water, p (H_2) = 50 bar, [100 mg levoglucosan or furfuryl alcohol (right graph only)]

3 – Aromatic Ring Hydrogenation

- **Objective:** Hydrogenate alkylated aromatic compound to be amenable to dehydration and determine the effect of alkylation on the rate
- **Relevance:** Bio-oil is expected to have both substituted and unsubstituted aromatics
- **Accomplishment:**
  - Determined that **ethylcatechol (substituted)** hydrogenation is **slower than catechol** hydrogenation; identified temperature at which they are about equal

Catechol hydrogenation rate

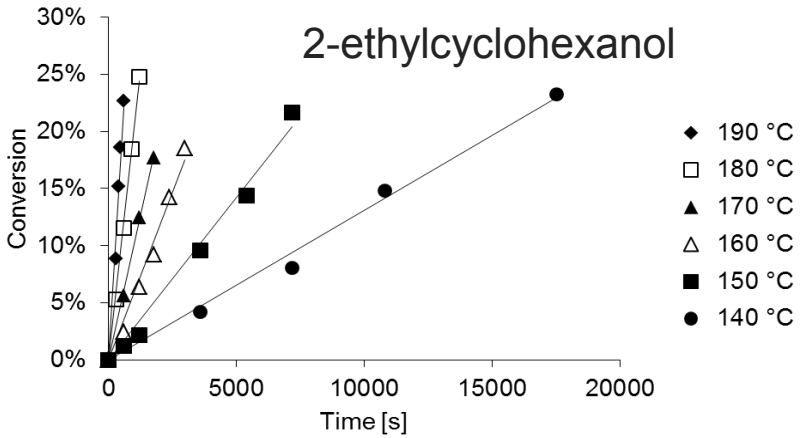
Temperature	Rate [mol / g_{Pd} s]
250 °C	6.48×10^{-3}
230 °C	2.34×10^{-3}
210 °C	7.32×10^{-4}

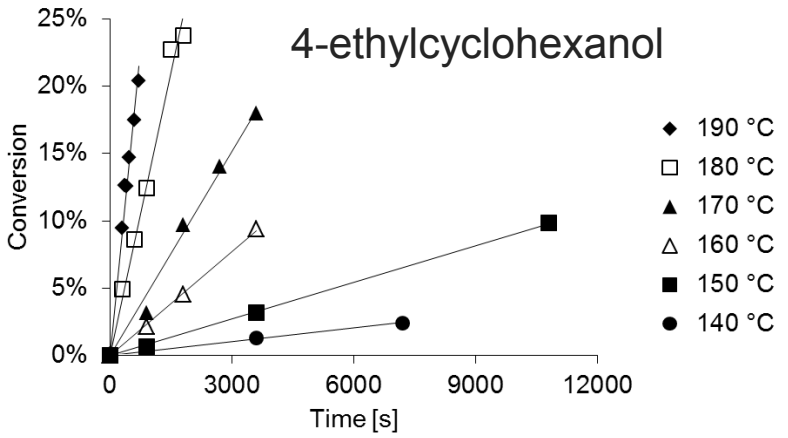
Ethylcatechol hydrogenation rate

Temperature	Rate [mol / g_{Pd} s]
250 °C	5.45×10^{-4}

3 – Dehydration

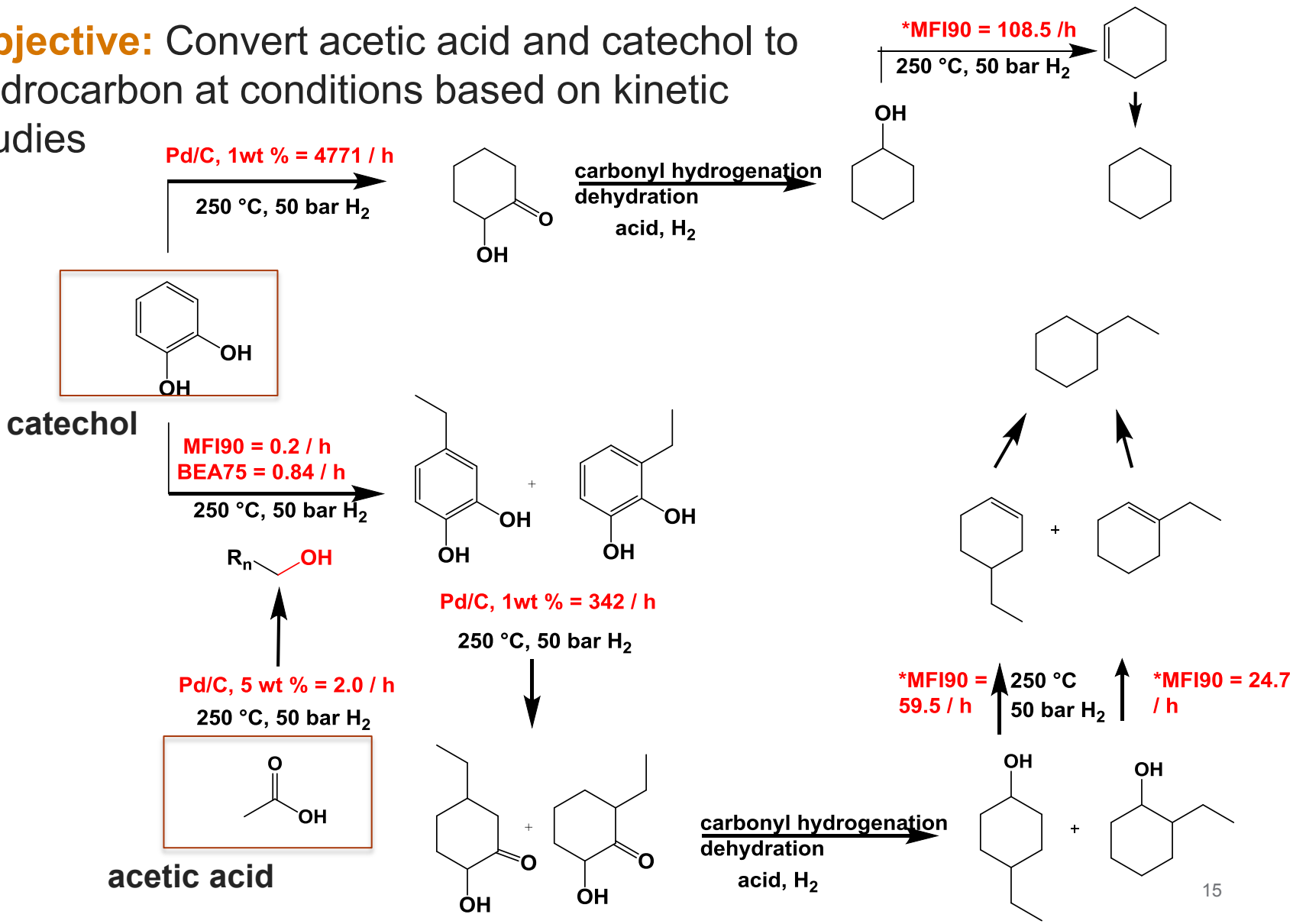
- **Objective:** Removal of O from alkylated cyclohexanol
- **Relevance:** Produce petroleum compatible compounds (hydrocarbons)
- **Achievement:**
  - Identified **dehydration** of naphthenic alcohol as a **low temperature, low pressure pathway to remove O**
  - Showed that 2-subtituted naphthenic alcohol reacts faster than 4-substituted (for methyl- and ethylcatechol)
    - Implied possible differences in dehydration reactivity based on biomass lignin structure
      - *p*-hydroxy vs. guaiacyl vs. syringyl





3 – Cascade Reactions in One-pot

- **Objective:** Convert acetic acid and catechol to hydrocarbon at conditions based on kinetic studies



3 – Cascade Reactions in One-pot

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Preliminary one pot result

$TOF_{\text{aromatic ring hydrogenation}} > TOF_{\text{dehydration}} > TOF_{\text{selective hydrogenation}}, TOF_{\text{alkylation}}$

- One-pot reaction results: directly hydrogenated and dehydrated products (i.e. cyclohexane and cyclohexene) dominate

PRODUCTS	YIELD [%]
CYCLOHEXANE	77.3
CYCLOHEXENE	6.0
CYCLOHEXANONE	1.4
DIRECT HYDROGENATED	**84.7**
METHYLCYCLOHEXANE	2.1
ETHYLCYCLOHEXANE	6.1
ALKYLATED HYDROGENATED	**8.1**

- Didn't achieve expected relative rates with current catalyst suite: **NEED to make aromatic ring hydrogenation less selective**

Importance: Insight into what other catalyst(s) properties can be modified to make project successful, i.e. molecular size effects

4 – Relevance

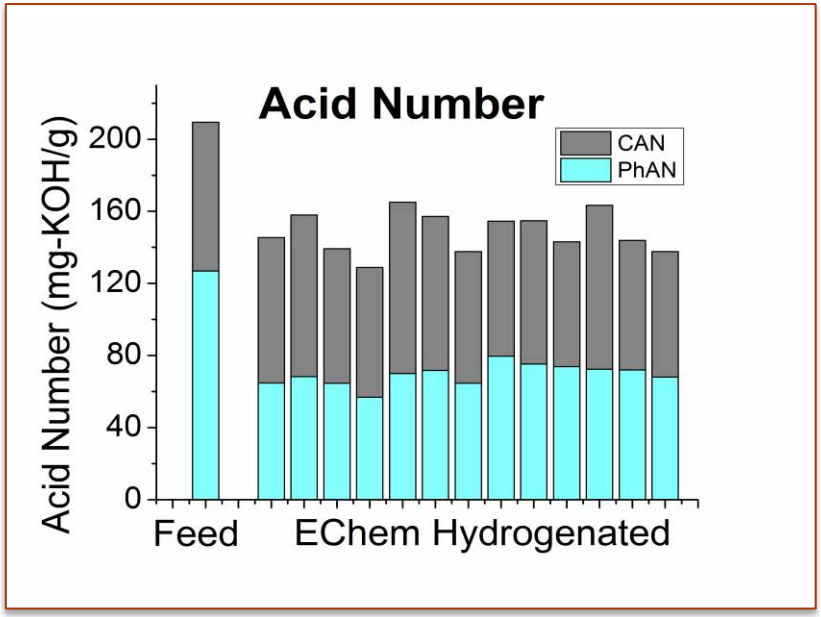
- Addresses BETO Barriers
  - Tt-F (Deconstruction of Biomass to Form Bio-oil Intermediates)
  - Tt-H (Bio-oil Stabilization)
  - Tt-J (Catalytic Upgrading to Fuels and Chemicals)
  - Tt-L (Knowledge Gaps in Chemical Processes)

- Graded approach can be used to determine insights to issues in more complicated systems.

- Reaction kinetics data **may inform other catalytic upgrading processes**
  - **Dehydration** is an attractive route for naphthenic alcohols due to activity at low T and P.

4 – Relevance

- May find application in processes which preferentially hydrogenate aromatics, i.e. electrochemical treatment of bio-oil.



Phenol amount decreases more than carboxylic groups.

- ❑ Acid functionality in the catalyst may also afford cracking.

Courtesy of 2.12.1.5

- Possible application for fractionated pyrolysis oils.

- The process still needs catalytic development and tuning with real bio-oil feeds and using continuous flow reactors.

5 – Future Work

- *Partner university – finish experiments and submit journal manuscripts.*
- *Collate data from partners. Submit final report. Closeout project.*

Summary

- **OVERVIEW**
  - Proposed an alternative pathway that has potential to use lower H_2 pressure and increase liquid product yield
- **APPROACH**
  - Systematic graded approach increasing in complexity
- **TECHNICAL ACCOMPLISHMENT**
  - Kinetic data for four reactions having functional groups relevant to bio-oil
  - Insights for possible application to other upgrading pathway
  - Directing catalyst development
- **RELEVANCE**
  - Potential for low temperature, low pressure catalytic upgrading of bio-oil
  - Inform other upgrading pathways
  - Identified possible alternative O removal for certain applications, e.g. electrochemical upgrading of biomass
- **Technology transfer:** Disseminate knowledge that is industrially relevant; publication of peer-reviewed manuscripts and presentation in conferences.

Acknowledgement

- Work reported herein were accomplished by the following researchers:
  - TUM
    - Sebastian Eckstein, Peter Hintermeier, Dr. Eszter Barath, Prof. Johannes A. Lercher
  - U of T
    - Junnan Shangguan, Yinan Xu, Prof. Cathy Chin

- Funding from BETO is gratefully acknowledged.

Additional Slides

Abbreviations

- TEA = Techno-economic analysis
- CAPEX = Capital expense
- OPEX = Operating expense
- MFSP = Market fuel selling price
- gge = gasoline gallon equivalent
- k = reaction rate (1/[concentration]$^{\text{reaction order-1}}$-hr)
- TOF = Turn-over frequency (mol compound/mol active site-hr)
- CAN = Carboxyllic acid number
- PhAN = Phenol acid number

Responses to Previous Reviewers' Comments

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- **2013 Review Comments**:
  - "The project addresses an important issue, which is converting low-value organic by-products into more valuable fuels. After a slow start caused by changing interests of a partner, the project has been rescoped and now appears to be on tack for successful completion"
  - "The use of alumina seems to be a false start. Need to get more active input/support from their industry partners."
  - "There is a key potential advance here (small fragments → alcohols and thence to fuels via alkylation of rings), but there is some ancillary work of less obvious value. Its not clear that the original partnership, which looked like a very good one, is still truly in place. Without that, it is really just more lab-directed work at PNNL on hydrotreating, which is useful but not terribly innovative or commercially promising."
  - "Think this is a good project. The slides were decently understandable."
  - **Response:** Thank you for the review and feedback on this competitively funded project. We agree that the industrial partnerships are valuable and will seek more active input from UOP and W.R. Grace as we move forward. It is unfortunate that the inherently low-value proposition of transportation fuels gives cause for industry to focus on developing higher-value products. However, we are fortunate to be working with world leaders in refinery technology and catalyst provision. We also believe that the novelty of this effort is the tying of fundamental reaction-kinetics studies of model compounds directed to bio-oil fractions, then whole bio-oils over the two-year period of performance. As such, the knowledge developed is expected to bolster the field of catalytic HDO, thereby facilitating commercially viable catalyst development for catalytic fast pyrolysis, hydropyrolysis, conventional fast pyrolysis and hydrothermal liquefaction of bio-oils. We are excited about moving the work forward with our academic and industry partners and note that there are aspects of the catalyst development that industry indentified as having value.

Publications, Patents, Presentations, Awards, and Commercialization

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- "Catalytic Pathways and Periodic Reactivity Trends for the Hydrogenation of Acetic Acid in Condensed Phase on Transition Metal Clusters" Shangguan, J, Olarte, MV and Chin, Y(C). *Poster presentation (to be presented).* 24th North American Meeting, Pittsburgh, PA.

2013 TEA funnel plot

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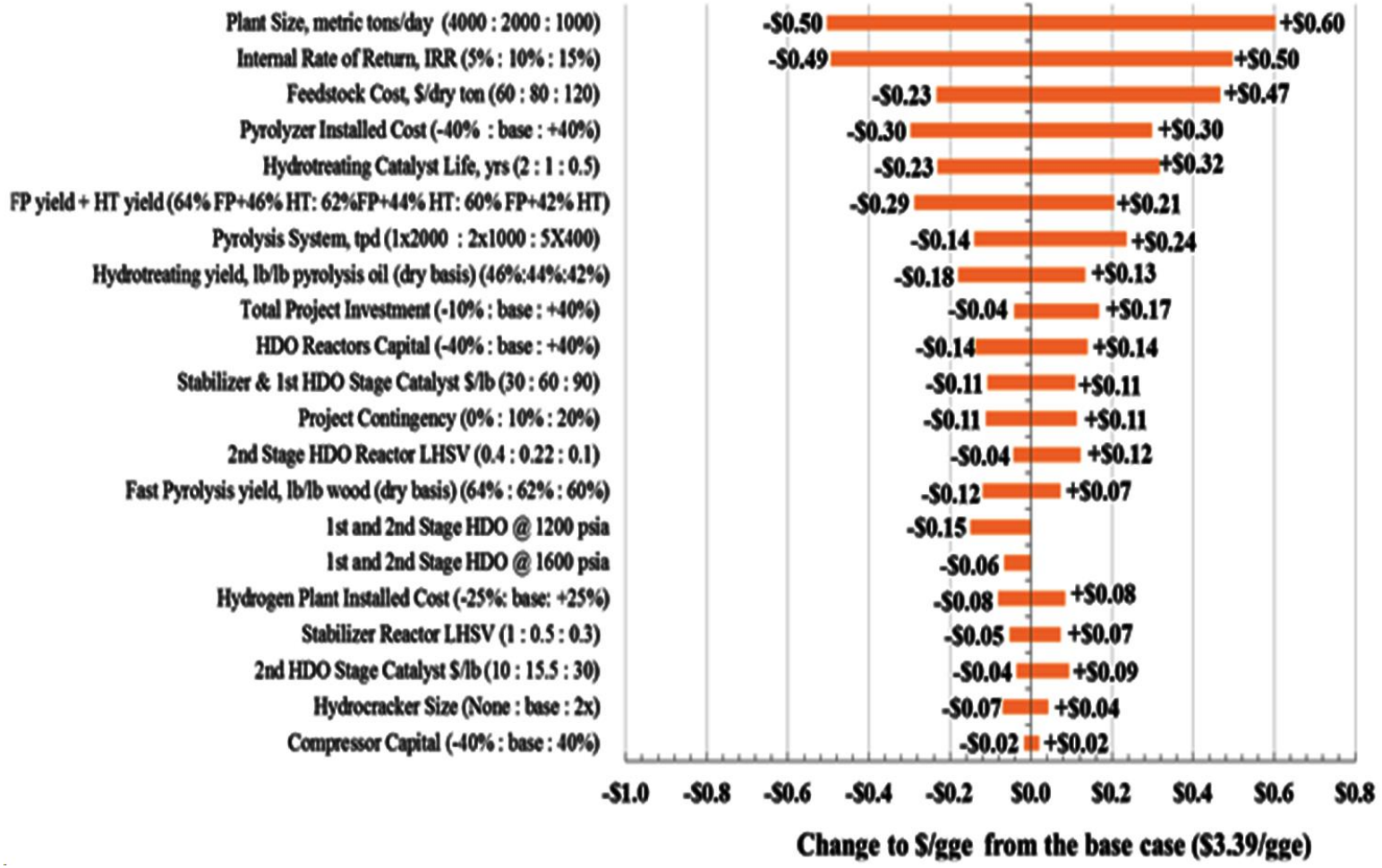
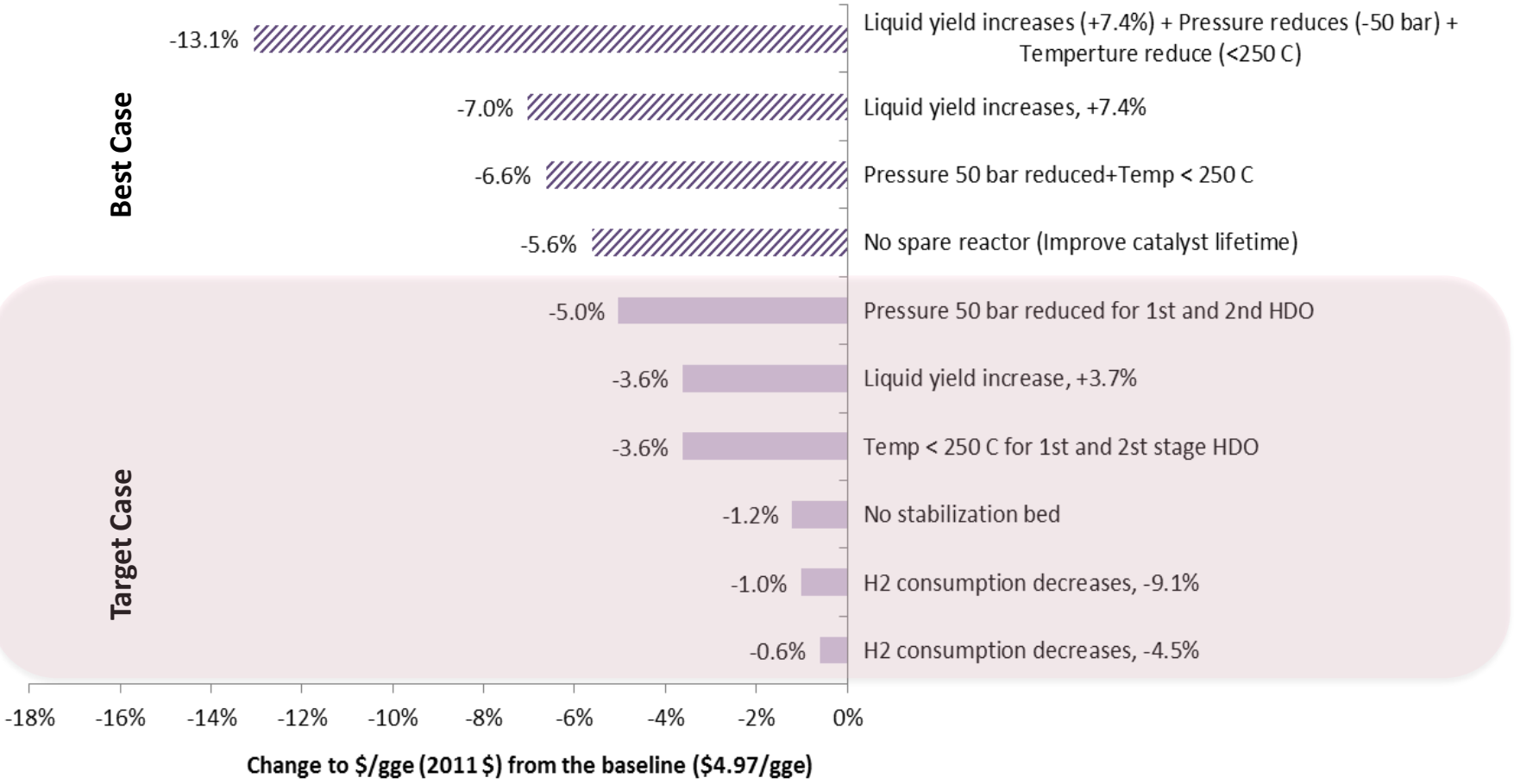
Production of liquid transportation fuel from biomass requires the process to be efficient and cost effective.



Potential for MFSP Reduction



- **Increased liquid yield** alone potentially reduces **MFSP by 3-7%**
- **Decreased CapEx** related to reduced operating conditions potentially reduces **MFSP by 3-7%**
- **Improvements** in liquid yield, catalyst stability, CapEx, and OpEx **combined** potentially reduces **MFSP by 10-20%**
- **If MFSP was $3/gge, this would be $0.30-$0.60/gal.**

Experimental Set-up: UofT

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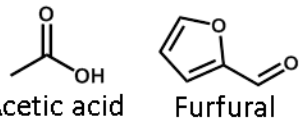
Model compounds aqueous solution



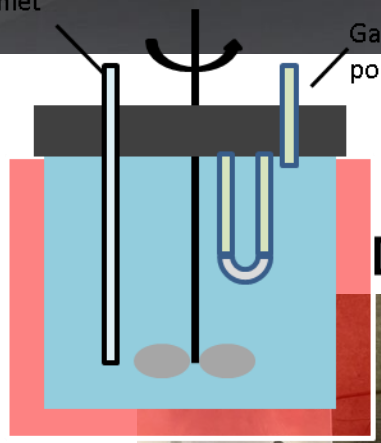
Acetic acid Furfural

Home-made carbon supported transition metal nano-clusters

Fe Ni Ru Pd Pt

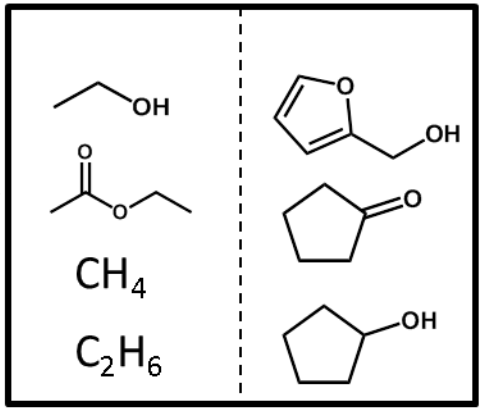
Co-feed

Pressurized with H_2



Parr reactor-high pressure batch reactor system

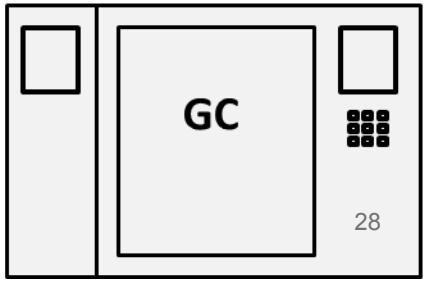
Ice-water quench



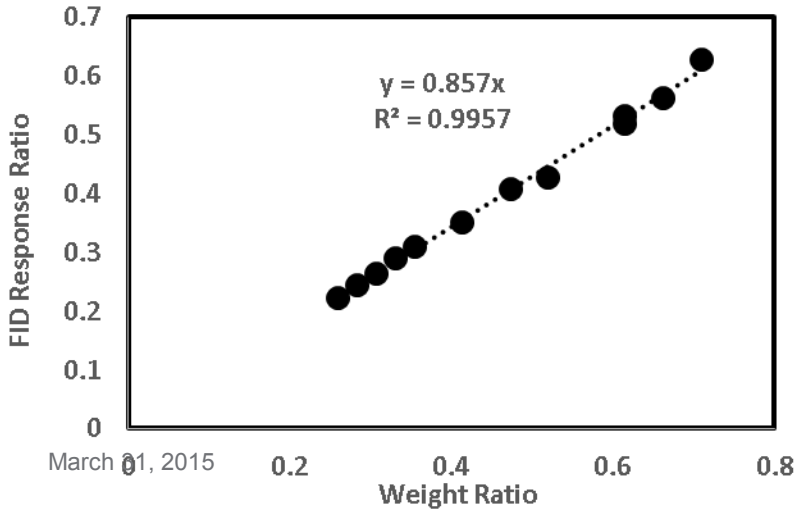
Adding internal standard

Ethyl acetate extraction

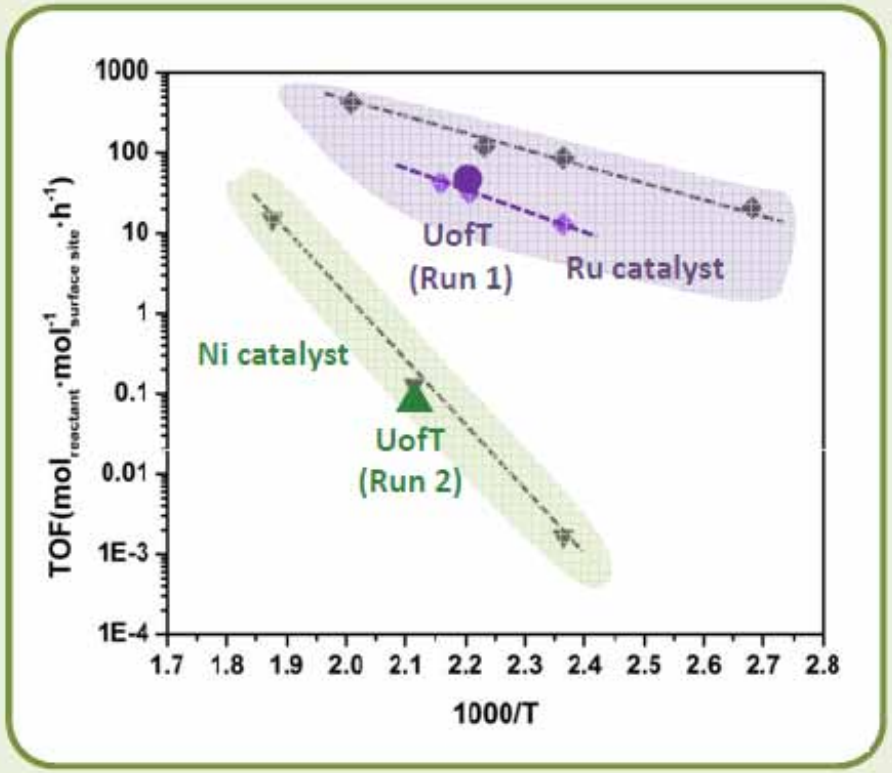
Off-line analysis



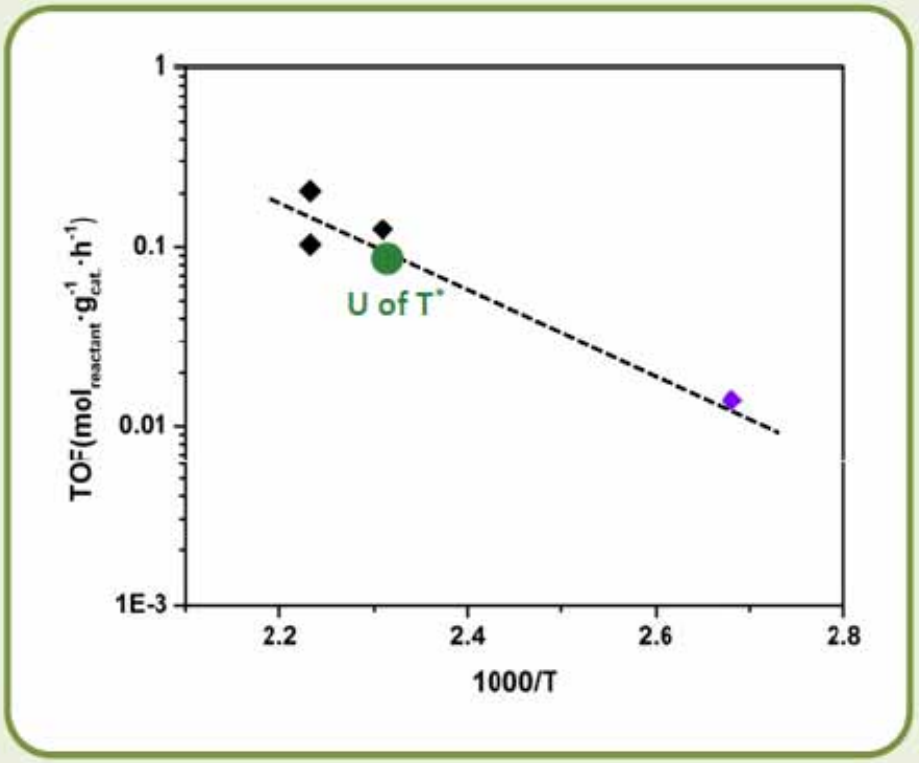
Ethanol calibration curve



Reactor Reproducibility Validation

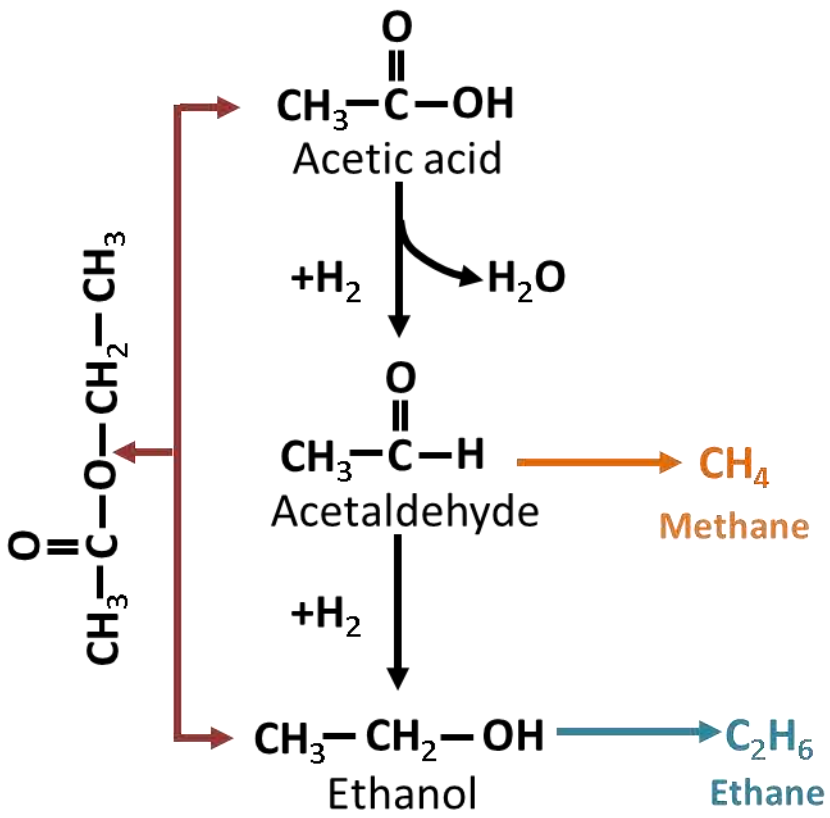


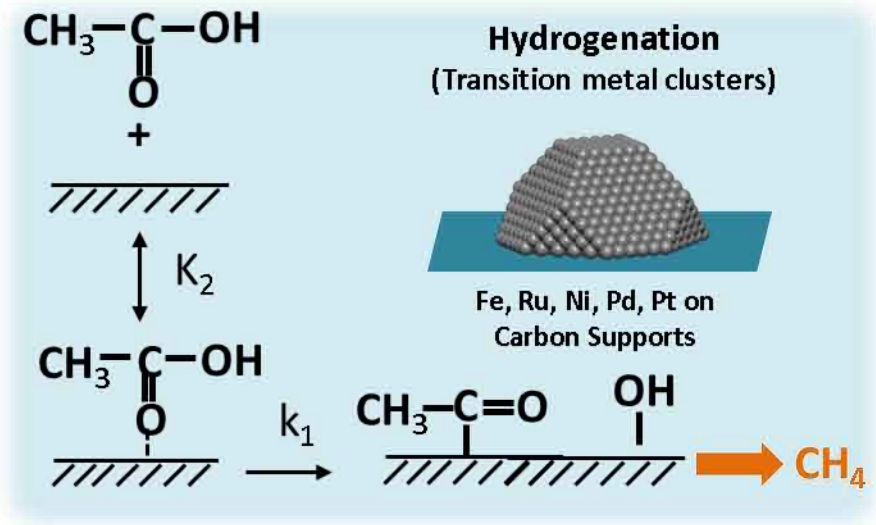
Acetic acid hydrogenation



Furfural hydrogenation

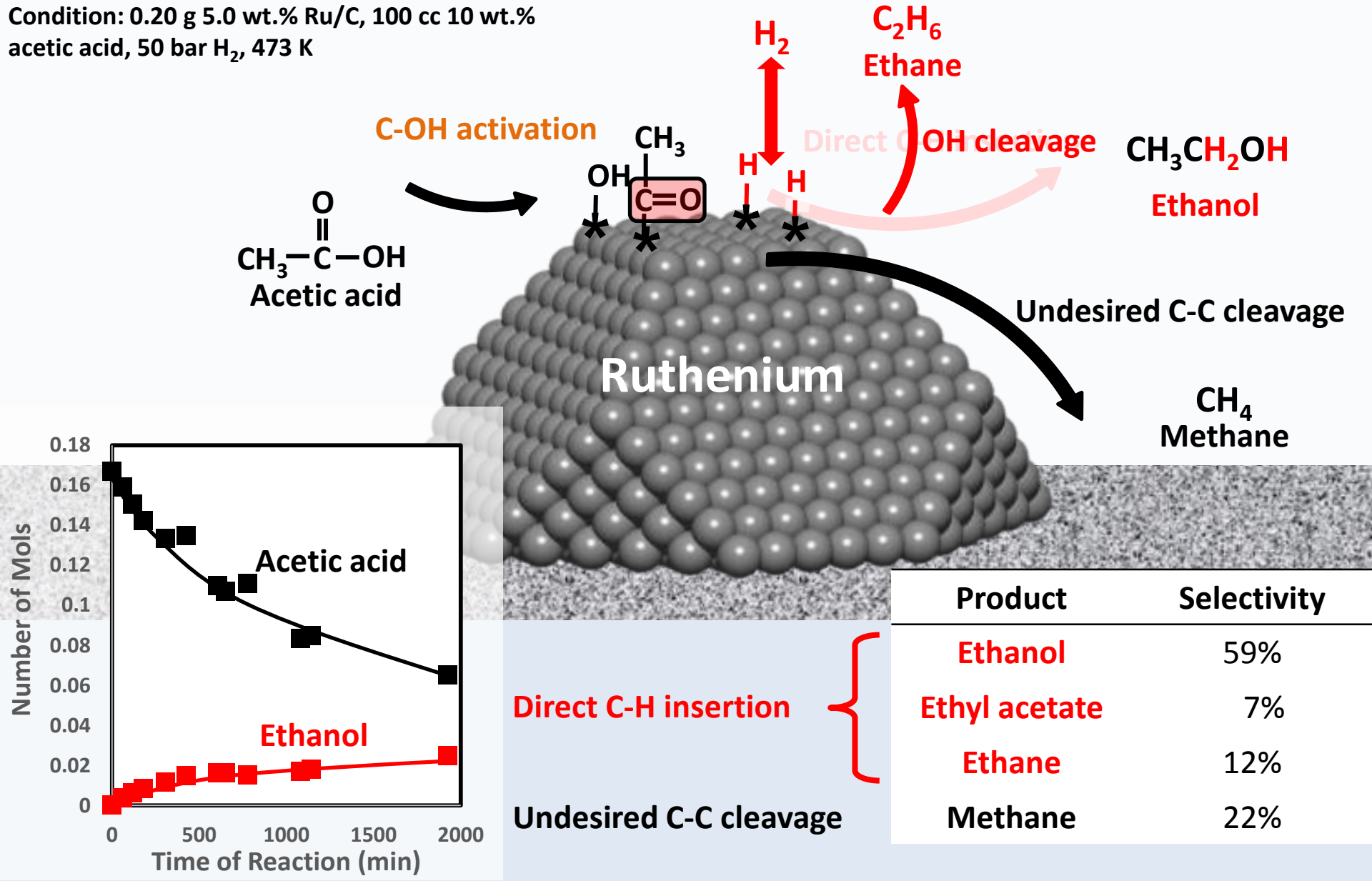
Selective hydrogenation of acetic acid





Acetic Acid Reaction Pathway

Condition: 0.20 g 5.0 wt.% Ru/C, 100 cc 10 wt.% acetic acid, 50 bar H_2, 473 K



	Product	Selectivity
Direct C-H insertion	Ethanol	59%
	Ethyl acetate	7%
	Ethane	12%
Undesired C-C cleavage	Methane	22%

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0.075 g Ru/C, 10 wt% acetic acid a.q., 473 K, 10-60 bar H_2

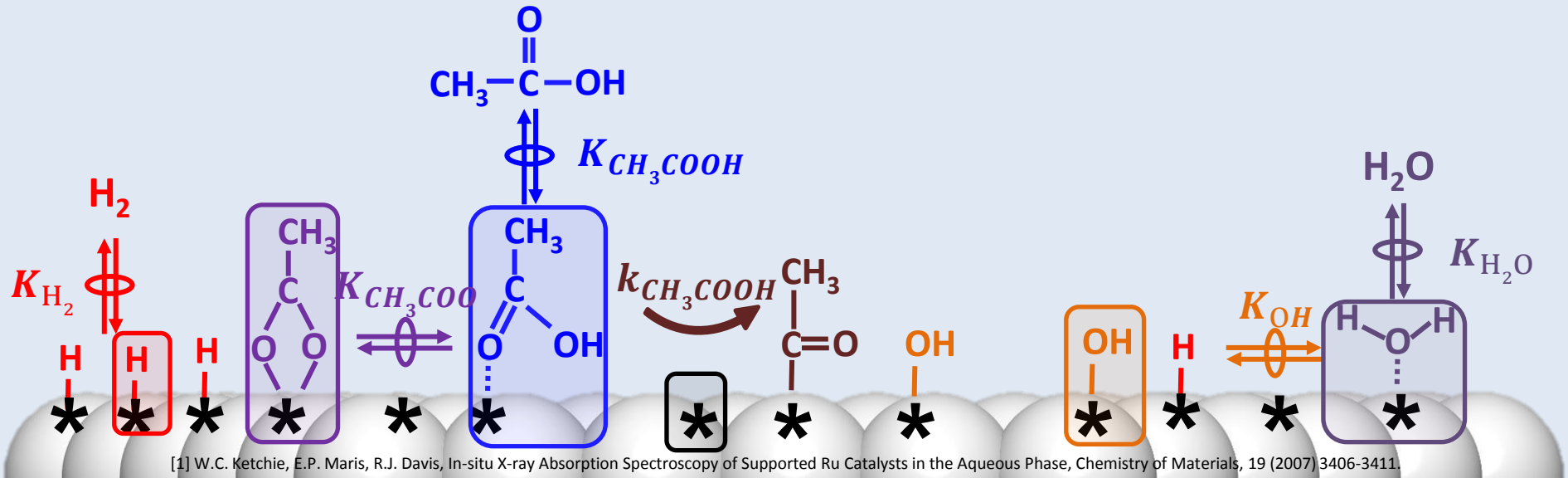
Surface Mechanism

$$r_{CH_3COOH} = k_{CH_3COOH}\frac{[CH_3COOH\ *][*]}{[T]}$$

$$TOR_{(CH_3COOH)} = \frac{r_{CH_3COOH}}{[T]} = \frac{k_{CH_3COOH}[CH_3COOH\ *][*]}{[T]^2}$$

$$TOR_{(CH_3COOH)} = \frac{r_{CH_3COOH}}{[T]} = \frac{k_{CH_3COOH}\ K_{CH_3COOH}[CH_3COOH]}{\left(\frac{K_{CH_3COO}K_{CH_3COOH}[CH_3COOH]}{(K_{H_2}[H_2])^{0.5}} + \frac{K_{OH}K_{H_2O}[H_2O]}{(K_{H_2}[H_2])^{0.5}}\right)^2}$$

$$[T] = \left((K_{H_2}[H_2])^{0.5} + \frac{K_{CH_3COO}K_{CH_3COOH}[CH_3COOH]}{(K_{H_2}[H_2])^{0.5}} + K_{CH_3COOH}[CH_3COOH] + 1 + \frac{K_{OH}K_{H_2O}[H_2O]}{(K_{H_2}[H_2])^{0.5}} + K_{H_2O}[H_2O] \right)[*]$$

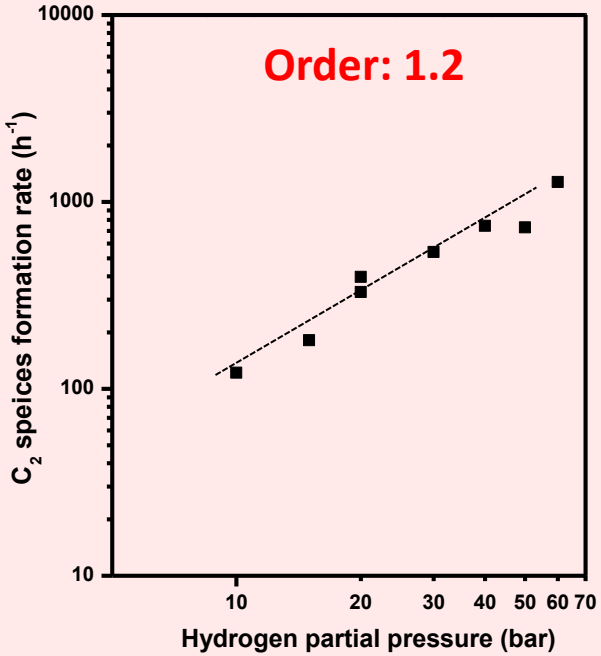


[1] W.C. Ketchie, E.P. Maris, R.J. Davis, In-situ X-ray Absorption Spectroscopy of Supported Ru Catalysts in the Aqueous Phase, Chemistry of Materials, 19 (2007) 3406-3411.

Fate of Surface Acetyl

$$TOR_{(CH_3COOH)} = \frac{k_{CH_3COOH}\ K_{CH_3COOH}[CH_3COOH]}{\left(\frac{K_{CH_3COO}K_{CH_3COOH}[CH_3COOH]}{(K_{H_2}[H_2])^{0.5}} + \frac{K_{OH}K_{H_2O}[H_2O]}{(K_{H_2}[H_2])^{0.5}} \right)^2}$$

Direct C-H insertion

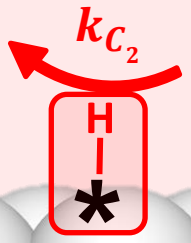


H_2 order= 1 - 1.5

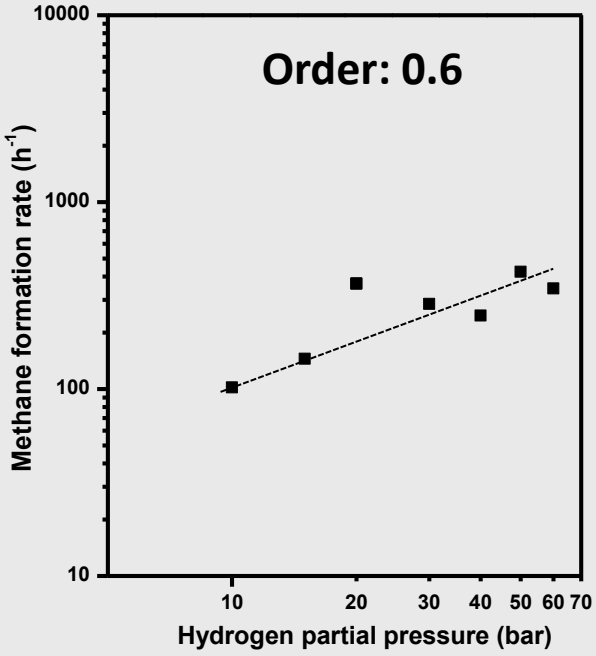
$$r_{C_2} = TOR_{(CH_3COOH)} \frac{k_{C_2}(K_{H_2}[H_2])^{0.5}}{k_{C_2}(K_{H_2}[H_2])^{0.5} + 2k_{CH_4}}$$

Ethanol

Ethyl acetate Ethane

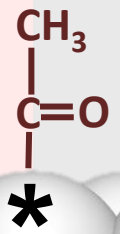


Undesired C-C cleavage



H_2 order= 0.5 - 1

$$r_{CH_4} = TOR_{(CH_3COOH)} \frac{2k_{CH_4}}{k_{C_2}(K_{H_2}[H_2])^{0.5} + 2k_{CH_4}}$$



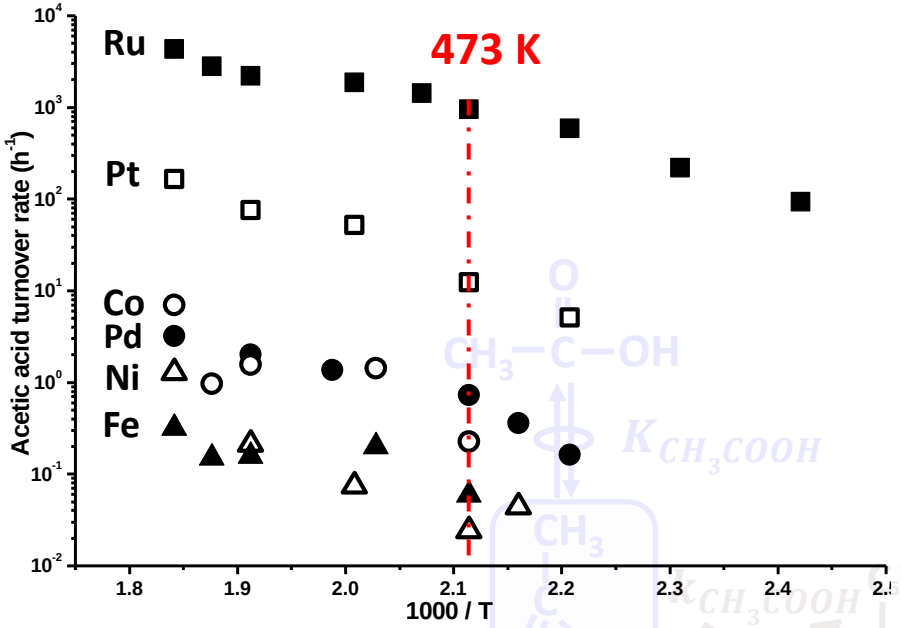
CH_4
Methane

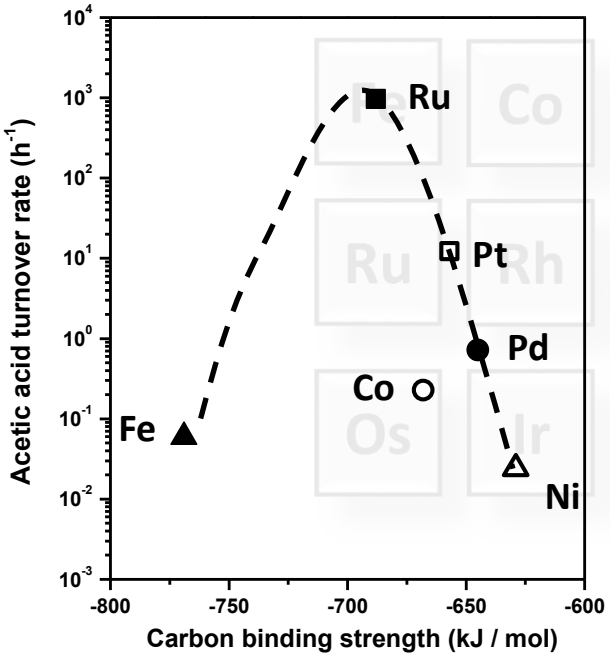
BEP Relation and Periodic Trend

BEP Relation: $\Delta E_a = \beta \Delta \Delta H$

ΔH= E(Acetic acid, C-OH)+**Ad(Acetyl*)+Ad(Hydroxyl*)-Ad(Acetic acid*)**

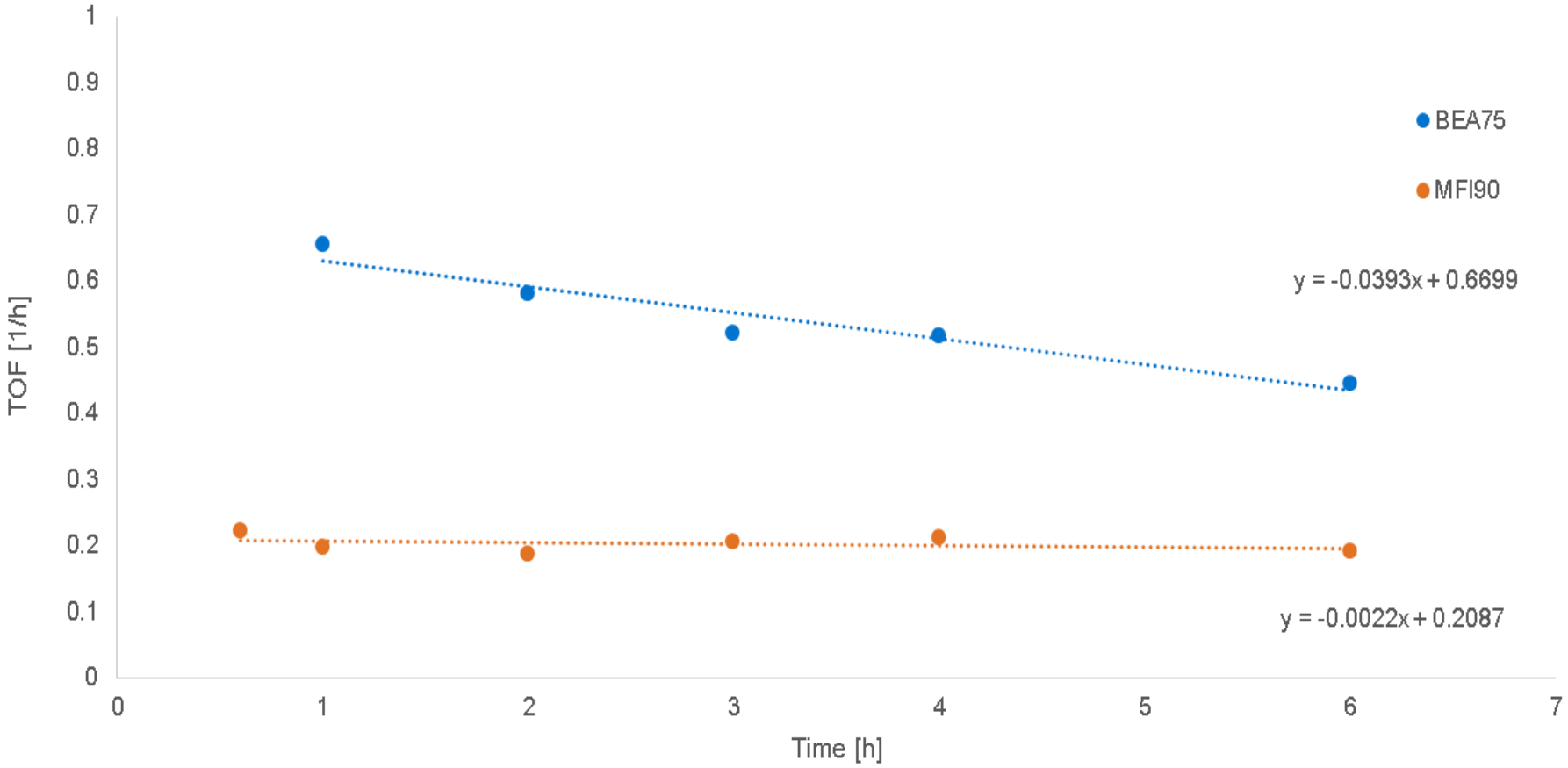
Carbon binding strength **Oxygen binding strength**





Stability of Zeolites

Reaction conditions: 250 °C, 0.5 g catalyst, 1.0 g catechol, 20 ml ethanol 80 ml water



MFI has more sustained performance

Kinetic data for alkylation over various types of zeolite at 250 °C

Pacific Northwest NATIONAL LABORATORY
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Catalyst	Si / Al ratio	initial Rate [$mol_{catechol}$/ $g_{catalyst}$ h]	K* [1 / h $g_{catalyst}$]	TOF
H-MFI	11.5	1.3×10^{-4}	1.4×10^{-2}	-
	45	7.3×10^{-5}	8.0×10^{-3}	0.20
	110	3.6×10^{-5}	4.0×10^{-3}	0.29
	200	1.3×10^{-5}	1.4×10^{-3}	0.17
H-BEA	12.5	1.6×10^{-3}	1.8×10^{-1}	1.21
	75	1.7×10^{-4}	1.9×10^{-2}	0.74
La-BEA	75	1.1×10^{-4}	1.2×10^{-2}	-
H-FAU	2.5	1.2×10^{-5}	1.3×10^{-3}	-
La-FAU	2.5	1.3×10^{-5}	1.4×10^{-3}	-

Alkylation of catechol with ethanol over MFI90 and BEA75

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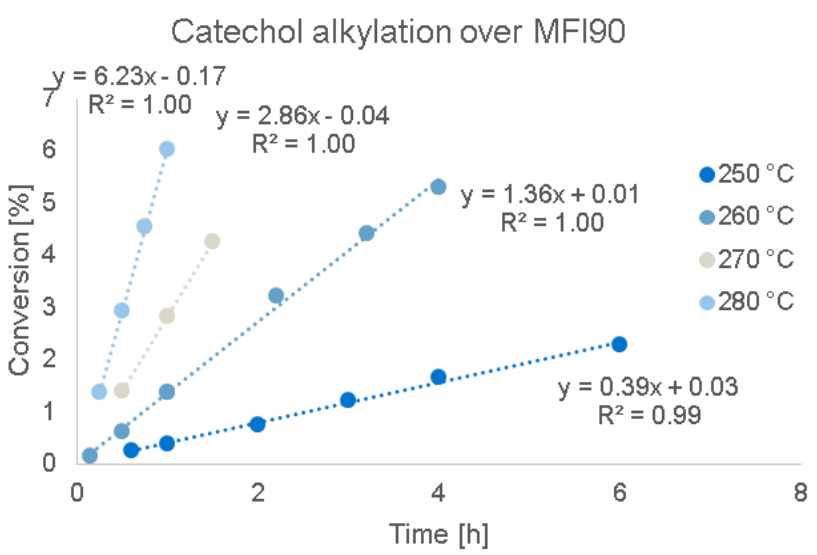
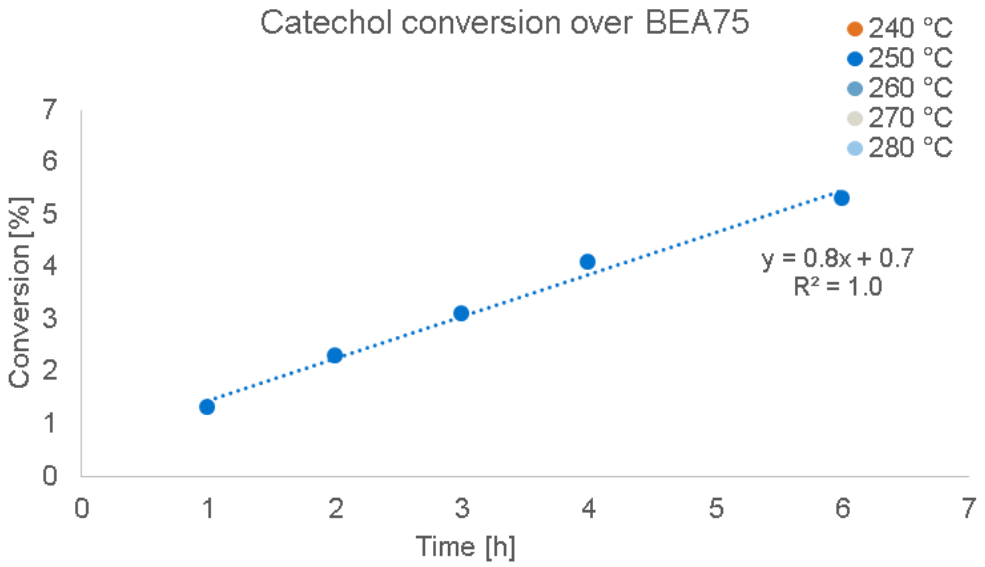
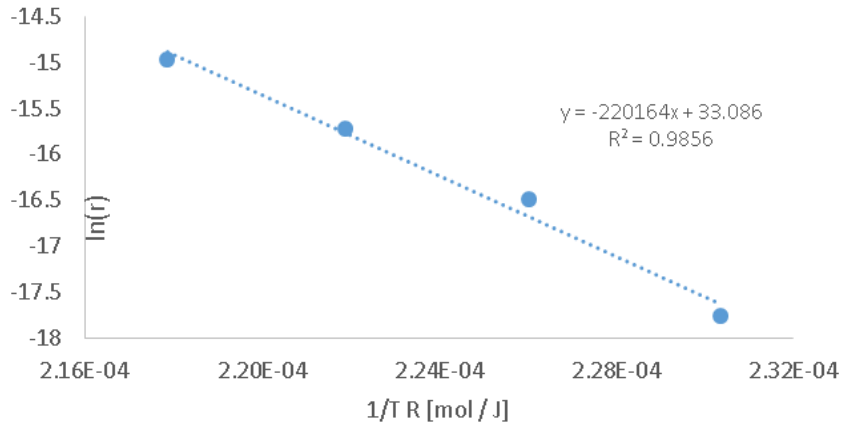
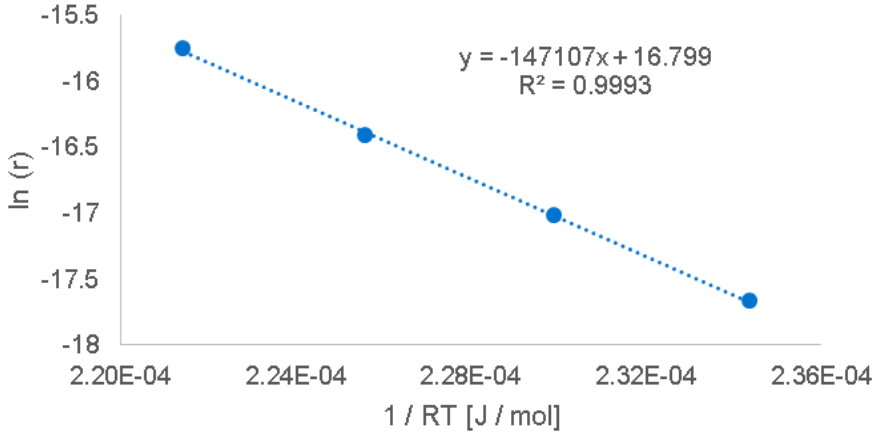


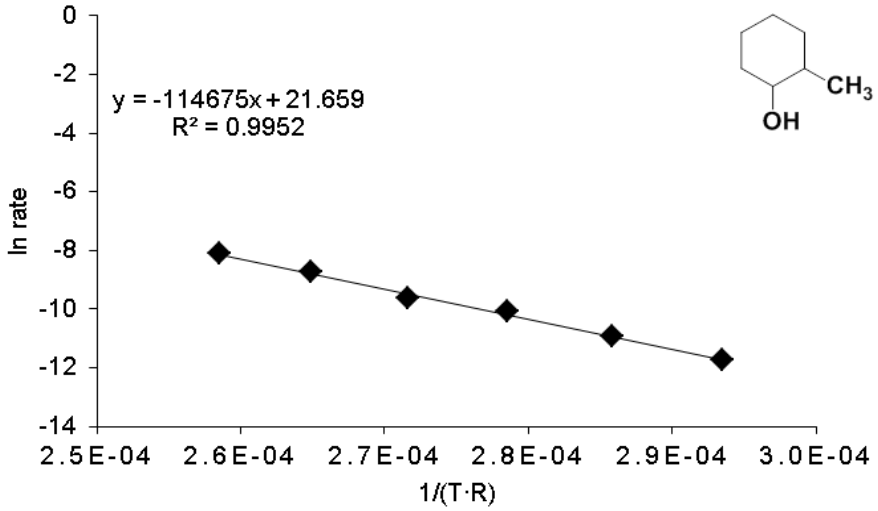


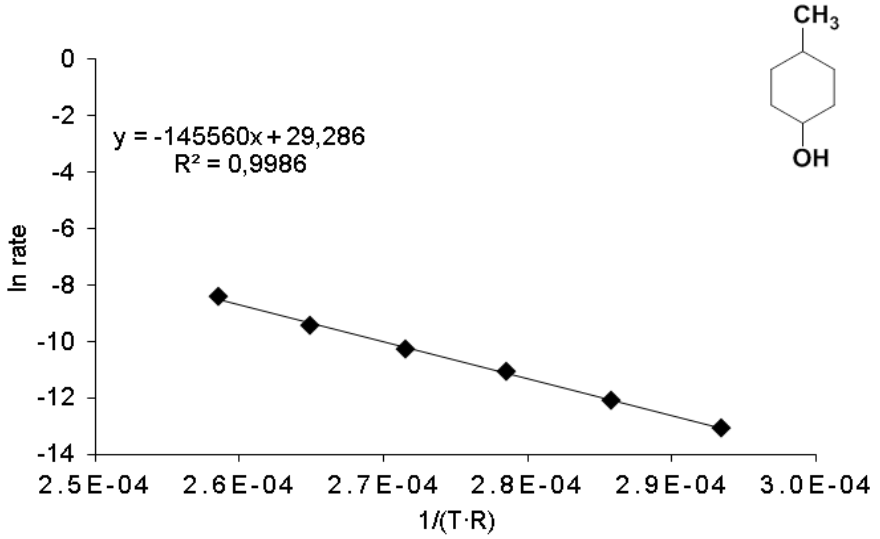
Reaction conditions: 0.5 g BEA catalyst, 1g catechol, 20 ml ethanol, 80 ml water, p (H_2) = 50 bar





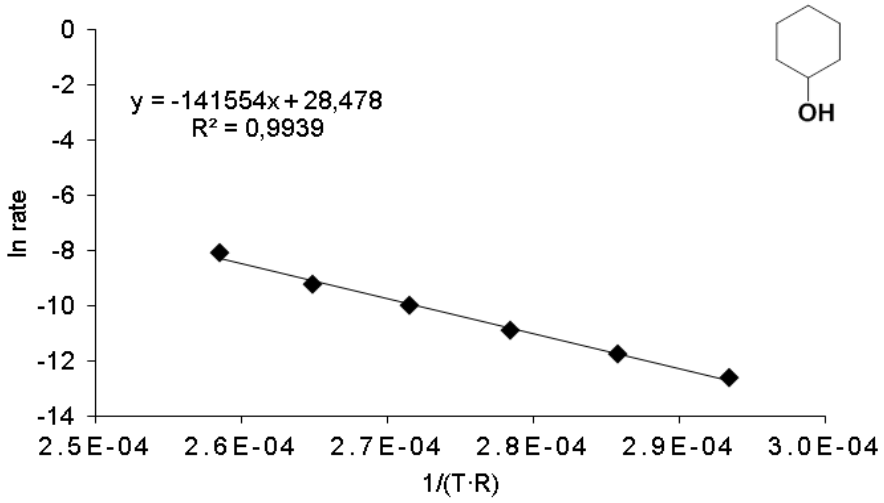
Dehydration with methyl substituents



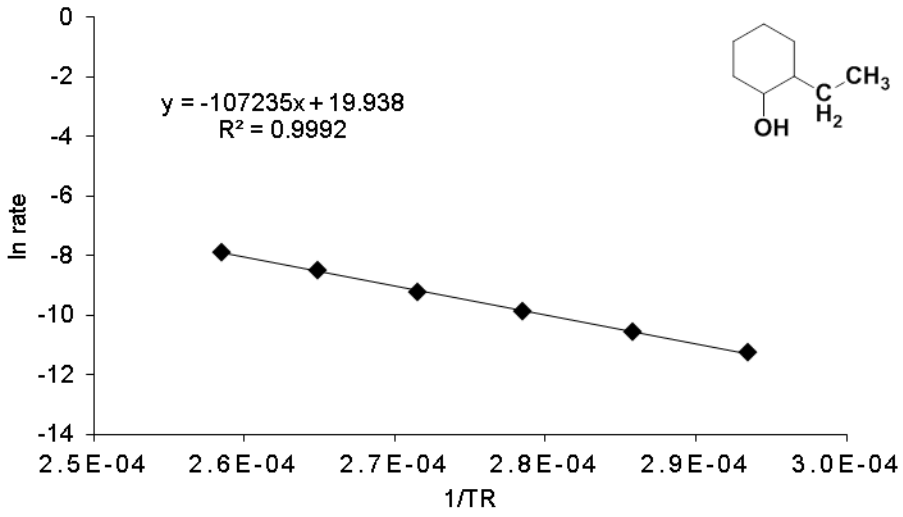


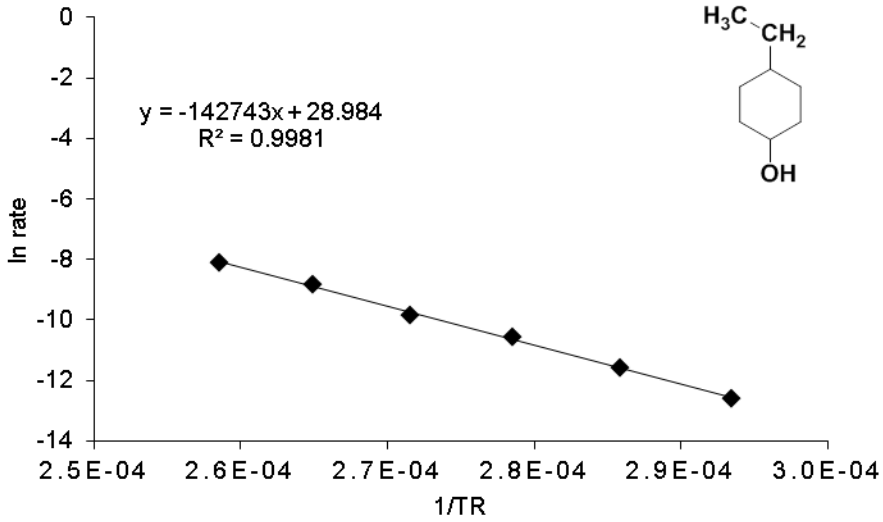
Activation energies:

Cyclohexanol	≈	142 kJ/mol
4-methylcyclohexanol	≈	146 kJ/mol
2-methylcyclohexanol	≈	115 kJ/mol



Dehydration with ethyl substituents

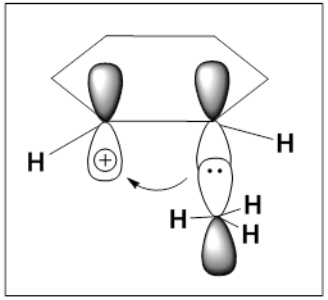




Activation energies:

4-ethylcyclohexanol ≈ 143 kJ/mol

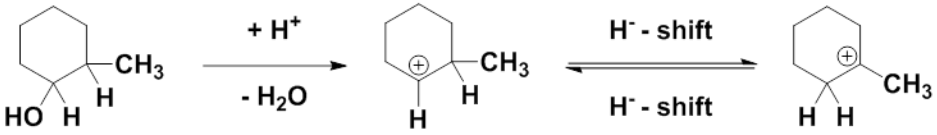
2-ethylcyclohexanol ≈ 107 kJ/mol



Activation energy of 2-substituted substrates significantly lower:

→ stabilizing effect (*hyperconjugation*) of substituent in position 2

→ ethyl (107 kJ/mol) slightly higher than methyl (115 kJ/mol)!



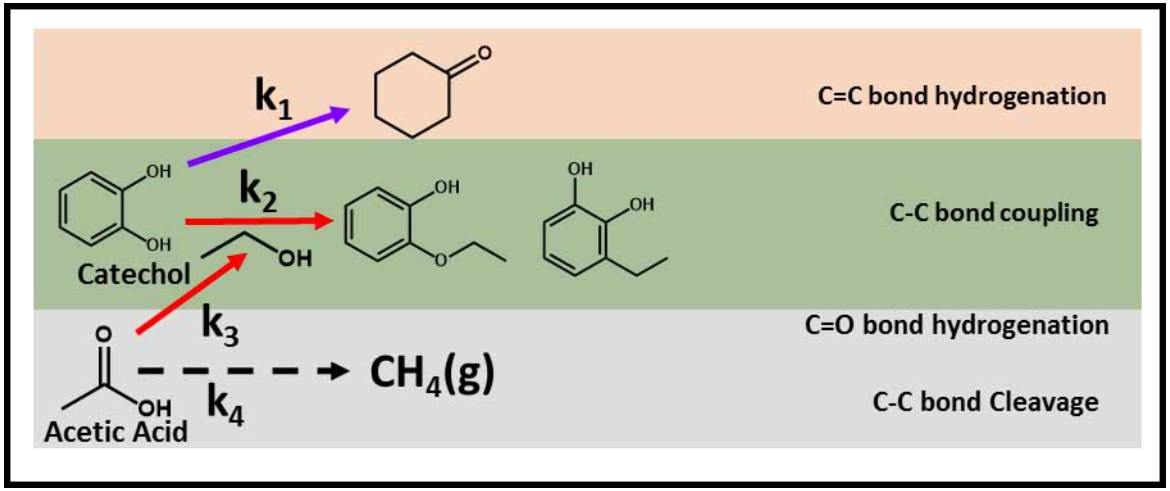
Cascade reactions starting with acetic acid (metal catalyst only)

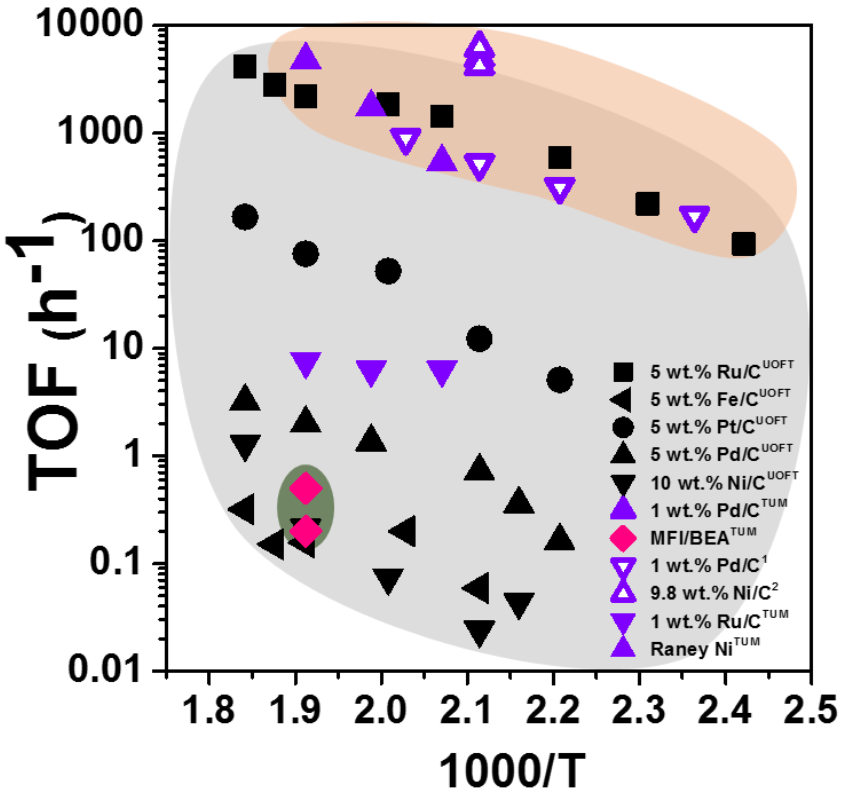
Reaction conditions: 1.0 g catechol, 20 ml acetic acid, 80 ml water, 200 °C, 17 h, 50 bar H_2

Catalyst	Pt/C, 10 wt %	Ru/C, 5 wt %	Pd/C, 10 wt %
Mass catalyst	0.3 g	0.1 g	0.3 g
Conversion Acetic acid	n.d.	n.d.	n.d.
Yield Ethanol	1.3 %	4.6 %	2.4 %
Yield Ethyl acetate	n.d.	n.d.	n.d.
Conversion catechol	99.8 %	93.2 %	97.7 %
	Yields		
Cyclohexane	-	28.4%	-
Cyclohexanol	0.5 %	3.0 %	3.5 %
Cyclohexanone	64.3 %	6.0 %	31.0 %
Cyclohexanediol	13.8 %		traces
Hydroxycyclohexanone	24.4%	30.4 %	51.2 %

Aromaticity is easily lost.

Kinetic Model

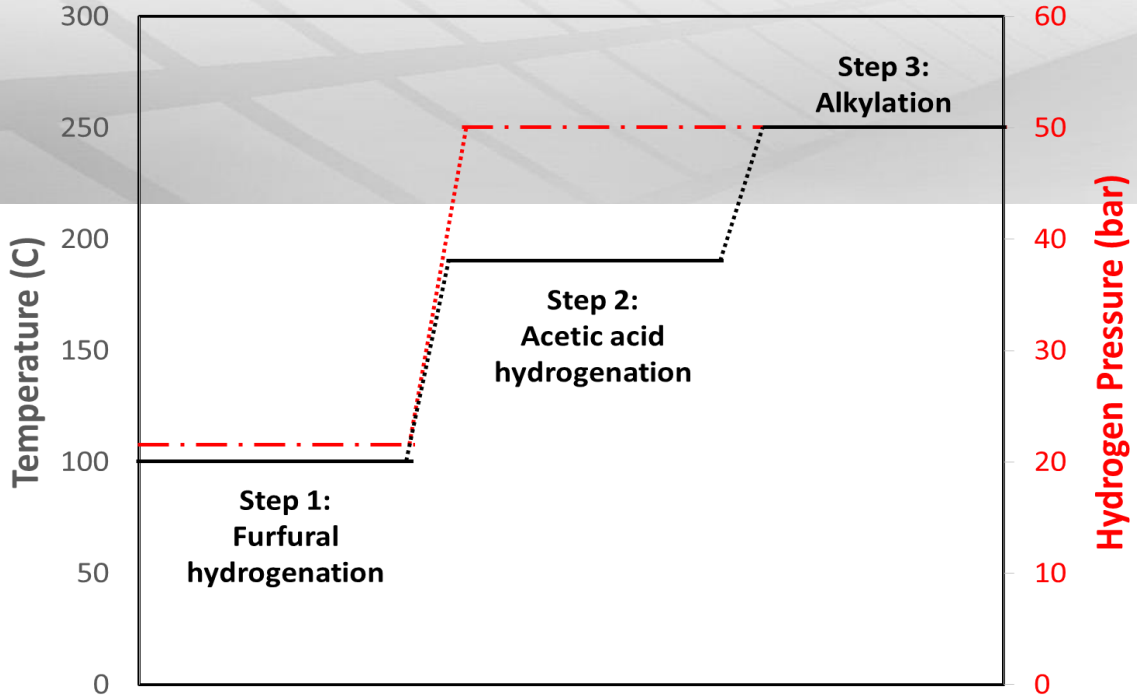




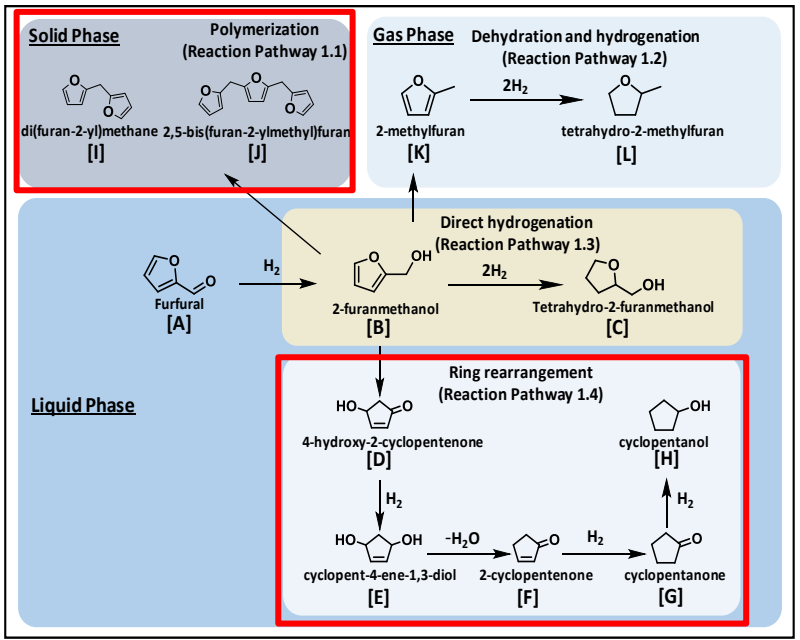
Reactions	1st order rate constant ($h^{-1} \cdot g^{-1}$) (at 523 K 50 bar H_2)
k_1 (C=C bond hydrogenation)	0.4- 223
k_2 (alkylation)	1.4×10^{-3} - 1.9×10^{-2}
k_3 (C=O hydrogenation)	1.9×10^{-2}- 0.3
k_4 (C-C bond cleavage)	3.6×10^{-3}- 0.7

1. Zhao, C., et al., *Comparison of kinetics, activity and stability of Ni/HZSM-5 and Ni/Al2O3-HZSM-5 for phenol hydrodeoxygenation.* Journal of Catalysis, 2012. **296**: p. 12-23.
2. He, J., C. Zhao, and J.A. Lercher, *Impact of solvent for individual steps of phenol hydrodeoxygenation with Pd/C and HZSM-5 as catalysts.* Journal of Catalysis, 2014. **309**: p. 362-375.

Temperature and Pressure Profile for Cascade Reaction



Step 1: furfural hydrogenation



Step 2: acetic acid hydrogentaion