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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This presentation does not contain any proprietary, confidential, or otherwise restricted information
Problem Statement

How can liquid transportation fuel from biomass be economically competitive?

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Contribution to TEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>▪ Reactor, heat exchanger (CAPEX); compressor (OPEX)</td>
</tr>
<tr>
<td>Catalyst</td>
<td>▪ Reactor (CAPEX); Material (OPEX)</td>
</tr>
<tr>
<td>Carbon yield</td>
<td>▪ Denominator in calculating MFSP! $\frac{\text{CAPEX} + \text{OPEX}}{\text{YIELD}}$</td>
</tr>
</tbody>
</table>

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 H₂ 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 H₂ 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

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

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

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

- **Rescope Project Flow**

  - **Bio-oil Production**
    - Task 1

  - **Corrosion Studies**
    - Task 6

  - **Preliminary Kinetic Information**
    - Tasks 2, 3, 4.1
    - 2014

  - **Bio-oil Fractions Testing**
    - Task 4.2

  - **Catalyst Optimization and Formulation**
    - Task 4.3

  - **Whole Bio-oil Testing**
    - Tasks 5.1, 5.2

  - **Refinery Insertion Studies**
    - Task 5.3

  - **TEA/LCA**
    - Task 7

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

Selectively hydrogenate 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

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

**TARGET:** Cascade reaction in one pot

Critical success factor:

\[ k_{\text{selective hydrogenation}} > k_{\text{alkylation}} > k_{\text{aromatic ring hydrogenation}} > k_{\text{dehydration}} \]
2 – Management Approach

► **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
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
Accomplishment:

- Identified a **threshold temperature** relationship with **activation energy**
- Informs temperature range for maximized conversion
3 – Selective Hydrogenation of Small Oxygenates (Acetic Acid)

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

**Condition:** 0.20 g 5.0 wt.% Ru/C, 100 cc 10 wt.% acetic acid, 50 bar H₂, 473 K

![Diagram of reaction pathway]

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

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

Is there potential for controlled molecular mass enhancement ($C_5 \rightarrow C_{10}$/diesel size)?
3 – Alkylation

**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

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**Catechol alkylation over MFI90**

- 250 °C
- 260 °C
- 270 °C
- 280 °C

**Cathecol alkylation in the presence of other compounds over MFI90**

- Furfuryl alcohol
- Levoglucosane
- Baseline

- 0.5 g catalyst, 1g catechol, 20 ml ethanol, 80 ml water, p (H₂) = 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

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rate [mol / g\text{Pd} s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 °C</td>
<td>6.48 x 10^{-3}</td>
</tr>
<tr>
<td>230 °C</td>
<td>2.34 x 10^{-3}</td>
</tr>
<tr>
<td>210 °C</td>
<td>7.32 x 10^{-4}</td>
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</table>

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rate [mol / g\text{Pd} s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 °C</td>
<td>5.45 x 10^{-4}</td>
</tr>
</tbody>
</table>
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-substituted 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

![Graphs showing conversion of 2-ethylcyclohexanol and 4-ethylcyclohexanol over time at different temperatures.](image-url)
Objective: Convert acetic acid and catechol to hydrocarbon at conditions based on kinetic studies.

Pd/C, 1wt % = 4771 / h

250 °C, 50 bar H₂

catechol

MFI90 = 0.2 / h
BEA75 = 0.84 / h

250 °C, 50 bar H₂

Rₙ-OH

Pd/C, 5wt % = 2.0 / h

250 °C, 50 bar H₂

acetic acid

Pd/C, 1wt % = 342 / h

250 °C, 50 bar H₂

carbonyl hydrogenation dehydration acid, H₂

OH

*MFI90 = 59.5 / h
250 °C
50 bar H₂

*MFI90 = 24.7 / h

OH
Preliminary one pot result

<table>
<thead>
<tr>
<th>PRODUCTS</th>
<th>YIELD [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CYCLOHEXANE</td>
<td>77.3</td>
</tr>
<tr>
<td>CYCLOHEXENE</td>
<td>6.0</td>
</tr>
<tr>
<td>CYCLOHEXANONE</td>
<td>1.4</td>
</tr>
<tr>
<td>DIRECT HYDROGENATED</td>
<td>84.7</td>
</tr>
<tr>
<td>METHYLCYCLOHEXANE</td>
<td>2.1</td>
</tr>
<tr>
<td>ETHYLCYCLOHEXANE</td>
<td>6.1</td>
</tr>
<tr>
<td>ALKYLATED HYDROGENATED</td>
<td>8.1</td>
</tr>
</tbody>
</table>

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

- 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.
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.

Possible application for fractionated pyrolysis oils.

The process still needs catalytic development and tuning with real bio-oil feeds and using continuous flow reactors.
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
- $k = \text{reaction rate} \left( \frac{1}{[\text{concentration}]^{\text{reaction order}} \cdot \text{hr}} \right)$
- TOF = Turn-over frequency (mol compound/mol active site/hr)
- CAN = Carboxylic acid number
- PhAN = Phenol acid number
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 track 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. It’s 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 identified as having value.
“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.
Production of liquid transportation fuel from biomass requires the process to be efficient and cost effective.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Change to $/gge from base case ($3.39/gge)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant Size, metric tons/day (4000 : 2000 : 1000)</td>
<td>-$0.50 to +$0.60</td>
</tr>
<tr>
<td>Internal Rate of Return, IRR (5% : 10% : 15%)</td>
<td>-$0.49 to +$0.50</td>
</tr>
<tr>
<td>Feedstock Cost, $/dry ton (60 : 80 : 120)</td>
<td>-$0.23 to +$0.29</td>
</tr>
<tr>
<td>Pyrolyzer Installed Cost (-40% : base : +40%)</td>
<td>-$0.30 to +$0.32</td>
</tr>
<tr>
<td>Hydrotreating Catalyst Life, yrs (2 : 1 : 0.5)</td>
<td>-$0.23 to +$0.32</td>
</tr>
<tr>
<td>FP yield + HT yield (64% FP + 46% HT: 62% FP + 44% HT: 60% FP + 42% HT)</td>
<td>-$0.29 to +$0.24</td>
</tr>
<tr>
<td>Pyrolysis System, tpd (1x2000 : 2x1000 : 5x4000)</td>
<td>-$0.14 to +$0.24</td>
</tr>
<tr>
<td>Hydrotreating yield, lb/lb pyrolysis oil (dry basis) (46% : 44% : 42%)</td>
<td>-$0.18 to +$0.17</td>
</tr>
<tr>
<td>Total Project Investment (-10% : base : +40%)</td>
<td>-$0.04 to +$0.17</td>
</tr>
<tr>
<td>HDO Reactors Capital (-40% : base : +40%)</td>
<td>-$0.11 to +$0.11</td>
</tr>
<tr>
<td>Stabilizer &amp; 1st HDO Stage Catalyst $/lb (30 : 60 : 90)</td>
<td>-$0.11 to +$0.11</td>
</tr>
<tr>
<td>Project Contingency (0% : 10% : 20%)</td>
<td>-$0.04 to +$0.07</td>
</tr>
<tr>
<td>2nd Stage HDO Reactor LHSV (0.4 : 0.22 : 0.1)</td>
<td>-$0.04 to +$0.12</td>
</tr>
<tr>
<td>Fast Pyrolysis yield, lb/lb wood (dry basis) (64% : 62% : 60%)</td>
<td>-$0.12 to +$0.07</td>
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<tr>
<td>1st and 2nd Stage HDO @ 1200 psia</td>
<td>-$0.12 to +$0.07</td>
</tr>
<tr>
<td>1st and 2nd Stage HDO @ 1600 psia</td>
<td>-$0.06 to +$0.08</td>
</tr>
<tr>
<td>Hydrogen Plant Installed Cost (-25% : base : +25%)</td>
<td>-$0.08 to +$0.08</td>
</tr>
<tr>
<td>Stabilizer Reactor LHSV (1 : 0.5 : 0.3)</td>
<td>-$0.05 to +$0.07</td>
</tr>
<tr>
<td>2nd HDO Stage Catalyst $/lb (10 : 15.5 : 30)</td>
<td>-$0.04 to +$0.09</td>
</tr>
<tr>
<td>Hydrocracker Size (None : base : 2x)</td>
<td>-$0.07 to +$0.04</td>
</tr>
<tr>
<td>Compressor Capital (-40% : base : 40%)</td>
<td>-$0.02 to +$0.02</td>
</tr>
</tbody>
</table>
Potential for MFSP Reduction

- **Best Case**
  - 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%

- **Target Case**
  - Pressure 50 bar reduced for 1st and 2nd HDO
  - Liquid yield increase, +3.7%
  - Temp < 250 °C for 1st and 2nd stage HDO
  - No stabilization bed
  - H2 consumption decreases, -9.1%
  - H2 consumption decreases, -4.5%

- If MFSP was $3/gge, this would be $0.30-$0.60/gal.
Experimental Set-up: UofT

Model compounds aqueous solution

\[ \text{Acetic acid} \quad \text{Furfural} \]

Home-made carbon supported transition metal nano-clusters

Fe  Ni  Ru  Pd  Pt

Parr reactor-high pressure batch reactor system

Gas inlet

Gas sampling port

Co-feed

Pressurized with H\(_2\)

Ice-water quench

Ethanol calibration curve

\[ y = 0.857x \]

\[ R^2 = 0.9957 \]

Adding internal standard

Ethyl acetate extraction

Off-line analysis

\( \text{GC} \)
Reactor Reproducibility Validation

Acetic acid hydrogenation

Furfural hydrogenation
Selective hydrogenation of acetic acid

Acetic acid + H₂ → H₂O
Acetaldehyde + H₂ → CH₄ (Methane)
Ethanol + H₂ → C₂H₆ (Ethane)

Hydrogenation (Transition metal clusters)
Fe, Ru, Ni, Pd, Pt on Carbon Supports

CH₃–C–OH + CH₃–C–OH → CH₃–C=O + OH

March 31, 2015
Acetic Acid Reaction Pathway

Condition: 0.20 g 5.0 wt.% Ru/C, 100 cc 10 wt.% acetic acid, 50 bar H₂, 473 K

1. C-OH activation
2. Direct C-H insertion
3. Undesired C-C cleavage

Product Selectivity

<table>
<thead>
<tr>
<th>Product</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>59%</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>7%</td>
</tr>
<tr>
<td>Ethane</td>
<td>12%</td>
</tr>
<tr>
<td>Methane</td>
<td>22%</td>
</tr>
</tbody>
</table>

Surface Mechanism

\[ r_{\text{CH}_3\text{COOH}} = k_{\text{CH}_3\text{COOH}} \frac{[\text{CH}_3\text{COOH} \ast \ast]}{[T]} \]

\[ \text{TOR}(_{\text{CH}_3\text{COOH}}) = \frac{r_{\text{CH}_3\text{COOH}}}{[T]} = \frac{k_{\text{CH}_3\text{COOH}}[\text{CH}_3\text{COOH}\ast\ast]}{[T]^2} \]

\[ \text{TOR}(_{\text{CH}_3\text{COOH}}) = \frac{r_{\text{CH}_3\text{COOH}}}{[T]} = \frac{k_{\text{CH}_3\text{COOH}} K_{\text{CH}_3\text{COOH}}[\text{CH}_3\text{COOH}]}{\left( \frac{K_{\text{CH}_3\text{COOH}} K_{\text{CH}_3\text{COOH}}[\text{CH}_3\text{COOH}]}{(K_{H_2}[H_2])^{0.5}} + \frac{K_{OH} K_{H_2}[H_2][O]}{(K_{H_2}[H_2])^{0.5}} \right)^2} \]

\[ [T] = (K_{H_2}[H_2])^{0.5} + \frac{K_{CH_3\text{COOH}} K_{CH_3\text{COOH}}[CH_3\text{COOH}]}{(K_{H_2}[H_2])^{0.5}} + K_{CH_3\text{COOH}}[CH_3\text{COOH}] + 1 + \frac{K_{OH} K_{H_2}[H_2][O]}{(K_{H_2}[H_2])^{0.5}} + K_{H_2}[H_2][O] \]

\[ [\ast] \]

\[ \text{Order}=1 \]

\[ 0.075 \text{ g Ru/C, 10 wt% acetic acid a.q., 473 K, 10-60 \text{ bar H}_2 \]

\[ T = \frac{r_{\text{CH}_3\text{COOH}}}{\text{TOR}(\text{CH}_3\text{COOH})} = \frac{k_{\text{CH}_3\text{COOH}} K_{\text{CH}_3\text{COOH}}[\text{CH}_3\text{COOH}]}{\left( \frac{K_{\text{CH}_3\text{COOH}} K_{\text{CH}_3\text{COOH}}[\text{CH}_3\text{COOH}]}{(K_{H_2}[H_2])^{0.5}} + \frac{K_{OH} K_{H_2}[H_2][O]}{(K_{H_2}[H_2])^{0.5}} \right)^2} \]

\[ [\ast] \]

Fate of Surface Acetyl

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

Direct C-H insertion

\[
r_{C_2} = TOR(CH_3COOH) k_c (K_{H_2}[H_2])^{0.5} + 2k_{CH_4}
\]

\[
H_2 \text{ order}= 1 - 1.5
\]

H_2 \text{ order}= 0.5 - 1

\[
r_{CH_4} = TOR(CH_3COOH) \frac{2k_{CH_4}}{k_c (K_{H_2}[H_2])^{0.5} + 2k_{CH_4}}
\]

Ethanol

Ethyl acetate

Ethane

CH_3

C=O

CH_4

Methane
BEP Relation and Periodic Trend

BEP Relation: \( \Delta E_a = \beta \Delta \Delta H \)

\( \Delta H = E(\text{Acetic acid, C-OH}) + Ad(\text{Acetyl*}) + Ad(\text{Hydroxyl*}) - Ad(\text{Acetic acid*}) \)

Carbon binding strength  Oxygen binding strength

Acetic acid turnover rate (h\(^{-1}\))

Acetic acid turnover rate (h\(^{-1}\))

Carbon binding strength (kJ / mol)

Metallic elements: Ru, Pt, Co, Pd, Ni, Fe

Temperature: 473 K
Stability of Zeolites

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

TOF [1/h] vs. Time [h]

- BEA75: $y = -0.0393x + 0.6699$
- MFI90: $y = -0.0022x + 0.2087$

MFI has more sustained performance
Kinetic data for alkylation over various types of zeolite at 250 °C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si / Al ratio</th>
<th>initial Rate $[\text{mol}<em>{\text{catechol}}/\text{g}</em>{\text{catalyst}} \cdot \text{h}]$</th>
<th>$K^*$ $[1 / \text{h g}_{\text{catalyst}}]$</th>
<th>TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-MFI</td>
<td>11.5</td>
<td>$1.3 \times 10^{-4}$</td>
<td>$1.4 \times 10^{-2}$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>$7.3 \times 10^{-5}$</td>
<td>$8.0 \times 10^{-3}$</td>
<td>0.20</td>
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<tr>
<td></td>
<td>110</td>
<td>$3.6 \times 10^{-5}$</td>
<td>$4.0 \times 10^{-3}$</td>
<td>0.29</td>
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<td>200</td>
<td>$1.3 \times 10^{-5}$</td>
<td>$1.4 \times 10^{-3}$</td>
<td>0.17</td>
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<tr>
<td>H-BEA</td>
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<td>$1.8 \times 10^{-1}$</td>
<td>1.21</td>
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<tr>
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<td>75</td>
<td>$1.7 \times 10^{-4}$</td>
<td>$1.9 \times 10^{-2}$</td>
<td>0.74</td>
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<tr>
<td>La-BEA</td>
<td>75</td>
<td>$1.1 \times 10^{-4}$</td>
<td>$1.2 \times 10^{-2}$</td>
<td>-</td>
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<tr>
<td>H-FAU</td>
<td>2.5</td>
<td>$1.2 \times 10^{-5}$</td>
<td>$1.3 \times 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>La-FAU</td>
<td>2.5</td>
<td>$1.3 \times 10^{-5}$</td>
<td>$1.4 \times 10^{-3}$</td>
<td>-</td>
</tr>
</tbody>
</table>
Alkylation of catechol with ethanol over MFI90 and BEA75

**Catechol alkylation over MFI90**

\[ y = 6.23x - 0.17 \]
\[ R^2 = 1.00 \]

\[ y = 2.86x - 0.04 \]
\[ R^2 = 1.00 \]

\[ y = 1.36x + 0.01 \]
\[ R^2 = 1.00 \]

\[ y = 0.39x + 0.03 \]
\[ R^2 = 0.99 \]

**Catechol conversion over BEA75**

\[ y = 0.8x + 0.7 \]
\[ R^2 = 1.0 \]

---

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

---

**Graphs showing data points and regression lines for conversion and reaction rate.**
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 $\approx 143 \text{ kJ/mol}$
- 2-ethylcyclohexanol $\approx 107 \text{ kJ/mol}$

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 H₂

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt/C, 10 wt %</th>
<th>Ru/C, 5 wt %</th>
<th>Pd/C, 10 wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass catalyst</td>
<td>0.3 g</td>
<td>0.1 g</td>
<td>0.3 g</td>
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<tr>
<td>Conversion Acetic acid</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
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<tr>
<td>Yield Ethanol</td>
<td>1.3 %</td>
<td>4.6 %</td>
<td>2.4 %</td>
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<tr>
<td>Yield Ethyl acetate</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Conversion catechol</td>
<td>99.8 %</td>
<td>93.2 %</td>
<td>97.7 %</td>
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</table>

Yields

<table>
<thead>
<tr>
<th>Product</th>
<th>Pt/C, 10 wt %</th>
<th>Ru/C, 5 wt %</th>
<th>Pd/C, 10 wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>-</td>
<td>28.4%</td>
<td>-</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>0.5 %</td>
<td>3.0 %</td>
<td>3.5 %</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>64.3 %</td>
<td>6.0 %</td>
<td>31.0 %</td>
</tr>
<tr>
<td>Cyclohexanediol</td>
<td>13.8 %</td>
<td>traces</td>
<td></td>
</tr>
<tr>
<td>Hydroxycyclohexanone</td>
<td>24.4%</td>
<td>30.4 %</td>
<td>51.2 %</td>
</tr>
</tbody>
</table>

Aromaticity is easily lost.
Reactions 1st order rate constant (h⁻¹·g⁻¹) (at 523 K 50 bar H₂)

k₁ (C=C bond hydrogenation) 0.4 - 223

k₂ (alkylation) 1.4 x 10⁻³ - 1.9 x 10⁻²

k₃ (C=O hydrogenation) 1.9 x 10⁻² - 0.3

k₄ (C-C bond cleavage) 3.6 x 10⁻³ - 0.7


Gas Phase

Liquid Phase

Solid Phase

Direct hydrogenation
(Reaction Pathway 1.3)

Dehydration and hydrogenation
(Reaction Pathway 1.2)

Polymerization
(Reaction Pathway 1.1)

Step 1: Furfural hydrogenation

Step 2: Acetic acid hydrogenation

Step 3: Alkylation

Temperature and Pressure Profile for Cascade Reaction

Temperature (°C)

Hydrogen Pressure (bar)

Di(furan-2-yl)methane 2,5-bis(furan-2-ylmethyl)furan

2-methylfuran

tetrahydro-2-methylfuran

Furfural

2-furanmethanol

tetrahydro-2-furanmethanol

4-hydroxy-2-cyclopentenone

cyclopentanol

cyclopentanone

cyclopent-4-ene-1,3-diol

2-cyclopentenone

Aqueous phase

Gas phase

Reactions:

Reaction 1:

Acetic acid

H₂ → H₂O

Acetaldehyde

H₂ ↔ Ethanol

Methane

Ethane

Step 1: furfural hydrogenation

Step 2: acetic acid hydrogenation

Step 3: alkylation