Aqueous-phase reforming – a pathway to chemicals and fuels

Laboratory of Industrial Chemistry and Reaction Engineering
Process Chemistry Centre
Åbo Akademi

POKE meeting, 14-th of August, 2014
Agenda

- Short Introduction, biomass, what is APR?
- Main tasks of the doctoral research
- Experimental methods
- Choice of catalytic systems
- Catalytic results
- Summary
Introduction - Biomass

Biomass

Biomass production 200 Gt/y
> 75 % of biomass carbohydrates

Fossil fuels extracted 7 Gt/y

huge potential in carbohydrates

Only ~ 4 % of annually produced biomass is used by man.
Rest decays and recycles natural pathways.

Carbohydrates $C_n(H_2O)_n$
hydrophilic
overfunctionalized with $OH^-$ groups

Hydrocarbons $C_nH_{2n+2}$
hydrophobic
lacking functional groups

→ due to different nature of carbohydrates compared to fossil resources,
different process technology is needed?
Catalytic transformation of biomass

Cellulose  Hemicellulose

Hydrolysis

Aldoses

Hydrogenation

Sugar alcohols

Oxidation

Sugar acids

Hydrolysis

Chemicals

Esterification

Lubricants

Aqueous reforming

Fuels

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Aqueous phase reforming (APR)

Biomass

Lignin

Cellulose

Hemicellulose

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RR=11/5
Aqueous phase reforming (APR)

Biomass

Lignin
Cellulose
Hemicellulose

6H₂ + 5CO

5CO + 5H₂O → 5H₂ + 5CO₂

C₅H₁₂O₅ + 6H₂O → 11H₂ + 5CO₂

RR=11/5

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The main tasks of the research

- Task 1. Investigation of reaction products and intermediates
- Task 2. Synthesis and characterization of catalysts
- Task 3. Catalyst stability studies
- Task 4. Investigation of reactant structure on process properties
- Task 5. Influence of a second metal (Re)
- Task 6. Modelling of reaction kinetics
Reaction conditions:
- 0.5 g of a catalyst
- 225°C
- 30 bar
- Carrier gas N₂ (30 ml/min)

✔ Continuous fixed-bed reactor
✔ 10 wt.% of xylitol used as a feed

Reagents in the liquid phase
Reactor’s scheme

H₂ (for reduction)

N₂ (1% He)

mass flow controller

catalyst

collector

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Volatile compounds were identified by means of Solid-phase microextraction (SPME) + GC-MS.

TOC – total organic carbon analysis
Mass balance – 95-100% (by carbon analysis)
Important parameters in APR

- Catalyst activity, stability and selectivity to H₂
- Product distribution between phases
- Ratio H₂/CO₂

Selectivity to H₂ (%) = \( \frac{v(H₂)}{v(C_{in\ gas})} \times 1 / RR \times 100\% \)

RR – reforming H₂/CO₂ ratio (11/5 for xylitol)
Choice of active metal and support

Based on catalytic activity in the APR of ethylene glycol

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>Pd</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Al$_2$O$_3$</th>
<th>TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>MgO</td>
<td></td>
</tr>
</tbody>
</table>
Choice of active metal and support

Based on catalytic activity in the APR of ethylene glycol

- C-C cleavage
- WGS activity

Pt/Al₂O₃, Pt/TiO₂, Pt/C and bimetallic catalyst PtRe/TiO₂
Catalyst showed stable performance within more than 120 h time on stream

<table>
<thead>
<tr>
<th>Time. h</th>
<th>CO₂[×10⁴]. mol</th>
<th>∑(X·CₓHᵧ)[×10⁵]. mol</th>
<th>∑CₓHᵧ/CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>1.7</td>
<td>6.9</td>
<td>0.4</td>
</tr>
<tr>
<td>123</td>
<td>1.6</td>
<td>6.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Distribution of carbon

benchmark catalyst – Pt/Al₂O₃

\[
\text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{APR} \quad \text{G} \\
\text{OH} \quad \text{OH} \quad \text{OH} \\
\]

\{ \text{H}_2, \text{CO}_2, \text{alkanes} \} \quad 100\%

\{ \text{Oxygenates} \}

\begin{align*}
\text{Carbon content, }% \\
\text{WHSV, h}^{-1}
\end{align*}

\text{Liquid}

\text{Gas}

\text{WHSV – weight hourly space velocity}
\text{g\text{sub}/g\text{cat}/hour [h}^{-1}\text{]}
Distribution of carbon

benchmark catalyst – Pt/Al₂O₃

\[
\text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{APR} \quad \text{G} \quad \text{H}_2, \text{CO}_2, \text{alkanes} \quad 100% \\
\text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{L} \quad \text{Oxygenates}
\]

Distribution of carbon content vs. WHSV (weight hourly space velocity) for various feedstocks and WHSV values. The graph shows the percentage of carbon content in the liquid and gas phases as WHSV varies. WHSV = \(\frac{g_{\text{subs}}}{g_{\text{cat}}/\text{hour}}\) [h⁻¹].

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Distribution of carbon

benchmark catalyst – Pt/Al₂O₃

\[ \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \rightarrow \quad \text{G} \]

\[ \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \rightarrow \quad \text{L} \quad \text{G} \quad \text{L} \quad \text{G} \quad \text{L} \]

- \text{G: } \text{H}_2, \text{CO}_2, \text{alkanes}
- \text{L: } \text{Oxygenates}

\[ \text{WHSV} \quad \text{weight hourly space velocity} \quad \text{g}_{\text{subs}}/\text{g}_{\text{cat}}/\text{hour} \quad [\text{h}^{-1}] \]

\[ \text{POKE meeting, 14-th of August, 2014} \]
Gas phase composition

Studied by micro-GC and GC-MS, benchmark catalyst – Pt/Al₂O₃
### Liquid phase

Studied by HPLC and SPME
benchmark catalyst – Pt/Al₂O₃

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂</td>
<td><img src="image1" alt="C₂ structure" /></td>
</tr>
<tr>
<td>C₃</td>
<td><img src="image2" alt="C₃ structure" /></td>
</tr>
<tr>
<td>C₄</td>
<td><img src="image3" alt="C₄ structure" /></td>
</tr>
<tr>
<td>C₅</td>
<td><img src="image4" alt="C₅ structure" /></td>
</tr>
<tr>
<td>C₆</td>
<td><img src="image5" alt="C₆ structure" /></td>
</tr>
<tr>
<td>Isoisorbid</td>
<td><img src="image6" alt="Isoisorbid structure" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbon in liquid. %</th>
<th>Alcohols</th>
<th>Diols</th>
<th>Triols</th>
<th>Ketons</th>
<th>Acids</th>
<th>Other</th>
<th>Total amount detected. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.4</td>
<td>17.3</td>
<td>49.9</td>
<td>4.2</td>
<td>5.0</td>
<td>4.9</td>
<td>18.7</td>
<td>90.6</td>
</tr>
</tbody>
</table>

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Higher selectivity to alkanes at lower space velocities

Yield of H$_2$, %

WHSV, h$^{-1}$

Reforming of xylitol

Reforming of sorbitol

Reforming of sorbitol

Reforming of xylitol

Higher yields of hydrogen for xylitol – substrate with shorter carbon chain

Conditions: 225°C, 30 atm., N$_2$ 30 ml/min, 10 wt.% solution, Pt/Al$_2$O$_3$
Influence of reactant structure

Higher yields of hydrogen for xylitol – substrate with shorter carbon chain

Higher selectivity to alkanes at lower space velocities

Conditions: 225°C, 30 atm., N₂ 30 ml/min, 10 wt.% solution, Pt/Al₂O₃
Influence of reactant structure

Higher yields of hydrogen for xylitol – substrate with shorter carbon chain

Conditions: 225°C, 30 atm., N₂ 30 ml/min, 10 wt.% solution, Pt/Al₂O₃

Higher selectivity to alkanes at lower space velocities
Catalysts

1. Effect of a second metal: series
   - Pt/TiO₂,
   - Pt-Re/TiO₂
   - Re/TiO₂

   Prepared by incipient wetness impregnation, from HReO₄ and or (NH₃)₄Pt(NO₃)₂

2. Effect of a support material and support structure

   one commercial Pt/C (Degussa) four prepared and characterized materials

   - 5% Pt/C (Degussa)
   - 2.5% Pt/TiC-CDC (CDC – carbide-derived carbon)
   - 5% Pt/Sibunit from (NH₃)₄ Pt (HCO₃)₂
   - 5% Pt/Sibunit H₂PtCl₆
   - 5% Pt/BAC (Birch active carbon)
Catalysts

1. Effect of a second metal: series
   - Pt/TiO$_2$
   - Pt-Re/TiO$_2$ ➢ *To enhance selectivity to hydrocarbons*
   - Re/TiO$_2$

2. Effect of a support material and support structure

one commercial Pt/C (Degussa) four prepared and characterized materials

- 5% Pt/C (Degussa)
- 2.5% Pt/TiC-CDC (CDC – carbide-derived carbon)
- 5% Pt/Sibunit from $(\text{NH}_3)_4 \text{Pt} (\text{HCO}_3)_2$
- 5% Pt/Sibunit H$_2$PtCl$_6$
- 5% Pt/BAC (Birch active carbon)
Higher yields of hydrogen for monometallic Pt catalyst

Higher selectivity to alkanes in the presence of bimetallic Pt-Re catalyst

Conditions: 225°C, 30 atm., N₂ 30 ml/min, 10 wt.% solution

In cooperation with prof. C. Hardacre from Queen’s University, Belfast
Example: APR of xylitol over Pt-Re/TiO$_2$

Higher yields of hydrogen for monometallic Pt catalyst

Slightly higher selectivity to alkanes in the presence of bimetallic Pt-Re catalyst

Conditions: 225°C, 30 atm., N$_2$ 30 ml/min, 10 wt.% solution

In cooperation with prof. C. Hardacre from Queen’s University, Belfast
Characterization

Transmission electron microscopy

Particle size distribution

~2 nm

Temperature programmed reduction (H₂)

Temperature programmed desorption (NH₃)

Particle size distribution

Pt/BAC

Concentration of NH₃, %

Temperature, K

Pt/BAC

Concentration of NH₃, %

Temperature, K

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Effect of acidity

![Graph showing the effect of acidity on the rate of alkanes formation and NH₃ desorption.]

- Supervised visiting PhD student Benjamine Hasse for 2 months

In cooperation with prof. B. Etzold from University of Erlangen-Nürnberg

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Effect of acidity

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Reaction pathways

Based on experimental data
Reaction pathways

Based on experimental data

▸ Pathway to hydrogen

Path 1:

- $\text{C}_6\text{O}_6\text{H}_{14}$
- $\text{H}_2$ → $\text{C}_6\text{O}_6\text{H}_{12}$
- $\text{CO}$ → $\text{C}_5\text{O}_5\text{H}_{12}$
- $\text{CO}_2 + \text{H}_2$
- $\text{C}_4\text{O}_4\text{H}_{10}$
- $\text{WGS} + \text{H}_2\text{O}$
- $\text{CO}_2 + \text{H}_2$

Path 2:

- $\text{C}_6\text{O}_5\text{H}_{12}$
- $\text{H}_2$ → $\text{C}_6\text{O}_5\text{H}_{14}$
- $\text{WGS} + \text{H}_2\text{O}$
- $\text{C}_5\text{O}_4\text{H}_{10}$
- $\text{CO}_2 + \text{H}_2$
- $\text{C}_4\text{O}_3\text{H}_{8}$
- $\text{H}_2$

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Reaction pathways

Based on experimental data

Pathway to hydrogen

Path 1:

\[ \text{C}_6\text{O}_6\text{H}_{14} \xrightarrow{-\text{H}_2} \text{C}_6\text{O}_6\text{H}_{12} \xrightarrow{-\text{H}_2} \text{C}_5\text{O}_5\text{H}_{10} \rightarrow \text{CO} + \text{H}_2 \]

Path 2:

\[ \text{C}_6\text{O}_5\text{H}_{12} \xrightarrow{-\text{H}_2} \text{C}_5\text{O}_4\text{H}_{10} \rightarrow \text{CO}_2 + \text{H}_2 \]

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Reaction pathways

Based on experimental data

Pathway to alkanes

**Path 1**

- **C₆O₆H₁₄** → **C₆O₆H₁₂** → **C₅O₅H₁₀** → CO + H₂O → CO₂ + H₂

**Path 2**

- **C₆O₅H₁₂** → **C₅O₄H₁₀** → **C₄O₃H₈**
  - WGS + H₂O → CO₂ + H₂
  - CO

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Reaction pathways

Based on experimental data

Pathway to alkanes

Path 1

$\text{C}_6\text{O}_6\text{H}_{14} \xrightarrow{-\text{H}_2} \text{C}_6\text{O}_6\text{H}_{12} \xrightarrow{\text{CO}} \text{C}_5\text{O}_5\text{H}_{12} \xrightarrow{-\text{H}_2} \text{C}_4\text{O}_4\text{H}_{10}$

Path 2

$\text{C}_6\text{O}_5\text{H}_{12} \xrightarrow{-\text{H}_2} \text{C}_5\text{O}_4\text{H}_{12} \xrightarrow{+\text{H}_2} \text{C}_4\text{O}_3\text{H}_{10}$

$\xrightarrow{\text{WGS} +\text{H}_2\text{O}} \text{CO}_2 + \text{H}_2$
Reaction pathways

Based on experimental data

➤ Pathway to hydrogen

Pathway to alkanes

Modelling of kinetics was performed at ÅA

Two main pathways are selected

Path 1:
- $\text{C}_6\text{O}_6\text{H}_{14}$
- $\text{C}_6\text{O}_6\text{H}_{12}$
- $\text{C}_5\text{O}_5\text{H}_{12}$
- $\text{C}_4\text{O}_4\text{H}_{10}$
- $\text{CO} + \text{H}_2\text{O}$
- $\text{WGS}$
- $\text{CO}_2 + \text{H}_2$

Path 2:
- $\text{C}_6\text{O}_6\text{H}_{14}$
- $\text{C}_6\text{O}_6\text{H}_{12}$
- $\text{C}_5\text{O}_5\text{H}_{10}$
- $\text{C}_4\text{O}_4\text{H}_{8}$
- $\text{CO}_2 + \text{H}_2$

$\text{H}_2$ and $\text{H}_2\text{O}$ are added or removed as indicated.
**Internal mass transport limitation (pore diffusion)**


Due to Weisz-Prater no pore diffusion limitation occurs, if Weisz modulus:

\[
\Phi = \frac{r_{obs} \cdot R^2}{c_s \cdot D_e}
\]

\(\Phi < 1\) first order reaction  
\(\Phi < 6\) zero-th order reaction  
\(\Phi < 0.3\) second order reaction

\[
\phi = R \cdot \sqrt{\frac{k \cdot c_s^{n-1}}{D_e}} \quad \rightarrow \quad \phi^2 \cdot \eta = \frac{r_{obs} \cdot R^2}{c_s \cdot D_e} = \Phi
\]
Weisz-Prater modulus

$$\Phi = \frac{r_{obs}R^2}{cD_{\text{eff}}}$$

Φ = maximal initial reaction rate
R = mean radius of the catalyst particle
c = substrate concentration.
In our case R = 1.25×10^{-4} m (125 µm)

effective diffusion coefficient (D_{\text{eff}}) of substrate
(sorbitol) in water

$$D_{\text{ef}} = D \frac{\xi}{\chi}$$

porosity (0.3-0.6)
tortuosity (2-5)

ϕ = 2.6 (water), M_B is molecular weight of solvent, η_B = 0.11888 cP is solvent
dynamic viscosity, T (K) = 498K, P=30 bar), V_{b(A)} = 122.15 cm^{3}×mol^{-1} is liquid molar
volume at solute’s normal boiling point.

Assuming \(\xi/\chi = 1/10\) the diffusion coefficient of sorbitol is calculated to be

$$D_{\text{ef}} = 1.18×10^{-9} \text{ m}^2/\text{s} \text{ (498 K and 30 bar).}$$

The concentration of the substrate in the solvent is equal to 0.515 mol×l^{-1}.

$$r_{\text{max}} = 1.93×10^{-4} \text{ mol}×\text{l}^{-1}×\text{s}^{-1} \text{ at 2.7 h}^{-1}$$

Φ=0.005 \rightarrow \text{substrate diffusion inside the catalyst pores does not affect the reaction rate}
Reaction pathways

\[ N^{(1)}: C_6O_6H_{14} = C_5O_5H_{12} + H_2 + CO \]

\[ N^{(2)}: C_5O_5H_{12} = C_4O_4H_{10} + H_2 + CO \]

\[ N^{(3)}: C_4O_4H_{10} = C_3O_3H_8 + H_2 + CO \]

\[ N^{(4)}: C_3O_3H_8 = C_2O_2H_6 + H_2 + CO \]

\[ N^{(5)}: CO + H_2O = CO_2 + H_2 \]

\[ N^{(6)}: C_4O_4H_{10} + 4H_2 = C_4H_{10} + 4H_2O \]

\[ N^{(7)}: C_3O_3H_8 + 3H_2 = C_3H_8 + 3H_2O \]

\[ N^{(8)}: C_2O_2H_6 + 2H_2 = C_2H_6 + 2H_2O \]
on metal sites:

\[ \theta_{C_6O_6H_{14}} = K_1 C_{C_6O_6H_{14}} \theta_V \quad \theta_{C_5O_5H_{12}} = K_3 C_{C_5O_5H_{12}} \theta_V \quad \text{and so on for each component} \]

on acid sites:

\[ \theta_{C_4O_4H_{10}}' = K_{12} C_{C_4O_4H_{10}} \theta_V' \]

Total coverage:

\[ \theta_V = \frac{1}{1 + K_1 C_{C_6O_6H_{14}} + K_3 C_{C_5O_5H_{12}} + K_5 C_{C_4O_4H_{10}} + K_7 C_{C_3O_3H_8} + K_9 C_{C_2O_2H_6} + K_{10} C_{H_2O}} \]

\[ \theta_V' = \frac{1}{1 + K_{12} C_{C_4O_4H_{10}} + K_{14} C_{C_3O_3H_8} + K_{16} C_{C_2O_2H_6}} \]

Rate for basic route 1:

\[ r^{(1)} = k_2 \theta_{C_6O_6H_{14}} = k_2 K_1 C_{C_6O_6H_{14}} \theta_V = \]

\[ = \frac{k_2 K_1 C_{C_6O_6H_{14}}}{1 + K_1 C_{C_6O_6H_{14}} + K_3 C_{C_5O_5H_{12}} + K_5 C_{C_4O_4H_{10}} + K_7 C_{C_3O_3H_8} + K_9 C_{C_2O_2H_6} + K_{10} C_{H_2O}} \]

Generation rate for compound: 

\[ - \frac{dC_{C_6O_6H_{14}}}{d\tau} = r^{(1)} \]
\[ r^{(1)} = k_2 \theta_{C_6O_6H_{14}} = k_2 K_1 C_{C_6O_6H_{14}} \theta_V = \]
\[ = \frac{k_2 K_1 C_{C_6O_6H_{14}}}{1 + K_1 C_{C_6O_6H_{14}} + K_3 C_{C_5O_5H_{12}} + K_5 C_{C_4O_4H_{10}} + K_7 C_{C_3O_3H_8} + K_9 C_{C_2O_2H_6} + K_{10} C_{H_2O}} \]

Simplification of the model because of overparametrization

\[ r^{(1)} = k_2' C_{C_6O_6H_{14}} \]
\[ \cdots \]
\[ r^{(9)} = k_1' C_{C_3O_3H_8} \]

\[ \frac{dC_{C_6O_6H_{14}}}{d\tau} = r^{(1)} + r^{(9)} \]

\[ \text{WHSV}h \]

D. Murzin & J. Wärnå
1. Aqueous-phase reforming of two most abundant polyols has been studied over stable catalysts

2. Effect of reactants structure on selectivity to main product formation reveals that higher selectivities to hydrogen can be achieved in APR of xylitol compared to sorbitol (up to 85%)

3. Addition of Re as a second metal component leads to enhanced alkane formation

4. Advanced reaction scheme was proposed on the basis of experimental data

5. For the first time reaction sensitivity in APR of xylitol was studied over Pt/C

6. The reaction kinetics was modeled based on kinetic data and mechanistic considerations for sorbitol transformation during APR.

✓ APR is a powerful method for hydrogen production from renewables
✓ Kinetic model proposed can be further developed and applied to description of APR data for other substrates as well as for APD/H process
Financial support

- Graduate School in Chemical Engineering (GSCE, 2010-2013)
- Fortum Foundation (2009-2011)
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- Haldor Topsøe Scholarship Programme (2010-2012)
- COST–Action CM0903 (UbioChem, 2010-2013)
Alexey Kirilin

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