Catalytic conversion of bio-sourced raw materials: homogeneous catalysis

Francois Jérôme

Castro, September 23rd 2011
Speaker: François Jérôme (Laboratoire de Catalyse en Chimie Organique)
LOCATION

Poitiers
Laboratoire de Catalyse en Chimie Organique

Director : Jean-Michel Léger

- Metal
  F. ERON
- Zeolites
  Y. POUILLOUX
- Catalysis and renewable carbon
  J. M. TATIBOUET
- Theoretical Chemistry
  G. FRAPPER
- Fluoration and hydrotreatment
  S. BRUNET
- Electrocatalysis
  B. KOHKOH
Group catalysis and renewable carbon

- Biomass, biogas, CO$_2$ and co-products
- Catalysis (heterogeneous/homogeneous)
- Plasma, microwaves, biphasic catalysis
- Stability of catalysts
- Selectivity
- Energiesaving
- Work-up procedure
- Biomass origin and purity
- Eco-efficient processes
- Atom economy

LACCO
Laboratoire de Catalyse en Chimie Organique
General context

Catalysis and lignocellulose
  - Fractionation process
  - Pre-treatment of cellulose - impact on the catalyst activity
  - Synergistic effect between homogeneous and heterogeneous catalysts

Catalysis and glycerol
  - Telomerization of glycerol
  - Etherification of glycerol

Renewably-sourced solvent for the recycling homogeneous catalysts
General context

Fossil reserves

85-90 %  10-15 %

ENERGY  Fine chemicals
General context

- Decrease of the fossil reserves
- Continual increasing of the fossil carbon consumption
- Environmental problems

- Increase of the barrel price
- Increase of greenhouse gases
Green chemistry

GREEN CHEMISTRY

(aim: design of products and processes that minimize the use and generation of hazardous substances)

12 principles of Green Chemistry
1. Prevention
2. Atom Economy
3. Less Hazardous Chemical Syntheses
4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis
10. Design for Degradation
11. Real-time analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention

In 2020: Green chemical industry is expected to soar to 98.5 billions dollars

Catalysis: 13 billion dollars

Biomass

Biomass production: 180 billions t/year

- Cellulose (45%)
- Lignin (20%)
- Hemicellulose, other polysaccharides (30%)
- Vegetable oils, Proteins, nucleic acids, etc… (5%)

Transportation fuels (ethanol, hydrocarbons, etc…)

Fine chemicals
Biomass and catalysis

**BIOMASS** → **Heterogeneous catalysis** → **BIOPRODUCTS**

- Pre-treatment of biomass
- Production of chemicals
- Combination homogeneous/heterogeneous catalysis
- Catalysis in a biphasic system
- Recycling

**HOMOGENEOUS CATALYSIS** (2008-2011)
HOMOGENEOUS CATALYSIS AND LIGNOCELLULOSE
Lignocellulose

Production: 170 billions t/year

Common processes: alkaline solution, ammonia, bisulfite, ozonolysis, acid treatment

Lecture Anna Raspoli, CIRCC
Homogeneously-catalyzed fractionation of lignocellulose

Reproduced with permission of Prof. Leitner

vom Stein T., Grande P.M., Kayser H., Sibilla F., Leitner W., Dominguez de Maria P. Green Chem., 2011, 13, 1772-1777
Valuability of chemicals

**Lignocellulose**

- **Phenolic compounds**
- **lignin**
- **Water-soluble sugars**
  - Xylose
    - (mannose, galactose, rhamnose, arabinose, glucose, among others)
  - **Energy**
- **Cellulose**
  - Microcrystalline cellulose
    - DP = 200
  - α-cellulose
    - DP = 1000
  - **Chemical platforms**
  - Glucose
Cellulose: a recalcitrant biopolymer

- Decrystallization Process
- Amorphous Cellulose
- Catalysis
  - Low Selectivity (severe conditions of temperature and pressure)
  - High Selectivity
Pre-treatment of cellulose

Decrystallization process

- Ball-milling
  - High energy input
- Ionic liquid
  - Toxic/expensive
- Acid solution
  - Environmental problems
- Basic solution

Non thermal atmospheric plasma

Combination homogeneous/heterogeneous catalysis
Non thermal atmospheric plasma

Radical, ions, excited species

Air depolution  Surface treatment

CELLULOSE?

Advantages
Low electricity consumption (mA)
Low energy input
No solvent/no catalyst
Non thermal atmospheric plasma

Microcrystalline cellulose
PH AVICEL 105 DP = 200
I_{index} = 78%

11kV, 2KHz, 3h
Power = 26 W

DP = 120
Increase of the crystallinity
I_{index} = 81%
Slight oxidation
-CHO: 0.6 mmol/g
-CO_{2}H: 0.5 mmol/g
Catalytic hydrolysis of cellulose treated by plasma

Pre-treatment | Yield of glucose (%) |
--- | --- |
- | < 1 |
[BMIM]Cl | 14 |
[BMIM]Et₂PO₄ | 9 |
[BMIM]OAc | 3 |
Ball-milling | 13 |
Plasma | 22 |
Plasma* with HCl | 25*

* with HCl

Selectivity of the reaction

- Levulinic acid (yield = 2.5 wt%)
- Water soluble carbohydrates (here mostly glucose) (yield = 22 wt%)
- HMF (yield = 1 wt%)
Transposition to other polysaccharides

<table>
<thead>
<tr>
<th>Polysaccharides</th>
<th>DP before Plasma</th>
<th>DP after Plasma</th>
<th>Yield of glucose (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH AVICEL 105</td>
<td>200</td>
<td>120</td>
<td>22</td>
</tr>
<tr>
<td>α-cellulose</td>
<td>1000</td>
<td>150</td>
<td>22</td>
</tr>
<tr>
<td>starch</td>
<td>&gt; 10000</td>
<td>&lt; 20</td>
<td>84</td>
</tr>
<tr>
<td>inulin</td>
<td>46</td>
<td>&lt; 6</td>
<td>16*</td>
</tr>
</tbody>
</table>

* fructose

Starch (a) before and (b) after plasma treatment

Size Exclusion Chromatography of inulin during the plasma treatment
Combination homogeneous/heterogeneous catalysis

\[ \text{cellulose} \rightarrow \text{glucose} \]

\[ \text{H}_3\text{PW}_{12}\text{O}_{40} \text{ in water, 2h, 180°C, HPA/cellulose = 0.42} \]


Homogeneous/heterogeneous catalyst
One pot process

Combination homogeneous/heterogeneous catalysis

Homogeneous catalysis

Low pH

Acid-catalyzed degradation

Heterogeneous catalysis

High content of Ru

C-C bond cracking

Efficiency = balance between acid and redox properties of the catalytic system

Combination homogeneous/heterogeneous catalysis

Homogeneous catalysis

Ball-milled cellulose

$\text{cellulose} \rightarrow \text{HPA} = \text{H}_3\text{PW}_{12}\text{O}_{40} \text{ or H}_4\text{SiW}_{12}\text{O}_{40}$

Ru/C (25 wt%), 190°C, 50 bar H$_2$

HEXITOL

Quantitative yield
60% yield
82% conversion of cellulose

Recovery by recrystallization → recycling

Heterogeneous catalysis

$\text{Cs-HPA} = \text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40} \text{ or Cs}_{3.5}\text{H}_{0.5}\text{SiW}_{12}\text{O}_{40}$

Ru/C (25 wt%), 190°C, 90 bar H$_2$

Hexitol

Side products stemming from C-C bond cracking

Integrated process
HOMOGENEOUS CATALYSIS AND VEGETABLE OILS
Vegetable oils

Less than 5% of the annual production of biomass

Fatty derivatives

Similar structure

hydrocarbon
Homogeneous catalysis and vegetable oils

\[
\text{triglyceride} \rightarrow \text{Glycerol} \downarrow \text{surfactant} \rightarrow \text{Fatty acid or esters}
\]

\[R = -\text{H or } -\text{OCH}_3\]

Mixture: C8-22:0-3

Lecture Eva Garrier, NOVANCE

Homogeneous catalysis and vegetable oils

**Surfactants**
10 millions t/year
Market estimated to 19 billions $

Non-ionic surfactants
Mostly based on ethylene oxide

Instable in water

**Glycerol as a renewably-sourced polyol**

Stable in water

**monoglycerides**

**Ethers of glycerol**
**Telomerization**

\[
\text{HO-CH}_2-\text{CH(OH) + 2 } \text{CH}_2=\text{CH}_2 \rightarrow \text{HO-CH}_2-O-\text{CH(OH)CH}_2-\text{CH(OH)CH}_2-\text{CH(OH)CH}_2-\text{CH(OH)}
\]

*Homogeneous palladium-based complexes*  
*Mixture of isomer (linear and branch)*

Catalytic cycle

Telomerization of glycerol with butadiene

58% yield

Low solubility of monomers in the aqueous phase

Easy recovery

High selectivity

Recycling of Pd(OAc)₂/TPPTS

Leaching of Pd=73ppm

Telomerization of glycerol with butadiene

\[
\text{HO-CH(OH)OH + 2 } \text{CH=CH}_2 \rightarrow \text{Pd(OAc)}_2 / \text{Ligand} \rightarrow \text{HO-CH(OH)O-CH=CH}_{n-1} \text{CH=CH}_2
\]

*Mixture of isomer (linear and branch)*

**TOF = 3418 h}^{-1}\)**
Yield of glycerol telomers: 92%
Yield monotelomer = 40%
Possible utilization of glycerin

**TOF = 260 h}^{-1}\)**
Yield monotelomer = 58%

**Palladium stabilized: 230h without appreciable loss of activity**

Etherification of glycerol with fatty alcohols

1) Glycerol and fatty alcohol are not miscible
2) Glycerol and fatty alcohol can be oligomerized or dimerized
Etherification of glycerol with fatty alcohols

Dodecylbenzene sulfonic acid: a surfactant-combined-catalyst

\[
\begin{align*}
\text{HO}_3\text{S} \quad \text{HO} \quad \text{HO} \\
\text{HO}_3\text{S} \quad \text{HO} \quad \text{HO}
\end{align*}
\]

Catalyst: A70, DBSA

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conv. gly</th>
<th>Conv. dode</th>
<th>Monoether</th>
<th>Diglycerol</th>
<th>Didodecylether</th>
</tr>
</thead>
<tbody>
<tr>
<td>A70</td>
<td>36%</td>
<td>5%</td>
<td>5%</td>
<td>22%</td>
<td>0%</td>
</tr>
<tr>
<td>DBSA</td>
<td>59%</td>
<td>50%</td>
<td><strong>25%</strong></td>
<td>9%</td>
<td>19%</td>
</tr>
</tbody>
</table>

Reaction conditions: 130°C / 24h, glycerol/dodecanol = 4

**Etherification of glycerol with fatty alcohols**

\[
\begin{align*}
\text{Glycerol} & \quad 130^\circ\text{C}, 24\text{h}, \text{CTAB} \\
\text{Glycerol/dodecanol} & = 4
\end{align*}
\]

**Bromination reaction**

- \(\text{H}_2\text{O}\)
- \(\text{Br}^{10}\text{mol}\%\)
- \(\text{HBr}\)

**Williamson’s reaction**

- Conv. dodecanol: 80%
- Yield monoglycerylethers: 50%
- Yield diglycerylethers: 10%
- Yield didodecylethers: 10%
NEW GENERATION OF BIO-BASED SOLVENTS FOR THE RECYCLING HOMOGENEOUS CATALYST
Green solvents

- Availability
- Flammability
- Eco-toxicity
- Recyclability
- Price
- Biodegradability

Green solvents

- Ionic liquids
- Switchable solvents
- Water
- PEG
- Supercritical fluids
- Renewably sourced solvents

P. G. Jessop, Green Chem. 2011, 13, 1391
**Glycerol**

- Available in large scale (≈ 2Mt/year)
- Renewable
- Cheap (<0.5€/Kg)
- Non-toxic
  - LD50 (oral rat) = 12600 mg/Kg
- Non-flammable

**Reactivity**

**Mass transfer**

**Work-up**
- Boiling point = 290°C

# Reactivity of glycerol

$$\text{O}_9 + \text{HO}_10 \xrightarrow{110^\circ C / \text{basic catalyst}} \text{O}_9 \xrightarrow{\text{+ regioisomer}}$$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Yield of ester (%)</th>
<th>Yield of ether (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>18</td>
<td>30</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Chitosane (c)</td>
<td>18</td>
<td>98</td>
<td>54</td>
<td>15</td>
</tr>
<tr>
<td>ZnO</td>
<td>18</td>
<td>80</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>18</td>
<td>70</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>SiO$_2$-NHMe</td>
<td>18</td>
<td>98</td>
<td>80</td>
<td>15</td>
</tr>
</tbody>
</table>

---


Confidential 39
**Emulsion**

Organic phase

Hydrophobic environment

Catalytic sites

Surfactant
Surfactant-Combined-Catalyst

Hydroxyethylcellulose (MS = 2.5)
R₁ = -(CH₂CH₂O)ₙH

MeOH/H₂O (80/20), fatty amine
Pd/C, H₂ (10bar), 25°C, 15h

30 µm
## Catalytic activity

\[ \text{O}_9 + \text{HO}_{10} \xrightarrow{110^\circ C / \text{basic catalyst}} \text{CO}_{10} \text{OH} \]

+ regioisomer

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
<th>Ester</th>
<th>Ether of glycérol</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(_2)CO(_3)</td>
<td>18</td>
<td>70</td>
<td>60</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>AP</td>
<td>3</td>
<td>98</td>
<td>95</td>
<td>Trace</td>
<td></td>
</tr>
</tbody>
</table>

**Work-up**

- **Instable emulsion** → **Easy purification**
  - Glycerol
  - Water

- **Stable emulsion** → **Complex purification**

**Selective extraction with scCO₂**

Solubility of glycerol in scCO₂ = 0.06 g/L
(vs 2.40 g/L for water)

*Green Chem. 2010, 5, 804*
Recycling of homogeneous catalysts in glycerol

β,β-diylation of acrylate over palladium nanoparticles

*Green Chem. 2010, 5, 804*

Catalytic synthesis of bio-based fungicides (1Kg scale)

PCT/FR2010/052867

Glycerol: an attractive solvent for carbohydrates

Zhao, H., Holladay, J. E., Brown, H. and Zhang, Z. C., Science, 2007, 316, 1597-1600

Ionic liquid, CrCl₂

Fructose → Levulinic acid

H⁺ / -H₂O

Ionic liquid

5-hydroxymethylfurfural (HMF)

Polymers, fuels, solvents, etc...

Ionic liquids: Advantages: high yield, easy isolation of HMF

Drawbacks: toxicity and price

GREENER SOLVENT?
Glycerol: as a renewably sourced co-solvent

1) 50mol % of [BMIM]Cl can be substituted by glycerol
2) Continuous extraction of HMF with MIBK
3) Isolated yield > 70%, purity 95%
Green solvents

Oxidation of carbohydrates

Waste of sugar beet industry

CATALYSTS


K. De Oliveira Vigier, A. Benguerba, J. Barrault, F. Jerome, manuscript in preparation

BIOMASS

DEEP EUTECTIC SOLVENT « biocompatible ionic liquids »

Yield up to 84%

1 Recovery by liquid-liquid extraction
2 Recyclable media

SAFE DERIVATIVES
Conclusion

**BIOMASS**

1. **HOMOGENEOUS CATALYSIS**
   - Fractionation of biomass
   - Production of fine chemicals (glucose, HMF, surfactant, etc...)

2. **HETEROGENEOUS CATALYSIS**
   - Recycling in a biphasic system
   - High selectivity/eco-efficient processes

**Green solvents** (glycerol, DES, H₂O)