Green hydrogen production – An investigation of autothermal reforming of native rapeseed oil

S. Martin, O. Jovalekic, J. Bürkle, A. Wörner

German Aerospace Center (DLR)
Institute of Technical Thermodynamics
Research Group „Alternative Fuels“
Table of Contents

- Towards a future hydrogen economy
- Reforming of liquid biofuels as an alternative option for green hydrogen production
- Biofuel consumption in Germany
- Rapeseed oil: Properties, Chemical structure
- Simulation results: Reformate gas composition, H₂-Efficiency, Coking tendency
- Experimental results: Variation of S/C, λ and GHSV
- Conclusion
Towards a future hydrogen economy

Requirements of a future hydrogen economy: Sustainability, EU long term commitment (2050): Reduction of emissions by 80-95 %, Low production costs, Simple production process, Availability of feedstock, Avoid food-fuel competition, Consider ecological impacts

A) Biomass

Biological or thermochemical conversion

B) Renewable Energy

Electrolysis of water

H₂
Thermochemical Conversion of Biomass

Solids (coal, wood, straw etc.)
- Pyrolysis ($\lambda = 0$)
  - partial Oxidation ($O_2/\text{Air}$)
  - autothermal g. ($H_2O, O_2/\text{Air}$)
  - steam gasification ($H_2O$)
  - Rawgas cleaning (dust removal, removal of tars)
  - Energetic use, Agricultural use

Gases/Liquids (natural gas, biodiesel, vegetable oil etc.)
- Gasification ($0 < \lambda < 1$)
  - partial Oxidation ($O_2/\text{Air}$)
  - autothermal r. ($H_2O, O_2/\text{Air}$)
  - steam reforming ($H_2O$)

Hydrogen rich product gas ($H_2, CO, CO_2, CH_4, H_2O, N_2 + \text{Impurities}$)
- Fine cleaning (CO-cleaning, sulphur removal, tar removal etc.)
  - CHP (Power, Heat)
  - Synthetic fuels and chemicals (BtL, Methanol, DME, SNG, NH$_3$)
  - Hydrogen cleaning (Pure hydrogen)
  - Fuel cell application (Power, Heat)
Biofuels in Germany (2010)

available biofuels on the market:

- **Vegetable oil**
- **Biodiesel**
- **Bioethanol**

1. Generation Biofuels

not available on the market:

- **Synthetic Biofuels (BtL, MtS etc.)**
- **Cellulosic Ethanol**
- **Bio SNG**

2. Generation Biofuels

Vegetable Oil as a promising option for green hydrogen production
Vegetable Oil

- Dominating vegetable oil in Europe and Germany: **Rapeseed oil**
- Area under cultivation in Germany (2010): 1.5 Mio ha
- Oil yield / hectare: ~1500 l/(ha a) → 2 Mio tons rapeseed oil
- High volumetric and gravimetric density (comparable to fossil fuels)
- Simple production process
- Low sulphur content

<table>
<thead>
<tr>
<th>Fatty Acid (R)</th>
<th>Total formula (Number of carbon atoms: double bonds)</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic Acid</td>
<td>(C_{18}H_{34}O_2) (18:1)</td>
<td>51-70%</td>
</tr>
<tr>
<td>Linolic Acid</td>
<td>(C_{18}H_{32}O_2) (18:2)</td>
<td>15-30%</td>
</tr>
<tr>
<td>Linolenic Acid</td>
<td>(C_{18}H_{30}O_2) (18:3)</td>
<td>5-14%</td>
</tr>
</tbody>
</table>

→ Chemical formula: \(C_{56.9}H_{101.8}O_6\)
→ Model Substance Trioleate: \(C_{57}H_{104}O_6\) (R=Oleic Acid)
ATR of Rapeseed Oil – Chemical Reaction System

Steam reforming reaction

\[ C_{57}H_{104}O_6 + 51 \text{ H}_2\text{O} \rightarrow 57 \text{ CO} + 103 \text{ H}_2 \quad \Delta H_{700^\circ C} = 8337 \text{ kJ/mol} \]

Partial oxidation reaction

\[ C_{57}H_{104}O_6 + 25.5 \text{ H}_2\text{O} \rightarrow 57 \text{ CO} + 52 \text{ H}_2 \quad \Delta H_{700^\circ C} = -4296 \text{ kJ/mol} \]

Total oxidation reaction

\[ C_{57}H_{104}O_6 + 80 \text{ H}_2\text{O} \rightarrow 57 \text{ CO}_2 + 52 \text{ H}_2\text{O} \quad \Delta H_{700^\circ C} = -33294 \text{ kJ/mol} \]

Methanation reaction

\[ \text{CO} + 3 \text{ H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H_{700^\circ C} = -165 \text{ kJ/mol} \]

Water gas shift reaction

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \quad \Delta H_{700^\circ C} = -125 \text{ kJ/mol} \]
Simulation of ATR with Aspen Plus®

- Aspen Plus Flowsheet of autothermal rapeseed oil reforming

**Fuel Supply**
- rapessed oil
- steam
- synthetic air

**ATR Reactor**
- chemical Equilibrium using „Gibbs“-Reactor

**Condensation of Liquids**
- water and organic phase
Experimental Test Setup
Experimental Test Setup

**Fuel Supply:**
- rapeseed oil (~10-30 g/h)
- steam (~30-200 g/h)
- synthetic air (0-1 l/min)

**Gas cleaning**
- condensation of water and organic phase
- aerosol filter
- activated charcoal trap

**Gas Analysis:**
- online measurement of H₂, CO, CO₂, CH₄
- + dry reformate gas volume flow

**ATR glas reactor:**
- equipped with zylindric honeycomb
- precious catalyst (Pt, Rh)
- P =1,2 bar
- T = 500 - 800 °C
Process variables and evaluation

- **Steam to carbon ratio**
  \[ \frac{S}{C} = \frac{\dot{n}_{H_2O}}{\dot{n}_{C,\text{rapeseedoil}}} \]

- **Air ratio**
  \[ \lambda = \frac{\dot{n}_{O_2}}{\dot{n}_{O_{2,\text{stochiometric}}} \dot{V}_{\text{reactor}}} \]

- **Gas Hourly Space Velocity**
  \[ \text{GHSV} = \frac{\dot{V}_{\text{feed}}}{\dot{V}_{\text{reactor}}} \]

- **Energetic H₂-efficiency**
  \[ \eta_t = \frac{\dot{m}_{H_2}(t) \cdot H_{u,H_2}}{\dot{m}_{\text{rapeseedoil}} \cdot H_{u,\text{rapeseedoil}}} \]

- **Mass balance**
  \[ \dot{m}_{C_{55}H_{100}O_6} + \dot{m}_{H_2O} + \dot{m}_{\text{Air}} = \dot{m}_{\text{reformate}} + \dot{m}_{\text{condensate,organic}} + \dot{m}_{\text{condensate,H_2O}} \]

- **Feed Conversion**
  \[ FC = 1 - \frac{\dot{m}_{\text{cond,organic}}}{\dot{m}_{\text{rapeseedoil}}} \]

- **Deactivation**
  \[ D = 1 - \frac{\eta_t}{\eta_0} \]
Simulation with Aspen Plus®

Dry reformate gas composition (ATR Trioleate, S/C=3)
Simulation with Aspen Plus® II

Comparison between calculated and measured **dry product gas composition** (nitrogen free basis, S/C=3)

![Graph showing comparison between calculated and measured dry product gas composition](image)

- H2 exp
- CO exp
- CO2 exp
- CH4 exp
- H2 calc
- CO calc
- CO2 calc
- CH4 calc
- T calc
Simulation with Aspen Plus® III

Energetic efficiency $\eta_{H2}$ (ATR Trioleate, S/C: 1…6, $\lambda$: 0…1)

- Optimum curve for $\lambda$ (at constant S/C)
- $\eta_{H2}$-maximum: 85% at $\lambda=0.175$
- Increasing $\eta_{H2}$ with increasing S/C-ratio (at constant $\lambda$)

Practical experience: Kinetic limitations, catalyst deactivation, incomplete fuel conversion
Simulation with Aspen Plus® IV

- **Coking boundaries** (ATR Trioleate, S/C: 0…2, \(\lambda\): 0…0,3)

  - Calculation of coking boundaries using Gibbs Minimization method
  - Consideration of solid carbon (graphite) as possible product

  High coking rates at low S/C and low \(\lambda\)

  Practical experience: Coking also occurs at higher S/C and \(\lambda\) (high temperatures)
Experimental Results

- **Reformate gas composition** (S/C=3, λ=0.15)

- H₂-concentration at t=0 lower than expected, decreasing continuously
- Catalyst deactivation with time → decrease of reformate volume flow, increase of product gas temperature
- H₂- and CO-concentration correlate
Experimental Results II

**Variation of S/C (λ=0.25)**

- Optimum curve (maximum at S/C = 3)
- Measured efficiency $\eta_0$ lower than thermodynamic value
- Temperature lower than expected
Experimental Results II

**Variation of S/C (λ=0.20)**

- **Findings "Variation of S/C":**
  - Optimum curves (maximum at S/C = 3)
  - S/C > 3: decrease of \( \eta_0 \) ↔ thermodynamics: Higher \( \eta_0 \) at higher S/C
  - S/C > 3: Temperature increase ↔ thermodynamics: Decrease of T with increasing S/C

**Hypothesis:** Kinetic Limitations → lower H\(_2\) yield, less energy needed for reforming reactions → increase of temperature
Experimental Results III

 Variation of Air Ratio $\lambda$ ($S/C=3$)

- Optimum curve (maximum at $\lambda = 0.15$)
- Efficiency $\eta_0$ lower than thermodynamically predicted
- Temperature lower than expected
Experimental Results III

Variation of Air Ratio $\lambda$ ($S/C=4$)

Findings „Variation of $\lambda$“:

- Optimum curves (maximum at $\lambda = 0.15/0.2$)
- Trend of $\eta_0$ and $T$ is similar to thermodynamic predictions
- Calculated efficiency significantly lower than measured efficiency

Catalyst deactivation, incomplete fuel conversion…
Experimental Results IV

Variation of GHSV (S/C=3, \(\lambda=0.15\))

- Optimum curve (maximum at GHSV = \(1.02 \times 10^5\) 1/h)
- Lower GHSV: Effect of heat losses and coke formation
- Higher GHSV: Kinetic limitations due to reduced reaction time
Experimental Results V

- **Mass balance and Conversion rates** (Feed Conversion FC and Carbon Conversion CC)

\[
FC = 1 - \frac{\dot{m}_{\text{cond,organic}}}{\dot{m}_{\text{rapeseedoil}}}
\]

\[
CC = 1 - \frac{\dot{m}_{\text{C, reformate}}}{\dot{m}_{\text{C, rapeseedoil}}}
\]

<table>
<thead>
<tr>
<th>S/C (-)</th>
<th>λ (-)</th>
<th>mass balance inaccuracy (%)</th>
<th>FC (%)</th>
<th>CC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0,1</td>
<td>15,3</td>
<td>88</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>0,15</td>
<td>17,5</td>
<td>83</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>0,2</td>
<td>27,4</td>
<td>93</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>0,25</td>
<td>19,7</td>
<td>89</td>
<td>56</td>
</tr>
<tr>
<td>4</td>
<td>0,15</td>
<td>22</td>
<td>83</td>
<td>26</td>
</tr>
<tr>
<td>4</td>
<td>0,2</td>
<td>25,8</td>
<td>87</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>0,25</td>
<td>9,3</td>
<td>97</td>
<td>55</td>
</tr>
</tbody>
</table>

- Carbon conversion (CC) significantly lower than Fuel Conversion (FC)
  
  Coke deposition on catalyst and inside tubings + formation of higher HCs?
Catalyst deactivation

- Deactivation Minimum at $\lambda_{\text{opt}} = 0.15$
- Continuous decrease of C- and S-deposition with increasing $\lambda$

Further deactivation mechanisms!
Summary

Alternative option for „green“ hydrogen production: Reforming of liquid biofuels

Rapeseed oil especially advantageous from an ecological and economical point of view

S. Martin et al. (2011): 6-8 % of the actual fuel consumption could theoretically be covered by hydrogen from rapeseed oil in Germany in the year 2020

Simulation results with Aspen Plus: Process efficiency of higher than 80 % can be achieved

Experiments proved feasibility of hydrogen production from rapeseed oil

Influence of S/C, λ and GHSV was investigated in detail. → Efficiency is significantly lower that thermodynamically predicted due to incomplete fuel conversion and catalyst deactivation

Catalyst deactivation cannot be solely attributed to coking and/or sulphur poisoning!

Next Steps: Investigate reasons for catalyst deactivation, enhance fuel conversion, catalyst development
Thank you for your attention!

Research Group „Alternative Fuels“

Antje Wörner (Antje.Woerner@dlr.de)
Tel.: +49 711-6862-484

Lecturer: Stefan Martin (Stefan.Martin@dlr.de)
Tel.: +49 711-6862-682