5th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry

CatchBio

Deoxygenation of stearic acid in the absence of H_2

The relevance of the anhydride reaction pathway

Stefan Hollak MSc

***Co-promotor:* Dr. Daan van Es**

***Promotor:* Prof.dr.ir. Krijn de Jong**

Karlsruhe, Germany, March 20, 2012

FOOD & BIOBASED RESEARCH WAGENINGEN UR

Universiteit Utrecht

Smart mix

Vegetable oils

- Wide variety of sources for vegetable oils
  - For instance: Sunflower oil, Soybean oil, Palm oil and Rapeseed oil

→ Land use issues; food vs. fuel

- Algae oil

  → Possible solution to these problems in future
  - No direct competition with food production
  - Rapid growth rates (10-200 times faster than terrestrial oil crops)[1,2]

→ AlgaePARC Wageningen UR

[1] *Huber et. al., Chem. Rev. 2006, 106, 4044-4098*
[2] *Christi, Biotechnol. Adv. 2007, 25, 294-306*

State of the art

1st generation biodiesel

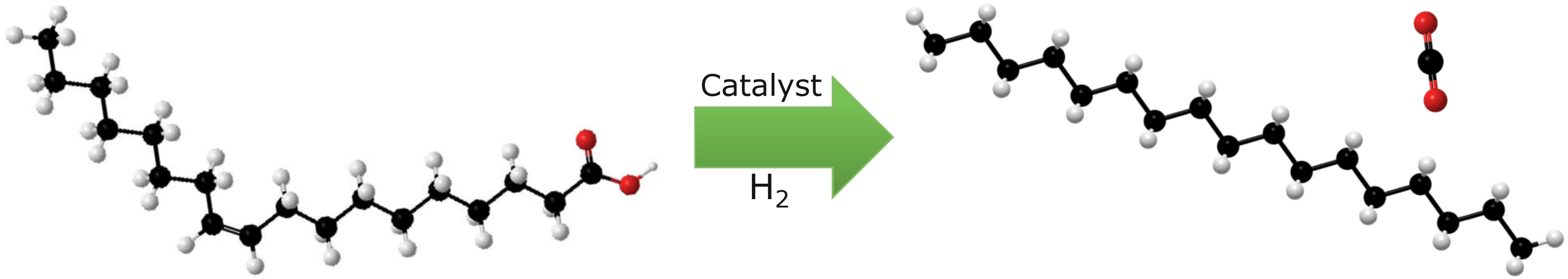
- 1st generation biodiesel: fatty acid methyl esters (FAME)
  - Derived from vegetable oils
  - Produced via transesterification of triglycerides with methanol

- Concerns
  - High purity feedstocks are necessary
  - Engine compatibility issues
    - Lower heat content
    - Poor storage stability

State of the art

2^{nd} generation biodiesel

- 2^{nd} generation biodiesel
  - Derived from vegetable oils or other fatty acid derivatives
  - Via catalytic hydrodeoxygenation using hydrogen



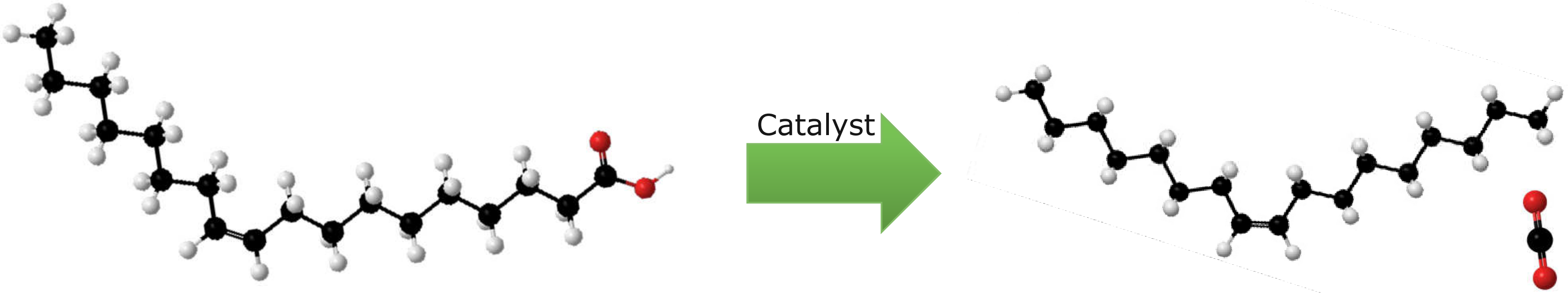
- Advantages
  - Low purity feedstocks possible
  - Higher fuel quality (heat content and storage stability)
  - Fully compatible with existing vehicles and infrastructure

- Concerns
  - Process requires (non-renewable) H_2
    - Reduction of double bond functionalities
    - Hydrodeoxygenation of glycerol to propane,
  - Process at elevated P and T *(3-10 MPa, 553-618 K)*

State of the art

CatchBio

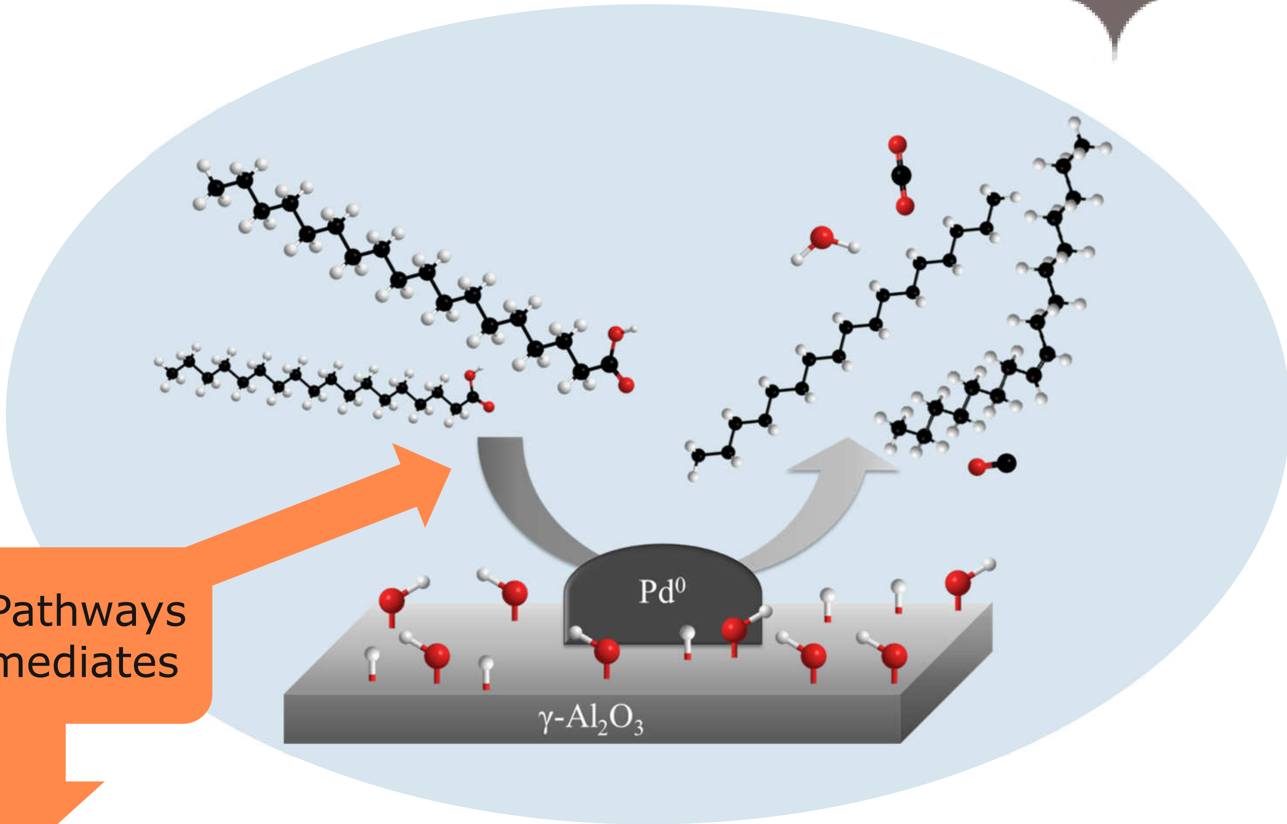
- A superior process would be the catalytic deoxygenation of fatty acids:
  - At low temperature (< 523 K)
  - With low/no hydrogen consumption
  - Yielding unsaturated hydrocarbons



- Advantages:
  - Excellent low-temperature properties as a fuel
  - Possible applications as chemical building blocks
  - Potential for glycerol valorization

Overview presentation

CatchBio



Reaction Pathways and Intermediates

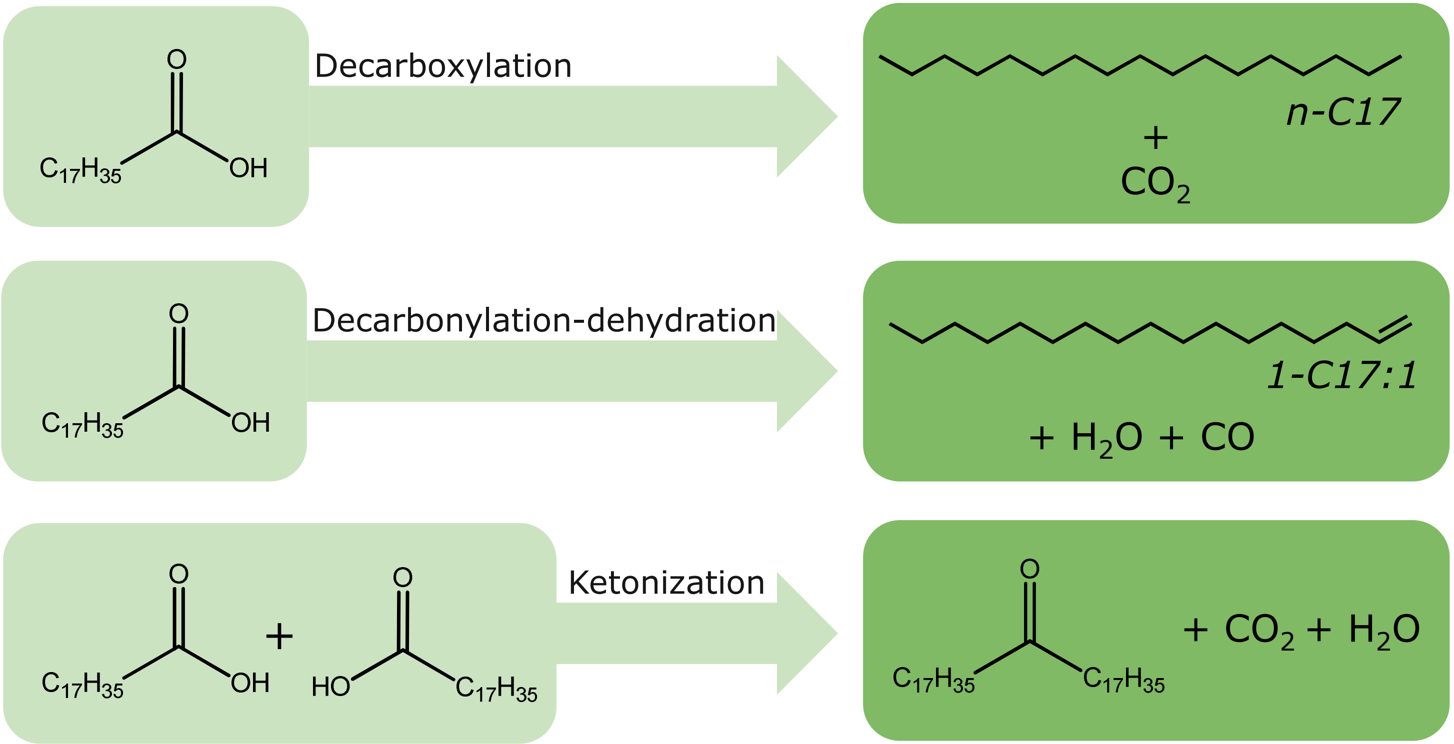
- Activity & Selectivity
  - Influence of feed conc.
- Deoxygenation reactions
  - Stearic anhydride intermediate

Catalyst:

4.5 wt% Pd/γ-Al_2O_3 (BASF)

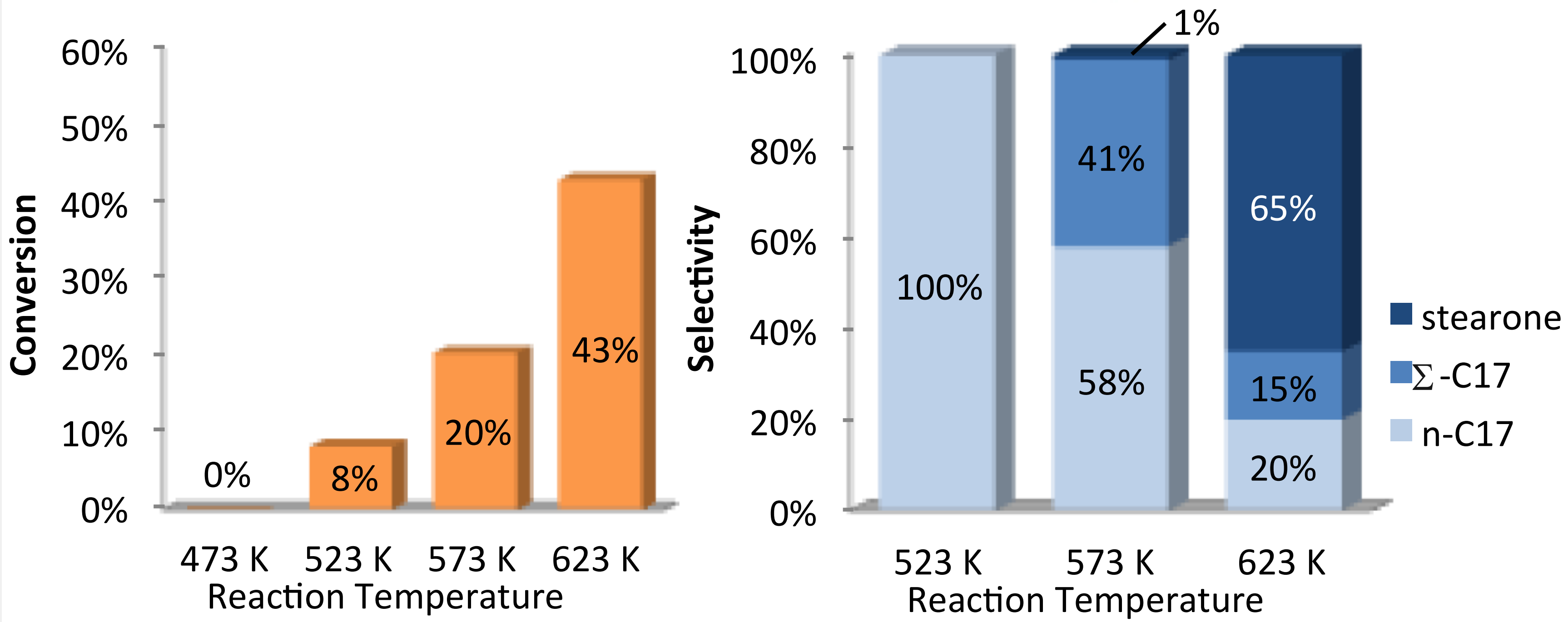
Surface area:	111 m^2/g
Av. Particle size:	6.7 nm
Dispersion:	17 %

Deoxygenation reactions



Results

Influence of temperature



Reaction conditions:

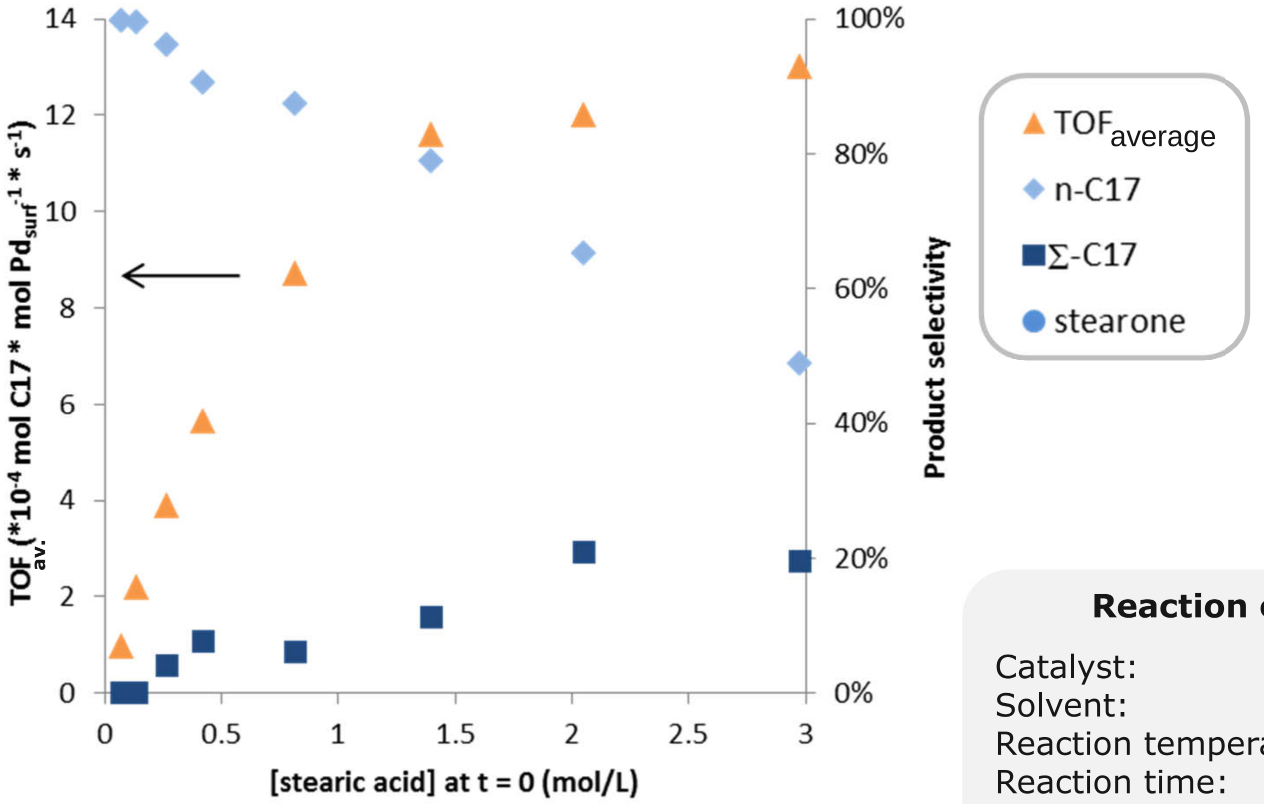
Catalyst:	Pd/γ-Al_2O_3
Solvent:	*dodecane*
Feed conc.:	*0.14 mol L^{-1}*
Reaction time:	*6 h*
Pressure:	*7 bar N_2*

- Lowest deoxygenation temperature at 523 K
  - *Heptadecane formed selectively*

Catalyst Activity & Selectivity

CatchBio

Influence of stearic acid concentration at 523 K



Reaction conditions:

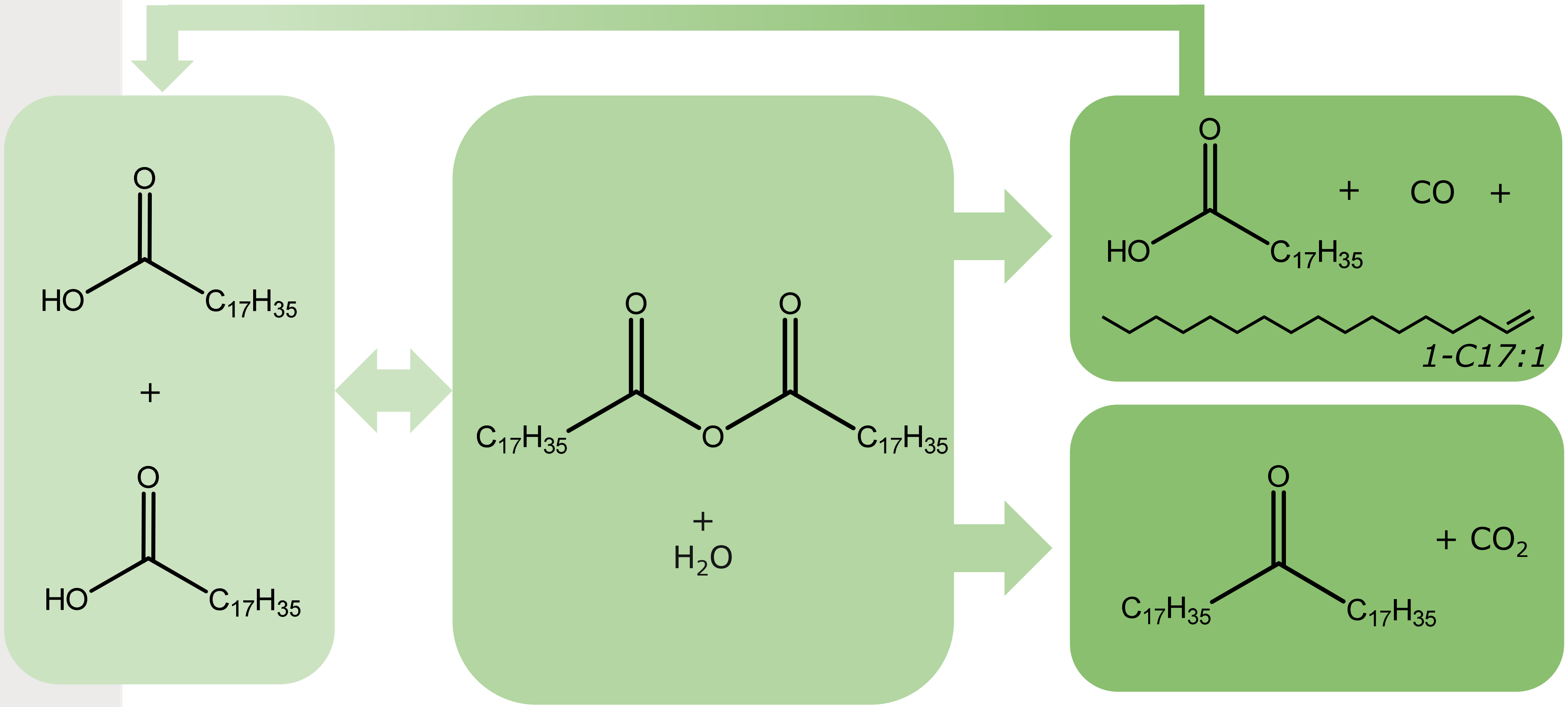
Catalyst:	$Pd/\gamma\text{-}Al_2O_3$
Solvent:	*dodecane*
Reaction temperature:	523 K
Reaction time:	*24h*
Pressure:	*7 bar N_2*

- Selective decarboxylation at low (<0.25 mol/L) stearic acid conc.
- >0.25 mol/L: Selectivity to n-C17 decreases
  - Decarbonylation products are formed
  - Ketonization to stearone

Anhydride intermediate

Hypothesis

- Possible explanation: Stearic anhydride as intermediate product
- Literature: Stearic anhydride suggested as intermediate product in homogeneous decarbonylation and ketonization reaction of stearic acid[1,2]

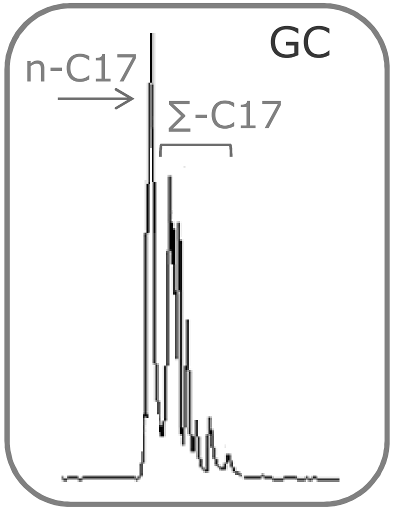


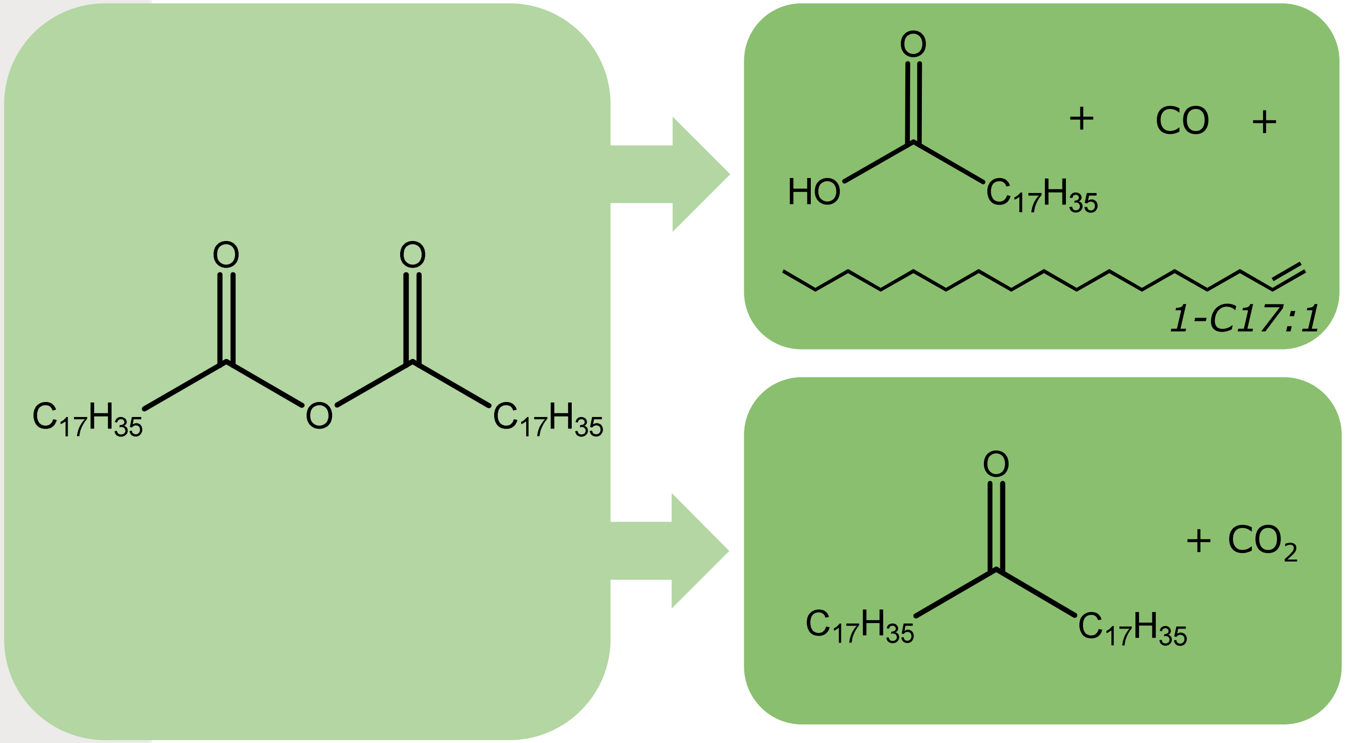
[1] Foglia et. al., *J. Am. Oil Chem. Soc.* 1976, *53*, 737-741
[2] Miller et. al., *J. Org. Chem.* 1993, *58*, 18-20

Anhydride intermediate

Model reaction

- Reaction wth stearic acid anhydride gives 100% conversion to:
  - Stearic acid
  - Heptadecenes *(Σ-C17)*
  - Heptadecane *(n-C17)*
  - Stearone *(C35)*



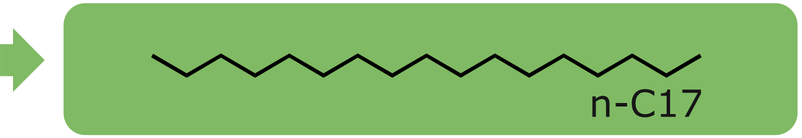


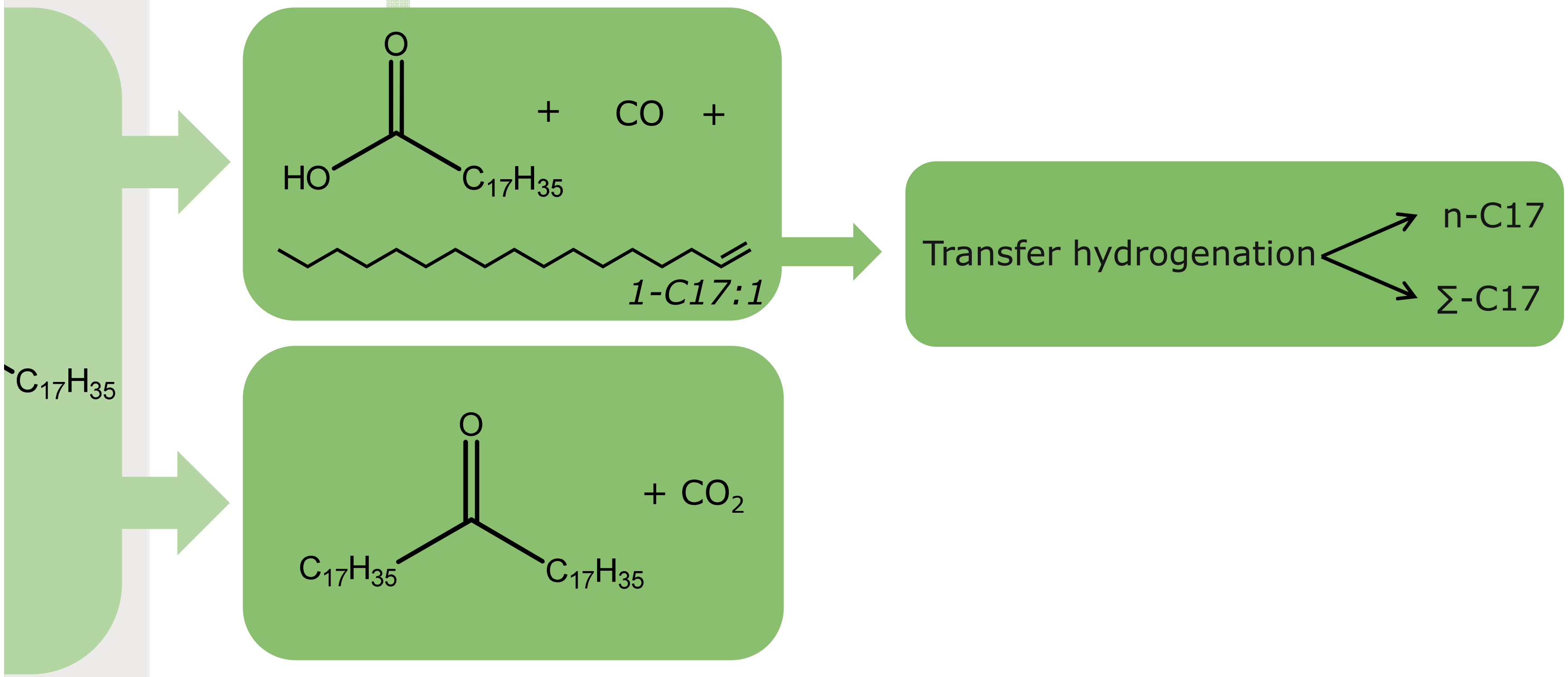
Reaction conditions:
0.14 mol/L stearic anhydride
523 K, 24h, 7 bar N_2

Anhydride intermediate

Model reaction

- Reaction wth stearic acid anhydride gives 100% conversion to:
  - Stearic acid
  - Heptadecenes *(Σ-C17)*
  - Heptadecane *(n-C17)*
  - Stearone *(C35)*





Reaction conditions:
0.14 mol/L stearic anhydride
523 K, 24h, 7 bar N_2

Anhydride intermediate

Overview model reactions

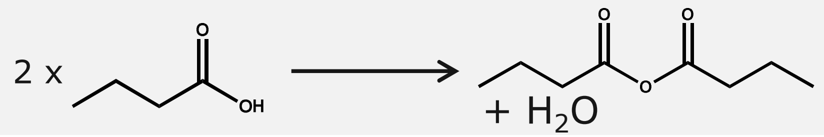
CatchBio

Catalyst	Stearic anhydride (g)	Reaction Temp (K)	Reaction time (h)	Conversion (%)	Selectivity (%)				
					n-C17	Σ-C17	SA	C35	heavies
Pd/γ-Al_2O_3	1.0	523	**5**	98	7	42	49	2	0
Pd/γ-Al_2O_3	1.0	523	**24**	100	27	25	46	2	0
γ-Al_2O_3	1.0	523	24	80	0	1	71	28	0
none	1.0	523	24	40	0	1	58	26	15
Pd/γ-Al_2O_3	**10.0**	523	24	62	14	20	35	12	19
Pd/γ-Al_2O_3	1.0	**473**	24	48	4	47	49	0	0

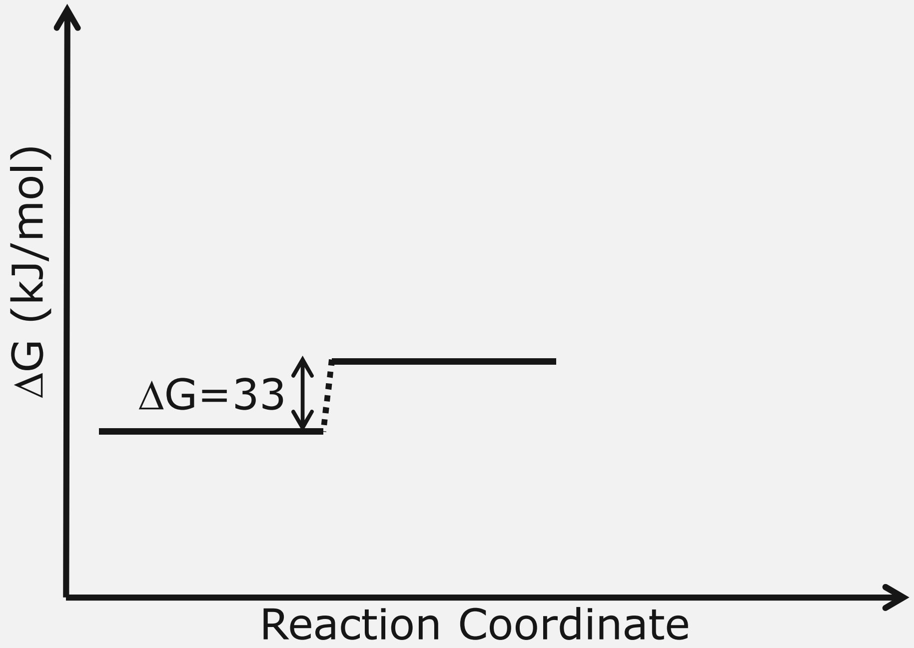
- Decarbonylation 10 times faster than when starting from stearic acid
  - Anhydride formation from stearic acid rate limiting step
- Pd essential for decarbonylation to HC’s.
  - Stearone and other heavies are formed in absence of Palladium
- High anhydride concentration: increase in side product formation
- Stearic anhydride is also converted at 473 K
  - Potential for low temperature decarbonylation of stearic acid?

Thermodynamics anhydride formation

Based on butyric acid at 523 K *



$\Delta H = 121$ kJ/mol

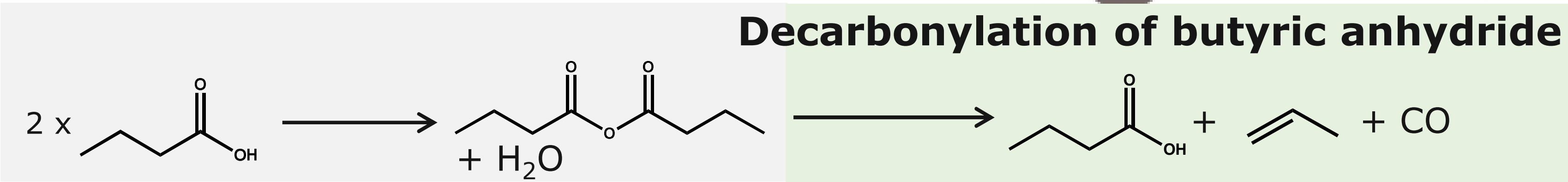


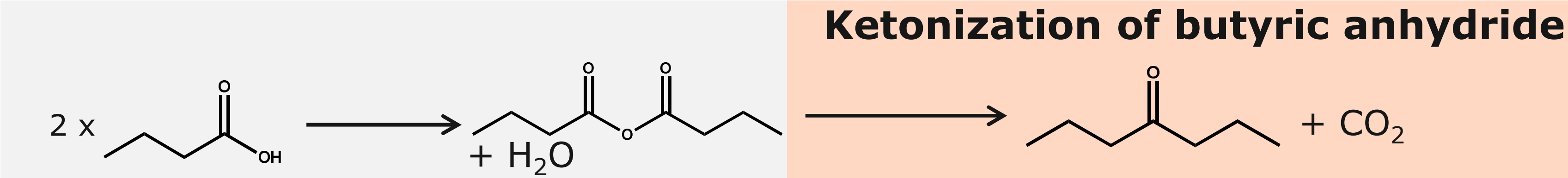
- Formation of butyric anhydride non-spontaneous at 523 K

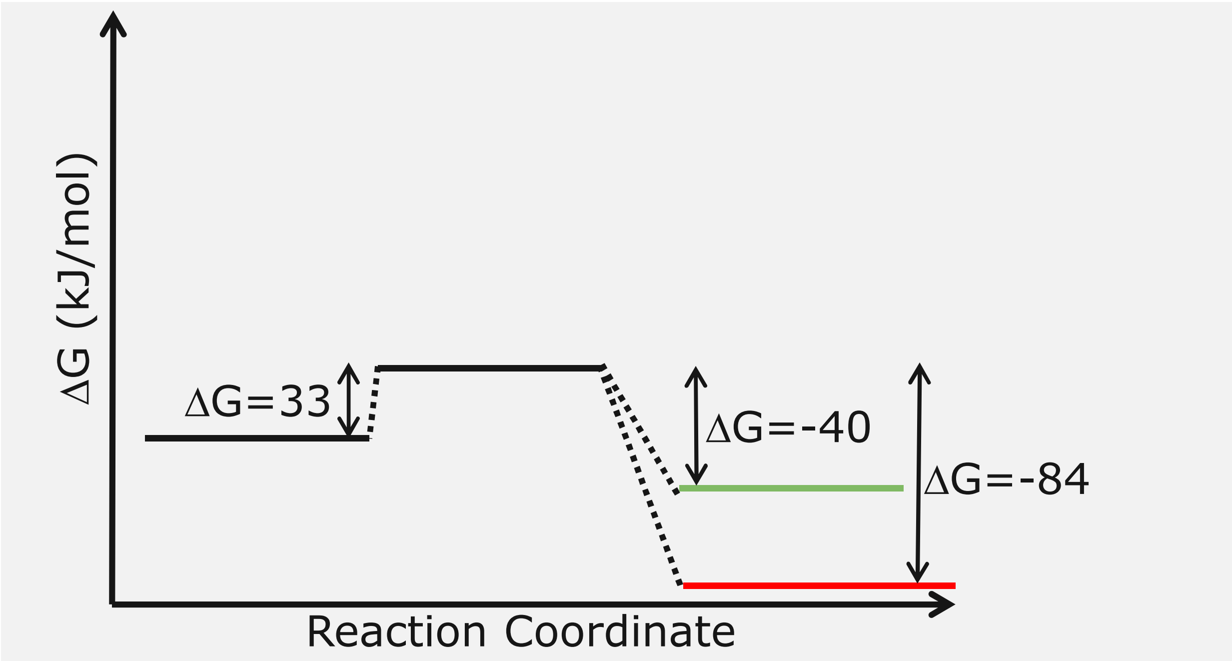
*Calculated by HSC

Thermodynamics anhydride conversion

Based on butyric acid at 523 K *





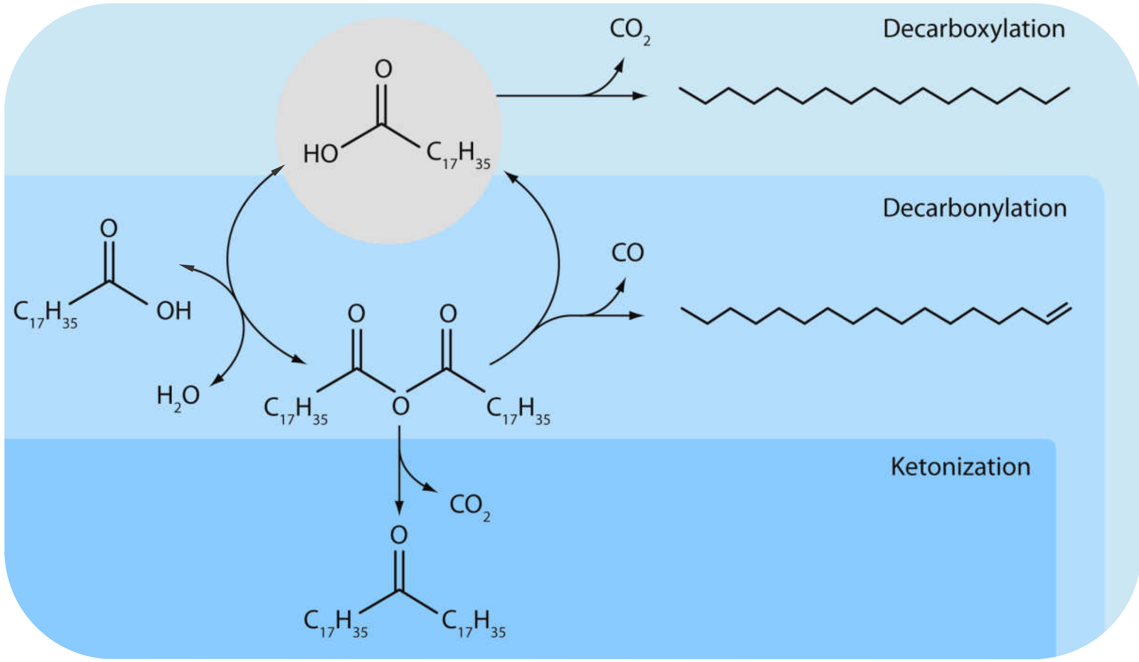


- Overall reaction pathway's are thermodynamically feasible

**Calculated by HSC*

Conclusions

- There are strong indications for the existence of stearic anhydride as reactive intermediate in the decarbonylation reaction of stearic acid at low temperatures
- Suggested deoxygenation reactions of stearic acid over Pd/Al_2O_3 at 523 K:



- Stearic anhydride is selectively converted to 1-heptadecene at 473 K
- Calculations on butyric anhydride show that pathway’s are thermodynamically feasible

Acknowledgements

Wageningen UR

- Frits van der Klis BSc
- Wouter Teunissen
- Dr. Adriaan van Aelst
- Dr. Jacco van Haveren

Utrecht University

- Rob Gosselink MSc
- Dr. Harry Bitter
- Jovana Zecevic MSc
- Dilek Ayse Boga MSc

BASF

- Dr. Bert Sandee

Funding

- This research has been performed within the framework of the CatchBio program. The authors gratefully acknowledge the support of the Smart Mix Program of the Netherlands Ministry of Economic Affairs, Agriculture & Innovation and the Netherlands Ministry of Education, Culture and Science.

email: stefan.hollak@wur.nl