# Upgrade processes for pyrolysis liquids obtained from ablative flash pyrolysis

Tim Schulzke


Denver, September 4th, 2014

# AGENDA

1. Fraunhofer Gesellschaft and Fraunhofer UMSICHT
2. Fraunhofer Innovation Cluster »Bioenergy«
3. Ablative Flash Pyrolysis
4. Staged Condensation
5. Catalytic Treatment
6. Summary




Fraunhofer
UMSICHT

# AGENDA

1. **Fraunhofer Gesellschaft and Fraunhofer UMSICHT**
2. Fraunhofer Innovation Cluster »Bioenergy«
3. Ablative Flash Pyrolysis
4. Staged Condensation
5. Catalytic Treatment
6. Summary




Fraunhofer UMSICHT

# Patron Joseph von Fraunhofer (1787 – 1826)

© Deutsches Museum

**Scientist**

➔ Discovery of the »Fraunhofer lines« in the Sun's spectrum

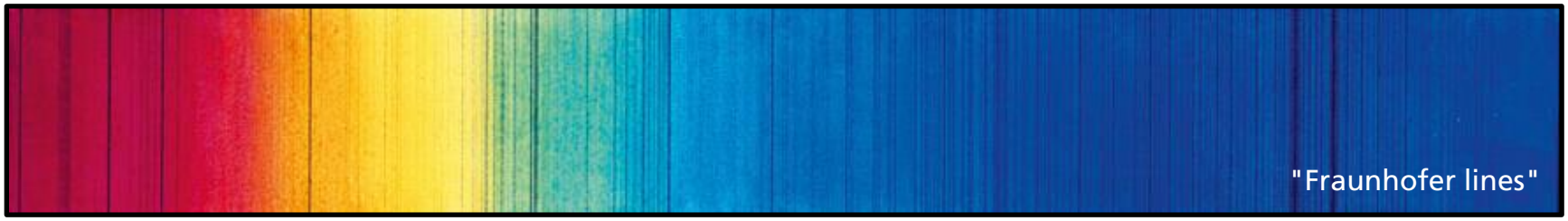
**Inventor**

➔ New manufacturing methods for lenses

**Businessman**

➔ Director and co-partner of a glass factory

© Fraunhofer-Gesellschaft







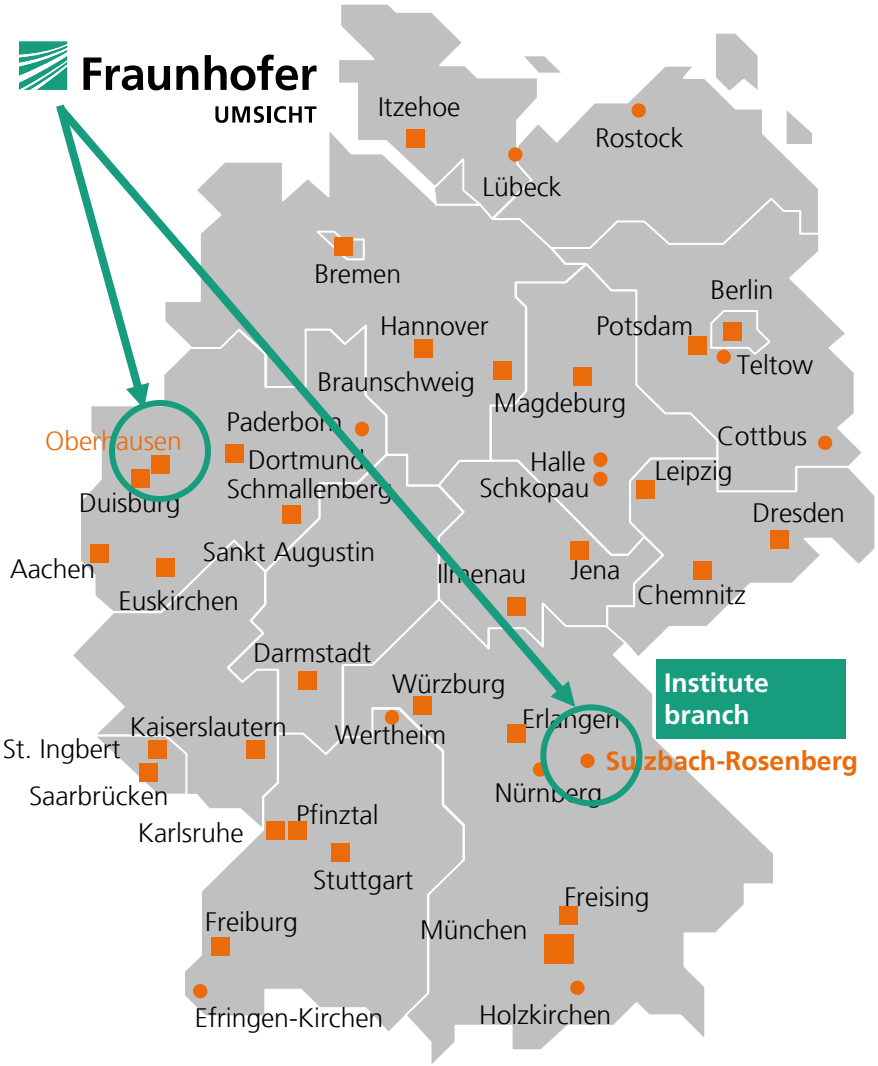
Fraunhofer UMSICHT

# The Fraunhofer-Gesellschaft

- 67 institutes and independent research facilities
- € 2 bn research funds
  - € 1.7 bn contract research
- More than 23 000 employees (m/f)[1]
- 40 facilities in Germany
- 13 institutes in North Rhine-Westphalia
- 4 institutes in the Ruhr area

more information under:

www.fraunhofer.de/en.html




[1] 23 236 (m/f) as per 12-31-2013 including fixed-term contracts of less than 18 months.




Fraunhofer
UMSICHT

# Facts and Data about Fraunhofer UMSICHT

## Fraunhofer-Institute for Environmental, Safety, and Energy Technology UMSICHT (= Prudence)

| | |
|---|---|
| Foundation | 1990 |
| Budget 2013 | € 35.2 m |
| Staff* | 528 (308 salaried) |
| Spin-off enterprises | 14 |
| Institute branch in Sulzbach-Rosenberg (SuRo) | integrated 1 July 2012 |

Site Oberhausen

Site Sulzbach-Rosenberg

* As per 1-9-2013




Fraunhofer UMSICHT

# Keynotes about Fraunhofer UMSICHT

| | |
|---|---|
| Founding | 1990 |
| Budget 2013 | € 29.5 m |
| Employees* | 427 (245 salaried) |
| Scientific | 192 |
| Administrative | 53 |
| Students, trainees | 166 |
| Apprentices | 16 |
| Spin-Offs | 14 |
| Projects | 300/year |
| Laboratory und technical area | 4 500 m² |
| Total area | 30 000 m² |

Site Oberhausen

more information under:

www.umsicht.fraunhofer.de/en.html

* As per 12-31-2012




Fraunhofer UMSICHT

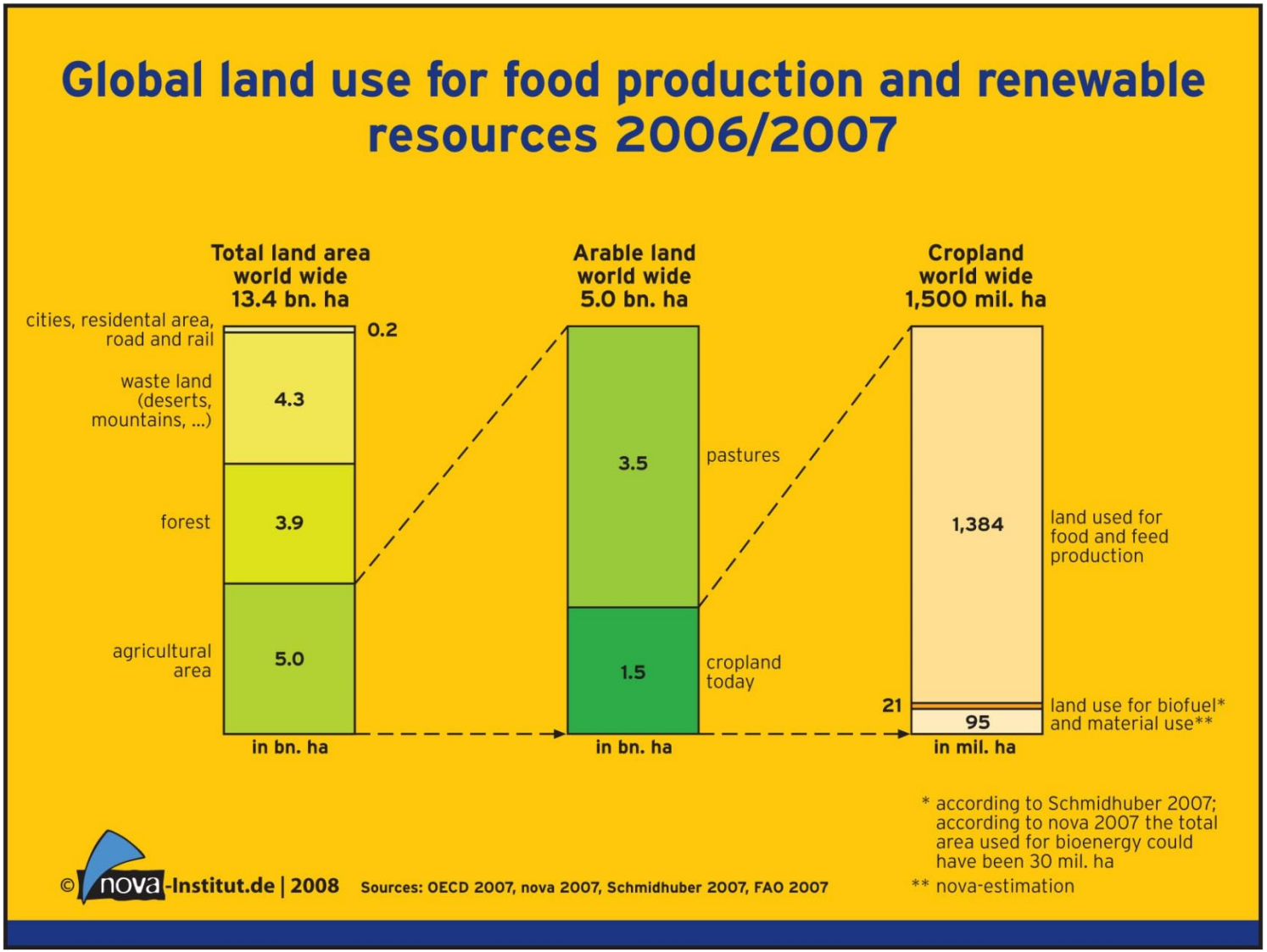
# AGENDA

1. Fraunhofer Gesellschaft and Fraunhofer UMSICHT
2. **Fraunhofer Innovation Cluster »Bioenergy«**
3. Ablative Flash Pyrolysis
4. Staged Condensation
5. Catalytic Treatment
6. Summary




Fraunhofer UMSICHT

# Fraunhofer Innovation Cluster »bioenergy« - Motivation







Fraunhofer UMSICHT

# Fraunhofer Innovation Cluster »bioenergy«

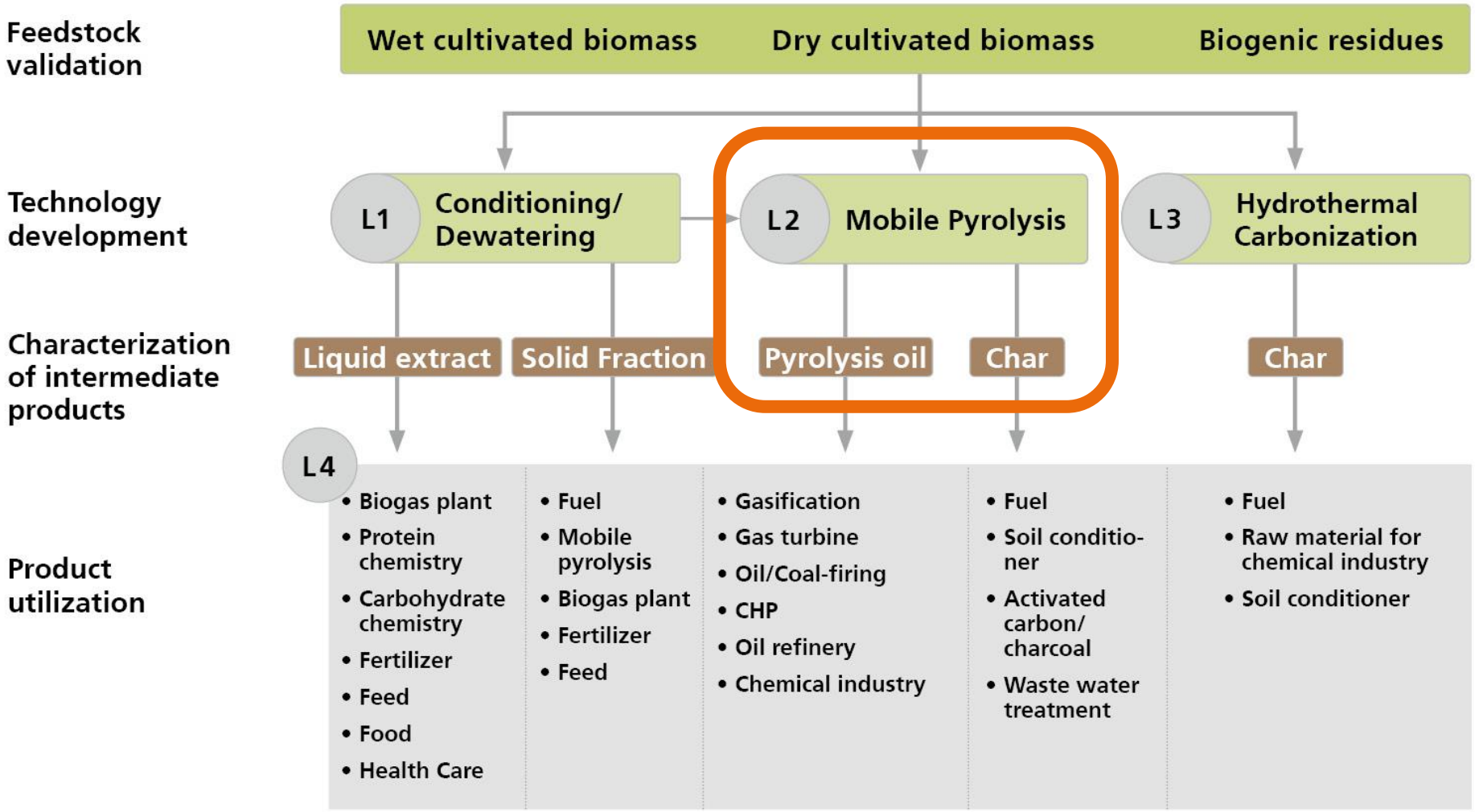
## Innovation Cluster »Bioenergy«

- Start 2012
- Duration: 3,5 Jahre
- Partner: 12 companies, 2 Universities/Institutes

## Content

- »Wet« biomass and residues as carbon source for material and energetic utilization
- storable intermediates which are worth transportation
- Technologies for  mobile/decentral Conversion

# Topics in Fraunhofer Innovation Cluster »bioenergy«







Fraunhofer UMSICHT

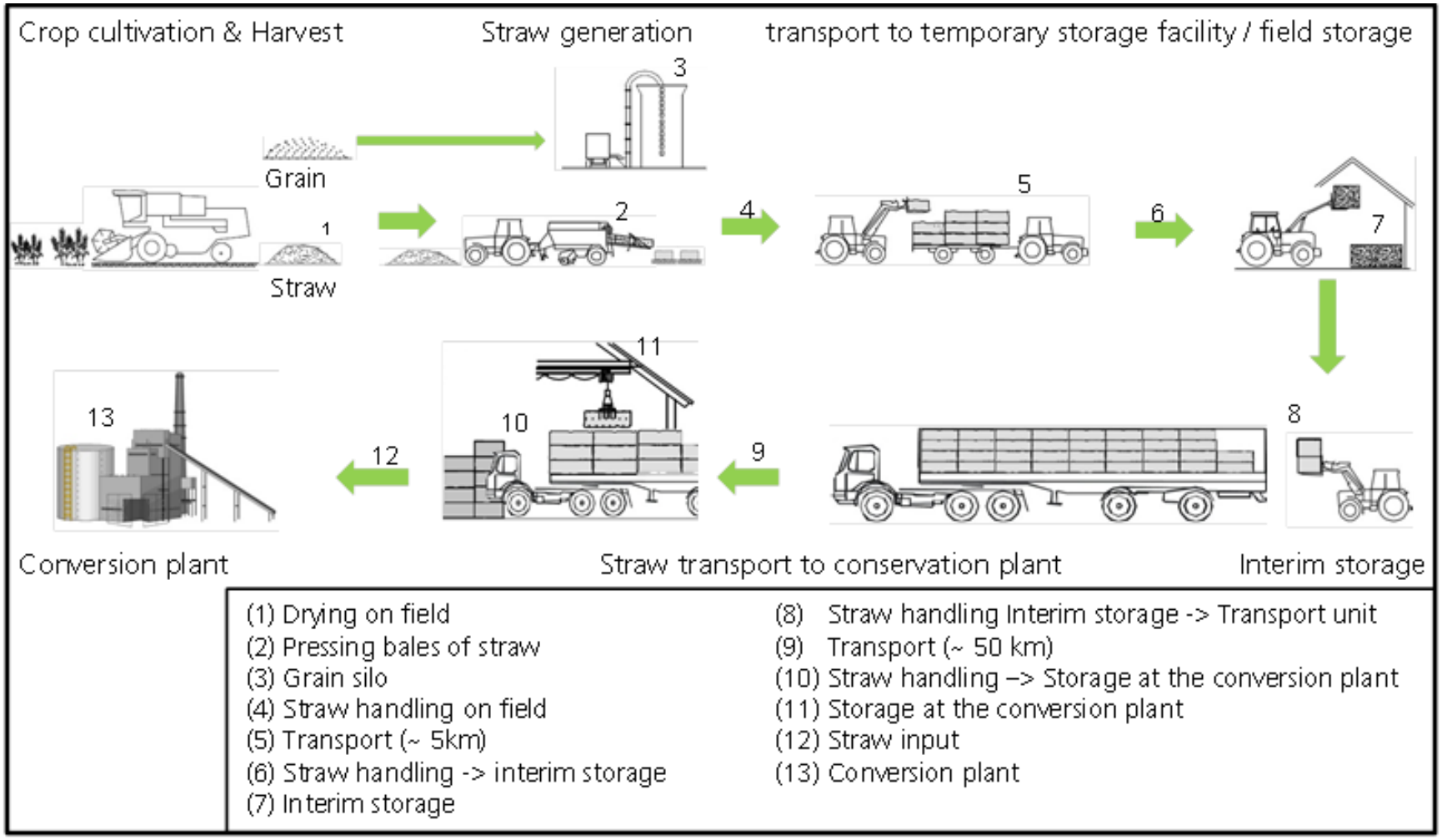
# AGENDA

1. Fraunhofer Gesellschaft and Fraunhofer UMSICHT
2. Fraunhofer Innovation Cluster »Bioenergy«
3. **Ablative Flash Pyrolysis**
4. Staged Condensation
5. Catalytic Treatment
6. Summary




Fraunhofer UMSICHT

# Conventional approach to straw utilization



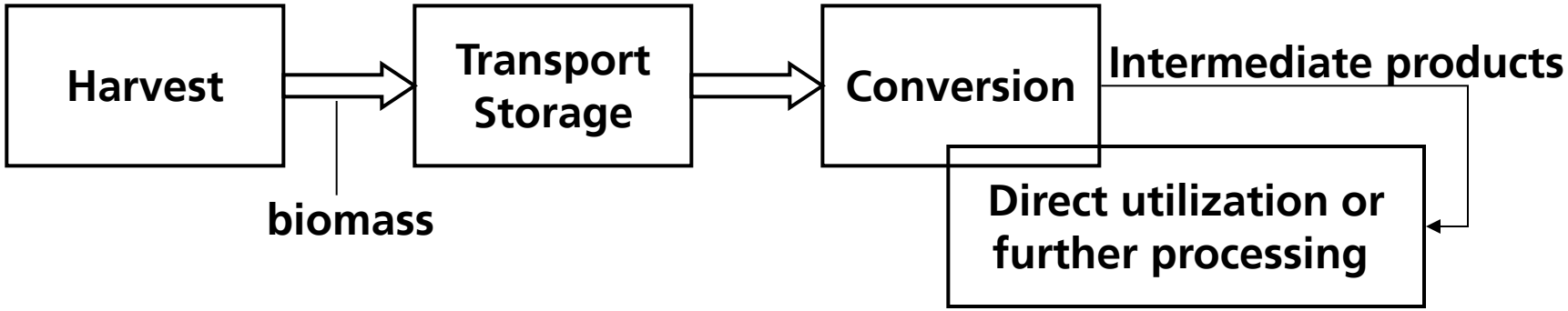

(1) Drying on field
(2) Pressing bales of straw
(3) Grain silo
(4) Straw handling on field
(5) Transport (~ 5km)
(6) Straw handling -> interim storage
(7) Interim storage
(8) Straw handling Interim storage -> Transport unit
(9) Transport (~ 50 km)
(10) Straw handling –> Storage at the conversion plant
(11) Storage at the conversion plant
(12) Straw input
(13) Conversion plant



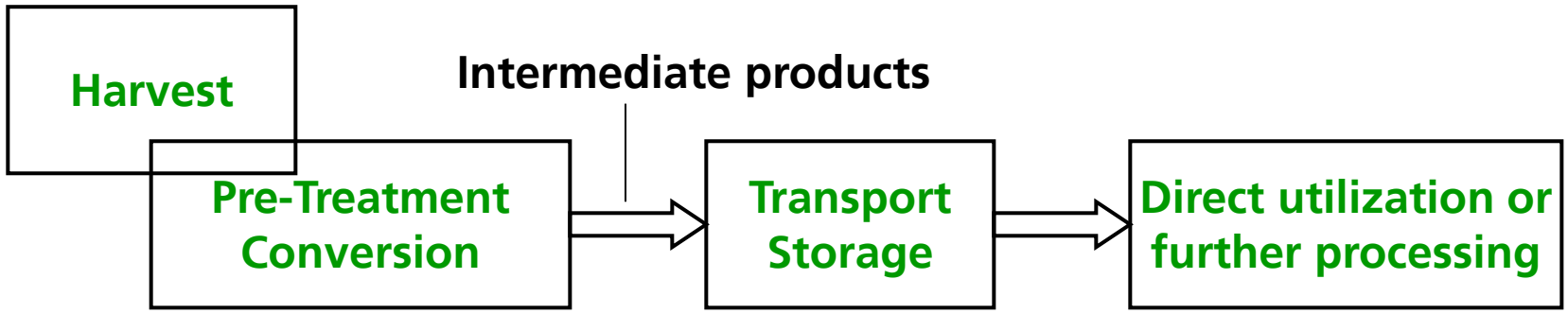

Fraunhofer UMSICHT

# Approach: On-site exploitation of intermediate products

## Conventional approach




## New cluster approach

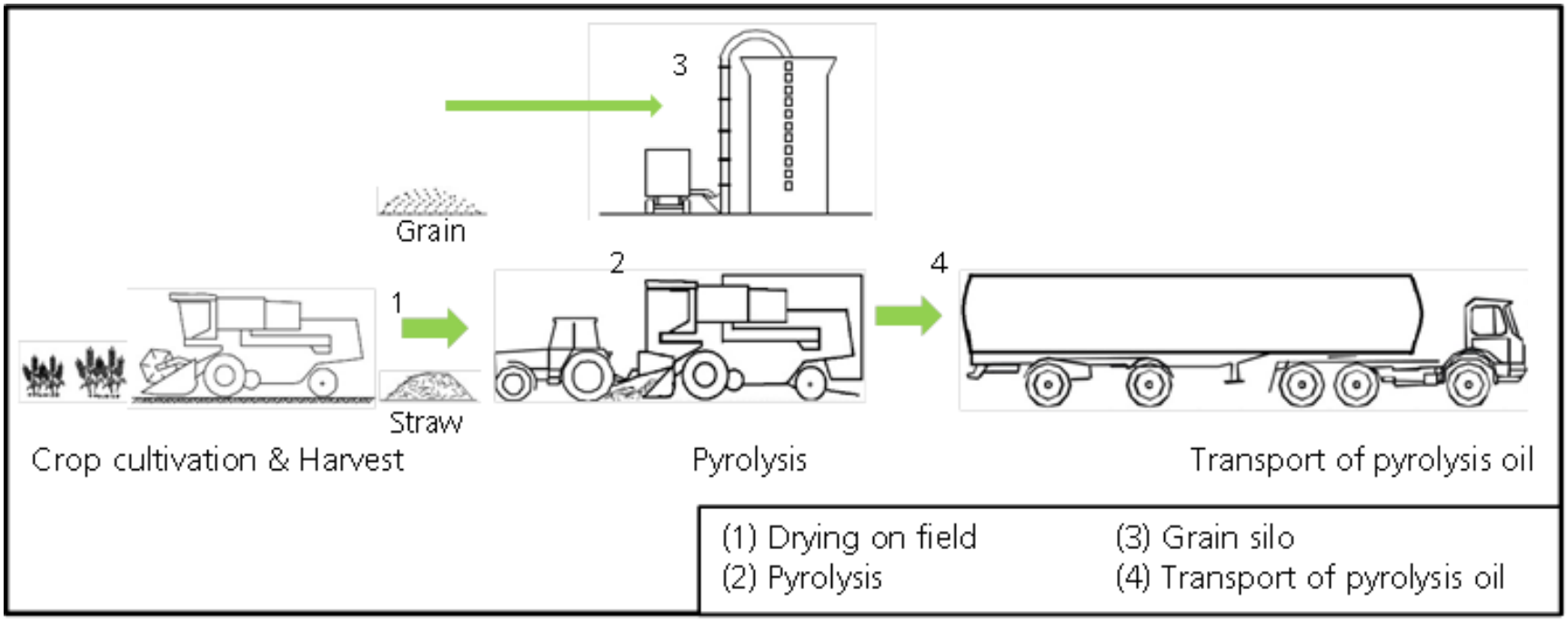






Fraunhofer
UMSICHT

# Approach: On-site exploitation of intermediate products

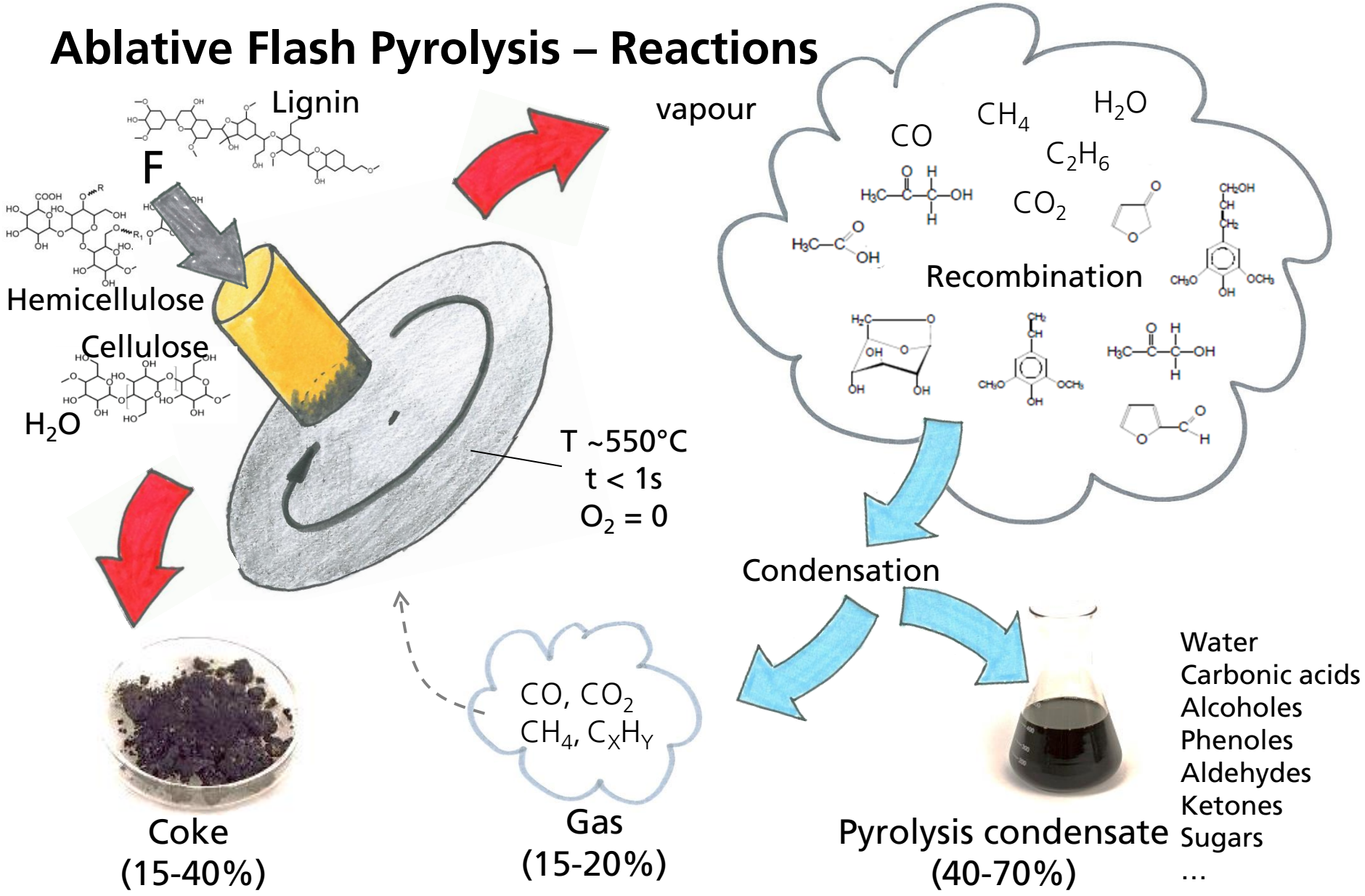






Fraunhofer UMSICHT

# Ablative Flash Pyrolysis – Reactions



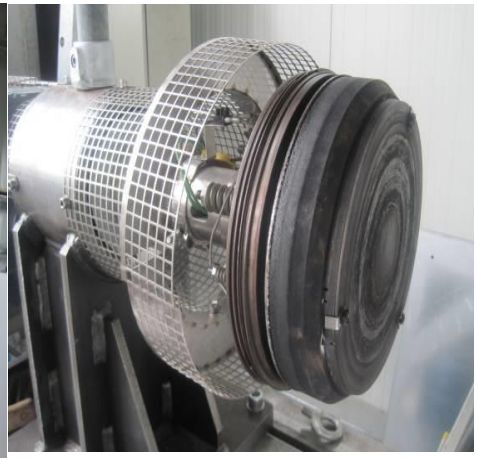


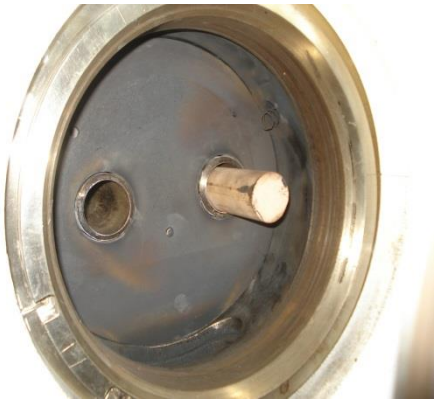


Fraunhofer UMSICHT

# Ablative Flash Pyrolysis – Laboratory plant

PYTEC



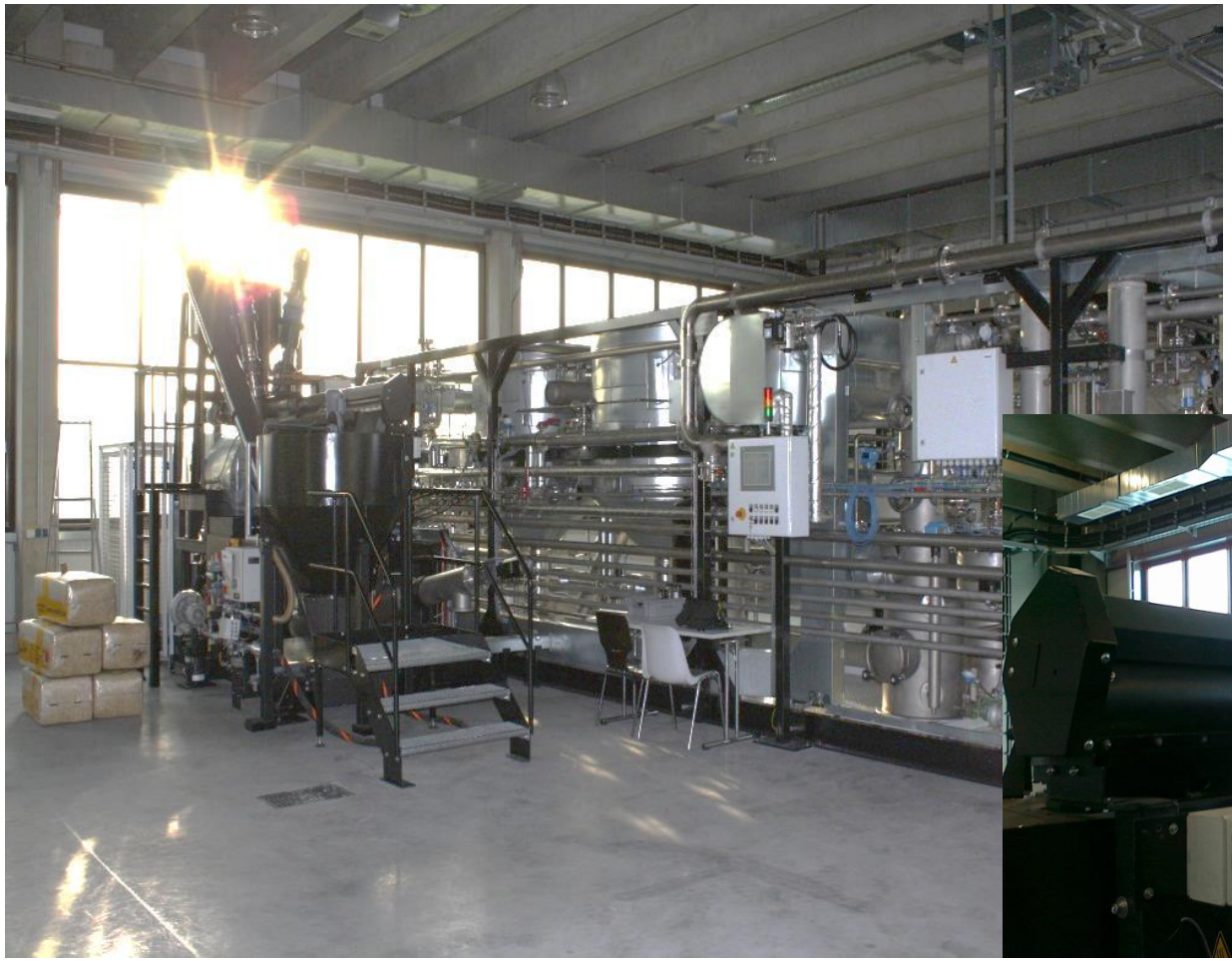





Fraunhofer UMSICHT

# Ablative Flash Pyrolysis – Functional model of mobile unit

## MBB Fertigungstechnik (former Claas Fertigungstechnik)






Fraunhofer UMSICHT

# AGENDA

1. Fraunhofer Gesellschaft and Fraunhofer UMSICHT
2. Fraunhofer Innovation Cluster »Bioenergy«
3. Ablative Flash Pyrolysis
4. **Staged Condensation**
5. Catalytic Treatment
6. Summary




Fraunhofer UMSICHT

# Pyrolysis Condensate - Properties

| | | |
|---|---|---|
| **Water** | | **24 %** |
| **C/H/O** | | **41 % / 8 % / 51 %** |
| **Heating Value** | | **16 MJ/kg** |
| **Pyrolysis Lignin** | | **13,7 %** |

Multitude of functional groups:

| | | |
|---|---|---|
| **Carbonic acids** | - acetic acid | **10,5 %** (9,5 %) |
| **Sugars** | - Levoglucosan | **5,7 %** (4,0 %) |
| **Aldehydes** | - Hydroxyacetaldehyde | **4,8 %** (4,0 %) |
| **Ketones** | - Acetol | **5,4 %** (3,5 %) |
| **Phenoles** | - Syringol | **7,4 %** (5,4 %) |

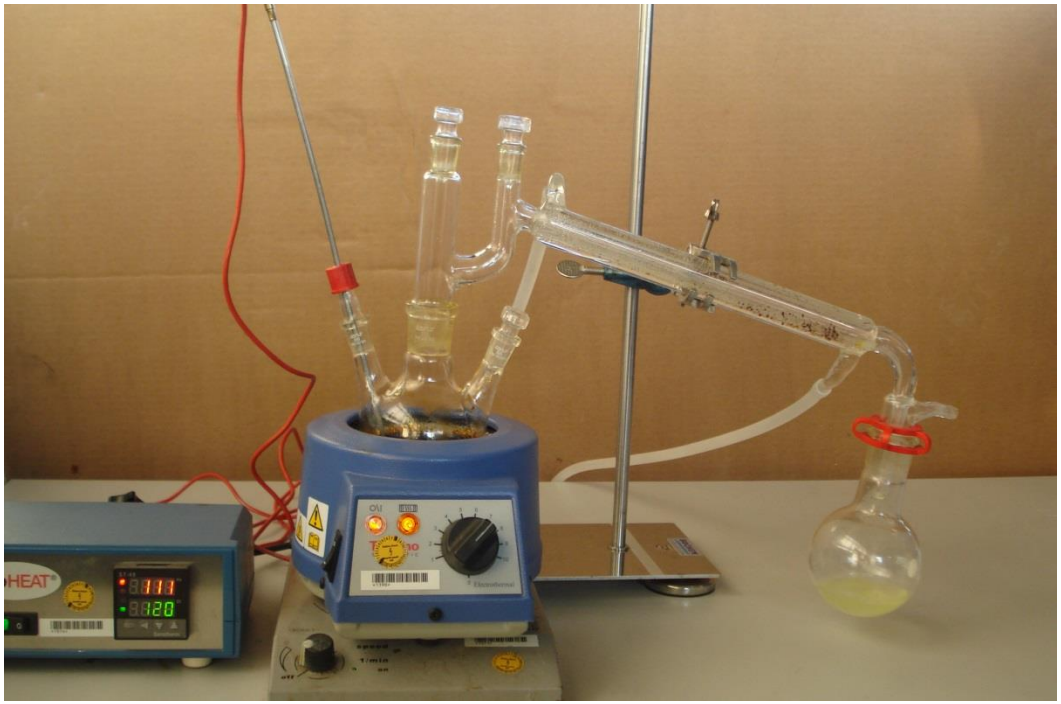
Mean values out of 9 Experiments
Beech wood, 450°C - 600°C, 20 – 50 bar




Fraunhofer UMSICHT

# Distillation

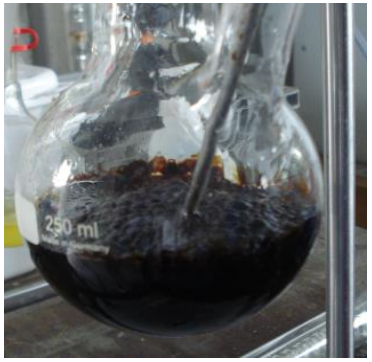
## Experimental Set-up



Pyrolysis condensate from spruce / fir
Distillation for 10 min at 160 °C

Distillate (38 %)

Sump residue (62 %)



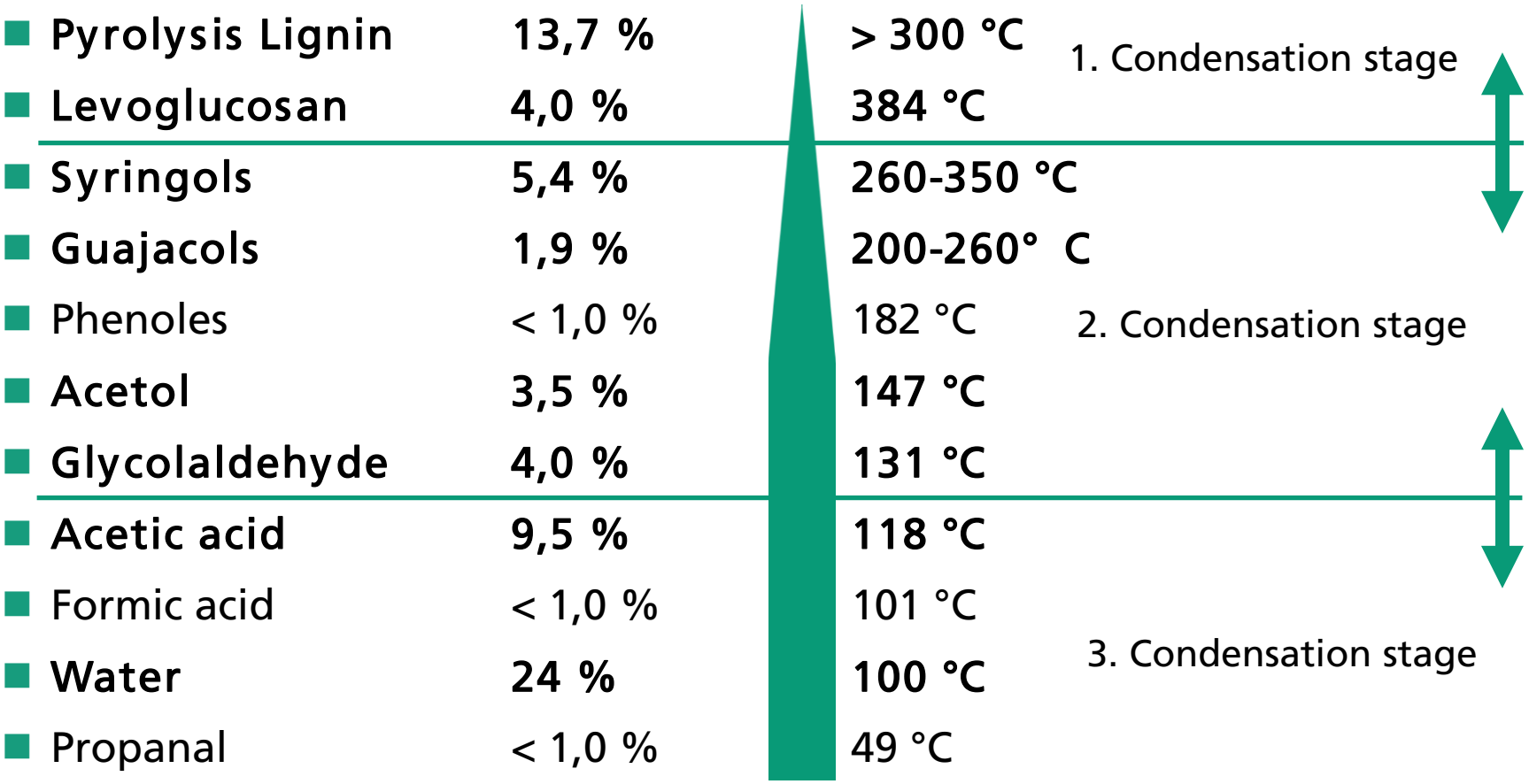




Fraunhofer UMSICHT

# Staged Pyrolysis Vapour Condensation - Motivation

## Boiling points



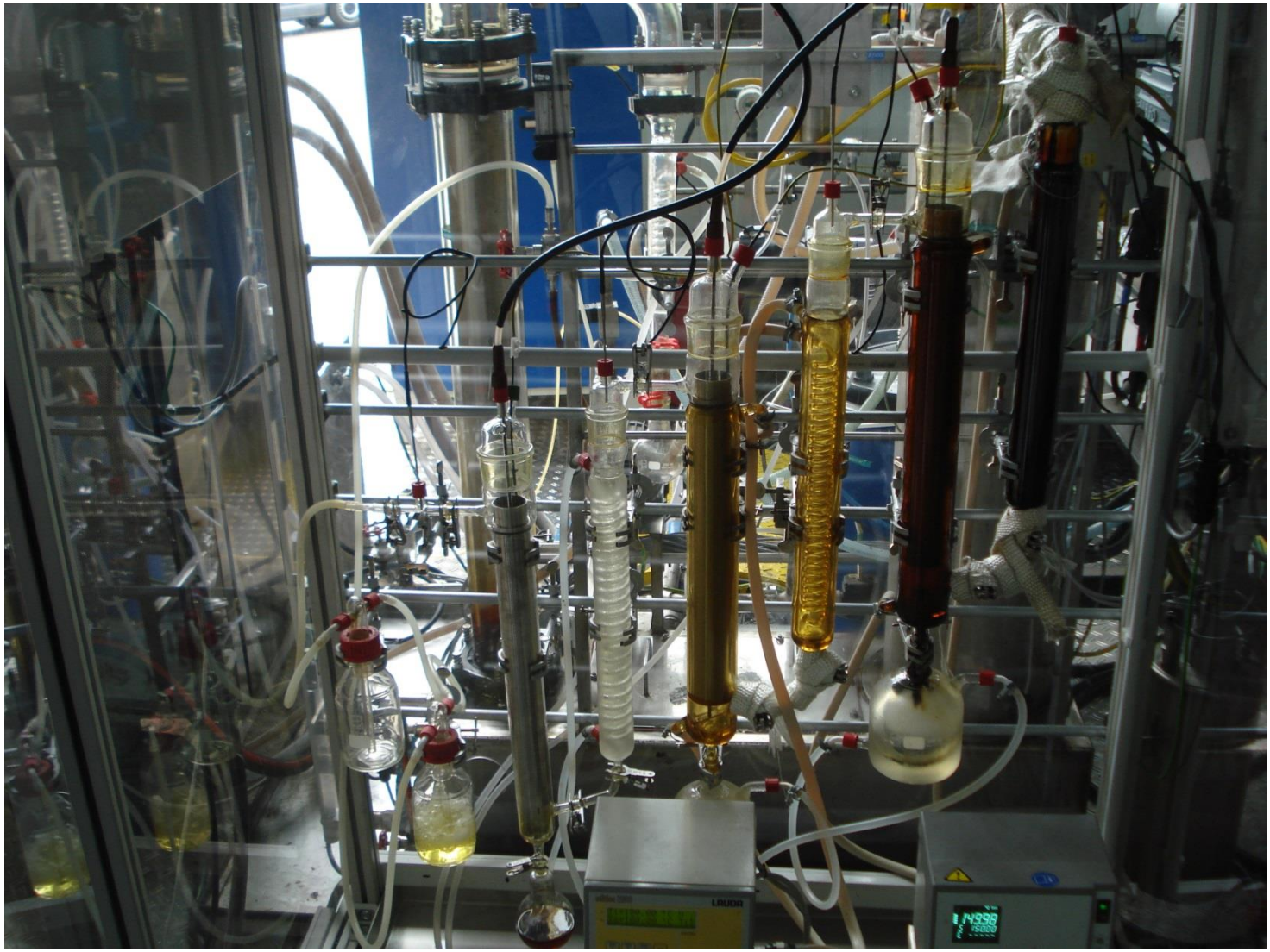




Fraunhofer UMSICHT

# Staged Pyrolysis Vapour Condensation– 1. Test run

1. Stage: 150 °C
2. Stage: 100 °C
3. Stage: 5 °C






Fraunhofer UMSICHT

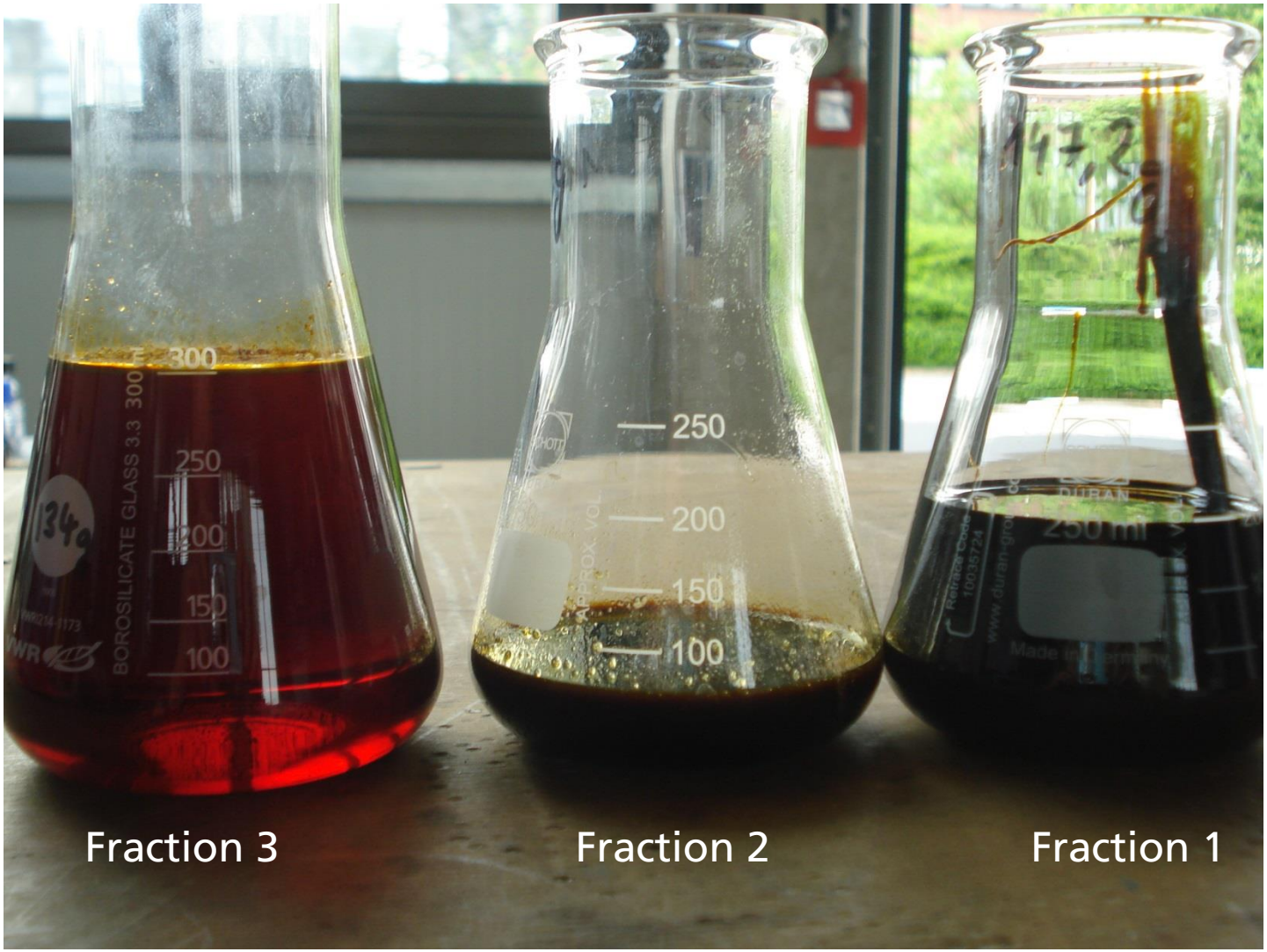
# Staged Pyrolysis Vapour Condensation - Products

Fractions

1. Stage
200 ml
Oligomers

2. Stage
75 ml
Phenols
23,4 MJ/kg

3. Stage
300 ml
Water
Acids
10,0 MJ/kg







Fraunhofer UMSICHT

# First results for staged condensation of pyrolysis vapours (beech)

| | Reference | Fraction 1 | Fraction 2 | Fraction 3 |
|---|---|---|---|---|
| Temperature | 5 °C | 150 °C | 100 °C | 5 °C |
| Ratio [weight-%] | 100 | 38,4 | 11,1 | 50,5 |
| Heating Value (LHV) | 15,4 MJ/kg | 23,6 MJ/kg | 20,6 MJ/kg | 9,2 MJ/kg |
| Water | 28,7 % | 3,7 % | 5,7 % | 51,0 % |
| C | 39,6% | 60,18 % | 52,39 % | 23,28 % |
| H | 7,96 % | 6,29 % | 7,07 % | 9,34 % |
| O | 52,35% | 33,39 % | 40,45 % | 67,38 % |
| Acids | 10,4 % | 1,1 % | 8,5 % | 16,9 % |
| Nonaromatic Aldehydes | 3,47 % | 0,39 % | 9,22 % | 0,33 % |
| Nonaromatic Ketones | 5,5 % | 0,9 % | 9,7 % | 6,3 % |
| Furans | 2,6 % | 1,8% | 6,1 % | 2,4 % |
| Pyrans | 0,18 % | 0,76% | 1,4 % | 0,1 % |
| Guaiacols | 2,0 % | 2,7 % | 7,2 % | 0,8 % |
| Syringols | 5,5 % | 12,3% | 9,1 % | 0,3 % |
| Sugars | 5,94 % | 17,5 % | 5,2 % | 0,02 % |

# First results for staged condensation of pyrolysis vapours (barley straw)

| | Ref. exp. aqueous | Ref. exp. organic | Ref. exp. Sum | Fraction 1 | Fraction 2 | Fraction 3 |
|---|---|---|---|---|---|---|
| Temperature [°C] | 5 | 5 | 5 | 150 | 100 | 2 |
| Ratio [%] | 62,8 | 37,2 | 100 | 22,8 | 9,8 | 67,4 |
| Heating Value (LHV) [MJ/kg] | 7,9 | 21,8 | 13,1 | 27,8 | 22,3 | 6,3 |
| Water [%] | 61,1 | 21,6 | 46,4 | 2,0 | 8,1 | 69,8 |
| C [%] | 19,85 | 51,46 | 31,61 | 65,94 | 54,4 | 15,00 |
| H [%] | 9,62 | 8,06 | 9,0 | 7,03 | 7,41 | 10,18 |
| O [%] | 70,28 | 39,91 | 58,98 | 25,91 | 37,53 | 74,76 |
| Acids [%] | 7,92 | 5,22 | 6,92 | 0,78 | 5,79 | 17,43 |
| Aldehydes [%] | 0,03 | 1,28 | 0,50 | 0,04 | 3,30 | 0,11 |
| Ketones [%] | 6,36 | 6,91 | 6,56 | 0,96 | 11,65 | 7,35 |
| Furans [%] | 1,75 | 2,04 | 1,86 | 0,58 | 4,95 | 1,35 |
| Pyrans [%] | 0,09 | 0,0 | 0,06 | 0,14 | 0,15 | 0,0 |
| Guaiacols [%] | 0,57 | 5,47 | 2,39 | 4,0 | 10,74 | 0,73 |
| Syringols [%] | 0,59 | 4,09 | 1,89 | 6,03 | 5,77 | 0,07 |
| Sugars [%] | 1,28 | 1,84 | 1,49 | 5,69 | 5,48 | 0,0 |

# Creation of Value from Fractions

- **aqueous fraction**
  reddish brown aqueous liquid, low heating value
  - Water
  - org. acids (acetic acid) ➡ pure acid (raw material for chem. Industry)
  - Alcohols, Ketones (Acetol) ➡ Solvents
  - fraction as a whole ➡ Fermentation (Biogas)

- **medium viscous fraction**
  darkbrown, honey-type liquid, medium heating value
  - Phenols (Syringols) ➡ raw material for Phenoplastic
  - Aldehydes (Acetaldehyde) ➡ raw material for Phenoplastic
  - fraction as a whole ➡ Refinery (transportation fuels)
    ➡ energetic utilization (power, heat)

# Creation of Value from Fractions

- **highly viscous fraction**
  black pasty liquid, high heating value
  - Sugars (Levoglucosan) ➡ raw material for chem. Industry
  - fraction as a whole ➡ Gasification (Synthesis gas)
    ➡ energetic utilization (heat)

# AGENDA

1. Fraunhofer Gesellschaft and Fraunhofer UMSICHT
2. Fraunhofer Innovation Cluster »Bioenergy«
3. Ablative Flash Pyrolysis
4. Staged Condensation
5. **Catalytic Treatment**
6. Summary




Fraunhofer UMSICHT

# Catalytic Treatment

joint project with Thuenen-Institute for Wood Research (Dr. Meier) titled

„Development of a combined procedure for the upgrade of pyrolysis liquids with alcohols and hydrogen “

two either competing or consecutive approaches:

- Esterification of carbonic acids and ketones/aldehydes (UMSICHT)
  - utilization of bio-based alcohols (e.g. bio-butanol)
  - reaction catalyzed by acids
    $\Rightarrow$ initially autocatalytic
  - later addition of homogeneous or heterogeneous (pref.) acid catalyst
  - complete raw pyrolysis condensate
  - single fraction from staged condensation

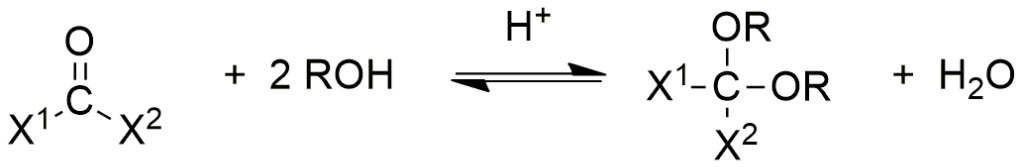
- Hydrogenation/Hydrotreatment (TI)
  - complete raw pyrolysis condensate
  - single fraction from staged condensation
  - mild hydrogenation of previously esterificated pyrolysis condensate

# 1st step: Esterification

Esterification/Acetal formation

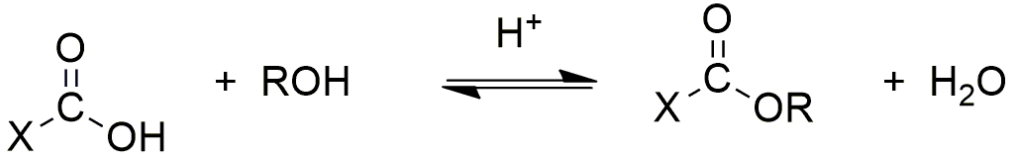
- Saturation of reactive/functional groups (Acids, Aldehydes, Ketones)
- Utilisation of higher alcohols (Butanol, Hexanol, etc.)

(better separation of water due to higher boiling point and hydrophoby)




Acetal formation

(Aldehydes, Ketones)




Esterification

(Acids)

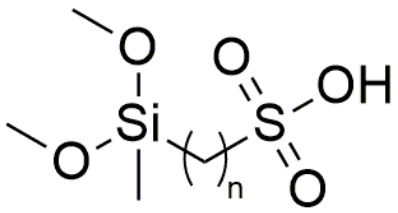



Fraunhofer UMSICHT

# 1st step: Esterification

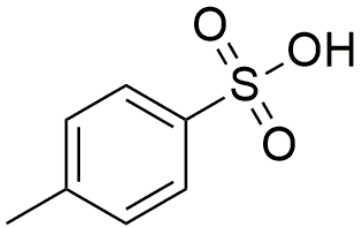
Catalyst Properties

- Sulfonic- or Carbonic acid groups
- varying strength of acid
- silicate or resins as solid support
- Homogeneous reference catalyst
- bleeding, conglutination, pore clogging




silicate supported sulfonic acid

(heterogeneous)




para-Toluene-sulfonic acid

(homogeneous)




Fraunhofer UMSICHT

# Pyrolysis Condensate Esterification – Experiments

Experimental Set-up

Dean-Stark-apparatus with

stirred flask with temperature control

reflux condenser for vapours

phase separator

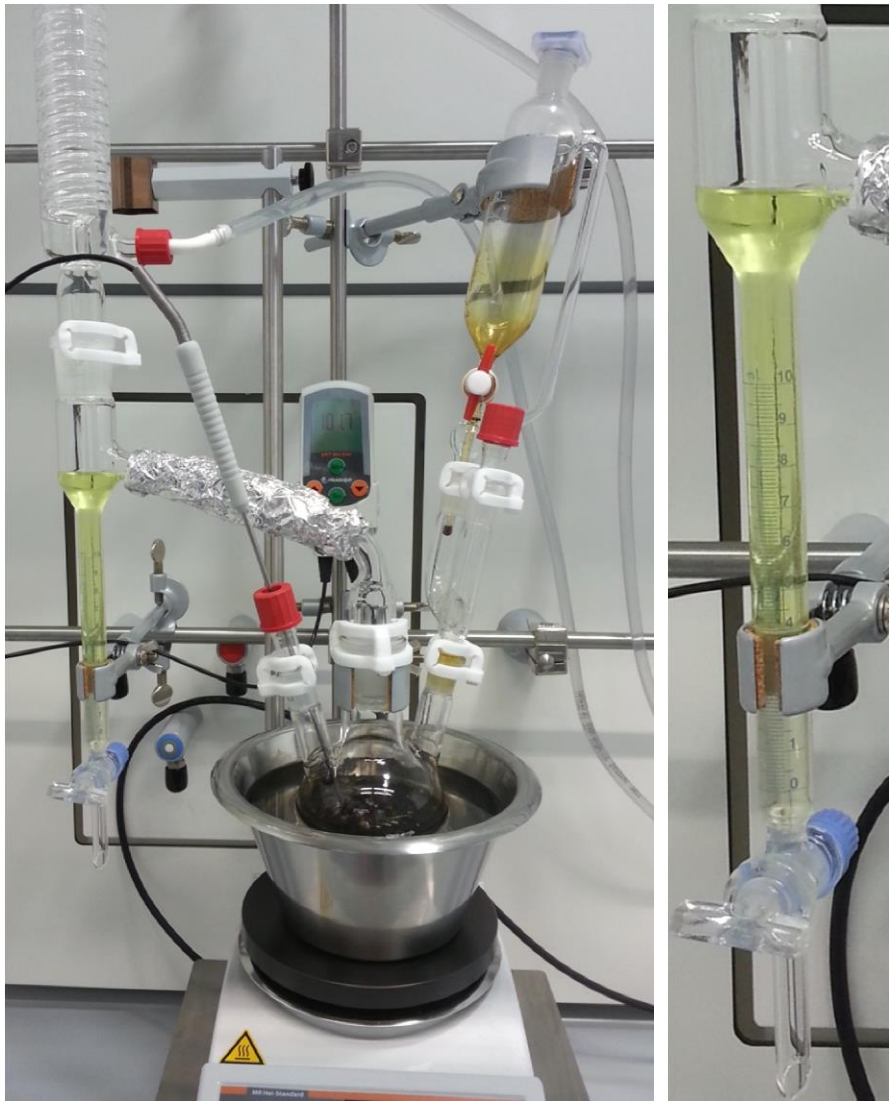
Experimental procedure

butanol + solid acid catalyst in flask

heating up to boiling point

pyrolysis condensate addition

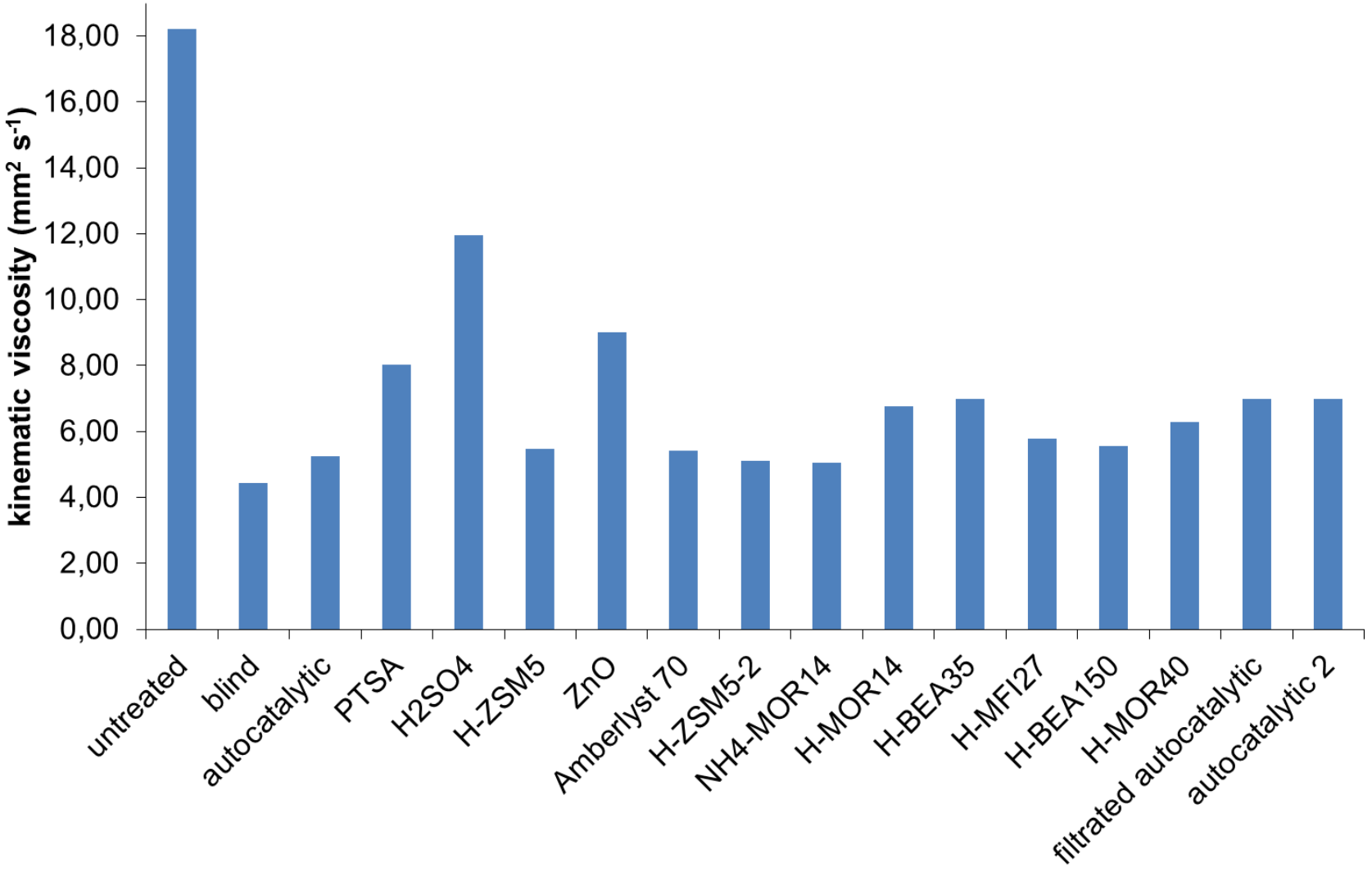
boiling until no more water condenses






Fraunhofer UMSICHT

# Pyrolysis Condensate Esterification – viscosity at 40 °C

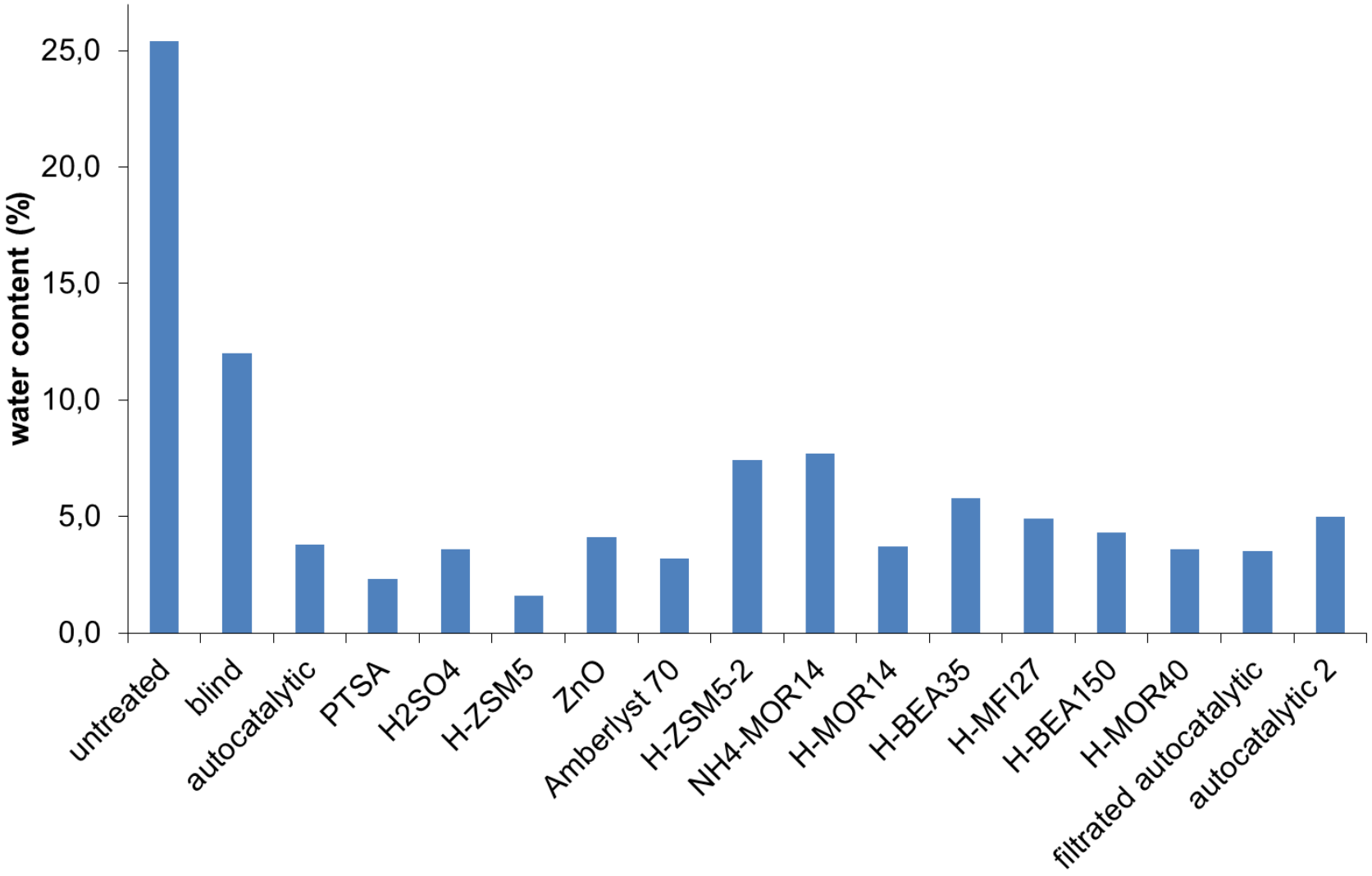






Fraunhofer UMSICHT

# Pyrolysis Condensate Esterification – water content

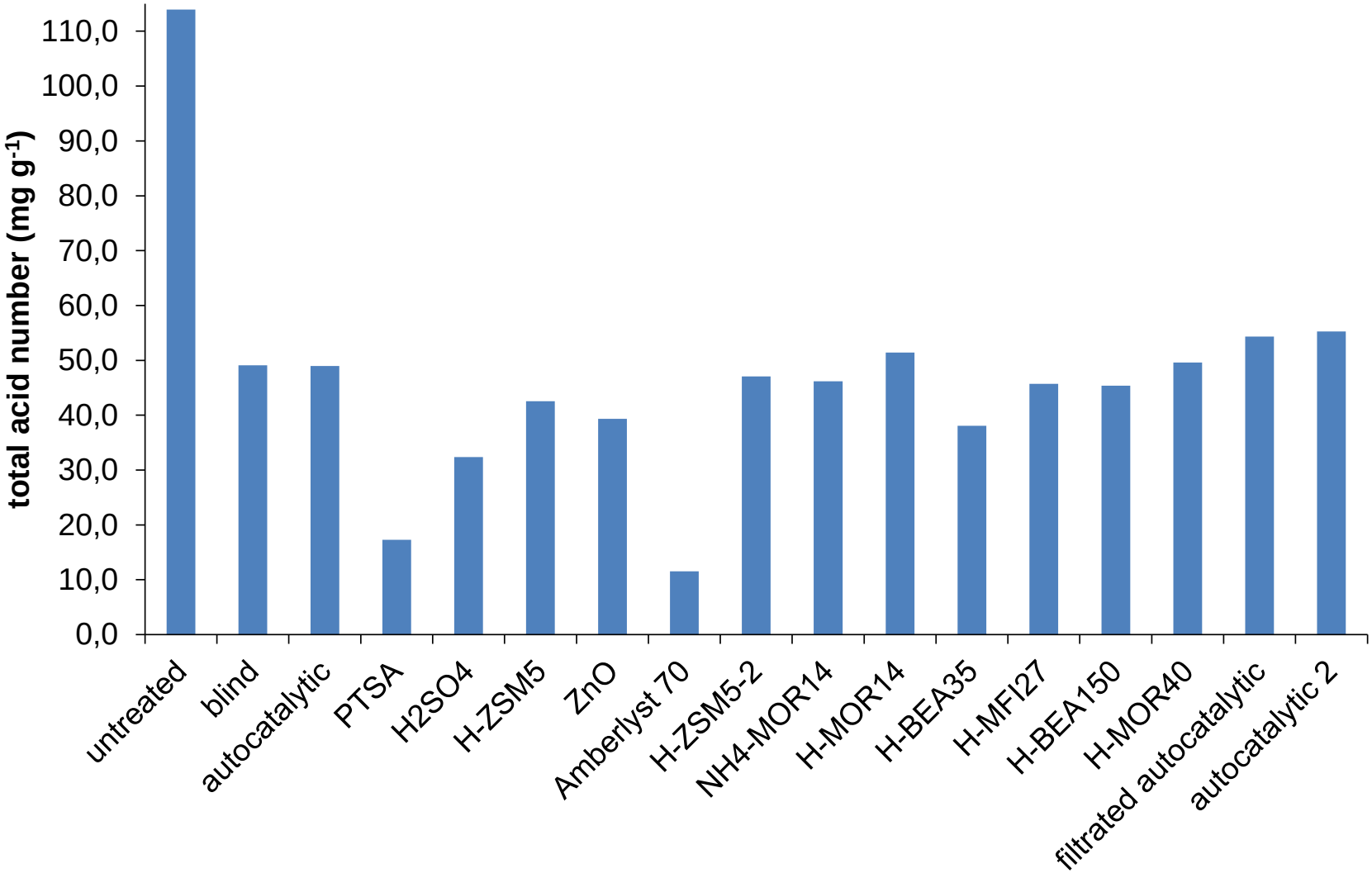






Fraunhofer UMSICHT

# Pyrolysis Condensate Esterification – total acid number







Fraunhofer UMSICHT

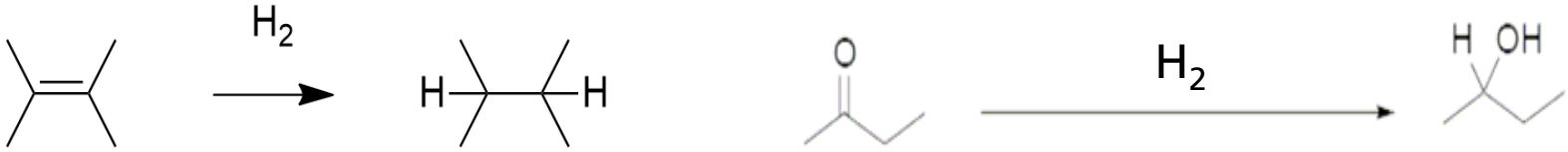
# 2nd step: Hydrogenation

Thuenen-Institute for Wood Research, Hamburg (D. Meier)

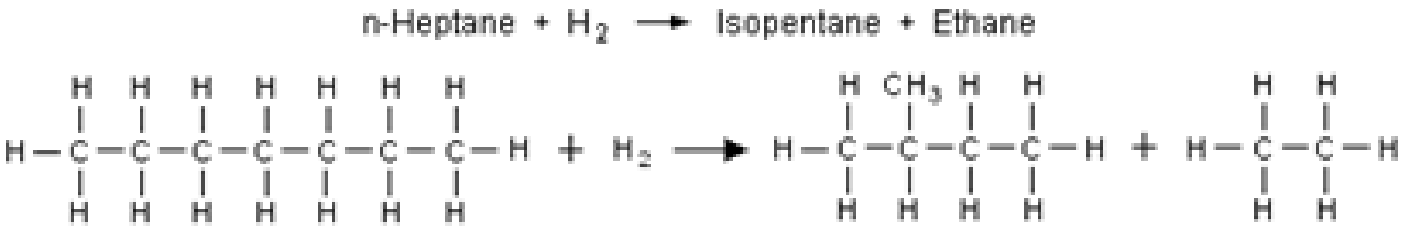
Hydrogenation of esterified pyrolysis liquid ($H_2$ from char reforming)

Two Options:

1. Hydrotreatment (mild reaction conditions / low $H_2$ partial pressure)




2. Hydrocracking (severe reaction conditions / high $H_2$ partial pressure)







Fraunhofer UMSICHT

# AGENDA

1. Fraunhofer Gesellschaft and Fraunhofer UMSICHT
2. Fraunhofer Innovation Cluster »Bioenergy«
3. Ablative Flash Pyrolysis
4. Staged Condensation
5. Catalytic Treatment
6. **Summary**

# Summary

- ablative flash pyrolysis
  - laboratory plant for different feedstock operational,
    tests for in-situ upgrade planned for near future
  - functional model for mobile plant (based on straw) in commisioning

- staged condensation of pyrolysis vapours
  - promising first result
    3 different fractions with high potential for value creation
  - future tests with varying temperatures and different feedstock

- esterification of pyrolysis condensate (catalytic treatment)
  - promising first results
    reduced acid number, water content, oxygen/carbon ratio
    increased heating value
  - future tests with varying catalysts and different feedstock

# FRAUNHOFER UMSICHT

## Biorefinery and Biofuels

# Thank You for Your attention!


### Funding notice

Fraunhofer Innovation cluster Bioenergy is partly funded by the Ministry of Innovation, Science and Research of North Rhein-Westphalia (MIWF) with funds from the European Regional Development Fund (ERDF) and by Fraunhofer Gesellschaft zur Förderung der angewandten Forschung e.V.
Catalytic treatment is funded by the Federal Ministry of Food and Agriculture through its funding agency FNR e.V. by decision of the German Bundestag.



**Contact:**

**Fraunhofer UMSICHT**
Osterfelder Straße 3
46047 Oberhausen, Germany
E-Mail: info@umsicht.fraunhofer.de
Internet: http://www.umsicht.fraunhofer.de

**Tim Schulzke**
Telefon: +49 208 8598-1155
E-Mail: tim.schulzke@umsicht.fraunhofer.de

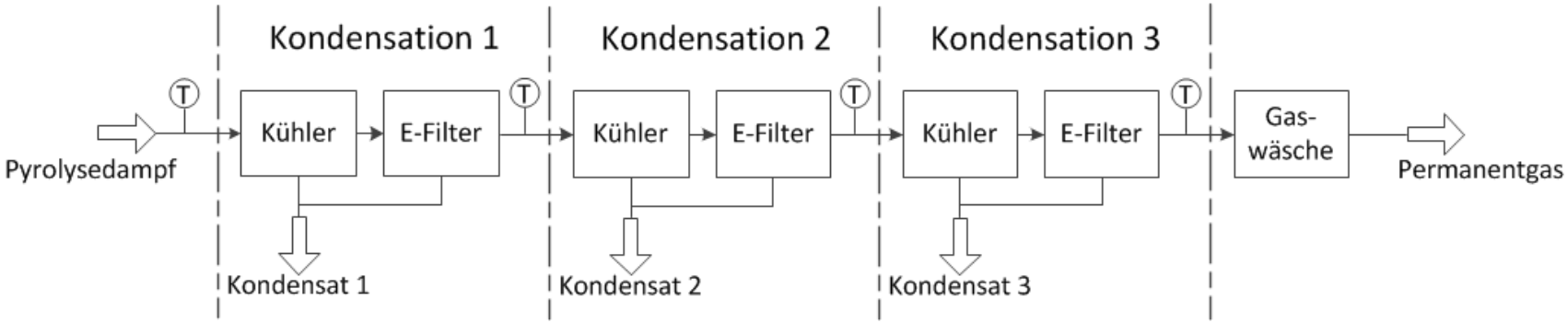




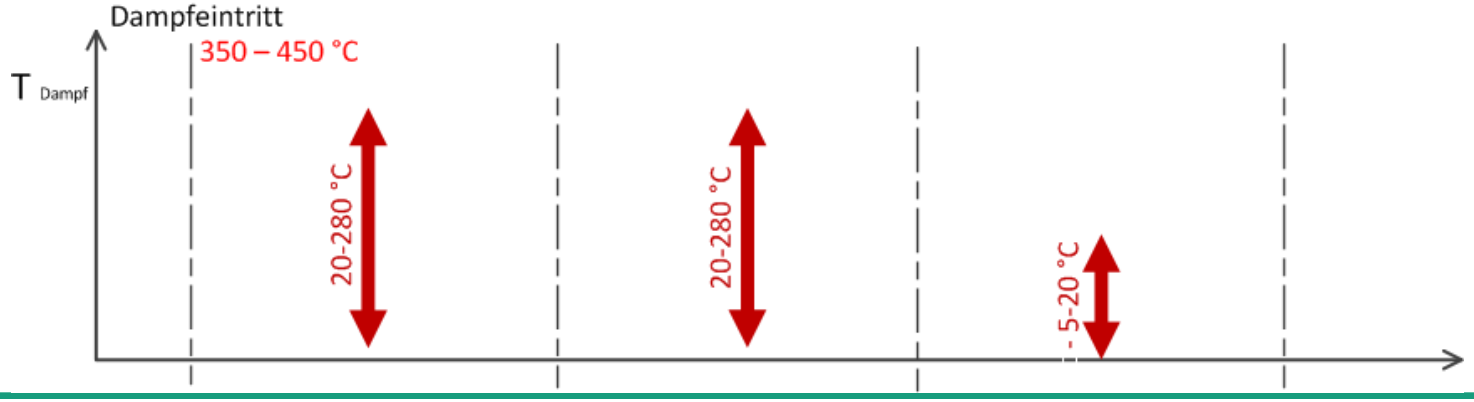
Fraunhofer UMSICHT

# Staged Pyrolysis Vapour Condensation - Approach

## Basic flow chart




## Condensation temperature



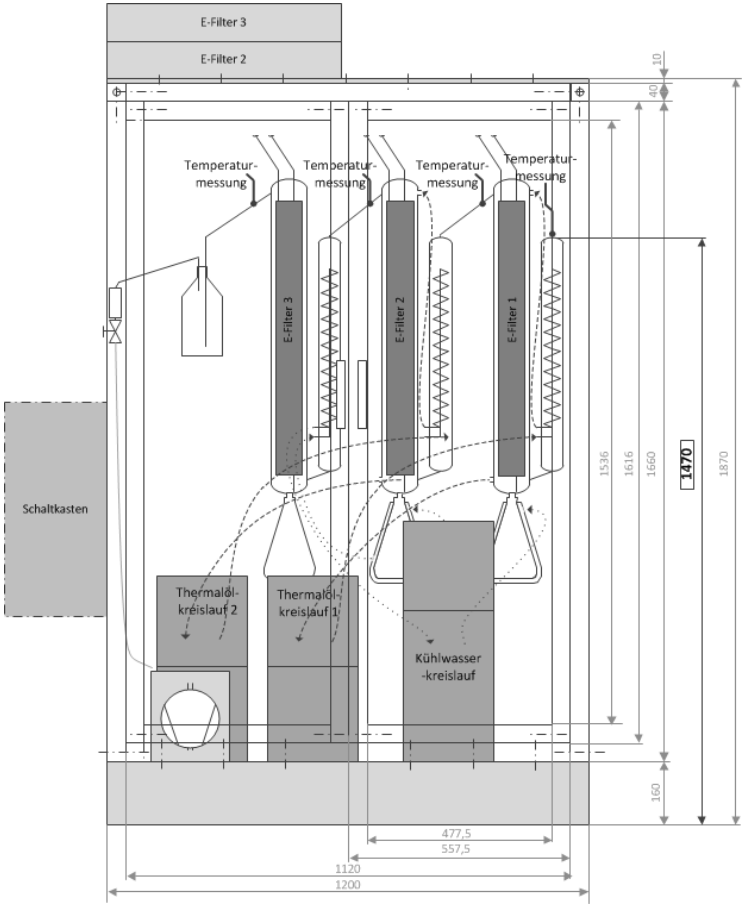


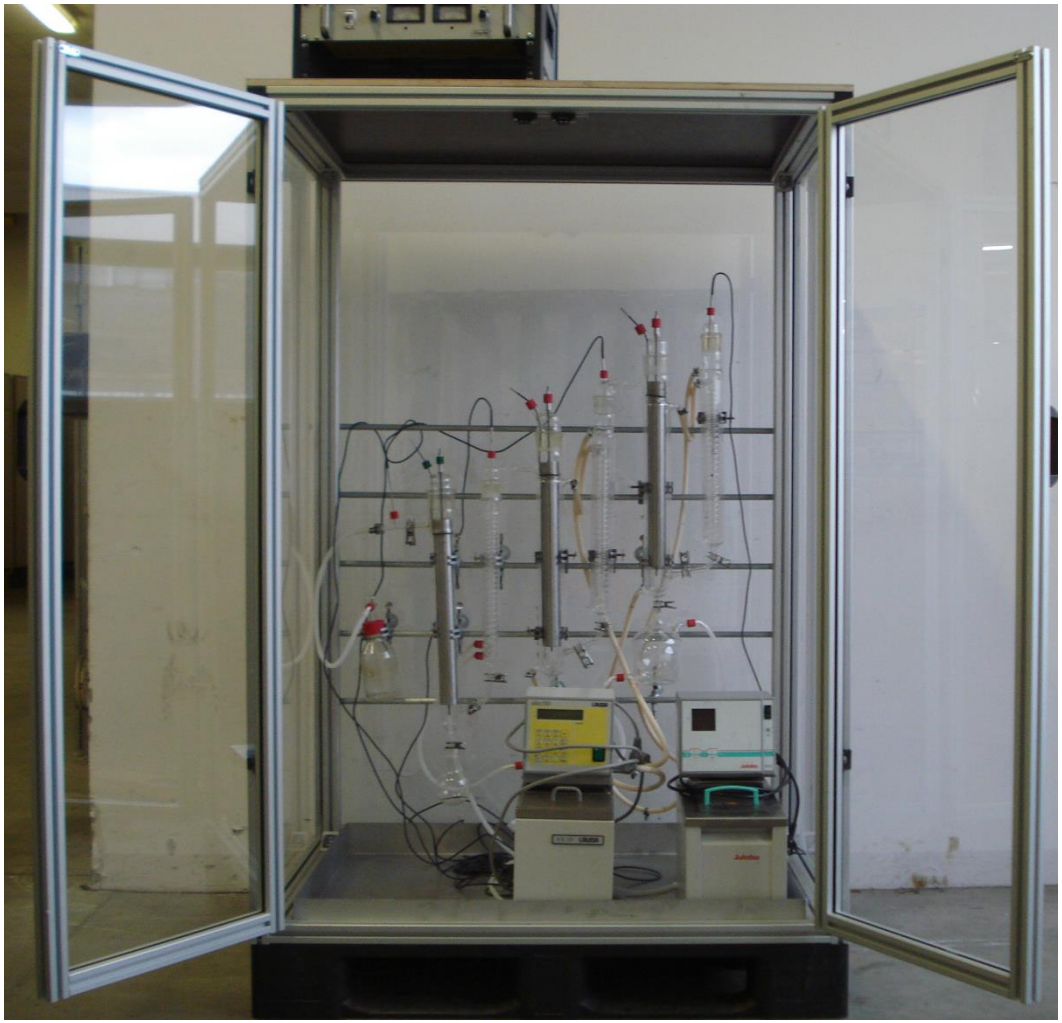


Fraunhofer UMSICHT

# Staged Pyrolysis Vapour Condensation - Assembly

## Test Plant






Fraunhofer UMSICHT