ABLATIVE FAST PYROLYSIS – PROCESS FOR VALORIZATION OF RESIDUAL BIOMASS

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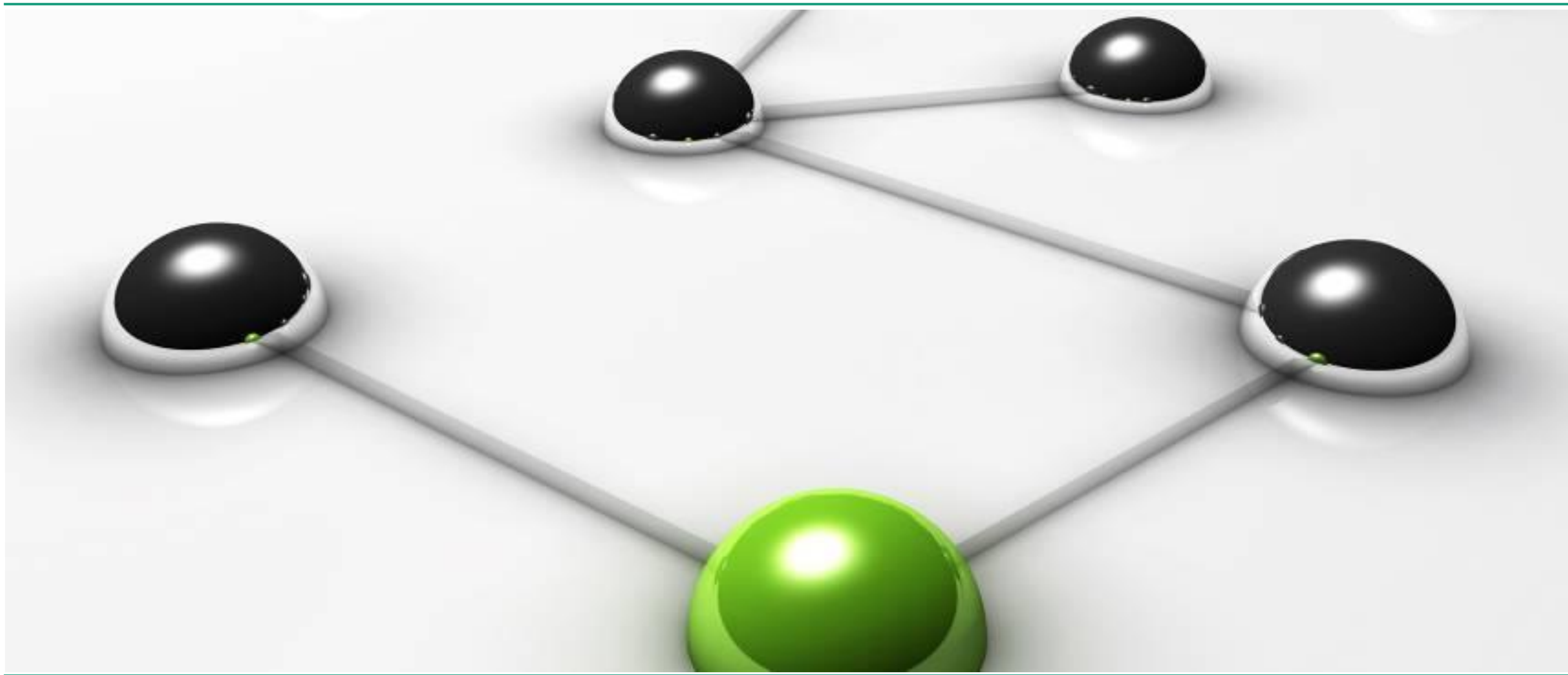

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Outline

1. Fundamentals of pyrolysis
2. Ablative fast pyrolysis – results from laboratory test rig
3. Application of biooil – Upgrade by staged condensation
4. Examples for application of biooil fractions
   - Phenolic resin for non-structural timber
   - Rigid polyurethane foams
5. Summary

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Definition of Pyrolysis

Pyrolytic decomposition means a thermo-chemical conversion, which - in contrary to gasification or combustion - takes place only under the influence of heat in absence of any additionally introduced oxygen (equivalence ratio = 0).

As *wet* biomass contains oxygen (wood ≈ 44 weight-%) and (*bound*) water, the reactions within pyrolytic decomposition may still be oxidation reactions (*at least part of them*).

During pyrolytic decomposition […] longchain organic compounds contained in the biofuel are cracked due to the introduced heat energy into shorter chain compounds which are mainly liquid or gaseous under normal conditions; additionally a solid residue called biochar occurs during this thermo-chemical process.

Translated from: Kaltschmitt, Hartmann, Hofbauer (Eds.): Energie aus Biomasse, 2nd Edtiton, Springer-Verlag Berlin, 2009, pp. 378-9

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Pyroloysis processes - Characteristics

The different pyrolysis processes are characterized by the following parameters:

- heating rate,
- residence time of original material within the reaction zone,
- residence time of primary products within the reaction zone and
- target products,

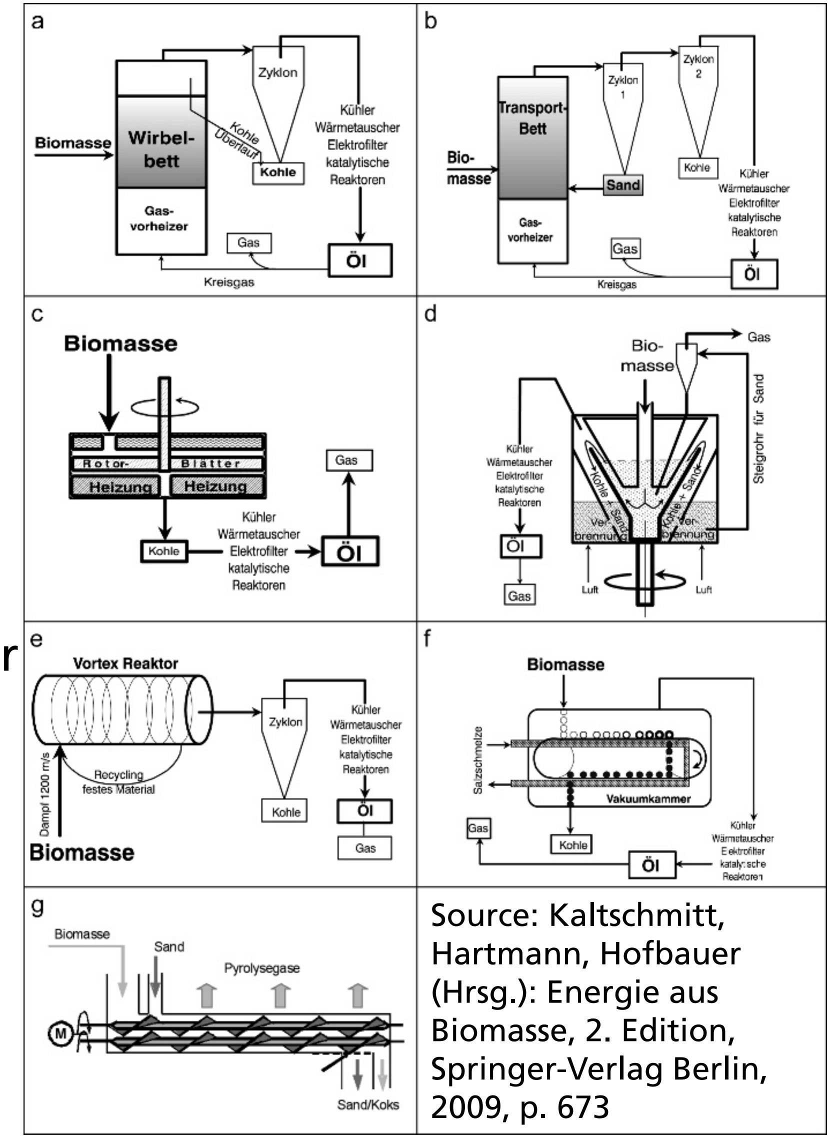
in which the parameters are not fully independent.

There are 2 larger groups of pyrolysis processes:

- Slow Pyrolysis (traditional: charcoal burning)
  target product charcoal
  low heating rate, long residence time in reactor
  (educt days + vapour minutes)
- Fast pyrolysis
  target product biooil
  high heating rate (≈ 1000 °C/s), short residence time vapour (< 1 s),
  medium residence time educt (minutes)

Reactor types for fast pyrolysis

- a) bubbling fluidized bed
- b) circulating fluidized bed
- c) ablative fast pyrolysis
- d) rotating cone reactor
- e) vortex reactor
- f) vacuum reactor
- g) twin screw reactor



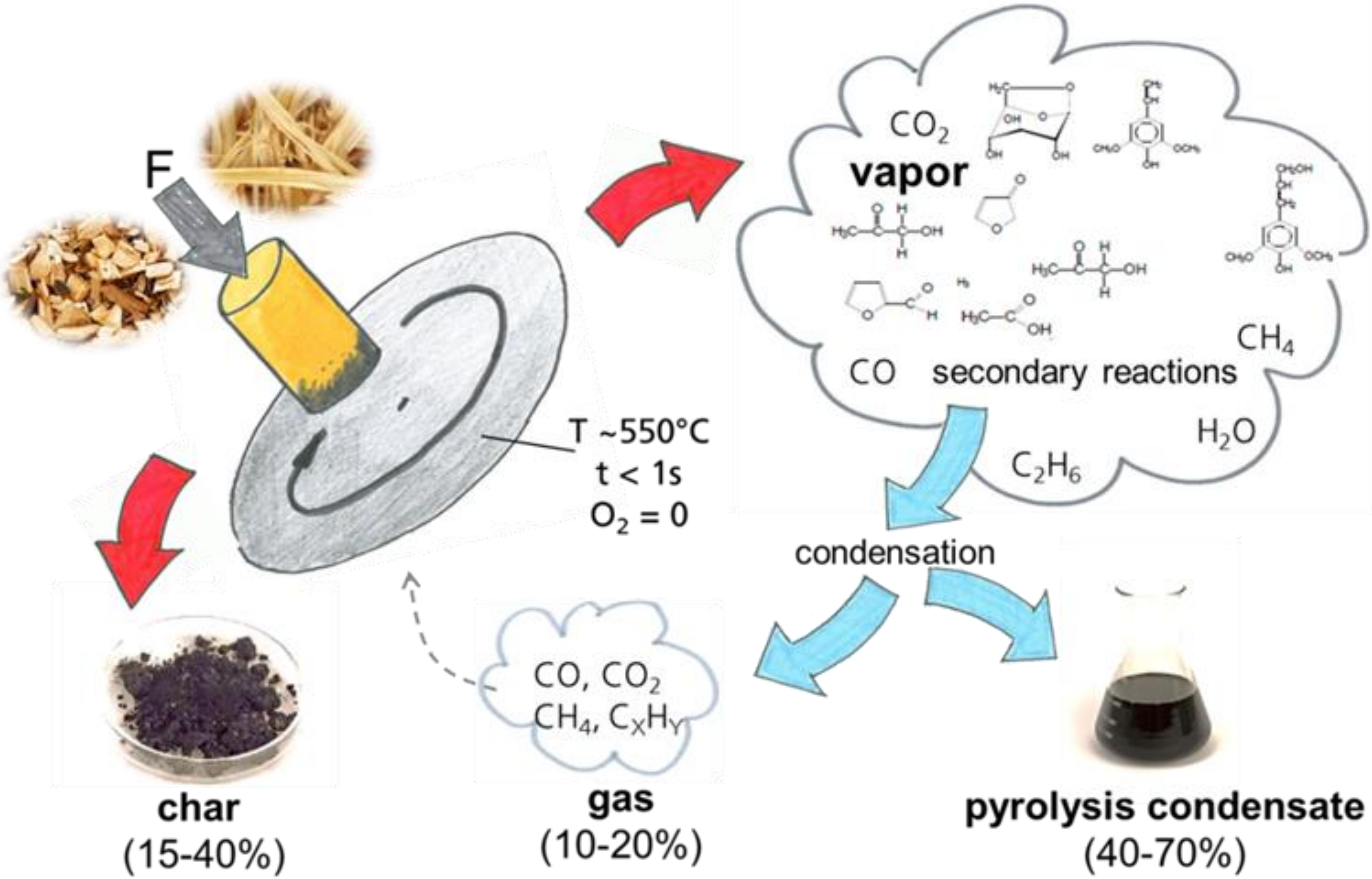
Source: Kaltschmitt, Hartmann, Hofbauer (Hrsg.): Energie aus Biomasse, 2. Edition, Springer-Verlag Berlin, 2009, p. 673

a, b, d, g need bed material as heat carrier

a, b, d, e, f, g require small particles to ensure high heating rates

While (dry) wood can be milled relatively efficient, herbaceous biomass needs very high milling energy.

Principle of ablative fast pyrolysis



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Ablative flast pyrolysis – Experimental facilities

Laboratory plant

10 kg/h

heat supply: electrical resistance heater

wood and straw

Functional model for mobile plant

100 kg/h (design capacity)

heat supply: flue gas (propane combustion)

straw only

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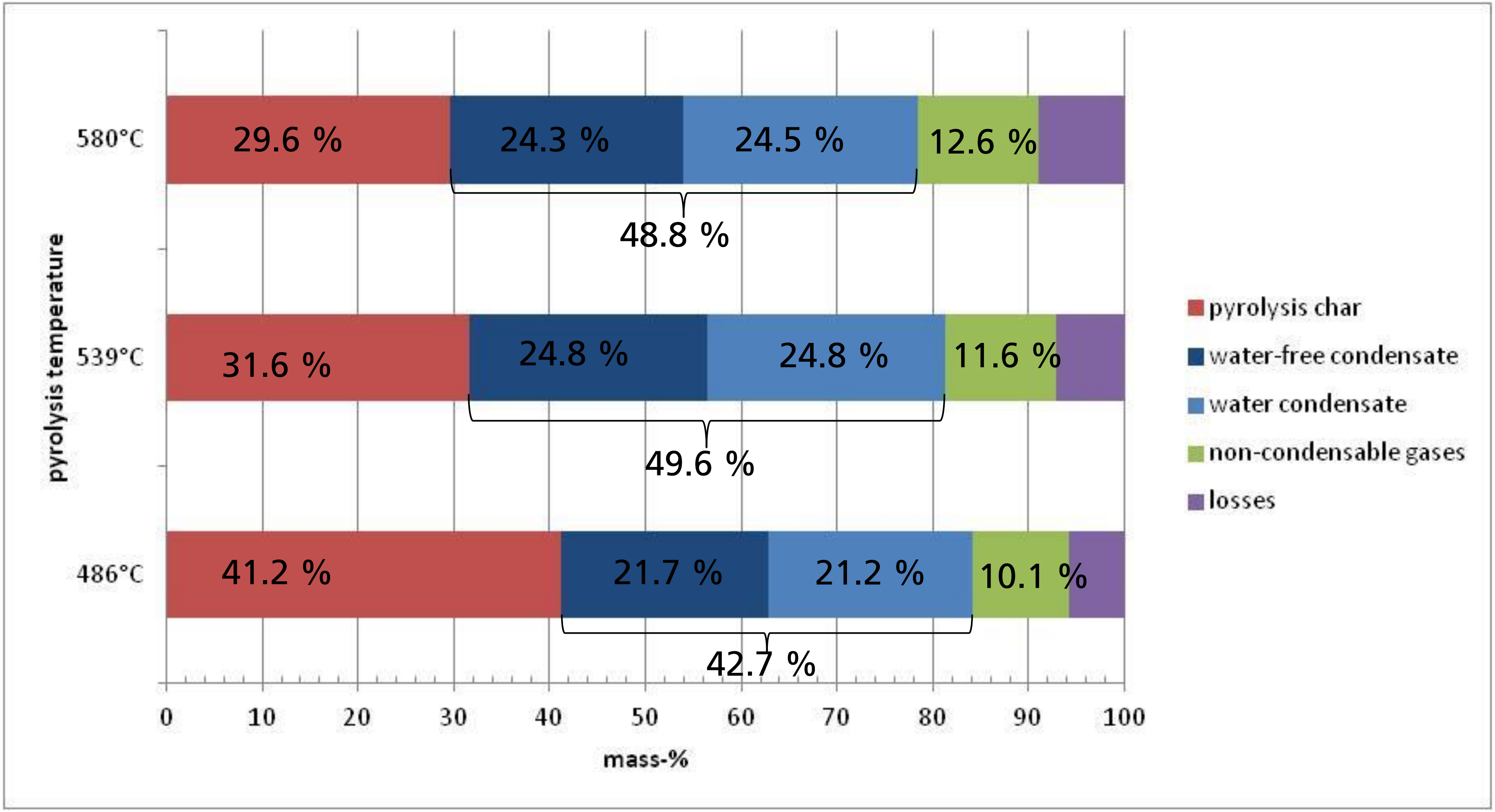
Mass balance – Results from pyrolysis of wheat/barley straw



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Ablative fast pyrolysis – Quality of pyrolysis biooil

Pyrolysis temperature	486 °C	539 °C	580 °C
total Water	49.4 %	49.9 %	50.3 %
reaction Water	31.6 % / 64 %	35.1 % / 70 %	34.4 % / 68 %
nonaromatic Acids	6.1 %	6.9 %	10.7 %
nonaromatic Alcohols	0.9 %	1.1 %	2.1 %
nonaromatic Aldehydes	0.4 %	0.4 %	0.4 %
nonaromatic Ketones	5.5 %	6.3 %	10.9 %
Phenols	4.1 %	4.7 %	4.4 %
Sugars	1.8 %	1.6 %	2.0 %
Heterocyclic Sub.	1.8 %	1.9 %	2.1 %
not GC-detectable Sub.	30.5 %	26.7 %	22.8 %

wheat / barley straw; original water content approx. 8 weight-%

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Ablative fast pyrolysis – Quality of pyrolysis biooil

	aqueous	organic	Beech wood
mass ratio	67.5 %	32.5 %	100 %
total Water	61.7 %	25.3 %	28.7 %
nonaromatic Acids	7.4 %	5.9 %	10.4 %
nonaromatic Alcohols	1.5 %	0.3 %	0.2 %
nonaromatic Aldehydes	0.0 %	1.1 %	3.5 %
nonaromatic Ketones	5.9 %	7.1 %	5.5 %
Phenols	1.2 %	12.0 %	7.7 %
Sugars	1.6 %	1.5 %	6.0 %
Heterocyclic Sub.	1.4 %	2.9 %	2.7 %
not GC-detectable Sub.	19.1 %	42.4 %	34.8 %
lower heating value	7.9 MJ/kg	22.3 MJ/kg	15.4 MJ/kg

wheat / barley straw at 549 °C, beech wood at 550 °C

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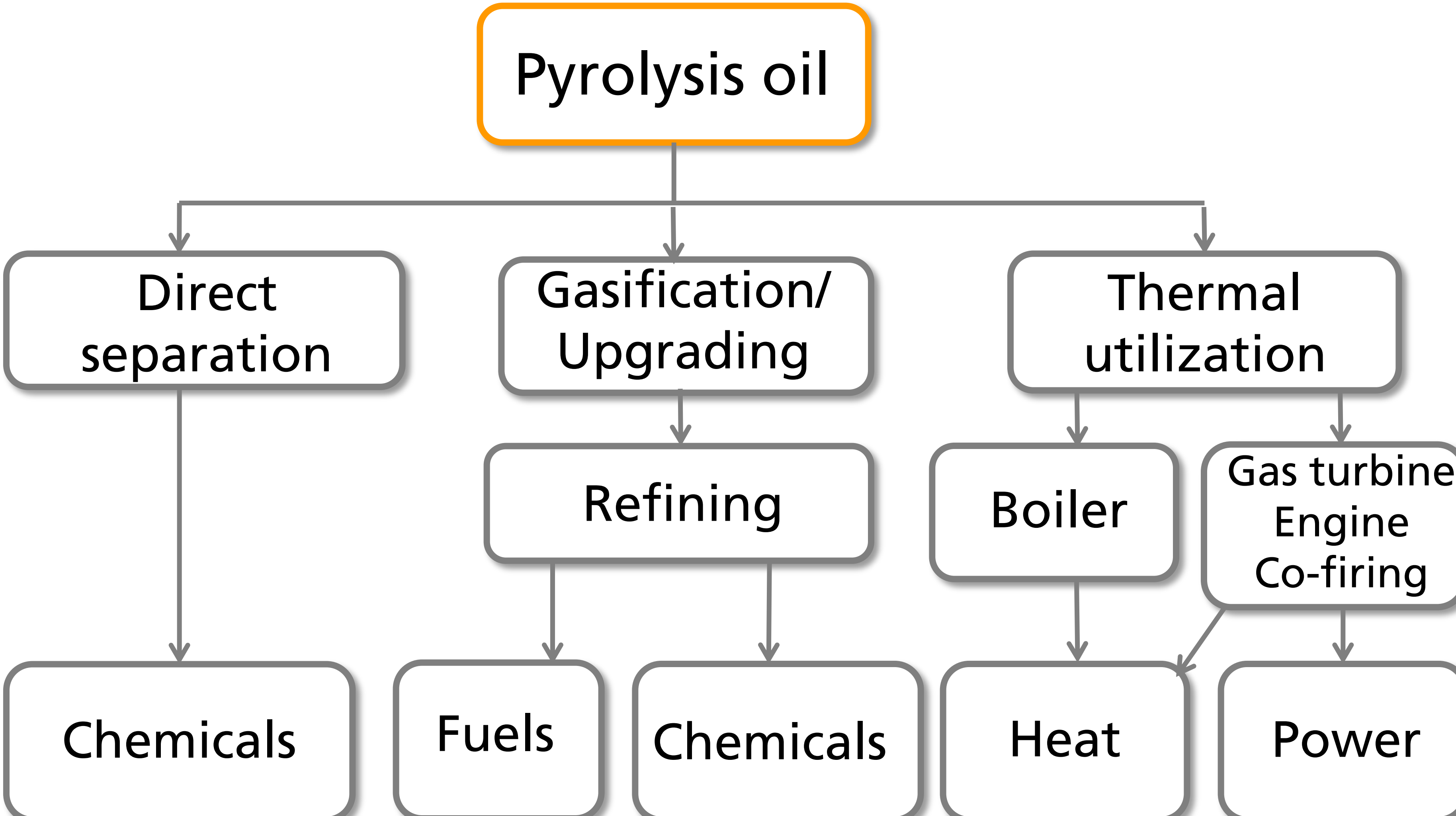
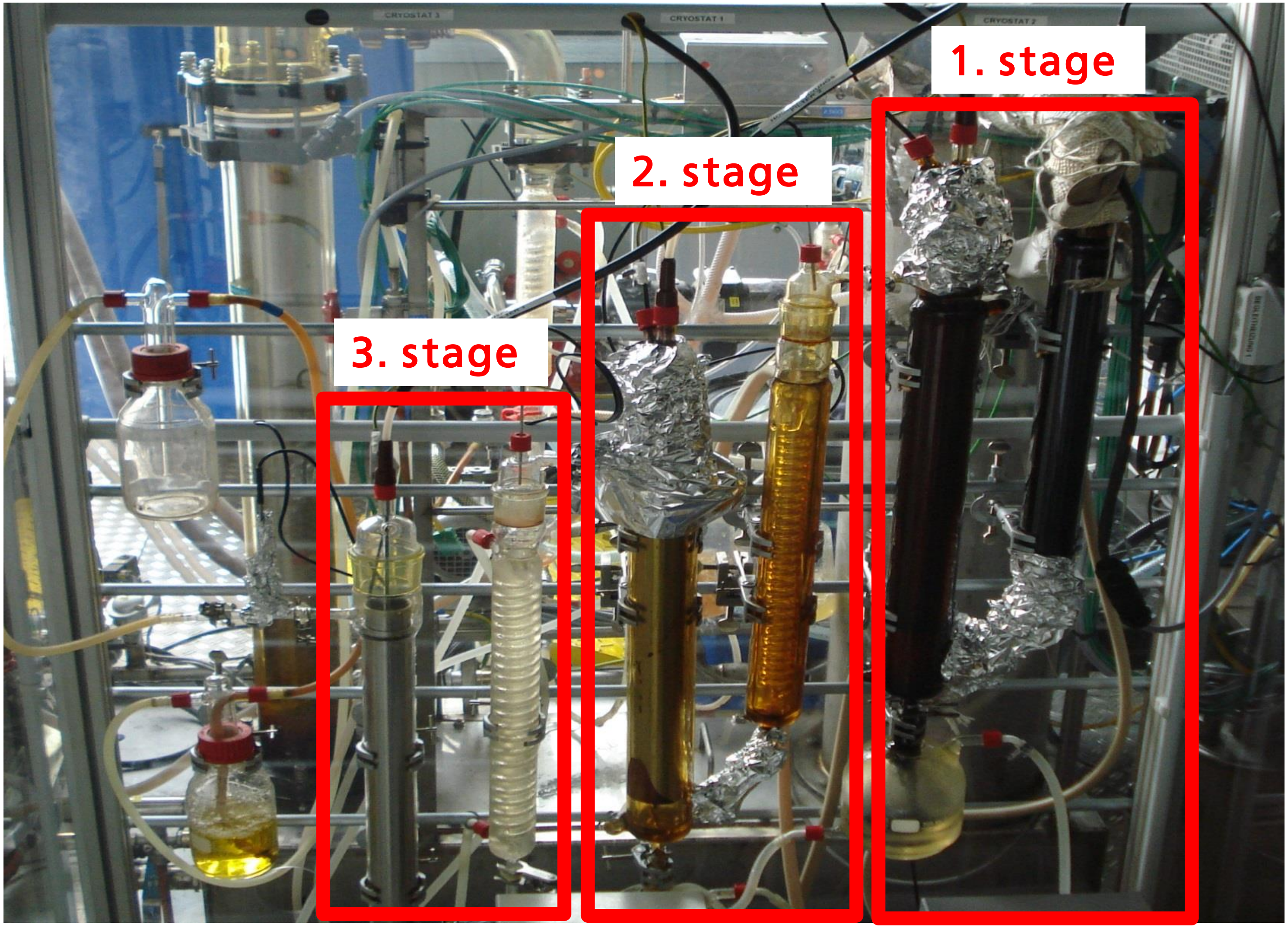
Applications for pyrolysis biooil



Staged condensation – Approach



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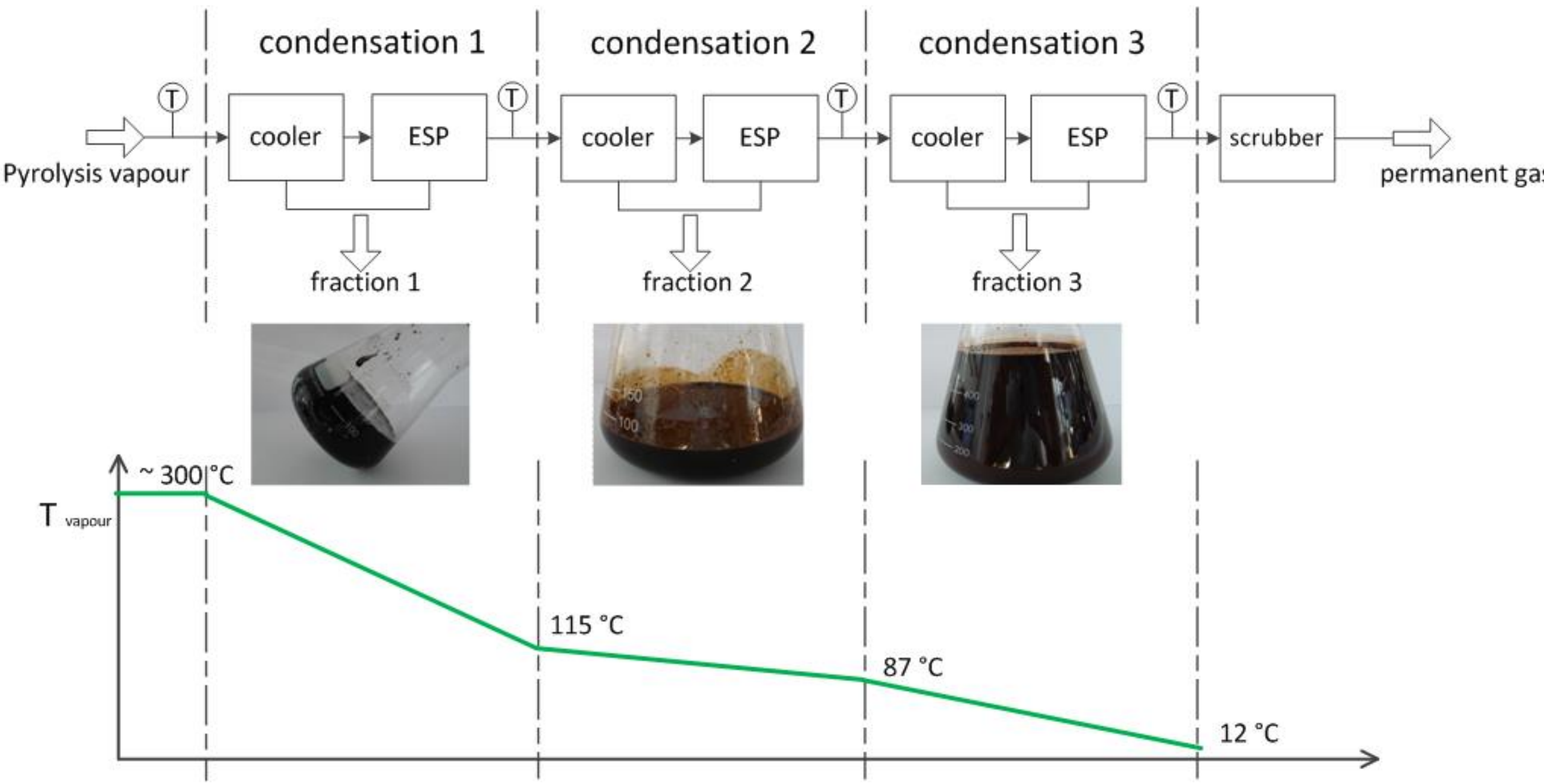
Staged Condensation – Three stages experiment



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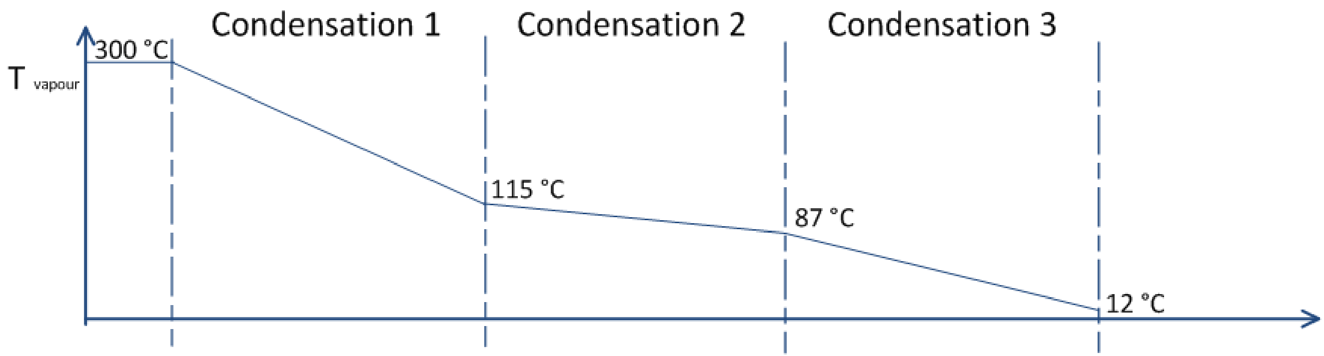

	Condensation 1	Condensation 2	Condensation 3	Total condensate (two-phase) weighted average values
Ratio [1]	23 %	10 %	67 %	
Water [2]	2 %	8 %	70 %	46 %
Acids [2]	1 %	6 %	9 %	7 %
nonaromatic Aldehydes [2]	0 %	3 %	0 %	1 %
nonaromatic Ketones [2]	1 %	12 %	7 %	7 %
Phenoles [2]	11 %	20 %	1 %	5 %
Sugars [2]	6 %	5 %	0 %	2 %
not detected substances [2]	79 %	38 %	10 %	30 %
Heating Value (LHV) [2]	28 MJ/kg	22 MJ/kg	6 MJ/kg	12 MJ/kg

[2] based on the fraction
[1] based on the raw material

Condensate of wheat/barley straw
550°C, 50 bar pressure

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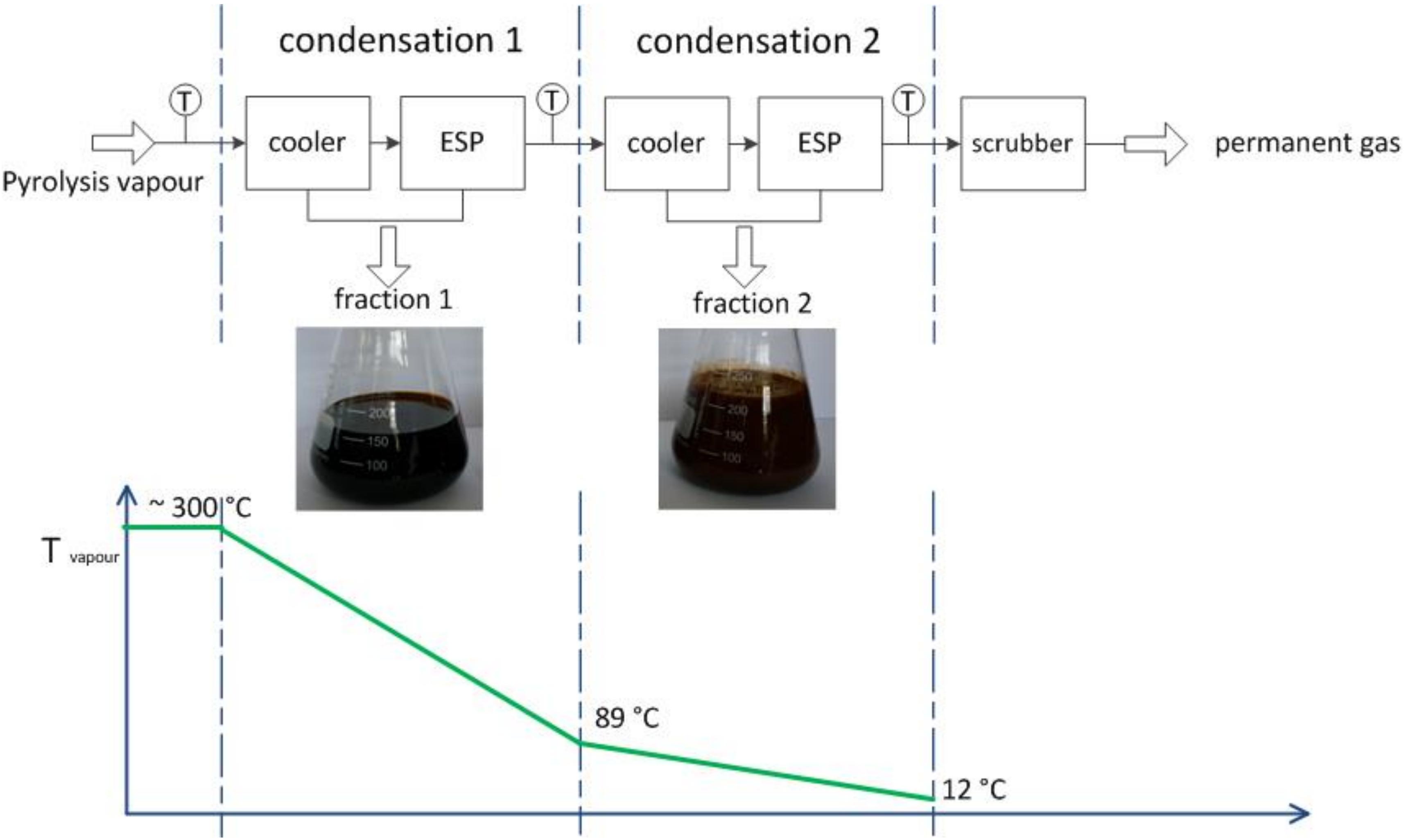
Staged Condensation – Two stages experiment



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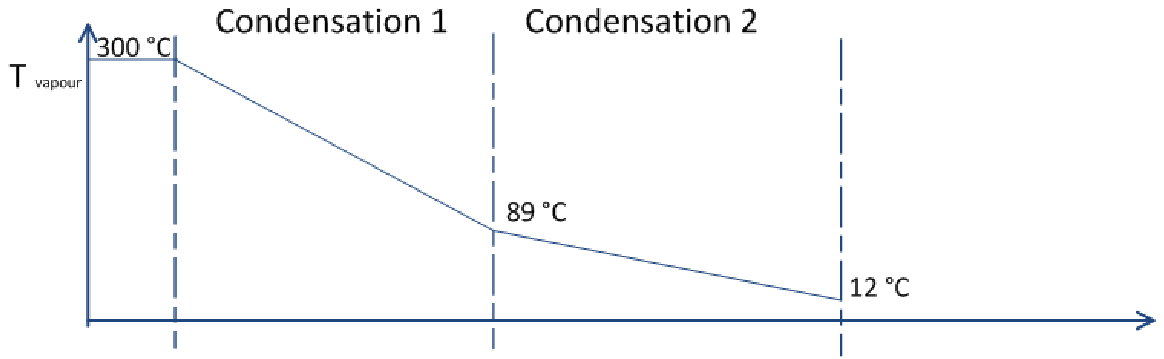
Staged Condensation – Two stages experiment



	Condensation 1	Condensation 2	Total condensate (two-phase) weighted average values
	45 %	55 %	
Water [2]	10 %	75 %	46 %
Nonaromatic Acids [2]	7 %	8 %	7 %
nonaromatic Aldehydes [2]	3 %	0 %	1 %
nonaromatic Ketones [2]	8 %	6 %	7 %
Phenoles [2]	12 %	0 %	5 %
Sugars [2]	4 %	0 %	2 %
not detected substances[2]	52 %	8 %	30 %
Heating Value (LHV) [2]	23 MJ/kg	5 MJ/kg	12 MJ/kg

[2] based on the fraction
[1] based on the raw material

Condensate of wheat/barley straw
539 °C, 50 bar pressure

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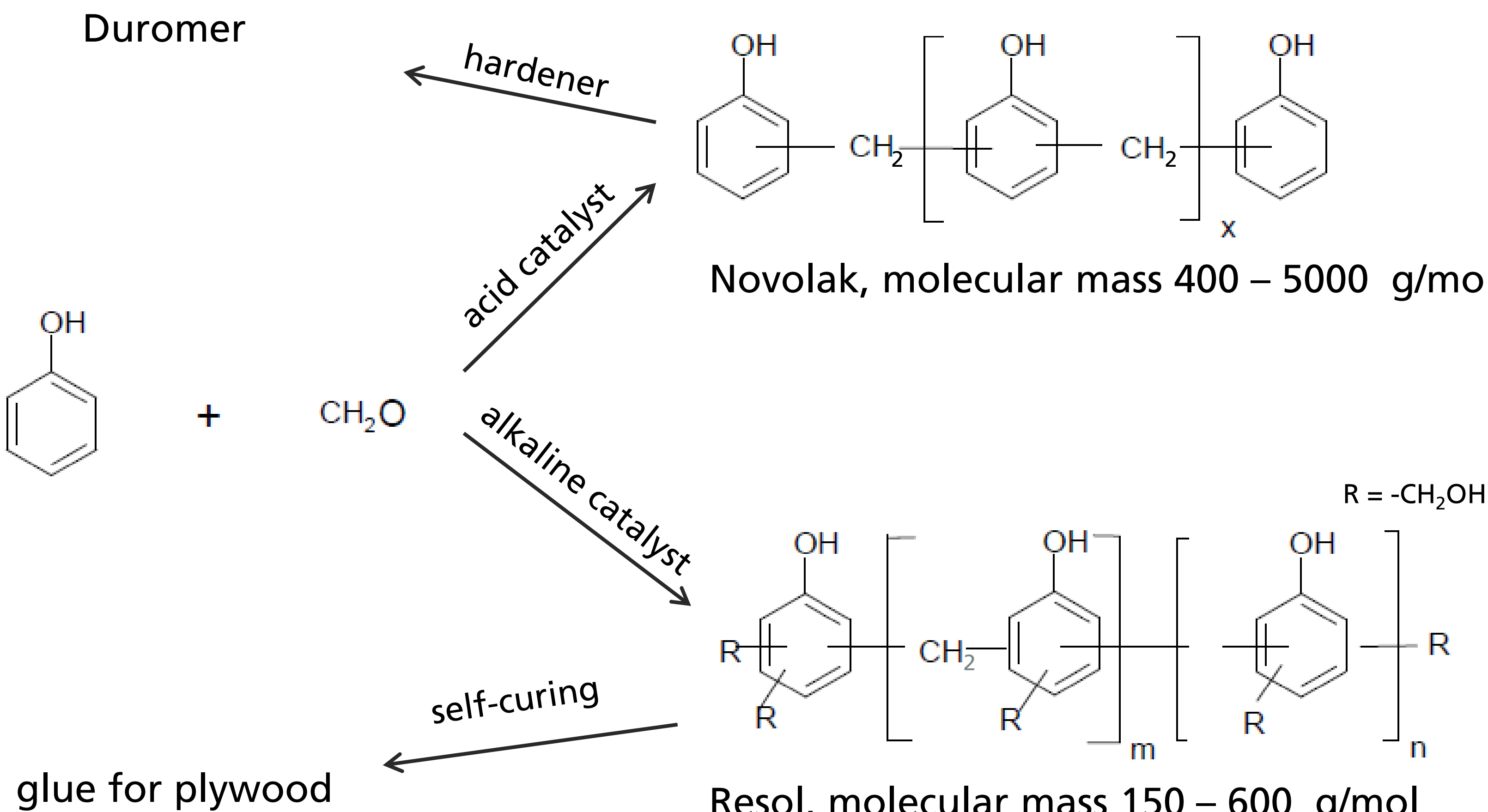
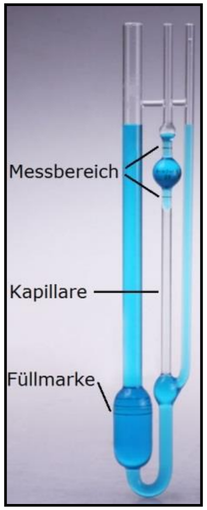
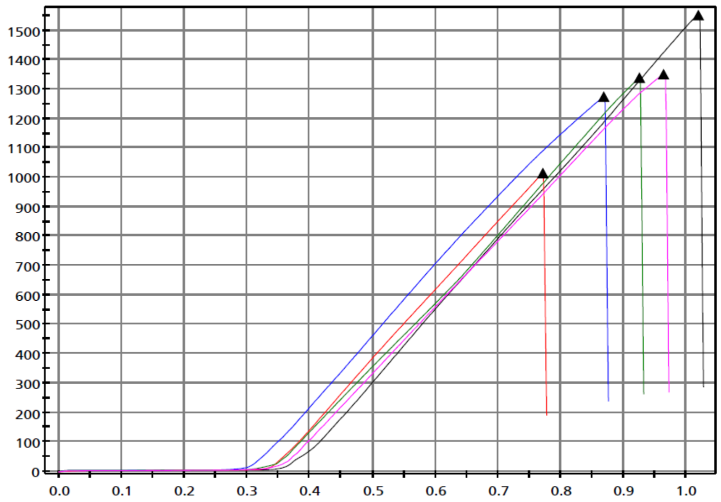
Phenolic resin as wood glue in non-structural timber



Phenolic resin as wood glue in non-structural timber



Tensile strength measurement according to DIN EN 205



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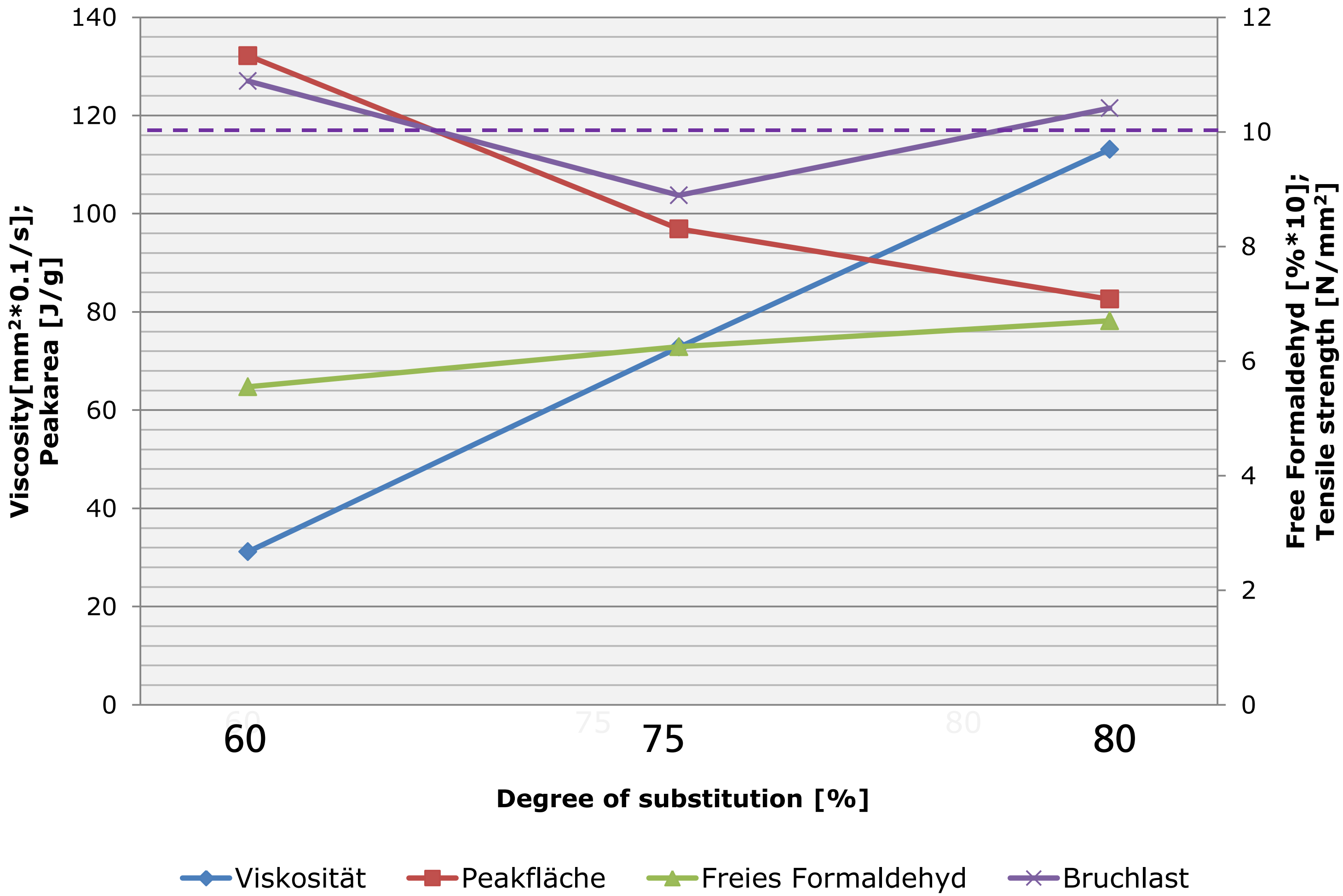

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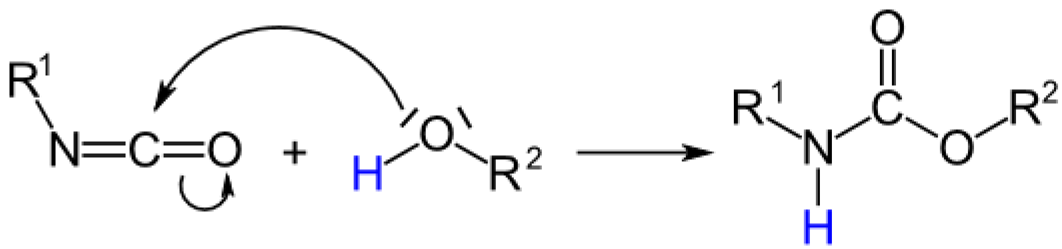
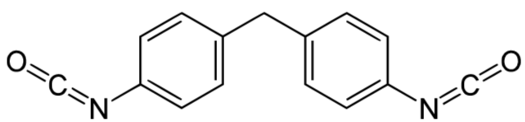
Rigid polyurethane foams

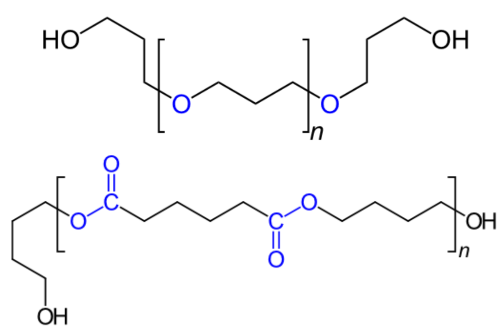


Isocyanate   Alcohol   Urethane

small amount of water releases CO_2



→ Di-isocyanate



→ Polyether-dialcohol / Polyester-dialcohol

to be substituted by pyrolysis oil

Rigid polyurethane foams

First tests were promising

- Poly-Dialcohol component substituted by weight without any modification
- Poly-Dialcohol component contains
  - catalyst
  - foaming agent
  - stabilizer

substitution rate: 0 % 50 % 80 %

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Rigid polyurethane foams

Structured set of experiments conducted:
3 different types of biomass, varying method of biooil drying

Component A	concentration	Component B
Pyrolysis oil	0-80% of active mass	PMDI (polymeric methylene diphenylene diisocyanate)
PEG 400	rest of active mass	
Blowing agent (water)	4.1% of component A	
Catalyst DABCO	0.5% of active mass	
Catalyst SnOct	1.5% of active mass	
Surfactant / Stabilizer	2% of active mass	
Mixing the constituents		
Mixing two components （A:B = 100 : 145）		
Mixing time, Rising time		

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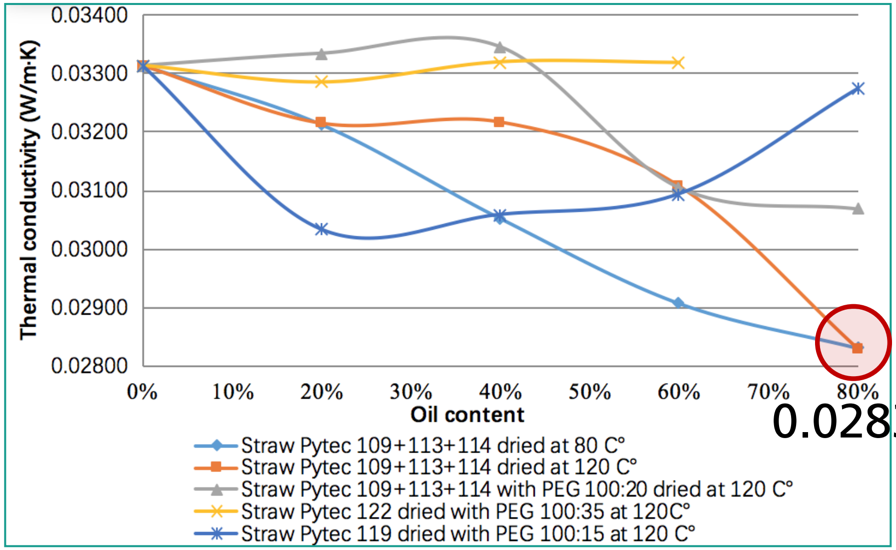
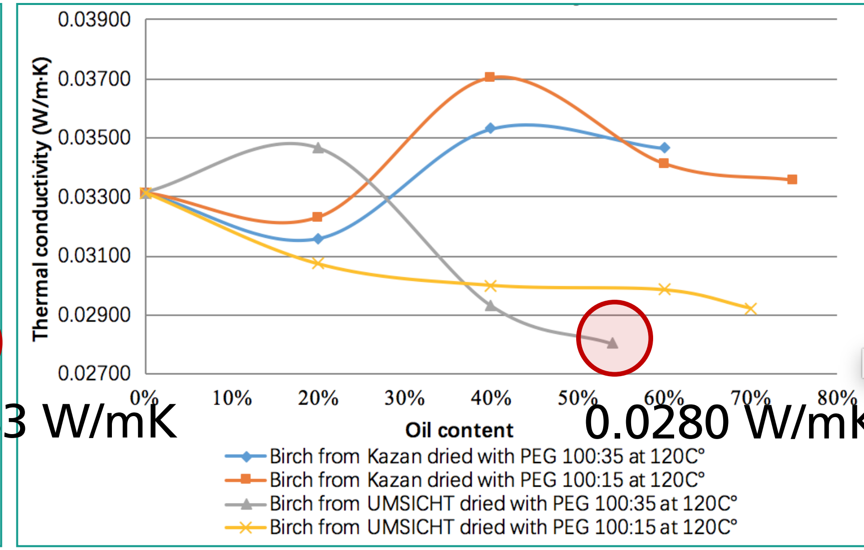
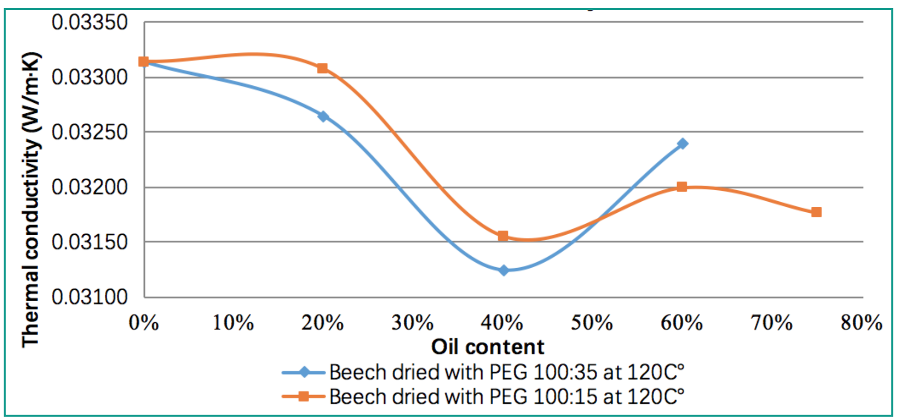
Rigid polyurethane foams

(1)Mixture of component A | (2)Adding component B | (3) Mixing | (4) Foaming beginning | (5) Foaming | (6) Foaming | (7) End

Rigid polyurethane foams







Commercial products : 0.02-0.03 W/mK

Sample with original recipe : 0.0308 W/mK

Benchmark material cut from insulation at Fraunhofer UMSICHT : 0.0282 W/mK

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Summary

- Economic assessment of decentraliced pyrolysis of straw showed general feasibility

- Principle of ablative Flash-Pyrolysis is well suitable for straw conversion

- Char can be used as catalyst, solid fuel or soil enhancer/fertilizer

- Condensates from flash pyrolysis of straw are always two-phase
  -> Utiliztation appears challenging, especially for aqeous phase

- Esterification yields single-phase product (stable, reduced corrosivity)
  -> higher value-added applications accessible (e.g. bunker fuel)

- staged condensation opens pathways to material utilization
  -> phenolic resins and rigid polyurethane foams partly based on biomass
  -> aqueous acidic residue can be valorized (e.g. in biogas plant)

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