Phenolic Resins Derived from Medium Boiling Fraction of Fast Pyrolysis Oil – Application as Wood Glue for Non-Load-Bearing Wooden Materials

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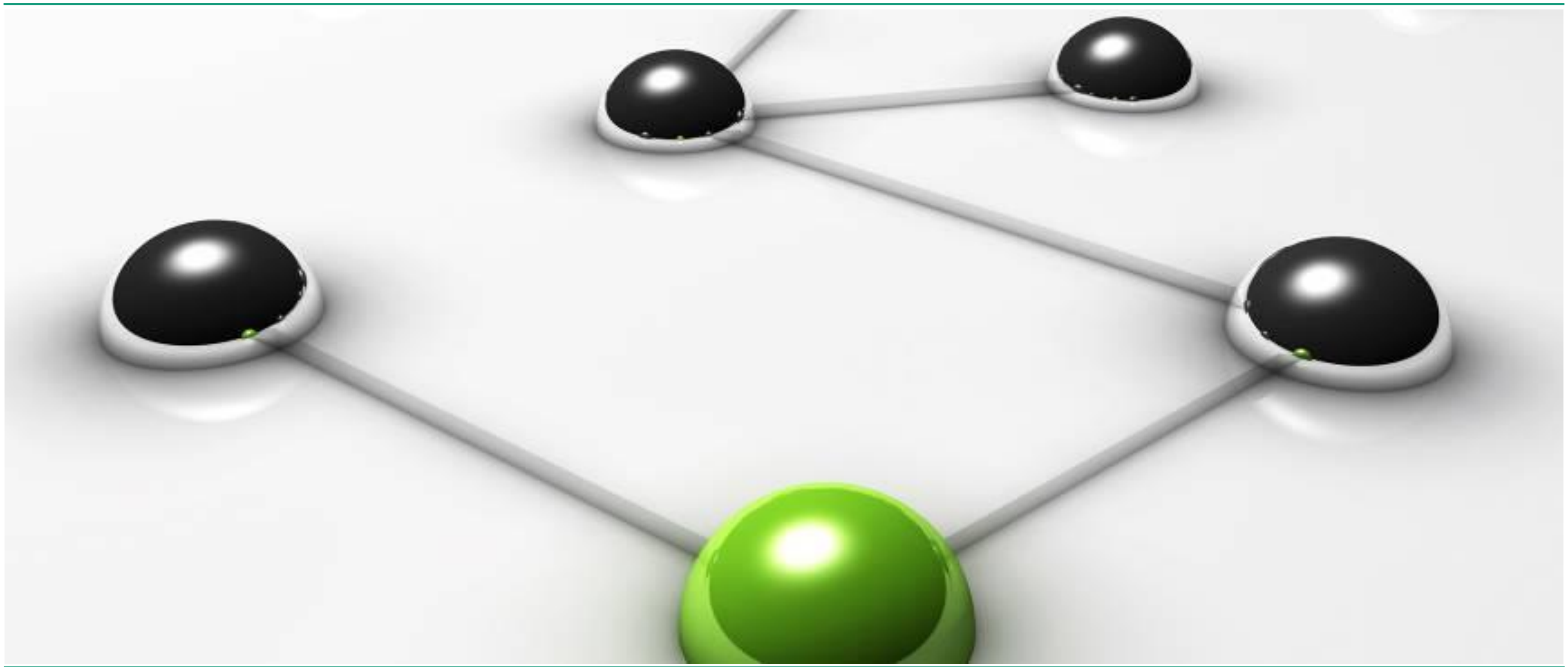

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Outline

1. Ablative Fast Pyrolysis of Herbaceous Biomass
2. Staged Condensation for Condensate Improvement
3. Phenol-Formaldehyde Resin
   - Preparation Procedure
   - Analytical Methods for Characterization
4. Orienting Tests
5. Parametric Study
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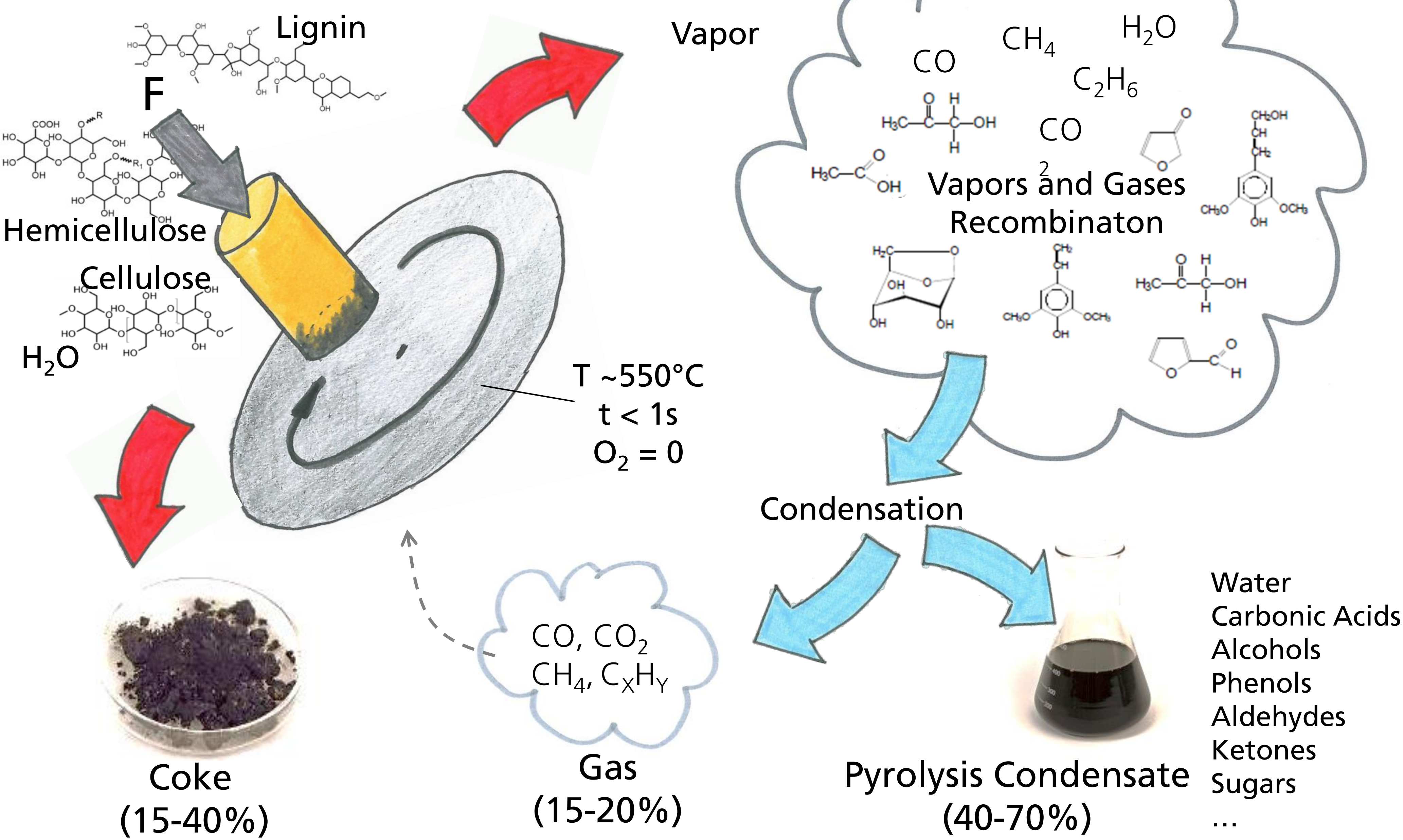
Principle of Ablative Fast Pyrolysis



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Main Reasons for Ablative Fast Pyrolysis

- Ablative fast pyrolysis does not need small particle sizes to acheive high heating rates at contact surface, because biomass has low heat conductivity, straw even lower than solid wood
  ⇒ no energy intensive grinding to < 1 mm necessary, easy briquetting instead

- Ablative fast pyrolysis does not require any heat transfer material
  ⇒ byproduct coke is received undiluted and does not need separation
  ⇒ reactor comparatively small

- Reactor for ablative fast pyrolysis works independent of orientation in space – potentially even mounted on a moving platform vehicle

- Quality of Condensates very similar to other fast pyrolysis concepts

- Only disadvantage: lower liquid yield compared to other fast pyolysis concpts (roughly 50 % instead of typically 60 % in the case of herbaceous biomass)

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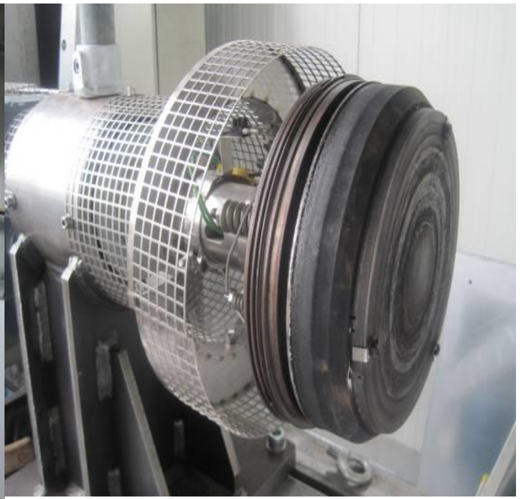
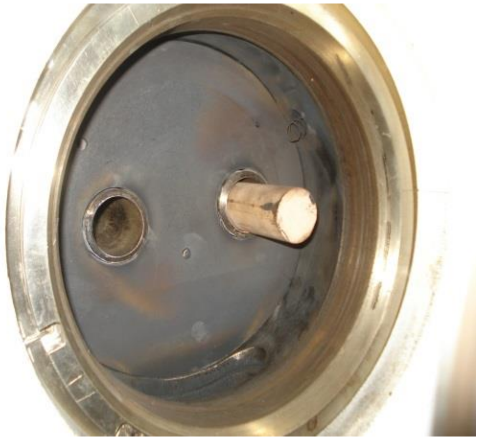
Laboratory Plant for Ablative Fast Pyrolysis

Enlargement of heated disc





Enlargement of biomasse entry
opposite side of heated surface

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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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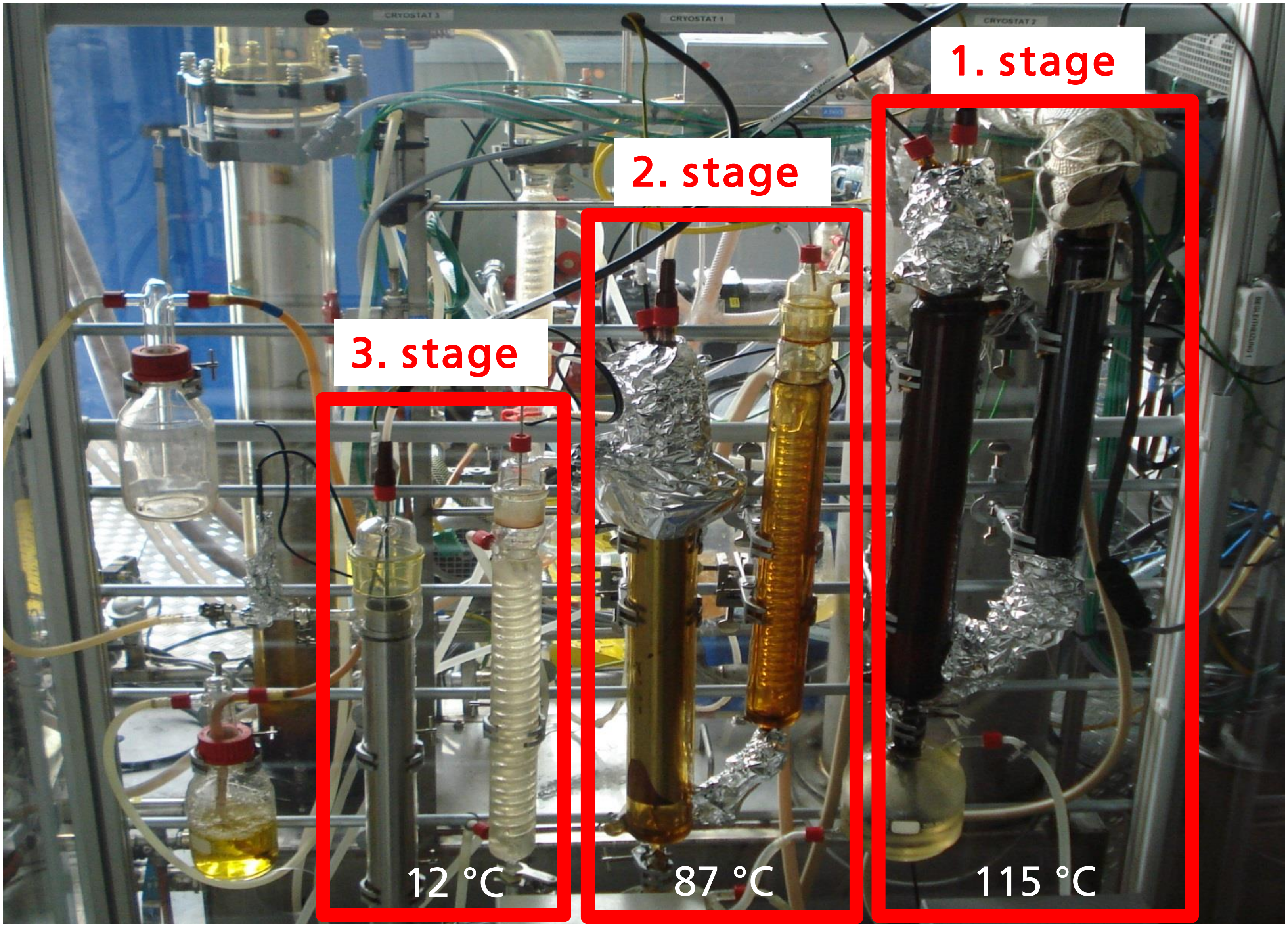
Staged condensation – Approach



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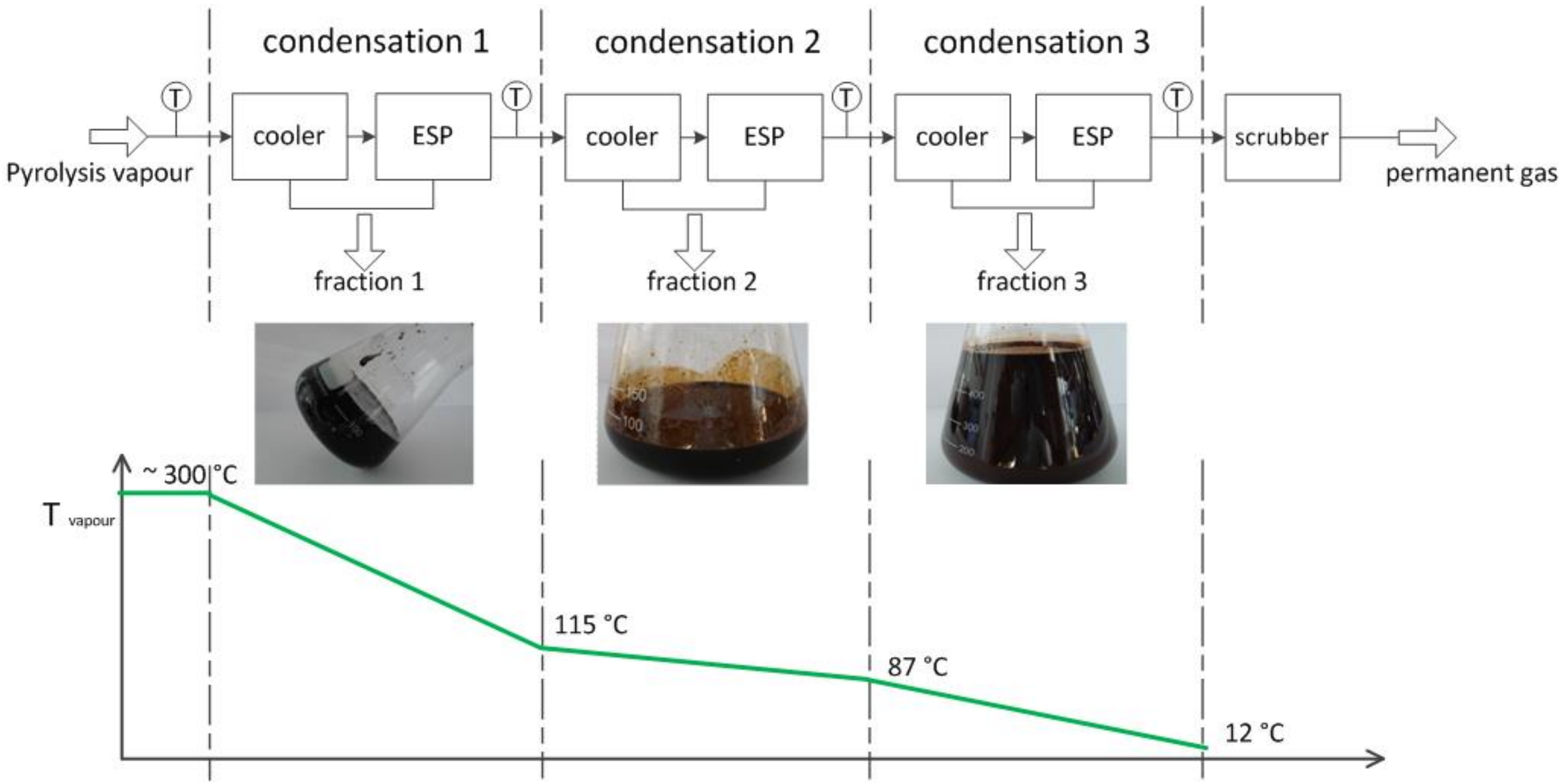
Staged Condensation – Three stages experiment



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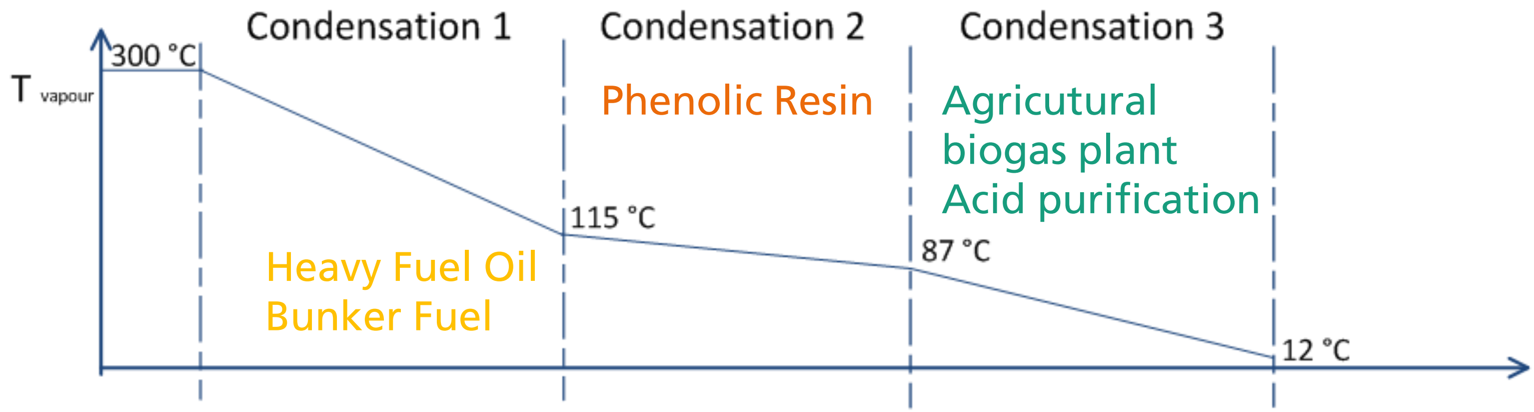
Staged Condensation – Three stages experiment



	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]	[illegible]	3 %	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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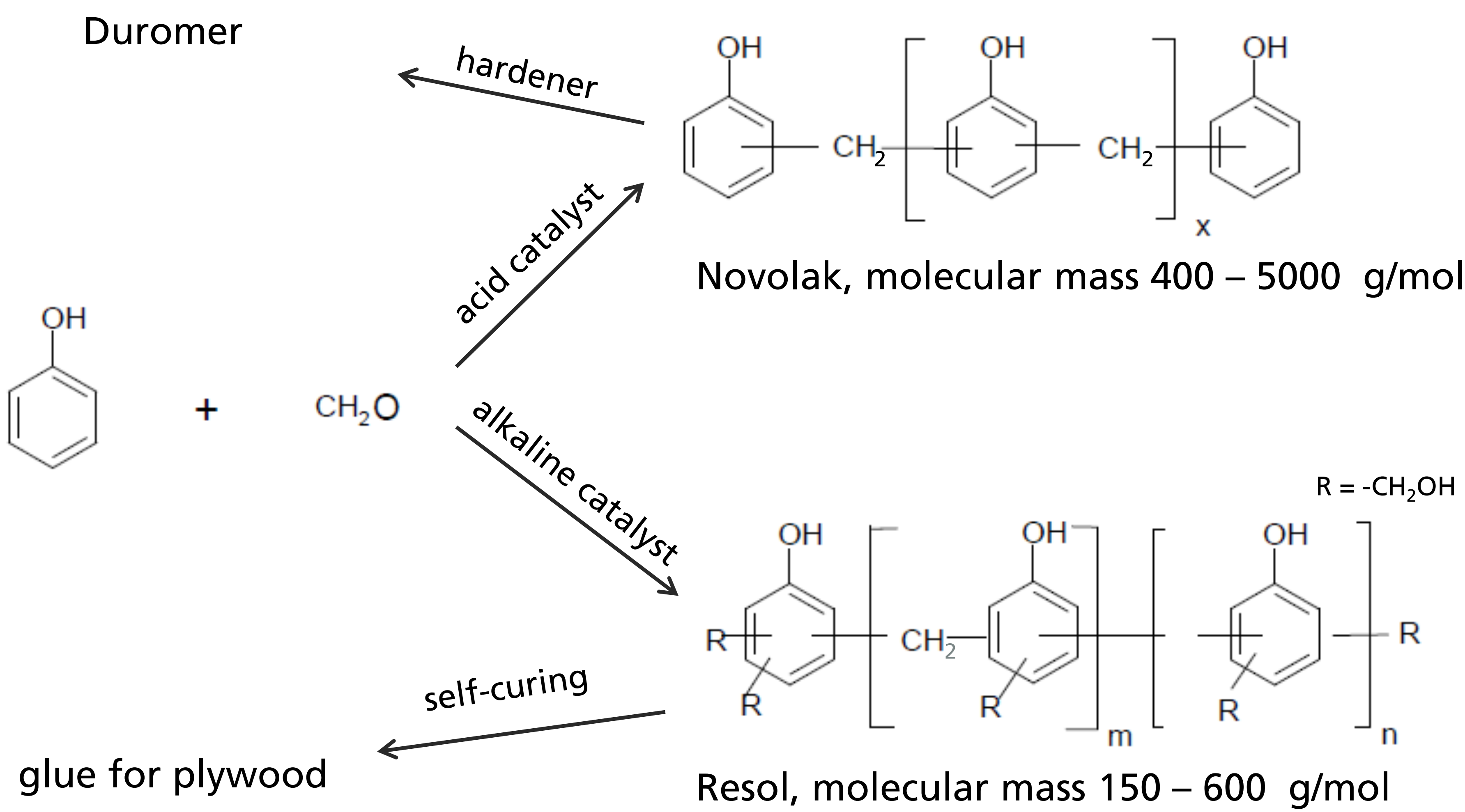
Phenolic resin as wood glue in non-structural timber



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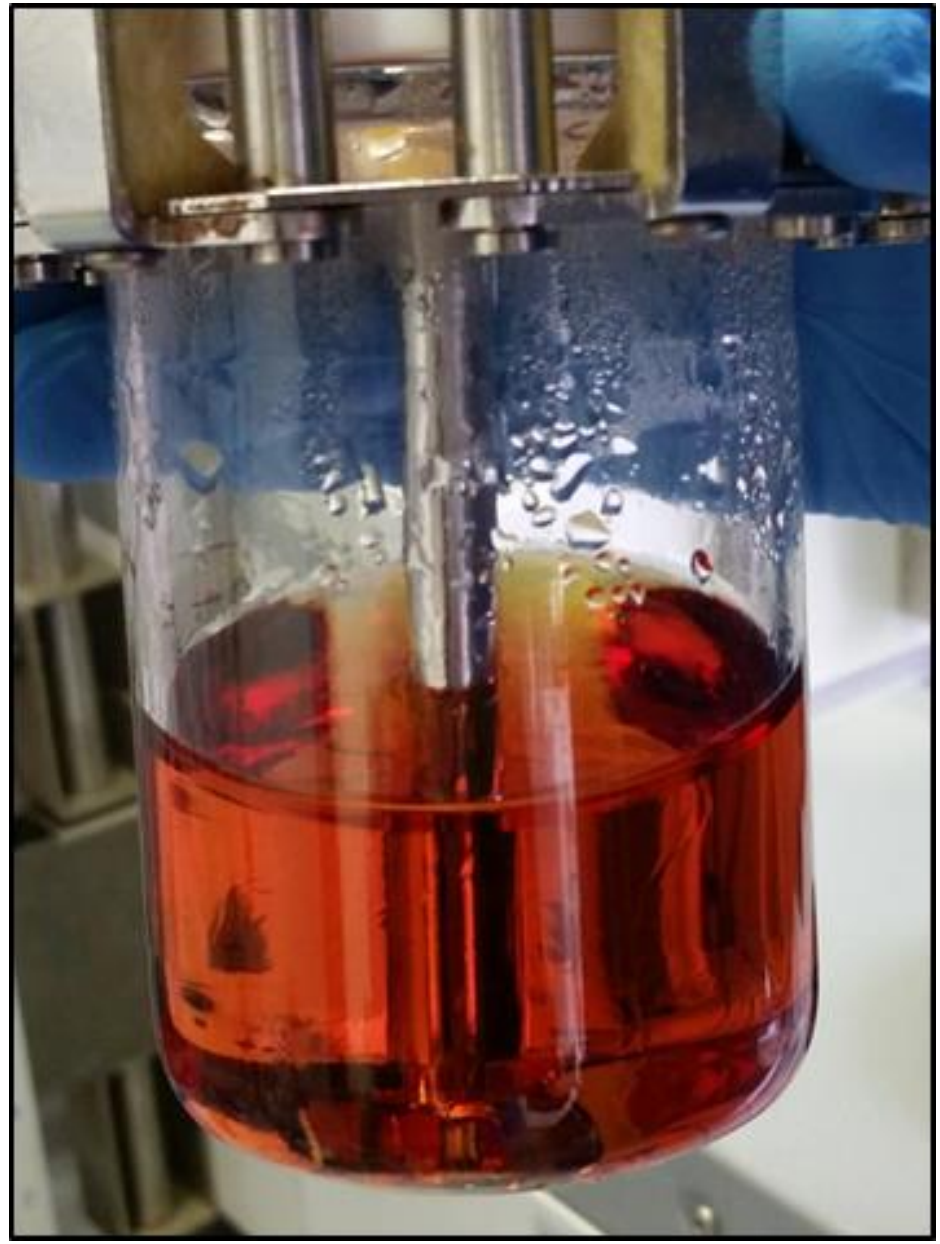
Base Recipe for Resol Preparation

Components:
30 g Phenol
12.8 g $NaOH_{aq}$ (50 % solution)
51.75 g $Formaldehyd_{aq}$ (37 % solution)

Resulting molar ratios:

Formaldehyd/Phenol:	2.0
NaOH/Phenol:	0.5

Procedure:
- $NaOH_{aq}$ put into vessel, stirrer started
- Phenol added
- Heating to 60 °C with 5K/min
- Formalin added over about 15 min (dropping funnel)
- Heating to 82 °C with 5K/min
- Reaction time at 82 °C for 3 h
- Cooling to room temp. with 5K/min



Automated Parallel Reactor for Resol Preparation

Mettler EasyMax102
2 replications per recipe

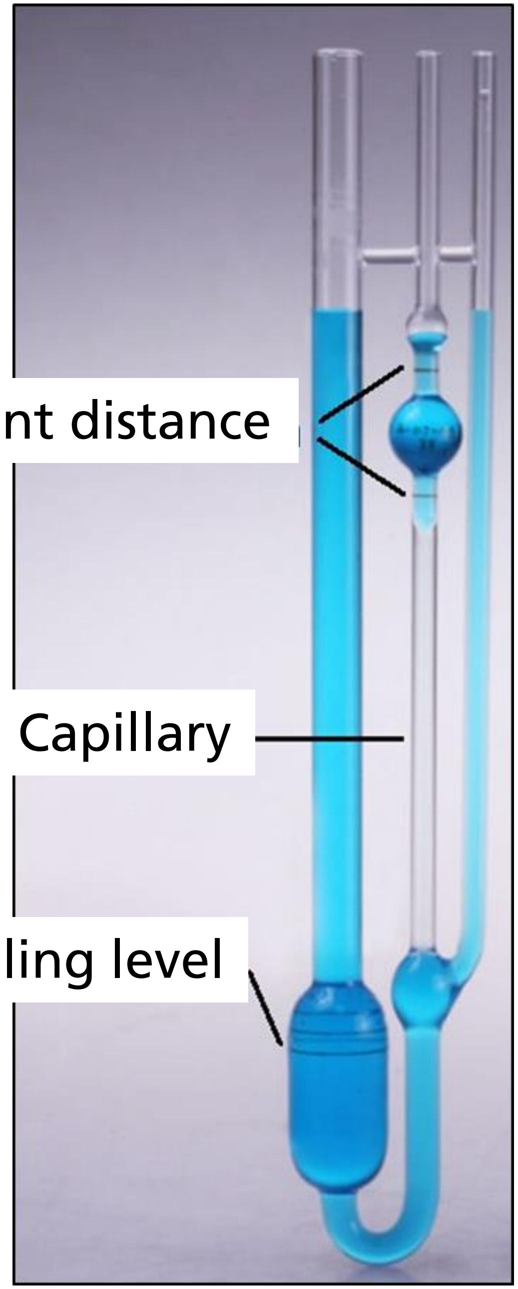
Main parameters influencing resol quality:
- Formaldehyd/Phenol-ratio F/P
- NaOH/Phenol-ratio NaOH/P
- Reaction time

- Degree of substitution

Quality Parameter Assessment for Resols I

Viscosity measurement with Ubbelohde viscosimeter to determine kinematic viscosity

Several caplillaries available to cover large range of viscosity



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Quality Parameter Assessment for Resols II

Hydroxylamine hydrochloride method

Determination of free formaldehyde by titration in %

5.0 g Resol dissolved in
50 ml Methanol

Add 0.1 m HCl until pH 3.5

25 ml 10 % $HONH_2 \cdot HCl$-solution

Stirr 10 min

Titrate with
0.1 m NaOH until pH 3.5

Repeat with blanc

$\omega = 3 \cdot 0.1 \cdot (V_1 - V_0) / 5.0$

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Quality Parameter Assessment for Resols III

Determination of curing characteristic by differential scanning calorimetry DSC

Onset Temperature
Peak Temperature
End Temperature

Peak Area eqal to Reaction Enthalpy

Set parameters:
Range 25 - 250 °C,
Heating rate 2 K/min

Source: www.netsch-thermal-analysis.com

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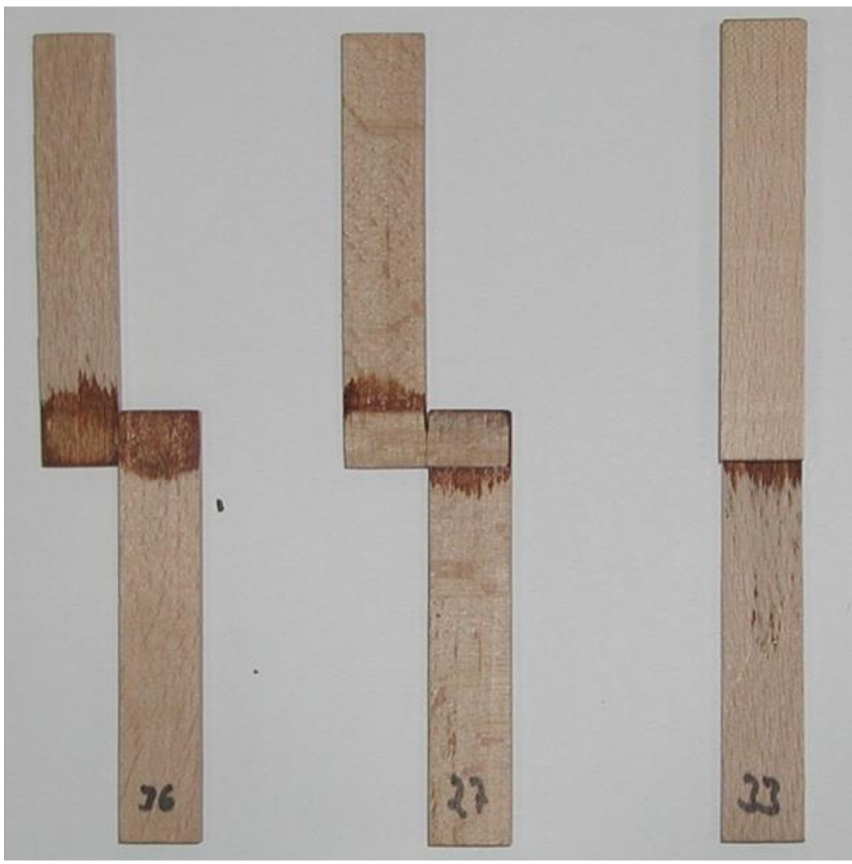
Quality Parameter Assessment for Resols IV

Determination of tensile strength

Specimen prepared according DIN EN 205



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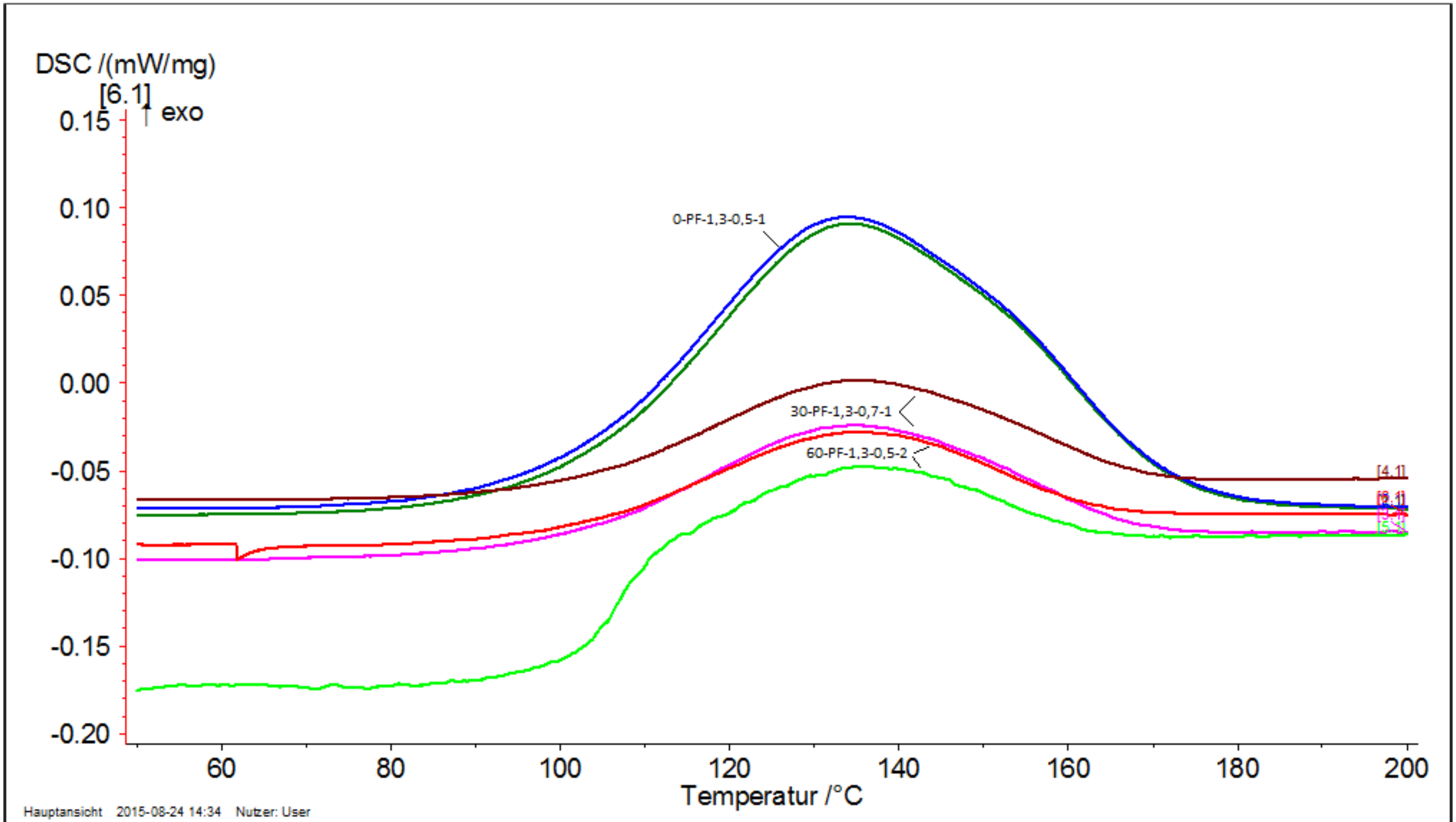
Orienting Tests (Master Thesis Kummert)

- Substituting phenol by condensate of second stage by weigth as received
- Water content in pyrolysis condensate not accounted for
- $NaOH_{aq}$-amount for neutralization based on earlier analysis for acid content
  NaOH-solution with 50 % NaOH used, water not accounted for

- Parameters varied (in green: typical values for commercial resols):
  - Degree of substitution: 0 %, 30 %, 60 %
  - F/P-ratio: 1.3, 2.0
  - NaOH/P-ratio: 0.3, 0.5, 0.7
  - Reaction time: 3 h, 4 h

Orienting Tests

Exemplary DSC-curves for some samples



[#] Gerät	Datei	Datum	Versuchs-ID	Probe	Masse/mg	Segment	Bereich	Atmosphäre	Korr.
[1.1] DSC 204F1 Phoenix	0PF-13_1.ngb-sd7	2015-08-15	0PF-13_1	Phenolharz	67.6	1/2	25°C/2.0(K/min)/250°C	N2, 40.0ml/min / N2, 20.0ml/min	---
[2.1] DSC 204F1 Phoenix	0PF-13_2.ngb-sd7	2015-08-15	0PF-13_2	Phenolharz	47.0	1/2	25°C/2.0(K/min)/250°C	N2, 40.0ml/min / N2, 20.0ml/min	---
[3.1] DSC 204F1 Phoenix	30PF-13_1.ngb-sd7	2015-08-14	30PF-13_1	Phenolharz	38.5	1/2	25°C/2.0(K/min)/250°C	N2, 40.0ml/min / N2, 20.0ml/min	---
[4.1] DSC 204F1 Phoenix	30PF-13_2.ngb-sd7	2015-08-14	30PF-13_2	Phenolharz	53.3	1/2	25°C/2.0(K/min)/250°C	N2, 40.0ml/min / N2, 20.0ml/min	---
[5.1] DSC 204F1 Phoenix	60PF-13_1.ngb-sd7	2015-08-14	60PF-13_1	Phenolharz	35.0	1/2	25°C/2.0(K/min)/250°C	N2, 40.0ml/min / N2, 20.0ml/min	---
[6.1] DSC 204F1 Phoenix	60PF-13_2.ngb-sd7	2015-08-14	60PF-13_2	Phenolharz	41.2	1/2	25°C/2.0(K/min)/250°C	N2, 40.0ml/min / N2, 20.0ml/min	---

Erzeugt mit NETZSCH Proteus Software

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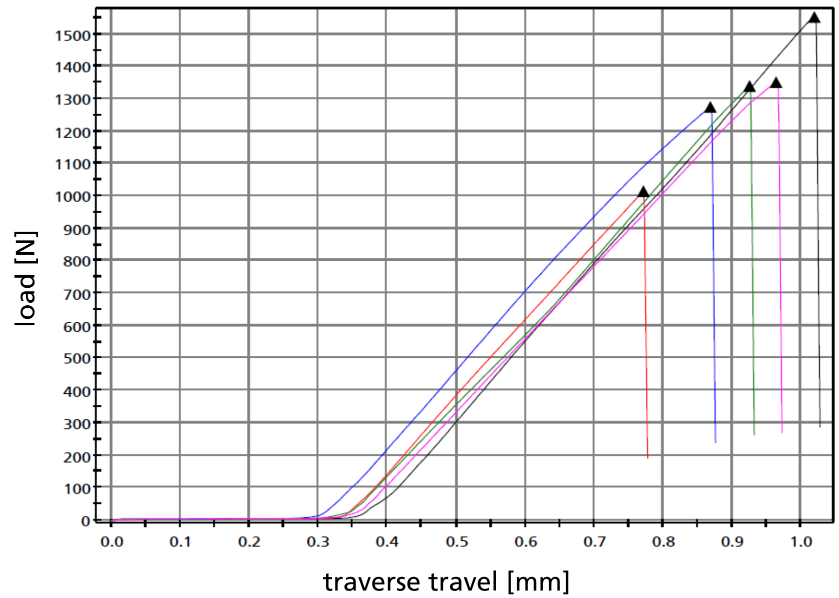
Orienting Tests
Tensile Strength for Sample 60-PF-1.3-0.5-2 (4 h)

DIN EN 205 Minimum value: 10 N/mm²



specimen	max. load [N]	area [mm²]	tensile strength [N/mm²]
1	1551	221	7.02
2	1274	255	5.00
3	1015	221	4.59
4	1338	187	7.16
5	1350	170	7.94

With all specimen the rupture occured in the glued joint, only specimen 1 showed a very small area, where the rupture occured in the adjacent wood.

Specimen pressed with screw clamp

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Orienting Tests

- Results:

Reduction of F/P-ratio due to aldehydes present in pyrolysis condensate

Change in NaOH/P-ratio no improvement concerning viscosity, free formaldehyde and curing characteristics

Free formaldehyd of resols in typical range of technical products

Curing temperature similar to technical products

Lower reactivity of substituted resols $\Rightarrow$ longer pressing times needed

Tensile strength for most promising resol: close to but below minimum value for application as wood glue in non-load bearing timber (10 N/mm^2)

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Parametric Study (Project Lenartowicz, Becker)

- Substituting phenol by condensate of second stage by weigth on dry basis
- Water content in pyrolysis condensate explicitly accounted for
- NaOH-amount for neutralization based on real TAN (total acid number) pure NaOH used, no water added

- Parameters varied (in green: typical values for commercial resols):
  - Degree of substitution: 0 %, 60 %, 65 %, 70 %, 75 %, 80 %, 100 %
  - F/P-ratio: 1.3 for substituted resols, 2.0 for pure phenol (control)
  - NaOH/P-ratio: 0.3, 0.4, 0.45, 0.453, 0.5
  - Reaction time: 0.75 h, 1.5 h, 1.75 h, 2.25 h, 3 h, 4 h

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Parametric Study – Overall Results

Viscosity

- Commercial Resol: 202 mm^2/s
- Resol with pure Phenol: 154 – 236 mm^2/s
  (orienting tests: 140 – 273 mm^2/s)
- Resol with pyrolysis oil: 58 – 2190 mm^2/s
  + 2 samples too high to measure
  (orienting tests: 30 – 107 mm^2/s)

Free Formaldehyde

- Commercial Resol: 0.2 % (typical range higher: 0.3 – 0.5 %)
- Resol with pure Phenol: 0.04 – 0.07 %
  (orienting tests: 0.03 – 0.09 %)
- Resol with pyrolysis oil: 0.33 – 0.99 %
  (orienting tests: 0.48 – 1.43 %)

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Parametric Study – Overall Results

Curing behaviour – Peak Temperature

- Commercial Resol: not reported
- Resol with pure Phenol: 128 – 129 °C
  (orienting tests: 126.4 – 134.1 °C)
- Resol with pyrolysis oil: 121.9 – 136.5 °C
  (orienting tests: 123 – 135.4 °C)

Curing Behaviour – Peak Area = Reaction Enthalpy

- Commercial Resol: 243.8 J/g
- Resol with pure Phenol: 118 – 191 J/g
  (orienting tests: 204 – 234 J/g)
- Resol with pyrolysis oil: 59.1 – 133.3 /g
  (orienting tests: 51.9 – 136 J/g)

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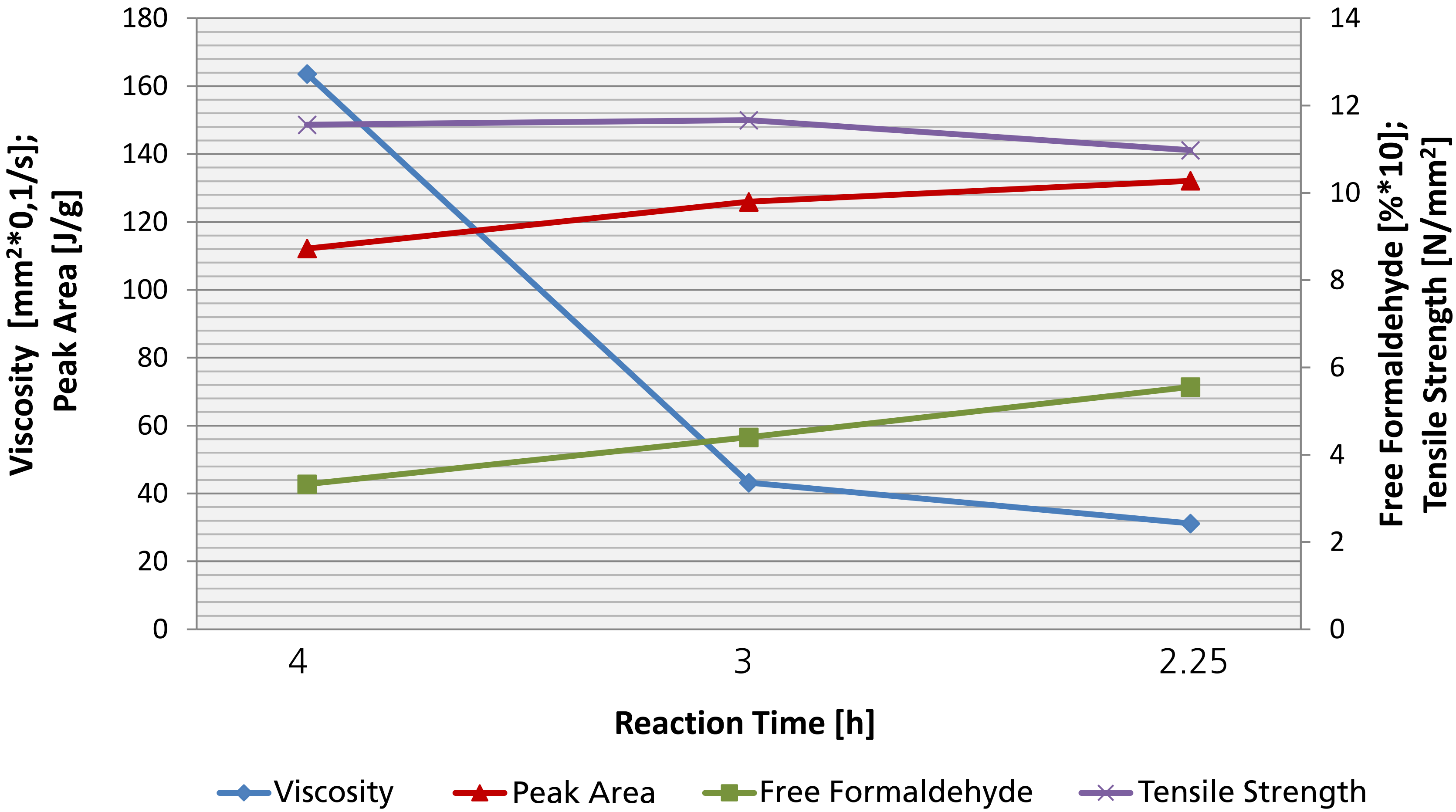
Parametric Study – Influence of Reaction Time

Constant parameters:
Degree of substitution: 60 %
F/P-ratio: 1.3
NaOH/P-ratio: 0.453



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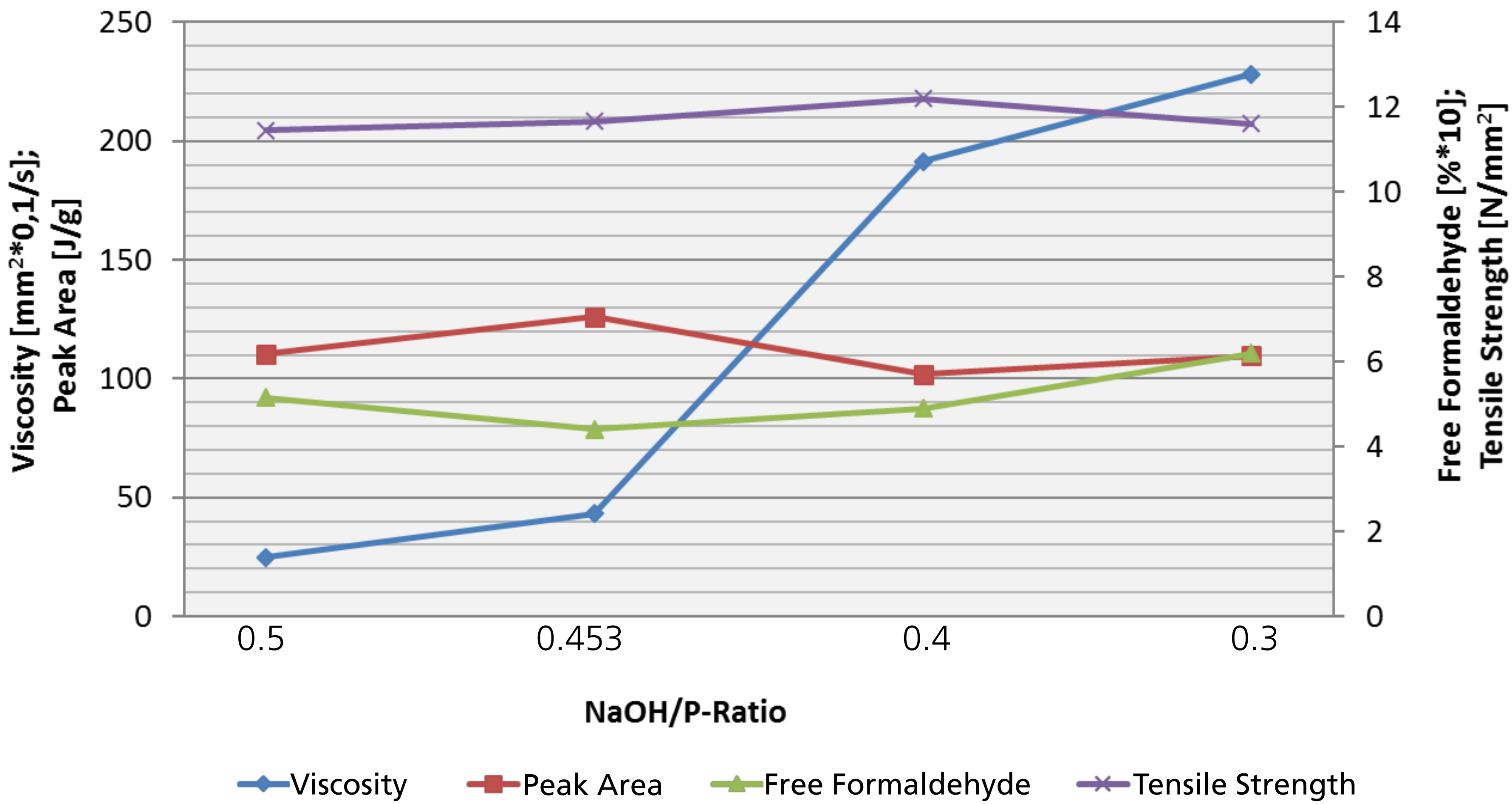
Parametric Study – Influence of NaOH/P-Ratio

Constant parameters:
Degree of Substitution: 60 %
F/P-ratio: 1.3
Reaction time: 3 h



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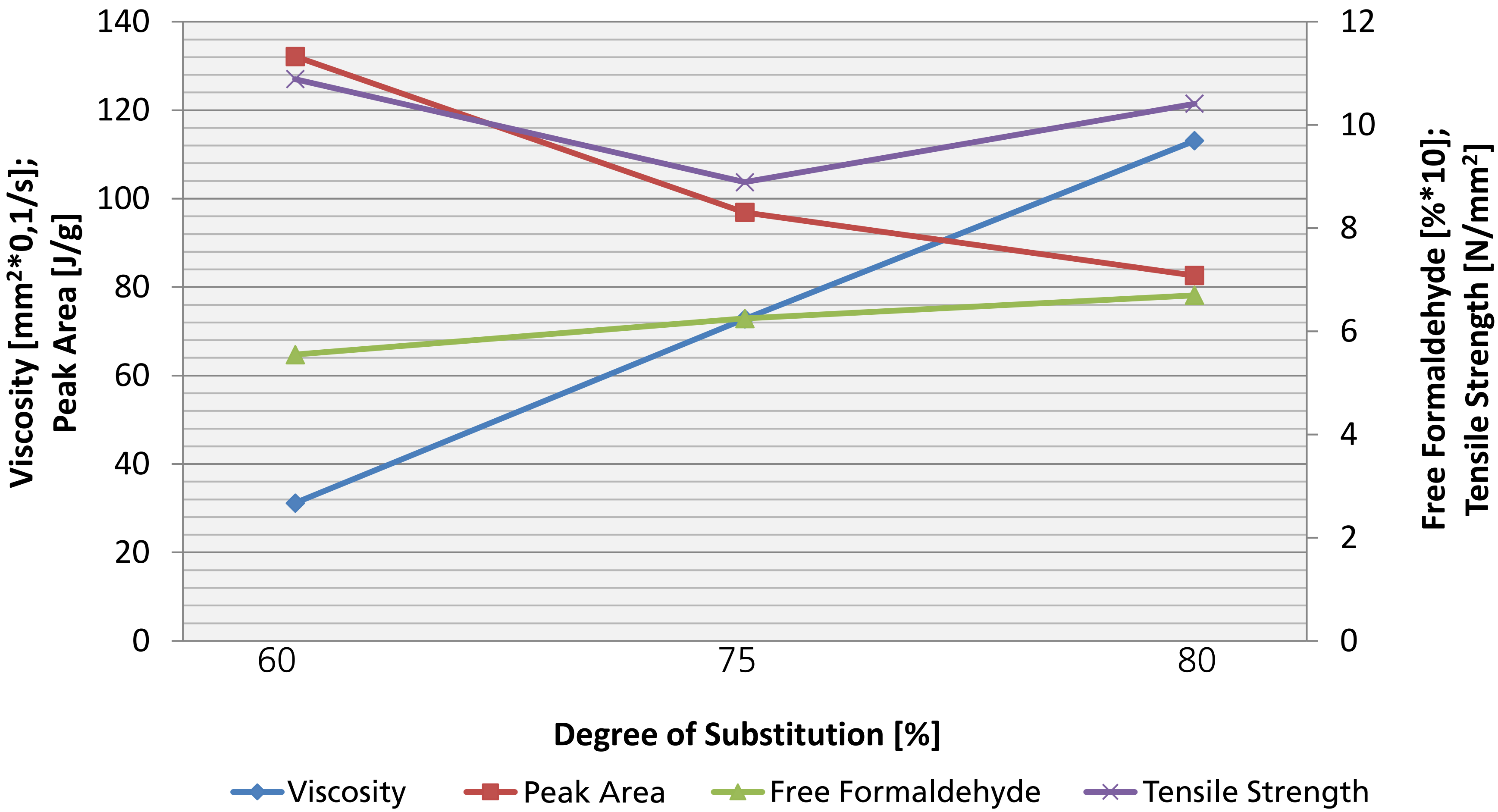
Parametric Study – Influence of Degree of Substitution

Constant parameters:
F/P-ratio: 1.3
NaOH/P-ratio: 0.453
Reaction time: 2.25 h



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Summary

- Ablative Fast Pyrolysis is a good means to convert herbaceous biomass.
- Liquid fraction condensed between 115 °C and 87 °C is suitable for the production of phenolic resins **without** further upgrade.
- Orienting tests showed promising results for phenol substitution above 50 weight-% and encouraged more detailed investigation.
- Parametric study showed only minor influence of reaction time, NaOH/P-ratio and degree of substitution on free formaldehyde, reactivity represented by peak area and tensile strength, while all parameters showed larger influence on viscosity, which is increasing with reaction time and degree of substitution and decreasing with NaOH/P-ratio.
- All results from tensile strength measurement are around the required minimum value of 10 N/mm² (the majority above), but without clear trend.

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Outlook

- In industry, resols are produced not with fixed reaction time but until a required viscosity is reached.
  ⇒ Production of larger samples with inline viscosity measurement could overcome this issue.

- In a next study, larger samples of e.g. plywood should be produced to charcaterize the glue application. For such investigation again larger amounts per batch of resol would be needed.

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Thank You for Your kind attention!

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