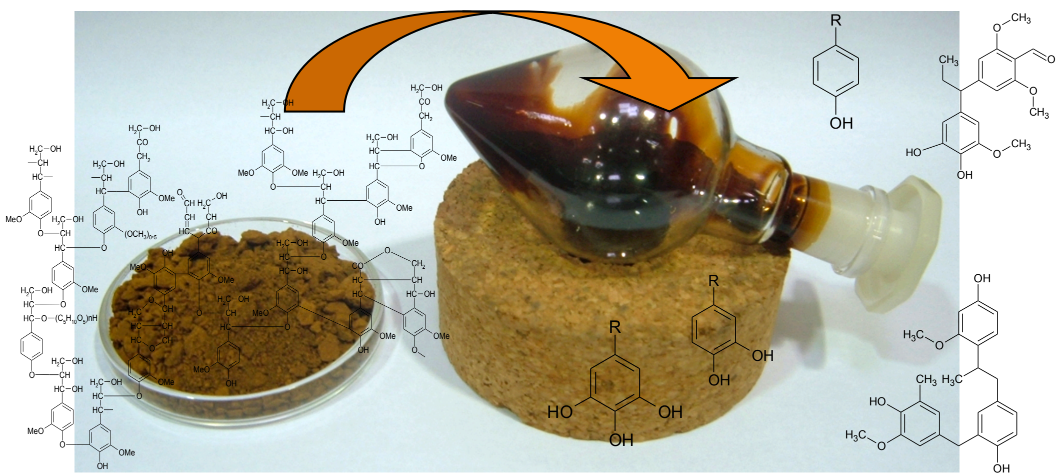
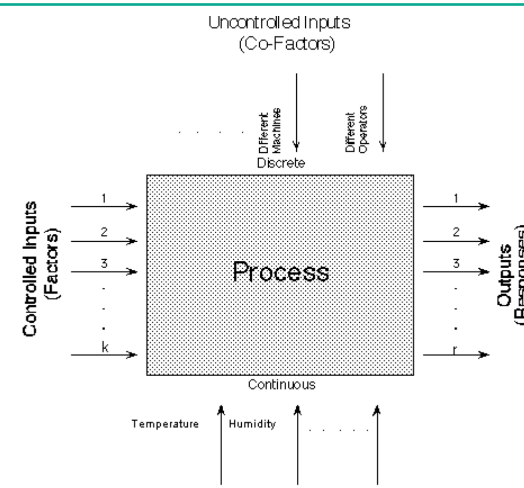
Lignin to aromatic compounds. The Base Catalysed Degradation in continuous reactors - a tentative review

Detlef Schmiedl[1]*, Gerd Unkelbach*[2]*, Sarah Böringer*[1]*, Detlef Rückert*[1]*, Rainer Schweppe*[1]

[1]*) Fraunhofer Institute for Chemical Technology ICT (Fh-ICT, Pfinztal, Germany),*

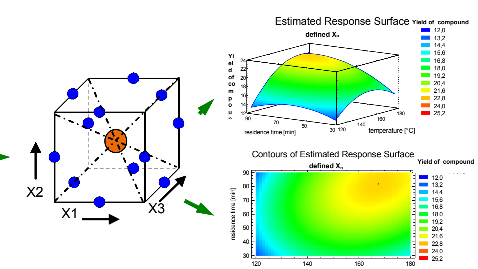
[2]) Fraunhofer Center for Chemical-Biotechnological Processes CBP (Fh-CBP, Leuna, Germany)





III Latin American Congress
Biorefineries
Ideas for a sustainable world
November 19th to 21st, 2012

Factors	Levels
X1 (e.g. Temperature)	-1; 0; +1
X2 (e.g. C_{NaOH})	-1; 0; +1
X3 (e.g. residence time)	-1; 0; +1



Fraunhofer CBP

Fraunhofer ICT

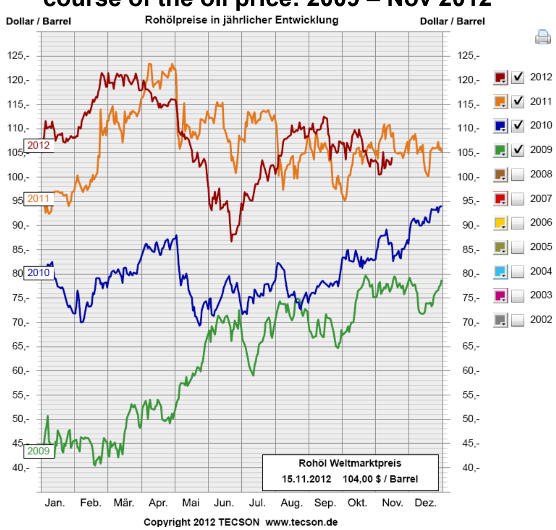
Biomass - A new feedstock for the 21. century ?

coal (> 1950) crude oil / natural gas biomass ?

From coal to crude oil - new efficient techniques have been developed for an economic production of chemicals

For the shift from oil & gas to bio mass based chemicals it has to be the same

course of the oil price: 2009 – Nov 2012



	Annual Production	Price of Product	Price of functionalized Carbon (2010)
ethylene	110 Mio. t/a	890 €/t	1035 €/t C
propylene	75 Mio. t/a	850 €/t	988 €/t C
benzene	45 Mio. t/a	830 €/t	902 €/t C
cellulose	320 Mio. t/a	500 €/t	1250 €/t C
starch	55 Mio. t/a	250 €/t	625 €/t C
sugar	143 Mio. t/a	300 €/t	750 €/t C
ethanol	36 Mio. t/a	365 €/t	700 €/t C
lignin	?	?	?

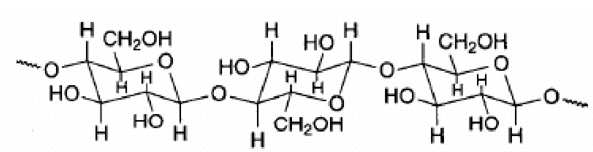
Fraunhofer CBP Fraunhofer ICT

Utilizing lignocellulose biomass

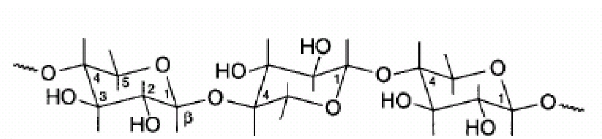
Fractionation of hardwood by a modified Organosolv-process

Pilot project “German lignocellulose bio refinery”

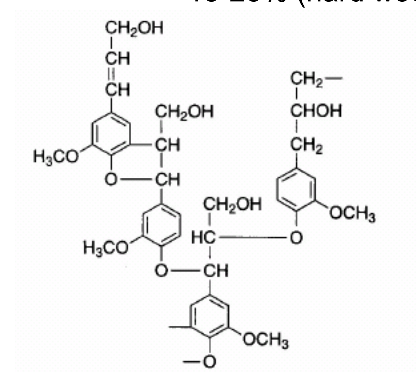
Cellulose
40-55%



Hemicellulose
15-35%



Lignin
28-31% (soft wood);
18-25% (hard wood)

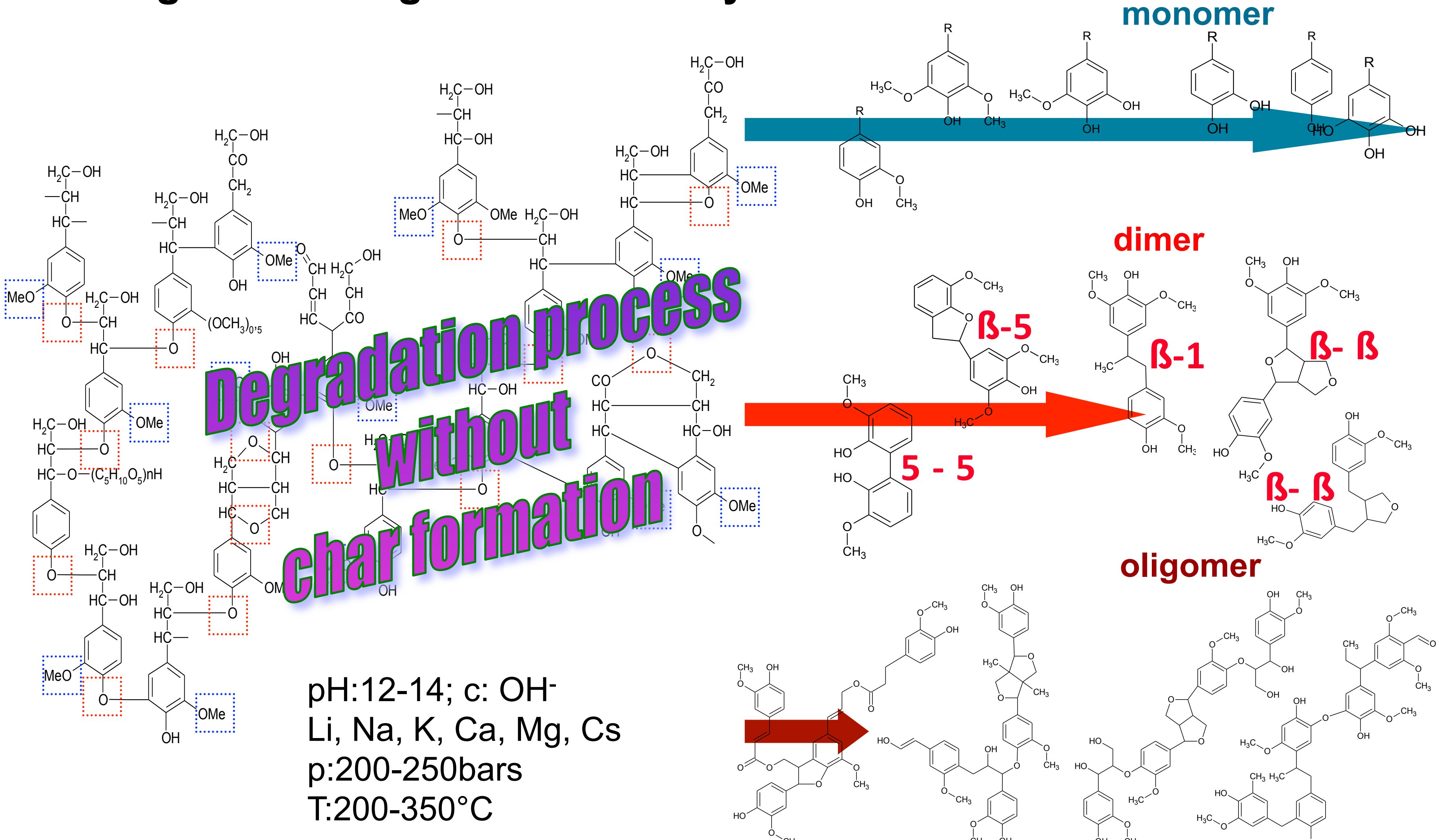


Hydrolysis results in C_6- and C_5-sugars as feedstock for fermentation or chemical reactions

Not yet an “easy” continuously degradation process for Lignin

Only material applications
(formaldehyde resins, PU foams, casting resins)

Chemical principle of an alkaline hydrolysis process (BCD) on Lignin for the generation of oxy aromatics



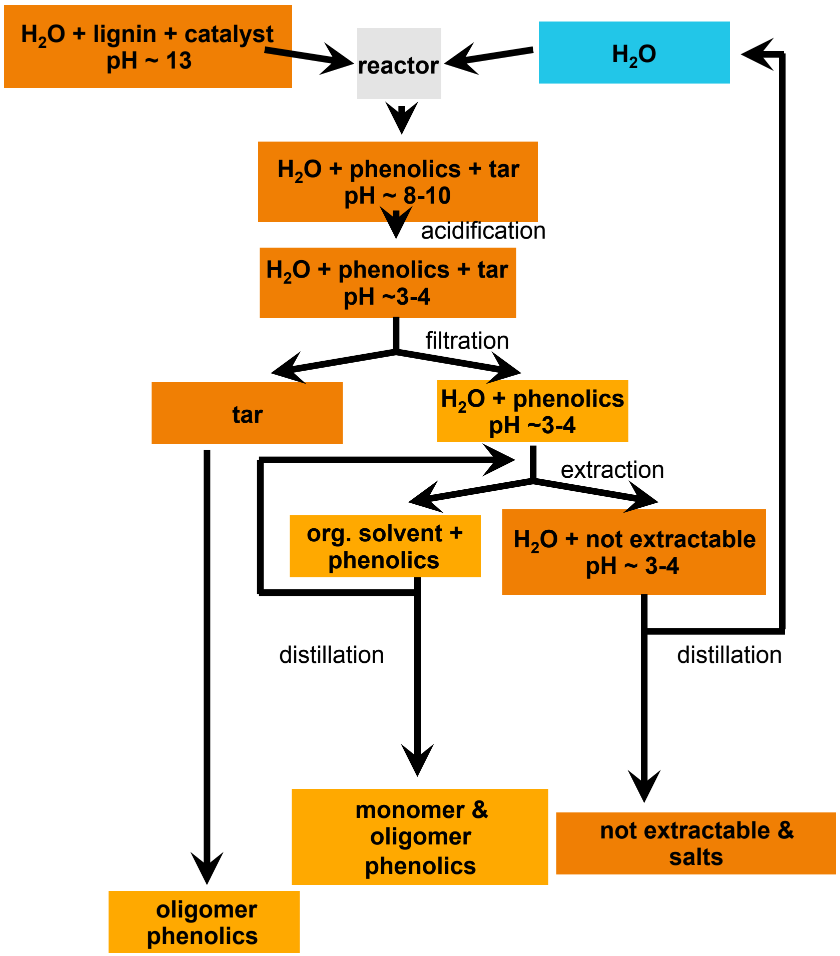
pH:12-14; c: OH^-
Li, Na, K, Ca, Mg, Cs
p:200-250bars
T:200-350°C

Fraunhofer CBP

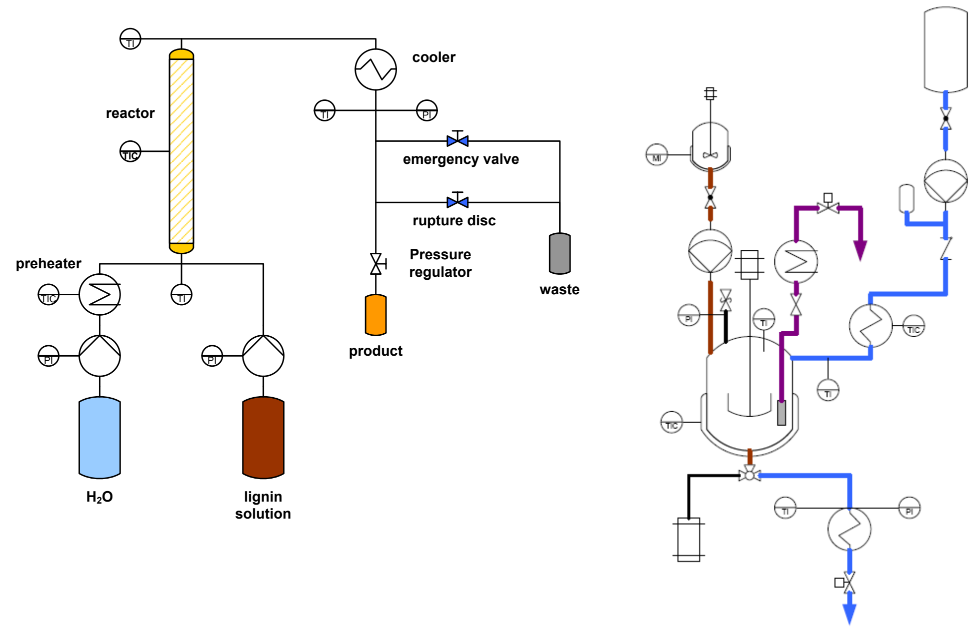
Fraunhofer ICT

<u>Engineering</u> principles of the BCD-process (Reaction & Separation Techniques)

BCD procedure & down stream



General flow diagram of a plug flow reactor & a continuously stirred tank reactor



T: 200-350°C,
p: up to 250 bar,
τ: 35sec to 15min dwell time
10 % Lignin

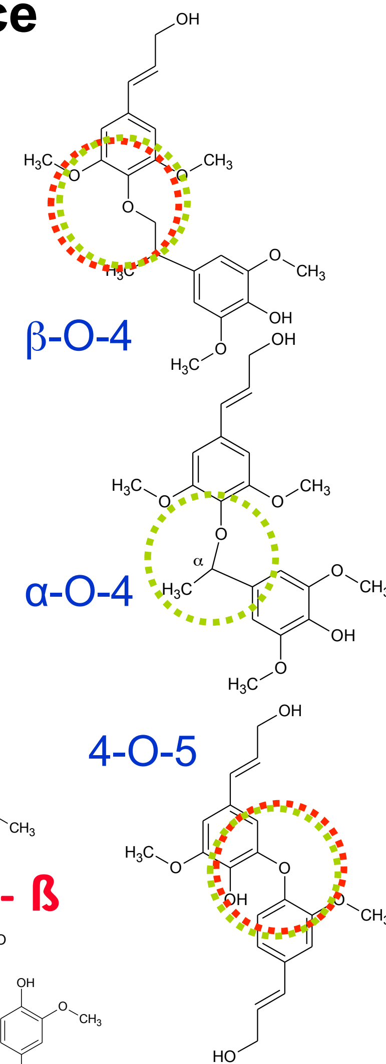
Fraunhofer CBP Fraunhofer ICT

Structural properties of lignin (botanical origin/incidence of bond type based on 100C_9 units)

bond type	dimeric structure	softwood (spruce) C_9 units of 100	hardwood (beech) C_9 units of 100
β-O-4	β-arylether	48	65
α-O-4	benzylarylether	6 – 8	
β-5	phenylcoumaran	[illegible] 12	6
5-5	biphenyl	10 – 11	2
4-O-5	diphenylether	4	2
β-1	1,2-diarylpropane	7	15
β-β	THF or resinol type	2	2 + 5

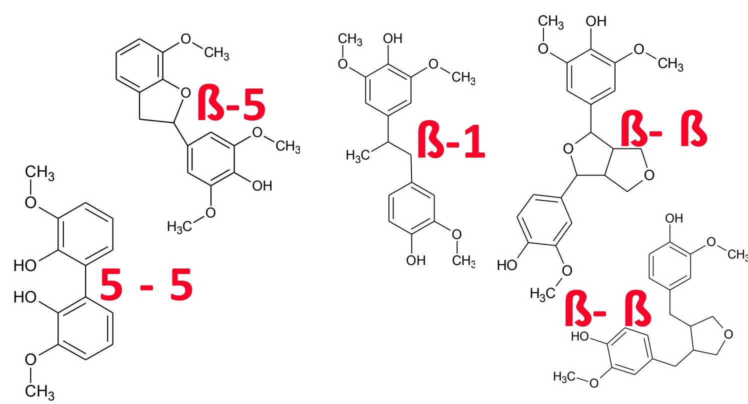
1/3 are alkyl bridges connecting 2/3 of aromatic rings - limitations for hydrolysis

Ref.: ERICKSON, M.; LARSSON, S.; MISCHKE, G.E. (1973)
NIMZ, H.; LÜDEMANN, H.D. (1974)



Structural properties of lignin

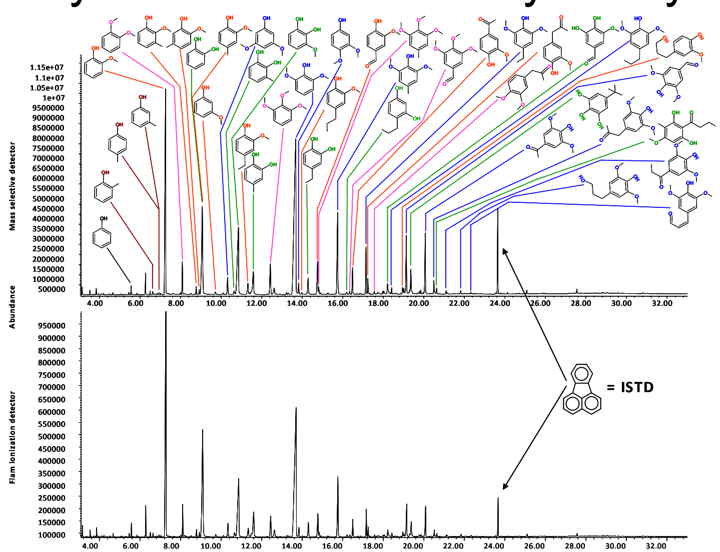
dimer & oligomer composition & functionality of BCD oil and tar



Analytical methods

- Reactor water, extracts and filter-cakes were characterized by gravimetric analysis
- Elemental analysis (CHONS) on the oil and tar fractions
- Monomers were identified and quantified by GC-MSD/FID
- Reactor water was analyzed by HPLC RID

  (formic acid, acetic acid, methanol)
- Oligomeric oxyaromatics were analyzed by LC MSD Ion Trap XCT+ / SEC

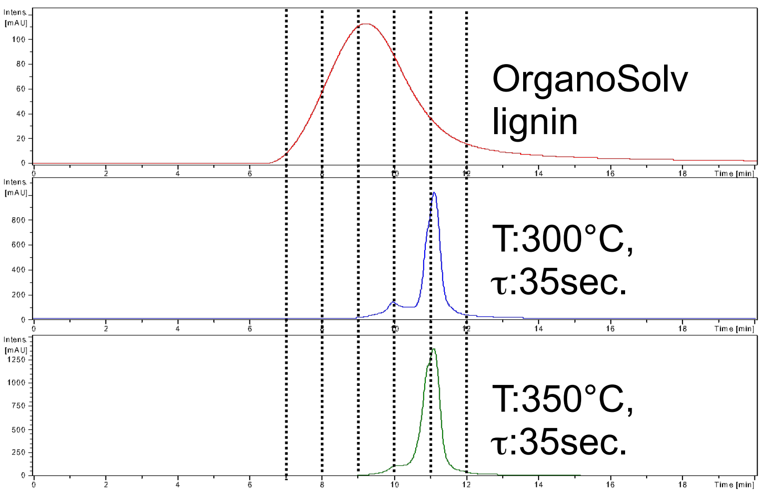


GC-MSD/FID analysis of monomer compounds in a BCD oil

Analytical methods

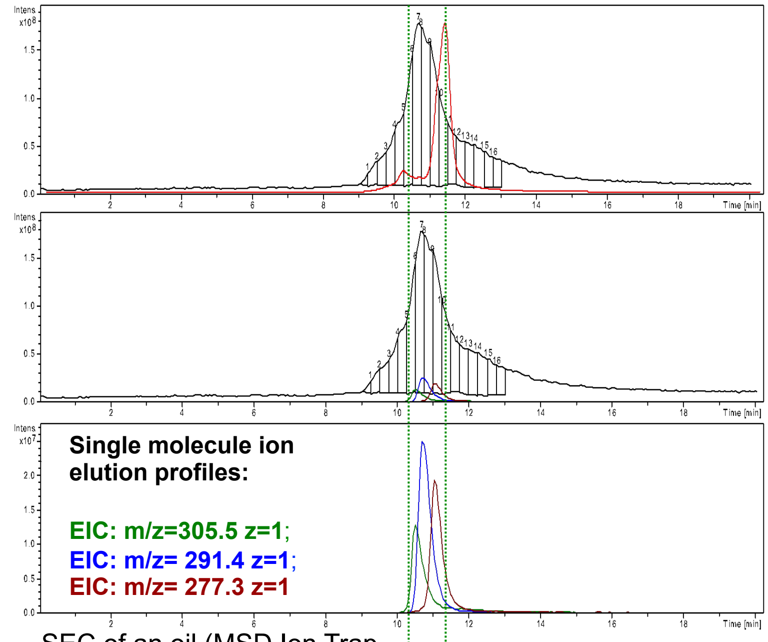
- Oligomeric oxyaromatics were analyzed on a SEC DAD MSD Ion Trap XCT+

Elution profile - SEC / DAD (oil):



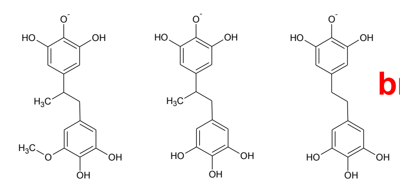
SEC of **lignin** (red), **oil L38**(blue), **oil L39**(green) on SDV micro, 4.6x30mm, 4.6x250mm, 3µ, 50 Å (PSS Mainz, Germany), mobile phase: THF non-stabilized, flow rate: 0.250ml/min;
DAD λ: 280nm ± 2nm, cell size: 5µl; Temp: 50°C, HPLC system: Agilent RR HT 1200SL.

SEC / DAD / ESI neg. MSD Ion Trap (oil):



SEC of an oil (MSD Ion Trap, ESI negative:
black: TIC: scan:100-2200 amu;
Dominant signals:
green: EIC: m/z=305.5 z=1;
blue: EIC: m/z= 291.4 z=1;
brown: EIC: m/z= 277.3 z=1)
TIC: Total **I**on **C**urrent
EIC: **E**xtracted **I**on **C**urrent

Possible molecules



m/z=305.5 **m/z= 291.4** **m/z= 277.3**

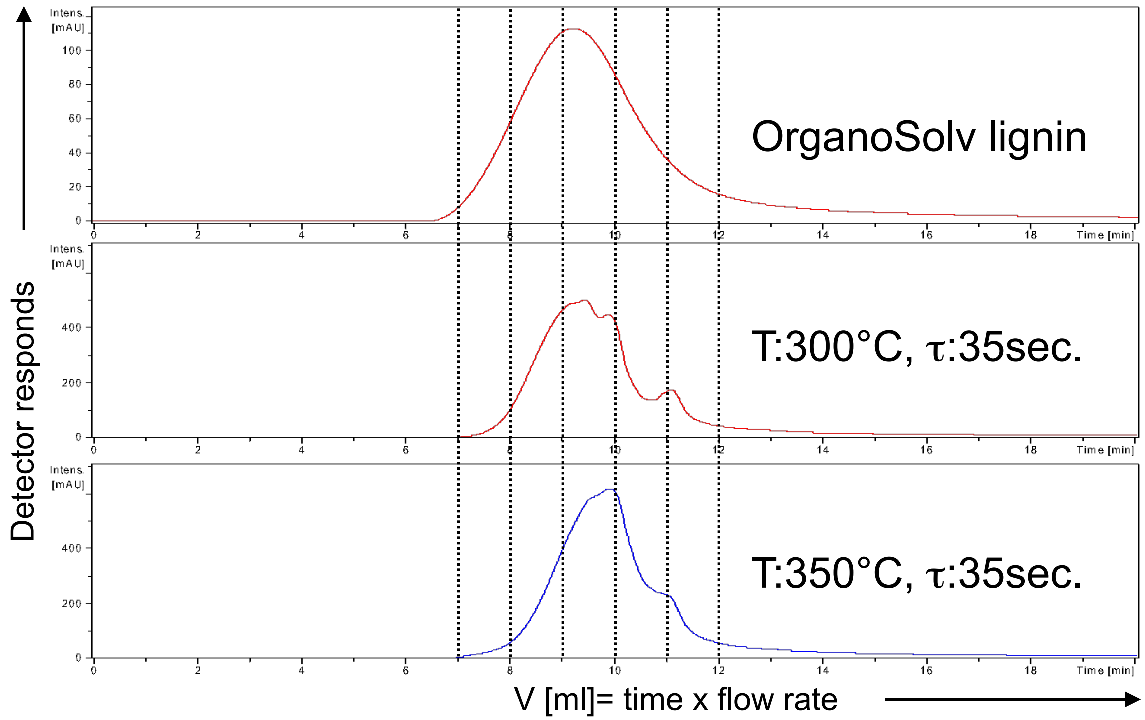
β-1 alkyl bridge

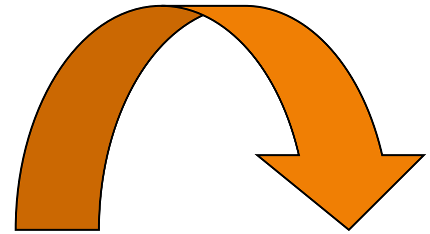
Fraunhofer CBP
Fraunhofer ICT

Analytical methods

- Oligomeric oxyaromatics were analyzed on a SEC-DAD-MSD Ion Trap XCT+

SEC / DAD (tar):





Process parameters

Molecular Characteristics (Mw, Mn) of Tar

SEC of **lignin** (upper), **tar L38** (red), **tar L39** (blue) on SDV micro, 4.6x30mm, 4.6x250mm, 3µ, 50 Å (PSS Mainz, Germany),mobile phase: THF non-stabilized, flow rate: 0.250ml/min; DAD λ: 280nm ± 2nm, cell size: 5µl; Temp: 50°C, HPLC system: Agilent RR HT 1200SL.

Structural properties of lignin (botanical origin/monomer type)

Botanical source of lignin:

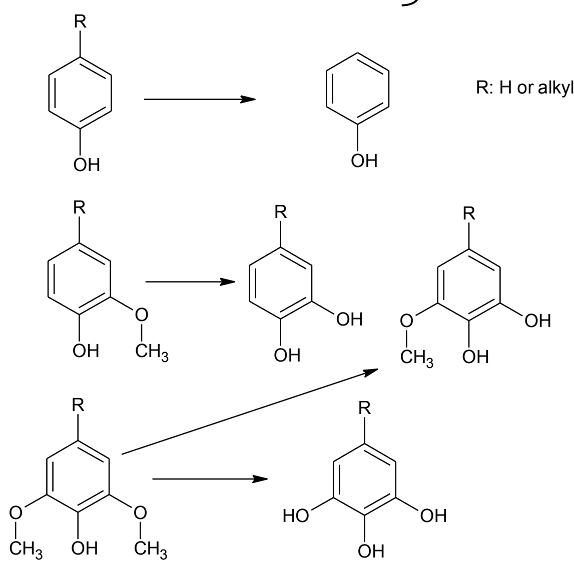
H/G/S-Lignin — annual plant

G/S or S/G-Lignin (hw), G-Lignin (sw) — perennial plant

H

G

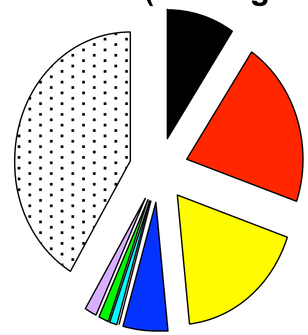
S



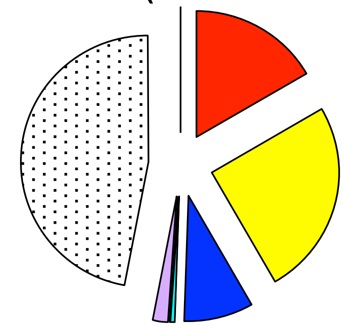
R: H or alkyl

Structural properties → **monomer composition of BCD oil**

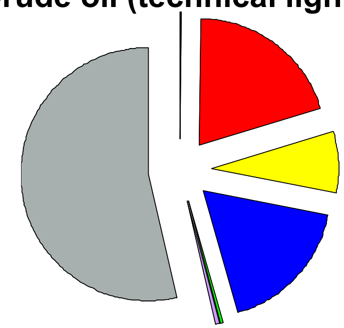
Crude oil (HGS lignin)



Crude oil (hard wood lignin)



Crude oil (technical lignin from a pulp mill)



T:300°C,

p:200-250bar,

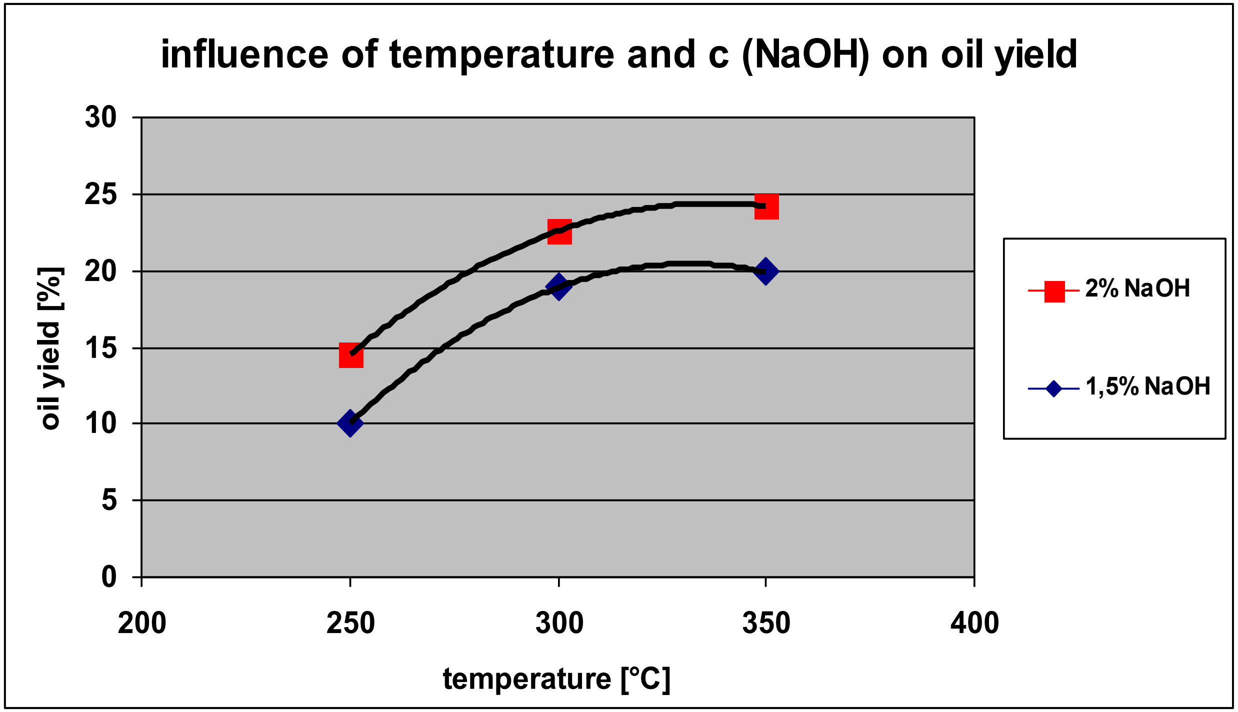
τ=10min;

ethyl acetate extract

- phenol
- guajacol & monomethoxyphenols
- syringol & dimethoxyphenols
- o-hydroxyphenol derivatives
- m-hydroxyphenol derivatives
- benzene; 1,2,3- triol derivatives
- alkylphenols
- di- & trimethoxy-alkylbenzenes; alkylbenzenes
- unknown & oligomers

Effect of Temperature & [NaOH] on oil yield

const. τ=600s, p=250bar; ethyl acetate extracted; BCD on beech lignin



- Highest oil yields (ethyl acetate extracts) at 350°C with 2% NaOH.
- Adding more base has no significant effect on oil yield / more acid is needed during downstream processing of the reactor water

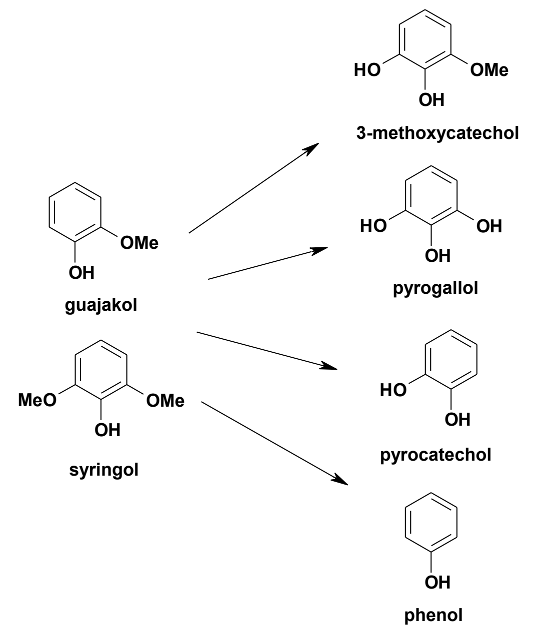
Fraunhofer CBP

Fraunhofer ICT

Effect of Temperature on oil composition

const. τ=600s, p=250bar; ethyl acetate extracted, BCD on beech lignin

Groups of compounds	wt.-% compared to oil		
	250°C	300°C	350°C
Phenol	0,1	0,1	0,4
Guaiacol & mono-methoxy phenol derivatives	8,8	16,4	22,9
Syringol & di-methoxy phenol derivatives	24,6	25,0	4,4
o-Hydroxy phenol derivatives	0,6	9,1	27,9
m-Hydroxyphenol derivatives	0,0	0,0	0,6
Benzene 1,2,3 –triol derivatives	0,0	0,5	0,8
Alkyl-phenol derivatives	0,0	0,0	0,4
Di- & Tri-methoxy-alkyl-benzenes, alkyl-benzenes	0,4	1,8	1,5
Unknown & Oligomer compounds	65,6	47,0	41,0



- Increasing reaction temperature increases hydroxy-functionalities in the oil ratification by experiments with model compounds

- The amount of oligomer compounds in the oil decreases by increasing T

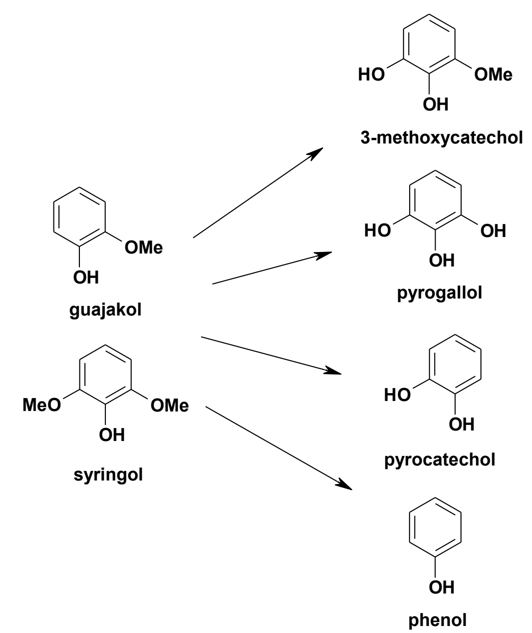
- Monomers were identified and quantified by GC-MSD/FID on column HP-5ms

Fraunhofer CBP Fraunhofer ICT

Effect of residence time on oil composition

const. T=300°C, p=250bar; ethyl acetate extracted; BCD on beech lignin

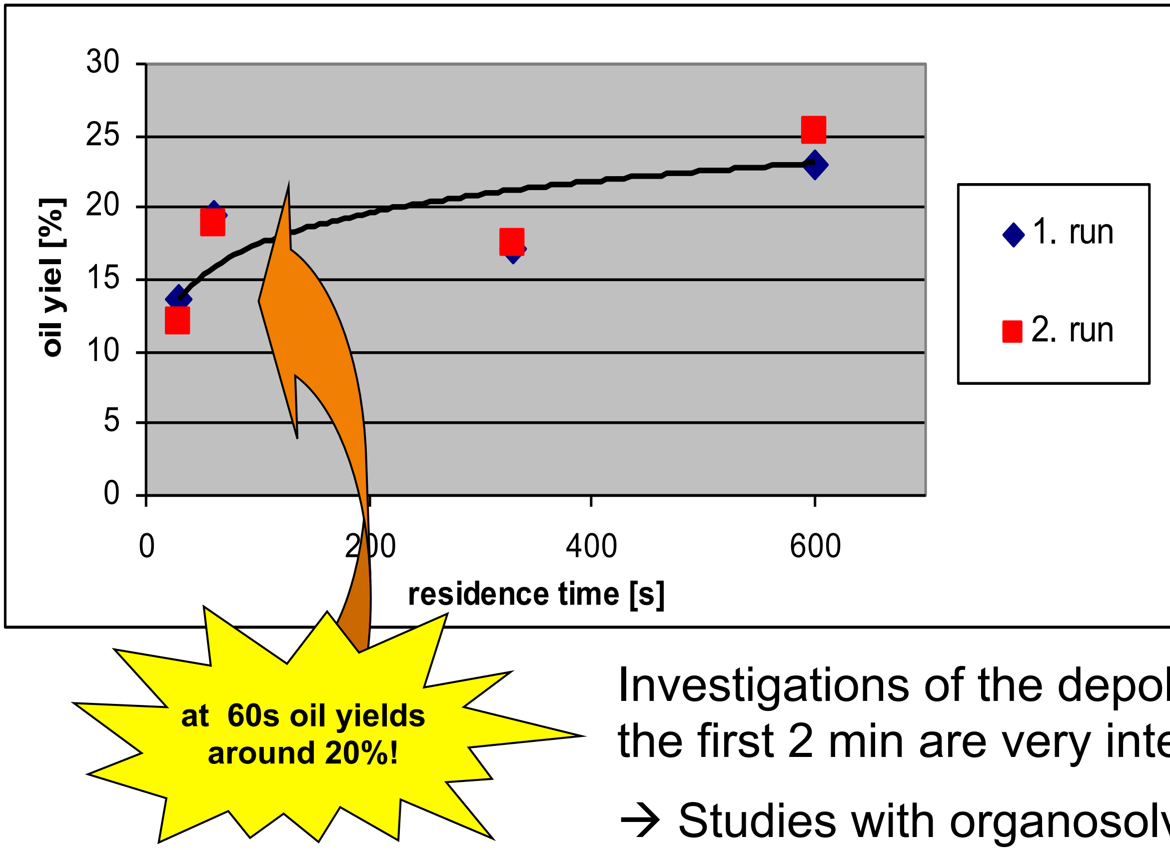
Groups of compounds	wt.-% compared to oil		
	300s	600s	900s
Phenol	0,2	0,1	0,2
Guaiacol & mono-methoxy phenol derivatives	17,4	16,4	14,4
Syringol & di-methoxy phenol derivatives	32,7	25,0	23,6
o-Hydroxy phenol derivatives	6,2	9,1	15,8
m-Hydroxyphenol derivatives	0,0	0,0	0,1
Benzene 1,2,3 –triol derivatives	0,6	0,5	0,9
Alkyl-phenol derivatives	0,1	0,0	0,2
Di- & Tri-methoxy-alkyl-benzenes, alkyl-benzenes	1,4	1,8	2,2
Unknown & Oligomer compounds	41,4	47,0	42,7



- Increasing residence time slightly increases hydroxy-functionalities in the oil ratification by experiments with model compounds
- The amount of oligomer compounds in the oil didn't change
- Monomers were identified and quantified by GC-MSD/FID on column HP-5ms

Effect of residence time on oil yield

const. T=350°C, p=250bar; ethyl acetate extracted; BCD on beech lignin



Investigations of the depolymerisation reactions in the first 2 min are very interesting

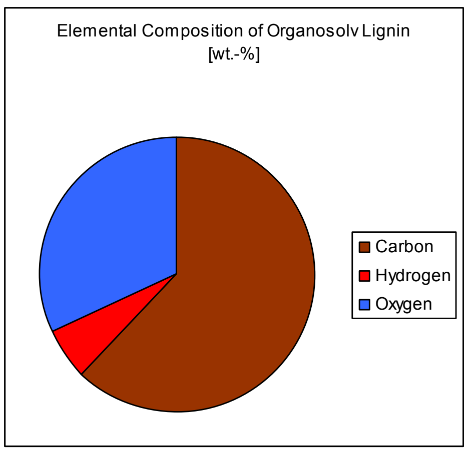
→ Studies with organosolv beech wood lignin and model compounds / detailed analytics is necessary !

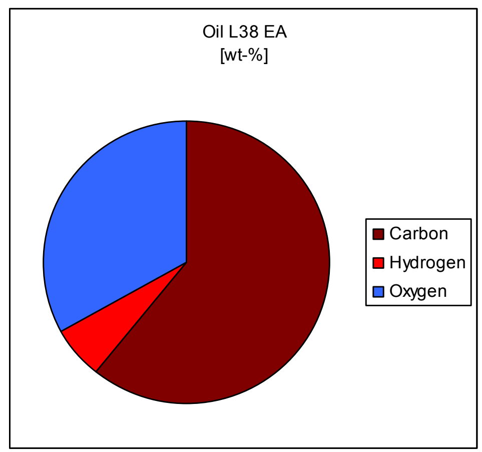
Fraunhofer CBP Fraunhofer ICT

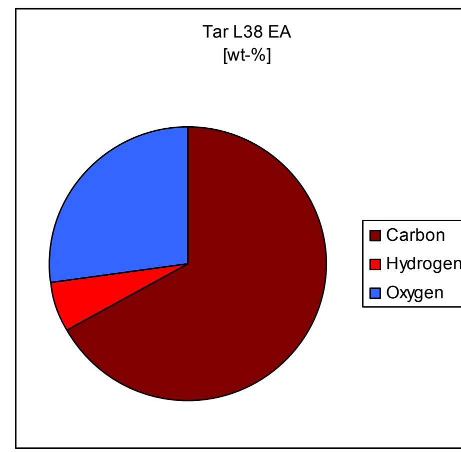
Carbon balance of BCD products

T=300 & 350°C, p=250bar, τ=35s; ethyl acetate extracted; BCD on beech lignin

Fractions / phases	300°C	350°C
Oil	10.5 % Carbon of Lignin	18.0% Carbon of Lignin
Tar	73.2% Carbon of Lignin	56.8% Carbon of Lignin
formic acid, acetic acid, methanol in reactor water	2,5% Carbon of Lignin	4.4% Carbon of Lignin
Carbon lost via gaseous phase / downstream pro.	13.8% Carbon of Lignin	20.8% Carbon of Lignin





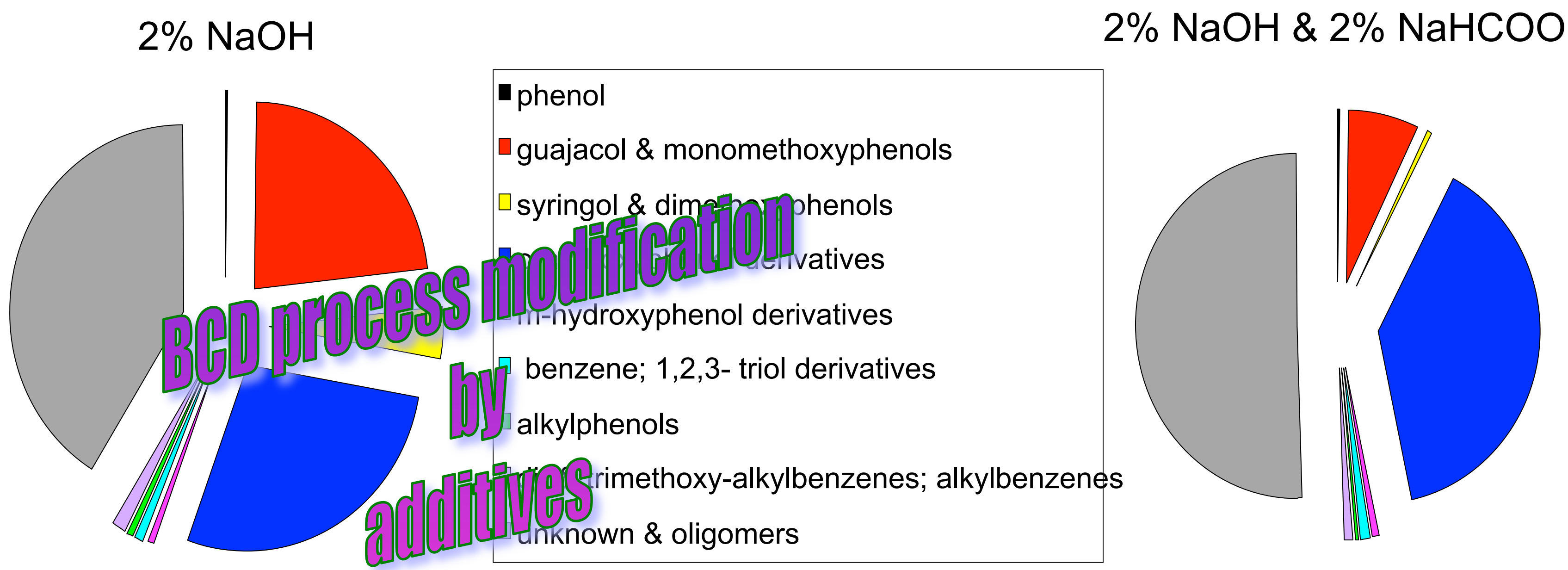


Carbon is the only element which is distributed during BCD !

Fractions are analyzed by HPLC-MS/RID/DAD and elemental analysis

BCD on beech lignin under reductive conditions / the Hydrogen donor effect

T=350°C, p=250bar, τ=600sec; ethyl acetate extracted; BCD on beech lignin



Adding formate for *in situ* H_2-generation decreases

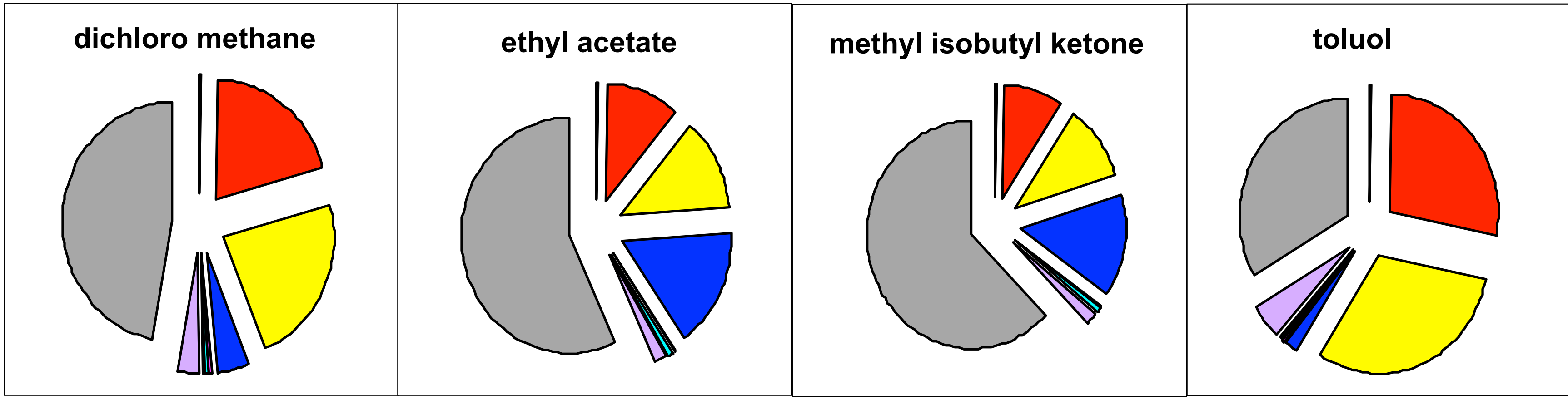
the oil yield from 25% to 19%,

but produces more catechols derivatives.

Fraunhofer CBP

Fraunhofer ICT

Compound distribution of oil depends also on extraction solvent



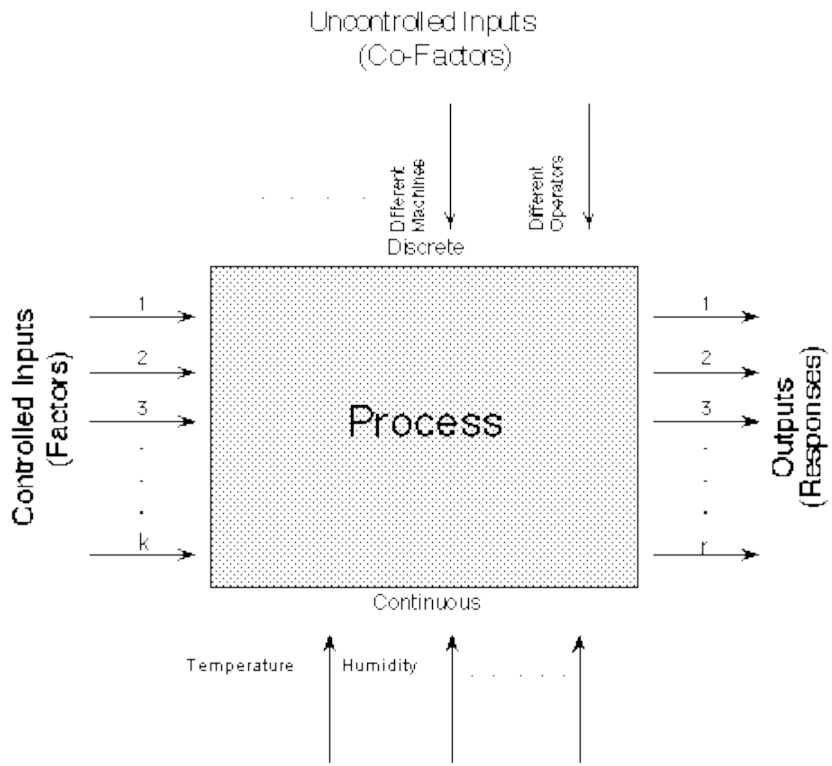
	wt.-% compared to oil			
	dichloro methane	ethyl acetate	methyl isobutyl ketone	toluol
Phenol	0,3	0,2	0,2	0,2
Guaiacol & mono-methoxy phenol deriv.	20,2	10,9	9,1	27,8
Syringol & di-methoxy phenol derivatives	23,4	12,7	10,9	31,1
o-Hydroxy phenol derivatives	4,6	16,5	14,7	2,1
m-Hydroxyphenol derivatives	0,4	0,3	0,2	0,3
Benzene 1,2,3 –triol derivatives	0,5	0,7	0,6	0,0
Alkyl-phenol derivatives	0,3	0,2	0,2	0,4
Di-&Trimethoxy-alkyl-benz., alkyl-benzenes	3,2	1,7	1,6	4,8
Oligomere compounds	47,1	56,9	62,5	33,4

Oil mass [mg] extratced from 750g reactor water	550	1070	1310	420

Fraunhofer CBP Fraunhofer ICT

Part II. Lignin cleavage for the production of oxy aromatics/ technical Lignin from a pulp mill

The BCD process as “Black Box” process on Kraft-Lignin



A `Black Box' Process Model Schematic

The Box-Behnken design

TABLE 3.24 Structural Comparisons of CCC (CCI), CCF, and Box-Behnken Designs for Three Factors

CCC (CCI)				CCF				Box-Behnken			
Rep	X1	X2	X3	Rep	X1	X2	X3	Rep	X1	X2	X3
1	-1	-1	-1	1	-1	-1	-1	1	-1	-1	0
1	+1	-1	-1	1	+1	-1	-1	1	+1	-1	0
1	-1	+1	-1	1	-1	+1	-1	1	-1	+1	0
1	+1	+1	-1	1	+1	+1	-1	1	+1	+1	0
1	-1	-1	+1	1	-1	-1	+1	1	-1	0	-1
1	+1	-1	+1	1	+1	-1	+1	1	+1	0	-1
1	-1	+1	+1	1	-1	+1	+1	1	-1	0	+1
1	+1	+1	+1	1	+1	+1	+1	1	+1	0	+1
1	-1.682	0	0	1	-1	0	0	1	0	-1	-1
1	1.682	0	0	1	+1	0	0	1	0	+1	-1
1	0	-1.682	0	1	0	-1	0	1	0	-1	+1
1	0	1.682	0	1	0	+1	0	1	0	+1	+1
1	0	0	-1.682	1	0	0	-1	3	0	0	0
1	0	0	1.682	1	0	0	+1				
6	0	0	0	6	0	0	0				
Total Runs = 20				Total Runs = 20				Total Runs = 15			

Part II. Lignin cleavage for the production of oxy aromatics/ technical Lignin from a pulp mill

The Box-Behnken design

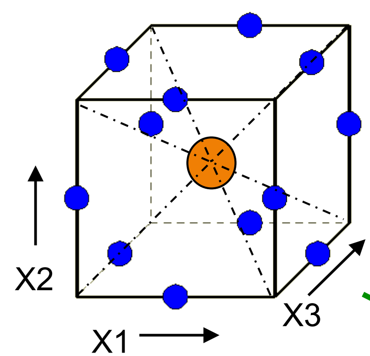
is an independent quadratic design (for the response surface methodology) based on combined statistical tests and quadratic equations.

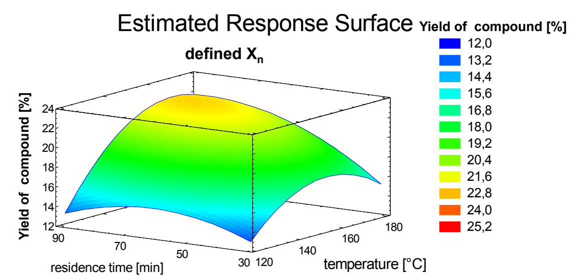
In this design the treatment combinations (combination of Process parameters (X_n))

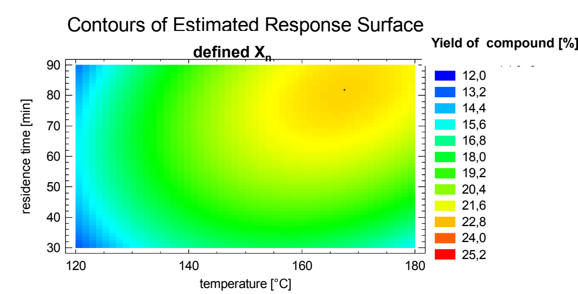
are at the **midpoints of edges (12)** of the process space and at the **center (3)**.

These designs are rotatable (or near rotatable) and require 3 levels of each factor:

Factors	Levels
X1 **(e.g. Temperature)**	-1; 0; +1
X2 **(e.g. c_{NaOH})**	-1; 0; +1
X3 **(e.g. residence time)**	-1; 0; +1





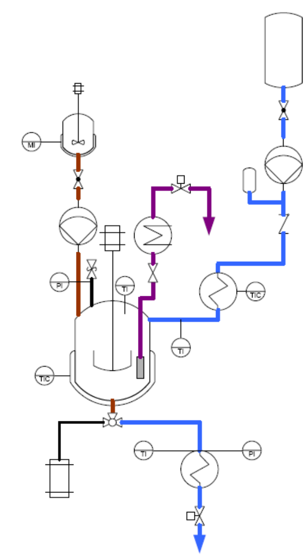


Fraunhofer CBP Fraunhofer ICT

Part II. Lignin cleavage for the production of oxy aromatics/ technical Lignin from a pulp mill

What are the goals of DoE in BCD of technical Lignin?

- Parametric studies (variable T, τ, $C_{catalyst}$) at const. p, $C_{technical\ Lignin}$ (**screening experiments to evaluate the reaction behavior**)
- **Effect of** the **variable process parameters/ controlled inputs** (T, τ, $C_{catalyst}$) & **Effect of a Co-factor** (mineral content:12wt.-%; (Na^+, K^+, Mg^{2+})) on:
  - Yield of Oil and Tar
  - Monomer composition of the Oil
  - Elemental composition of Lignin, Oil and Tar
  - Carbon balance / Carbon distribution over phases
  - Molecular weight of Tar



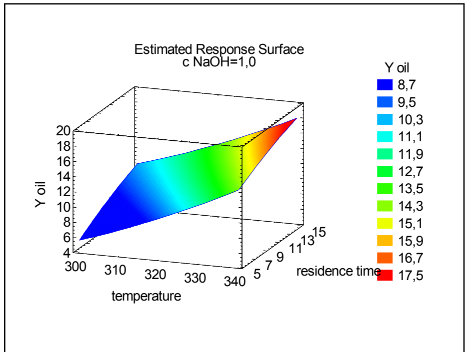
Fraunhofer CBP

Fraunhofer ICT

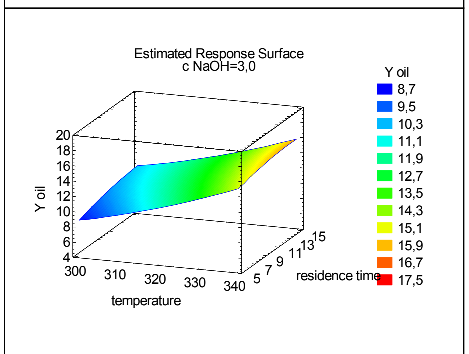
Part II. Lignin cleavage for the production of oxy aromatics/ technical Lignin from a pulp mill

[NaOH]

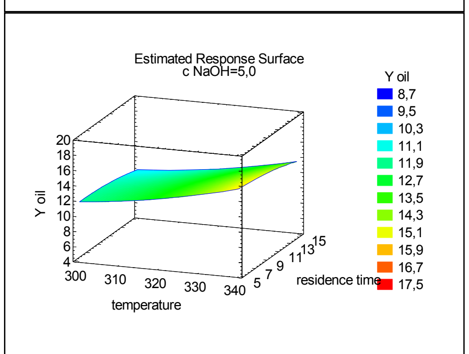
Low
(1%)



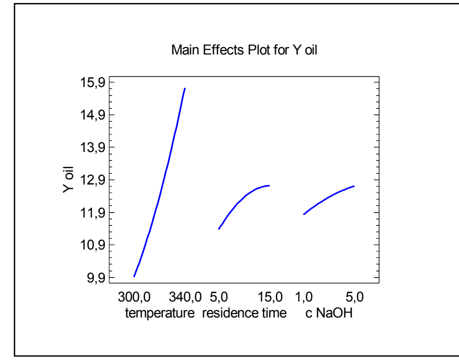
Medium
(3%)

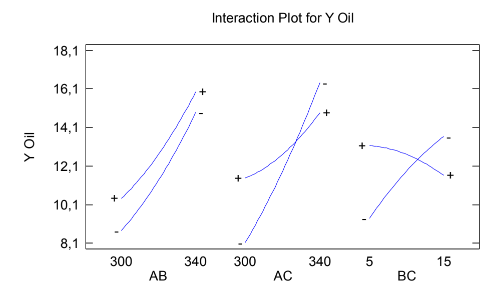


High
(5%)



Effect of C $_{NaOH}$ on the oil Yield





Optimize Response
Goal: maximize Yield of Oil [wt.-%]

Estimated optimum value = 17,94 [wt.-%]

Correlation: R^2 = 95,44 %

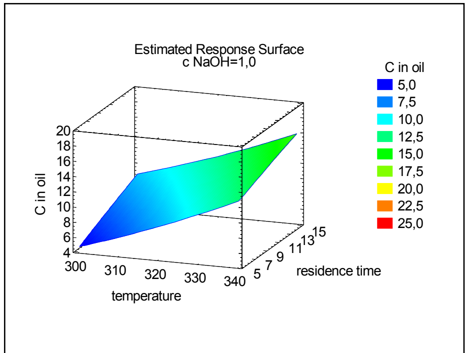
Factor		*Low*	*High*	*Optimum*
Temperature	[°C]	300,0	340,0	339,433
Dwell time	[min]	5,0	15,0	15,0
c_{NaOH}	[%]	1,0	5,0	1,0

Fraunhofer CBP   Fraunhofer ICT

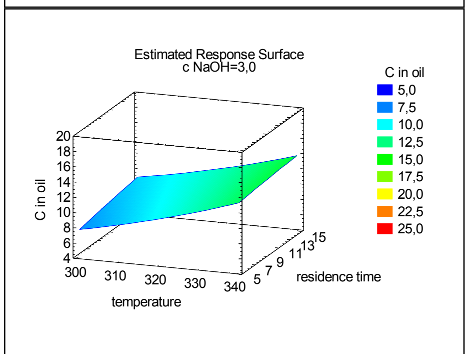
Part II. Lignin cleavage for the production of oxy aromatics/
technical Lignin from a pulp mill

[NaOH]

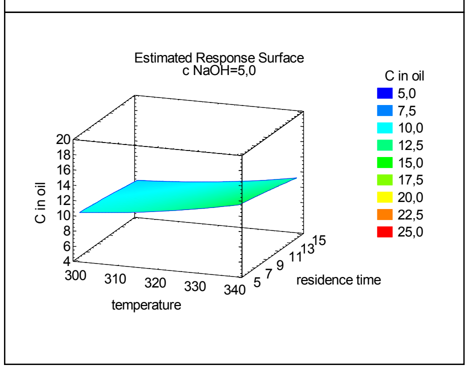
Low
(1%)



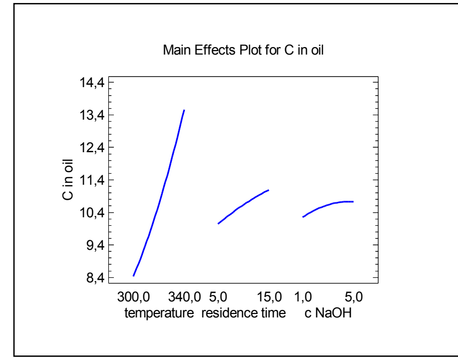
Medium
(3%)

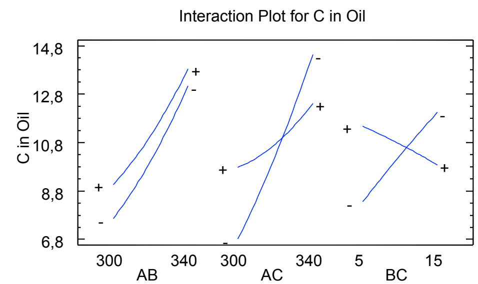


High
(5%)



Effect of C_{NaOH} on the relative Carbon content in oil





Optimize Response

Goal: maximize Carbon in Oil originating from Lignin [wt.-%] –

Conversion degree into Oil

Estimated optimum value = 15,91 [wt.-%]

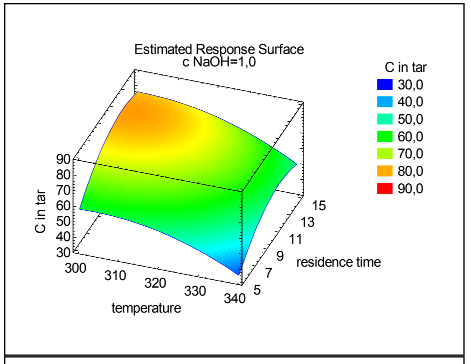
Correlation: R^2 = 94,32 %

Factor	*Low*	*High*	*Optimum*
Temperature [°C]	300,0	340,0	**339,437**
Dwell time [min]	5,0	15,0	**15,0**
c_{NaOH} [%]	1,0	5,0	**1,0**

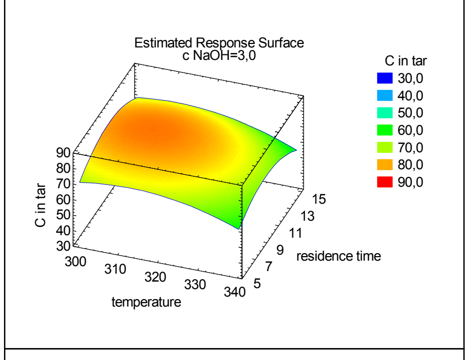
Part II. Lignin cleavage for the production of oxy aromatics/ technical Lignin from a pulp mill

[NaOH]

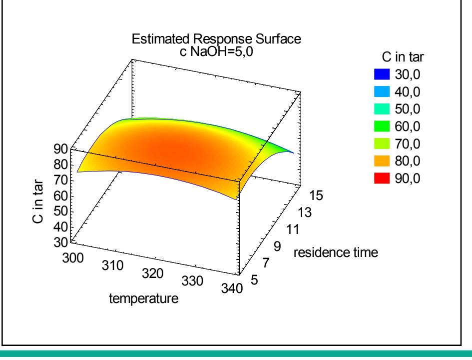
Low
(1%)



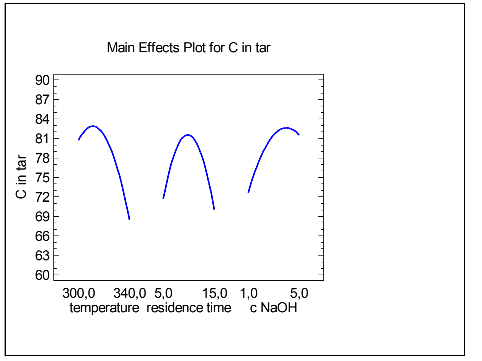
Medium
(3%)



High
(5%)



Effect of C_{NaOH} on the relative Carbon content in Tar



Optimize Response
Goal: maximize Carbon in Tar originating from Lignin [wt.-%] –
Conversion degree into Tar

Fraunhofer CBP

Fraunhofer ICT

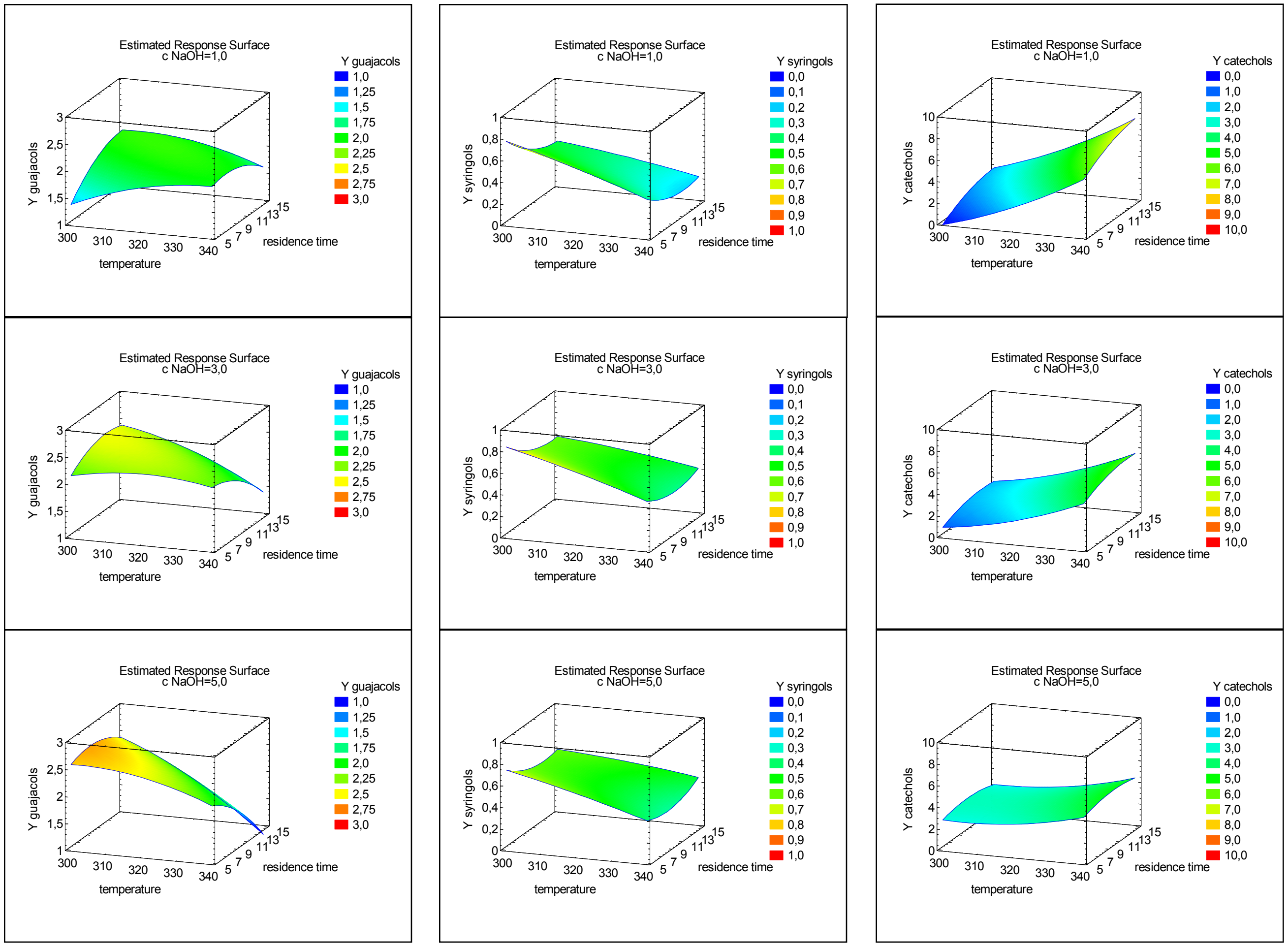
Part II. Lignin cleavage for the production of oxy aromatics/ technical Lignin from a pulp mill

[NaOH] | Guaiacol type monomers | Syringol type monomers | Catechol type monomers

Low (1%)

Medium (3%)

High (5%)



Effect of C_{NaOH} on the Yield of selected monomer compounds in BCD oil

Fraunhofer CBP

Fraunhofer ICT

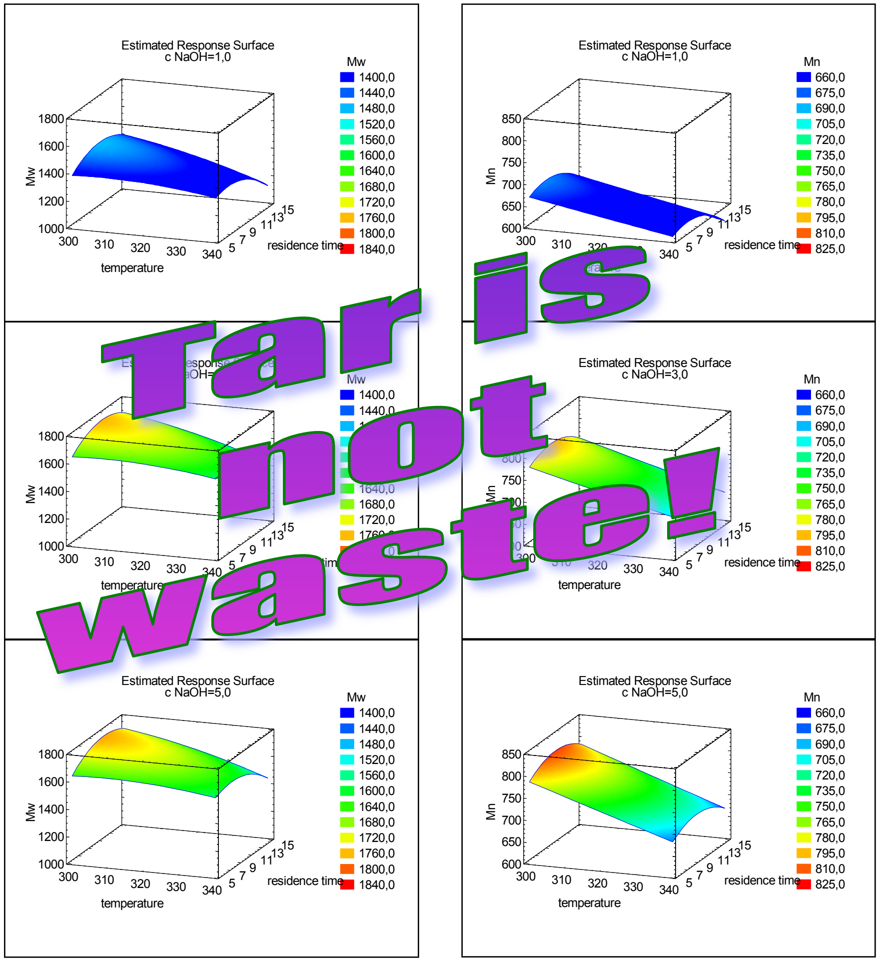
Part II. Lignin cleavage for the production of oxy aromatics/
technical Lignin from a pulp mill

[NaOH] **Mw** **Mn**

Low (1%)

Medium (3%)

High (5%)



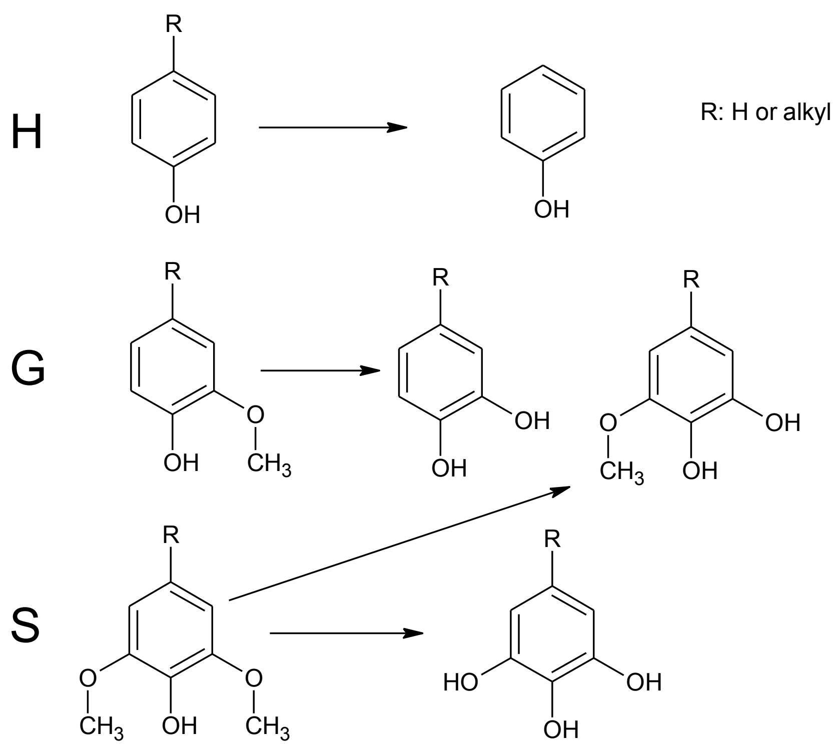
technical Lignin:
Mw: 3592g/moles
Mn: 1022g/moles
PD: 3.54

Effect of C_{NaOH} on the molecular characteristic (Mw, Mn) **of Tar**

Fraunhofer CBP Fraunhofer ICT

Summary: Process factors / substrate factors effect during BCD on Lignin

- Generally process parameters & the type of lignin influence the yield, composition & properties of the fractions (tar , oil)



process parameters:

T, τ, p, catalyst

presence of additives

Botanical source/ Pulping conditions:

HGS-Lignin (annual plants)

GS/SG-Lignin (hard wood)

G-Lignin (soft wood)

Mixtures

Summary

- Oil yields are around 20 wt% in short residence times by BCD on OrganoSolv Lignin (beech)
- The yield of water insoluble (pH=3) oligomeric compounds (tar) is approx. 50wt% of Lignin
- Addition of sodium formiate favors the cleavage of aryl-methyl-ether bonds → increase of hydroxy functionalities in oil and tar
- Depending on the process parameters (T, p, residence time, catalyst) and the downstream processing a defined product distribution can be reached
- The downstream processing / extraction has to be optimized
- Only combined processes (- subsequent bond splitting by hydro cracking, pyrolysis or oxidation of Tar) will be successful for high monomer aromatic yields
- BCD on Lignin is also a pretreatment step for biotechnological conversion routes.

Acknowledgment:

Agency for Renewable Resources (Ministry for Agriculture, Forestry, Fishery & Consumer protection), Germany, for financial support

Dow Chemical for cooperation

Nordic pulp mill & paper industry for cooperation and financial support

vTI, Hamburg, Germany (D. Meier (PhD)) for the references & advice

International Lignin Institute, (A. Abaecherli) for the Lignin of an annual plant

Colleagues of Fraunhofer ICT (Pfinztal, Germany) for the team work

Contact

Detlef Schmiedl, PhD
Fraunhofer Institute for Chemical Technology ICT
Environmental Engineering
Joseph-von-Fraunhofer-Str.7
D-76327 Pfinztal
Phone ++49(0)721/4640-747
Fax ++49(0)721/4640-111
E-mail: detlef.schmiedl@ict.fraunhofer.de
http://www.ict.fraunhofer.de

Gerd Unkelbach
Fraunhofer Center for Chemical-Biotechnological Processes CBP
Am Haupttor (Bau 4310)
06243 Leuna
Phone ++49 (0)721/4640-605
E-mail:gerd.unkelbach@cbp.fraunhofer.de
http://www.cbp.fraunhofer.de

Thank you for your attention!