biocoup

Resins from pyrolysis oil to make wood panels

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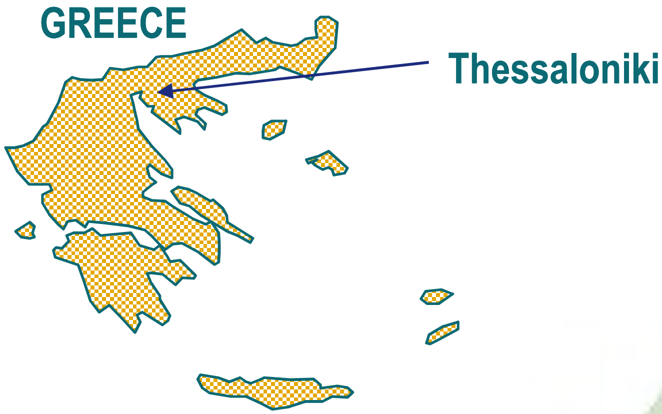
Chimar Hellas

Chimar Hellas S.A. is a private research institute serving the wood-based panels industry

Its activities include:

- **Development and licensing of technology for thermosetting resins and additives (hardeners, formaldehyde scavengers, fire retardants, wetting agents for paper impregnation etc).**
- **Technical support remotely and on site both at resin and wood-based panels producers.**
- **Training of client personnel.**
- **Services on knowledge protection and installation of Quality Management Systems.**



Chimar is also active in industrial engineering and plant procurement for formaldehyde, UFC, resins and chemical additives.

Chimar Hellas has 33 years expertise in

36 countries all over the world.

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- Composition of wood pyrolysis liquid-variations
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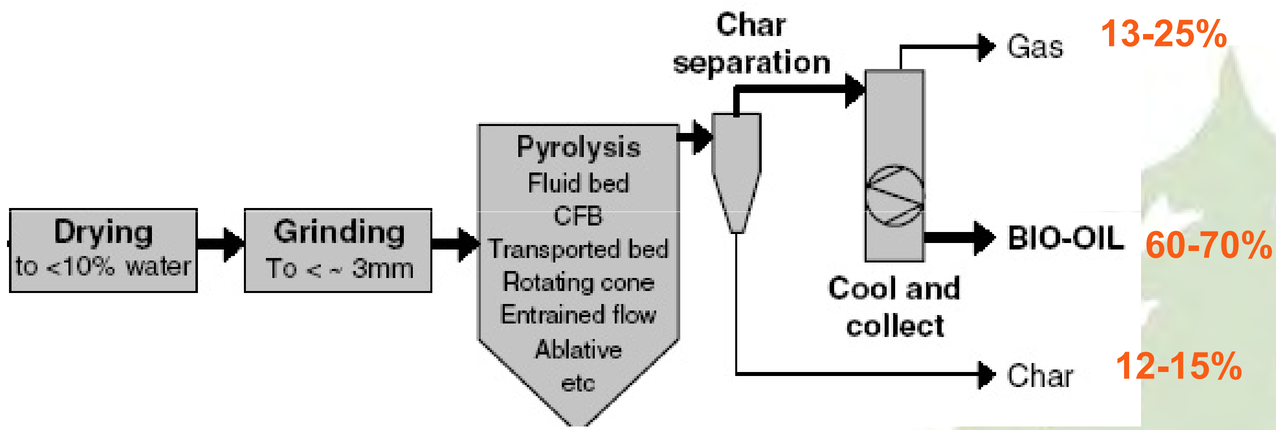
- Conclusion

Biomass and pyrolysis products

The total global live biomass has been estimated as 2000 billion tones of which 1600 billion tones are found in forests



In 2002, more than **80% of primary bioenergy production** in the EU came **from wood-based feedstocks**, while 13% came from municipal solid waste and the rest from biogas and other sources. *(http://www.thegreenpowergroup.org/eu.cfm)*

Composition of wood pyrolysis liquid

Pyrolysis liquid from wood is a complex mixture mainly comprised of the cellulose, hemicellulose and lignin degradation products and water (appox. 25%) that cannot be easily removed.

Fraction	Major components		Mass, %
	Water		**20-30**
Water insoluble	**Lignin fragments**	Insoluble pyrolytic lignin	**15-30**
Water soluble	Aldehydes	Formaldehyde, acetaldehyde, hydroxyacetaldehyde, glyoxal, methylglyoxal	**10-20**
	Carboxylic acids	Formic, acetic, propionic, butyric, pentanoic, hexanoic, glycolic (hydroxyl acetic)	**10-15**
	Carbohydrates	Cellobiosan, a-D-Levoglucosan, oligosaccharides, 1,6 anhydroglucofuranose	**5-10**
	Phenols	Phenol, cresols, guaiacols, syringols	**2-5**
	Furfurals		**1-4**
	Alcohols	Methanol, ethanol	**2-5**
	Ketones	Acetol (1-hydroxy-2-propanone), cyclopentanone	**1-5**

Variations in pyrolysis liquid composition

1. Feedstock

	Molecular weigh		
lignin	weight average, Mw	number average, Mn	polydispersity, Mw/Mn
WIF (softwood **bark residues**)	**1163**	**577**	2.0
Biomass Technology Group (BTG) – mixed softwood	1317	592	2.2
MWL (**spruce**)	**5720**	**3270**	1.8

2. Process

	Yield (wt % anhydrous feed basis-birch)				
stepwise pyrolysis (°C)	solid residue	pyrolysis oil	gas	water	**phenols**
1. 25-200	93.96	6.02	0.02	5.91	0.00
2. 200-275	70.46	18.14	5.36	6.19	0.40
3. 275-350	37.85	27.28	5.33	6.95	2.18
4. 350-450	25.67	9.47	2.71	0.70	1.83
5. 450-550	23.25	1.48	0.94	0.41	0.01
cumulative (steps 1-5)	25.25	62.39	14.36	20.16	**4.42**
one-step, 25-500	24.79	63.43	11.78	19.79	**2.51**

3. Storage

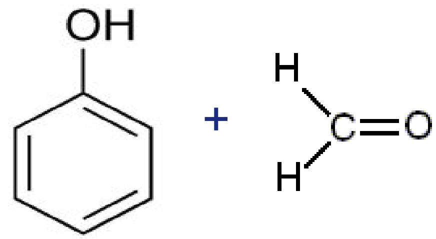
(*reactions between the different components*)

Not all pyrolysis liquids are the same !

PF resins

What is a phenol formaldehyde resin?

Oligomeric product resulted from the polycondensation of phenol with formaldehyde.

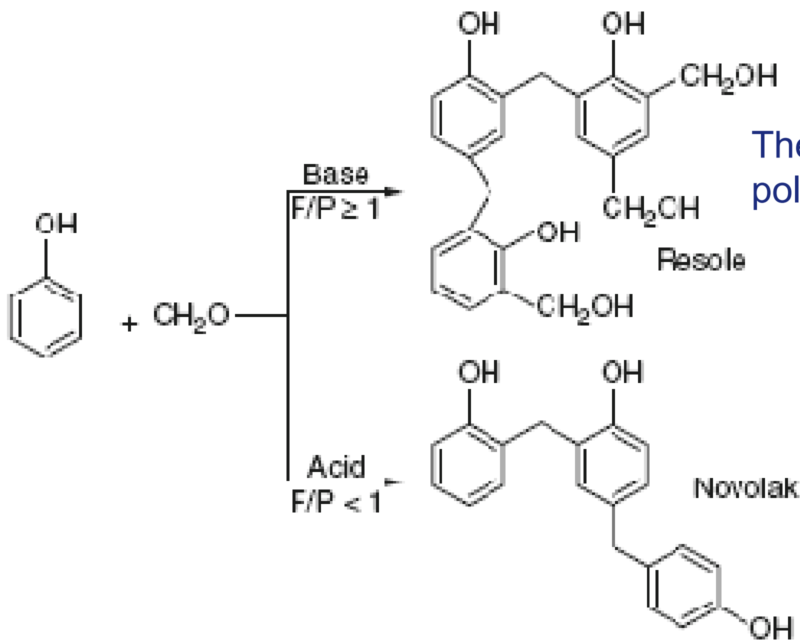


How does it look like??

Wide range of flow from liquid to hard

a) Novolak: Acid catalyzed reaction, mole ratio F/Ph<1

b) Resols: Base catalyzed reaction, mole ratio F/Ph>1 *(in practice 1.6-2.6)*



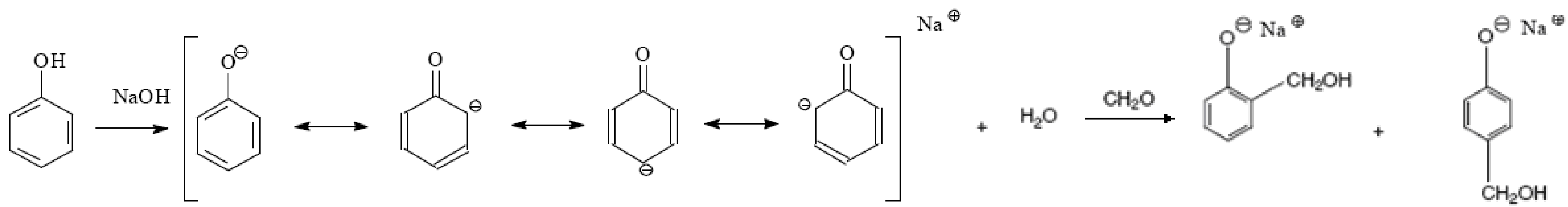
Thermosetting polymer

Thermoplastic polymer

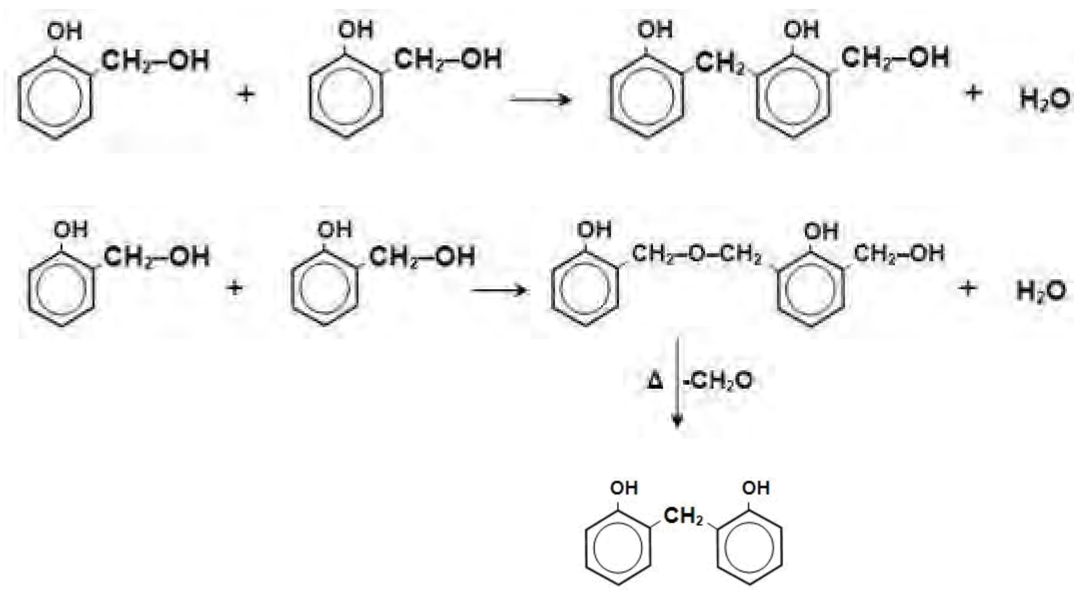
Wood-based panels industry uses resol resins

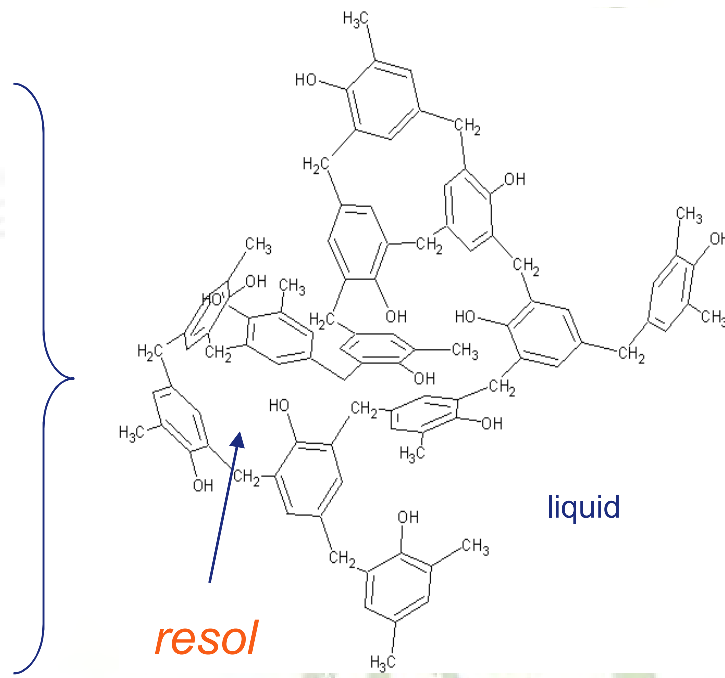
Synthesis process of resol resins

Step 1-Addition reactions



Step 2-Polycondensation reactions





Step 3 – Completion of crosslinking *(during PW production)*

Typical process for the synthesis of a PF resol resin

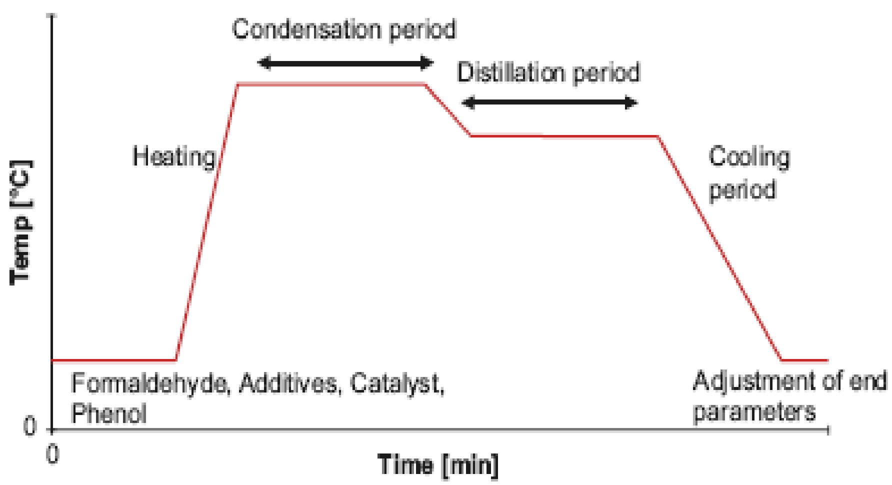
- Dosing and addition of raw materials.
- Heating to about 60°C for a certain period of time, as to allow the conduction of addition reactions (stage A).
- Heating to about 100°C for a certain period of time for the polymerization stage (stage B).
- Distillation of excess water, if needed.
- Cooling.
- Adjustment of final parameters (e.g. pH)

Lab synthesis of a PF resin at Chimar premises

Synthesis process of resol resins

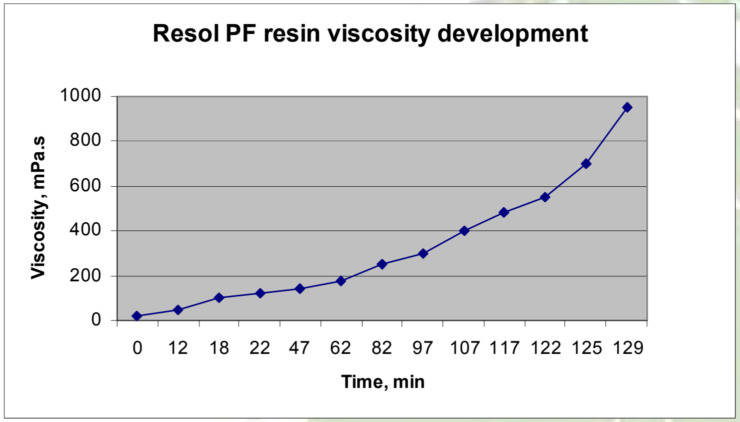
Characteristics of the synthesis process

- Strongly exothermic reactions: good temperature control is required.
- In common practice, the polycondensation reaction is stopped when a target viscosity is reached.
- The polycondensation reaction is ceased by rapid cooling; ***but*** polymerization reactions continue even at ambient temperatures, although at much slower rates ⟹ short storage life of the resin.



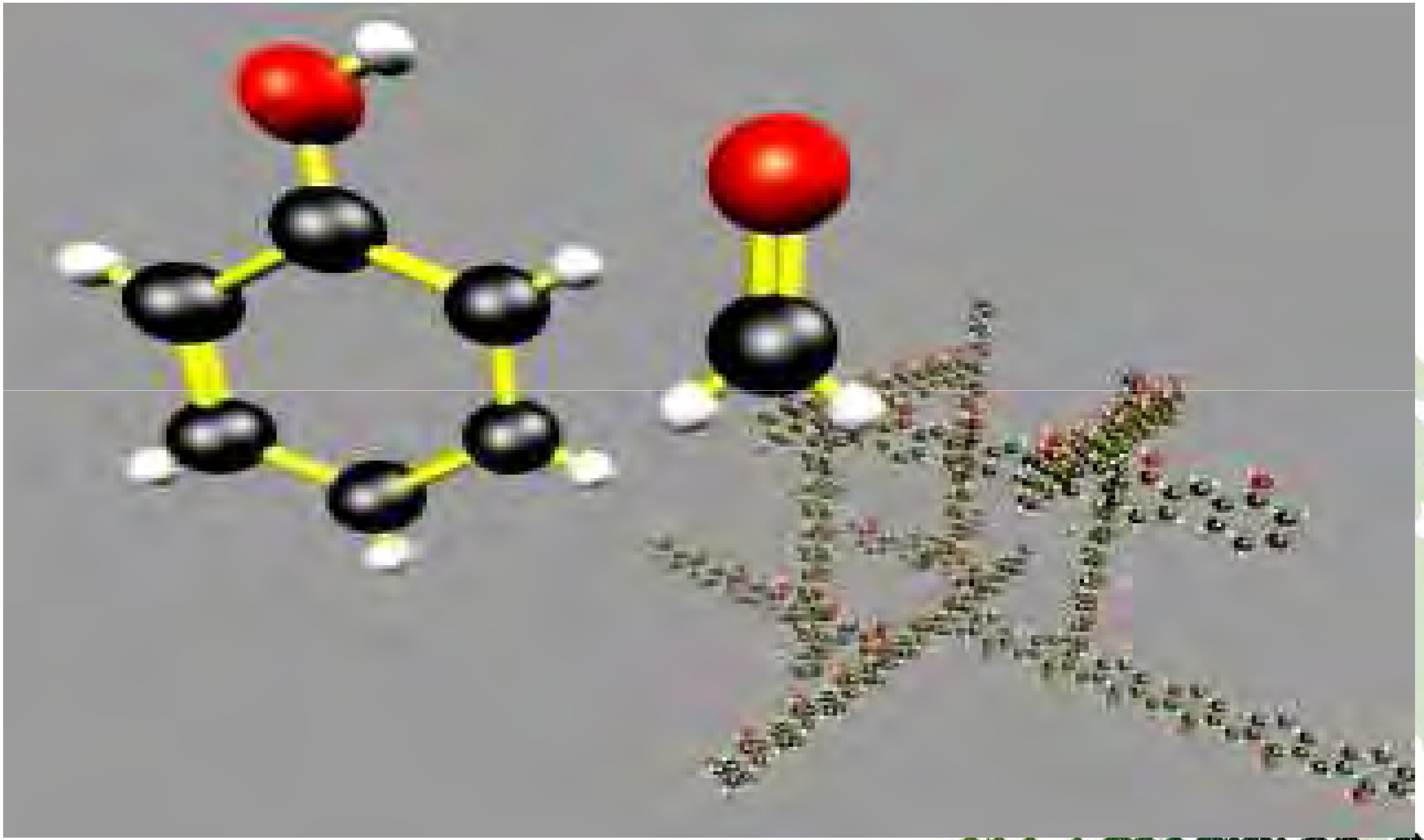
Time-temperature scheme of a resole resin synthesis

Source: Jürgen Lang Marc Cormick, resole production (chapter 6) in Phenolic resins: a century of progress, L. Pilato (Ed), Spinger-Verlag, Heidelberg, 2010.



Indicative viscosity development during the synthesis of a resol PF resin

3D visual synthesis of a PF resin



http://www.youtube.com/watch?v=NpO2DAvMWi4&feature=related

Resin properties for quality control

- Resin content
- pH
- Viscosity
- Water dulability
- Specific gravity
- Gelation time
- Alkalinity
- Conductivity

Other sophisticated analysis methods are: Infrared Spectroscopy (IR), Mass Spectroscopy (MS), High Performance Liquid Chromatography (HPLC), Themogravimetric Analysis, Differential Scanning Calorimetry, etc.

BIOCOUP EU funded project

BIOCOUP: “Co-processing of upgraded bio-liquids in standard refinery units”.

EU funded & VTT coordinated.

17 partners from various countries.

The aim of BIOCOUP is to develop a chain of process steps, which would allow biomass feedstock to be co-fed to a conventional oil refinery. Energy and oxygenated chemicals will be co-produced. The overall innovation derives from integration of bio-feedstock procurement with existing industries (energy, pulp and paper, food) and processing of upgraded biomass forms in existing mineral oil refineries.

Experimental resins with pyrolysis liquid

Samples tested by Chimar Hellas within the framework of BIOCOUP project:

- Crude bio oil from pine and forestry residues delivered by VTT in Finland.
- Phenolic fractions provided by the Slovenian Institute of Chemistry.
- Aldehydic fraction recovered by the Eindhoven University of technology in the Netherlands.

All samples were compatible with phenol and formaldehyde.
Not all of them gave smooth reactions.

- Crude bio oils performed irregularities at substitution levels higher than 25%.
- The phenolic fraction gave a smooth synthesis even at 50% phenol substitution levels.
- The aldehydic fraction did not created any problems in the synthesis of the resin but it was tested only at a 10% formaldehyde substitution.

Requested properties of raw materials & resins

The pyrolysis oil materials **<u>have not</u>** to:

- be very viscous because otherwise it is difficult to be handled (e.g. transportation & weigh of the material).
- perform cohesion properties with glass or metals, because otherwise they stick on the surface of their container.
- have irksome odour.
- have inherently high reactivity, because it will lead to very rapid reactions during the synthesis of the resin, that is undesirable.

Quality control of "bio resins" (*besides the standard properties*)

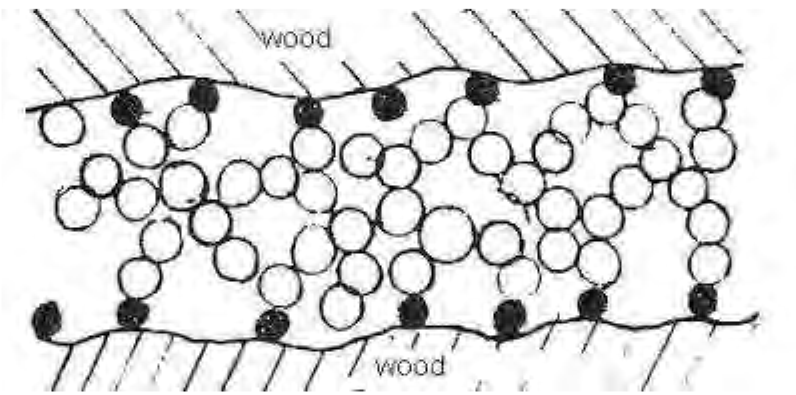
- easy free flow.
- no agglomerations.
- easy washing out from the reactor and
- acceptable storage life (above 1 month).

Properties of synthesised bio-resins

Provider of the sample	CHIMAR	TUe	VTT	VTT	SIC	VTT	VTT	SIC	SIC	SIC	SIC	SIC
sample	PF std	Aldehydic fraction	Bio –oil from Pine	Bio-oil from Forestry residue	Ph. fraction	Bio –oil from Pine	Bio –oil from Forestry residue	Ph. fraction	Ph. fraction	Ph. fraction	Ph. fraction	Ph. fraction
Code of sample		Aldehydic fraction	PF/PDN 35-06	PF/PDU 5-07	OP1 03-09	PF/PDN 35-06	PF/PDU 5-07	PMO 12-08	PMO 12-08	OP1 03-09	OP1 03-09	PMO 12-08
Level of Phenol sub., %	-	5	15	15	15	25	25	25	25	25	35	50
Solids, %	45.7	50.87	45.4	45.0	45.48	44.9	45.0	46.4	51.09	50.02	49.8	46.3
Viscosity @ 25°C, cP	560	485	550	490	410	400	580	520	525	325	365	610

Wood adhesion theories

Adhesion theory	Adhesion method	Production stage
Mechanical interlocking	Sufficient penetration	Cold pressing
Adsorption/specific adhesion	wood-adhesive interaction	During wetting of wood substrate
Chemical bonding	wood-adhesive interaction	Hot pressing



- Active groups of wood
- Active groups of adhesive
- Adhesion bonds
- Cohesion bonds

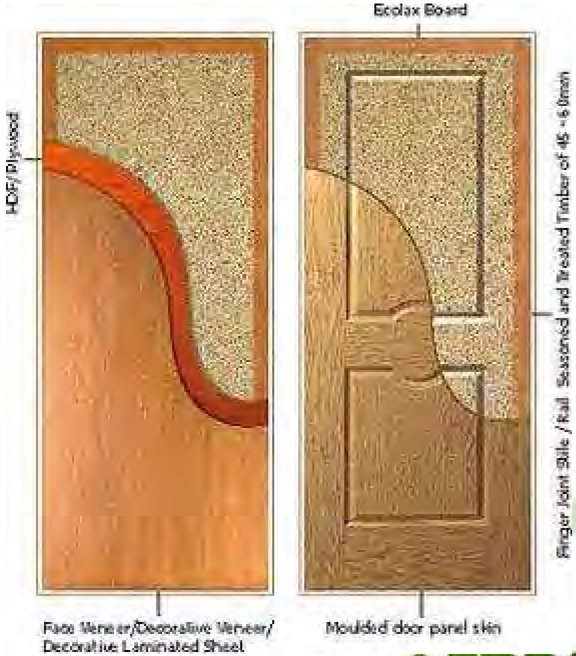
Good bonding ⇨ adhesion + cohesion of resin > cohesion of wood

What is it?

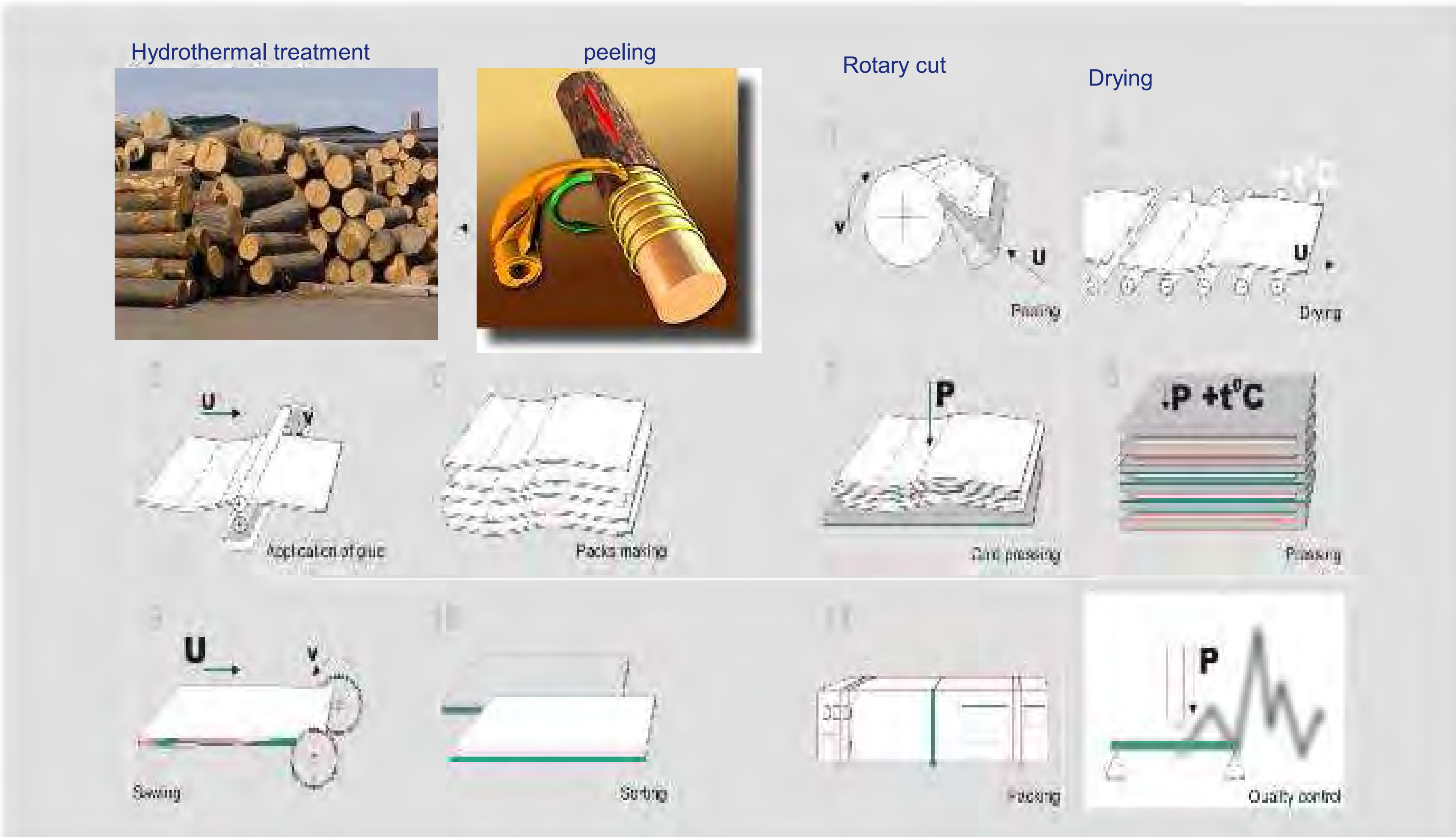
Veneers-odd number

Cross bonding – face to face

Applications



Typical production process



Application of resin

Mixture of resin + extender + hardener + water.

Critical points: viscosity, pot life, short time curing.

Assembling

Resin application and stacking of veneers at right angles.

(waiting time 15 min-1h)

Cold pressing

Pressure 5-7kg/cm^2. Expedite the penetration of the resin in wood pores.

Critical point: good tack.

(Waiting time >1h)

Hot pressing

The temperature and time of pressing depends on the type of veneers. The optimum temperature for the curing of a phenolic adhesive is above 125°C.

Critical point: water balance.

Visual production of PW

Classification, testing & evaluation methods of PW

- Testing of plywood = testing of the glue line.
- Plywood panels are classified according to their application.
- Different testing conditions depending on the application or the class of plywood.

The basic European standards for the testing and evaluation of plywood panels as per their shear strength, wood failure performance and free formaldehyde emissions are:

EN 314.1
Plywood - Bonding quality - Part 1: Test methods (June 1993). Revision published in 2004.

EN314.2
Plywood - Bonding quality - Part 2: Requirements (June 1993).

EN 717-1
Wood-based panels - Determination of formaldehyde release - Part 1: Formaldehyde release - Part 1: Formaldehyde emission by the chamber method (Published in 2004).

EN 717-2
Wood -based panels - Determination of formaldehyde release - Part 2: Formaldehyde release by the gas analysis method (April 1995). (Corrigendum published in 2002).

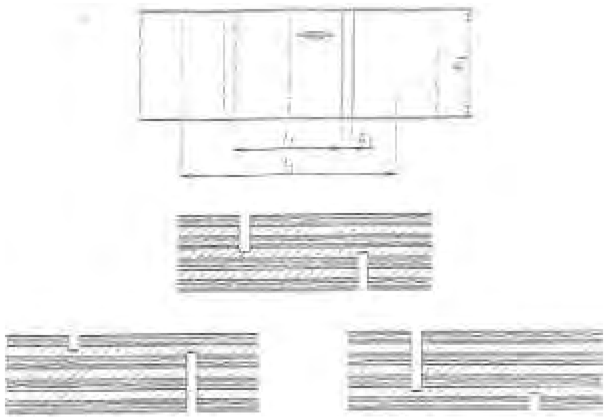
Full list of standards for PW: http://**europlywood.satelithost.be/index.php?page=technical-information**

Depending on the application there are different pre-treatments before the measurement of the shear strength and wood failure performance.

The pretreatments for each class of plywood are specified by the standard EN314.2. The testing is carried out following the procedure described in the standard EN314.1

Category	Application	Pretreatment
Class 1	Use in dry conditions	Immersion in water for 24h (20±3°C)
Class 2	Covered panels for exterior use	Immersion for 6 h in boiling water followed by cooling in water at (20 ± 3) °C, for at least 1 h
Class 3	Non covered panels for exterior use	Immersion for 4 h in boiling water, then drying in the ventilated drying oven for 16 h to 20 h at (60 ± 3) °C, then immersion in boiling water for 4 h, followed by cooling in water at (20 ± 3) °C for at least 1 h.

Shear strength test



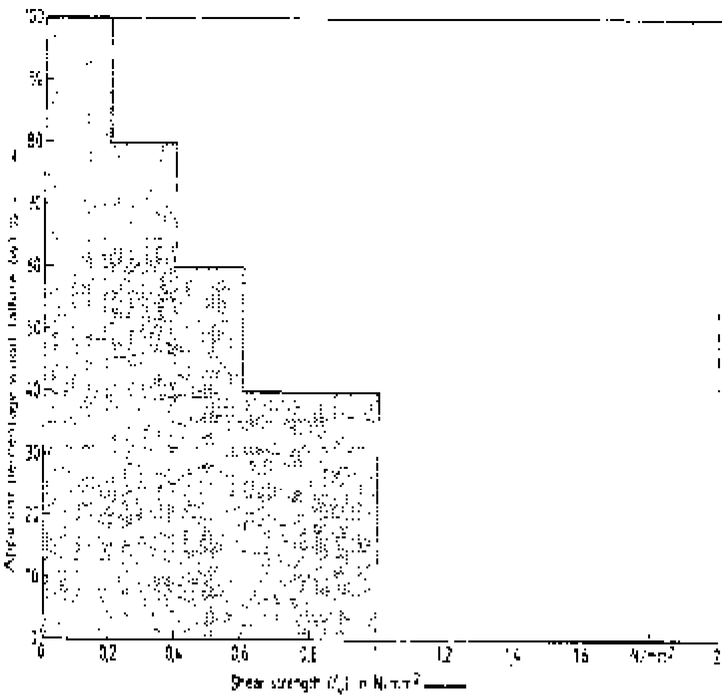
Testing of plywood for shear strength at Chimar premises

Wood failure test

Grade = % area covered with fibers.

100% corresponds to a very strong bonding and a complete wood failure.

Plywood bonding and free formaldehyde requirements



The threshold values for plywood evaluation as per EN314.2

Mean shear strength fv, N/mm²	Mean apparent cohesive wood failure w, %
0.2 ≤ fv < 0.4	≥ 80
0.4 ≤ fv < 0.6	≥ 60
0.6 ≤ fv < 1.0	≥ 40
1.0 ≤ fv	no requirement

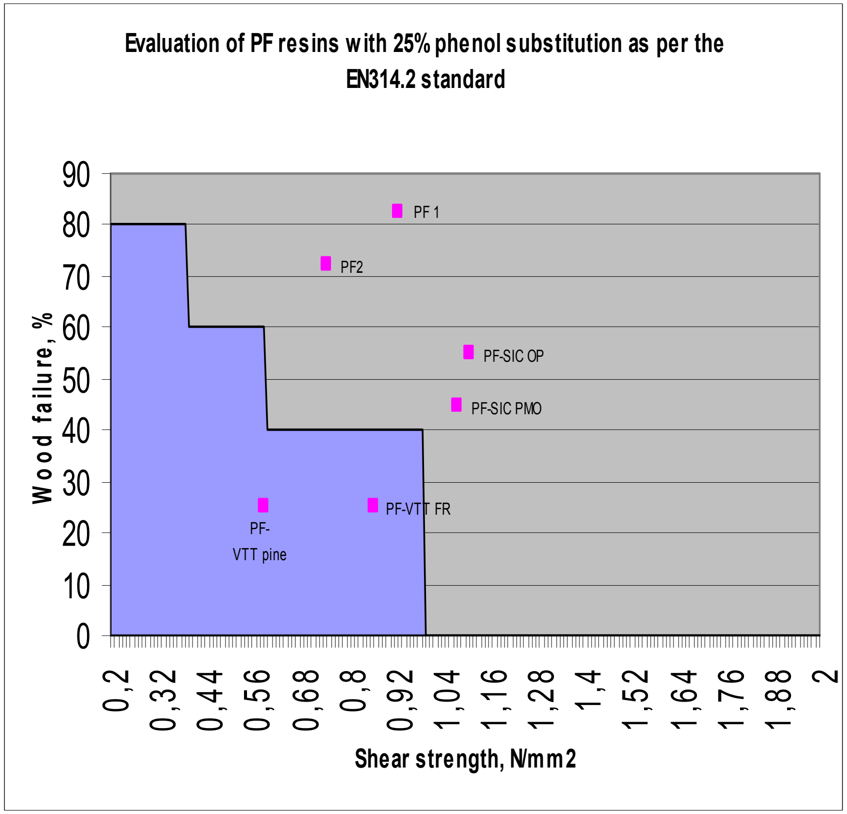
Class	Limit of free formaldehyde emissions	Test method
E1	≤0.1ppm ≤3.5 mg/h*m²	EN 717-1 EN 717-2
E2	>0.1ppm >3.5 ÷ ≤0.8mg/h*m²	EN 717-1 EN 717-2

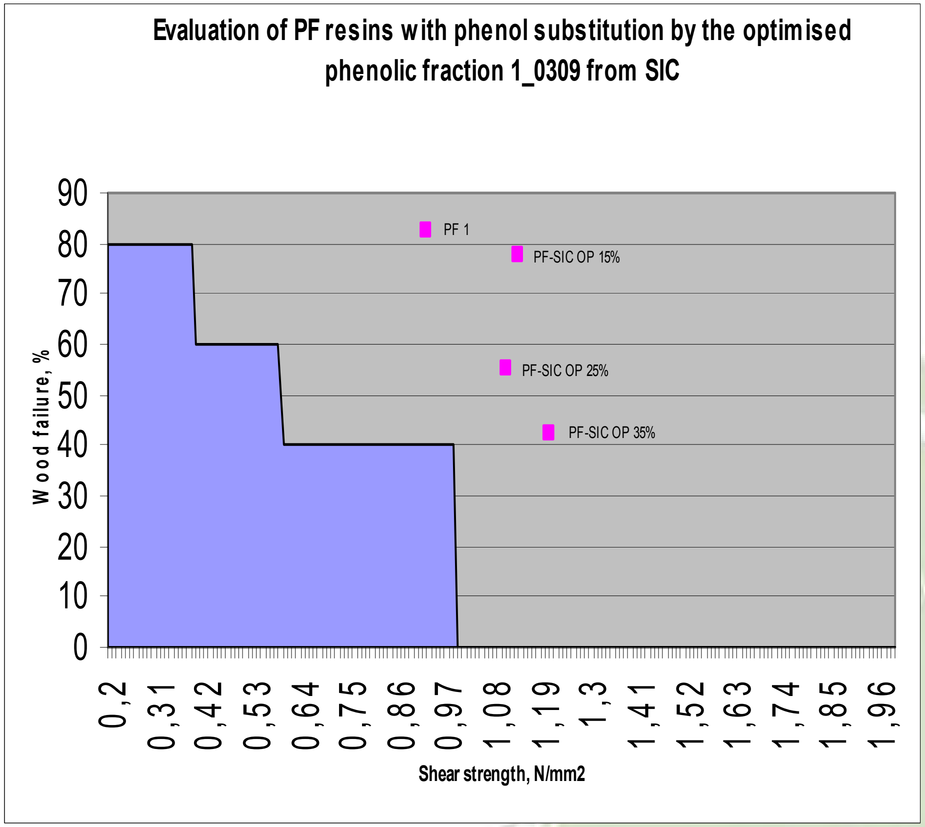
PW with BIOCOUP bioresins

Resin-Sample provider		PF 1 Chimar	PF 2 Chimar	PF-VTT	PF-VTT	PF -SIC	PF -SIC
Sample		-	-	Pine	Forestry residues	Ph. fraction PMO 12-08	Ph. fraction OP 1-0309
Ph. sub., %		-	-	**25**	**25**	**25**	**25**
EN 314.1	Shear strength N/mm^2- Fv	0.93	0.75	0.59	0.87	1.08	1.1
	Wood failure, %	82.5	72.5	25	25	45	55

Resin-Sample provider		PF std Chimar	PF -SIC	PF -SIC	PF -SIC
Sample		-	Ph. fraction PMO 12-08	Ph. fraction PMO 12-08	Ph. fraction PMO 12-08
Ph. sub., %		**-**	**15**	**25**	**35**
EN 314.1	Shear strength N/mm^2- Fv	0.93	1.14	1.08	1.21
	Wood failure, %	82.5	77.5	45	42.5

Evaluation of BIOCOUP bioresins





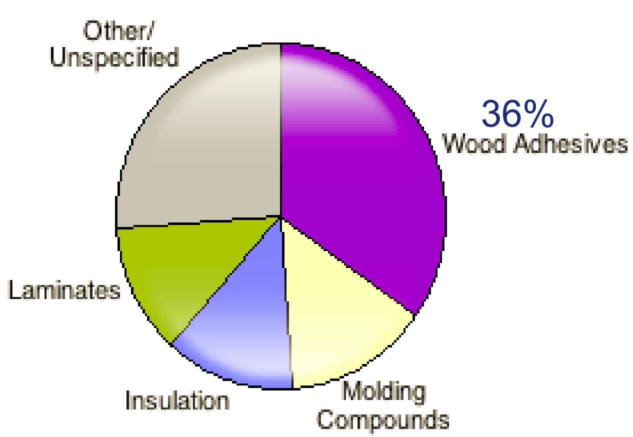
Market prospects

Today, not many phenolic resins from bio oil or its fractions are available on the market yet.

The global production and consumption of PF resins in 2009 were approximately 3.0 to 3.1 million metric tons, respectively.

It is expected an average growth of 3.9% per year from 2009 to 2014, with slower demand growth of around 2.9% per year from 2014 to 2019.

World Consumption of Phenol-Formaldehyde Resins - 2009



Generally, by 2025 it is predicted that the biochemical market will worth €175-420bn equal to a chemical production market share of 7-17%.

(Source:Nieuwenhuizen/Little, 2010)

Source: SRI consulting, World Petrochemical (WP) report on PF Resins, January 2010

Future of pyrolysis liquid products

Just being “green” or bio-derived from a renewable source are not enough to be accepted in the market place.

Necessary pyrolysis liquid optimizations

•Availability at large quantities through out the year.
•Standard quality.
•Competitive cost.
•Improvement of some physicochemical properties like odour and high viscosity.

Conclusion

The biorefinery process is a very promising concept for biomass exploitation.

Not only more research and process development are still required but also political incentives, economical support and legal regulations.

Success requires synergy !!

Thank you very much

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