UNIVERSITÀ DEGLI STUDI DI PADOVA
DIPARTIMENTO DI INGEGNERIA INDUSTRIALE
Corso di Laurea Magistrale in Ingegneria Chimica e dei Processi Industriali

Polyols synthesis from waste by microwave lignin liquefaction

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Relatore: Prof.ssa Alessandra Lorenzetti

Laureanda: Lorenza Catini

Summary

- Introduction
- Polyols synthesis: **lignin liquefaction**
- Production and characterization of **polyurethane foams**
- Conclusions

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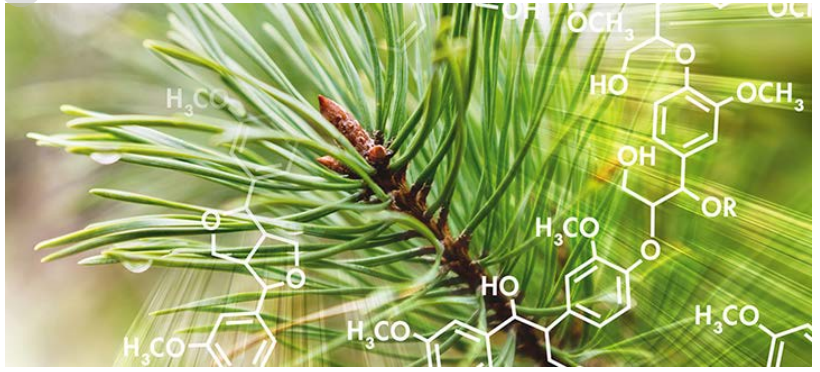
Environmental problems

Limited **fossil sources** and
environmental problems

Platform molecules

Lignin



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Lignin

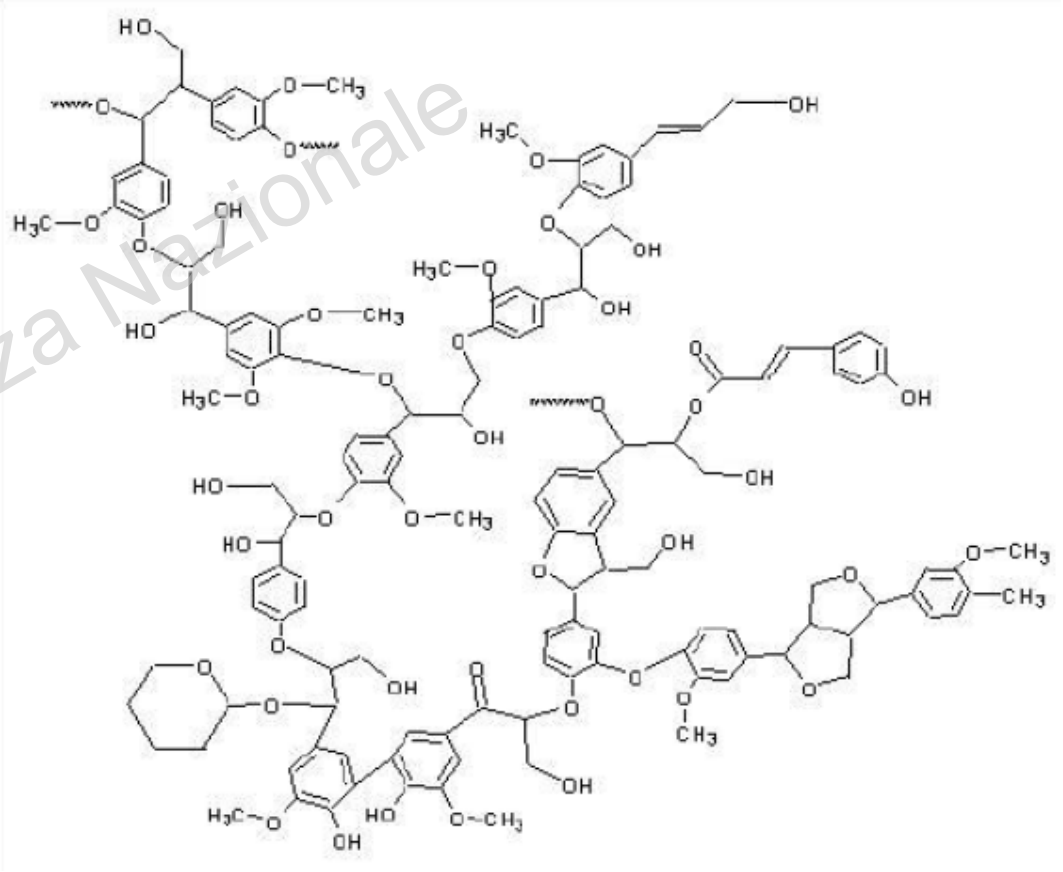
Lignocellulosic **biomass**

- Cellulose
- Emicellulose
- **Lignin** ~ 20-30%

But

- High availability
- Reach of phenolic group

Only 5% is used for chemical production



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Objectives

Optimization of lignin **liquefaction** process

Polyols synthesis

Polyurethane foam preparation and characterization

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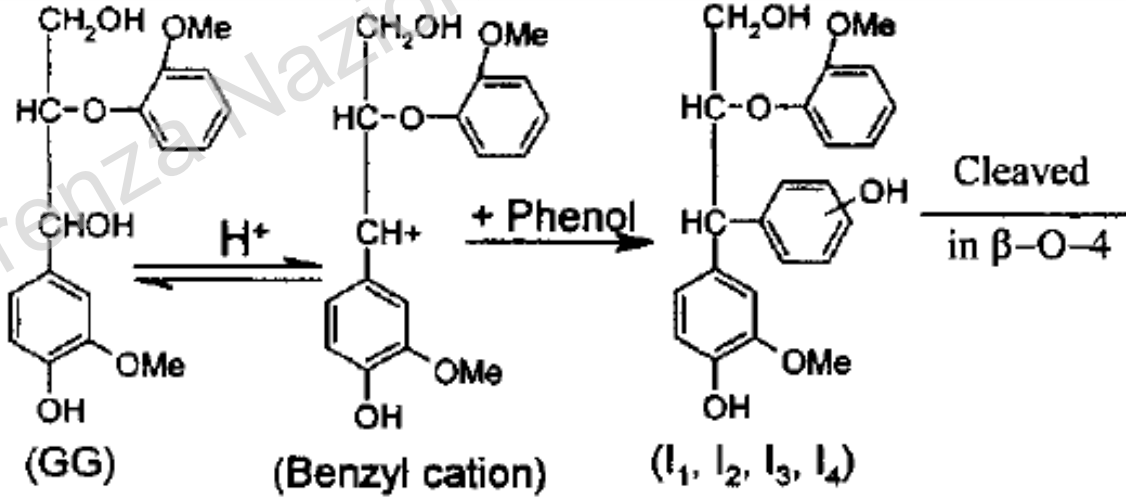
Liquefaction process

High molecular weight of lignin

Solvolysis process : C-C and C-O **bounds cleavage**

Decreasing nOH number and MW



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Liquefaction process

Reactions involved

- Depolymerisation
- Polycondensation

Literature conditions

- → High temperature: 150-170°C
- → Short time: 5-30 minutes
- → Acid or basic catalysis
- → Solvent-to-solid ratio between 5:1÷6:1
- → Solvent: PEG400/glycerine mixture

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Materials

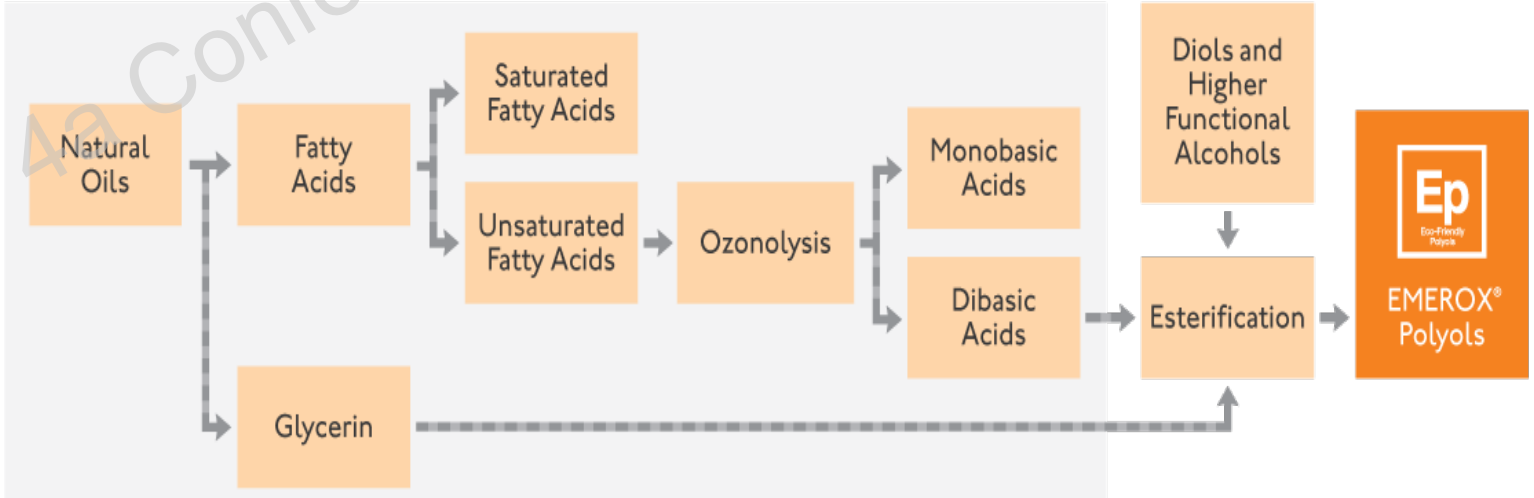
Lignin **INDULIN® AT**

EMEROX® polyols from **azelaic acid**

- Functionality
- Molecular weight
- Hydroxyl number

Solvents	nOH [mgKOH/g]	f	MW [g/mol]
EMEROX® 14270	356	2.7	425
EMEROX® 14280	274	2.7	502
EMEROX® 14511	107	2.0	1043
EMEROX® 14535xp	352	2.0	318
EMEROX® 14737xp	371	2.3	347
EMEROX® 14730	295	2.3	437

Glycerine



Catalysts

- Sulphuric acid
- Caustic soda

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Multimode **microwave** reactor

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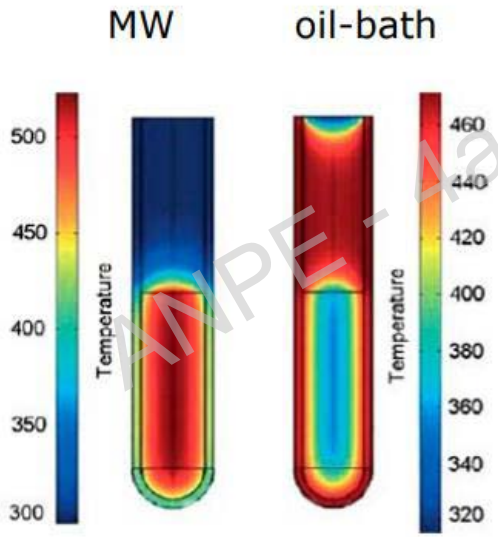
Methods

Multimode **microwave** reactor

- Rapid and uniform heating
- Lower reaction time
- Lower temperature



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Polyols characterization

Determination of nOH number with **potentiometric titration** → $nOH = \frac{56100 * f}{MW}$

nOH= **400-500** mgKOH/g in rigid foam

Calculation of **yield** → $\eta = 1 - \frac{M}{M_0}$

Gel permeation chromatography (**GPC**) → **Molar weight** distribution of polyols

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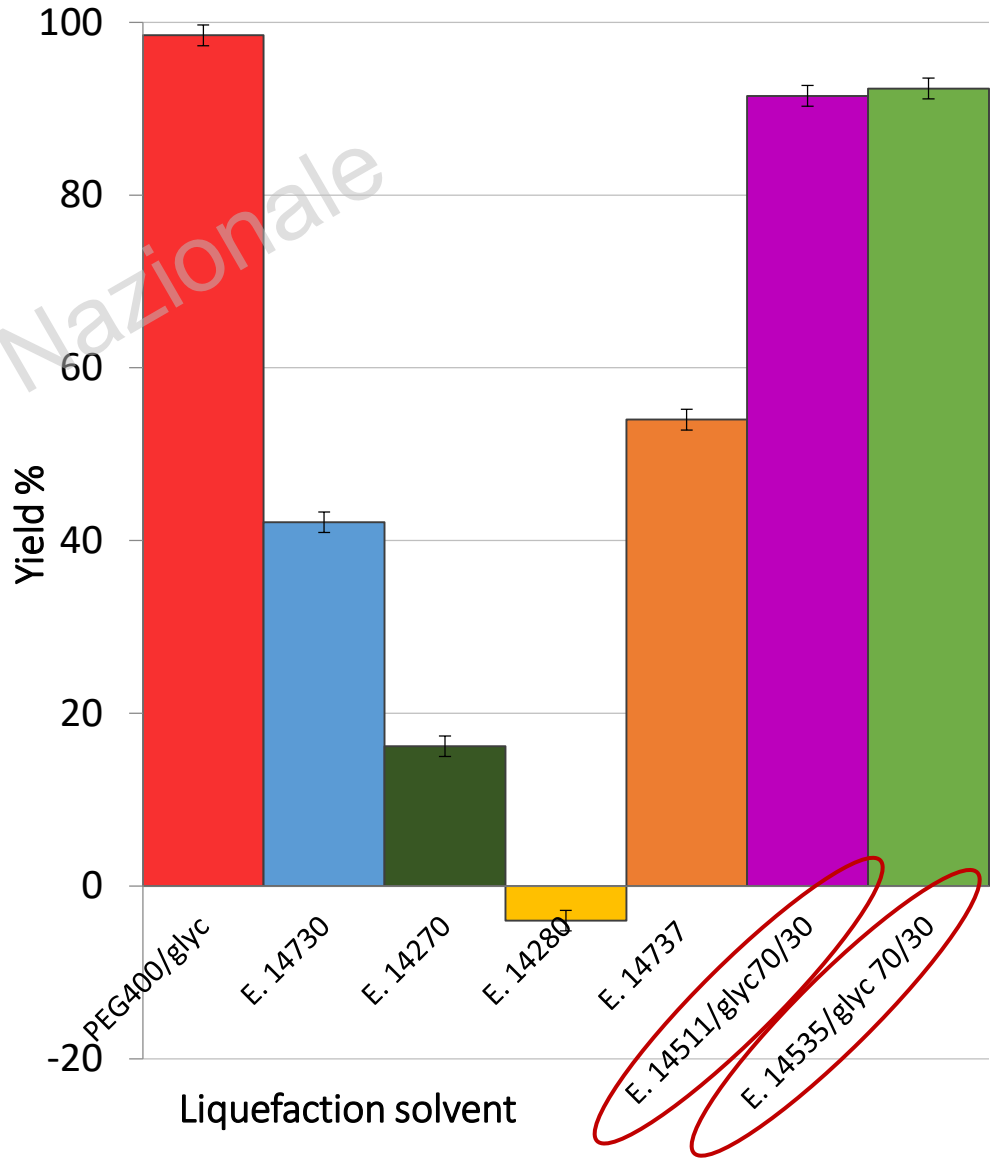
Liquefaction solvent effect

- T = 150°C
- Solvent-to-solid ratio = 5/1
- Catalyst= 3% H_2SO_4
- Reaction time = 20 min

Literature | Bio-based solvents

Solvents	PEG400/ glyc	Em. 14730	Em. 14270	Em. 14280	Em. 14737	Em. 14511/glyc (70/30)	Em. 14535/glyc (70/30)
Products nOH [mgKOH/g]	396	101	62	80	172	195	372



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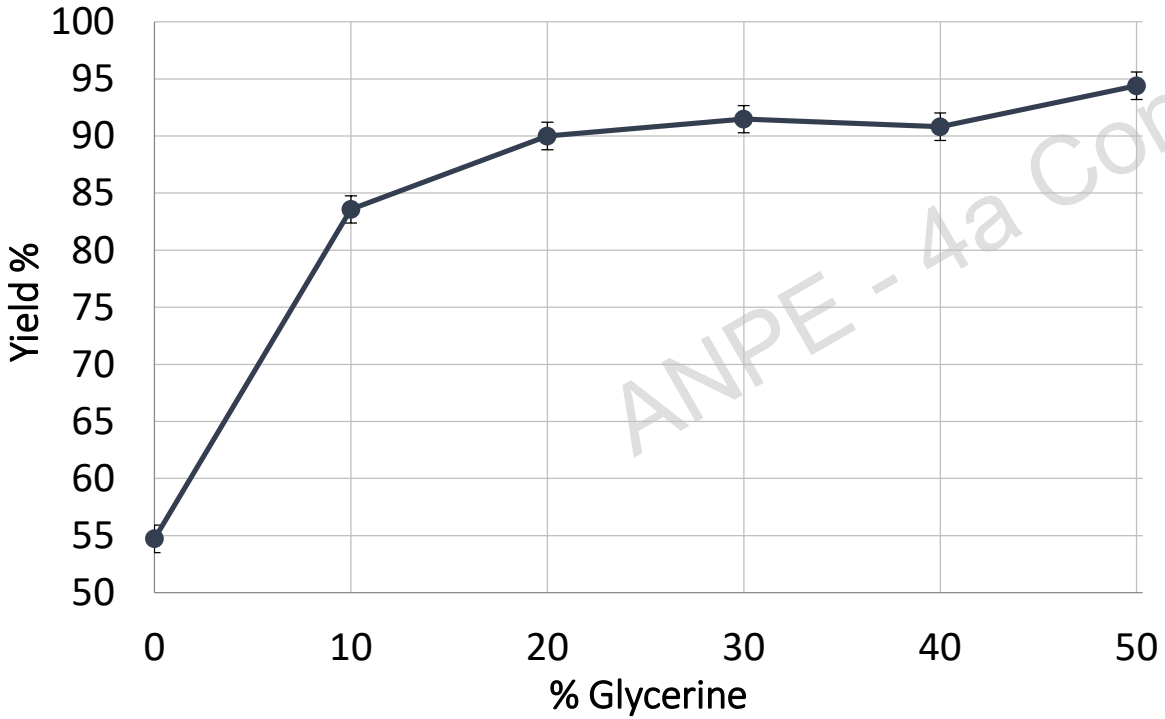
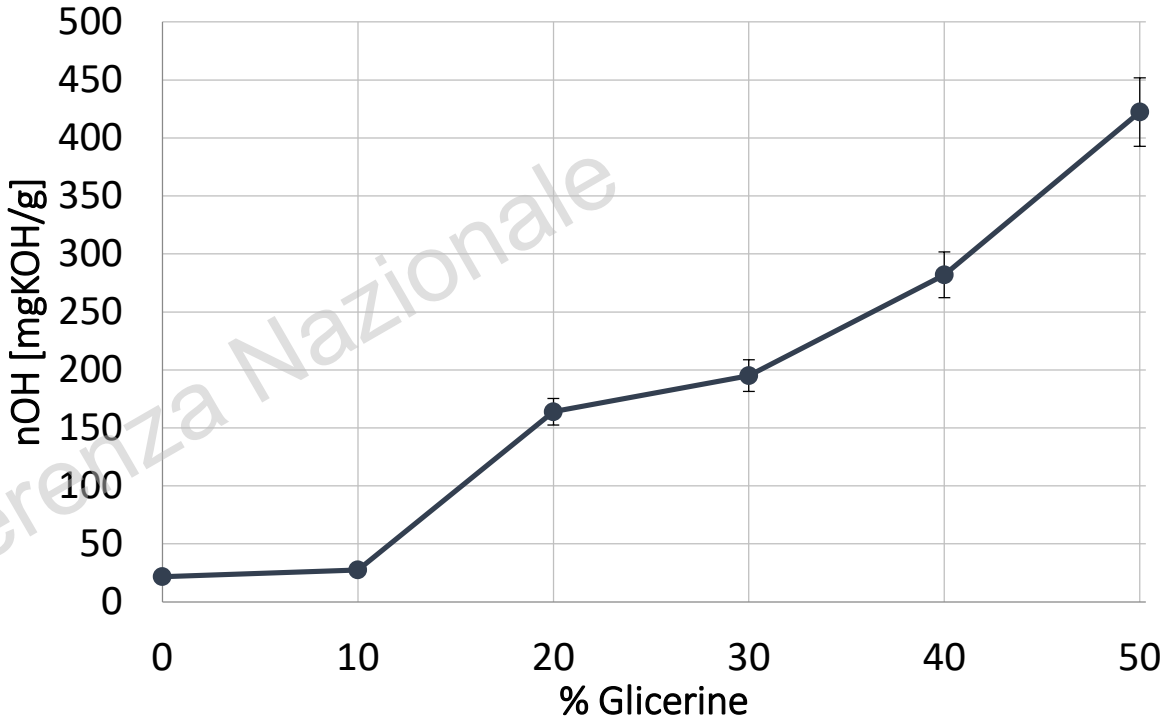
Solvent-to-glycerol ratio effect

- T = 150°C
- Solvent-to-solid ratio = 5/1
- Sulphuric acid = 3%
- Reaction time = 20 min
- Bio-based polyols: EMEROX® 14511





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Mixture **EMEROX®** 14511/Glycerol 50/50

Liquefaction results

3% H_2SO_4 as catalyst

↓

pH ≃ 1

↓

Drawback:

✗ PU synthesis

⇒

Solutions:

✓ Decrease of H_2SO_4 to 1%

✓ Use of **NaOH** as catalyst

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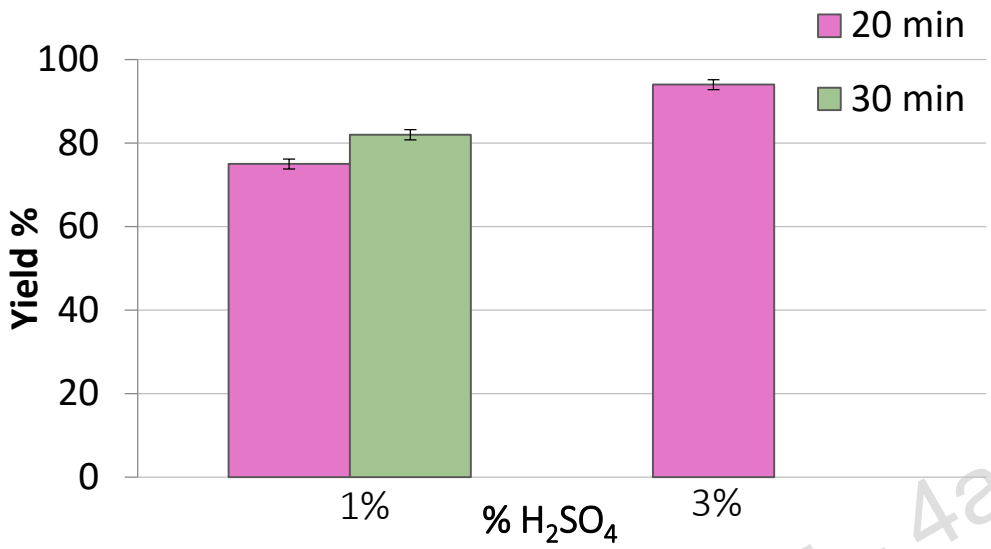
T = 150°C
Solvent = 14511/glycerol (50/50)
Solvent-to-solid ratio = 5/1

Liquefaction catalysis

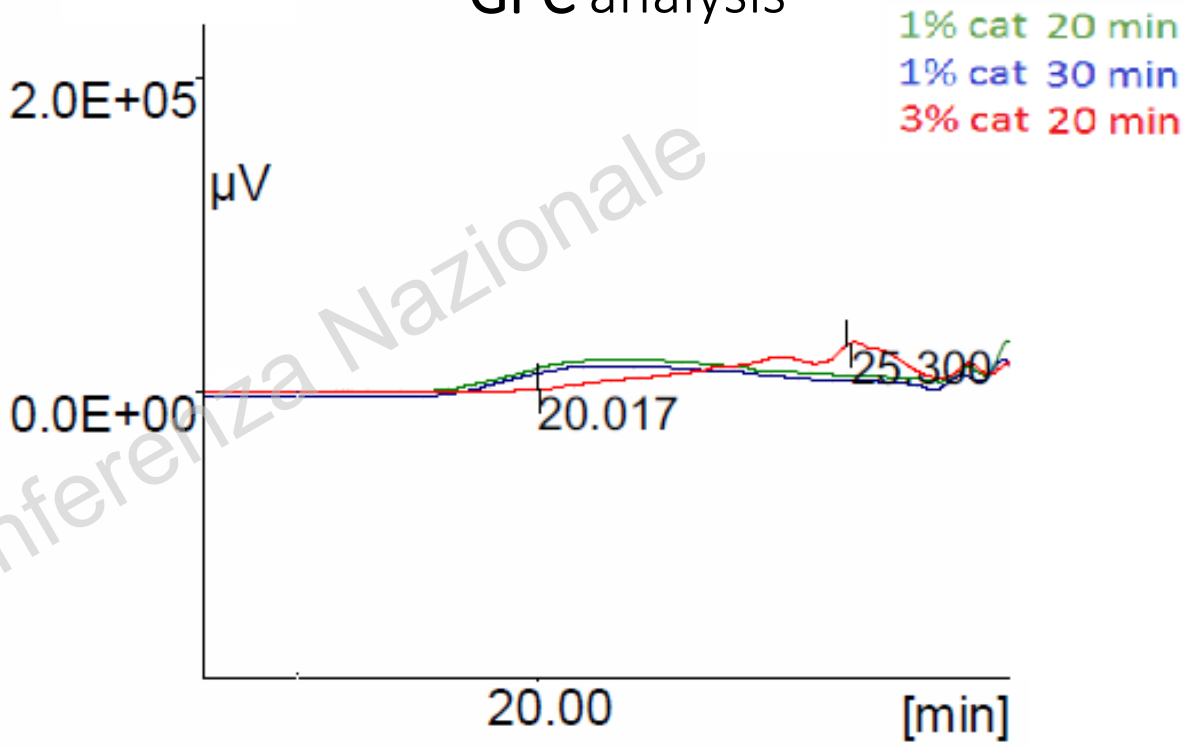
1% H_2SO_4 as catalyst

Two different reaction times



Time [min]	20	30	20
% H_2SO_4	1%	1%	3%
nOH [mgKOH/g]	676	628	422

GPC analysis



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⇨ Reaction time of **30** minutes

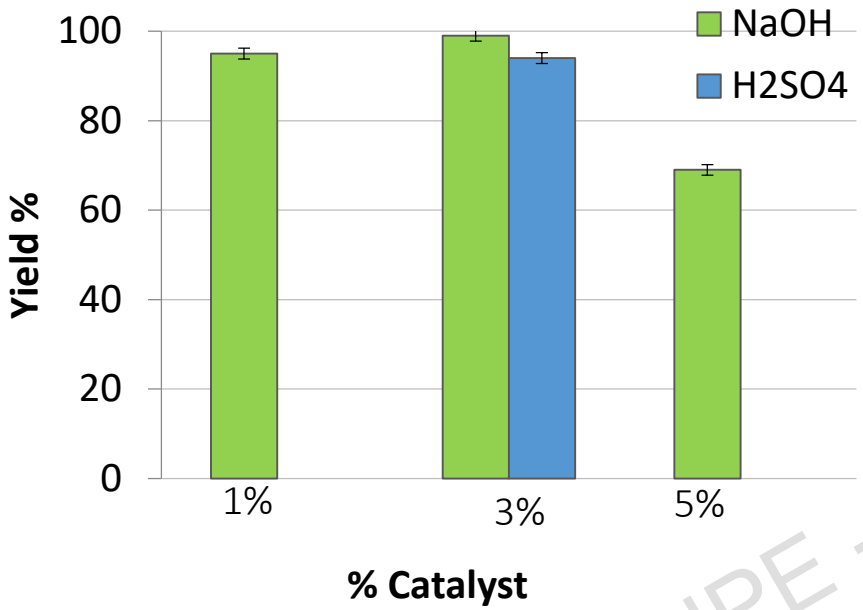
⇨ pH ≃ 5

T = 150°C t= 20 min
Solvent = 14511/glycerol (50/50)
Solvent-to-solid ratio = 5/1

Liquefaction catalysis

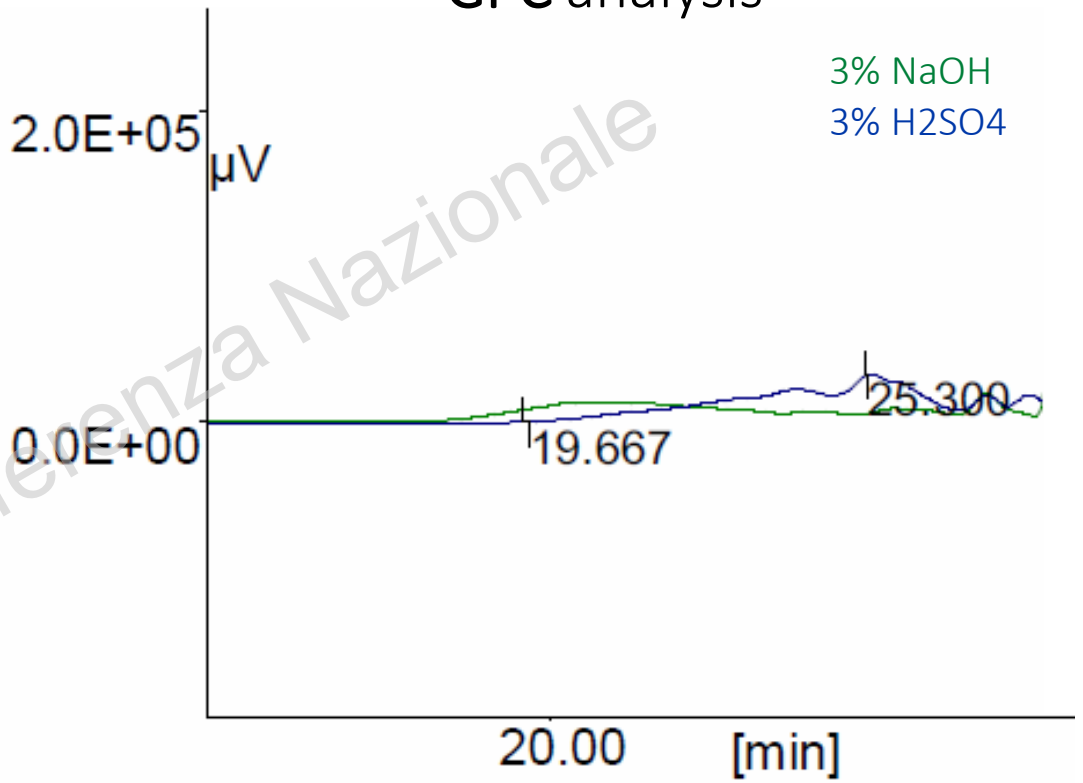
NaOH as catalyst

Three different concentrations



% NaOH	1%	3%	5%	% H_2SO_4	3%
nOH [mgKOH/g]	878	858	834	nOH [mgKOH/g]	422

GPC analysis



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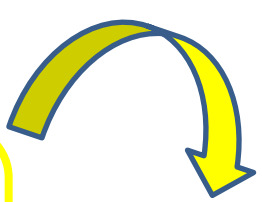
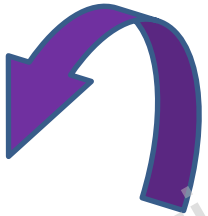
3% of NaOH as catalyst

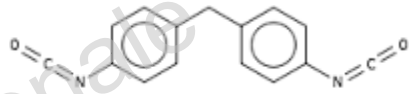
pH ≃ 7

Polyurethane foams production

Polyols
H_2O
Catalysts
Surfactant







Isocyanate MDI

Mix for 15 sec

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Polyurethane foams production

Polyols

EMEROX® polyols

- 14511 nOH = 110 mgKOH/g
- 14535 nOH = 353 mgKOH/g
- 14511/glycerol (50/50) nOH= 960 mhKOH/g
- 14535/glycerol (70/30) nOH= 795 mgKOH/g

Polyols from lignin

- 3% of H_2SO_4 for 20 min nOH = 422 mgKOH/g
- 1% of H_2SO_4 for 20 min nOH = 661 mgKOH/g
- 1% of H_2SO_4 for 30 min nOH = 629 mgKOH/g
- 1% of NaOH for 20 min nOH = 858 mgKOH/g

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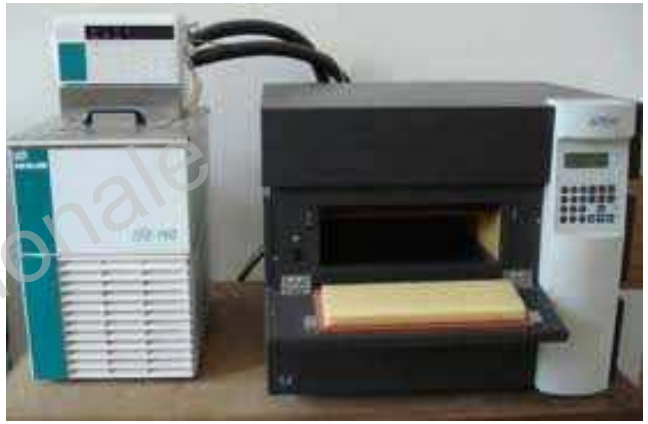
Polyurethane foams characterization

Physical properties → Density
Thermal conductivity



Reaction to fire → LOI test

Thermal stability → TGA analysis

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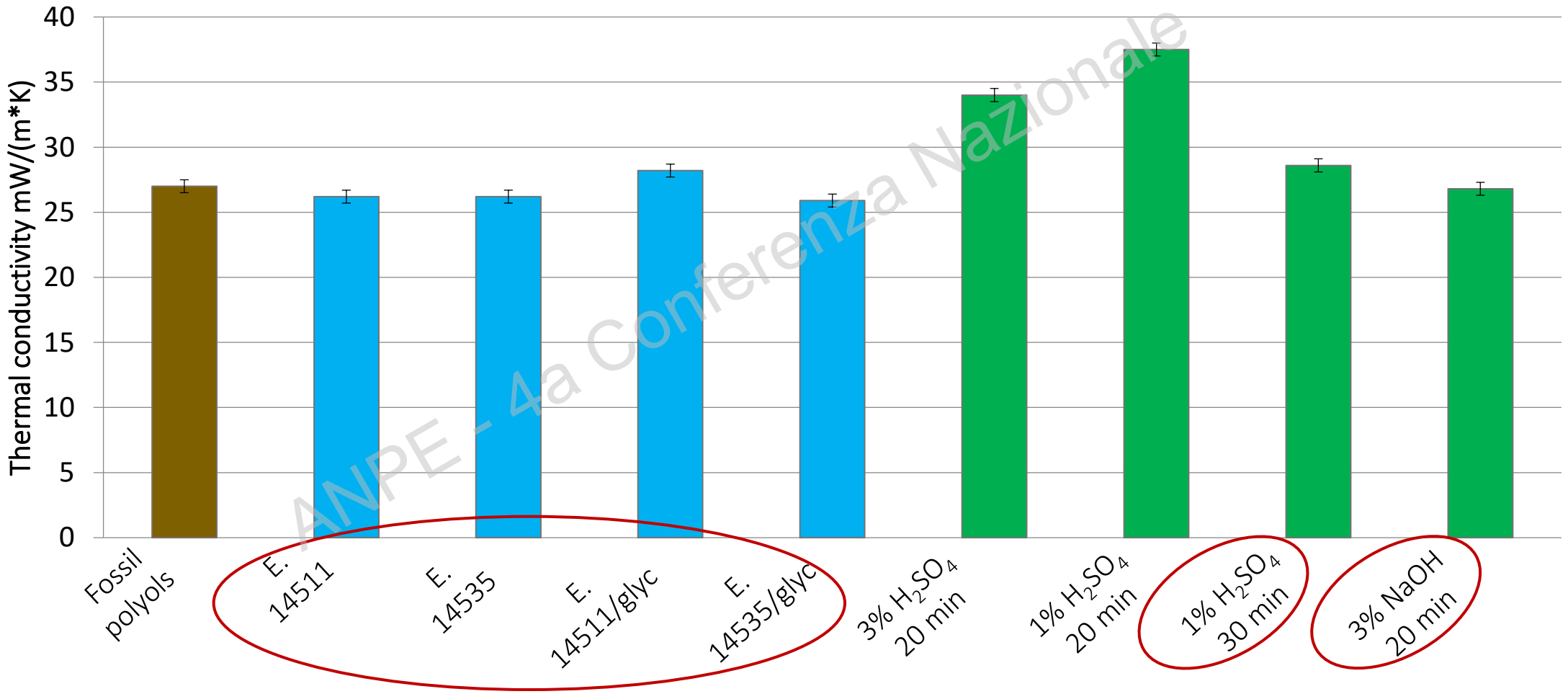
Thermal conductivity



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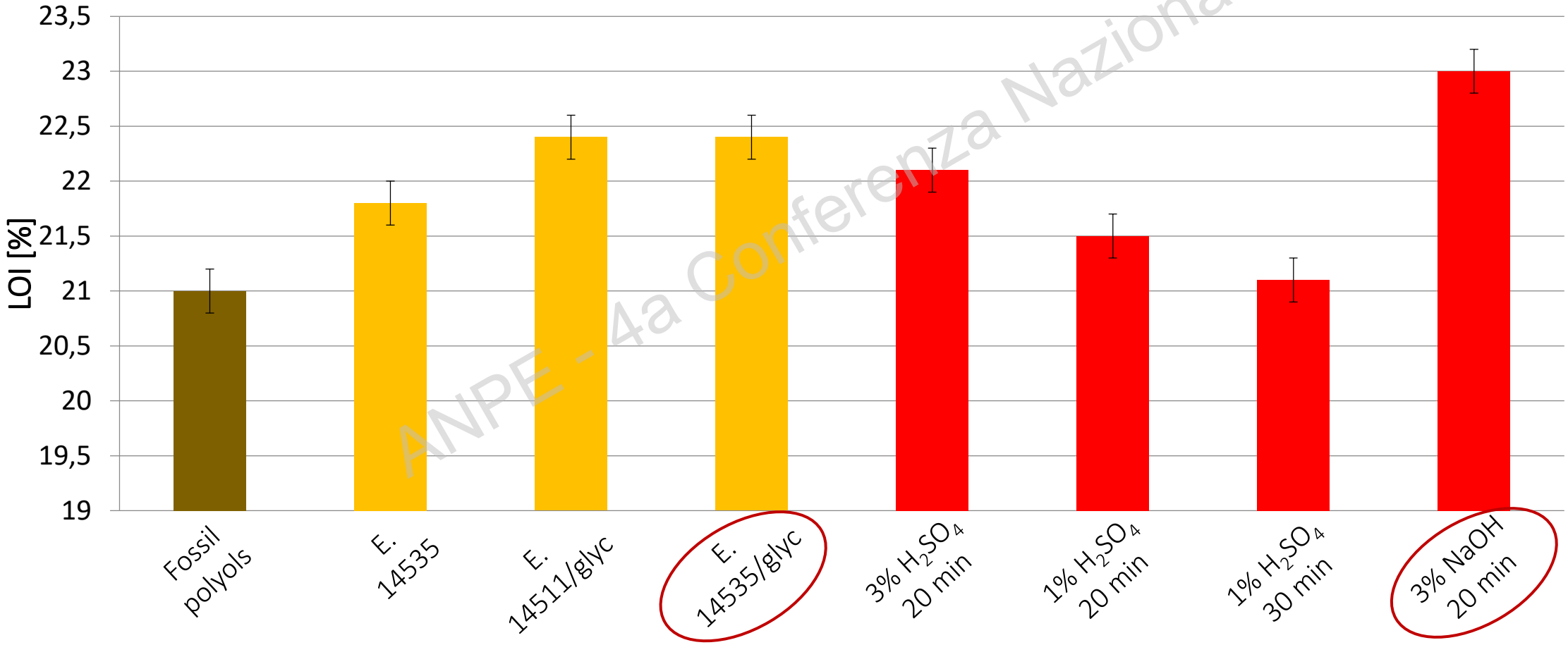
Lower Oxygen Index (**LOI**)

Minimum concentration of oxygen, expressed as a percentage, that will support combustion of a polymer.



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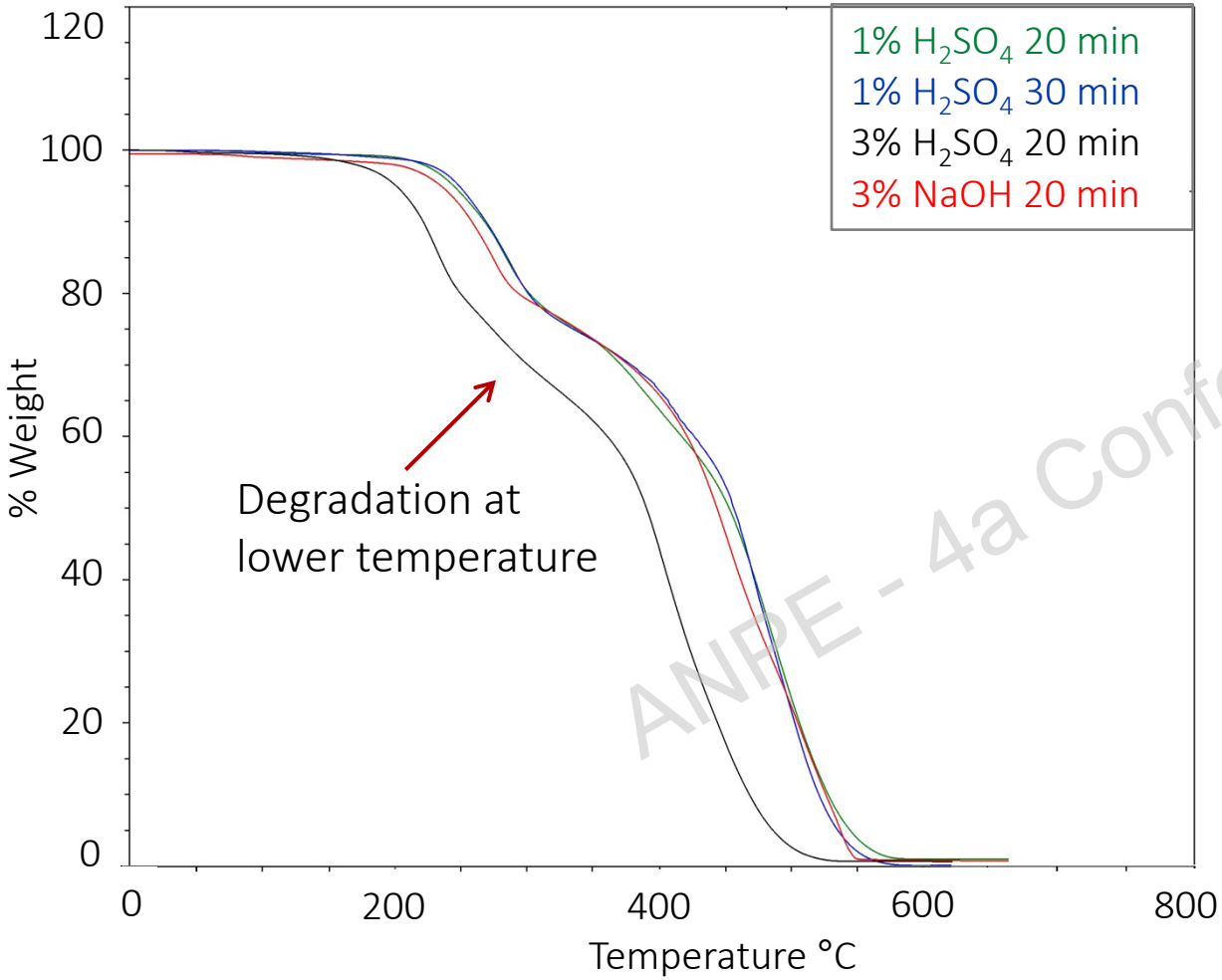
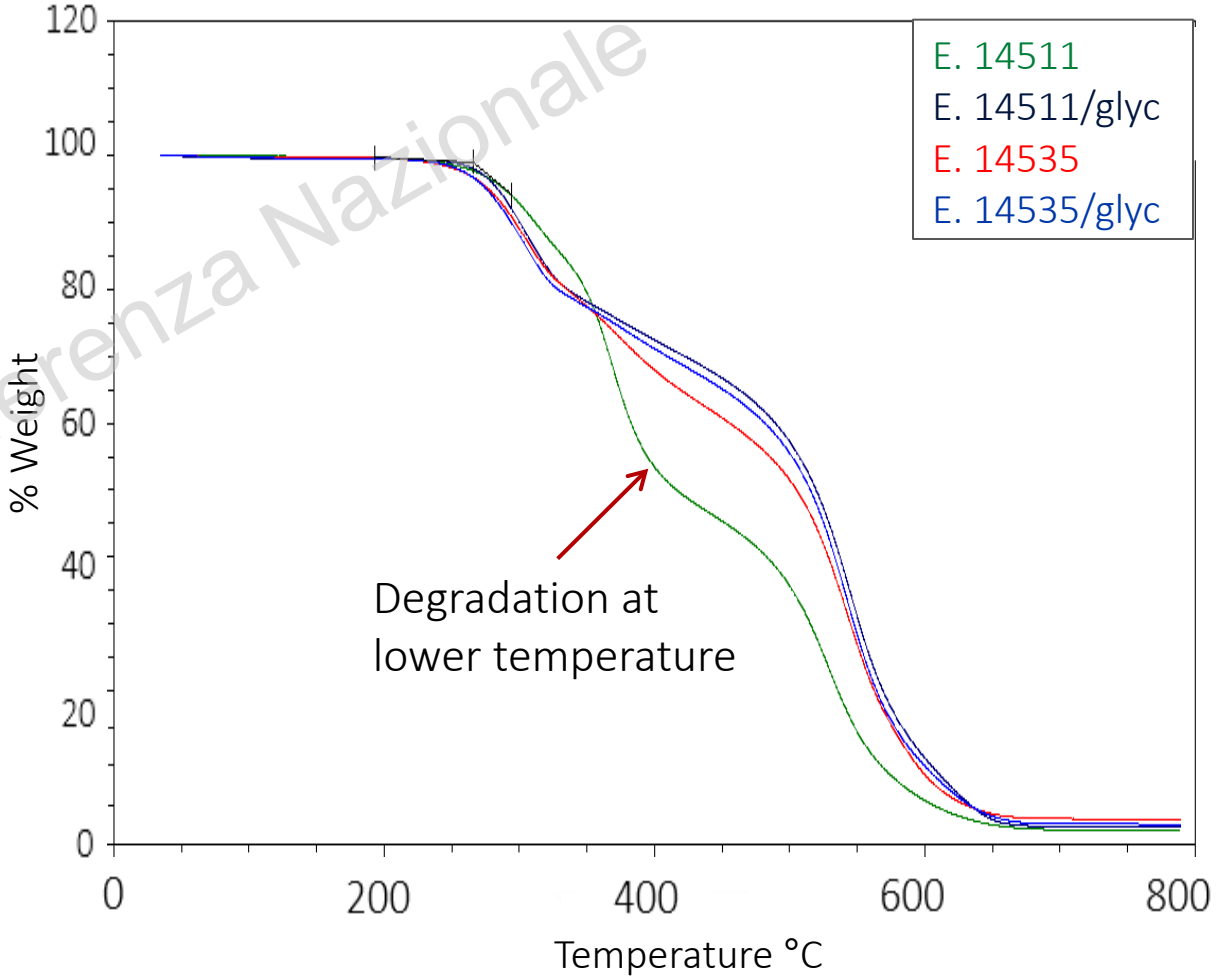
TGA analysis

Oxidant atmosphere **(air)**





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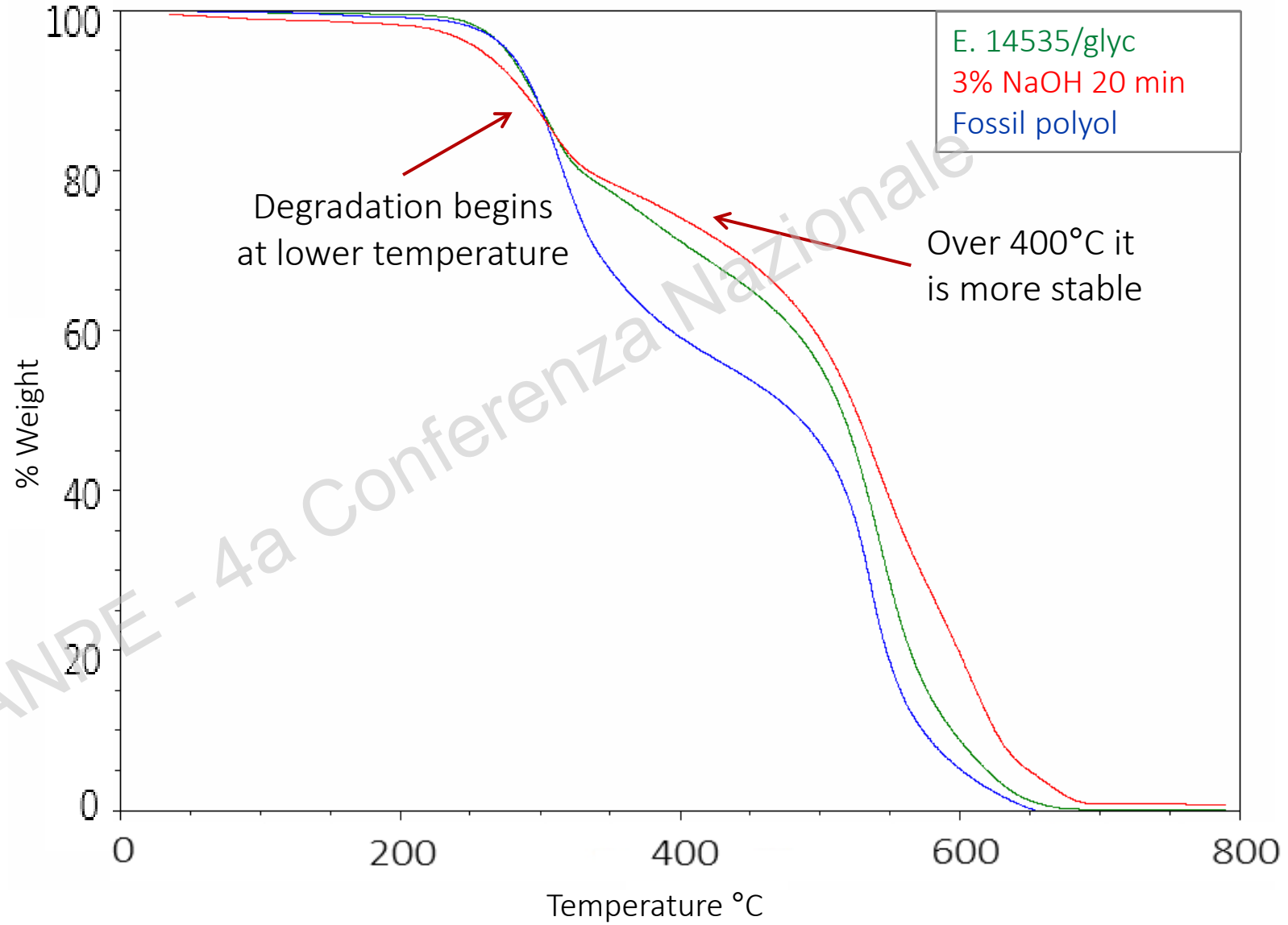
Polyurethane foams characterization

TGA analysis



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Conclusions

- Optimization of liquefaction catalysis
- Optimization of polyurethane foam formulation

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Polyurethane foams from liquefied **lignin**

- Good physical properties
- Improved reaction to fire
- Improved thermal stability over 400°C

Thank you for your attention!

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