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Modified Lignin for Advancing the Properties of particleboards containing UF adhesive

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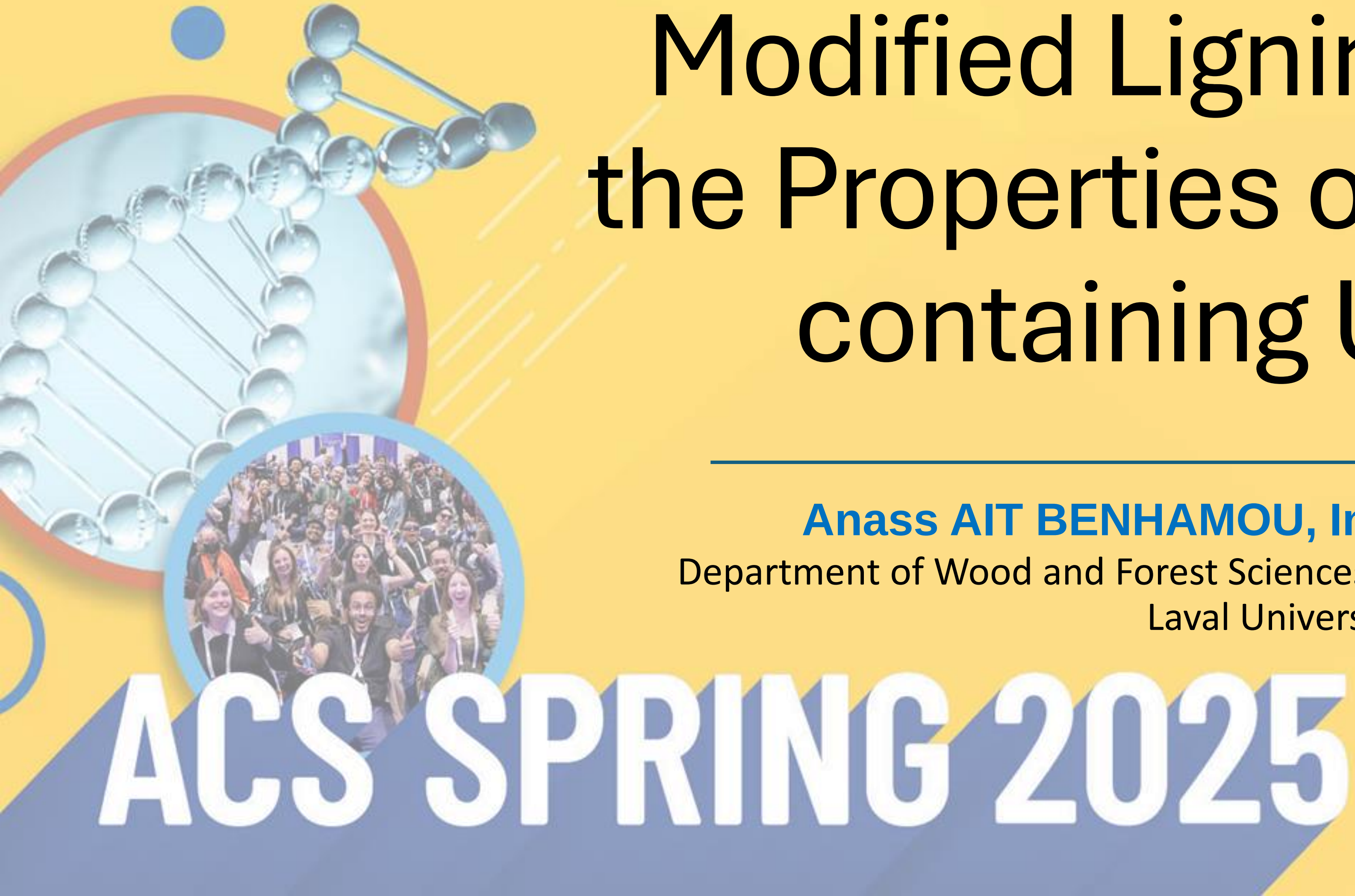


OUTLINE

1. Introduction
2. Lignin modification:history and characterisation
3. Lignin Application
4. Conclusion

I. Introduction : **Towards sustainable materials**

Petroleum resources

I. Introduction : **Wood-based composites**

Worldwide annual production of about 416 million cubic meters in 2016*

- **Availability from several sources**
- **Nature origin**
- **Non-toxicity**
- **Good dimensional stability**

Oriented strand board (OSB)

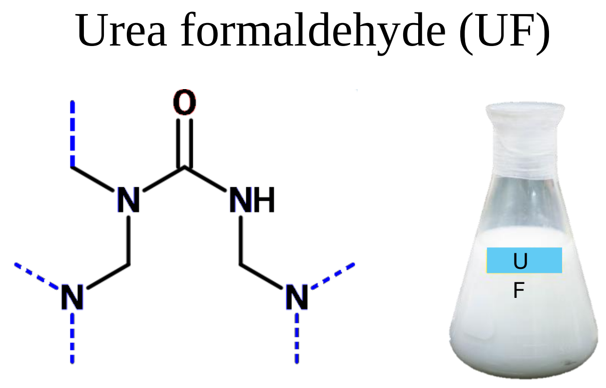
Medium density fiberboards (MDF)

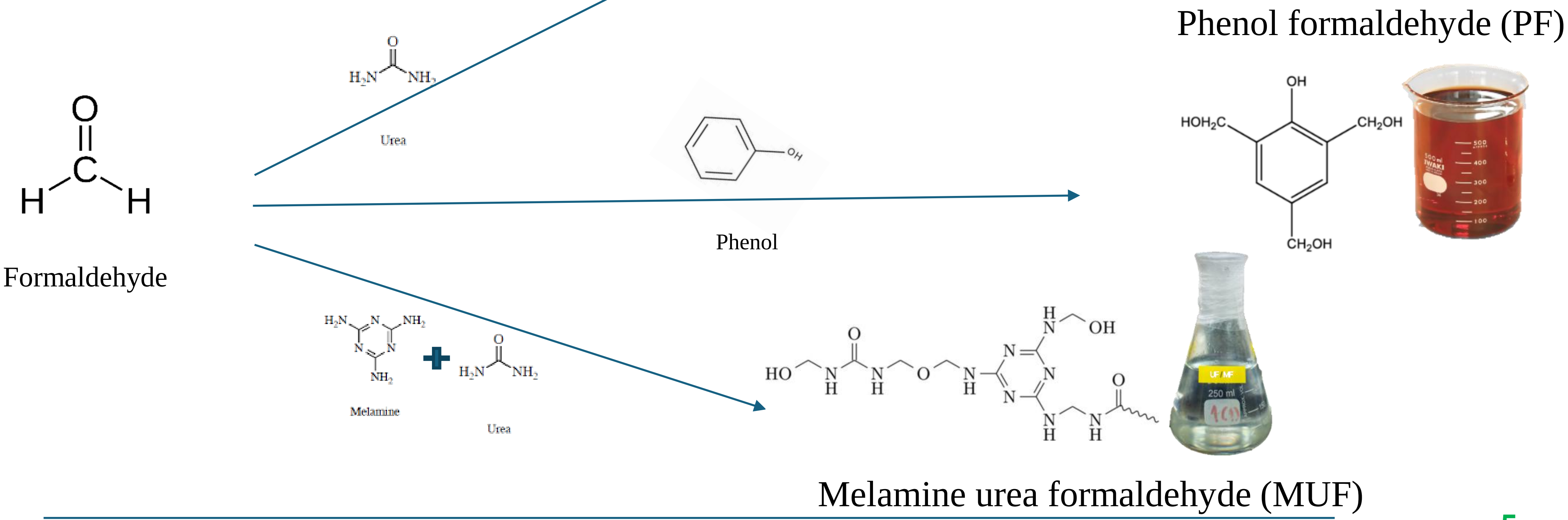
Plywood

Particleboard

I. Introduction : Most used adhesives

- The panel industry, is the larger user of products based on formaldehyde
- More than 50% of the formaldehyde produced in the world is used in the production these resins

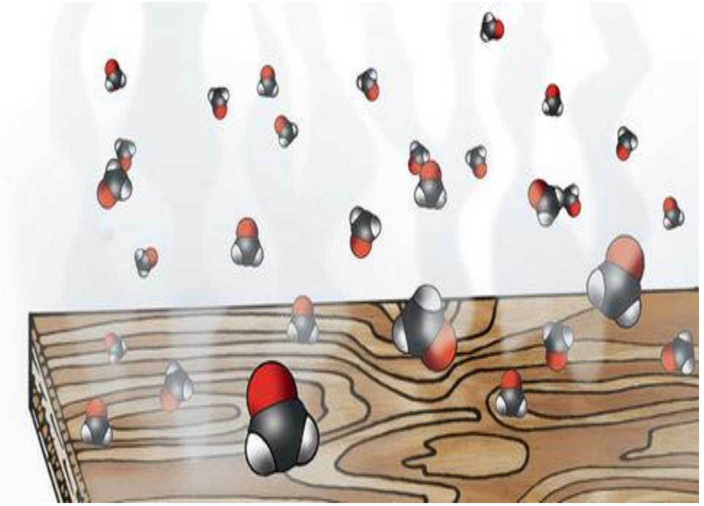




A, Ait benhamou et al., (2021), International *Journal of adhesion and adhesives, 10.1016/j.ijadhadh.2021.102940*

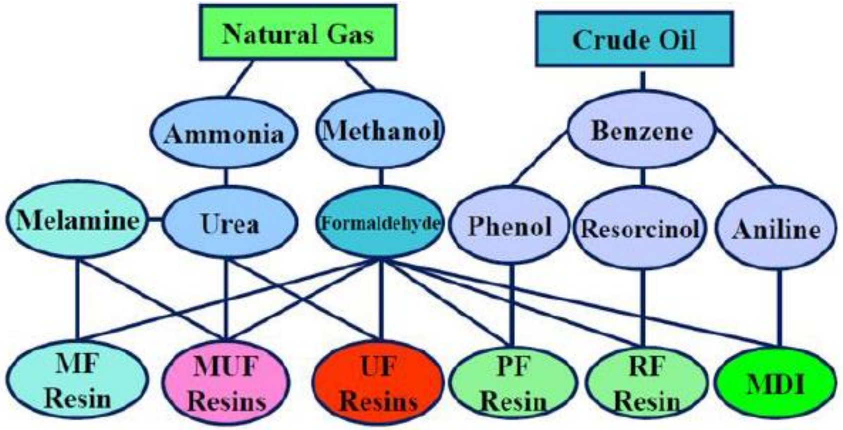
I. Introduction **Synthetic adhesive - Source and toxicity**

Formaldehyde emission from wood products are the major concern



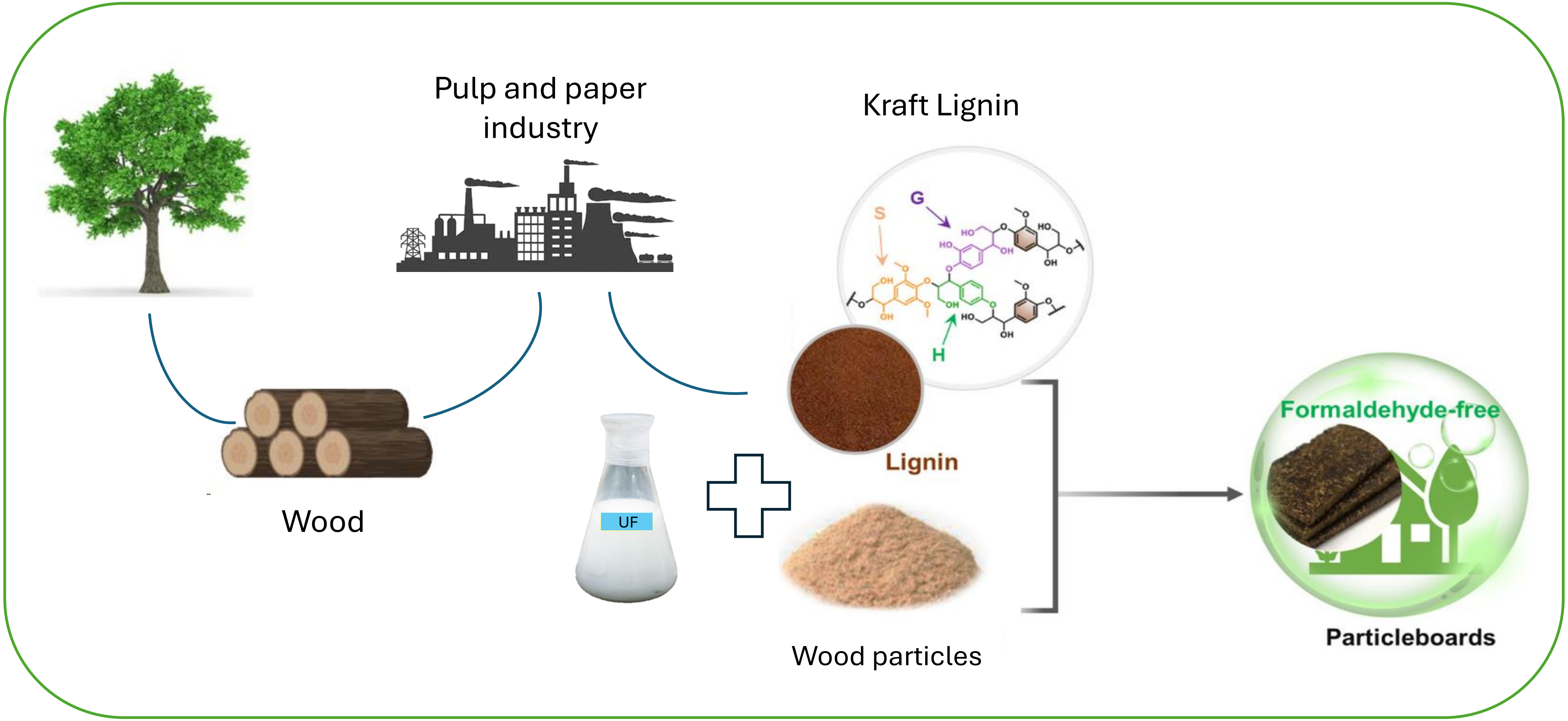
V. **Hemmila** et al., (2017), Royal society advances, *10.1039/c7ra06598a*

Major source of formaldehyde based adhesives



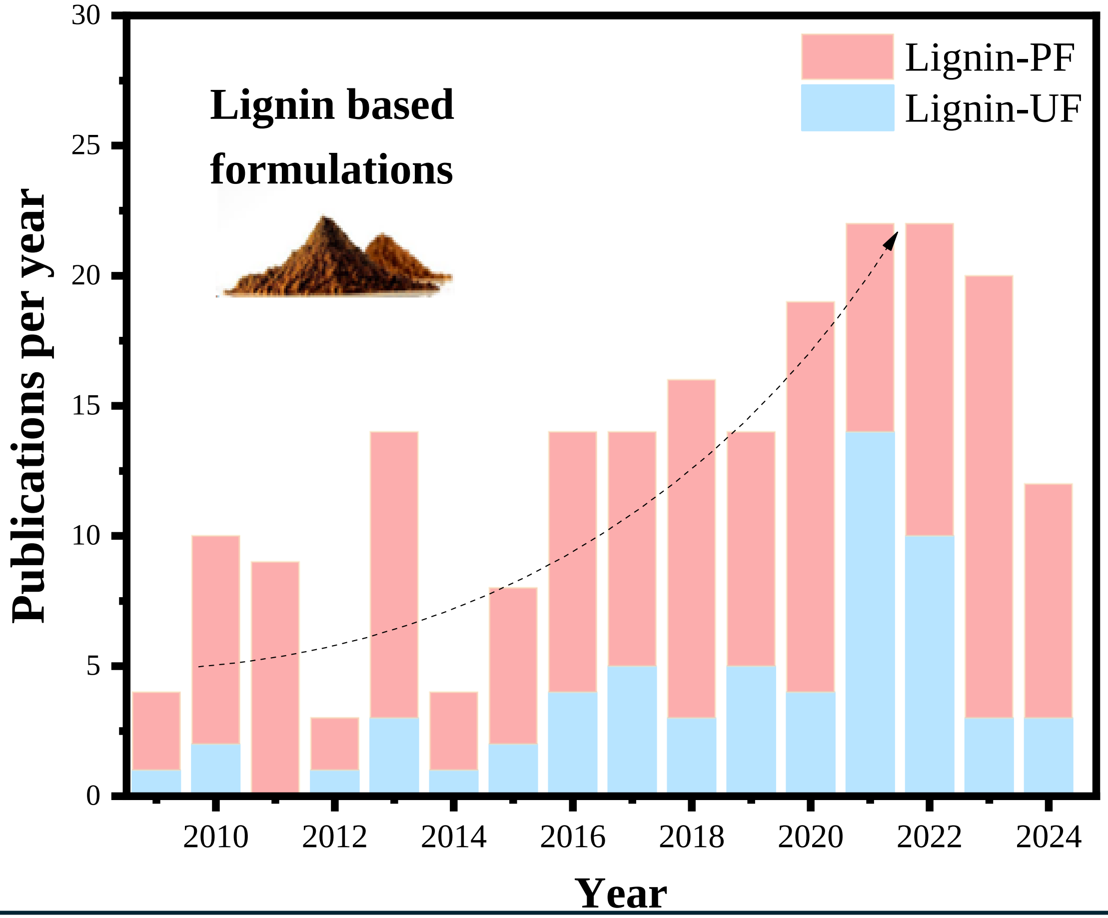
Resine	Quality	Water resistance	Cost (€/t)	Formaldehyde emissions
UF	+	+	300-400	+++
PF	++	++	500-750	+++
MUF	+++	++	500-1000	+++
pMDI	+++	++	1500	-

Context of the current work



Statistics and History of Lignin in UF adhesive

Annual number of scientific publications in the last decade, Using the following key-words **Lignin** and **UF adhesive**, in Web of Science



Historically

First introduction of Lignin in UF adhesive has been performed in the 1994th by Chen et al at University of Quebec at Trois-Riviéres,

Modified Lignosulfonate as Adhesive

RUBIE CHEN* and QUOXIONG WU

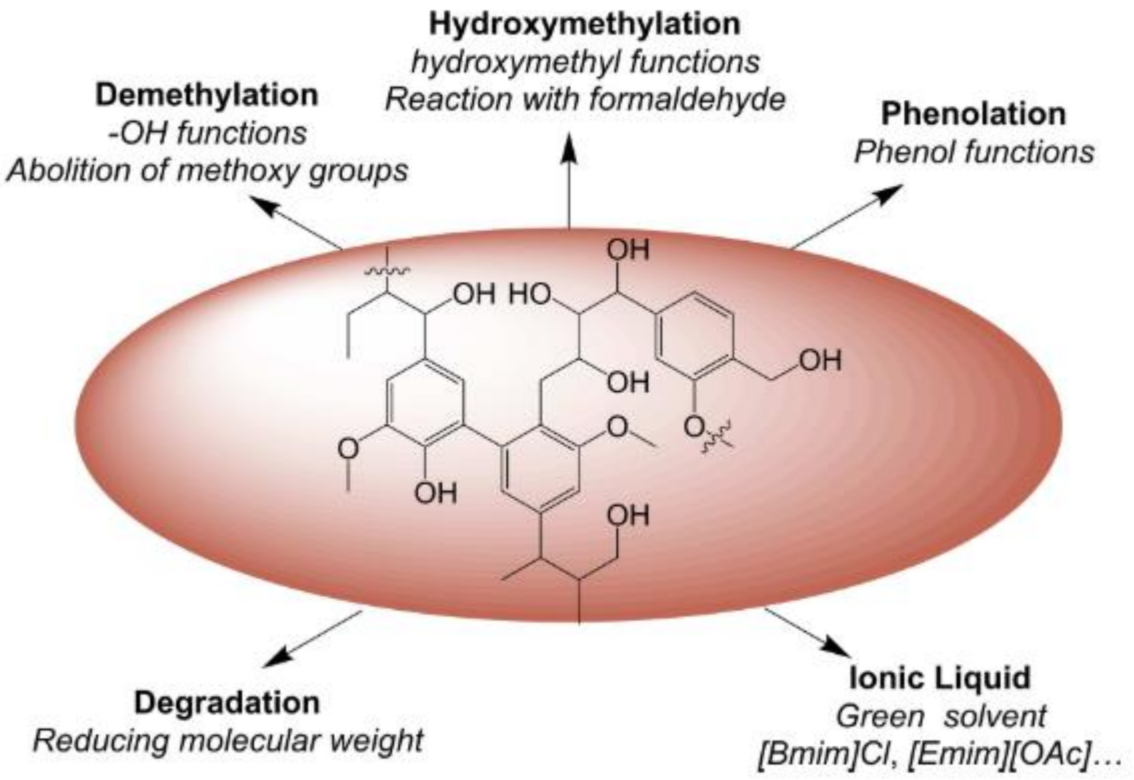
Pulp & Paper Research Centre, University of Québec at Trois-Rivières, Trois-Rivières, Québec, Canada G9A 5H7

Bibliography on Lignin in UF adhesive

According to web of science using the following keywords: *Lignin and UF adhesives*.

1. **Oxidized lignosulfonate** (30-40 wt.%) + UF ➔ Positive effect on IB and TS (1994)
2. **Glyoxalated** soda bagass **lignin** (10-20 wt.%) during UF synthesis ➔ Improved WA, SS and decreased FE of plywood (2015)
3. **Phenolated** kraft **lignin** (10-20 wt.%) during UF synthesis ➔ Less FE with no changes in IB of the Particleboards (2016)
4. **Ionic liquid modified lignin** (10-20 wt.%) during UF synthesis ➔ Improved SS, lower WA and FE of plywood (2017)
5. Nanoclay (0.5-1 wt%) + **Glyoxalated lignin-UF adhesive** ➔Improved MOE, MOR, IB and Less FE of Particleboards (2017)
6. pMDI (2-6 wt%) + **Ionic liquid lignin- UF adhesive** ➔ Improved SS in wet and dry states, lower FE of plywood (2018)
7. **Hydroxymethylated sulfite liquor** + UF resin ➔ Less FE with no Improvement in mechanical ppt of Particleboards (2019)
8. commercial **Sulfonated kraft lignin** + UF resin ➔ Improved thermal behaviour of the resins (2019)
9. Amphiphilic **Lignosulfonate** (20 wt%) + UF ➔ SS and FE was not influenced of the elaborated plywood (2020)
10. **Hydroxymethylated–maleated lignin** + UF ➔ Improved tensile ppt of plywood (5%) and MDF (7.5%) with less FE (2020)
11. **Mg/Na-Lignosulfonate** (0-100 wt%) + UF ➔ 30% of Na-LS highly decrease FE with no effect on tensils ppt of PB (2021)
12. **Ammonium-Lignosulfonate** + UF ➔ 10% showed best tensile ppt and less FE of Particleboards (2019)
13. **Alkali lignin from bagass**(5-15 wt%) + UF ➔ 10% leads to improved tensile ppt and less FE of Particleboards (2021)
14. **Lignosulfonate** + UF ➔ 6% leads to improved MOR, MOE and less WA, TS and FE of Particleboards (2021)
15. **Aceton fractionated kraft lignin** + UF ➔ Soluble lignin Showed great potential as green additive in UF (2023)
16. **Soda and Kraft lignin (20-40 wt%)** + UF ➔ 20% leads to improved MOR, MOE, IB and FE of Particleboards (2023)
17. **Alkali lignin from weeds** (5-20 wt%) + UF ➔ 15% leads to improved MOR, MOE, IB and less FE of Particleboards (2023)
18. Commercial **Lignin** (5%) and **Lignosulfonate** (10%) + UF ➔ Acceptable physical and mechanical properties of elaborated panels as well as in improvement in fire resistance properties (2023)

Chemical modifications of lignin in Wood adhesives

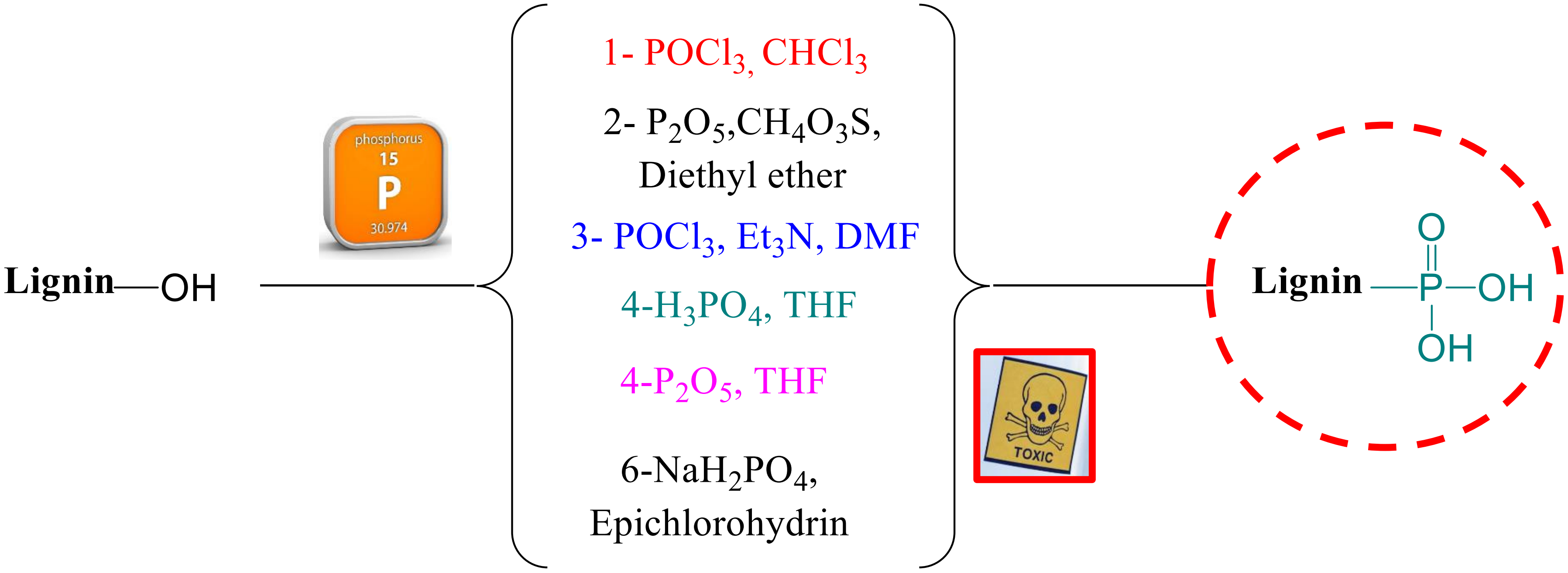


Summary of the most applied chemical reactions for the functionalization of lignin in adhesives

To our knowledge No work presented till now a Phosphorylation of Lignin to be applied in UF adhesives !!!

Peng et al., Chemsuschem (2023), doi.org/10.1002/cssc.202300174

Lignin Phosphorylation : Stat of the art

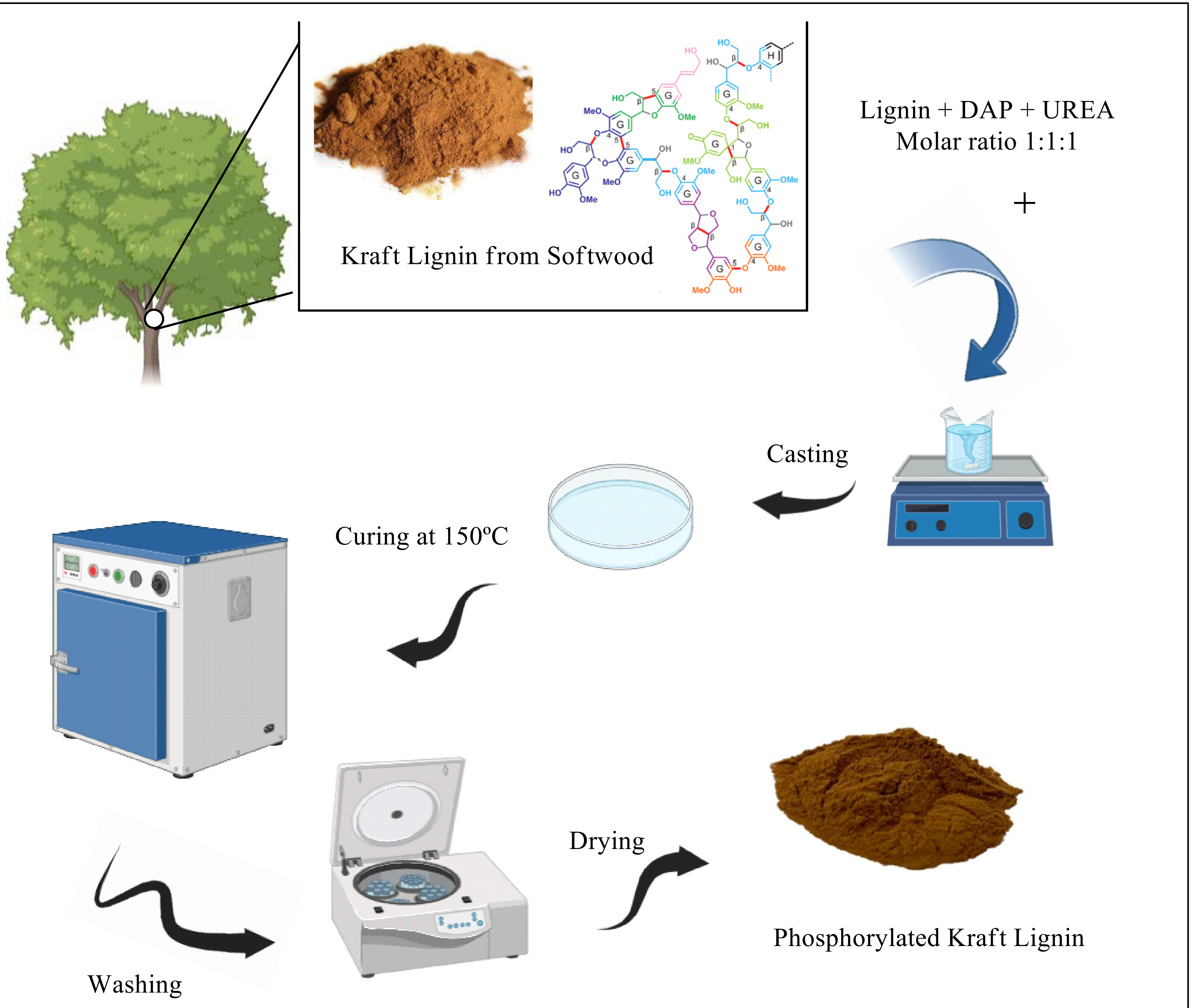


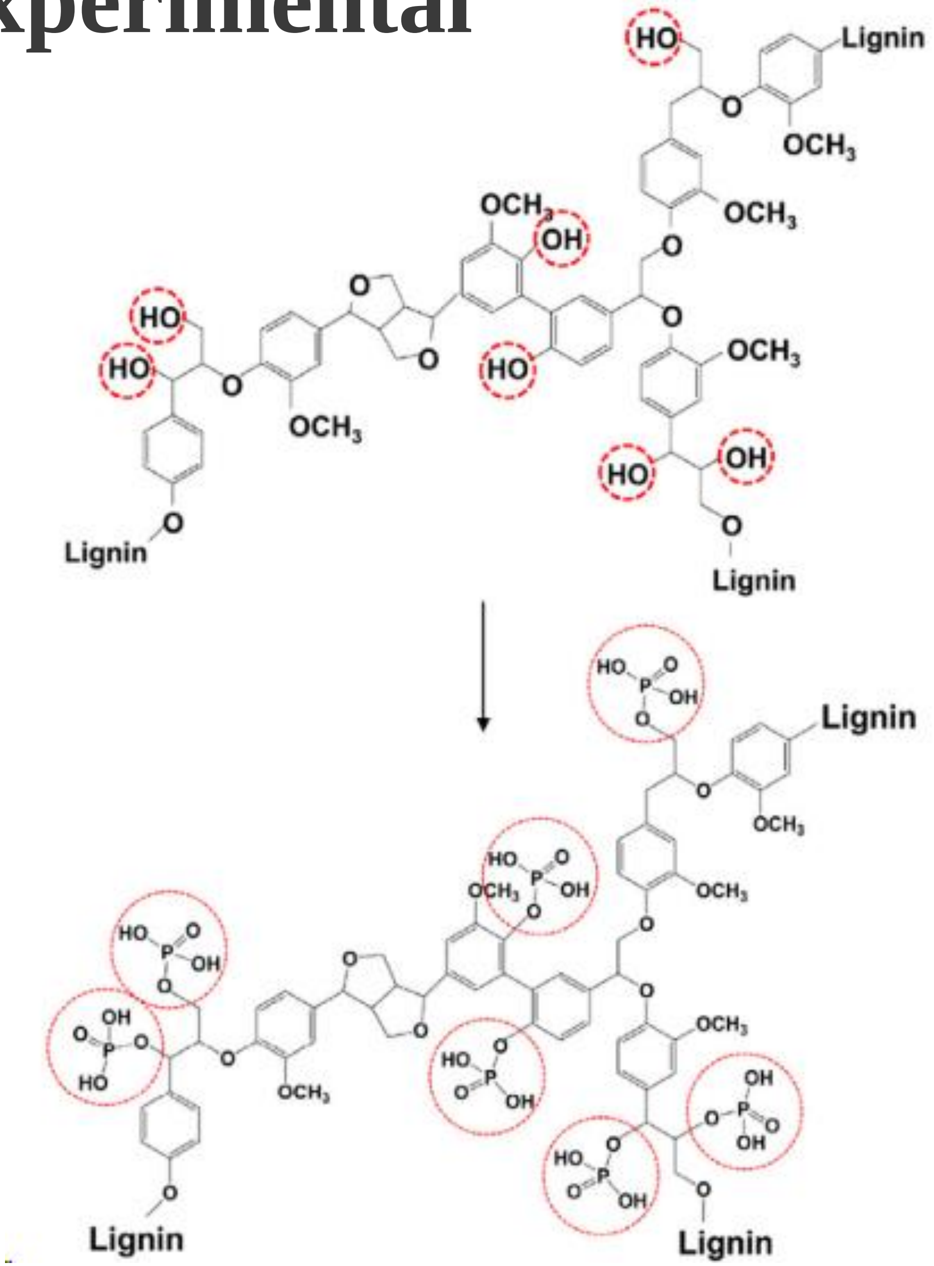
Historically

Lignin structure have been widely functionalized since the 1980’s by different chloro-phosphorus containing-compounds through Williamson reaction for different applications*

*__Illy__ el al., (2015), Phosphorylation of bio-based compounds: state of the art\ ***Polymer Chemistry*** *10.1039/C5PY00812C*

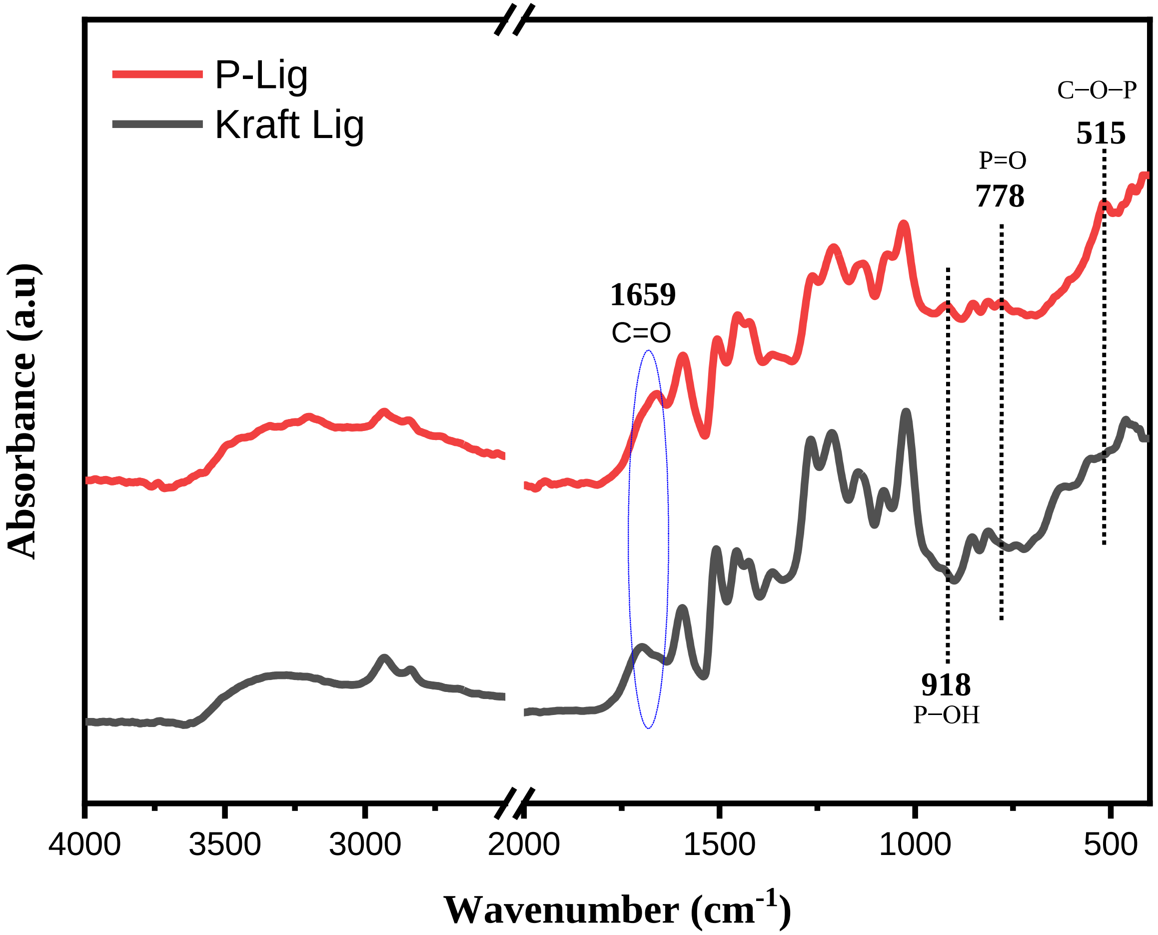
Lignin Phosphorylation : Experimental





Lee et al., 2022 10.1002/app.52519

Lignin Phosphorylation : Results



FTIR analysis

-Appearance of new peaks correspond to C-O-P (515cm^{-1}), P=O (778cm^{-1}); P-OH (918cm^{-1}) indicative of the successful phosphorylation of kraft lignin

-Usually, phosphate moieties do not show intense bands in the IR spectroscopy*

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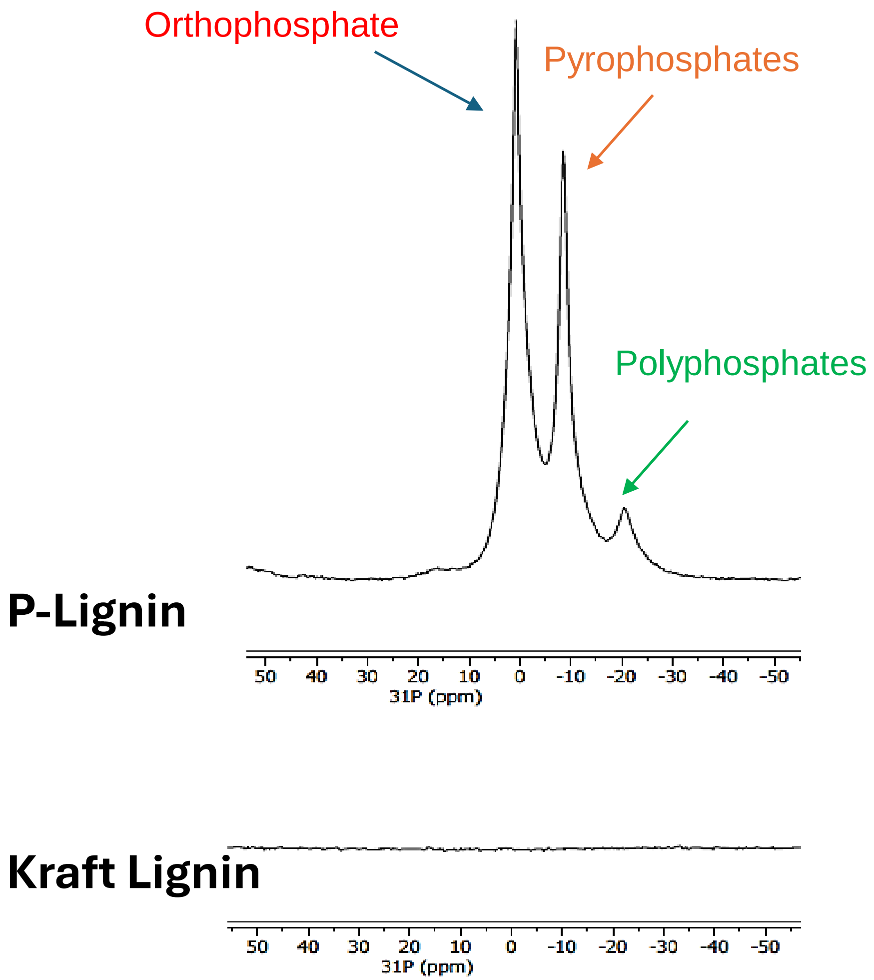
*G. Nourry, et al, Cellulose 23 (6) (2016) 3511–3520.

Lignin Phosphorylation : Results



Solid state ^{31}P NMR analysis

-As expected, no peak corresponding to phosphorus was present in the spectrum of unmodified Kraft Lignin,

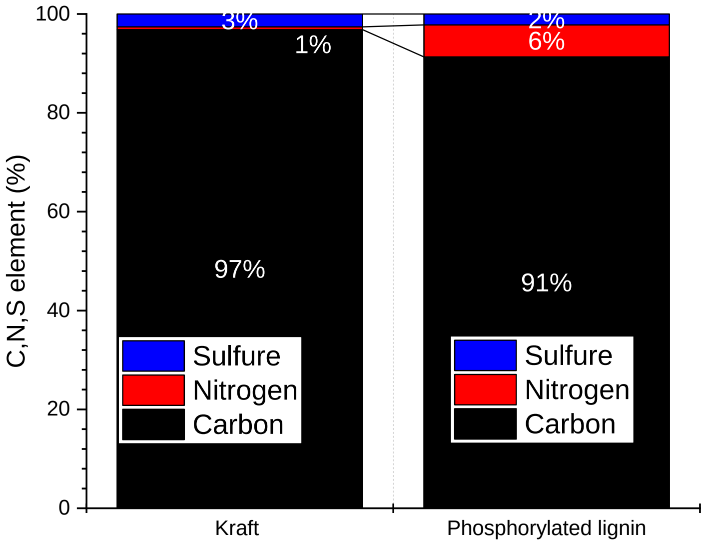
-Referring to literature data, An intense signal between **10 and 0 ppm** is attributed to the orthophosphate groups and a medium intense signal between **-5 and -10 ppm** is due to the presence of pyrophosphate groups. [2,3]

-After phosphorylation, the content of **phenolic** and **aliphatic** hydroxyl groups in KL decreased significantly and nearly 60% after phosphorylation

[2]Ablouh et al ., (2021) RSC Advances, 10.1039/d1ra02713a
[3]Barbara J. Cade-Menun (2004), Talanta, 10.1016/j.talanta.2004.12.024

Lignin Phosphorylation : Results

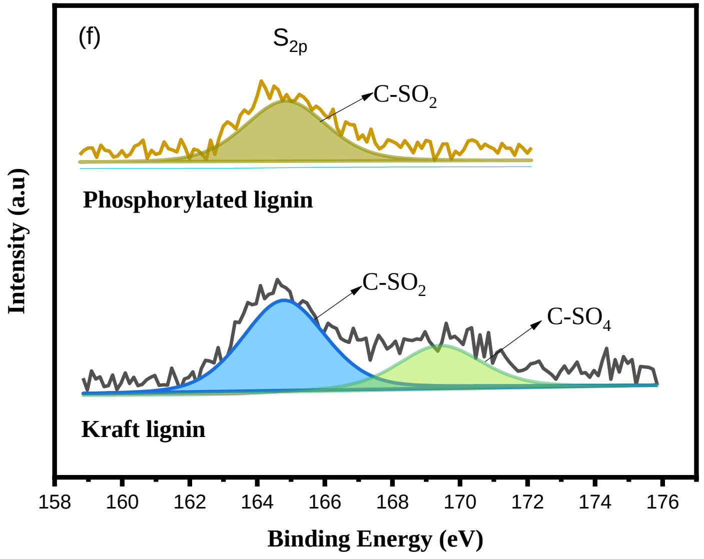
XPS analysis

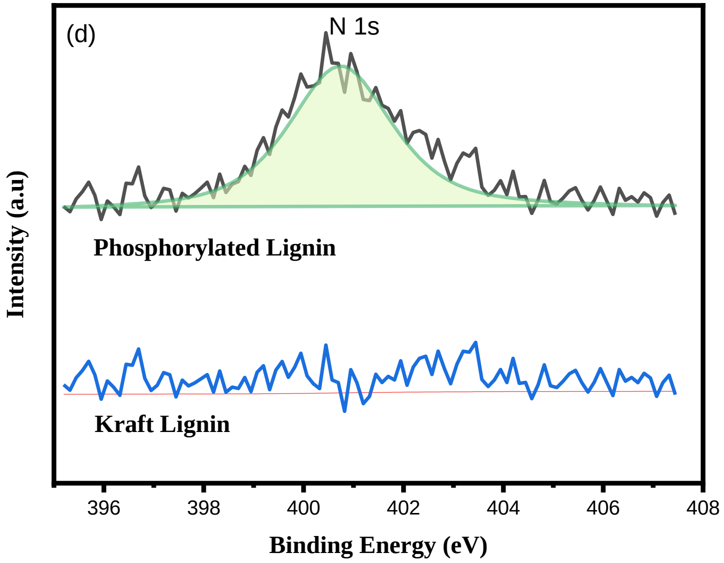


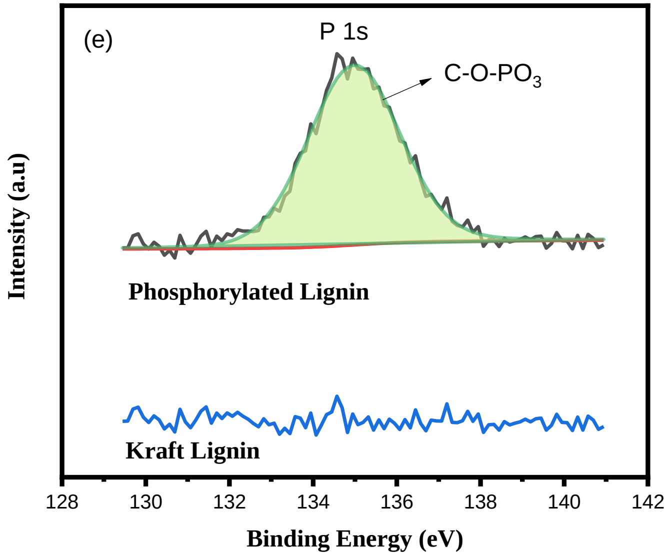
-As expected, no peak corresponding to phosphorus was present in the spectrum of unmodified Kraft Lignin,

-Referring to literature data, a new peaks was found at 135 eV for P 2p in the spectrum of the PKL, indicating that the phosphate group was successfully introduced onto the lignin molecule. The appearance of N 1s at 401 eV was also found in PKL. *

-Probable formation of carbamate (-NH-CO-O-) group on lignin due to the presence of Nitrogen on its structure.







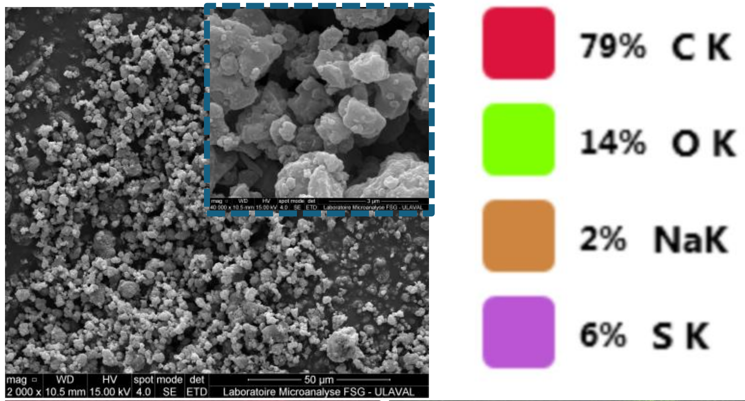
*Barbara J. Cade-Menun (2004), Talanta, 10.1016/j.talanta.2004.12.024

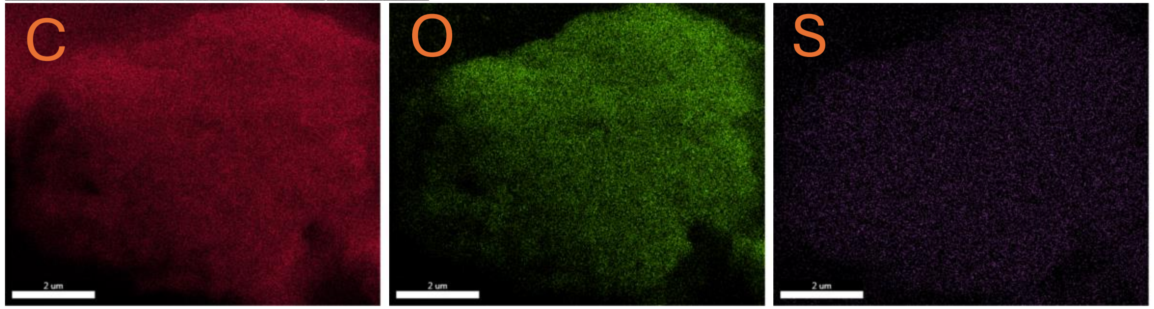
Lignin Phosphorylation : Results

SEM analysis

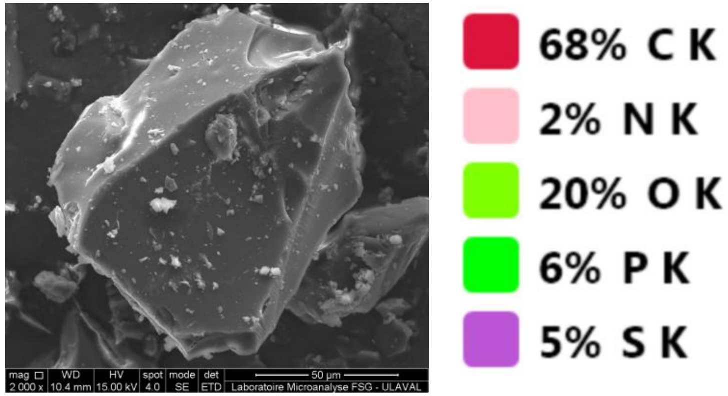
SEM observations and elemental analysis

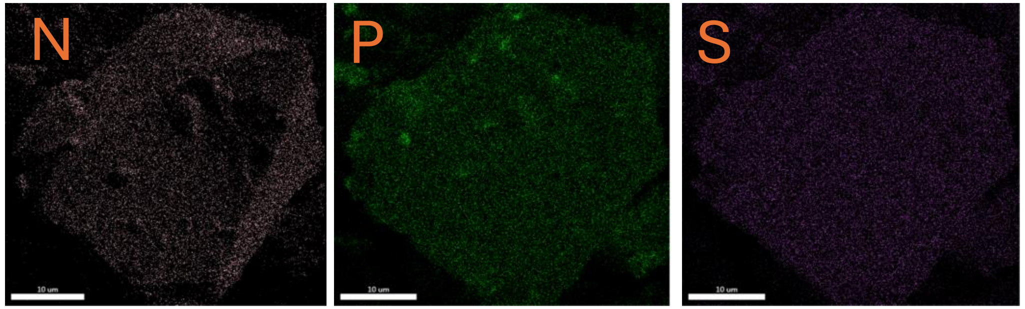
Kraft-Lignin





P-Lignin



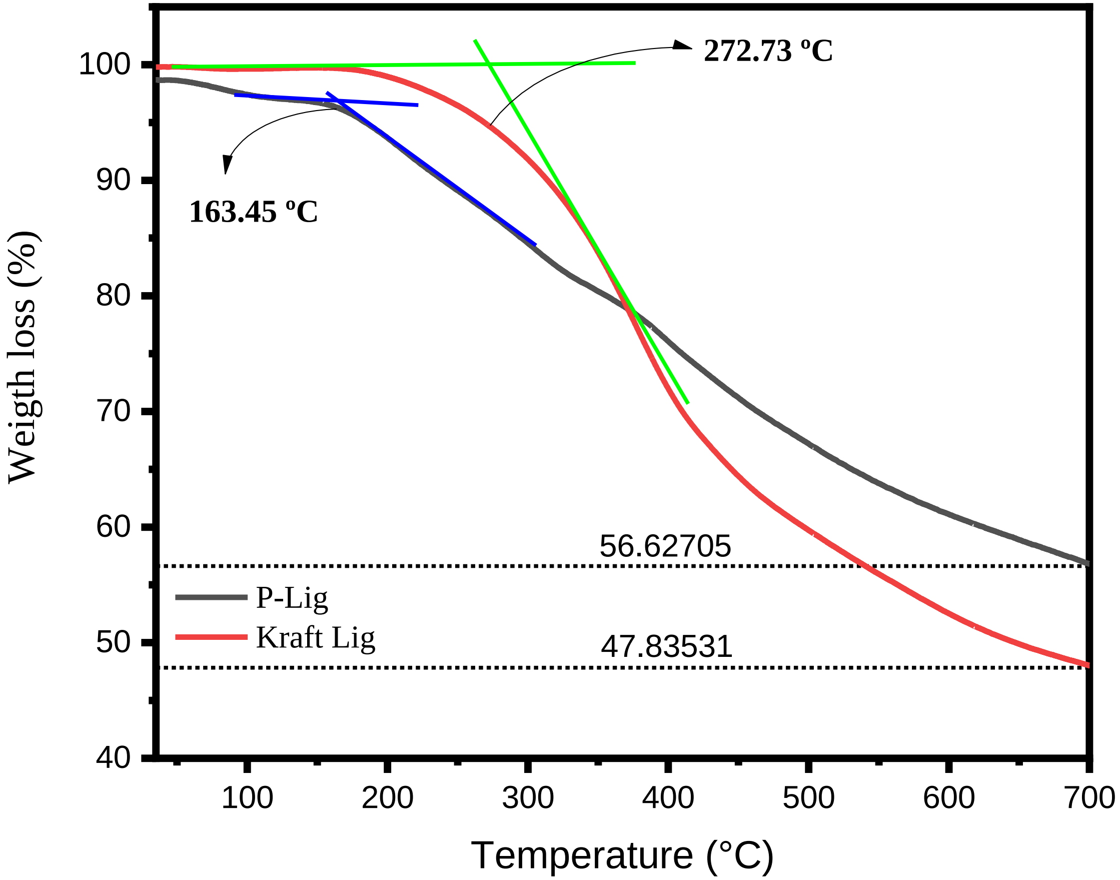


*CNS and ICP analysis confirmed the obtained data in SEM and NMR analysis

	C (%)	N (%)	S (%)	P (ug/g)
Kraft Lignin	66.605	0.38944	1.78	<LQM
P-Lignin	59.656	4.2215	1.44	14888

Lignin Phosphorylation : Results

TGA analysis

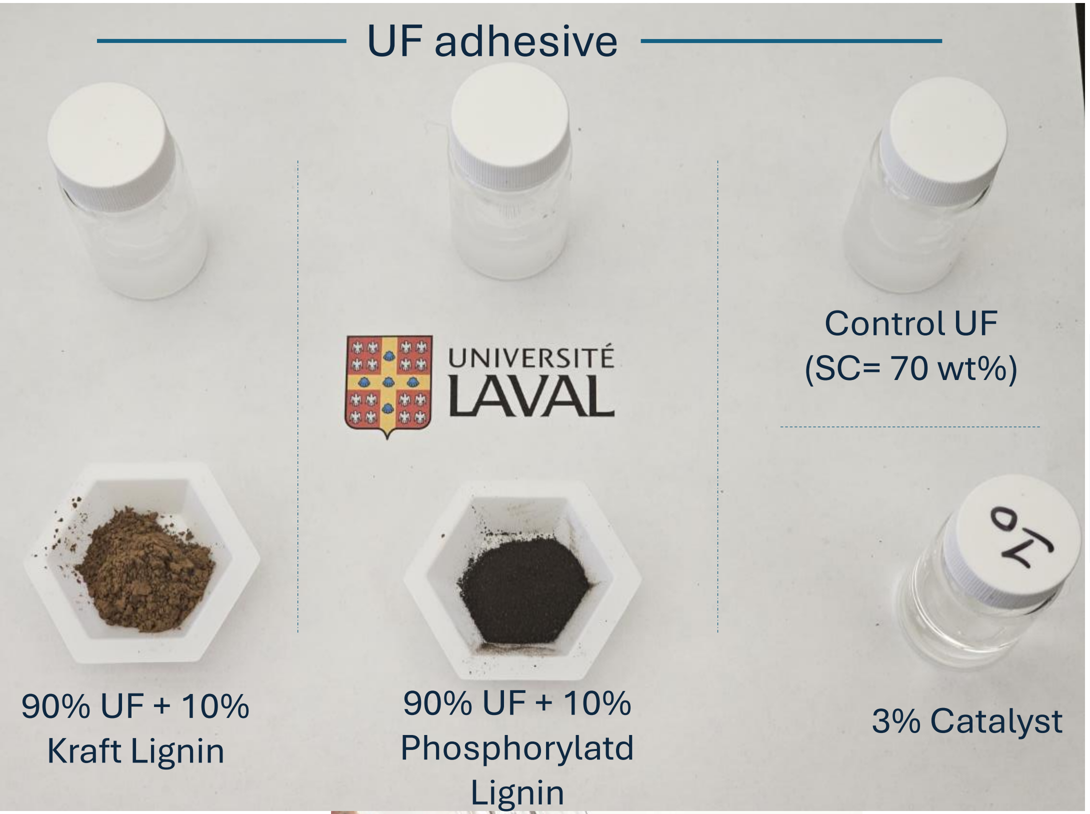


1. -Low onset temperature after phosphorylation,

2. -High residual mass loss formation even before the chemical modification due to the presence of Sulfate groups ([SO_4^{2-}] = 369 µg/g) in the structure of lignin,

3. -The phosphate insertion plays an important role in giving a fire-retardant behaviour to the lignin ([PO_4^{2-}] = 14888 µg/g) ,

Lignin UF formulation: Results



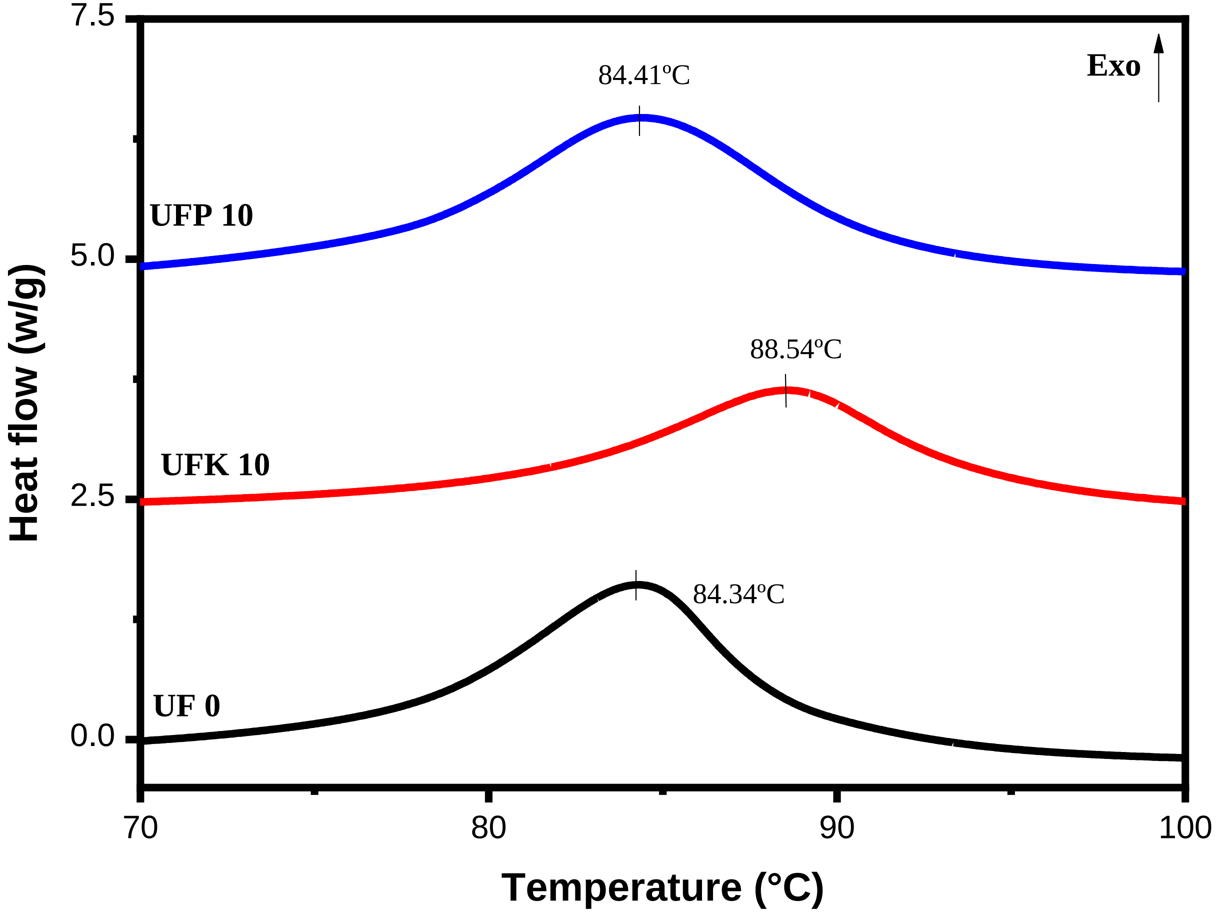
Lignin-UF formulation

Physico-chemical analysis of all formulations

Formula (%)	Solid content (%)	pH	Gel time (s)	SD (±)
UF 0	70.11	8.12	132	13
UFK 10	70. 95	8.15	163	18
UFP 10	70.96	8.32	125	10

Lignin UF formulation: Results

DSC analysis of UF + kraft lignin



1. Neat UF had an exothermic curing peak of 84ºC, which can be attributed to the heat released from the polycondensation reaction of primary amino groups of free urea with hydroxymethyl groups *,
2. The curing temperature increased regardless of the addition level, which indicates a lower reactivity of **Kraft Lig** *

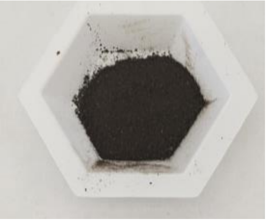
Sample code	Curing peak temperature (º)	Heat of curing reaction (J/g)
UF 0	84.34	86.84
UFK 10	88.54	70.85
UFP 10	84.41	97.27

*Antov et al.,2021. https://doi.org/10.3390/polym13162775

IV. Wood adhesive development and bounding application

90% UF Adhesive (70% Solid Content)

Or



10% Lignin

1

Wood particles

Lignin:UF resin

2

3

Mat formation

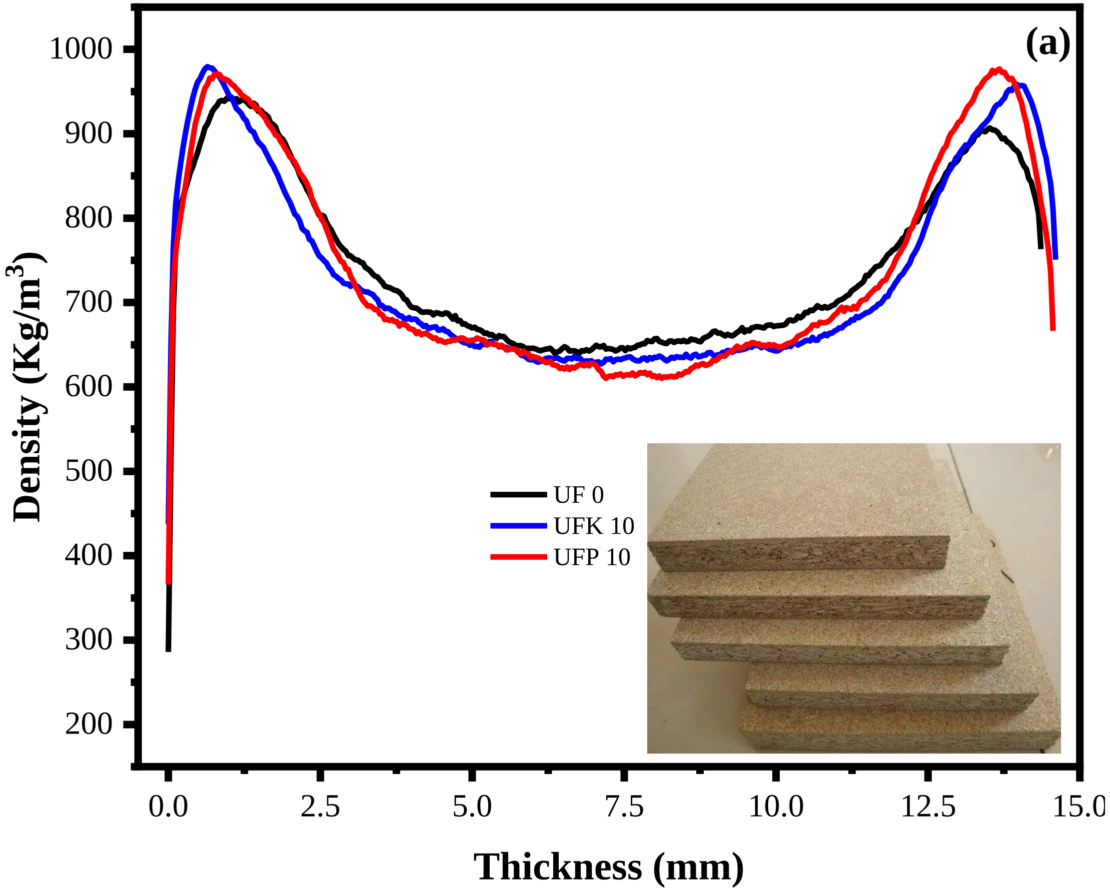
4

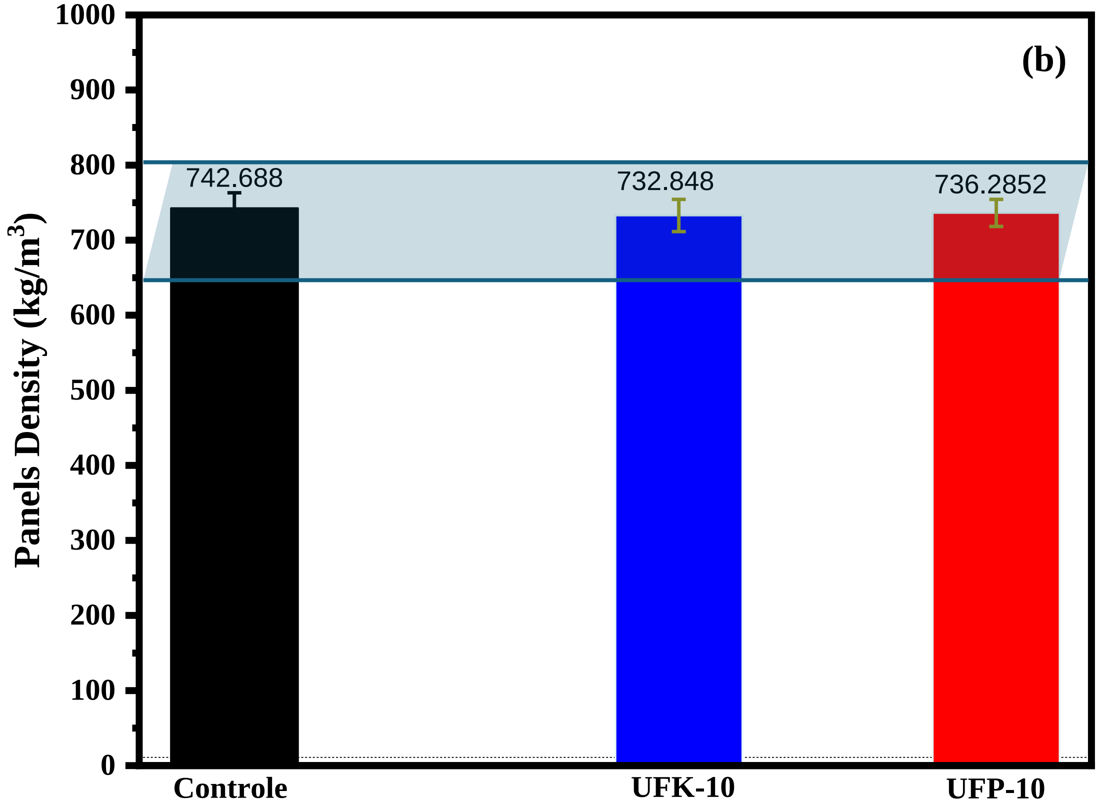
Elaborated panel

Density profile of the panels

Targeted Density was 700 kg/m³

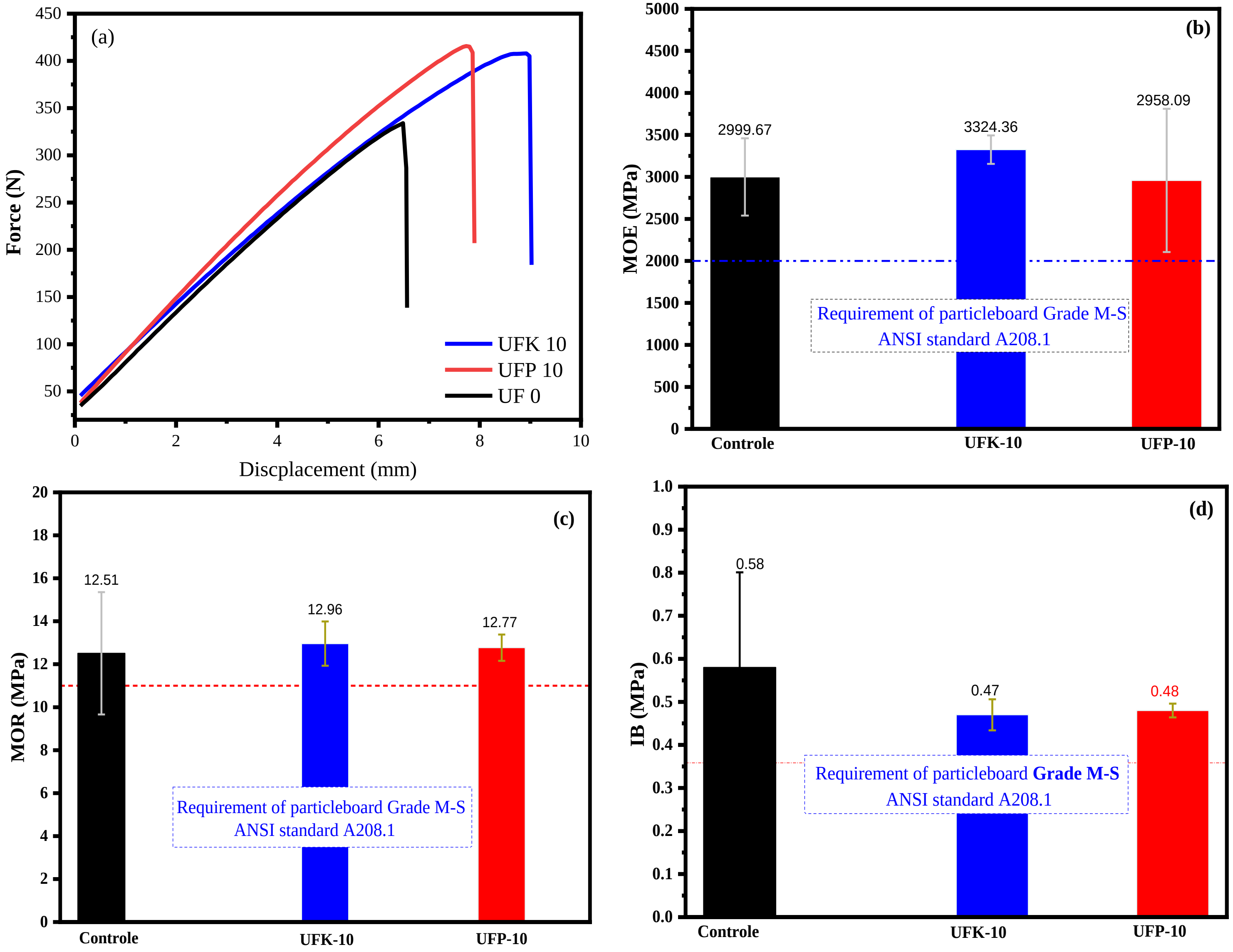
All panels meet the ANSI A208.1 (2022) standard for medium density panels





Mechanical properties

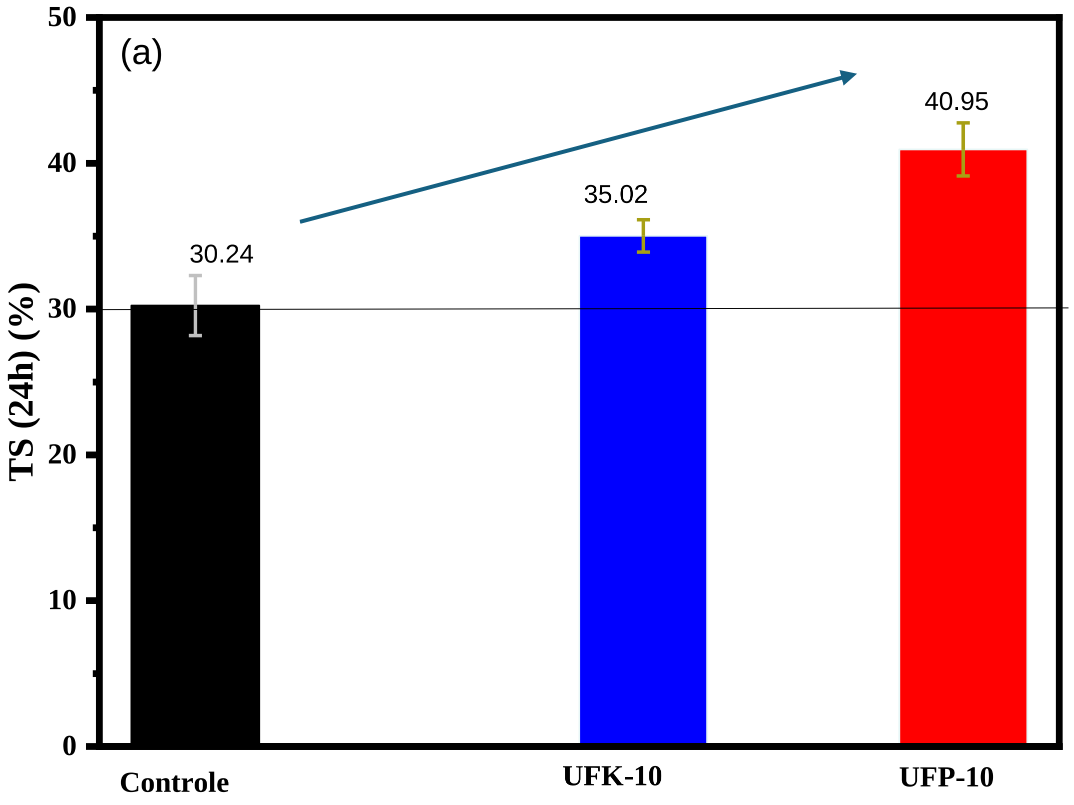
MOE: modulus of elasticity, MOR: Modulus of resistance, IB: Internal bounding

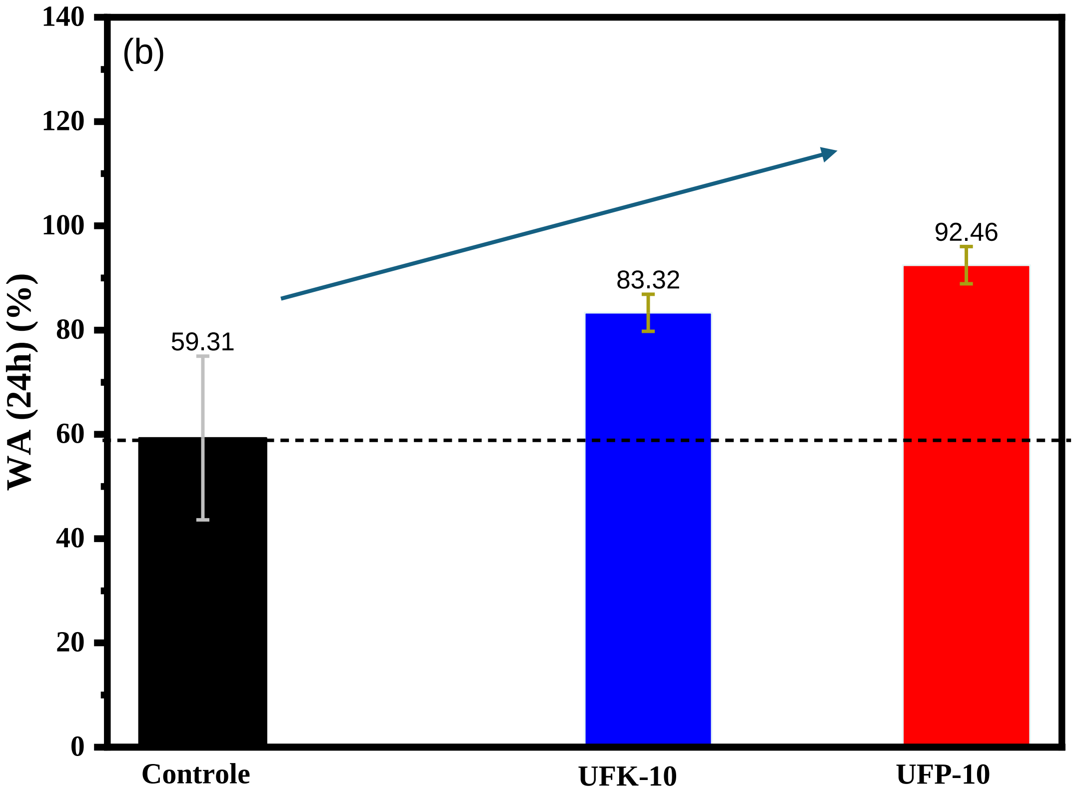


According to the ASTM D1037-12(2020) Standard

Physical properties

Thickness swelling (TS) and water absorption (WA) After immersion in water (20ºC) for 24h According to the ASTM D1037-12(2020) Standard

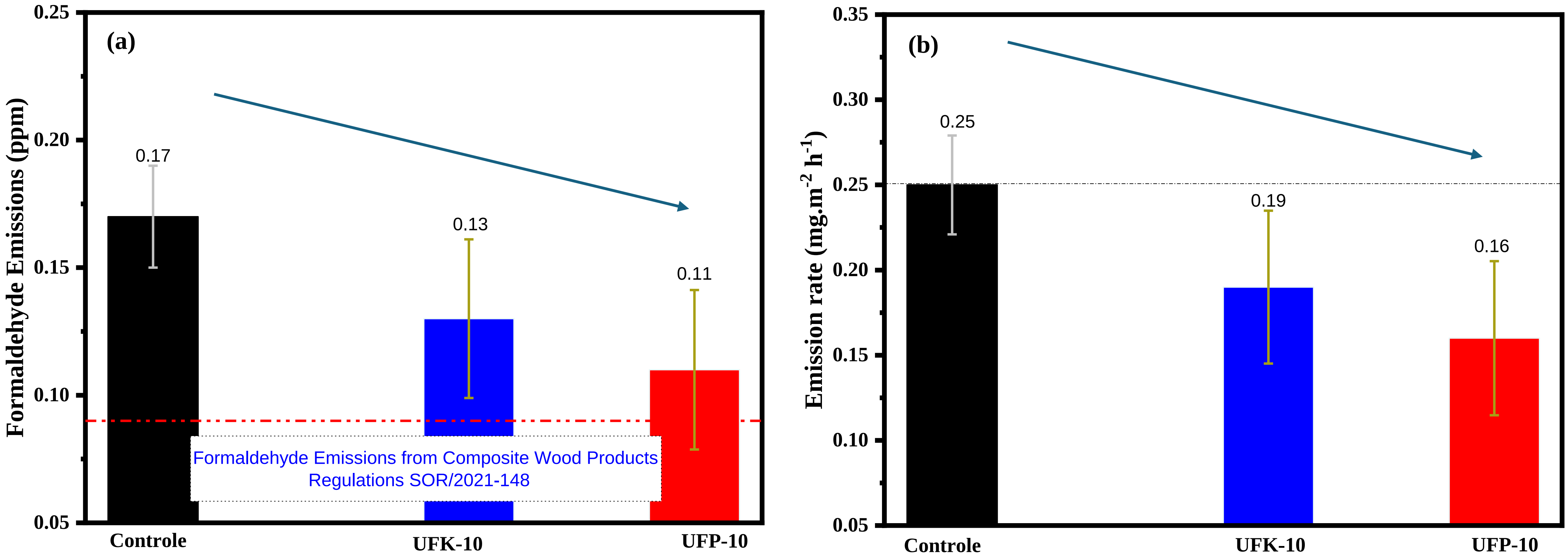




Formaldehyde Emissions

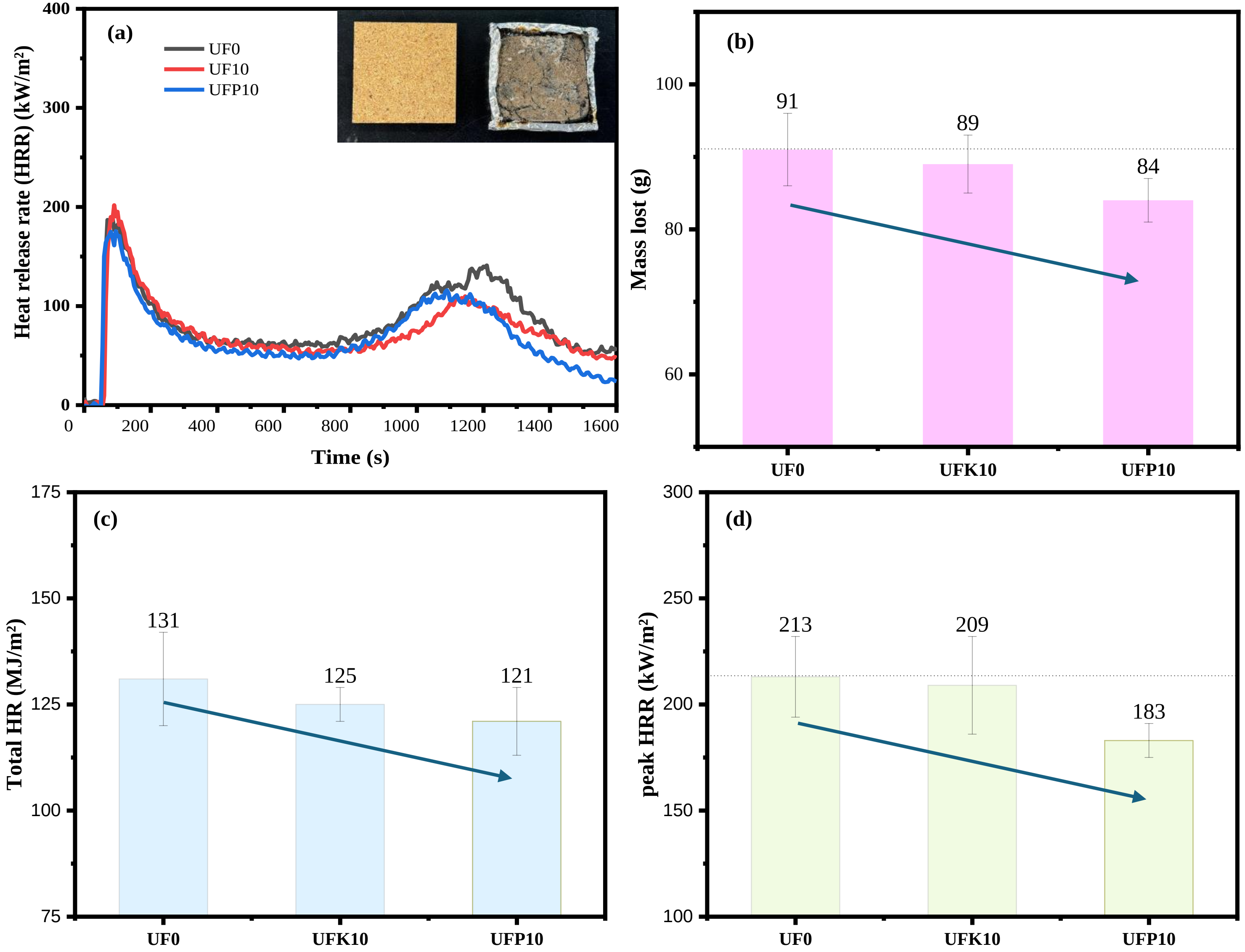
According to the ASTM D6007 standard for small chambers

- **HCHO ppm** tells you how much formaldehyde is in the air of the chamber.
- **ER mg/(m^2·h)** tells you how fast the formaldehyde is being emitted from the material's surface into the air.



Fire retardant properties

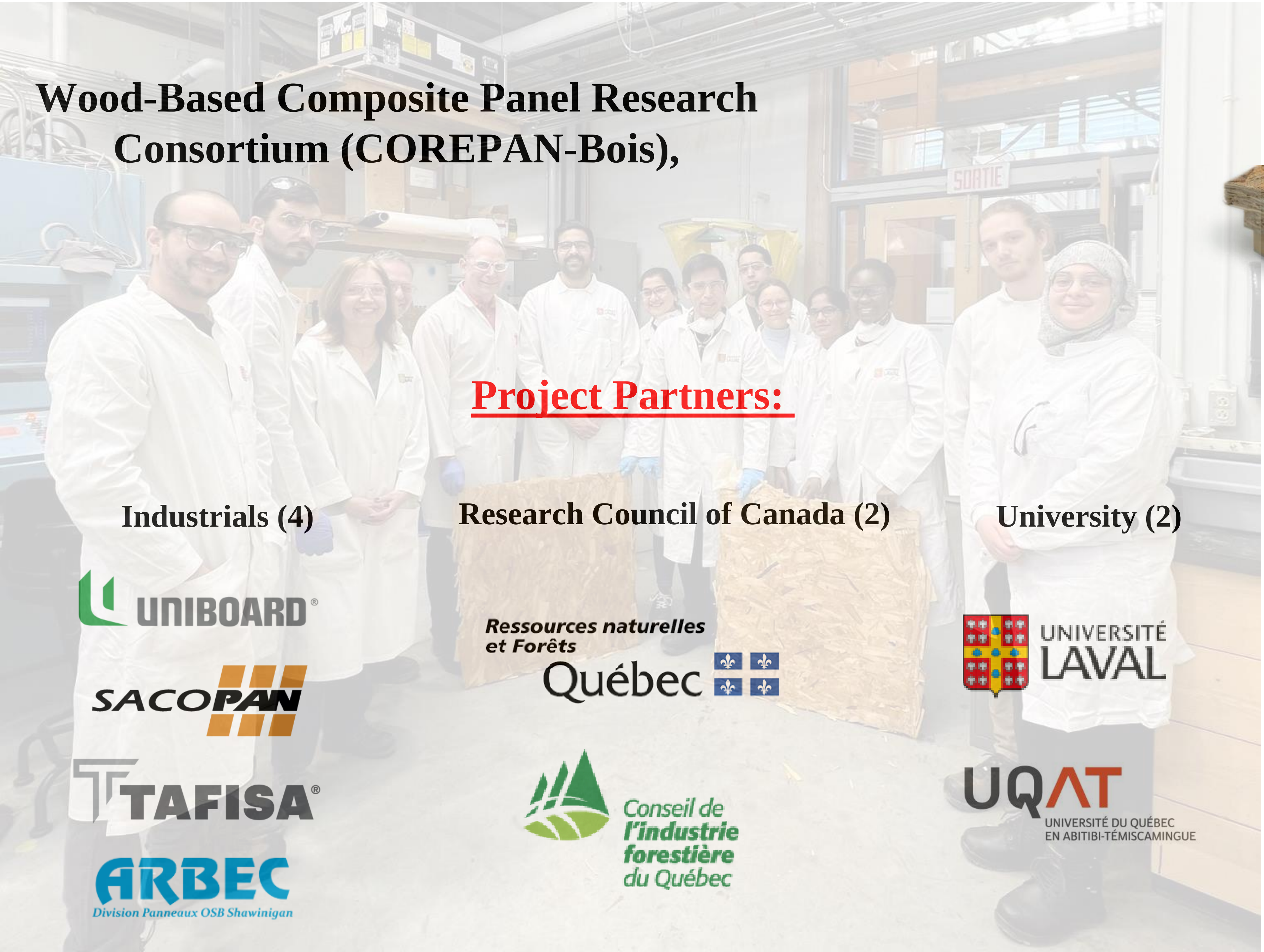
according to **ASTM E1354**



- **PhRR** indicates the **maximum rate** at which a material releases heat during combustion
- **THR** It represents the **total amount of energy** released over the entire burning period

Conclusions

Acknowledgement



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- SACOPAN
- TAFISA®
- ARBEC Division Panneaux OSB Shawinigan

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- Ressources naturelles et Forêts Québec
- Conseil de l'industrie forestière du Québec

University (2)

- Université Laval
- UQAT Université du Québec en Abitibi-Témiscamingue

Federal Laboratory (2)

- FPInnovations®
- SEREX L'innovation au service du bois

Acknowledgement

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