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MNEXT MATERIALEN & ENERGIE X TRANSITIE

Lignin as Flame Retardant

Modification of lignin & Encapsulation of ammonium polyphosphate (APP)

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Project/Research Group: Better Biobased Building Blocks (B4)

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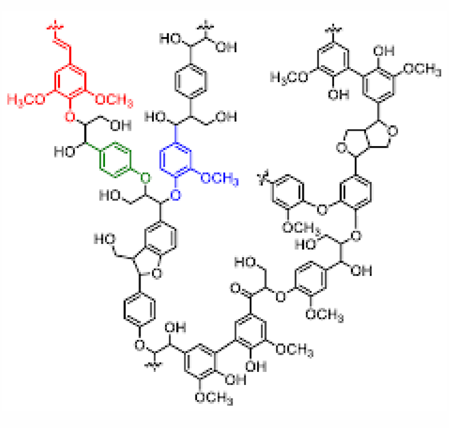
Introduction

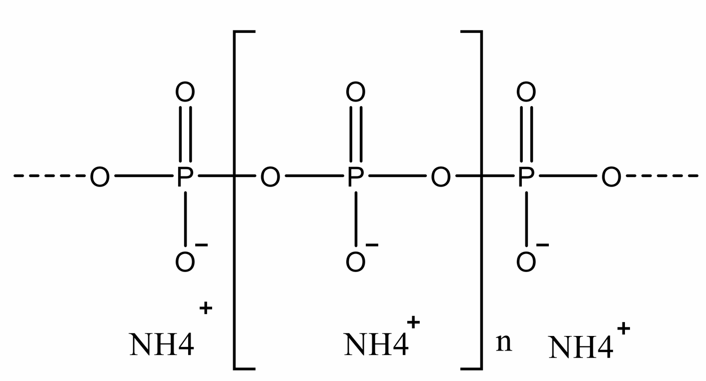
Nowadays the most used flame retardants (FR) are halogen based FRs (bromide and chloride), which are used in polymers, furniture, coatings and more. The problem of these flame retardants is that there not good for the health and the environment. [1]
A flame retardant is important in the society, because it ensure that a fire spreads less quickly, thereby increasing the chances of survival [2]. Therefore, more research needs to be conducted on a halogen free and biobased flame retardant.

Goals & Hypothesis
The goals of this research are to improve chemical modification of lignin with nitrogen and phosphorus (NP-modification) to make a better flame retardant, varying in amount and time of phosphorus. And to explore the encapsulation of APP with lignin and polyurethane (PU) to improve the flame retardancy. This is done by varying in copolyol and isocyanate.

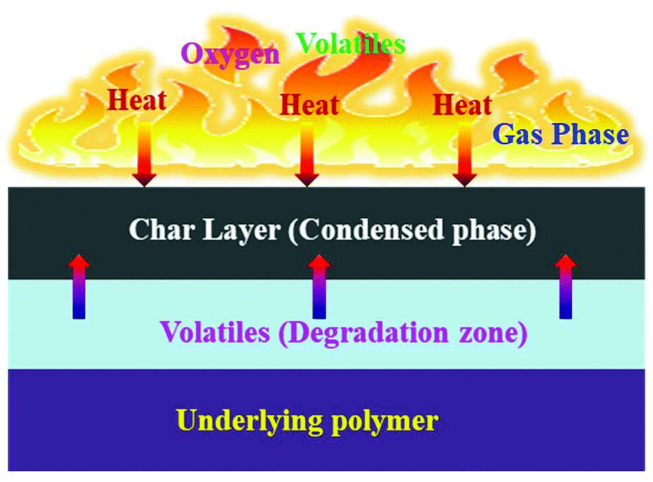
It is expected that the modified lignin has a higher char residue than the unmodified lignin. The char residue will increase by 25 wt%, because of the nitrogen and phosphorus molecules attached to the lignin [3][4]. The char residue of the encapsulated APP will increase with 20 wt%, because of the PU shell around the APP [5]. These expectations are based on TGA analysis at 600/800 °C under N2.



Lignin structure



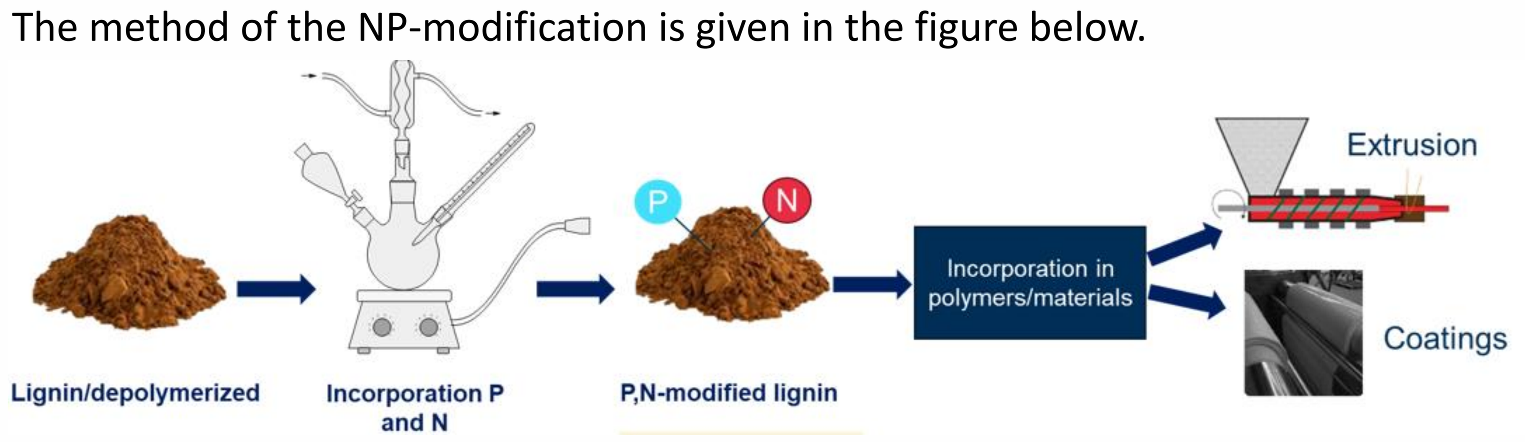
Ammonium polyphosphate structure



Combustion model for a flame retardant

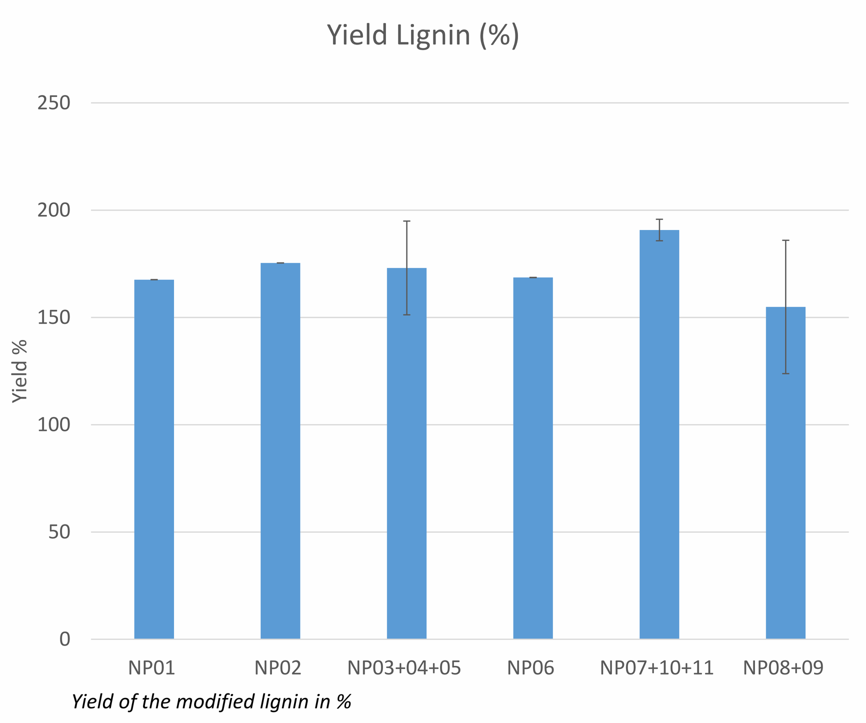
NP-modification

The method of the NP-modification is given in the figure below.

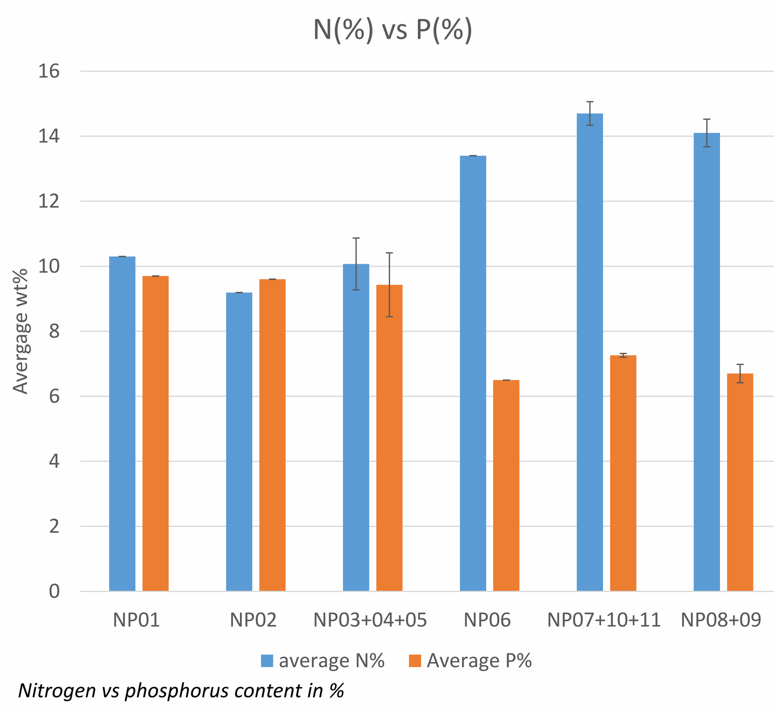


Scheme of the lignin modification

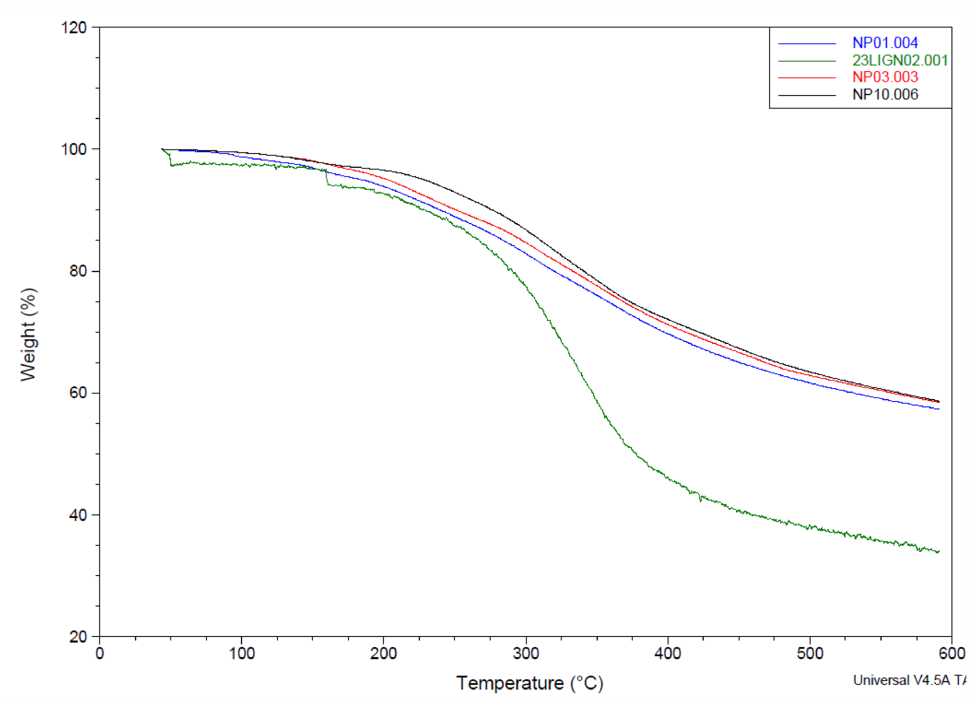
During the reaction, the amount of phosphorus is varied from 3:1 with the nitrogen to 1:1. This changes the wt% of P and N. N is higher when amount of P is lower. The yield doesn't change when the time or amount of P is varied.



Yield of the modified lignin in %



Nitrogen vs phosphorus content in %

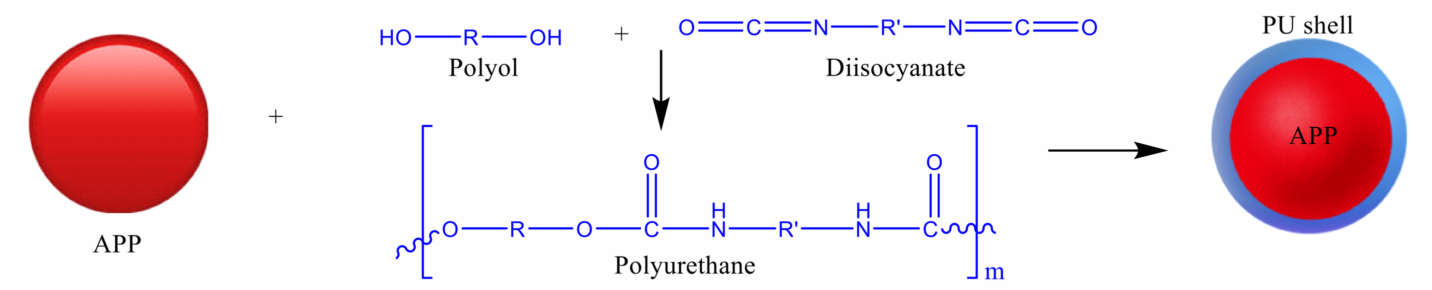


TGA overlay lignin with modified lignin

A TGA is taken to see what the char residue of the lignin and modified lignin is. The lignin has a char residue of 34 wt% and the modified lignin is 58 wt% at 600 °C in air.

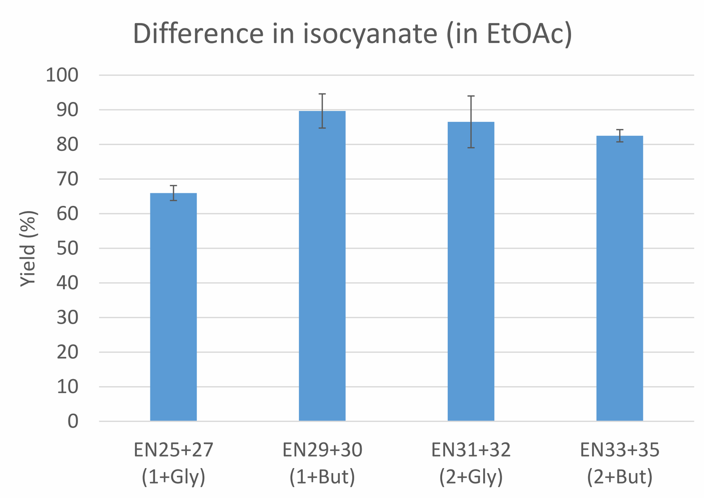
Encapsulation of APP

The reaction scheme of the encapsulation of APP is given in the figure below. This shows the shell that forms around the APP.

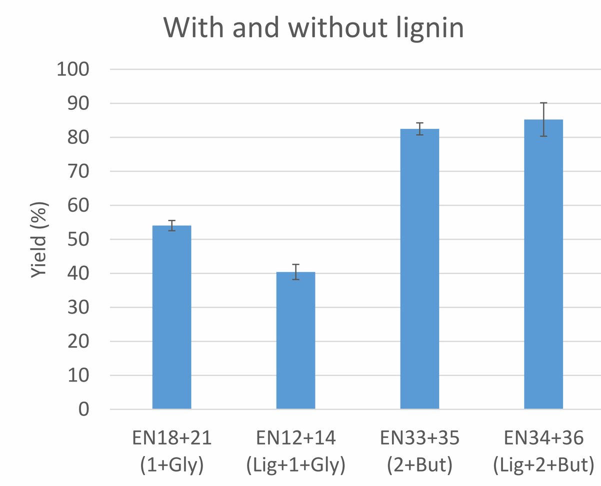


Reaction scheme of APP with PU

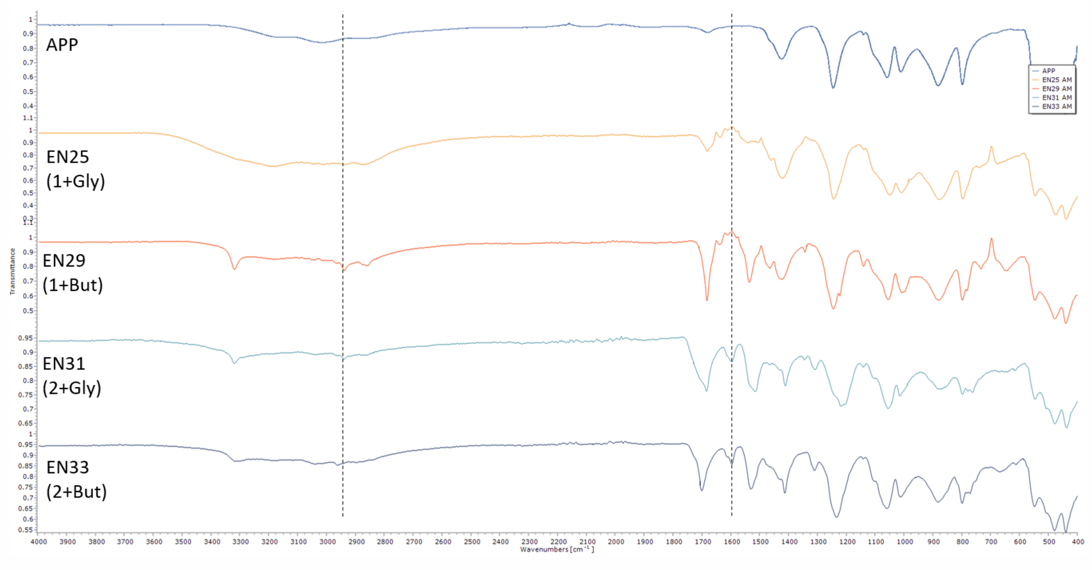
For the encapsulation there is varied in isocyanate (1/2) and copolyol (Gly/ But). The left graphic shows that the combination of EN25+27(1+Gly) gives a lower yield. The right graphic shows that with lignin and without lignin has few differences.



Difference in isocyanate and copolyol in %



Difference in encapsulation with lignin and without lignin



FT-IR stacked of APP and encapsulated APP

The 1st dot line represents a peak that is not visible in APP but is visible in the encapsulated APP. The 2nd dot line is from the HN-C=O peak. Typical for a PU bond.

Conclusion

For the modification of the lignin the expectation was that the char residue will increase with 25 wt% at 600/800 °C. The TGA showed that the char residue of lignin 34 wt% is at 600 °C and the modified lignin is 58 wt%. This is a difference of 24 wt%. Also the yield of the modified is above the 150% and the N and P content is higher than 6 wt%. So, it can be concluded that the NP-modification of lignin worked and can be used as biobased flame retardant.

The encapsulation of APP is done with different isocyanates and copolyols. This means that the 1+Gly yielded the lowest yield of 65,95 ± 2,16 %. The 1+But (89,67 ± 4,93%) and 2+Gly (86,52 ±7,46%) gave the highest yield. The FT-IR showed that the HN-C=O peak from the PU can be seen in the encapsulated APP and is not shown in APP. This concluded that PU has formed, only the SEM can say if the PU shell is formed around the APP.

References

[1]] N. Levinta, Z. Vuluga, M. Teodorescu en e. al, „Halogen-free flame retardants for application in thermoplastics based on condensation polymers," Discover Applied Sciences, April 2019.
[2] A. Morgan en J. Gilman, „An overview of flame retardancy of polymeric materials: application, technology, and future directions," Fire and Materials, pp. 259-279, June 2013.
[3] J. Sameni, S. Krigstin, D. Rosa en e. al, „Thermal characteristics of lignin residue from industrial processes," BioResources, pp. 725-737, 2014.
[4] W. d. Lange, „The synthesis of lignin-based flame retardants and the incorporation in polymers.," Final Report, pp. 1-46, June 2024.
[5] T. N. Thanh, Z. Yusifov, B. Tóth en e. al, „Preparation and characterization of microencapsulated ammonium polyphosphate with polyurethane shell and its flame retardance in polypropylene," Fire, 2024.