Partially depolymerized enzymolysis lignin: Preparation, Characterization and Application

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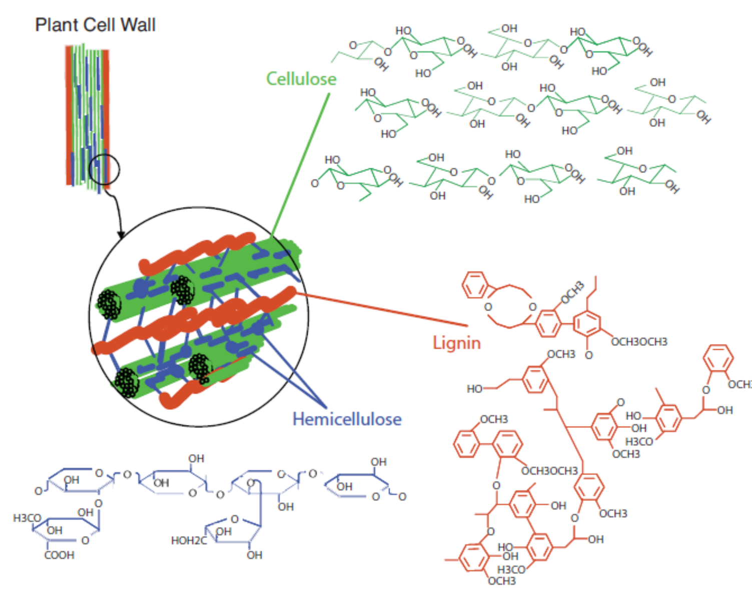
1. Introduction



1. Second-generation bioethanol is focused on lignocellulosics;
2. The process makes use of the cellulose and hemicelluloses, leaving lignin as byproduct;
3. Lignin is currently utilized as a low-grade boiler fuel to provide heat and power in pulp process;
4. The chemical structure of lignin be broken into smaller molecular units.

2. Partial depolymerization

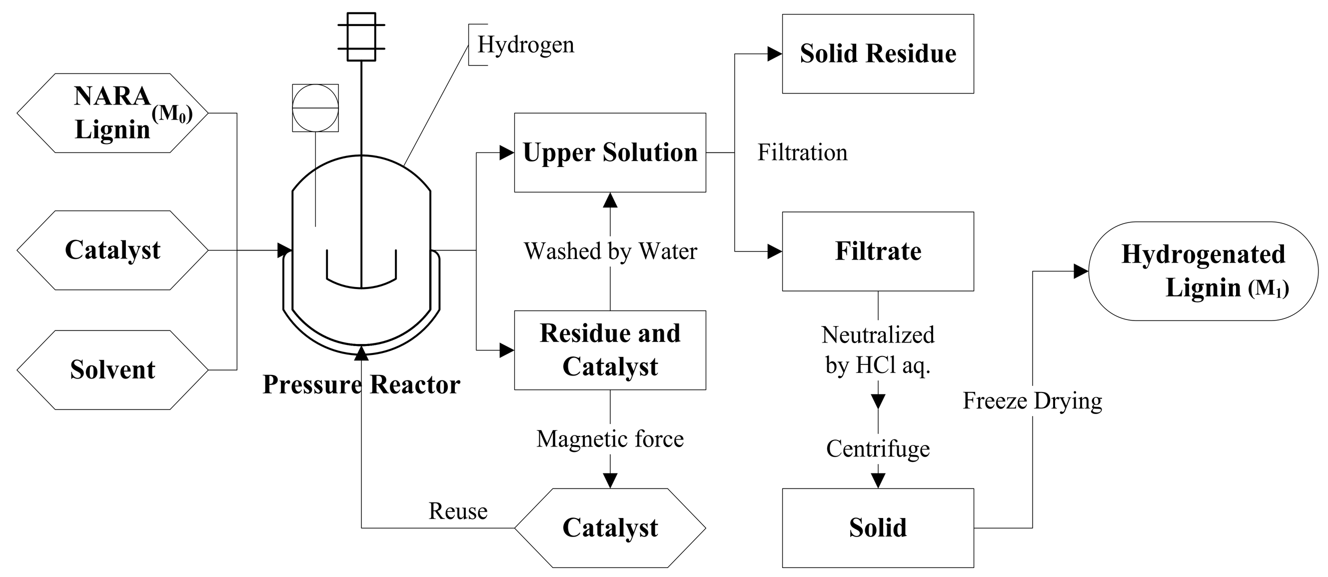


Figure 1: Process diagram for hydrogenolysis reaction

Process 1: partial hydrogenolysis [1,2]

1. Mild conditions: 120-250 ºC, H_2 pressure <2.0 MPa;
2. Raney Ni catalyst: high active and easy to separate;
3. Selective hydrogenolysis: cleavage C-O rather than C-C.

Process 2: Base-catalyzed depolymerization (BCD)

1. Temperature 150-250 ºC;
2. 1N NaOH solution.

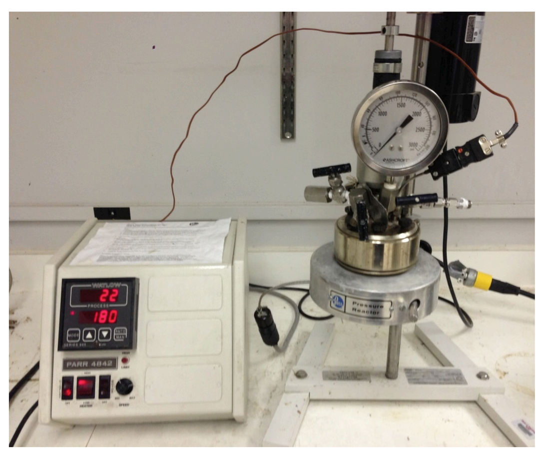


Figure 2: Reactor and temperature controller.

Figure 3: Freeze-drying samples

3. Results and Discussion

Preparation

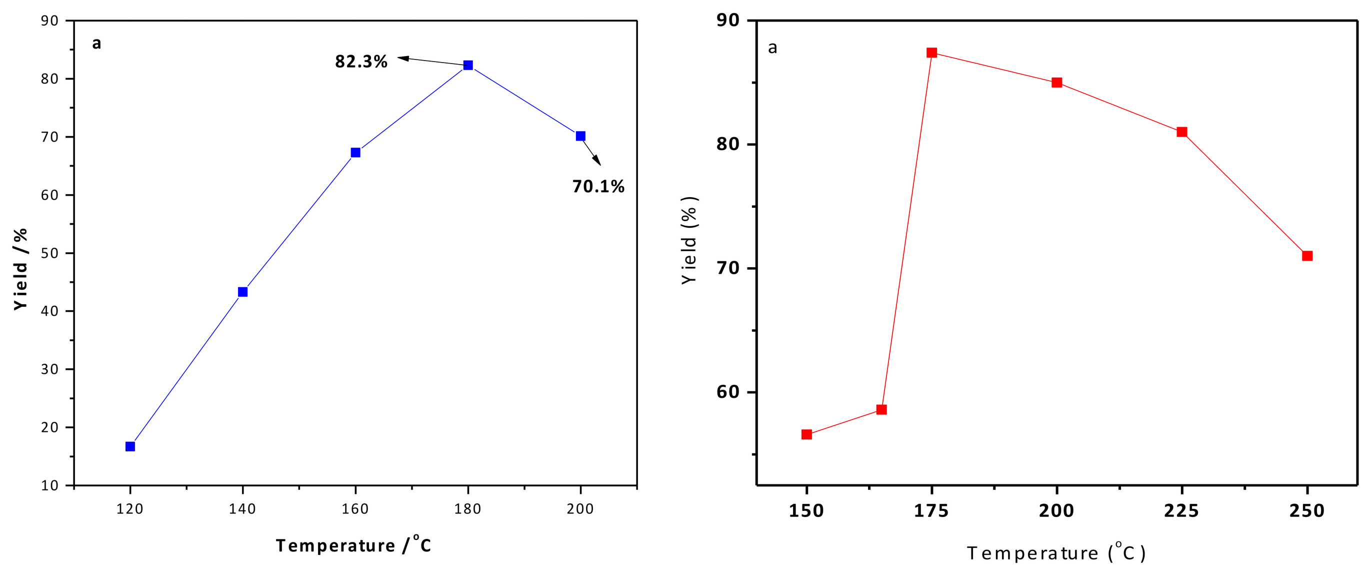


Figure 4. Effects of temperature on yield of hydrogenation (a) and BCD (b).

Determination of hydroxyl value by ^{31}P NMR

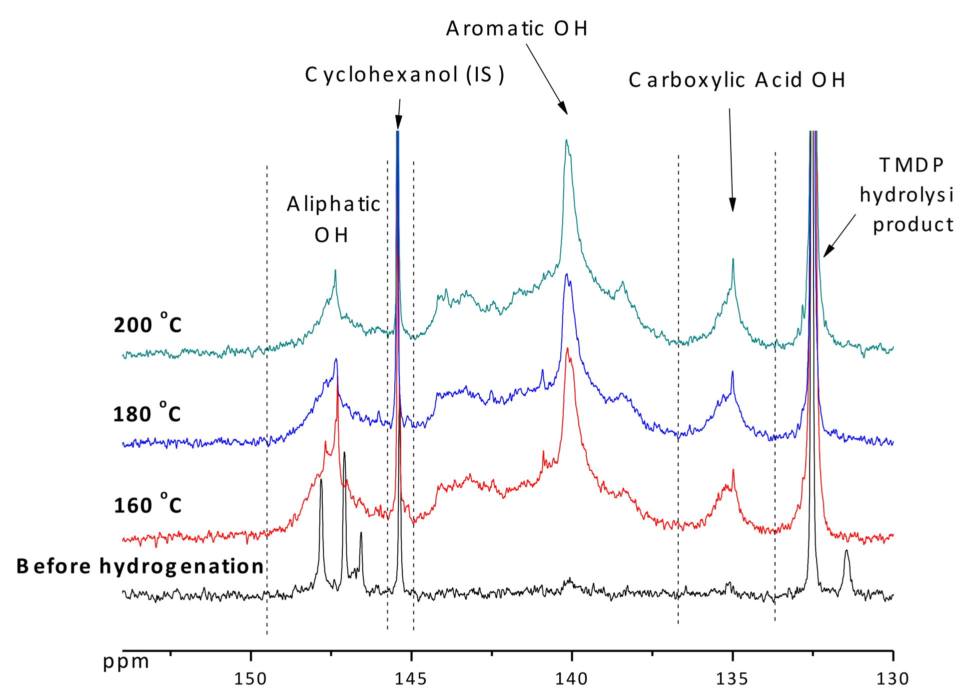
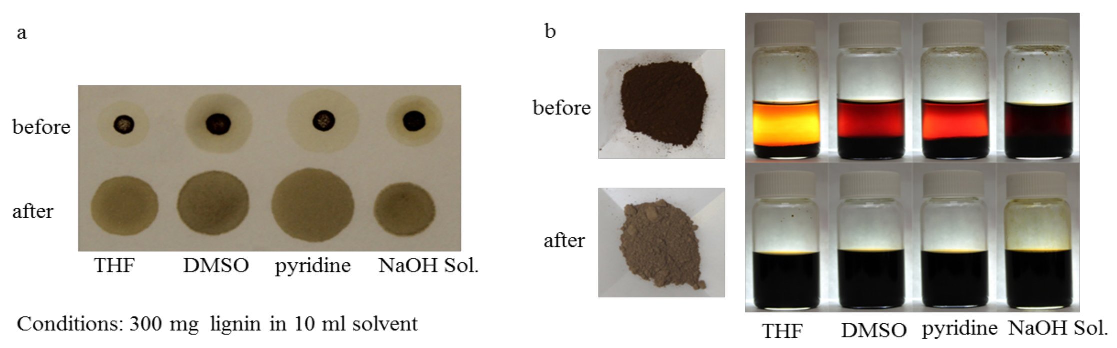


Table 1. Hydroxyl values of partial depolymerized lignins (PDL)

Structure	δ ^{31}P NMR (ppm)	OH value (mmol/g)		
		160 ºC	180 ºC	200 ºC
Aliphatic OH	145.5-150.0	0.81	0.71	0.66
Aromatic OH	136.6-144.7	2.40	2.68	3.22
Carboxylic acid OH	133.6-136.6	0.37	0.44	0.50
Total		3.58	3.83	4.38

Applications

Solubility of lignin before and after hydrogenolysis



Adhesives

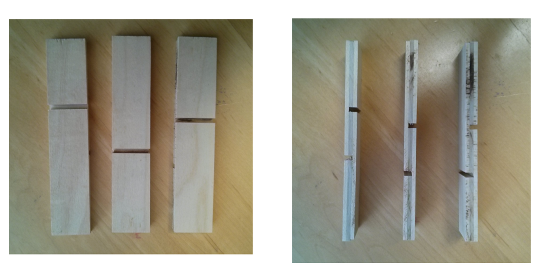


Figure 5: dry samples (Maple veneers, PDL/SPI)

Figure 6: samples after soaking in the water (60 ºC)

Polyurethane foams

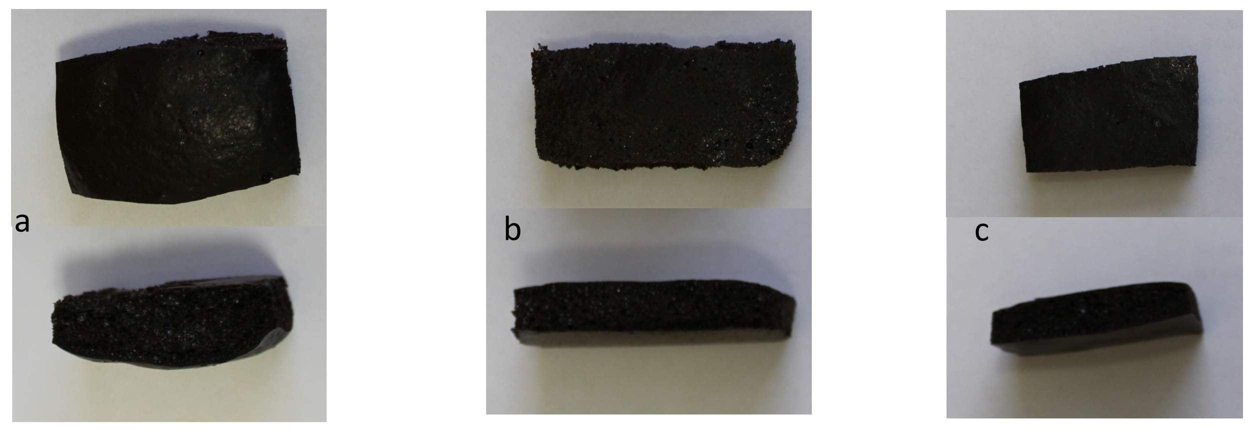
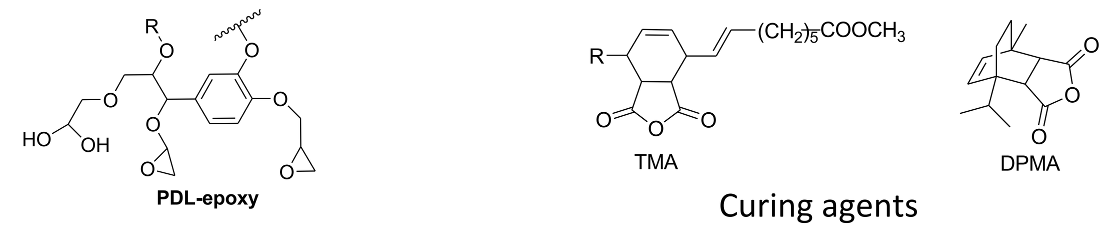


Figure 7. polyurethane foams based on PDL/PCL/TDI (a: 30% PDL; b: 20% PDL; c: 15% PDL)

Lignin epoxy and application in asphalt



Curing agents

Dynamic mechanical analysis (DMA)

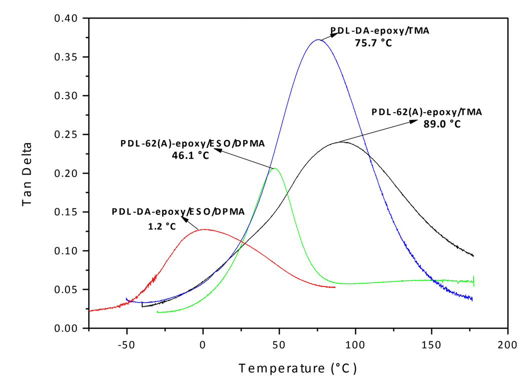


Figure 8. tan δ *versus* temperature for PDL-epoxy with DPMA and TMA

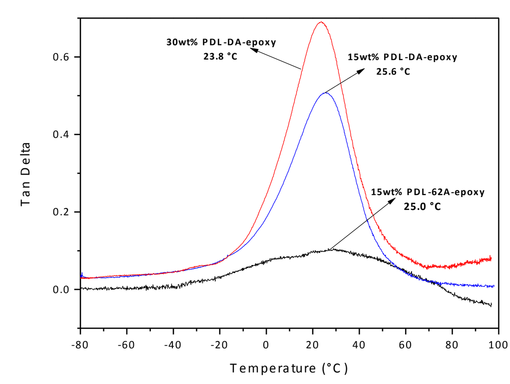
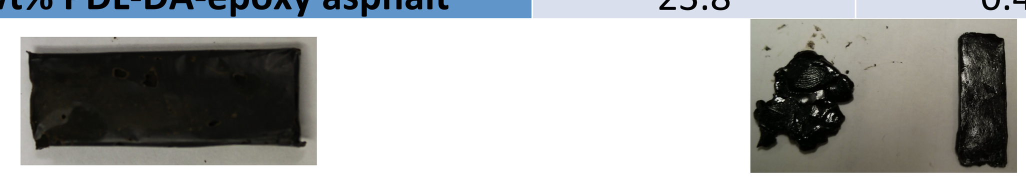


Figure 9. Preliminary results of PDL-based epoxy asphalt

Table 2. Thermal properties of cured PDL-epoxy resin and PDL epoxy asphalt

Systems	DMA	
	T_g /ºC	G′ (Gpa, 25 ºC)
PDL-62(A)-epoxy/TMA	89.0	0.61
PDL-DA-epoxy/TMA	75.7	0.35
PDL-62(A)-epoxy/ESO/DPMA	46.1	0.47
PDL-DA-epoxy/ESO/DPMA	1.2	0.20
Neat asphalt	-12.8	-
15wt% PDL-62A-epoxy asphalt	25.0	0.72
15wt% PDL-DA-epoxy asphalt	25.6	0.10
30wt% PDL-DA-epoxy asphalt	23.8	0.42



4. Conclusions

- Partial depolymerization of enzymolysis lignin (PDL) was effectively performed under mild conditions.
- The obtained PDL demonstrated low molecular weight, high hydroxyl value and good solubility in organic solvent and were further converted into epoxies and polyurethanes.
- Green adhesives based on PDL and SPI exhibited excellent performance in terms of strength and water resistance.

Acknowledgements
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