VOC and odor reduction for lignin plastic products

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VOC and Odor Reduction for Lignin Plastic Products

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Outline

- Challenges for lignin blends in plastic applications:
  - VOC and odor issues in the plastic processing and industrial applications
- NRC solutions for VOC/odor reduction
  - Multi-level treatment approach
  - Examples
- Conclusions
- Acknowledgement

This work is undertaken with the collaboration of Canadian Forest Services

Canada
Natural Resources Canada
Canadian Forest Service

Forest bioeconomy & NRC contributions

NRC
- **Lignin thermoplastics**
- **Biocomposites**

NRC
- **Greener extraction**
- **New applications**

NRC
- **Laminated/coated paper packaging**
- **Paper foam packaging**

Source: Anne-Helene Mathey, Room to grow: The forest bioeconomy in Canada, NRCan-CFS, 2019

Lignin plastic blends

- Lignin is a plastic itself
- 2nd abundant renewable resource after cellulose

Raw lignin

Lignin plastic blends

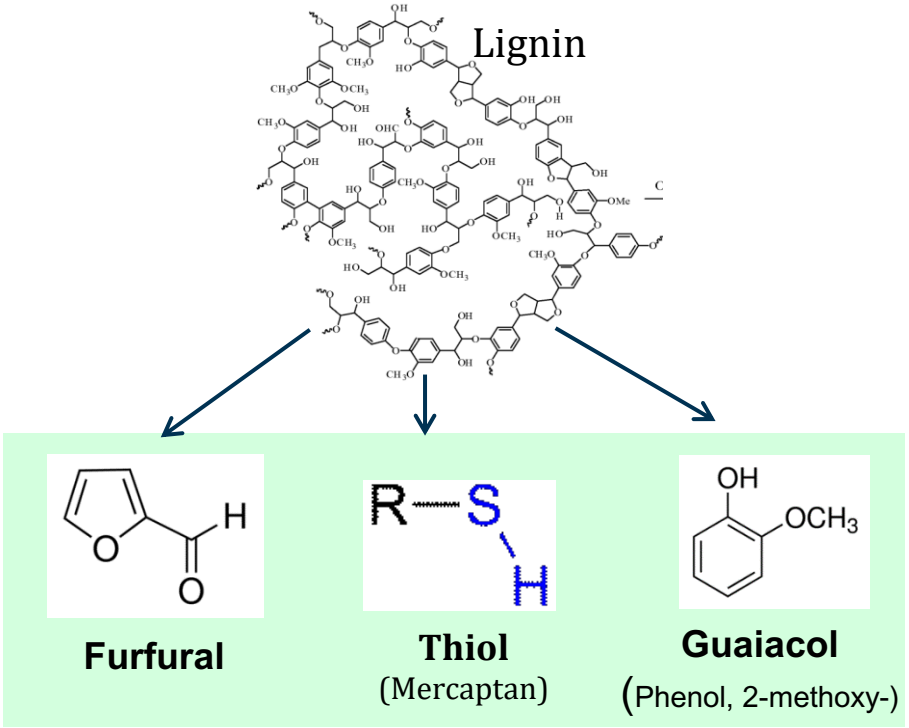
Lignin can be used to replace a part of plastic in plastic products

Outdoor applications
- Renewable
- Cost reduction

Indoor applications
- VOC and odor issue

VOCs and odor in lignin plastic blends

- Melt compounding lignin with plastics to form lignin plastic blends and also molding it into final plastic products are executed at elevated temperatures: *180 - 200 °C*
  - Lignin is very sensitive to thermal degradation and oxidation at such temperature thus producing VOCs (with strong odor)
  - Very limited fundamental understanding and no practical and cost-effective solution in VOC and odor removal for industrial applications



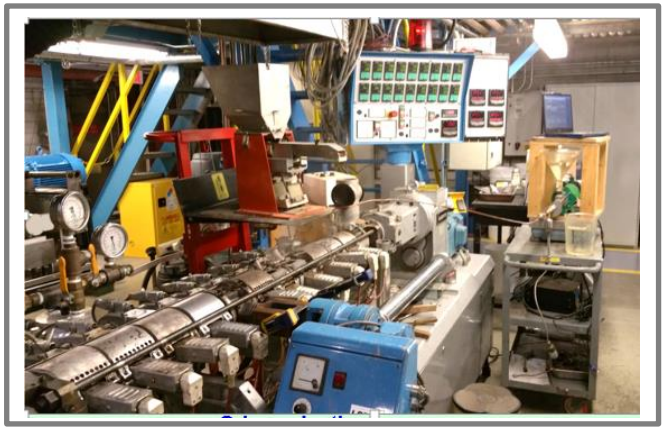
NRC strategies for VOCs and odor reduction

MULTI-LEVEL TREATMENT APPROACH

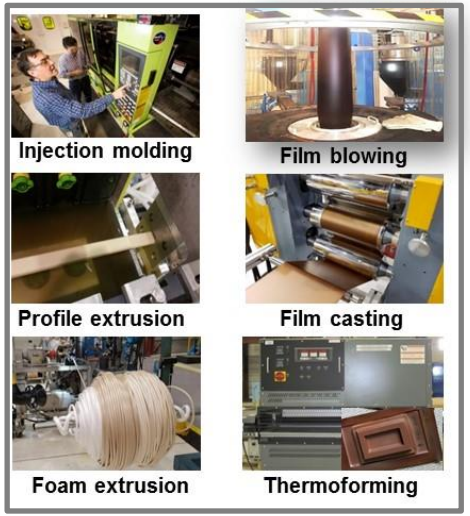
Reduce VOC/odor in raw lignin

Raw lignin

Reduce VOC/odor during compounding of lignin/plastic blends



Reduce VOC/odor during making final products

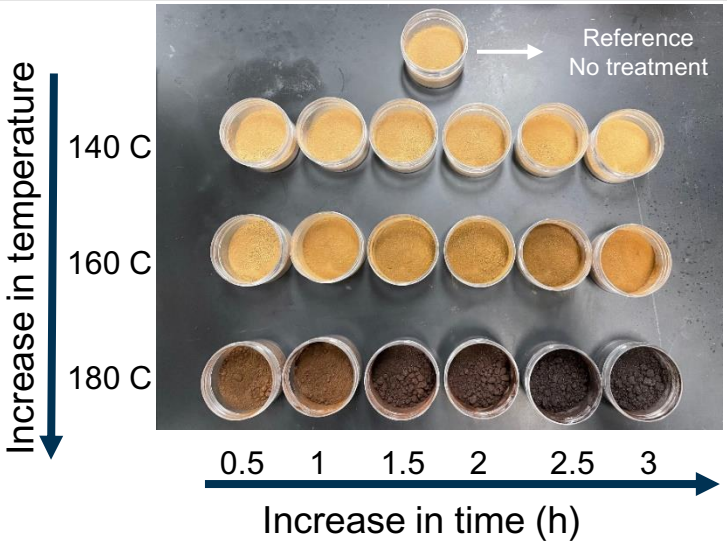


VOCs and odor reduction for the raw lignin

By thermal treatment under vacuum

Reduce VOC/odor in raw lignin

Raw lignin



Methodology:

Heating lignin under vacuum at different temperatures for different time to remove VOCs and odor presented in lignin

Odor rating on a scale of 1 to 10:

- Inhouse smell test
- Lignin without treatment (reference) is rated 10

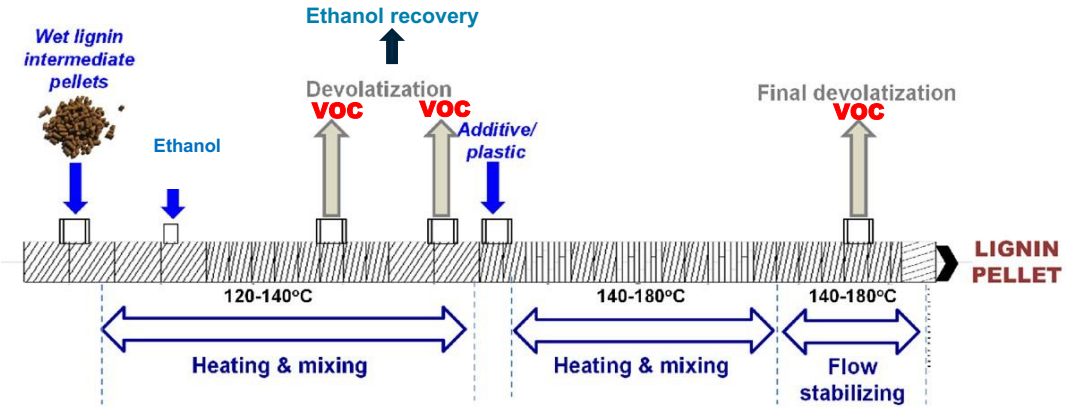
	0.5 h	1 h	1.5 h	2 h	2.5 h	3 h
140°C	10	10	9	9	7	6
160°C	10	8	7	5	4	4
180°C	6	4	2	2	1	1

Although VOCs and odors are reduced by this method, they are reproduced when process at high temperatures.

VOCs and odor removal for lignin plastics

By extrusion

- VOC reduction by degassing during extrusion with the addition of organic solvent
  - Fine-turned NRC Patent pending technology, WO/2018/035598



- Significantly reduce VOCs in lignin : > 95%
- Reduce odor but not sufficient for in door applications → further development is required

VOCs and odor reduction for lignin plastics

By reactive extrusion

Reduce VOC/odor for lignin plastic blends during compounding

- Reactive extrusion methodology

Extruded lignin blends

Odor reduction

Lignin blends	Odor index #
Without additives	54
With additives	40-50

Not effective because of

- Low residence time thus not permitting the complete interaction with odor molecules
- Only low concentration of reactive additives can be used due to the cost issue

Odor test

Odor Intensity	Odor index #
No odor	0
Negligible	0-24
Acceptable	25-49
Disturbing	50-74
Unacceptable	75-99
Unbearable	100

Odor reduction in lignin plastic blends using polar materials

Typical VOC compositions in PP lignin blends

Chemical	CAS	Concentration at 50°C (ng/L)/g
Acetic acid	000064-19-7	348
Cyclotrisiloxane, hexamethyl-	000541-05-9	24
Furfural	000098-01-1	3,556
Ethanol, 2-butoxy-	000111-76-2	75
2-Furancarboxaldehyde, 5-methyl-	000620-02-0	39
Phenol	000108-95-2	10
C13 branched hydrocarbon		33
Pentanoic acid, 4-oxo-, ethyl ester	000539-88-8	67
Phenol, 2-methoxy-	000090-05-1	22
Nonanal	000124-19-6	53
Benzoic acid, ethyl ester	000093-89-0	118
Oxiniacic Acid	002398-81-4	48
Octanoic acid, ethyl ester	000106-32-1	75
Decanal	000112-31-2	29
Vanillin	000121-33-5	22
Total VOC		**4,893**

Observation:

All the odors are polar organic molecules, consisting of carboxylic acid, aldehyde, ketone, ester, etc.

Hypothesis:

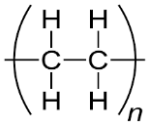
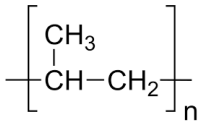
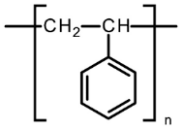
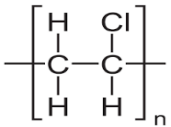
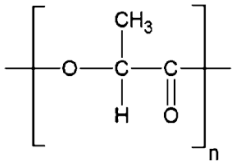
May foreign polar molecules interact with odor molecules via hydrogen bond or strong Van der Waals bond thus reducing odor issue?

Note:

- Red color dedicated to irritating smell
- Blue color dedicated to pleasant smell

Odor reduction in lignin plastic blends using polar materials

- *Blend lignin with various plastics that have different polarities*

LDPE  PP  PS  PVC  PLA 

Increasing polarity

LDPE/lignin

Extremely irritating odor

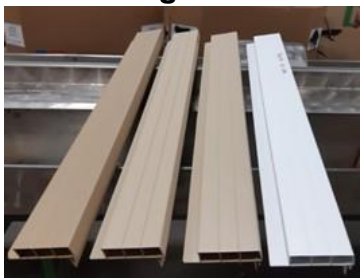
PP/lignin

Very irritating odor

PS/lignin

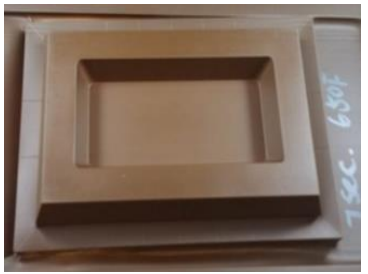
Irritating odor

PVC/lignin



Mild odor

PLA/lignin



Extremely mild odor

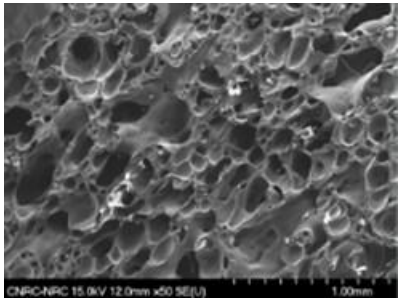
Significant odor reduction as the material polarity increases !

VOC and odor reduction for lignin

By creating active biochar from lignin

- Developed novel biochar from lignin for absorbing VOCs and odor in lignin plastics
  - Carbonization of lignin to produce biochar
  - Activization without harmful chemical treatment and maximization of the absorption of VOC and odor molecules
  - Execution of carbonization and activation in one equipment to reduce energy consumption and operation cost

Lignin Carbonization with/without Activation



Biochar with high porosity

VOC and odor reduction for lignin plastics

By creating active biochar from lignin

Pilot scale production: Active biochar from lignin

Lignin

Carbonization and activation

Active biochar

VOC and odor reduction for lignin plastics

By creating active biochar from lignin

Novel active biochar from lignin

- Effectively reduce the odor in lignin plastic products
- Promote the utilization of lignin → increasing lignin consumption
- Reinforce stiffness and enhance thermal stability of the thermoplastics

Lignin plastic prototypes without odor

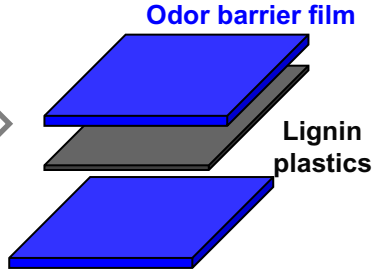
VOC and odor reduction for lignin plastics

By adding an odor barrier film

Lignin plastic prototypes without odor using barrier layer

- Effectively reduce the odor emission from lignin plastic products
- Easily applicable to current plastic processing via co-injection or co-extrusion or compression molding

Sheet casting



Compression Molding

Lignin PP prototype without odor

Summary

- NRC developed multi-level treatment approach to address VOCs and odor in lignin plastic applications:
  - Reduce VOC and odor in raw lignin
    - Vacuum heating effectively reduces odor and increases thermal stability in lignin but VOC and odor regenerate at high temperatures > 180^{o}C
  - Reduce VOC and odor in lignin plastic blends during compounding
    - Significant VOC and odor reduction using NRC patent pending technology but it is not enough for indoor application
    - Reactive extrusion is not effective as reaction kinetics become the limiting factor
    - Lignin-based VOC absorbents are the promising and cost-effective solutions while increasing bio content in final products
  - Reduce odor in lignin plastic final products
    - Achieving almost odor free final product with post process treatment, however, additional operation is required

Acknowledgement

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- Matthew Schacker
- Allan Ding
- Jean-François Levasseur

Thank you!

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