

# Liquefied Wood: What is it, and what can be done with it?

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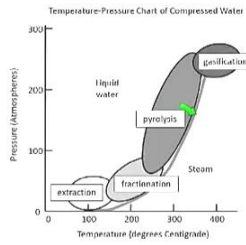
## Conventional Liquefaction

Conversion of Biomass to Drop In Biofuels

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Hydrothermal Processing (HTP)

- Processing in hot, compressed liquid water or supercritical water
  - Carbohydrate from HTP: 200°C and 20 bar yields carbohydrate that can be hydrolyzed to fermentable sugars
  - Biocrude from HTP: 330°C and 150 bar yields hydrocarbons suitable for production of diesel fuel
  - Syngas from HTP: 600°C and 230 bar yields hydrogen, carbon monoxide, and methane



Temperature-Pressure Chart of Compressed Water

Pressure (Atmospheres)

Temperature (degrees Celsius)

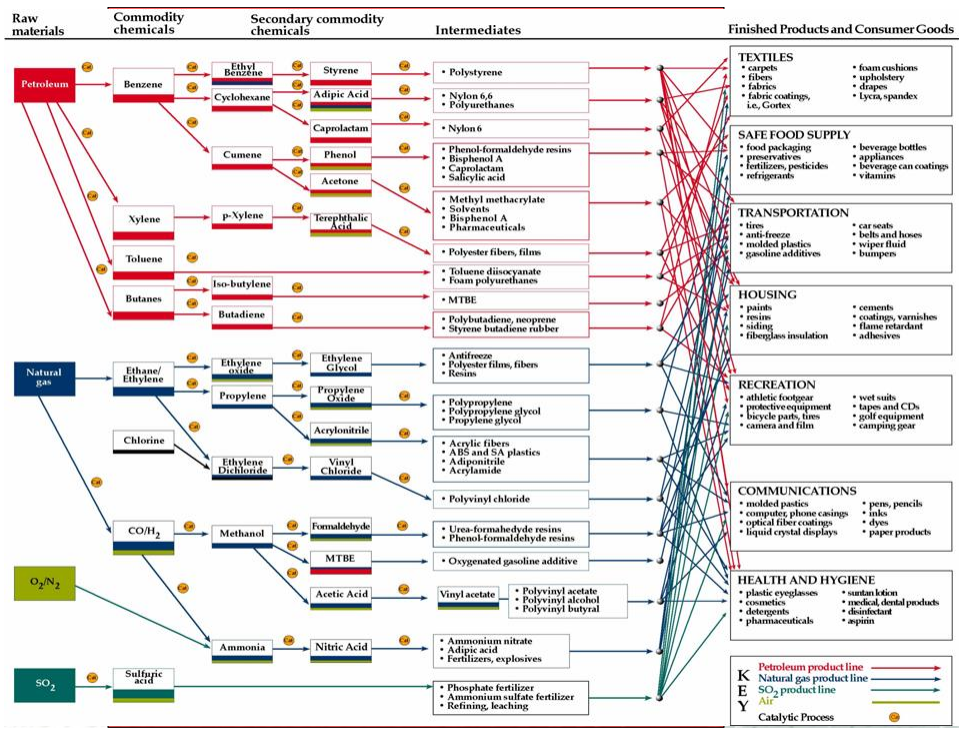
Credit: Robert Brown, CenUSA BioEnergy & Iowa State University

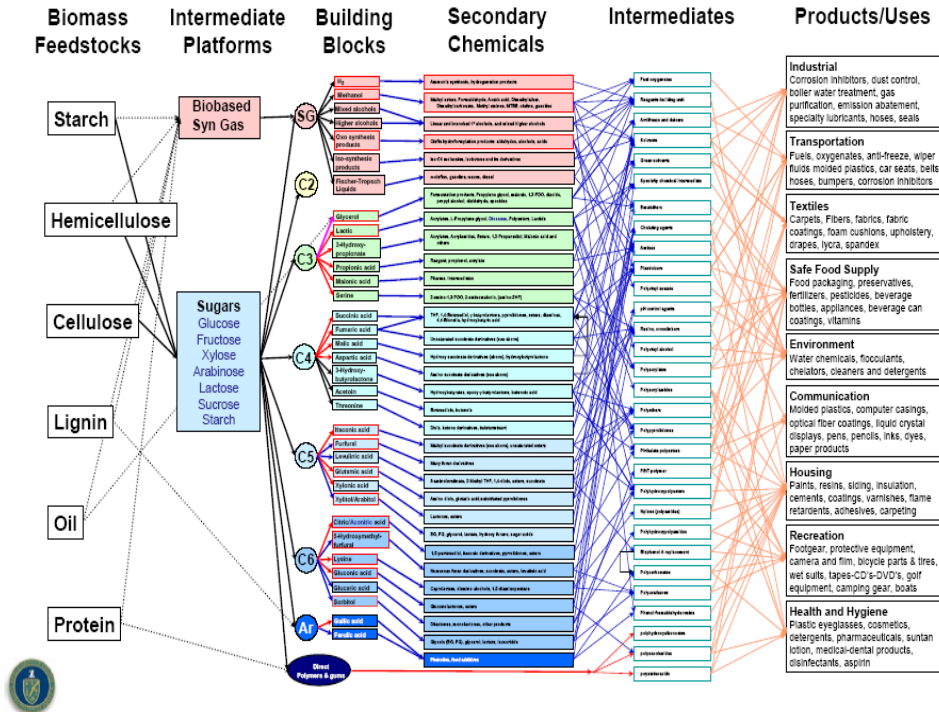
<https://www.youtube.com/watch?v=Ua8She55qTc> 2/14/2013



# Major Problems

- Energy input / Efficiency
- Do we really want to burn a valuable product?





## Heat Required

- Energy efficiency = \$\$\$\$\$



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## Microwave

- **Energy efficient**
- **More even heating**
- **More controlled heating**
- **Can still use solvents**
  - **Acids**
  - **NaOH, H<sub>2</sub>O<sub>2</sub>**
  - **Glycerin**



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## Microwave

- **Energy efficient**
- **Easier to develop a valuable product**
  - **Carbon nanofibers**
  - **Polyurethane Foam**
- **End of Service treated wood**
  - **Extract metals from CCA treated wood**

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# 3-step Converting CCA Treated Wood into High-value Added Products

**Xingyan Huang**

**School of Renewable Natural Resources  
Louisiana State University**



## **Chromate Copper Arsenate (CCA)**

**C: Chromium (Cr) : a fixing agent**

**C: Copper (Cu) : an effective fungicide**

**A: Arsenic (As) : insecticide and fungicide**

**(Kazi and Cooper, 2002)**

## **A Mixture of HEAVY METALS**



Fence



Deck



Pole





## BACKGROUND

- **Why should we recycle CCA treated wood?**



**Diffusing heavy metals into environment and threatening human health** (Kakitani et al., 2006)



Estimated spent CCA-treated wood in the U.S. would **increase to  $16 \times 10^6 \text{ m}^3$  by 2020** (Copper 1993)

- **What the traditional ways to recycle?**



## • STEP 1 DETOXIFICATION

### Traditional Means of Detoxification

Biological, chemical, steam explosion, electro-dialytic

- Previous recycling methods are **too costly** and/or too slow to be commercially viable
- **Not really “green”**



## Our Approach: Microwave-enhanced Detoxification



**Microwaves can generate** high temperatures and relatively high pressure rapidly, resulting in a higher liquefaction efficiency with a **faster reaction rate** and a **shorter reaction time**, compared to conventional heating.

**Economical and Eco-friendly.**



### • STEP 2 DELIGNIFICATION

#### Traditional Means of Delignification

Biological, **chemical**, **steam explosion**, electro-dialytic

- **Acidic/alkaline pretreatment** (Saha et al. 2007)
- **Wet oxidative** (Lissens et al. 2004)
- **Liquid hot water** (Perez et al. 2007)
- **Team explosion** (Sun et al. 2008)
- **Ultrasound delignification**

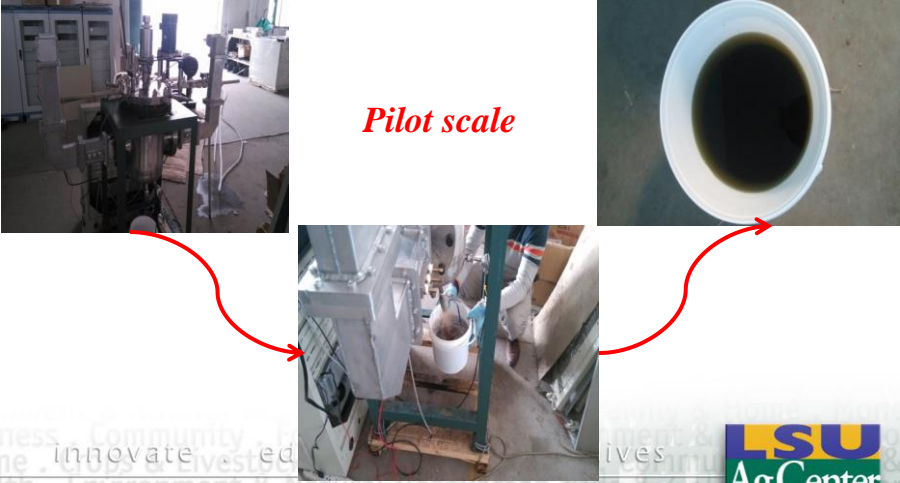
• **Disadvantages:**

- **Cannot be in industrial scale**
- **Low efficiency**
- **Expensive**
- **environmentally-friendly**



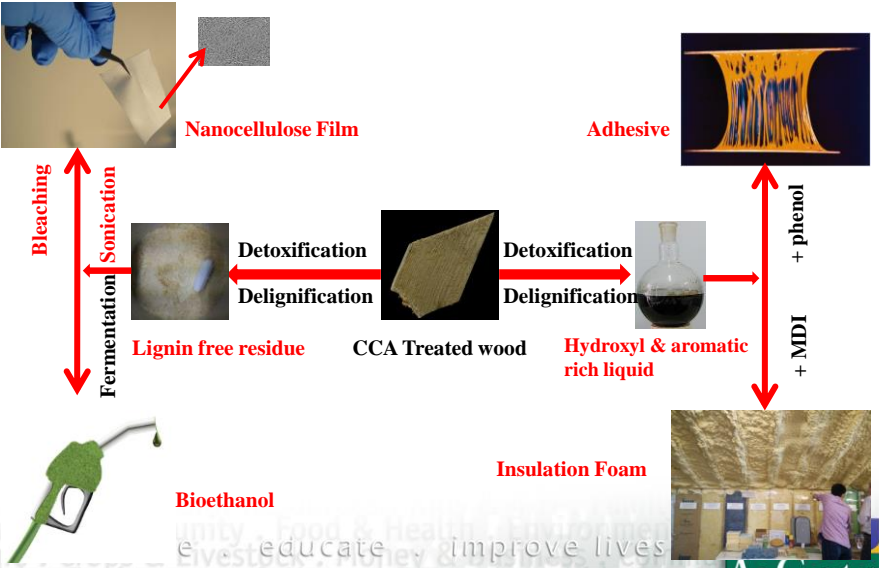
# Our Approach: Microwave-assisted Delignification

*Pilot scale*



The image shows a pilot-scale delignification process. On the left, a piece of industrial equipment is used to process wood chips. A red arrow points from this equipment to a white bowl containing a dark, viscous liquid. Another red arrow points from the bowl to a larger piece of equipment in the center, which appears to be a microwave reactor. The background features a watermark with the text 'Innovate, Educate, Improve Lives' and the LSU AgCenter logo.

## • STEP 3 CONVERTING



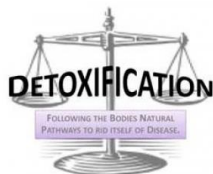
The flowchart illustrates the conversion of CCA Treated wood into various products. The central starting point is 'CCA Treated wood'. From this point, three paths emerge:

- Left Path:** 'Detoxification' and 'Delignification' lead to 'Lignin free residue'. From 'Lignin free residue', 'Bleaching' and 'Sonication' lead to 'Nanocellulose Film'. 'Fermentation' leads to 'Bioethanol'.
- Right Path:** 'Detoxification' and 'Delignification' lead to 'Hydroxyl & aromatic rich liquid'. This liquid is then combined with '+ phenol' and '+ MDI' to produce 'Adhesive'.
- Bottom Path:** 'Hydroxyl & aromatic rich liquid' is used to produce 'Insulation Foam'.

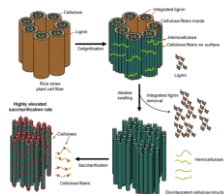
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- **REVIEW**



**DETOXIFICATION**



**DELIGNIFICATION**



**CONVERSION**

Thank you, Xingyan Huang

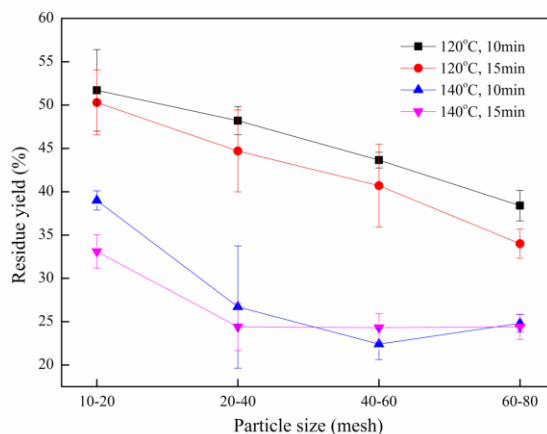


## Liquefied Bamboo

- **Jiulong Xie, Xingyan Huang**
  - **Research Assistant**
  - **LSU AgCenter**



## Residue Content (cellulose)



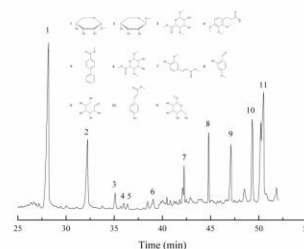
Note: Error bars represent the standard deviations

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## Chemical composition of biopolyols

- Presence of C5 & C6 sugars from hemicellulose & cellulose indicate degradation of carbohydrates.
- Aromatics indicate decomposition of lignin.



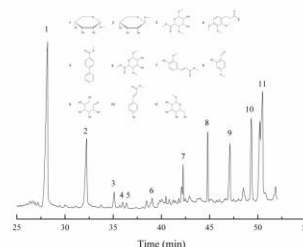
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## Chemical composition of biopolyols

- Since the sugar derivatives processed 2-5 hydroxyl groups, the biopolyols have potential in polyurethane foams because of their large amount of hydrogen bonds.



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### Characteristics of liquefied residues

The liquefied residues mainly exhibited a fiber structure with remaining cellulose and recondensed lignin fragments indicated by damaged cell wall and small granules.

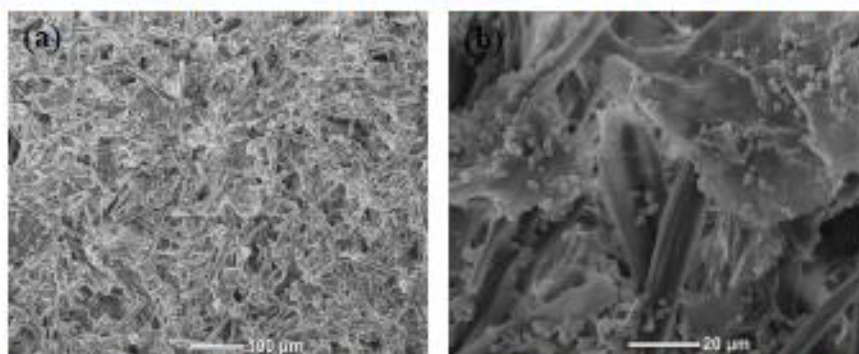


Figure 3. SEM images of traced cellulose structure of liquefied residues obtained from 140°C, 60-80mesh, 10min. (a) 150×; (b) 800×.

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## Production of nanofibers from residues

Table 1. Yield of chemically purified cellulose fibers and nanofibrillated cellulosic fiber from microwave liquefied bamboo residues.

Sample	Yield of chemically purified cellulose (%)	Yield of nanofibrillated cellulosic fiber (%)
120°C/2.0%	85.69	10.75
120°C/25%	77.78	31.96
120°C/45%	69.59	37.18
140°C/2.0%	78.07	37.17
140°C/25%	67.09	50.20
140°C/45%	65.61	52.02

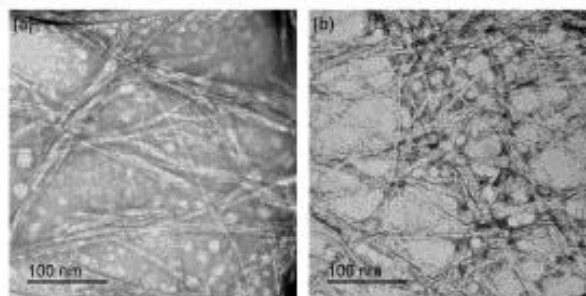


Figure 5. Transmission electron microscope (TEM) images of the nanofibrillated cellulosic fiber extracted from microwave liquefied bamboo residues; (a) 120°C/2%, ultrasonic time, 25 min; (b) 140°C/25%, ultrasonic time, 5min

## Polyurethane Foam from Lignin from Switchgrass

- Thank you Jiulong Xie and Xingyan Huang

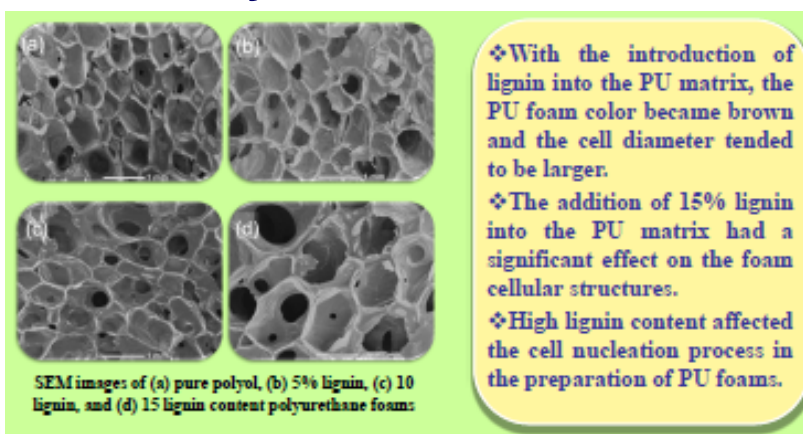


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## Morphological Structures – Polyurethane Foam



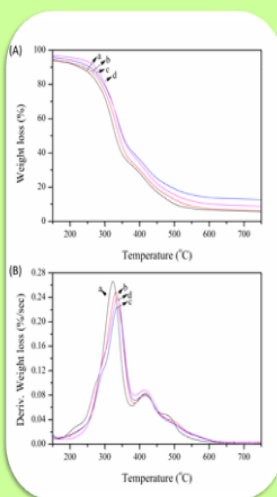
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### Thermal stability

Temperature and residue yield of the PU foams with different lignin content



(a) pure polyol, (b) 5% lignin,  
(c) 10% lignin, (d) 15% lignin

Lignin content (%)	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	Char yield (%)
0	132.60	323.17	5.37
5	139.93	331.74	5.80
10	177.55	334.97	12.42
15	223.52	333.95	8.42

❖ Lignin could improve the thermal stability of the foams, and the foam with 10% lignin had the best thermal stability.

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## Conclusions

- **Using microwave energy simplifies liquefaction.**
- **Promising uses:**
  - **Recover CCA**
  - **Polyurethane foam (insulation)**



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## Thanks to

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- **Xingyan Huang, LSU AgCenter**
- **Chung-yun Hse, USDA Forest Service, Southern Experiment Station**



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