“Another Look at Products from Plant Materials”

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Outline

- Historical uses of wood
- Before Petrochemical Industry
- Today’s take on plants’ (wood) role
- Charcoal Industries Today
- A contribution to Bio-Oils
- Wood as Advanced Material Template
“In spite of the rapid introduction of wood substitutes, new uses are being constantly found for wood”

Written in 1919!

I suspect similar conversations occurred in centuries before and even occur now!

N.C Brown, Forest Products, Their Manufacture and Use, John Wiley and Sons, Inc, N.Y., 1919
Wood Attributes

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\[ (C_6H_{10}O_5)_n \]
Engineering with Wood

- Cut, sawn, planed, carved and joined; has built our homes and vehicles for millennia
- Has heated our homes for millennia
- Has been turned to Charcoal for millennia...
- Began chemical industries
- Wood products in many present applications referred to as “Engineered Wood” products
- Charcoal use now in filtration and cooking (except for “developing” countries)
- Recent activity in conversion to Ceramics and Carbon Composites
Charcoal Industry

HEAT ENERGY AND FUELS

PYROMETRY, COMBUSTION, ANALYSIS OF FUELS AND MANUFACTURE OF CHARCOAL, COKE AND FUEL GASES

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Charcoal Industry, Evolved

CHAPTER XVIII.

LIQUID FUELS.

To this class belong oil (petroleum), tar from destructive distillation of coal and wood, schist-oil, and to a small extent certain vegetable oils, alcohol, turpentine, benzine, etc.

The liquid fuels have the advantage of burning up without residuum. Such a residuum as remains of solid fuels might obstruct the grate, cause uneven air supply and incomplete combustion.

The utilization however, of liquid fuels presents some serious difficulties and makes the construction of well designed and carefully tested burners imperative. The main difficulty is the atomization, otherwise carbon is deposited, which will cause stoppages and block the flow of the liquid.

A general use of liquid fuel is prevented by high cost. However, under certain local conditions it can be used economically.

The experiments for introducing alcohol as fuel on a large scale have so far not been successful.

Table CVIII contains some data relating to the use of liquid fuels.

<table>
<thead>
<tr>
<th>TABLE CVIII. COMPOSITION OF LIQUID FUELS.</th>
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<tbody>
<tr>
<td></td>
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<tr>
<td>American crude oil</td>
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<tr>
<td>Caspian crude oil</td>
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<tr>
<td>Refined American oil</td>
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<tr>
<td>Coal tar</td>
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<tr>
<td>Heavy oil from Caspian petroleum</td>
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<tr>
<td>Heavy oil from American petroleum</td>
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<tr>
<td>Schist oil</td>
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<tr>
<td>Tar oil</td>
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<td>Rape oil</td>
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Charcoal Industry; the Old Still Exists

Brazil: Scaling up Renewable Charcoal Production
LAST UPDATED 03.22.2012

CHALLENGE
Charcoal is one of the main sources of energy used in the production of pig iron for steel in Brazil. The vast majority of the current charcoal production is from unsustainable and often illegal harvest of native forests, leading to severe environmental degradation and deforestation. However, there have been successful business cases of forest plantation for charcoal production in Brazil, including one Clean Development Mechanism (CDM) project financed by the Prototype Carbon Fund in Minas Gerais. Expanding the area of forest plantations for charcoal on idle or degraded pasture land would reduce the pressure on native forests in Brazil.

http://www.profor.info/profor/knowledge/brazil-scaling-renewable-charcoal-production

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Charcoal production in Brazil: Does it pass the sustainability bar?
Social Sustainability

Working conditions in charcoal production

- The charcoal production technique has not evolved, it remains basic and primitive, and implies nomadism. It is the same as one century ago.
- The working conditions are precarious. Charcoal workers do not use PPE and work 12 hours a day, including weekends.
- Charcoal workers have respiratory diseases and a permanent eye irritation caused by the smoke they breathe in long working hours.
- Charcoal workers are underpaid and there are accounts of slavery and child labor.

Rabo-quente kilns for charcoal production
Another problem caused by deforestation
Today’s Attention Towards Plant Use
From the earliest days of internal-combustion engines, technological visionaries dreamed that engines would run on fuel made from plants. Experiments conducted in the 19th century showed that it was possible, and both Henry Ford and Rudolf Diesel supported the notion. Interest has waxed and waned for decades. These days, it is running high once again, and the fuels have acquired a modern moniker: biofuels.


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George Huber, the Armstrong Associate Professor at University of Massachusetts at Amherst, likely the most prolific chemical engineering researcher today has published a paper in Science outlining a new pyrolysis oil process that yields chemical feedstock and fuel type products.

http://newenergyandfuel.com/2010/12/03/pyrolysis-oil-gets-more-practical-refining/

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Energy-Efficient Manufacturing Technology

Big Island Carbon is building a modern, energy-efficient plant for converting biomass feedstock into activated carbon. Our plant is set up to produce activated carbon in a two-stage process: an initial pyrolysis, followed by a steam (thermal) activation to enhance the porous structure. The pyrolysis, or carbonization, of macadamia nut shells produces a large amount of natural oils and other volatile and condensable organic compounds. At Big Island Carbon, these materials are collected and used as biofuel to generate electricity and steam used for the energy-intensive thermal activation process. This allows us to exert a high degree of control over the process, as well as conserve resources by minimizing our overall energy use.

http://www.bigislandcarbon.com/sustainability/
Industries to Benefit

From developing better technologies for use of pyrolysis “byproducts”

• Activated Carbons (ie Big Island)
• Charcoal (ie Kingsford)
• Those requiring “Green” Fuels and Chemicals
An Effort in Bio-Fuels

- Objective to look at chemical modifications of wood prior to carbonization with intent of enhancing fuel value of pyrolysis vapors
- Chemistry Graduate student Prahba Grade set out to identify benefits
Importance of thermal degradation of plants

- Considered carbon-neutral and uses a renewable feedstock.

- Growing concerns over worldwide carbon emissions

- Depleting fossil resources
Figure 1.1. Applications of Bio-oil.[12]

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Volatile Products from Pyrolysis of Untreated Wood

• Most of the volatile products obtained from the pyrolysis of untreated wood were the phenols.
• The overall volatile products obtained from wood pyrolysis by using Flash, Fast and Slow heating rates were the same.
• But the volatile products obtained at different temperature ranges like Room temperature-300°C, 300°C-400°C, 400°C-500°C in Flash, Fast and Slow Pyrolysis were different.
Furan derivatives for Biofuel

- Furan based biofuels – FURANICS.
- Furanics - heteroaromatic compounds derived from the chemical intermediate HMF (hydroxymethylfurfural, C6H6O3).
- Furan derivatives have higher energy density than ethanol.
- Different catalytic processes were developed for the efficient production of furan derivatives from untreated biomass.

➢ Furan derivatives from treated wood ?????
10% sulfuric acid pretreatment of wood with slow pyrolysis produced maximum yield of charcoal.
II. Comparisons of Volatile Products

- Yellow Pine - Fast - Treated Vs Untreated

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Yellow Pine - Treated - Fast Vs Slow
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Yellow Pine –Slow- Treated –

20% Vs 10% Vs 7%
Sulfuric acid pre-treatment of wood –

- Decreased the abundance of Phenols.
- Increased the abundance of Furan derivatives.
Thermo Gravimetric Analysis

Fast heating rate: (5°C/min)

Yellow Pine Treated Vs Untreated

The treated samples of wood undergo decomposition at much lower temperatures.

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Charcoal Product Altered

Figure 3.1. Shrinkage of wood block by 600°C treatment for Yellow Pine
• Original (B) treated with sulfuric acid (C) without sulfuric acid

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Semi-Summary

The volatile products obtained by different heating rates from wood pyrolysis were different at different temperature ranges but the overall volatile products obtained from wood pyrolysis by using Flash, Fast and Slow heating rates were the same. The compounds which we found were consistent with the literature.

The advantages of the pre-treatment of wood with sulfuric acid on the pyrolysis products:

- Improved charcoal yield by using 10% sulfuric acid.
- Decrease in phenols and increase in furan derivatives.
- The TGA results showed that the treated samples of wood undergo decomposition at much lower temperatures when compared to that of untreated samples of wood.
Next Category
New Materials Process Approach

• Developed in 1995, uses plants as template
• Carbonization creates carbon skeleton
• Skeleton creates framework for processing into variety of “advanced” materials
• Research has been conducted across the world in creating ceramics from wood
• This presentation will focus on carbon/polymer for musical instruments (and other)
The Technology

• Builds upon naturally formed materials
• Produces materials widely used in industry
• Produces materials with unique properties
• Can enable simplification of production
• Is in its early stages of development
• Is not being developed by other companies
• Is Patented
Cellulose Derived Composites
A revolutionary materials processing technology

1. **Wood (wood products)**

2. **Pyrolysis**

3. **Pre-shape**

- **Metal matrix ceramic composite**
- **Ceramics, carbides, nitrides**
- **Carbon-polymer composite**
- **Structural Porous Carbon**
- **Carbon/carbon composite**

- **Finished product**

- **Patented 3-step process creates variety of new materials**
  - Step 1: select renewable wood-based starter
  - Step 2: proprietary pyrolysis stage to transform wood
  - Step 3: conversion to one of many advanced materials

Finished products include ceramics, composites, carbons and **ForestPlate**

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Carbonization Process

- Converts to carbon without forming cracks
- Dimension change is predictable
- Density of carbon structure depends on wood selected
- All plant and wood species have been demonstrated

**Graph:**
- X-axis: Wood Density (g/cc)
- Y-axis: Normalized Value
- Graph markers for Balsa Wood and Carbonized Balsa

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Conversion to Ceramic

- Conversion to ceramic by infiltration and reaction at elevated temperature

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Ceramics from Wood

- Liquid metal infiltration and conversion
- Metal particulate preforms, heat to convert
- Metal vapor infiltration and conversion
- Sol-gel infiltration before and after carbonization and conversion
- Carbon/Carbon by
  - Liquid infiltration densification
  - Chemical Vapor Infiltration densification
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Carbon-Polymer Composites, *ForestPlate*

- Infiltration with resin to form carbon-polymer composite
- Process scaled up with new technologies for impregnation

• This product has been extensively developed at WKU
• Grain structure is retained
• Pieces can be joined and machined
• Exceptional appearance and feel

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Microstructures of *ForestPlate*

- Micrographs of carbon/epoxy composite derived from southern yellow pine. Longitudinal view, left, of earlywood region revealing pit apertures left intact. These allow for fluid transport between adjacent cells. Tangential view, right, of earlywood region indicating the thorough wetting of the carbon cell walls by the epoxy.
Limited test data is shown, but:

- Strength of carbonized wood is exceptional
- *ForestPlate* composite is three times stronger than original wood
- Carbon stage is machinable
- Failure mode of composite is similar to that of wood
Manufacturing **ForestPlate**

- Carbonized wood
- Composite
- ForestPlate

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“ForestPlate” Demonstration Pieces

- Chessboard
- Desk/Table Top
- Counter Top Sample
- trophy-base, handle, bookend
- Pick Guard
- Nameplate

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Targeted Markets

• *ForestPlate* Carbon-Polymer Composites
  • There is no similar material
  • Can sustainably use natural resources of North America

• Initial Market - Decorative Products
  • Veneers and Inlays, Countertops
  • Musical Instruments, string and Woodwind
  • Artists Medium (jewelry, sculptures, boxes, statues, etc)
  • Handles for stick shifts, knifes, guns, cabinets

• Status
  • Ready to scale up production for entering market
  • Continued discussions with potential customers
Enough for Now?

• Thank you for allowing me to convey some of my thoughts
• Appreciation to ISTC and Manohar Kulkarni
• Grateful to Dr. Ryan Farris, Matt Seibert, Brandon Bibelhauser and Dr. Eric Conte
• These are exciting times for research in this arena
• Questions?