Current and Future Products for Pyrolysis Oils

Philip Steele and Leonard Ingram

Department of Forest Products

Mississippi State University

Production:

- Bio-oil results from fast pyrolysis of cellulosic biomass
- Applied temperatures 400 to 650^{o}C
- Absence of oxygen
- Rapid cooling
- Particles are less than or equal to 2 mm

Bio-oil Reactor

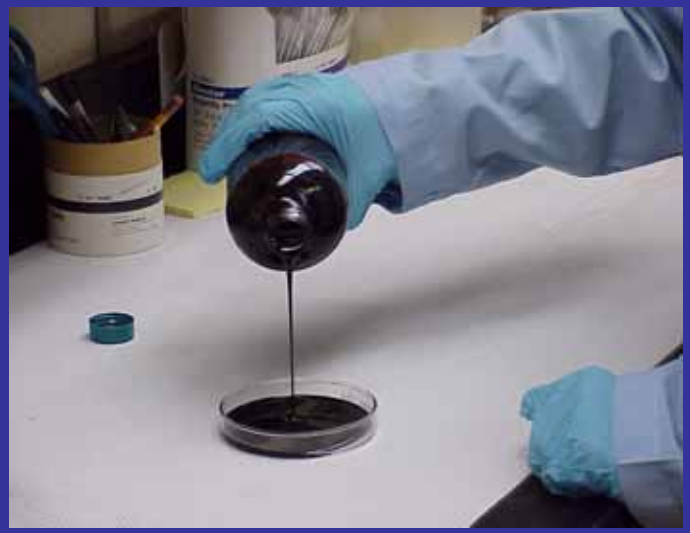
Bio-oil is best produced with biomass high in lignin content:

Wood!

What are bio-oils?

- Bio-oils are dark brown liquids; complex "microemulsions comprised of char particles, waxy materials, aqueous droplets, and micelles formed of heavy compounds in a matrix of hollocellulose-derived compounds and water."

- Not an oil as it is immiscible in petroleum oils



What are bio-oils, cont'd

- A typical bio-oil may contain more than 200 chemical compounds
- Compound classes are more easily defined:
  - water 10 – 25%
  - aldehydes and ketones 15-35%
  - sugars 6-10%
  - carboxylic acids 15-35%
  - phenols 6-15%
  - lignin 15-30%

Bio-oil yields:

- 40 – 65 % organic condensate
- 10 – 20 % char
- 10 – 30 % gases (CO, CO_2, CH_4)
- 10 – 25 % water

Char and gases

- Can be combusted to provide the process heat for pyrolysis

Water removal:

- Problematic; because bio-oil heating results in rapid polymerization and increased viscosity

Bio-oil Challenges:

- Production viscosities are variable
- Viscosity changes over time
- Highly acid: 2.2 to 2.5
- Odor is considered unpleasant

Acknowledgements:

Stefan Czernik and Tony Bridgewater
"Applications of Biomass for Pyrolysis Oil", 2005

Desmond Radlein
"The Production of Chemicals from Fast Pyrolysis Bio-oils", 1999

Oxygen in bio-oil: 45-50% by weight

- **incorporated in oxygenated compounds**

Causes most of the negative properties:

- **variable viscosity**
- **acidity**
- **odor**
- **low energy density (50% that of fuel oils)**

Current products:

– food flavors

Current products (continued):

– fuels

Dynamotive Corp. demonstration project in Ontario, Canada sited at Erie Flooring and Wood Products.

Utilizes wood waste to produce BioOil to fuel an Orenda Corp. turbine for electricity production.

Bio-oils as fuels:

- Difficult to ignite
- Burn readily after ignition
- Support fuels for ignition and smoother burning are helpful
- Higher particulate and CO_2 levels
- Results are variable but most suggest lower NO_X

Bio-oils as boiler fuels:

- **Research:**
  - **Boiler combustion tests in Finland successful with one test using pure bio-oils**
  - **Coal-firing test in Wisconsin with bio-oil as 5% of fuel value was successful**
- **Current:**
  - **Red Arrow products produces food flavourings (liquid smoke) and has for 10 years fueled a boiler with a bio-oil by-product from this process**

Bio-oil as diesel fuel:

- **Research:**
  - **Several studies have demonstrated that bio-oil can fuel slow-speed diesel engines**
  - **Higher speed engines perform best with dual fuels, or bio-oils with alcohol added**
  - **Diesel emulsions with up to 50-percent bio-oil have been tested with some damage to injectors and fuel pumps not observed for pure bio-oils**
- **Current:**
  - **No current commercial installations**

Bio-oils as turbine fuel:

- **Research:**
  - **Successful tests conducted with pure bio-oils and in dual-fuel modes**
  - **Some problem with deposits in the combustion chamber and on blades**
- **Current:**
  - **Orenda turbine is successfully fueled by Dynamotive bio-oil in a commercial operation**

Stirling Engines:

- **Research:**
  - **A combined heat and power application fueled a Stirling engine successfully with bio-oil; However, electrical and thermal efficiencies were a somewhat disappointing 50-60%**

Bio-oils for transport fuels:

Research:

- **Diesel fuel/bio-oil micro-emulsion via surfactants with diesel fuel**
  - **good fuel characteristics but surfactant costs high and significant engine corrosion**

Bio-oils for transport fuels, cont'd:

- **Deoxygenation**
  - **Catalytic hydrogenation of bio-oil but rapid catalyst deactivation and low yields**
  - **Catalytic pyrolysis vapor cracking with zeolytes but similar catalyst deactivation and low yields; also PAHs produced**
  - **Recent successful research results have initiated new interest in hydrogenation with new catalysts**

Resins and adhesives:

- Research to substitute bio-oil for petroleum phenols up to 30% are successful but not commercialized with odor as the road block

Road deicers:

– Calcium salts of carboxylic acids can be produced but process not economically viable

Fertilizers:

- Reaction of bio-oil or pyrolysis vapors incorporates 10% nitrogen into a biodegradable fertilizer. Not commercially practiced

Wood Preservatives:

- Several researchers have demonstrated the synergistic fungicidal properties of bio-oils as a potential substitute for creosote. Not yet commercialized

Synergism:

pentachlorophenol 10X more effective with bio-oil

Levoglucosan and levoglucosenone:

- Yields of 50% and 25% from cellulose. Yields are about ½ for lignocellulosic biomass. Value-added potential but levoglucosan is difficult to separate; lower levoglucosenone yields have prevented commercialization

Summary

- The complex chemistry of bio-oils have limited commercialization
- Researchers and corporate entrepreneurs have begun to develop technology to overcome commercialization barriers
- Further technological development will gradually remove barriers to bio-oil commercialization

Current and Future Products for Pyrolysis Oils

Philip Steele and Leonard Ingram

Department of Forest Products

Mississippi State University