Pyrolysis: A method for Mixed Polymer Recycling

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Outline

- Value and Supply Chain of Waste
  - What's recycled and what's not?
- Pyrolysis Process
  - How it works for plastics?
- Literature Review
  - Current research in the area, 2009-present
- Technology Status
  - Who's producing?
  - Where?
  - When?

Plastic Solid Waste (PSW)

- 2007 Statistics
  - 260 million tons/yr of plastic are produced in the world.
  - This figure rises at a rate of 5% yearly.
  - 60% of all PSW goes to landfill.
- EU has already mandated that by 2020 all plastic waste must go to mechanical, thermal or chemical processing facilities.
  - No more waste will be allowed in landfills.
- Plastic usage accounts for 4-8% of all fossil fuels yearly.

Resource Facts: S.M. Al-Salem , P. Lettieri & J. Baeyens, Progress in Energy and Combustion Science, Feb. 2010

Value of Plastic Waste

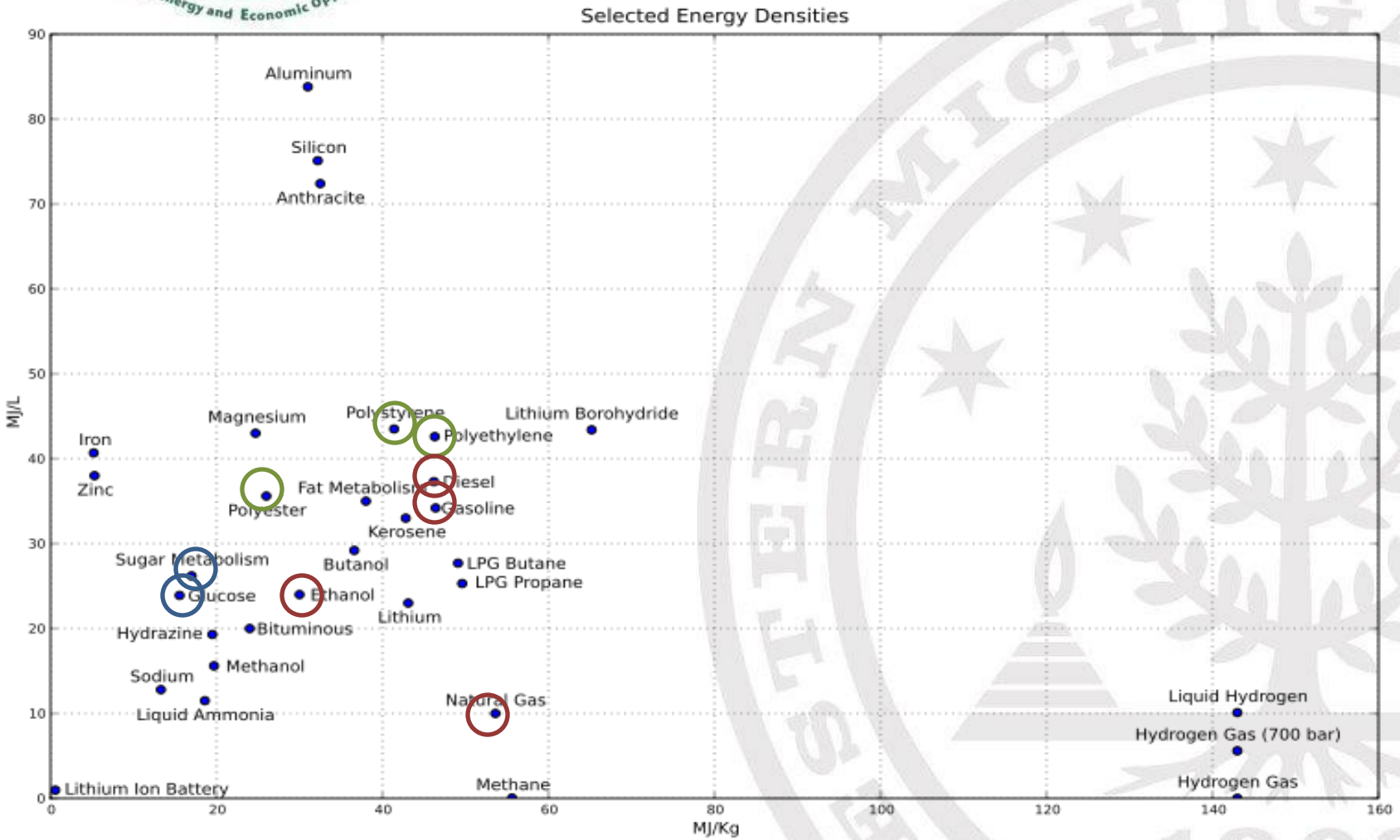


Image Source: "Energy Density" Wikipedia, 2010 http://en.wikipedia.org/wiki/Energy_density

Value of Plastic Waste (Normalized)

- Plastics
  - PE-46.3 MJ/kg
  - PP-46.4 MJ/kg
  - PET-23.5 MJ/kg
  - Polyester-PA66- 26 MJ/kg
  - PVC-18 MJ/kg
  - PS-41.4 MJ/kg
- Biomass
  - Glucose-15.55 MJ/kg
  - Wood-18 MJ/kg

- Fuels
  - Coal-32.5 MJ/kg
  - Ethanol-30 MJ/kg
  - Crude Oil-46.3 MJ/kg
  - Biodiesel- 42.2 MJ/kg
  - Natural Gas- 53.6 MJ/kg
  - Methane-55.6 MJ/kg
  - Hydrogen Gas- 143 MJ/kg
  - Gasoline- 46.4 MJ/kg

Reference Values: "Energy Density" Wikipedia, 2010 http://en.wikipedia.org/wiki/Energy_density

Reusing Plastic Waste

- Plastic Sorting
  - Often very difficult
  - Some ways that have been used to sort.
    - Adding modifier to water
    - Density sorting (hydroclones)
    - Triboelectric separation
    - X-Ray Fluorescent Spectroscopy
    - Manual Sorting

- Most is manually sorted.

Britannica Encyclopedia, 2010

Mechanical Recycling

- Milling, grinding, or shredding polymers into small pieces.
  - Re-extrusion of plastics.
- Cryogenic grinding plastics to powder fillers.
  - Commonly used in recycling tires.

www.diytrade.com, 2010

Thermal-Chemical Recycling

- Typically will reduce polymers down to monomers or create derivative petro-based chemicals.
  - Common Processes
    - Pyrolysis
    - Gasification
    - Liguid-Gas Hydrogenation
    - Viscosity Breaking
    - Steam or Catalytic Cracking
    - Reduction Blast Furnaces

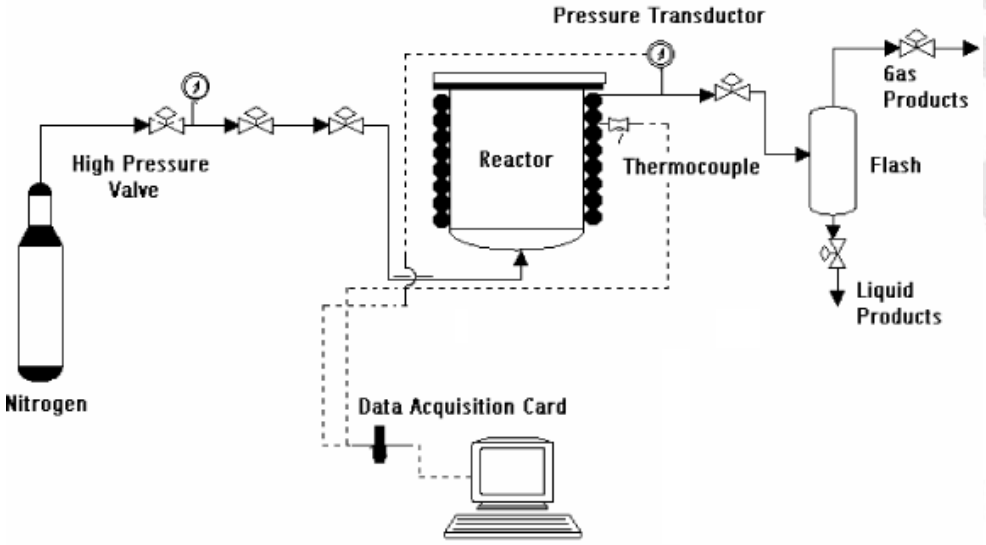


Figure 1: Schematic diagram of the pyrolysis process.

A Study of Paint Sludge Deactivation by Pyrolysis Reactions; L.A.R. Muniz et al, 2003. Brazilian Journal of Chemical Engineering.

What is Pyrolysis?

Definition: *Chemical decomposition of organic substances by heating to high temperatures*

- Breaks “cracks” polymer chains into smaller chains under heat and pressure.
- Same reaction that happens when you inside the earth to form crude oil from organic matter.
- Greek-derived terminology
  - Pryo “Fire”
  - Lysis “decomposition”

3 Forms of Pryolysis

- Hydrous Pyrolysis
  - Known as Steam Cracking
  - Heats organic compounds in presence of steam

    Temp: 300-350°C Pressure: <12MPa

    Time: 30+min Product: Light Alkenes
- Hydrothermal Liquefaction
  - Converting biomass to oily liquid
  - Aqueous solvent remains liquid during process

    Temp: 300-350°C Pressure: 12-20MPa

    Time: 30min Product: Hydrocarbon slurry
- Anhydrous Pyrolysis
  - Does not use any water just high temperature and pressure

    Temp: 350+°C Pressure: >12MPa

    Time: 30+min Product: Biochar, light crude, gaseous alkenes

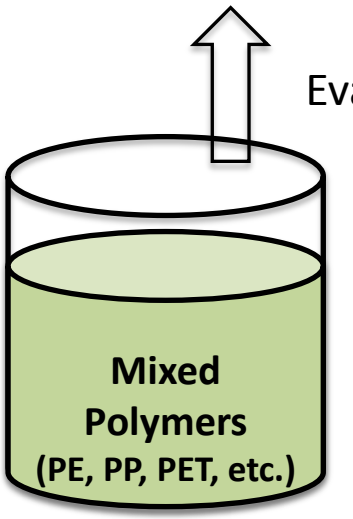
Mixed Polymer Pyrolysis

Goal: Reduce mixed polymer inputs into short chain light crude oils for alternative uses

- Uses Anhydrous Pyrolysis to obtain light crude
- Light crude can be reprocessed into:
  - Virgin polymer feedstock (PS, PE, PP)
  - Short chain fuel products (Gasoline, Jet Fuel)
  - Esters (Diesel) with addition of process catalyst

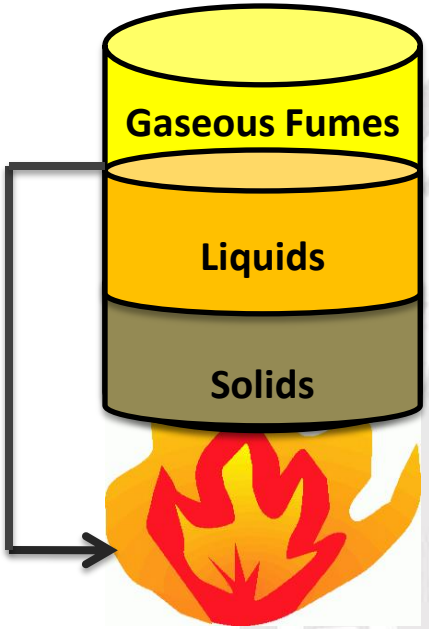
- Depending on the processing company the waste material is sorted in similar polymers (ie: PE, PP).
- Some processes cannot use certain polymers due to their depolymerization characteristics.
- Some processors use a proprietary catalytic pyrolysis method which can handle hard to depolymerize materials.
- After sorting the material, it is chopped, pulverized or ground and loaded into reactor vessel.

Anhydrous Pyrolysis w/o Catalyst



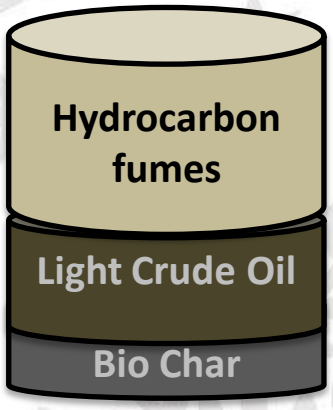
Stage 1

Raw mixed polymers are added to reactor. Vessel is then evacuated to remove moister and oxygen. Typically Gaseous fumes from other reactors or "dry" gasses are used to pressurize vessel.



Stage 2

Vessel is sealed and heated to above 350°C @ > 12MPa is maintained. Mixed material depolymerizes into light crude liquid. Inorganics and radicals combine to form solids that sink or fume off.



Stage 3

Process Complete

- Hydrocarbon fumes can be burnt as Syngas.
- Light crude contains various polymer chains for reprocessing.
- Biochar solids can be used on farm fields.

Recent Research

- Key Areas
  - Process Recipes
    - What is the highest yield?
    - Cost productive
    - What plastics can be used.
  - Co-pyrolysis
    - Wood, manure, biomass..
  - Safety and Environmental
  - Hydrogen
  - Chemical Remediation
  - Scalability

- Summarized articles over wide spectrum from 2008-present.
  - 12,800+ publications.

- **Wood/plastic co-pyrolysis in an auger reactor: Chemical and physical analysis of the products**
  - P. Bhattacharya et al. Fuel, July 2009
  - Consisted of an experiment with a 1:1 blend of plastic polymers with yellow pine wood. The plastics used were PP, PS and HDPE. Discusses the process design and specifies that the temperature of the process needs to be very high to produce decomposition vapors of the plastic that will not bind to the pine char derivatives and exit the exhaust stack.
- **Tertiary recycling of PVC-containing plastic waste by copyrolysis with cattle manure**
  - Apinya Duangchan and Chanatip Samart, Waste Management, November 2008
  - Conducted studies of mixing PVC waste plastics with cow manure in a pyrolytic environment to study the yields of useable liquids, solids and gases.

- **Dechlorination of fuels in pyrolysis of PVC containing plastic wastes**
  - A. López et al. Fuel Processing Technology,Article In Press, 2010
  - Discusses methods for chlorine reduction in pyrolysis liquids.
- **The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals**
  - S.M. Al-Salem , P. Lettieri & J. Baeyens, Progress in Energy and Combustion Science, Feb. 2010
  - Discusses an in depth overview of the process of value to plastic waste.

- **Co-pyrolysis of pine cone with synthetic polymers**
  - Mihai Brebu, Suat Ucar, Cornelia Vasile & Jale Yanik, Fuel, Aug. 2010
  - Suggested the combination of pine cones/polymers results in higher yields of useable product along with less char. The paper suggests a synergistic partnership between biomass and synthetic polymers.
- **Study of the slow batch pyrolysis of mixtures of plastics, tyres and forestry biomass wastes**
  - F. Paradela et al. Journal of Analytical and Applied Pyrolysis, May 2009
  - The mix of plastics, tires and forest biomass led to an increase reaction time. This increased time reduced the amount of liquid yield but increases solids and gases.

- **Study of kinetics of co-pyrolysis of coal and waste LDPE blends under argon atmosphere**
  - **Sumedha Sharma and Aloke K. Ghoshal, Fuel, Article In Press, 2010**
  - Provides a study of using coal and LDPE in a mixture for pyrolysis. The coal content appeared to increase the reaction time.
- **The pollution characteristics of odor, volatile organochlorinated compounds and polycyclic aromatic hydrocarbons emitted from plastic waste recycling plants**
  - Chung-Jung Tsai et al., Chemosphere, Feb. 2009
  - A study investigating the pollution coming of pyrolytic plastic recycling facilities. The investigation focused on PVC constituents for the most part. Found most facilities currently have inadequate filtration for exhausts coming off the process.

- **Pyrolysis–gasification of plastics, mixed plastics and real-world plastic waste with and without Ni–Mg–Al catalyst**
  - Chunfei Wu and Paul T. Williams, Fuel, Oct. 2010
  - The authors are using PE, PS and HDPE with a Ni-Mg-Al catalyst in a pyrolysis environment to investigate hydrogen gas production. Using steam catalytic pyrolysis to generate the hydrogen gas. Achieved volumes of gas at 0.196 g H_2 per 1g of PS. About a 20% yield of gas.
- **Study of the co-pyrolysis of biomass and plastic wastes**
  - F. Paradela et al., Clean Technologies and Environmental Policy, July 2010
  - The authors are investigating using pyrolysis with a mixture of waste polymers and pine wood (biomass). Preliminary results show the polymers provided higher efficiency in slow pyrolysis of pine. Achieved higher liquid yields with much lower solid product waste (char). Liquids achieved heating values similar to fuel oils, gases had heating values similar to producer gases and solids had heating values close to some coals.

Pyrolysis Companies

- Linda Corporation, Hudson Ohio
  - Catalytic Anhydrous Pyrolysis
  - Accepts all polymer and organic wastes.
  - Specializing in powder paint, PS, and #7 polymers
  - Fully operational *TBA*
- Ozmotech, Melbourne Australia
  - Proprietary Continuous Anhydrous Pyrolysis
  - Accepts all from consumers but rejects onsite
  - Fully Operational and runs 24/7
- Polymer Energy®LLC, Minneapolis MN
  - Anhydrous Pyrolysis
  - Accepts PET, HDPE, LDPE, PP, Limited #7 polymers
  - Operational small batches

Green Manufacturing Initiative

Pursuing Environmental, Energy and Economic Opportunities

- Questions?