Fast Pyrolysis and Bio-oil Production from Agricultural Residues and Energy Crops

Charles A. Mullen and Akwasi A. Boateng

USDA-ARS, Eastern Regional Research Center, Crop Conversion Science and Engineering RU
600 East Mermaid Lane, Wyndmoor, Pennsylvania 19038, USA
www.ars.usda.gov/naa/errc

Abstract

Fast pyrolysis is rapid heating in the absence of oxygen resulting in decomposition of organic material. When applied to biomass fast pyrolysis produces liquids (bio-oil), charcoal and gas. Bio-oil is a complex mixture of hundreds of oxygenated organic compounds resulting from the decomposition of the cellulose, hemicellulose, and lignin of which the biomass is composed. Raw bio-oil has energy contents about half of that of diesel fuel and can be burned in boilers or turbines. It can also be further upgraded into transportation fuels. The Agricultural Research Service (ARS) of the USDA is studying the fast pyrolysis of potential perennial energy crops and animal wastes for bio-oil production. For forage biomass materials, effects of variables such as maturity at harvest and genotype have been studied both analytically and in a bench scale pyrolysis reactor. Process parameters for the reactor including material and energy balances will be presented. Furthermore, the chemical compositions and fuel properties of the bio-oil produced from different forage plants and poultry wastes will be compared and contrasted.

Background

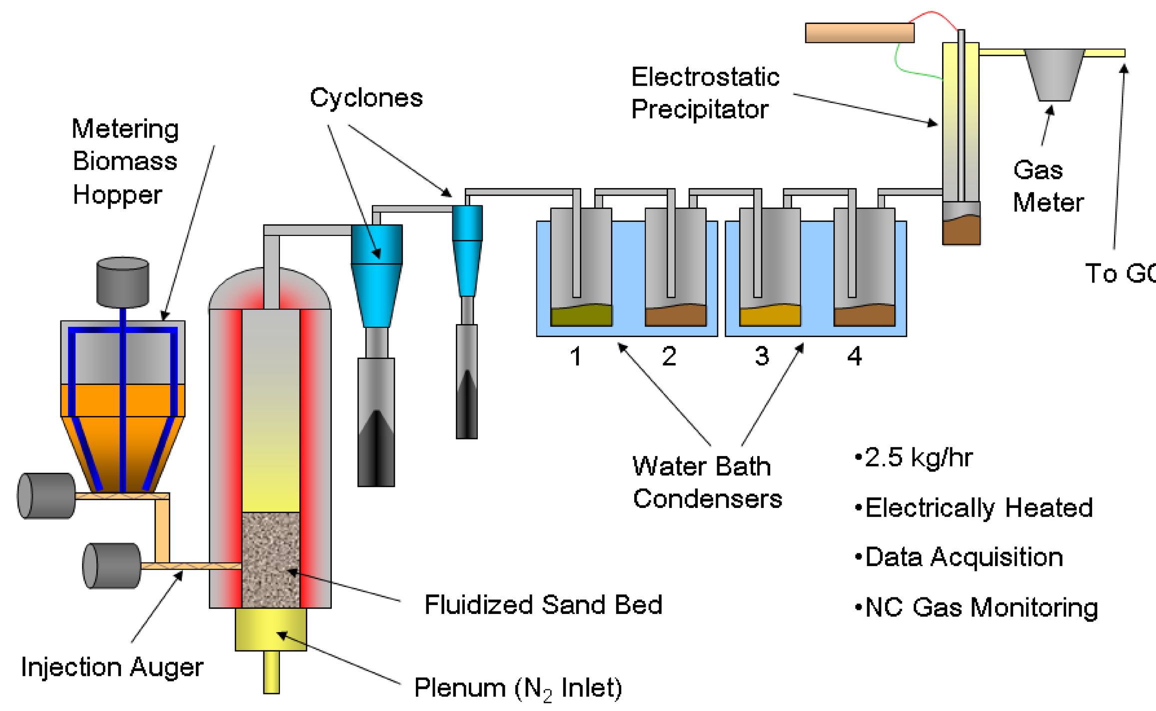
Thermochemcial conversion of biomass is an alternative method to biological conversion (fermentation) to produce usable energy from lignocellulosic biomass. Fast pyrolysis is the mode of thermochemical conversion that produces the highest yields of liquid product (bio-oil). Because bio-oil is much denser than biomass, it can be more cost-effectively transported to centralized refineries, where bio-oil could be upgraded to hydrocarbon fuels directly or through a gasifcation/Fischer-Tropsch process. However, bio-oil is plagued with the problems of corrosiveness, compositional changes with aging, and phase separation due to high water content that make its use as a fuel or further processing challenging. Therefore evaluating different feedstocks and process conditions that can consistently produce high yield and high quality bio-oil is extremely important.

A 2.5 kg/h bench scale fluidized bed pyrolyzer has been developed at ERRC for the production of bio-oil from agricultural residues including energy crops being developed within ARS. This system allows for the study of both feedstock characteristics and process conditions including feed rates, temperatures, and quenching mechanisms. The bio-oil produced is characterized for physical properties and chemical compostion, factors that are important for further upgrading. Feedstocks from which bio-oil has been produced include switchgrass, alfalfa stems, bamboo, guayule, and chicken litter.

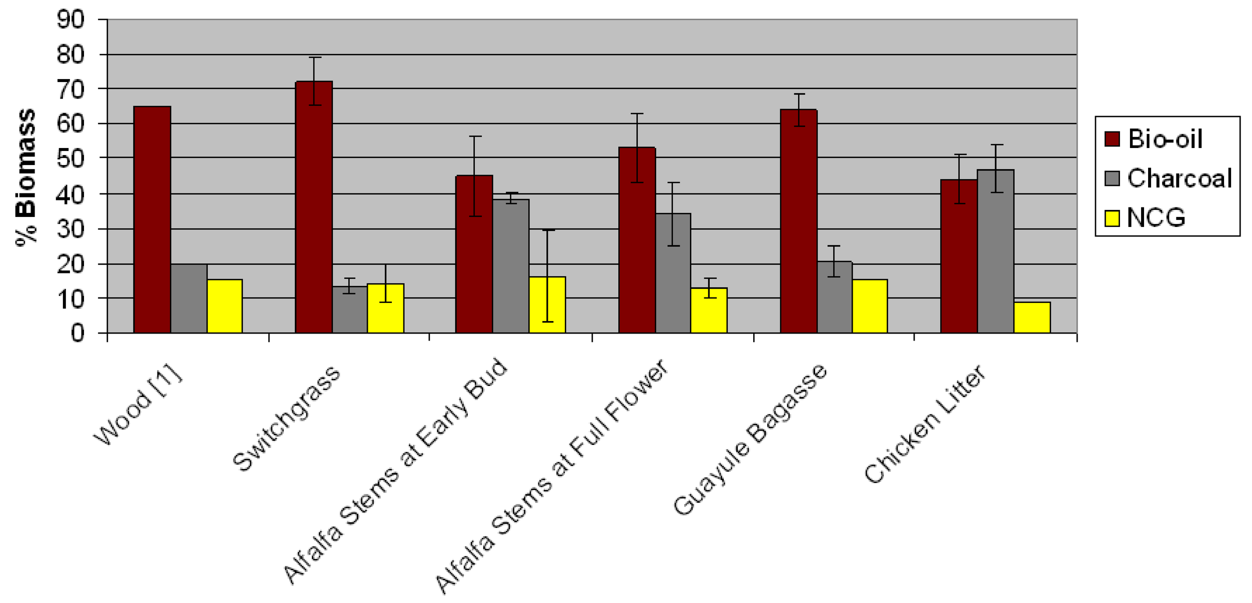
Methods

- Fluidized Bed Pyrolysis Conditions:
  - Biomass materials were dried to <5% moisture and ground in a Wiley Mill through a 2 mm screen.
  - Bed Medium: Silica Sand ~ 800 microns
  - Bed Temperature: 450 – 500°C
  - Heating Rates: ~ 3800 – 4600°C/s
  - Residence time in fluidized bed ~0.1 s
  - Quench Rates: 35 – 51°C/s
  - Total residence time from injection to ESP ~ 8.5 s.
- Bio-oil analysis include GC/MS, HPLC, Karl-Fisher Water, Elemental Analysis, and Calorific Value

Bench Scale Bio-Oil Production



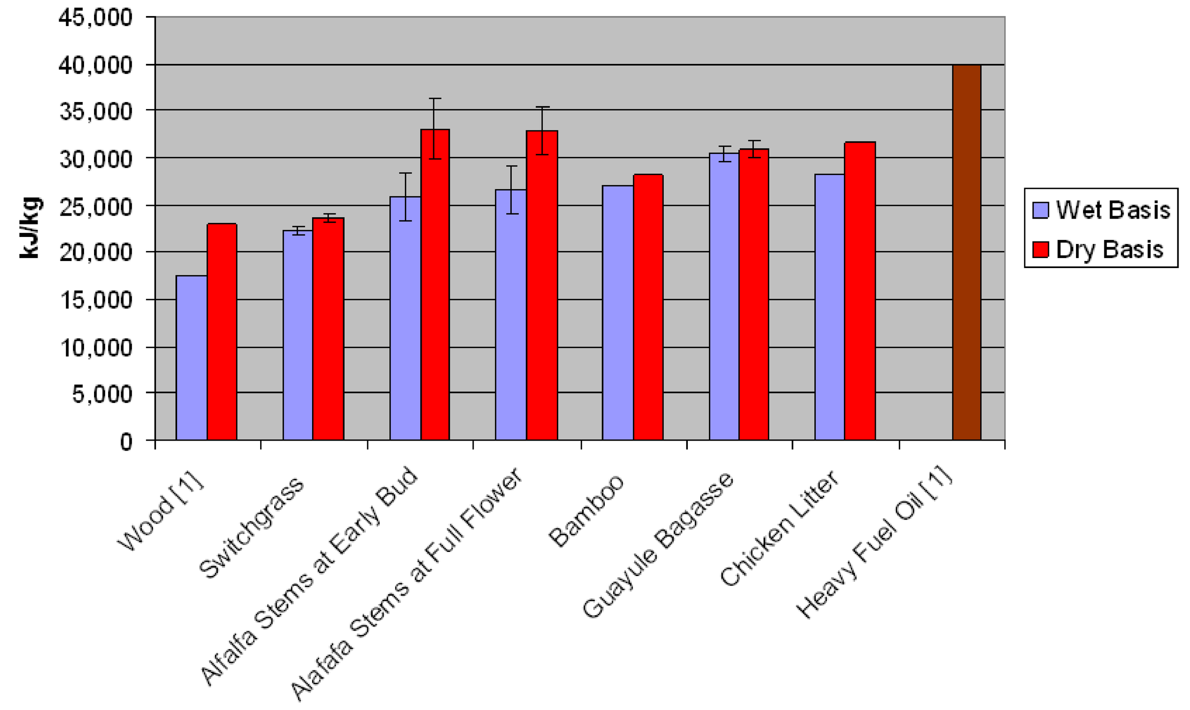
Pyrolysis Product Yields



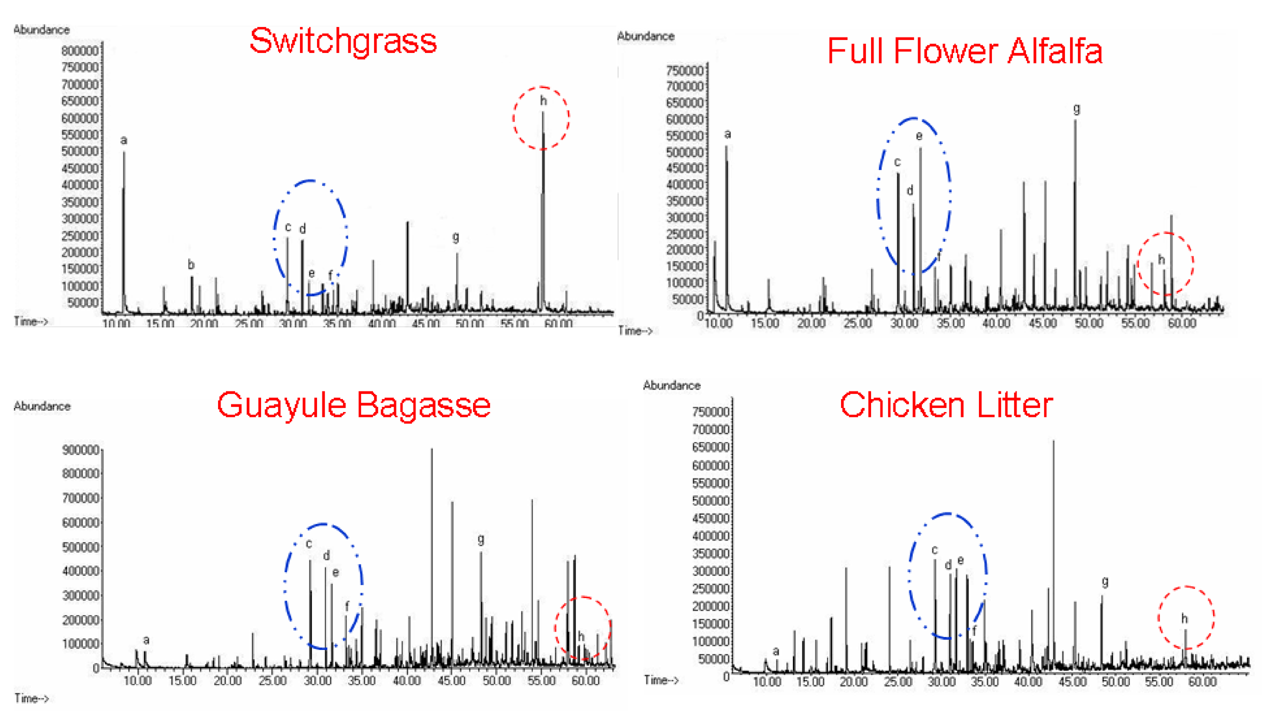
Bio-oil

- Bio-oil is a complex mixture of oxygenated organic compounds, the composition of which depends on feedstock characteristics, and process conditions
- Analytical screening (Py-GC/MS) of herbaceous grasses has shown that theromchemical conversion (ratios of bio-oil:charcoal:gas products) is dependant on lignin content of the feedstock and therefore can be related to plant maturity
- Four condenser train system allows for fractionation of bio-oil -- Removal of large amounts of water at the condensers results in the ESP containing the highest quality and largest fraction of bio-oil
- Bio-oil from wood generally has a high heating value (HHV) about 50% that of heavy fuel oil. Bio-oils produced at ERRC from agricultural feedstocks have had HHV values up to 75% of heavy fuel oil
- Preliminary results show that reaction of bio-oil with alcohols over solid acid catalysts show enhanced energy content over bio-oil/alcohol mixtures
- *In situ* catalytic pyrolysis of lignin over HZSM-5 has shown in increase in aromatic hydrocarbon production over pyrolysis over sand

Bio-oil High Heating Value



Total Ion Chromatograms for Bio-oil



Labeled Peaks: **a**. acetol; **b**. furfural; **c**. 2-hydroxy-3-methyl-2-cyclopenten-1-one; **d**. phenol; **e**. guaiacol; **f**. cresols; **g**. isoeugenol; **h**. levoglucosan

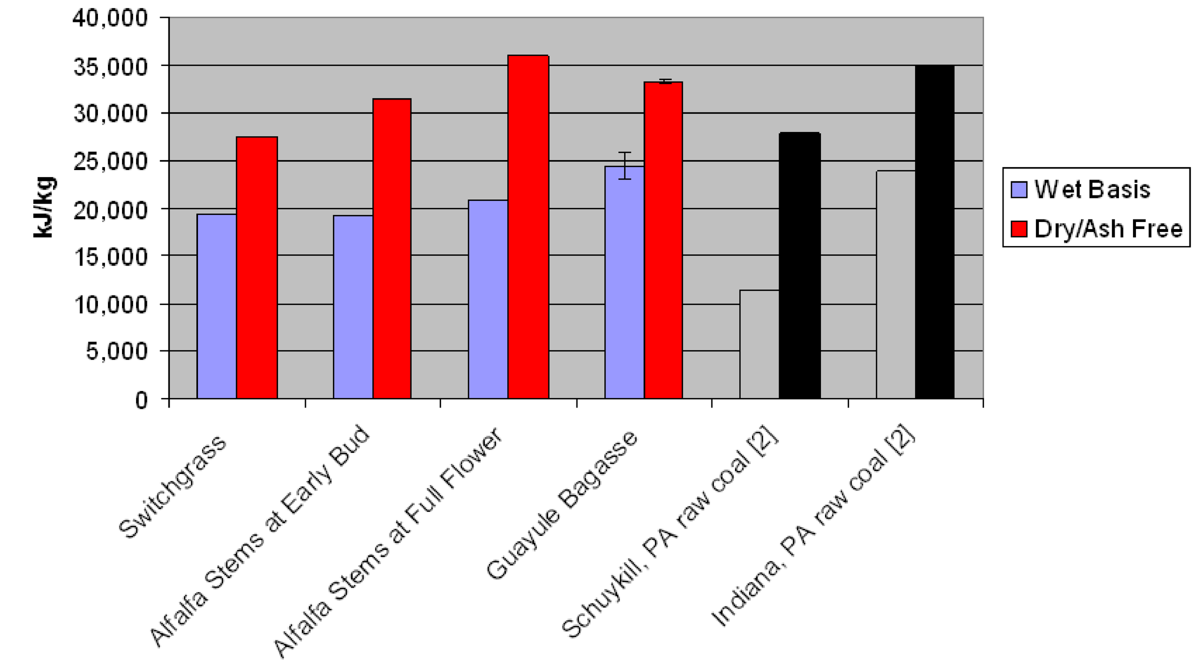
Some Bio-oil Components

Compound (wt %)	Switch-grass	Alfalfa Stems Full Flower	Guayule Bagasse	Chicken Litter
water	11.04	18.45	1.44	24.46
Cellulose/Hemicellulose Derived Compounds				
acetic acid	2.94	3.49	1.29	0.70
furfural	0.62	--	--	--
hydroxyacetaldehyde	2.40	--	--	0.04
acetol	2.75	2.35	0.73	0.05
levoglucosan	6.38	0.37	1.37	0.27
Lignin Derived Compounds				
guaiacol	0.18	0.46	0.39	0.41
isoeugenol	0.45	0.73	0.65	0.24
2,6-dimethoxyphenol	0.20	0.43	0.73	0.11
phenol	0.66	0.95	0.65	0.51
Protein Derived Compounds				
pyrrole	--	--	--	0.07
benzylnitrile	Trace	0.06	Trace	0.06
indole	--	0.01	--	0.13

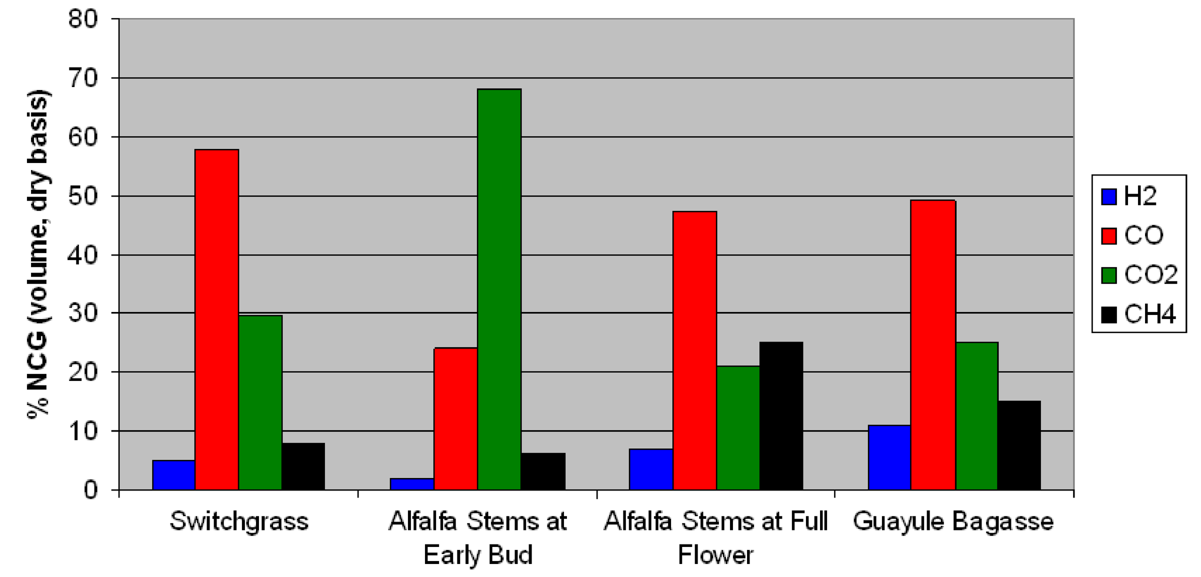
Charcoal and Non-Condensable Gases

- Charcoal has numerous potential uses including carbon sequestration, soil amendment, and for nutrient delivery in fertilizers or as a solid fuel
- Pyrolysis conditions can be modified to optimize for charcoal, fast pyrolysis is optimum for bio-oil production
- Fast pyrolysis produces charcoal that has low surface areas without further activation
- Charcoal has HHV values comparable with coal
- Non-condensable gas contains various amounts of H2, CO, CO2, and light hydrocarbons, dependant on feedstock.
- Charcoal and/or non-condensable gas co-products can be combusted to provide enough heat to power a pyrolysis system for bio-oil production

Charcoal High Heating Value



Non-condensable Gas Compositions



References

1. Average Literature Value. Mohan, D.; Pittman, C. U.; Stelle, P. H. Energy and Fuels, 2006, 20, 848.
2. Weston, K. C. Energy Conversion West Publishing Company, New York: 1992, p. 93.
3. Boateng, A. A.; Hicks, K. B.; Vogel, K. P. Pyrolysis of switchgrass harvested at several stages of maturity. J. Anal. Appl. Pyrolysis, 2006, 55 – 64.
4. Boateng, A. A.; Daugaard, D. E.; Goldberg, N. M.; Hicks, K. B. Bench-Scale Fluidized-Bed Pyrolysis of Switchgrass for Bio-oil Production. Ind. Eng. Chem. Res., 2007, 46, 1891 – 1897.
5. Boateng, A. A. Characterization and Thermal Conversion of Charcoal Derived from Fluidized-Bed Fast Pyrolysis Oil Production of Switchgrass. Ind. Eng. Chem. Res. 2007, 46, 8857 – 8862.
6. Mullen, C. A.; Boateng, A. A. Chemical Composition of Bio-oils Produced by Fast Pyrolysis of Two Energy Crops. Energy and Fuels, 2008, In Press.
7. Boateng, A. A.; Mullen, C. A.; Goldberg, N.; Hicks, K. B.; Jung, H. G.; Lamb, J. F. S. Production of Bio-oil from Alfalfa Stems by Fluidized-Bed Fast Pyrolysis. Ind. Eng. Chem. Res. 2008, In Press.

Acknowledgements

Neil Goldberg, Dr. Kevin Hicks, Rich Cook, Mike Mandel, Johnny Morphew, Ken Schaffer, and Jhanel Wilson.