

Fractional pyrolysis of biomass for high-valued products

F.A. Agblevor

Department of Biological Systems Engineering, Virginia Polytechnic Institute & State University
Blacksburg, VA 24061

Phone: 540-231-2578; Fax: 540-231-3199; fagblevo@vt.edu

Conventional biomass pyrolysis maximizes the conversion of all biomass components into liquid products. Liquid product (biocrude oil) yields as high as 70% have been reported with char and gases constituting the rest of the products. Biocrude oil is a complex mixture of carbohydrate, lignin, and extractives decomposition compounds, which is usually very unstable. The poor stability of biocrude oils is attributed to char and alkali metals, which catalyze secondary reactions during storage at room temperature. Reduction of char levels in biocrude oils have been shown to improve the storage stability of these oils. Because of their poor stability, biocrude oils cannot be easily upgraded using conventional petrochemical process technologies. There have been extensive studies on the catalytic upgrading of biocrude oils to higher-value products such as methyl-aryl ethers and gasoline-like products. However, product yields from such upgrading processes were very low because of char and coke formation.

In this paper a fractional pyrolysis approach is used to convert the lignin fraction of hybrid poplar wood into high yields of cresols and phenols while the carbohydrate fraction was selectively converted into gaseous products and char. The goal of this research is to produce specialty chemicals from residual materials generated from the bioconversion of biomass to bioethanol.

Hybrid poplar wood was air-dried at room temperature and ground in a Wiley mill to pass –20-mesh screen. Fractional pyrolysis of the feedstock was carried out in a 2in-fluidized bed reactor. The reactor consisted of a 2-in (50mm) schedule 40 stainless steel pipe, 500 mm high including a 140 mm preheater zone below the distribution plate. The unit was equipped with a 100- μ m porous metal gas distributor. The fluidizing media was a proprietary catalyst and the bed was fluidized with nitrogen. The reactor was electrically heated with a three-zone furnace. Biomass was fed from a hopper and conveyed by twin-screw feeder into an entrainment zone where a high velocity nitrogen gas entrained the feed and carried it through a jacketed air-cooled feeder tube into the fluidized bed. The reactor tube contained a bubbling fluid bed with back-mixing of feed and catalyst.

The pyrolysis temperature was maintained at 500C and the apparent vapor residence time was one second. Run time was 2-3 h at a feed rate of 100 g/h. Gas flow rate, feed rate, and reactor temperature were maintained constant during each run. Temperature and gas flow rates were controlled by an Omega data acquisition system. Pyrolysis vapors and gases exiting the reactor were first passed through a cyclone followed by passage through, a hot gas filter, two water condensing units, electrostatic precipitator, and a wet test meter. The gases were analyzed on line on a Shimadzu GC14A gas chromatograph. The oil samples were analyzed by gas chromatograph/mass spectrometry, ¹³C NMR and gel permeation chromatography.

The total liquid yield was 30%; gas yield 60% and char/coke yield 11.5%. The liquid products were collected in three condensers. The products collected in the first water-cooled condenser and the electrostatic precipitator (ESP) were brown low viscosity liquids that flowed freely at room temperature. These liquids were immiscible with water. The product from the second water-cooled condenser was light yellow low viscosity liquid containing 95% water and 5% dissolved organics. The product from the second water-cooled condenser was immiscible with the products from the ESP and first water-cooled condenser. Total water yield was 30%.

The product from the second water-cooled condenser was mostly the carbohydrate decomposition products such as hydroxyacetaldehyde, hydroxyacetone, and small fractions of phenol and cresol.

The GC/MS analysis of the products from the first condenser and ESP showed similar composition. The liquids were almost pure phenolics with very little or no detectable carbohydrate decomposition products. The major components were phenol, cresols, methyl substituted phenols, and small fractions of indene and substituted naphthalenes. Neither, benzene, toluene, nor xylenes were detected in the products. NMR analysis of the oils confirmed the GC/MS results.

Comparison of the NMR data of the fractional pyrolysis products with conventional pyrolysis products showed that whereas all the signals between 60-100 ppm due to carbohydrate decomposition products were present in the conventional pyrolysis products, these were either absent or in low levels in the fractional pyrolysis liquids. The methoxyl content of the fractional pyrolysis products were extremely low (25% of the conventional products). It appears there was demethoxylation and demethylation of the oils.

Elemental composition and higher heating value (HHV) clearly showed that there was partial deoxygenation of the oils. The carbon content was very high (71%) and the oxygen content was 21% compared to 53-55% carbon and 38-40% oxygen for conventional pyrolysis oils. The HHV was consequently very high (30.5 kJ/kg) compared to 23 kJ/kg for conventional hybrid poplar pyrolysis oils.

The gas content was mostly hydrocarbons, carbon dioxide and carbon monoxide. About 90 wt% of the gaseous products was carbon monoxide and carbon dioxide and the rest a mixture of hydrocarbons. The hydrocarbons were methane, ethane, ethylene, butene, and some unidentified peaks. Butene was the most abundant hydrocarbon and constituted 30% of the products.

These oils are very stable, low viscosity and could be potentially used for several applications including phenol formaldehyde resins, phosphate esters, magnetic wire, cleaning and disinfectant compounds, ore floatation, and miscellaneous applications. Special applications of these oils are currently under investigation.