IOWA STATE UNIVERSITY
Center for Sustainable Environmental Technologies

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# Time-Resolved Sampling of Pyrolysis Vapors and Aerosols from a Free-fall Reactor

## Introduction

Pyrolysis of biomass yields a large variety of volatile and non-volatile chemical compounds that likely change as a result of secondary reactions. The goal of this research is to (1) determine the effect of operating conditions on pyrolysis product yields; and (2) evaluate the temporal profile of both volatile and non-volatile compounds in the pyrolysis stream.

## Reactor Design

- 316 1¼" schedule 40 stainless steel pipe
- GC/MS sampling ports positioned every 15.2 cm
- 3.05 m reactor length
- Temperature range: 300-1000˚C
- Pressure range: 0-100 kPa
- Feed rate range: 0.25-2 kg/h
- Maximum heating time of 2.5 seconds
- Ability to operate continuously
- Ability to manipulate particle velocities
- Ability to manipulate reaction duration

## Reactor Advantages

- Time resolved sampling of pyrolysis products
- Simple manipulation of important pyrolysis variables
- Identification and semi-quantification of both volatile land non-volatile pyrolysis products
- Reactor can be used with a variety of analytical methods
  - Mass Spectroscopy (MS)
  - Gas Chromatography/Mass Spectroscopy (GC/MS)
  - Mass Spectroscopy/Mass Spectroscopy (MS/MS)
  - Solid Phase Micro Extraction (SPME)
- Fast turn-around of experiments

Free-fall Reactor System

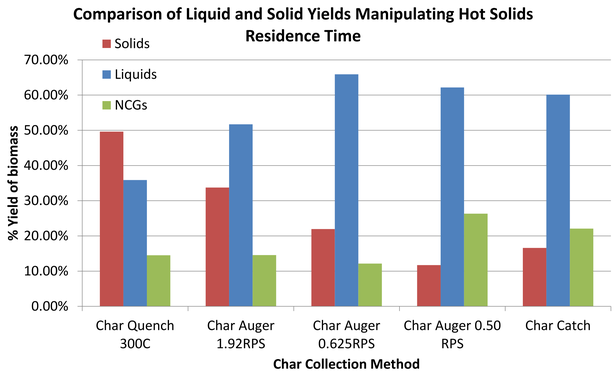
## Char Collection

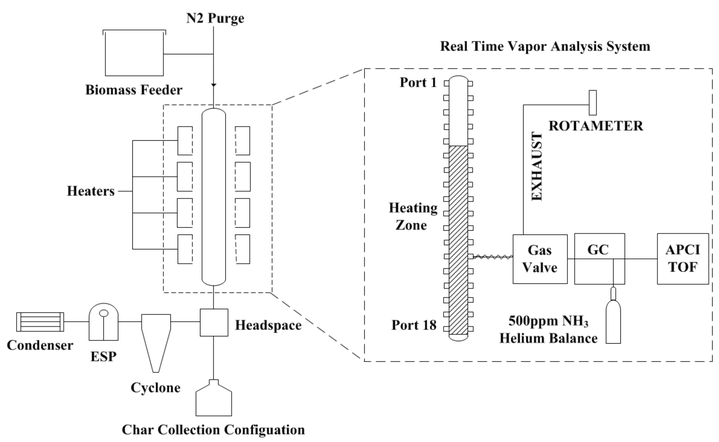
Hot solid residues fall directly into a catch-pot at the bottom of the free-fall reactor, with the balance entrained in the sweep gas and recovered by the gas cyclones. It is generally thought that rapid heating of the biomass followed by rapid quenching of products is important to high bio-oil yields. The effect of residence time and temperature of hot solids in the catch-pot on bio-oil yield was investigated by either cooling the catch-pot or augering the solids out at different rates.

**Reactor Conditions**
Reactor temperature: 550°C; sweep gas flow rate: 5 SLPM; Heated length of reactor: 2.13 m (1.8 s heating time)

## Results from Different Char Collection Methods

The residence time and the temperature of the char in the catch-pot was found to dramatically influence bio-oil yield. As shown in the figure below, moderately long residence times in the catch-pot at elevated temperature favored high bio-oil yield.




Schematic of Free-fall Reactor With On-line Sampling System

## Time-Resolved Measurements of Py Products

If the free-fall reactor is operated in steady state, then vertical positions along the axis of the reactor can be related to residence time of falling particles in the heated zone. Gas sampled from the reactor also contain condensable organic vapors and aerosols, which constitute bio-oil when recovered. A Time-of-Flight Mass Spectrometer (TOF MS) is used to analyze this gas stream because it is able to detect a wide range of both volatile and non-volatile compounds in virtually real-time. The TOF MS is located on an elevator that brings the instrument very close to the desired sampling port, which are located at 15.2 cm intervals along the height of the reactor, providing equivalent temporal resolution of about one-tenth second in pyrolysis reactions.

The first time-series data of molecular weight distribution of pyrolysis products are displayed to the right. The reactor had a heated length of 1.8 m with heated wall temperature of 600°C. Sweep gas was 18 SLPM. Average particle heating time was1.06 s.

## Observations From Time-Resolved Tests

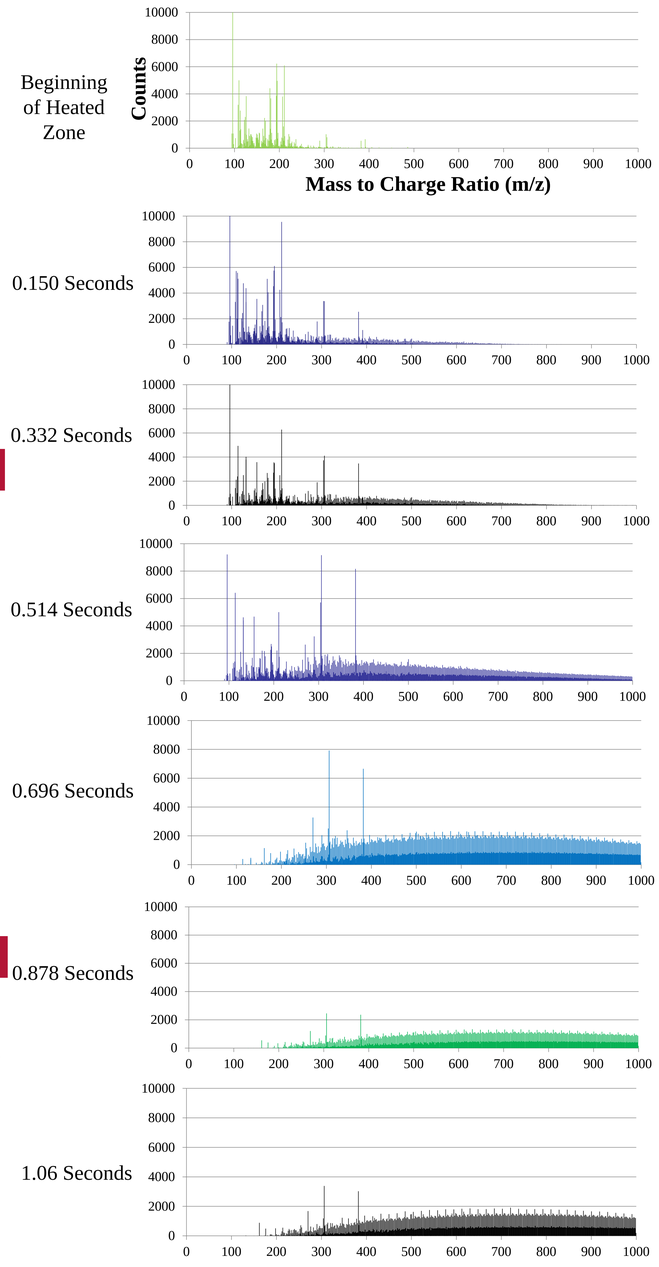
- Upon initial heating pyrolysis vapors containing relatively low molecular weight (MW) compounds are released very quickly;
- Many of these initial low MW (100-250 Da) compounds reach their maximum concentrations within 0.5 seconds of initial heating;
- As time further increases, these low MW compounds disappear. Since these are thought to be phenolic monomers and dimers, they are likely polymerizing to higher MW oligomers;
- The number of high MW compounds (250-1000 Da) increases dramatically after 0.5 s. Since the data has not been quantified, it is difficult to conclude whether their mass accounts for the loss of mass from low MW compounds. Residence time tests with the char catch-pot suggests that some of this increase in high MW compounds is due to "slow devolatilization" of the hot solids;
- After 0.7 s the high MW compounds reach their maximum concentration after which they decline or shift to MW > 1000 Da (detector limited to 100-1000 Da for the present test)

## Other Experiments in Progress

A Design of Experiments (DOE) is being performed to create an Response Surface Methodology (RSM) to better understand the relationship between reactor conditions and the pyrolysis products. The dependent variables include yields of liquid, solid, and non-condensable gases. The independent variables of reactor temperature, particle heating time, and sweep gas dilution.

Fixed parameters for DOE
- Feedrate: 1 kilogram per hour
- Reactor headspace purge: 3 standard liters per minute
- Solids collection configuration: Char Auger at 0.5 RPS
- Liquid collection configuration: Cold Quench Version 2.1

## MW Distribution from TOF Mass Spectrometer

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