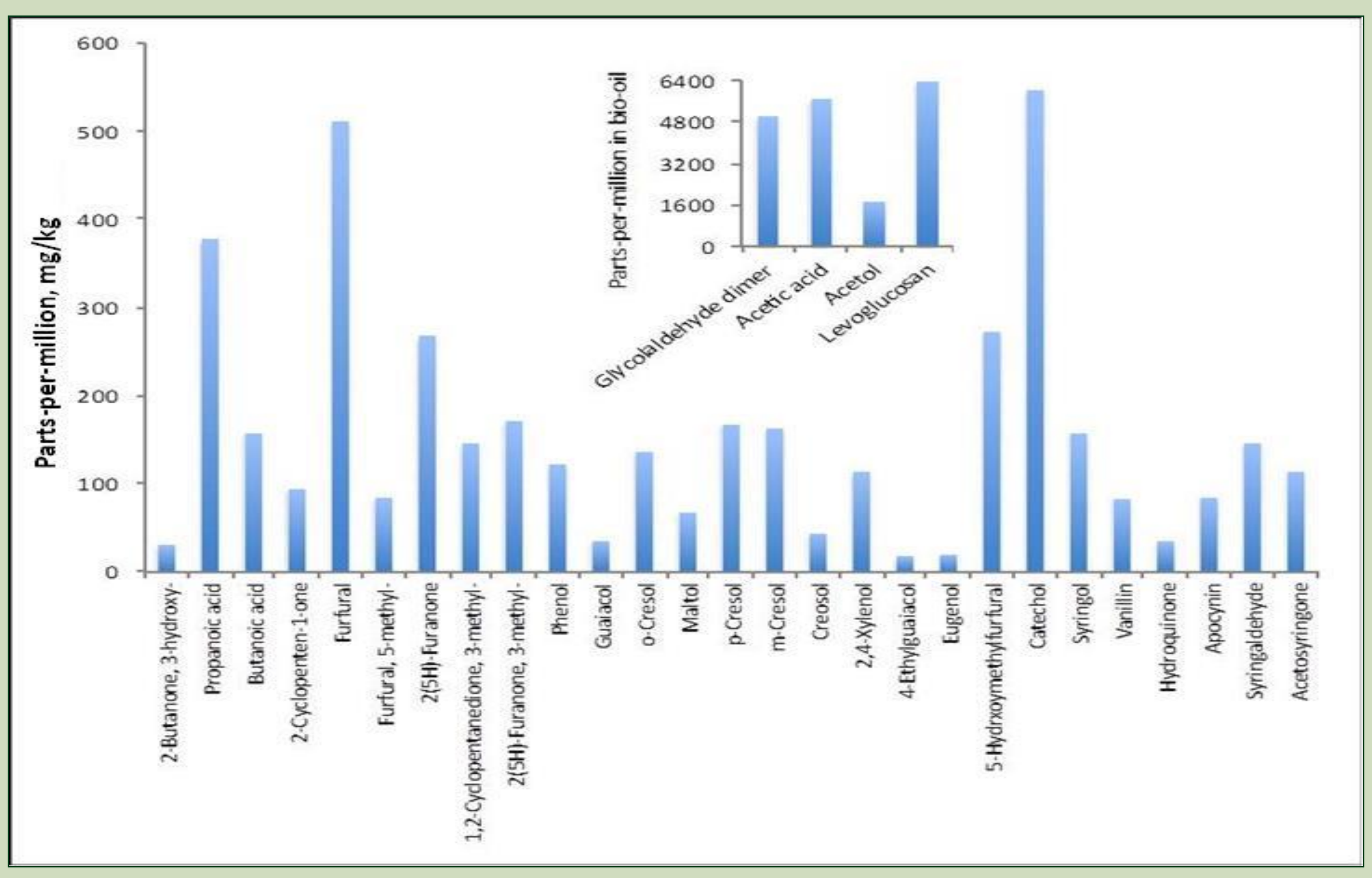
Compatibility of Fast-Pyrolysis Bio-oil with Infrastructure Plastic Materials

Mike Kass (kassmd@ornl.gov), Chris Janke, Maggie Connatser, Sam Lewis, Jim Keiser
Oak Ridge National Laboratory, Oak Ridge, TN 37831

Background

Bio-oil derived via fast pyrolysis is being developed as a renewable fuel option for petroleum distillates, such as diesel. The compatibility of plastic materials was investigated since these materials are used extensively in fuel systems seals, valves and structural components. Their performance, when exposed to a new fuel chemistry, is critical to ensure leak-tight joining and effective containment of fuel. Failure may lead to leakages (or fugitive emissions).

Bio-oils contain a complex mix of ketones, carboxylic acids, furans, phenols and other oxygenates. This complex blend makes it difficult to apply standard solubility methodologies to assess compatibility. Therefore empirical-based exposure studies are needed.



Partial polar oxygenate composition of bio-oil used in this study

Objective: generate a database of key compatibility properties to guide plastic selection and identify potential risks

Materials and Methods

Nineteen common types of plastics were evaluated in an off-highway diesel (baseline) and a mixed-oak feedstock bio-oil derived via fast pyrolysis (sans aqueous phase). Specimens were exposed to liquid and vapor phases.

Plastic Type and Grade	Trade Name	Application
Permeation Barrier Plastics		
Polyphenylene sulfide (PPS)	Techtron™	Permeation barrier material
Polyethylene terephthalate (PET)	Mylar™	Permeation barrier material
Polytetrafluoroethylene (PTFE)	Teflon™	Permeation barrier and seal material
Polyvinylidene fluoride (PVDF)	Kynar™	Permeation barrier material
Nylons and Acetals		
Nylon 6		Plastic piping and seal material
Nylon 6/6	Zytel™	Plastic piping and seal material
Nylon 11		Fuel tank material
Nylon 12		Automotive fuel lines & plastic piping material
POM acetal homopolymer	Delrin II™	Fuel line valves, pump and tank components
POM acetal co-polymer	Acetron GP™	Fuel line valves, pump and tank components
Other Infrastructure Plastics		
Polypropylene (PP)		Fuel containment and cable insulation
Polybutylene terephthalate (PBT)		Fuel tank materials
High density polyethylene (HDPE)		Fuel tank materials
PET glycol (PETG)	Spectar™	Sheathing material for automotive applications
Polythiourea (PTU)		Steel coating material
Thermosetting Fiberglass Resins		
Novolac vinyl ester		Resin for rigid fiberglass piping/tanks
Terephthalic polyester		Resin for rigid fiberglass piping/tanks
Isophthalic polyester (1:2)		Resin for rigid fiberglass piping/tanks
Isophthalic polyester (1:1)		Resin for rigid fiberglass piping/tanks

Experimental Protocol

Measure for mass, volume & hardness (unexposed)

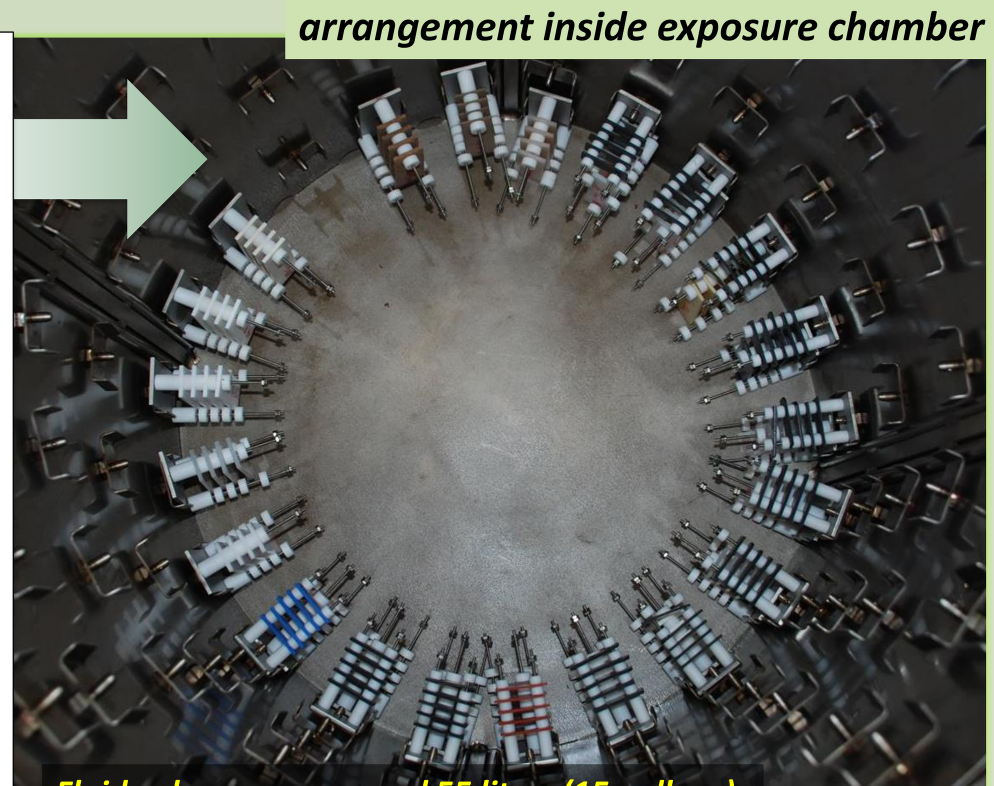
Test fuel exposure 60°C for 4 weeks

Re-measure properties (while wet)

Oven dried at 60°C & 65h in open atmosphere

Re-measure properties (dried)

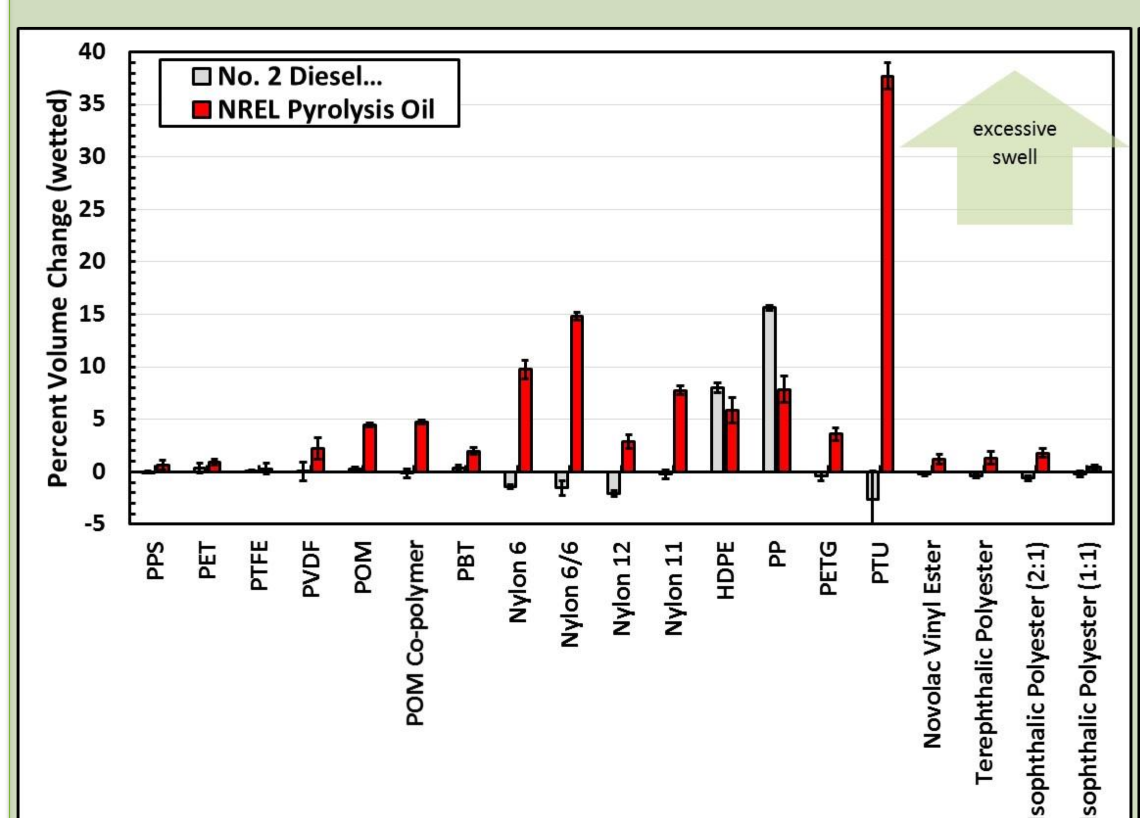
Top-down view showing specimen arrangement inside exposure chamber



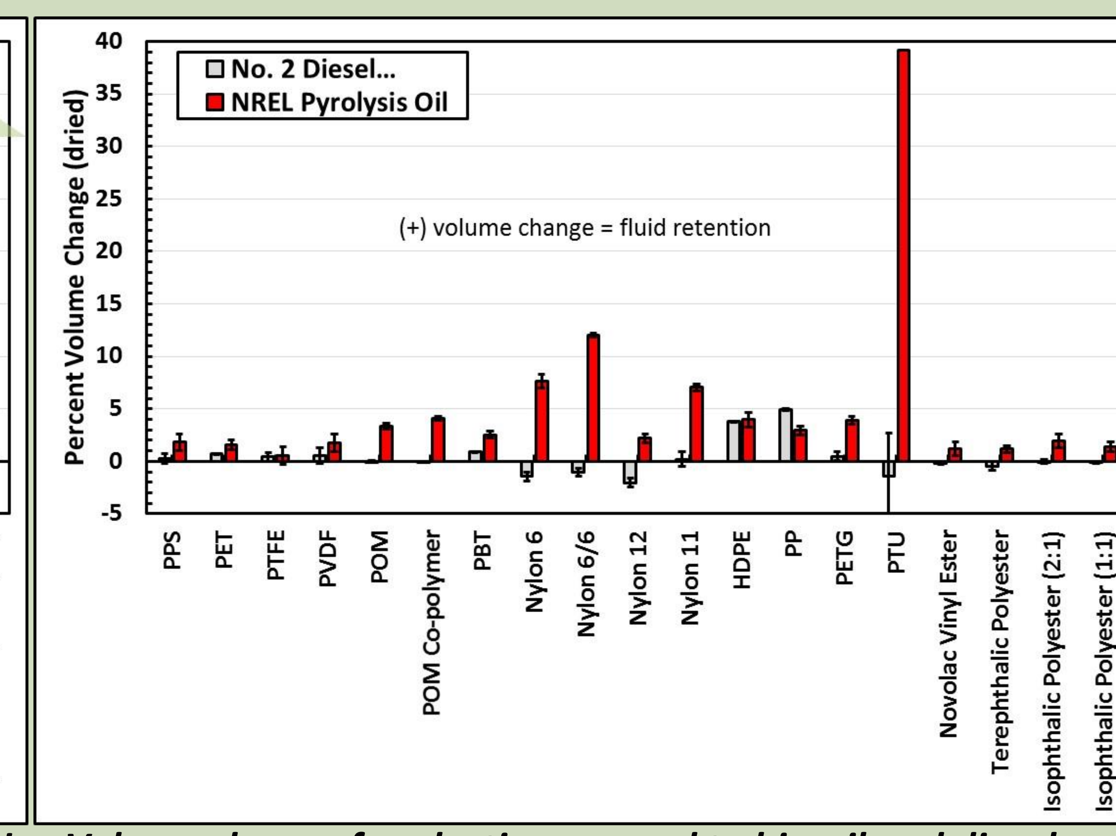
Results and Discussion

The wetted and dried volume change results show that:

- Diesel did not significantly affect the high-performance permeation barriers, nylons and acetals, resins, PBT, PETG, or PTU. However, moderate swelling was observed for the two nonpolar plastics, HDPE and PP. This swelling was higher than observed with bio-oil and remained even after drying. The higher volume expansion in diesel fuel is attributed to the heighted solubility of these plastics in diesel, which in turn is due to their matching nonpolar natures.
- The bio-oil produced modest swelling in PVDF, the acetals, Nylon 12 and PETG. More moderate swelling occurred in Nylon 6, Nylon 6/6, HDPE and PP. For the nylons and acetals, much of this swelling remained even after drying.
- Nylon 6, Nylon 6/6, and Nylon 12 exhibited a small decrease in volume and mass following exposure to diesel.
- Plastics which exhibited the best compatibility (minimal volume change) in bio-oil were PPS, PET, PTFE, and the four thermosetting resins.
- Interestingly, isophthalic polyester (1:1) showed a slight volume (but no mass) increase after drying. This effect indicates that physical restructuring of the polymer chains occurred during the drying process.
- PTU experienced pronounced and excessive swelling when exposed to the bio-oil fuel.



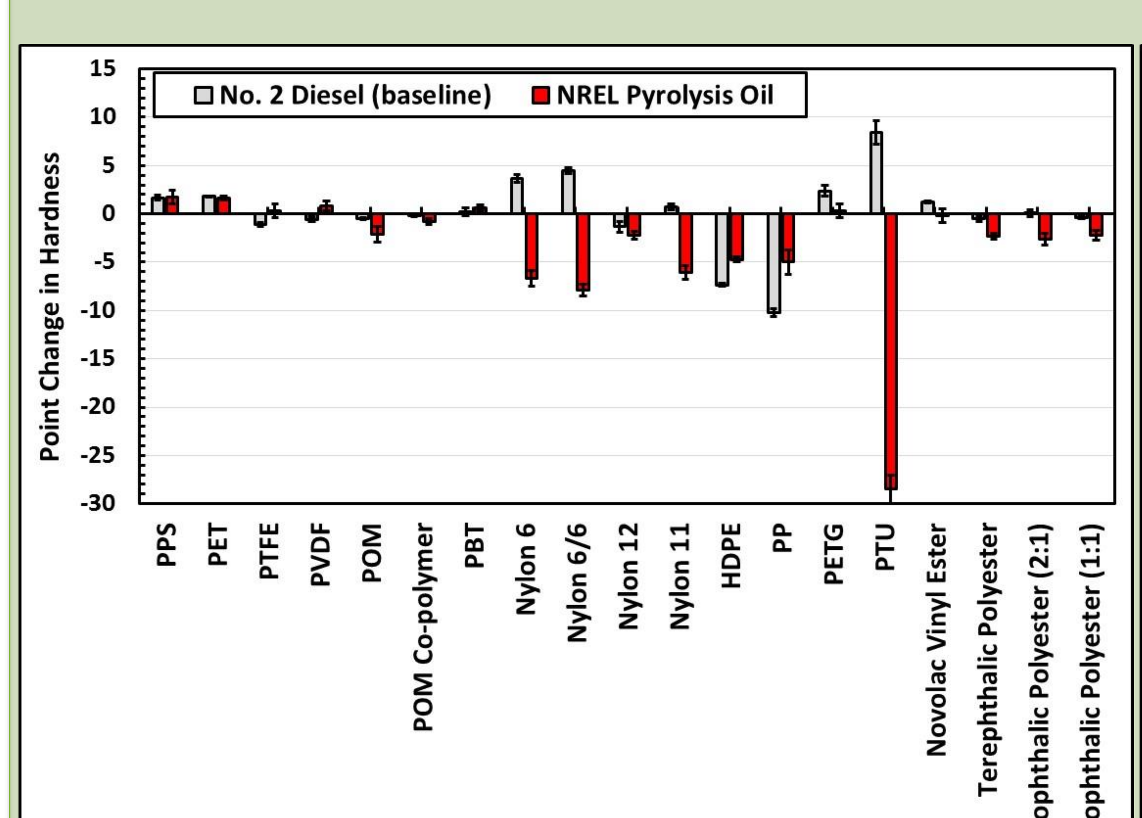
Volume change for plastics exposed to bio-oil at 50°C and diesel at 60°C for 16 weeks



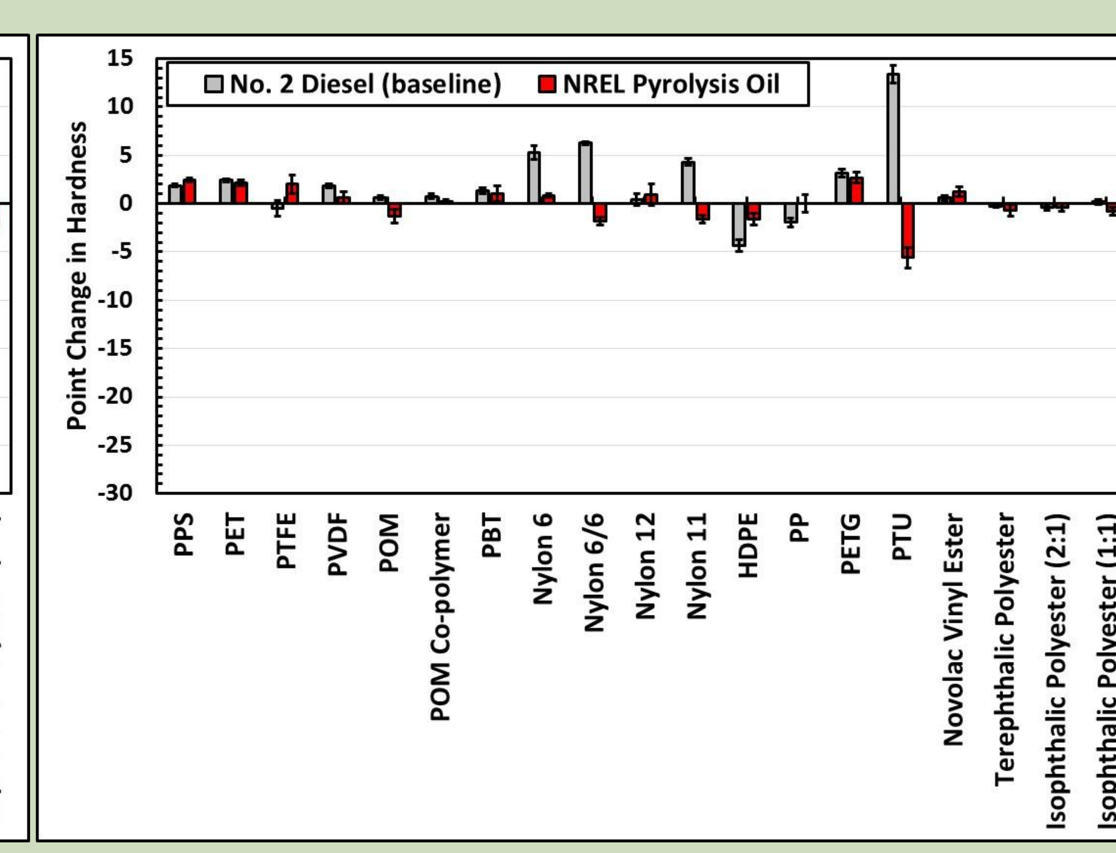
Volume change for plastics exposed to bio-oil and diesel exposed for 16 weeks and then dried at 60°C for 65h

The wetted and dried point change in hardness results show that:

- In general a decrease in hardness (increased softening) roughly corresponded with volume swell results for the plastics. Noticeable exceptions were Nylon 6, Nylon 6/6 and PTU specimens exposed to diesel. For these three materials the observed embrittlement carried over following dry-out.
- When dried, the hardness values of the nylon and resin specimens exposed to the bio-oil returned to their starting values.
- The PTU specimens exhibited pronounced softening when exposed to bio-oil. When dried the hardness values for these specimens increased approximately 25 points, even though the volume & mass were relatively unchanged. The reason for this increase is attributed to the extraction of plasticizer and the replacement of plasticizer volume by the bio-oil fluid.
- The high performance permeation barrier materials, acetals, PBT, Nylon 12, PETG, and resins did not experience significant changes to their original hardness values.



Hardness results for for plastics exposed to bio-oil at 50°C and diesel at 60°C for 16 weeks



Hardness results for elastomers exposed for 16 weeks and then dried at 60°C for 65h

Impact

- ***PPS, PET PTFE and the thermosetting reins (used in fiber-reinforced plastics) showed negligible property changes when exposed to bio-oil. The implication is that these materials are acceptable for use with bio-oil.***
- ***A slight, but noticeable volume increase was observed for PVDF, PET, Nylon 12, and PETG specimens exposed to bio-oil. These materials are likely to be compatible with bio-oil in most applications.***
- ***Acetals (POM and POM co-polymer) showed modest volume expansion when wetted. As such they are compatible for many sealing applications, but may have limitations in low volume swell applications.***
- ***HDPE, PP, Nylon 11, Nylon 6 and Nylon 6/6 all exhibited moderate levels of volume expansion. Their applications should be limited to use as seals. Some hose applications may be acceptable depending the strength requirements.***
- ***PTU experienced excessive swelling in bio-oil. This material will not be compatible for use with bio-oil in most applications.***

Contact information: kassmd@ornl.gov; 865-946-1241; Oak Ridge National Laboratory, The NTRC Bldg., 2360 Cherahala Blvd., Knoxville, TN, USA, 37932
Oak Ridge National Laboratory; 1 Bethel Valley Rd., Oak Ridge, TN, USA 37830
Research sponsored by the U.S. Department of Energy, Bioenergy Technologies Office