RESEARCH & DEVELOPMENT TO PREPARE AND CHARACTERIZE ROBUST COAL/BIOMASS MIXTURES FOR DIRECT CO-FEEDING INTO GASIFICATION SYSTEMS

FINAL SCIENTIFIC/TECHNICAL REPORT

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ABSTRACT

This project was initiated on October 1, 2010 and utilizes equipment and research supported by the Department of Energy, National Energy Technology Laboratory, under Award Number DE-FE0005349. It is also based upon previous work supported by the Department of Energy, National Energy Technology Laboratory, under Award Numbers DOE-DE-FG36-01GOl1082, DE-FG36-02G012011 or DE-EE0000272. The overall goal of the work performed was to demonstrate and assess the economic viability of fast hydrothermal carbonization (HTC) for transforming lignocellulosic biomass into a densified, friable fuel to gasify like coal that can be easily blended with ground coal and coal fines and then be formed into robust, weather-resistant pellets and briquettes. The specific objectives of the project include:

- Demonstration of the continuous production of a uniform densified and formed feedstock from loblolly pine (a lignocellulosic, short rotation woody crop) in a hydrothermal carbonization (HTC) process development unit (PDU).
- Demonstration that finely divided bituminous coal and HTC loblolly pine can be blended to form 90/10 and 70/30 weight-percent mixtures of coal and HTC biomass for further processing by pelletization and briquetting equipment to form robust weather resistant pellets and/or briquettes suitable for transportation and long term storage.
- Characterization of the coal-biomass pellets and briquettes to quantify their physical properties (e.g. flow properties, homogeneity, moisture content, particle size and shape), bulk physical properties (e.g. compressibility, heat transfer and friability) and assess their suitability for use as fuels for commercially-available coal gasifiers.
- Perform economic analyses using Aspen-based process simulations to determine the costs for deploying and operating HTC processing facilities for the production of robust coal/biomass fuels suitable for fueling commercially-available coal-fired gasifiers.

This Final Project Scientific/Technical Report discusses and documents the project work required to meet each of these objectives.

TABLE OF CONTENTS

ABSTRACT iii
TABLE OF CONTENTS iv
LIST OF FIGURES vi
LIST OF TABLES xiv
ACRONYMS AND ABBREVIATIONS xvii
EXECUTIVE SUMMARY 1
ACCOMPLISHMENTS 3
1. Background and Introduction 3
2. Project Objectives 5
3. Project Activities 5
3.1 Overview 5
3.2 Tasks 5
3.2.1 Task 1: HTC Operating Condition Optimization for Pellet Formation 7
Development and Use of DRI's PDU 7
Design and Fabrication of the DRI PDU 7
Feedstock Sorter 9
Water/Solid Separator 11
Solar Oven for Drying Hydrochar 11
Pellet Press and Die 12
Optimizing PDU Operating Conditions 14
2 x 2 Experimental Matrix 16
Characterization of Hydrochar and Aqueous Products 19
Sugars Analyses 21
Organic Acids 22
Other Batch PDU Experiments and Results 23
Hydrochar and Mass Balance 24
Characterization of Gaseous Products 27
Hydrochar Characterization and Pelletization 36
Pellet Durability Tests 37
Water Immersion Tests 42
Effect of HTC Process Temperature upon Pellet Durability 48
Extraction of Hydrochar 50
Effectiveness of Acetone Extracts as Pellet Binder 52
Characterization of Acetone Extracts 56
Leaching of Organic Acids from Hydrochar 62
Effectiveness of Hydrochar as Pellet Binder 64
3.2.2 Task 2: Characterization of Pelletized HTC Process Solids/Extractables with Coal 68
The GTI Continuous, Fast Hydrothermal Carbonization (FHTC) PDU 71
Continuous Production of FHTC Biomass 77
Assessment of FHTC Products from the GTI TSE-Based PDU 79
FHTC Experiments in February, 2013 80
FHTC Product Characterization by DRI 80
Pelletization of FHTC hydrochar 83
FHTC PDU Experiments in May, 2013 86

Assessment of Process Severity 90
FHTC Experiments in July, 2014 94
Sample Preparation 95
Characterization of FHTC Solid Products 97
Characterization of FHTC Aqueous Products 103
Characterization of FHTC Gaseous Products 109
Mass Balance for July, 2014 FHTC Testing 116
3.2.3 Task 3: PDU Modification for Online Coal/FHTC Biomass Fuel Production 121
3.2.4 Task 4: Forming & Characterization of Coal/HTC Biomass Briquettes 125
Briquette Forming 125
Briquette Characterization 126
3.2.5 Task 5: HTC Biomass and Offline Briquetting/Characterization 127
Offline Production of Coal/FHTC Biomass Blends 127
Drying the HTC Prior to Mixing with Pulverized Coal 127
Mixing of Dried HTC with Coal 127
Briquette Production 127
Briquetter Operating Trials 127
Drop Test Evaluation of Briquettes 129
Evaluation of Offline Briquettes by CONSOL 133
3.2.6 Task 6: HTC Biomass and Online Mixed Fuel Production/Characterization 135
Online Production of Coal/FHTC Briquettes 135
Briquette Analyses 135
Evaluation of Online Briquettes by CONSOL 135
Drop-Shatter Testing of Briquettes 141
3.2.7 Task 7: Economic Feasibility and Assessment of Environmental Impacts 142
Summary 142
Process Overview 142
Techno-economic Analysis (TEA) 142
Total Capital Investment 144
Annual Operating Expenses 145
Minimum Selling Price of Briquettes of Blended Hydrochar & Coal Fines 146
Sensitivity Analysis of Plant Size on MSP of Coal Fines Briquettes 147
Case 1 147
Case 2 147
Sensitivity Analysis of Wood Chips Cost on MSP of Briquette 147
Sensitivity Analysis of Coal Fines Cost on MSP of Briquette 148
Sensitivity Analysis of Mixing Ratio on MSP of Briquettes 149
Energy Costs (MSP/GJ) 149
TEA - Conclusions 149
Calculations 150
3.4 Conclusions and Recommendations 151
3.5 Publications and Presentations 155
3.6 References 156
Appendix 160

LIST OF FIGURES

Figure 1. Schematic of PDU showing heating zones, ports, fittings, and sampling locations. (Drawing not to scale.) 8

Figure 2. Location and fabrication of DRI's PDU: (A) Outside view of DRI's REDD Workshop, which houses the PDU, (B) frame for holding reactor, (C) PDU mounted on frame, (D) close-up of heating band. 9

Figure 3. Control system of PDU: (A) Assembled unit with heaters, auger motors, and insulation installed, (B) solid state relays for heating bands, (C) PID temperature controllers, (D) control boxes for power control, heater relays, heater control, and auger frequency converter. 10

Figure 4. Photos of PDU gas sampling system (A) and (B) and liquid sampling system (C). Ancillary Equipment for Support of the PDU 10

Figure 5. Top (left) and side (right) schematic views of wood chip sorter 11

Figure 6. Schematic (left) and photograph (right) of wood chip sorter 11

Figure 7. Sieve for separating solid and liquid products 11

Figure 8. Solar oven for drying hydrochar produced in the PDU. (A) Schematic of indirectly-heated oven. (B) Photo of oven installed in the DRI REDD Facility 12

Figure 9. Carver Laboratory Press Model M, with Wika Model 232.34 pressure gauge 12

Figure 10. Across™ heated die with temperature controller 13

Figure 1. Schematic of Across™ heated die 13

Figure 2. Carver Pellet Press with heated die and controller 13

Figure 13. PDU schematic showing locations of thermocouples, heaters, and water level. (Drawing not to scale.) 15

Figure 14. Temperature monitoring and control of PDU (235 °C reaction temp. run) 16

Figure 15. Four hydrochar fractions recovered from HTC experiment in PDU 17

Figure 16. Effect of HTC reactor temperature on energy content of produced hydrochar. Star symbols represent PDU experiments with Slash Pine feedstock; all other experiments were conducted in a stirred, 2-L Parr reactor, with a 30-min. hold time. 19

Figure 17. Sugar yields in aqueous PDU fractions from HTC treatment of Slash Pine 21

Figure 18. Sugar concentrations in aqueous PDU fractions from HTC treatment of Slash Pine 22

Figure 19. Organic acid yields in aqueous PDU fractions from HTC treatment of Slash Pine 23

Figure 20. Organic acid concentrations in aqueous PDU fractions from HTC treatment of Slash Pine 24

Figure 21. Mass recovery of hydrochar and NVR from PDU experiments. All experiments conducted with fast auger speed except those indicated by "(S)" 26

Figure 22. Effect of HTC reactor temperature on energy content of produced hydrochar. Star symbols represent PDU experiments; all other experiments were conducted in a stirred, 2-L Parr reactor, with a 30-min. hold time 26

Figure 23. Schematic of sampling system for collecting hot, pressurized gaseous products from PDU 28

Figure 24. Gas chromatogram of headspace sample taken from PDU after HTC treatment of Loblolly Pine at 255 °C 29

Figure 25. Schematic of 10-bag PDU sparging experiment to collect gaseous products from HTC treatment of P-J at 235 °C 29

Figure 26. CO and CO_2 concentrations measured by GC in the PDU 10-bag experiment 30

Figure 27. CO concentrations measured by GC in the PDU 10-bag experiment 30

Figure 28. Chromatograms from GC-MS analysis of bag samples of gaseous products from the PDU after HTC treatment of P-J at 235 °C. Peaks: 1 – Butene-1 + isobutene; 2 – guanidine (?); 3 – furan; 4 – 2-methyl-2-butene; 5 – isobutylamine (?); 6 – 2-methylfuran; 7 – unknown; 8 - unknown; 9 – Furfural +?; 10 – isopropylbenzene; 11 – dimethylphenol; 12 – a-pinene; 13 – dimethylethylbenzene; 14 – unknown 31

Figure 29. Chromatogram from GC-MS analysis of gaseous products from Changing World Technologies (CWT) HTC treatment of Loblolly Pine at 260 °C. Peaks: 1 – Butene-1 + isobutene; 2 – guanidine (?); 3 – furan; 4 – 2-methyl-2-butene; 5 – isobutylamine (?); 6 – 2-methylfuran; 7 – methylbutanal (?); 8 – 3-methylcyclopentene; 9 – 2-ethylfuran; 10 – 2,5-dimethylfuran; 11 – dimethyldisulfide; 12 – Furfural, 13 – unknown; 14– a-pinene; 15 – limonene (or camphene) 33

Figure 30. GC-MS TIC chromatogram of gaseous products from HTC treatment of Pinyon-Juniper in the PDU at 235 °C 34

Figure 31. Measurement of pellet height by digital Vernier Calipers 37

Figure 32. Laboratory protocol for assessing pellet durability 39

Figure 33. (A) Thumbler Model A-R1 tumbler used for pellet durability tests; (B) 40-hydrochar pellets on analytical balance 39

Figure 34. Pellets used in tumbler durability tests: (a) raw wood pellets, hydrochar pellets, and 3 "filler pellets": (steel, wood, and plastic; (b) tumbler drum containing wood filler pellets 40

Figure 35. Effects of water immersion on stability of pelletized woody biomass materials. All pellets had diameters of 13 mm and heights of 6-7 mm prior to immersion 42

Figure 36. Set of 18 pellets for water immersion tests 43

Figure 37. Effect of water immersion on the behavior of HTC and torrefied pellets. (A) Percent increase in pellet length; (B) pellet density; (C) pellet durability. Error bars represent standard deviations from triplicate experiments. (No durability results are shown for torrefied materials as these pellets did not survive tumbling.) 44

Figure 38. Effect of HTC process temperature upon behavior of hydrochar pellets after immersion in water for 60-min. Hydrochar was produced by treatment of Loblolly Pine at indicated temperature for 30-min. in a 2-L stirred Parr reactor. Error bars represent ± 1 std. dev. from measurement of 3 pellets produced from a single HTC experiment.....48

Figure 39. Effect of HTC process temperature upon mass and volumetric densities of pellets. Hydrochar was produced by treatment of Loblolly Pine at indicated temperatures for 30-min. in a 2-L stirred Parr reactor. All measurements were made prior to water immersion. Error bars represent ± 1 std. dev. from measurement of three pellets produced from a single HTC experiment.....50

Figure 40. Effects of acetone extract addition upon pellet behavior after immersion in water for 60-min. (A) Increase in pellet length; (B) pellet durability. Error bars represent ± 1 std. dev. from triplicate experiments. (No durability results are shown for pellets made from raw loblolly as they did not survive a tumbling test.) 53

Figure 41. Effect of acetone extract addition on stability of pellets produced from Integro torrefied biomass. Percentage values indicate the amount of acetone extract added to the torrefied Tahoe Mix. "Tumbled" indicates pellet was tumbled for 3000 revolutions, after 60-min. immersion in water 56

Figure 42. Effect of acetone extract addition on stability of pellets produced from extracted hydrochar. "60 min" indicates pellet was immersed in water for 60-minutes. "Tumbled" indicates pellet was tumbled for 3000 revolutions, after 60-min. immersion in water.....56

Figure 43. IR spectra of Tahoe Mix HTC-275 before acetone extraction, after extraction, and acetone extracts.....57

Figure 44. IR spectra of torrefied Tahoe Mix before acetone extraction, after extraction, and acetone extracts.....58

Figure 45. 1H NMR spectra of acetone extracts from HTC-275 and torrefied Tahoe Mix wood.....59

Figure 46. 13C NMR spectra of acetone extracts from HTC-275 and torrefied Tahoe Mix wood.....59

Figure 47. TIC from GC/MS analysis of acetone extracts from (A) Tahoe Mix HTC-275 and (B) torrefied Tahoe Mix 60

Figure 48. Measurement of pH during leaching of hydrochar.....62

Figure 49. Leaching of acidic components from bio-chars into water. Monitoring of pH vs. time. (A) HTC-215°C, (B) HTC-255°C, (C) HTC-275°C, (D) Torrefied char 63

Figure 50. Effect of hydrochar blend amount on pellet swelling after water immersion for 60-min. Hydrochar was produced from HTC treatment of Tahoe Mix wood at 275 °C 64

Figure 51. Effect of hydrochar blending on stability of pellets produced from Tahoe Mix wood.....66

Figure 52. Effect of hydrochar blending on stability of pellets produced from Astec torrefied biomass. Percentage values indicate the fraction of Tahoe Mix hydrochar included in the blend. "50% Tumbled" indicates a pellet that was tumbled for 3000 revolutions, after immersion in water for 60-min 67

Figure 53. Effect of hydrochar blending upon stability of pellets produced from various solid biomass materials. The hydrochar was produced from treatment of Tahoe Mixed woods at 275°C for 30-min. 68

Figure 54. Effect of hydrochar blending on stability of pellets produced from pulverized Galatia coal. Percentage values indicate the fraction of Tahoe Mix hydrochar included in the blend. All pellets were immersed in water for 60-min. 68

Figure 55. Behavior of pellets produced from blends of biomass and Galatia coal. Effects of blending ratio upon pellet behavior after immersion in water for 60-min. (A) pellet swelling; (B) pellet durability. Data points are averages of three pellets from a single HTC experiment; error bars represent ± 1 std. dev.....69

Figure 56. Effect of biomass blending upon stability of pellets produced from pulverized Galatia coal. "Raw" indicates untreated loblolly pine; "HTC" indicates hydrochar from loblolly pine at 275 °C 70

Figure 57. Photos of starting feedstock blends and products from HTC co-processing experiments 71

Figure 58. Cross-section view of the Clextral BC-21 twin-screw extruder obtained to prepare FHTC biomass. A separate volumetric feeder and water heater are not shown 72

Figure 59. Schematic cross-section drawing of the BC-21 TSE (top) and (bottom) the configuration of one of the two intermeshing screw sets configured along splined shafts that moved particulate biomass introduced at the left to the right as the CHTC reaction proceeded and was completed with the ejection of the CHTC product 73

Figure 60. Segment of the two co-rotating TSE shafts illustrating the appearance of forward-pitch, and reverse-pitch screw elements 73

Figure 61. End View of a Typical TSE Barrel Section Removed from the BC-21 74

Figure 62. Manually-operated, dual-function variable restriction pressure-sustaining valve.....76

Figure 63. Custom-Built manual valve located at the exit of the BC-21 TSE.....76

Figure 64. Process charts for first-generation HTC exhaust VRPSV, April 21, 2013.....78

Figure 65. Process charts for second-generation FHTC exhaust VRPSV, March 21, 2014.....78

Figure 66. Process charts for third-generation FHTC exhaust VRPSV, July 15, 2014 79

Figure 67. Analysis of sugars in aqueous products from HTC treatment of Loblolly Pine in GTI's FHTC PDU: (A) concentrations in liquid samples, (B) normalized distribution of identified constituents – Feb. 2013 82

Figure 68. Analysis of sugars in aqueous products from HTC treatment of Loblolly Pine in GTI's FHTC PDU: (A) concentrations in liquid samples, (B) normalized distribution of identified constituents – Feb. 2013 83

Figure 69. Effects of water immersion (60-min.) upon characteristics of pellets produced from FHTC hydrochar from Loblolly pine – February, 2013. All results expressed as % change from behavior of pellets that did not undergo water immersion 84

Figure 70. Effect of water washing upon behavior of pellets produced from FHTC hydrochar of Loblolly Pine.....84

Figure 71. Comparison of raw Loblolly Pine and hydrochar produced 2/21/13 in GTI's FHTC PDU. "Immersed" indicates the pellet was immersed in water for 60-minutes. "Tumbled" indicates the pellet was tumbled for 3000 revolutions, after 60-min. of immersion in water 85

Figure 72. Energy densities of hydrochar produced from loblolly pine using DRI's 2-L Parr reactor and GTI's FHTC PDU:(A) mass energy density of powders, (B) volumetric energy density of pellets. (All hydrochar samples from GTI were used as received, without water washing.).....86

Figure 73. Sampling schematic for the GTI FHTC PDU.....87

Figure 74. Analysis of sugars in aqueous products from treatment of Loblolly in the GTI FHTC PDU – May, 2013. (A) concentrations in units of μg/ml; (B) concentrations normalized to 100%.....88

Figure 75. Concentration of organic acids in aqueous products from treatment of Loblolly pine in the GTI FHTC PDU.....89

Figure 76. Normalized concentrations of organic acids in aqueous products from treatment of Loblolly pine in GTI's FHTC PDU.....89

Figure 77. Relationship between HTC reaction temperature and hydrochar energy content. Experiments with Loblolly pine and Tahoe Mix feedstocks were conducted in different reactor systems under various conditions. Trend lines are shown for 2-L Parr reactor experiments.....90

Figure 78. Relationship between reaction severity factor and hydrochar energy content. Experiments with Loblolly pine and Tahoe Mix feedstocks were conducted in different reactor systems under various conditions. Trend lines are shown for 2-L Parr reactor experiments and PDU experiments.....91

Figure 79. Sugar profiles from HTC treatment of Loblolly Pine at different temperatures in DRI's 2-L stirred Parr reactor. All experiments had 30-min. hold times 92

Figure 80. Effect of reaction severity upon sugar profiles from HTC treatment of Loblolly pine. Data points connected with trend lines are from DRI's 2-L Parr reactor with 30-min. hold times. Data points at a severity factor of 3.9 represent the average profile of rinsate and filtrate from GTI's "fiber" samples. Data points at a severity of 4.1 represent the average profile of rinsate and filtrate from GTI's "paste" samples.....93

Figure 81. Organic acid profiles from HTC treatment of Loblolly Pine at different temperatures in the DRI 2-L stirred Parr reactor. All experiments had 30-min. hold times 94

Figure 82. Effect of reaction severity upon organic acid profiles from HTC treatment of Loblolly pine. Data points connected with trend lines are from the DRI 2-L Parr reactor with 30-min. hold times. Solid lines (lactic, acetic, and formic acids) are on left axis; dashed lines are on right axis. Data points at a severity factor of 3.9 represent the average profile of rinsate and filtrate from GTI's "fiber" samples. Data points at a severity of 4.1 represent the average profile of rinsate and filtrate from GTI's "paste" samples 94

Figure 83. Sampling setup at GTI's FHTC Laboratory: (A) hot gas sampling; (B) cold gas sampling; (C) hydrochar slurry samples 96

Figure 84. Schematic of collection, processing and analysis of samples collected from GTI's FHTC in July, 2014 97

Figure 85. Relationship between severity factor and hydrochar energy content (MJ/kg) 99

Figure 86. Van Krevelen diagram of hydrochar products from different reactors/conditions. Severity factors noted are for 2-L Parr reactor experiments 101

Figure 87. Relationship between O/C ratios and severity factor for hydrochar produced from Loblolly pine. Curve shown is fitted to the 2-L Parr reactor data 101

Figure 88. Pellets from hydrochar produced in GTI's FHTC PDU in July, 2014 102

Figure 89. Durability of pellets from hydrochar slurries produced by the GTI FHTC PDU (July, 2014 103

Figure 90. Analysis of sugars in aqueous products from July 2014 HTC treatment of Loblolly Pine in the GTI FHTC. Shown as (A) percentage of starting dry mass, (B) measured concentration (μg/mL), and (C), concentration normalized to 100% 105

Figure 91. Comparison of sugar results between the GTI FHTC and DRI 2-L Parr treatment of loblolly pine. The numbers directly beneath each bar are calculated reaction severity factors. FHTC results are the sum of sugars from slurry and condensate 106

Figure 92. Effect of reaction severity upon sugar profiles from HTC treatment of Loblolly Pine. Data points connected with trendlines are from the DRI 2-L Parr reactor with 30-minute hold times. Data points at severity factors of 3.9 and 4.1 represent the average profiles of rinsate/filtrate from GTI's "fiber" and "paste" samples, respectively from May, 2013. The average profile of the FHTC slurry rinsate from the July, 2014 sampling campaign is shown at a severity of 5.3 107

Figure 93. Organic acids measured in aqueous products from operation of GTI's FHTC PDU with Loblolly pine in July, 2014 108

Figure 94. Comparison of organic acid results between GTI's FHTC and DRI's 2-L Parr treatment of Loblolly pine. (A) Percentage of starting dry mass; (B) concentrations normalized to 100% 109

Figure 95. Effect of reaction severity upon organic acid profiles from HTC treatment of Loblolly Pine. Data points connected with trendlines are from DRI's 2-L Parr reactor with 30-minute hold times. Data points at severity factors of 3.9 and 4.1 represent the average profiles of rinsate/filtrate from GTI's "fiber" and "paste" samples, respectively from May, 2013. The average profile of the FHTC slurry rinsate from the July, 2014 sampling campaign is shown at a severity of 5.3 110

Figure 96. GC-MS TIC chromatogram of cold gas sample I014 from FHTC experiment No. 3, July 15, 2014 111

Figure 97. GC-MS TIC chromatogram of cold gas sample I008 from FHTC experiment No. 5, July 16, 2014 112

Figure 98. GC-MS TIC chromatogram of hot gas sample I009 from FHTC experiment No. 5, July 16, 2014 113

Figure 99. Isometric view of the twin-auger, cut-flight blender/conveyor as configured with the Clextral BC-21 TSE 121

Figure 100. Top and side views of the twin-auger, cut-flight blender/conveyor as configured with the Clextral BC-21 TSE 122

Figure 101. The blender/conveyor unit as delivered 122

Figure 102. Overview of assembled and insulated blender/conveyor unit installed with the Clextral BC-21 TSE 123

Figure 103. Detail of the assembled and insulated blender/conveyor unit installed with the Clextral BC-21 TSE 124

Figure 104. Schematic representation of a roller-press briquetter 125

Figure 105. Komarek, Inc. Model B100QC briquetting machine used in laboratory trials..... 125

Figure 106. Overview from briquetting head side with vent line installed 126

Figure 107. Photographs of (a): the pulverized coal, (b): dried FHTC powder, and the two blends produced from them (c): 90% pulverized coal/10% FHTC, and (d): 70% pulverized coal/30% FHTC 128

Figure 108. Photograph of briquettes with tabs formed around the center seam of the briquettes 129

Figure 109. Briquettes formed from 100% pulverized coal prior to the drop tests 130

Figure 110. Briquettes formed from 90% pulverized coal/10% HTC prior to the drop tests 130

Figure 111. Briquettes formed from 70% pulverized coal/30% HTC prior to the drop tests 130

Figure 112. Results of the drop test evaluations of the briquettes formed from 100% pulverized coal, 90% pulverized coal/10% HTC, and 70% pulverized coal/30% HTC 132

Figure 113. Briquette fragments (each having a mass <20% of the original mass) from a 100% coal briquette after two drops. A 1 cm x 1 cm grid is shown under the striking plate 132

Figure 114. After four drops, 85% of the original briquette mass was contained in the two major pieces of this briquette formed from 70% coal/30% FHTC. A 1 cm x 1 cm grid is shown under the striking plate 133

Figure 115. Online coal/HTC biomass briquettes produced in July, 2014 136

Figure 116. Fragments of ~1 in. air-dried 70/30 coal/HTC biomass produced in July, 2014 136

Figure 117. Consol Energy, Inc. test report for offline coal/FHTC briquettes produced in April, 2014 137

Figure 118. Consol Energy, Inc. test report for online coal/FHTC briquettes produced in July, 2014.....137

Figure 119. Comparison of proximate and ultimate analyses of coal/HTC briquettes and fragments of air-dried wet 70/30 coal/biomass mixture as reported in Figures 4 and 5.....139

Figure 120. Comparison of sieve analyses of tumbled coal/HTC briquettes and fragments of air-dried wet 70/30 coal/biomass mixture as reported in Figures 4 and 5.....139

Figure 121. Hardgrove grindability index measurements for offline and online coal/HTC briquettes and fragments of air-dried wet 70/30 coal/biomass mixture.....140

Figure 122. High heating value determinations for offline and online coal/HTC briquettes and fragments of air-dried wet 70/30 coal/biomass mixture 140

Figure 123. Process flow diagram of co-forming of coal fines with FHTC hydrochar.....143

LIST OF TABLES

Table 1. Matrix of PDU Experiments 16

Table 2. Hydrochar Recovery from PDU Experiments with Slash Pine Micro-Chips 17

Table 3. Properties of Solid Hydrochar from HTC Treatment of Slash Pine in the PDU 20

Table 4. Analysis of Aqueous Product Fractions from HTC Treatment of Slash Pine in the PDU. (NVR and TOC results expressed as percent of starting dry feedstock mass) 20

Table 5. Matrix of HTC Experiments Conducted in DRI's PDU 24

Table 6. Mass Recovery and Energy Densification Results from HTC Experiments in PDU 25

Table 7. Molar Concentrations of Selected VOCs from GC/MS Analyses in the PDU 10-Bag Experiment, ppbv 32

Table 8. GC-MS Analysis of Gaseous Products from HTC Treatment of P-J in the PDU at 235 °C 35

Table 9. Characterization of Raw and Thermally Treated Feedstocks 38

Table 10. Pellet Durability Results from Tumbler Tests, % Mass Remaining 41

Table 11. Durability of Pellets from Mixed Hardwood, % mass remaining (Comparison of laboratory-produced and commercially-produced pellets) 42

Table 12 (a). Pellet Water Immersion Test Results 45

Table 12 (b). Pellet Water Immersion Test Results 46

Table 12 (c). Pellet Water Immersion Test Results 47

Table 1. Effect of HTC Process Temperature upon Properties of Loblolly Pine Pellets 49

Table 2. Extractable Mass from Hydrochar and Torrefied Tahoe Mix Wood, % 51

Table 3. Acetone-Extractable Mass from Tahoe Mix Hydrochar (All hydrochars produced in 2-L stirred Parr reactor, with 30-min. hold time) 51

Table 16. Acetone Extraction of 255°C Hydrochar Produced from Tahoe Mix 52

Table 17. Part 1. Effect of Acetone Extract Addition upon Pelletization Properties of Raw and HTC loblolly Pine 54

Table 17. Part 2. Effect of Acetone Extract Addition upon Pelletization Properties of Torrefied and Raw Tahoe Mix Wood 55

Table 18. GC/MS Analysis of Acetone Extracts Obtained from Tahoe Mix HTC-275 and Torrefied Tahoe Mix. 61

Table 4. Effect of Hydrochar Blend Level upon Pellet Properties (Hydrochar was produced from Tahoe Mix Wood at 275 °C) 65

Table 20. Improvements in FHTC reactor stability over three generations of the VRPSV 79

Table 21. Characterization of Solid Products from the GTI FHTC Process – Feb. 2013 81

Table 22. Operating Conditions and Sample ID for July 2014 Runs of GTI's FHTC PDU 96

Table 23. Solids and Energy Contents of Products from GTI's FHTC PDU in July, 2014 98

Table 24. Proximate Analysis of Solid Products Produced by GTI's FHTC PDU in July, 2014 100

Table 25. Ultimate Analysis of Solid Products Produced by GTI's FHTC PDU in July, 2014 100

Table 26. Water Immersion Tests of Pellets from Hydrochar Produced in the GTI FHTC PDU (July, 2014) 102

Table 27. NVR and TOC of Aqueous Products from GTI's FHTC PDU (July, 2014). Results expressed as percentage of starting dry feedstock 104

Table 5. GC-MS Analysis of Gaseous Products from the GTI FHTC Treatment of Loblolly Pine at 290 °C. Top 5 Compounds Highlighted in Yellow; Next 5 Highlighted in Green 114

Table 6. Molar Concentrations of Selected VOCs from GC-MS Analysis of Gaseous Products from DRI's PDU and GTI's FHTC Reactor, ppm. 115

Table 30. Mass Balance for FHTC Experiments Conducted in July, 2014. All results expressed as a percentage of starting dry feedstock (Loblolly pine). All moisture contents used in mass calculations are based on measurements taken at DRI 117

Table 31. Moisture content comparisons from samples measured at GTI and at DRI 118

Table 32. HTC Drying and Reducing Procedures 128

Table 33. Procedure for Mixing Pulverized Coal and Dried, Chopped FHTC Powder 128

Table 34. Bulk Densities of Source Powders and Pulverized Coal/FHTC Blends 129

Table 35. Summary of Off-Line Briquette Production for Subsequent Analysis 130

Table 36. Briquette Drop Test Procedures 131

Table 37. Chemical Analyses of Off-Line Briquettes 133

Table 38. Size Analyses of Off-Line Briquette Fragments by Screening 134

Table 39. Comparison of drop-shatter test results for online and offline test series. (breakage of a briquette is defined as multiple pieces containing 20% or more of the original briquette mass.) 141

Table 40. Installed Equipment Costs (coal fines/hydrochar: 90/10, dry mass basis) 144

Table 41. Total Capital Investments (TCI), (Coal Fines/Hydrochar: 90/10, on a Dry Mass Basis) 145

Table 42. Annual Operating Expenses (Coal Fines/Hydrochar: 90/10, on a Dry Mass Basis) 146

Table 43. Parameters for Determining Minimum Selling Price of Char (Coal Fines/Hydrochar :90/10, on a Dry Mass Basis) 146

Table 44. Minimum selling price[1] (MSP/MT) of Briquette Based on Various Feedstock Costs (Coal Fines @ $10/MT, on a Dry Basis, Mixing Ratio: 90% Coal Fines/10% Hydrochar 148

Table 45. Minimum selling price[1] (MSP/MT) of Briquette Based on Various Feedstock Costs (Coal Fines @ $10/MT, on a Dry Basis, Mixing Ratio: 70% Coal Fines/30% Hydrochar 148

Table 46. Minimum Selling Price [1] (MSP/MT) of Briquettes Based on Three Coal Fines Costs (Wood Chips[2] @ $35/MT, Mixing Ratio: 90% Coal Fines/10% Hydrochar) 148

Table 47. Minimum Selling Price [1] (MSP/MT) of Briquettes Based on Three Coal Fines Costs(Wood Chips[2] @ $35/MT, Mixing Ratio: 70% Coal Fines/30% Hydrochar) 148

Table 48. Minimum Selling Price[1] (MSP/MT) of Briquettes Based on Two Mixing Ratios of Coal Fines and FHTC hydrochar (Wood Chips[2] @ $35/MT, Coal Fines @ $10/MT, Dry Basis.....149

Table 48. Minimum Selling Price[1] (MSP/GJ) of Briquettes Based on Two Mixing Ratios of Coal Fines and FHTC hydrochar (Wood Chips[2] @ $35/MT, Coal Fines @ $10/MT, Dry Basis.....149

ACRONYMS AND ABBREVIATIONS

5-HMF	5-(Hydroxymethyl) furfural
ASE	Accelerated solvent extraction
BDT	Bone dry ton
CO	Carbon monoxide
CO_2	Carbon dioxide
CWT	Changing World Technologies
DI	De-ionized (water)
DOE	U.S. Department of Energy
DRI	Desert Research Institute
DTPD	Dry tons per day
FHTC	Fast HTC
FID	Flame ionization detector
FTIR	Fourier transform infrared (spectroscopy)
GC	Gas chromatography
GC/MS	Gas chromatography/mass spectroscopy
GHG	Greenhouse gas
GTI	Gas Technology Institute
HC	Hydrocarbon
HHV	Higher heating value
HPLC	High performance liquid chromatography
HTC	Hydrothermal carbonization
HTP	Hydrothermal pre-treatment
IC	Ion chromatography
MS	Mass spectroscopy
NDIR	Non-dispersive infra-red
NI	National Instruments
NMR	Nuclear magnetic resonance (spectrometry)
NPOC	Non-purgeable organic carbon
NETL	National Energy Technology Laboratory
NVR	Non-volatile residue
PDU	Process development unit
pH	Measure of acidity in an aqueous solution
PID	Proportional integral derivative
P-J	Pinyon-juniper
PM	Particulate matter
REDD	Renewable Energy Deployment and Display (facility at DRI)
RI	Refractive index

RPM	Revolutions per minute
SEM	Scanning electron microscopy
SVOC	Semi-volatile organic compounds
TCD	Thermal conductivity detector
TGA	Thermogravimetric analysis
TIC	Total ion current
TOC	Total organic carbon
TSE	Twin-screw extruder
VOCs	Volatile organic compounds

EXECUTIVE SUMMARY

This project was carried out by the Gas Technology Institute (GTI), with a project team composed of GTI as the prime contractor and the Desert Research Institute (DRI) as a subcontractor. In addition, Parker Towing Company, Incorporated, an Alabama-based company with extensive experience in forestry, coal handling, and transport, supported the project as a significant cost share contributor and adviser.

This project commenced on October 1, 2010, and utilized equipment and research supported by the Department of Energy, National Energy Technology Laboratory, under Award Numbers DE-FE0005349, DE-FG36-0IGOl 1082, DE-FG36-02G012011 or DE-EE0000272. The project concluded on December 31, 2014

The overall objective of the project was to demonstrate and assess the economic viability of a novel technology based on the hydrothermal carbonization (HTC) of lignocellulosic biomass with hot compressed water that quickly (<1 minute) transforms any such biomass into a densified, friable fuel that has been shown to gasify like coal. In a novel Process Development Unit (PDU), the project team demonstrated and validated a novel Fast biomass Hydrothermal Carbonization (FHTC) technology based on twin-screw reactive extrusion (TSE) to create densified biomass fuels that equal the energy density of coal, gasify like coal, and create robust pellets and briquettes from coal/FHTC biomass mixtures that are infrastructure compatible with conventional coal handling, transport, and feeding equipment. This development provides a blended coal/biomass fuel that will significantly expand biomass utilization and introduce a new energy-dense, fossil carbon lowering fuel for commercially-available coal gasification equipment without the requirement for process or equipment modification.

To complete this project, the following tasks were carried out:

- Production, analysis, and characterization of HTC loblolly pine in a small (2L) batch-based laboratory Parr reactor and a larger batch-based, pilot-scale, PDU. Batch processing times range from one to five hours, depending on scale and process severity.
- Evaluation of the binding properties of HTC loblolly pine prepared at various levels of process severity to determine optimal processing conditions for creating robust pellets and briquettes of a blended coal/HTC biomass solid fuel product.
- Continuous, fast production of HTC (FHTC) loblolly pine in a novel TSE-based PDU developed and validated on previous DOE projects and shown to produce FHTC loblolly pine that was physically and chemically identical to HTC loblolly pine of similar severity produced by conventional batch-based HTC reactors.
- Design, construction, and incorporation of an online mixing stage downstream of the TSE-based PDU to facilitate mixing of FHTC loblolly pine with finely ground coal.
- Demonstration of online blending of finely divided bituminous coal and FHTC loblolly pine to form 90 wt. % coal/10 wt. % FHTC loblolly pine and 70 wt. % coal/30 wt. % FHTC loblolly pine mixtures of coal/HTC biomass with further processing by briquetting equipment to form robust, weather-resistant briquettes with the ability to withstand transportation and piling..
- Characterization of the coal-biomass pellets and briquettes made by direct extrusion of the 90/10 and 70/30 coal/FHTC biomass mixtures from the PDU to quantify their physical properties (e.g. flow properties, homogeneity, moisture content, particle size and

shape), bulk physical properties (e.g. compressibility, heat transfer and friability) and assess their suitability for use as fuels for commercially-available coal gasifiers.

- Completion of a techno-economic analysis using Aspen®-based process simulations to determine the costs for deploying and operating FHTC processing facilities for the ultimate production of robust coal/biomass fuels suitable for fueling commercially-available coal-fired gasifiers.

ACCOMPLISHMENTS

1. Background and Introduction

To address national concerns with respect to energy security, energy availability, and greenhouse gas (GHG) mitigation, it is of increasing interest to develop mixtures of biomass and coal that can be effectively utilized as fuel for combustion and gasification. Therefore, an economical technology is needed that can quickly transform any form of lignocellulosic biomass into a densified fuel that gasifies and combusts like coal, can be easily blended with coal, and after blending can be formed into robust, weather-resistant pellets and briquettes. Numerous biomass feedstocks can be considered, each with varying degrees of inherent moisture, morphology (size and shape), and composition. These feedstocks exhibit significant differences in their handling characteristics, energy content, and recalcitrance to comminution and thermochemical conversion, all of which are factors that must be accommodated within a context where biomass is combined with coal to produce a uniform, acceptable fuel that requires minimal process modifications when substituted for coal. It is of particular interest to develop biomass/coal blends containing up to 30% biomass material that can be utilized with existing infrastructure for coal handling, storage, and use.

In most cases, it is necessary to pretreat raw biomass to ease handling and assure uniform chemical and physical properties before use in a biochemical or thermochemical conversion process. The diversity of physical shapes, densities, and other handling properties among different forms of biomass creates significant challenges in feeding these materials into gasification, pyrolysis, and combustion processes. Biomass pretreatment also densifies the material in terms of mass density (kg/m^3) and energy content (kJ/kg). Raw lignocellulosic biomass typically contains about 40% oxygen (dry basis), which contributes nothing to its energy content. Thus, one desired result of a pretreatment process is the reduction of oxygen content, thereby increasing overall energy content.

Pretreatment also improves the handling, transportation, and storage of thermochemical feedstocks. Certainly, diversity of sources (forest thinnings, agricultural residues, energy crops, etc.), and the seasonal availability of some biomass, introduce logistical and supply challenges. These problems can be mitigated by pre-treatment processes that convert raw lignocellulosic material into a densified biochar that is more easily transported and stored. Our overall interest in the pretreatment of lignocellulosic material is the enhancement of its suitability for use as a solid feedstock for subsequent combustion, gasification, soil amendment, and carbon sequestration.

Presently, there are two major paths for biomass pretreatment: torrefaction and hydrothermal carbonization (HTC). Both processes produce solid char products having similar external appearance. Either process may be able to prepare a more or less universal fuel from virtually any form of lignocellulosic biomass. Torrefaction is a mild pyrolysis of biomass that is carried out at atmospheric pressure in an inert atmosphere, usually at temperatures between 230 – 300 °C, with residence times extending from 10 minutes to several hours.[1-3] Lower temperatures require longer processing times. Under these conditions, the hemicellulose fraction of wood decomposes into CO_2, H_2O, CO, acetic acid, methanol, furans, and hydrocarbon tars (similar to those produced in biomass gasification) so that a carbon-rich solid (torrefied wood) and volatiles are formed. Torrefaction avoids the problems associated with feeding and handling of diverse forms of raw biomass by improving grindability and increasing the energy density of the biomass

from 17-19 MJ/kg to 19-23 MJ/kg. Experiments with torrefied wood have shown that the grinding energy is reduced by 50-80% when compared to raw biomass.

Hydrothermal carbonization (HTC) involves treatment of raw biomass materials in a hot, pressurized, aqueous environment. In recent years, HTC of woody biomass has been investigated by several groups, with the objective of transforming the material into a more suitable feedstock for subsequent thermal conversion processes such as gasification and combustion.[4-8] At first glance, products of the HTC process appear visually similar to biomass that has been subjected to mild pyrolysis or torrefaction. This has led some researchers to refer to HTC as "wet torrefaction," however, this oversimplification is incorrect.[9,10]

The char produced by the HTC process is known by several terms - including biochar, biocoal, HTC-char, and others. However, to avoid confusion with other processes and products, the term "hydrochar" is used here, as recommended by Libra et al.[11] While hydrochar is typically viewed as a solid biofuel, it has been investigated in several other applications including catalysis,[12] water purification, [13-15] carbon sequestration,[16] soil amendment,[17-19] and other uses.

Both torrefaction and HTC are useful pre-treatment methods for converting a diverse range of biomass feedstocks into a more homogeneous and 3energy-dense form, suitable for subsequent thermochemical processing. This energy densification is achieved principally by removal of oxygen from the lignocellulosic structures through a variety of hydrolysis, dehydration, and decarboxylation reactions - resulting in a solid having significantly higher carbon content than the starting feedstock.[20]

Typical HTC process temperatures are 200-300 °C and reaction times vary from a few minutes to several hours.[7,11] As with torrefaction, a friable solid char product is produced by HTC, called hydrochar, that has substantially increased energy content, compared to raw biomass.[9,21] Depending upon process conditions, hydrochar contains approximately 55-90% of the original biomass feedstock dry mass, and 75-95% of the original fuel value. In addition to the solid hydrochar product, as opposed to torrefaction, the HTC process produces gases (mainly CO_2) and a wide variety of water-soluble organic products, including sugars, organic acids, furans, furfurals, etc. A significant advantage of HTC over torrefaction is its inherent accommodation of wet feedstocks, thus avoiding the complexity and costs of pre-drying the raw lignocellulosic biomass. Several excellent reviews of the HTC process are available in the literature.[7,8,6,11]

Pelletization is commonly used to increase the mass and energy density of biomass. In addition, the uniform shape and size of pelletized biomass improves handling and storage, and reduces transportation costs. However, raw biomass pellets have relatively low energy content, as compared to coal, and exhibit very poor water tolerance. These problems can be partially overcome by torrefaction, which involves mild pyrolysis conducted in an inert atmosphere.[22-24] However, while torrefied biomass is somewhat hydrophobic, and has a higher energy density compared to raw biomass, it is quite friable and can create a dust hazard when handled. As opposed to hydrochar, torrefied biomass is challenging to pelletize without the addition of an external binder material.[25-29] On the other hand, hydrochar produced by the HTC process is strongly hydrophobic, and requires no binder to produce robust, water-resistant pellets.[30,31]

2. Project Objectives

The overall objective of this work was to demonstrate and assess the economic viability of a novel, rapid technology based on HTC treatment of lignocellulosic biomass to quickly transform (<1 minute) any such biomass into a densified, friable fuel that has been shown to gasify like coal, can be easily blended with ground coal and coal fines, and then be formed into robust, weather-resistant pellets and briquettes. These pellets and briquettes are meant to be rugged enough to withstand transportation and piling, and to possess an average Hardgrove grindability index (HGI) of 50 or greater for processing this material into a pulverized product. Specific goals of the overall project included the following:

- Utilize HTC technology and facilities developed under other DOE Cooperative Agreements (DE-FG36-01GO11082, DE-FG36-02GO12011, and DE-EE0000272) to produce a densified, uniform feedstock from Loblolly pine (a lignocellulosic, short rotation woody crop). This hydrothermally pretreated feedstock has been shown to chemically resemble coal and gasify like lignite.
- Combine the hydrochar produced from Loblolly pine with finely divided bituminous coal to form a uniform coal/biomass mixture containing 10% by weight dry biomass and another mixture containing 30% by weight dry biomass. From the two coal/biomass mixtures, form robust, weather resistant pellets and/or briquettes (stable forms suitable for transportation and storage).
- Characterize the coal-biomass pellets and briquettes to quantify their physical properties (including flow properties, homogeneity, moisture content, particle size, shape, and bulk physical properties including compressibility, heat transfer, and friability) and assess their suitability as fuels for commercially-available coal-fired gasifiers.
- Using Aspen-based process simulations, perform techno-economic analyses to determine the costs for deploying and operating HTC processing facilities for the ultimate production of robust coal/biomass fuels suitable for fueling commercially-available coal-fired gasifiers.

3. Project Activities

3.1 Overview

Gas Technology Institute (GTI) and its subcontractor, the Desert Research Institute (DRI) carried out the technical efforts described in this report. These technical efforts are briefly summarized below, with more detailed descriptions that follow. Note that in this project only loblolly pine was subjected to HTC, primarily because of its wide availability in the Southern US. Therefore, HTC biomass is synonymous with HTC loblolly pine.

First, using small laboratory-scale batch HTC reactors and later, a much larger batch process development unit (PDU), DRI determined optimal HTC processing conditions for processing loblolly pine, and then investigated the pelletization of the resulting hydrochars – both alone and blended with bituminous coal.[32] This was an extensive effort that provided a thorough understanding of the HTC process and the propensity of HTC biomass for pelletization with itself and coal.

Second, in a parallel effort, GTI utilized and modified a novel PDU for the fast production of HTC (FHTC) biomass that is based on a twin-screw extruder (TSE). This PDU was developed on two previous DOE Cooperative Agreements (DE-FG36-01GO11082, DE-FG36-02GO12011) and in this project was modified to permit FHTC loblolly pine produced by this PDU to be mixed with pulverized coal for subsequent briquetting and characterization. Two biomass-coal mixtures were prepared. The first mixture was composed of 10 wt. % FHTC biomass and 90 wt. % pulverized coal and the second mixture was composed of 30 wt. % FHTC biomass and 70 wt. % pulverized coal. Multiple batches of each mixture were prepared: First, trial "off-line" mixtures were made where FHTC biomass was produced, set aside, manually mixed with pulverized coal, dried to various levels of moisture, and then briquetted. Then, after the mechanics of FHTC biomass production, mixing with coal, drying, and briquetting were understood and quantified, "on-line" mixtures were prepared and briquetted. In on-line mixing, FHTC biomass was made, mixed with pulverized coal in a heated twin-screw mixer, dried (if necessary) and briquetted. Briquettes of both types and mixtures were characterized.

When the FHTC PDU was operated to produce FHTC biomass for on-line briquetting, DRI visited GTI's facilities and carried out sampling activities to thoroughly characterize the solids, liquids, and gases produced in the FHTC process. The results of these measurements and simultaneous process measurements for the FHTC PDU provided process information that was essential for informing a techno-economic analysis of the production of FHTC biomass/coal briquettes which was the final technical task for this project.

3.2 Tasks

In the order of their execution, the technical tasks that comprised this project included:

1. HTC Operating Condition Optimization for Pellet Formation
2. Characterization of Pelletized HTC Process Solids/Extractables with Coal
3. PDU Modification for Online Coal/HTC Biomass Fuel Production
4. Forming & Characterization of Coal/HTC Biomass Briquettes
5. HTC Biomass and Offline Briquetting/Characterization
6. HTC Biomass and Online Mixed Fuel Production/Characterization
7. Economic Feasibility and Assessment of Environmental Impacts

The first two tasks were carried out mainly by DRI, with the remaining five tasks carried out mainly by GTI, with analytical and testing assistance provided by DRI. In addressing Project Tasks 1 and 2, DRI focused primarily on defining optimum process conditions for the preparation of HTC lignocellulosic biomass by batch-based processes, characterizing the products resulting from batch-based HTC process, and studying the pelletization properties of hydrochar and hydrochar blended with coal. In subsequent tasks, continuous HTC production by the GTI Fast HTC process (FHTC biomass) is addressed. First, in Task 3, to show that FHTC biomass is physically and chemically the same as HTC biomass produced by batch processes, particularly when pelletized and briquetted with coal. Tasks 4 through 6 address the briquetting of FHTC biomass with pulverized coal and this report concludes with Task 7, a techno-economic analysis of the production of coal/FHTC briquettes.

Note that while Tasks 1 and 2 address the HTC of a variety of pine and coniferous biomass, Task 3 and subsequent tasks address only the FHTC of loblolly pine, per project requirements.

3.2.1 Task 1: HTC Operating Condition Optimization for Pellet Formation

To carry out this task, DRI developed and deployed a small, laboratory-scale, batch-based reactor system to define an envelope of optimal process conditions for the HTC treatment of Loblolly pine feedstocks. This batch-based process development unit (PDU) is meant to treat 2-3 kg of raw biomass within a single run – a scale sufficient to investigate the effects of process parameters (temperature and time) upon product quality and composition, but not large enough to produce samples for mixing with coal and assessing the properties of such mixtures.[32]

Products resulting from HTC treatment of lignocellulosic biomass were characterized using a variety of standard and advanced analytical methodologies developed on previous DOE-supported projects. Substantial characterization efforts were devoted to defining the chemical and physical properties of the solid hydrochar product. Energy contents of all solid products were determined by calorimetry. Proximate and ultimate analyses were carried out, and complete mass balances were determined for each biomass feedstock when subjected to various HTC process conditions.

In Task 1, DRI's technical efforts were focused primarily on defining optimum HTC process conditions for treating lignocellulosic biomass using the DRI batch-based PDU, characterizing the products resulting from producing HTC biomass in the PDU, and investigating the pelletization properties of this HTC biomass. We begin with a description of the DRI PDU and the comparison of HTC biomass produced by this PDU with HTC biomass produced in small-scale Parr Reactors.

Development and Use of DRI's PDU

With funding from previous DOE contracts (DE-EE0000272 and DE-0003248), a laboratory-scale, semi-continuous PDU was fabricated and installed in the Workshop of DRI's Renewable Energy Deployment and Display (REDD) Facility. However, considerable additional efforts were required in this project to improve operational features – especially temperature control, auger control, and data acquisition/processing – and to develop ancillary equipment and processes to support operation of the PDU. These efforts are summarized below, but are described in more detail in a recent publication.[32]

Design and Fabrication of the DRI PDU: The laboratory-scale PDU operates with hot compressed water under sub-critical conditions – typically 200-300 °C. To avoid complications of feeding biomass across a large pressure gradient, the feeding assembly and the solid product receiving assembly operate at the same pressure as the reactor. The reactor vessel itself is temperature controlled. Inclined augers are used to convey the biomass material through the reaction zone where it is contacted with hot compressed water. After exiting the reactor vessel, the wet product is deposited into a cooled collection vessel. This system permits characterization of material produced at different times throughout a single pretreatment experimental run. The reactor system is also designed to allow for periodic collection of gas and water samples during operation.

A schematic of the PDU showing locations of heating zones, thermocouple ports, disconnect points, and sampling points is shown in Figure 1. The main pressure vessel portion of the PDU was fabricated by Custom Metalcraft of Springfield, MO. The vessel was built and certified to

operate at pressures up to 1300 psi. The tubular portion of the PDU was constructed of Schedule 80, 316 stainless steel pipe. 4-in. IPS diameter pipe was used for the inclined auger sections; 6-in. IPS diameter pipe was used for the accumulator vessel. The pressure-disconnect joints used for loading, unloading, and cleaning the system were obtained from Grayloc Products of Houston, TX.

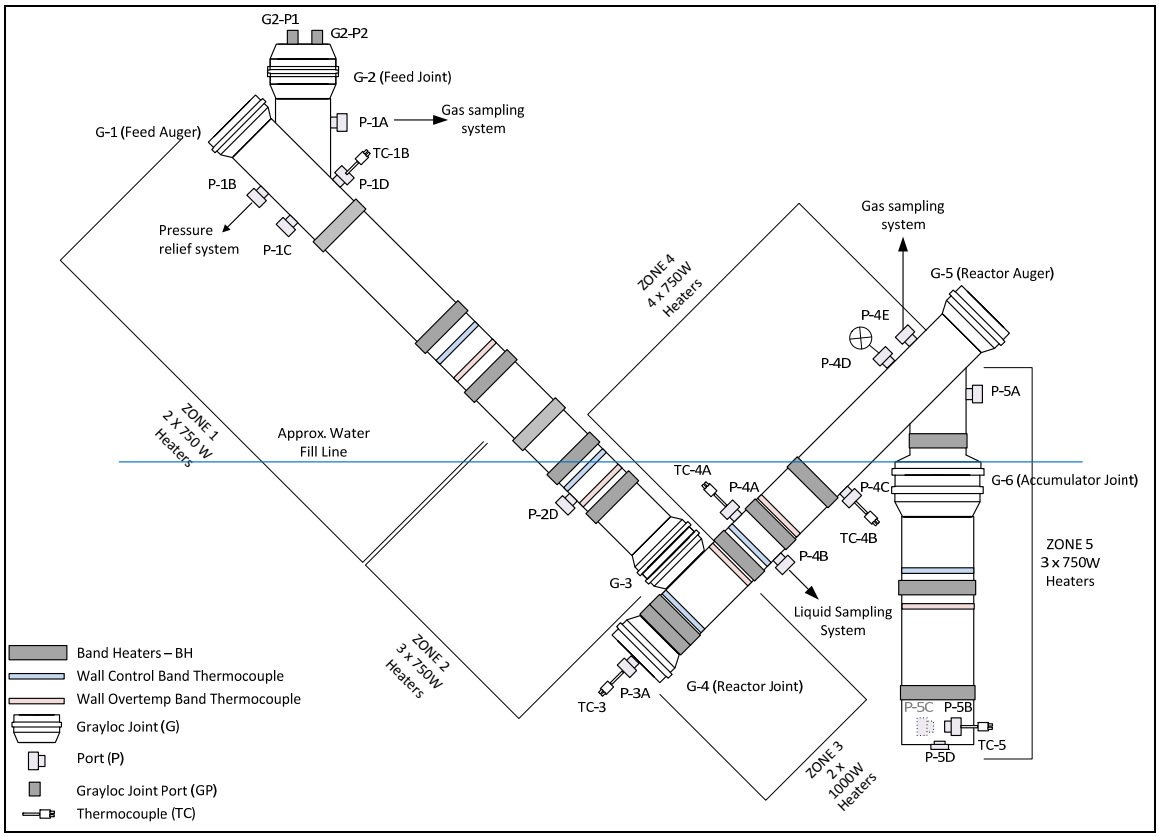

Figure 1. Schematic of PDU showing heating zones, ports, fittings, and sampling locations. (Drawing not to scale.)

Once the pressure vessel was received from the manufacturer, it was assembled at DRI, attached to a steel frame, and installed in the Renewable Energy Deployment and Display (REDD) facility. Photos of this assembly and installation are shown in Figure 2.

Two augers are used to convey the feedstock (raw wood chips) into the reaction zone containing hot, pressurized water, and convey the solid hydrochar product out of the reactor zone and into the accumulator vessel. The feed-side auger is 8-ft. in length; the product side auger is 5-ft. in length. Both augers are operated with Dayton ½ HP, 90 V permanent magnet DC motors and variable speed DC controls.

As shown in Figure 1, the PDU was divided into five independent temperature zones. Each zone was heated by electric band heaters from the Tempco Electric Heater Company of Wood Dale, IL. Both 750-W and 1000-W band heaters were used. Each of the five temperature zones was monitored and controlled by means of band thermocouples, internal thermocouples, and a National Instruments LabView-based monitoring and control system. Some of the hardware used in monitoring and control of the PDU is shown in Figure 3.

Figure 2. Location and fabrication of DRI's PDU: (A) Outside view of DRI's REDD Workshop, which houses the PDU, (B) frame for holding reactor, (C) PDU mounted on frame, (D) close-up of heating band.

At DRI, gas and liquid sampling systems were fabricated to enable collection of hot, pressurized samples during operation of the PDU. The gas sampling system consists of a 1-L Parr pressure vessel connected to the top of the PDU at Port P-1A through ¼ inch stainless steel tubing. Opening a high pressure valve in the sampling line allows gaseous products from the PDU to enter the 1-L collection vessel. The liquid sampling system consists of a 150-mL cylindrical pressure vessel (Swagelok 316L 500 F4-150), with high pressure valves on both ends. This vessel was connected to the PDU at a port located in Zone 4, partway up the reactor auger, at a point that was expected to always be beneath the water level (Port P-4B in Figure 1). Photos of the gas and liquid sampling systems are provided in Figure 4. CAD drawings and other details of these sampling vessels (and the rest of the PDU) are provided in a recent publication. [32]

Feedstock Sorter: As part of a student project, a simple, manually operated system was built for sorting raw loblolly chips. This sorter consisted of two screens/grates of different sizes mounted within a conventional, 35-gallon aluminum garbage can. Over-sized material does not pass through the top screen, while very small material passes through both screens and is removed. By proper sizing of these two screens, wood chips having the desired size range are isolated. Schematics and photos of this wood chip sorter are included in Figure 5 and Figure 6.

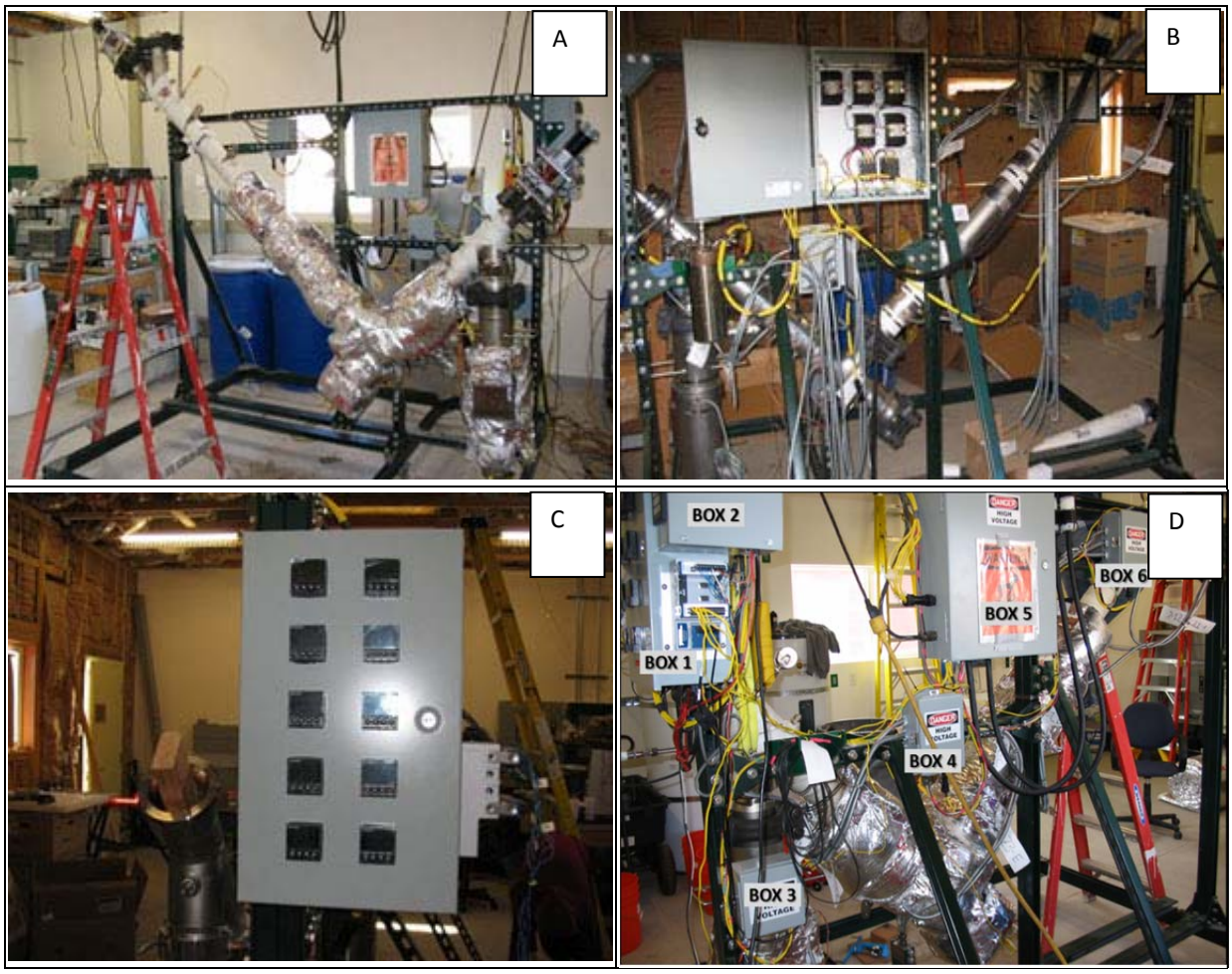

Figure 3. Control system of PDU: (A) Assembled unit with heaters, auger motors, and insulation installed, (B) solid state relays for heating bands, (C) PID temperature controllers, (D) control boxes for power control, heater relays, heater control, and auger frequency converter.

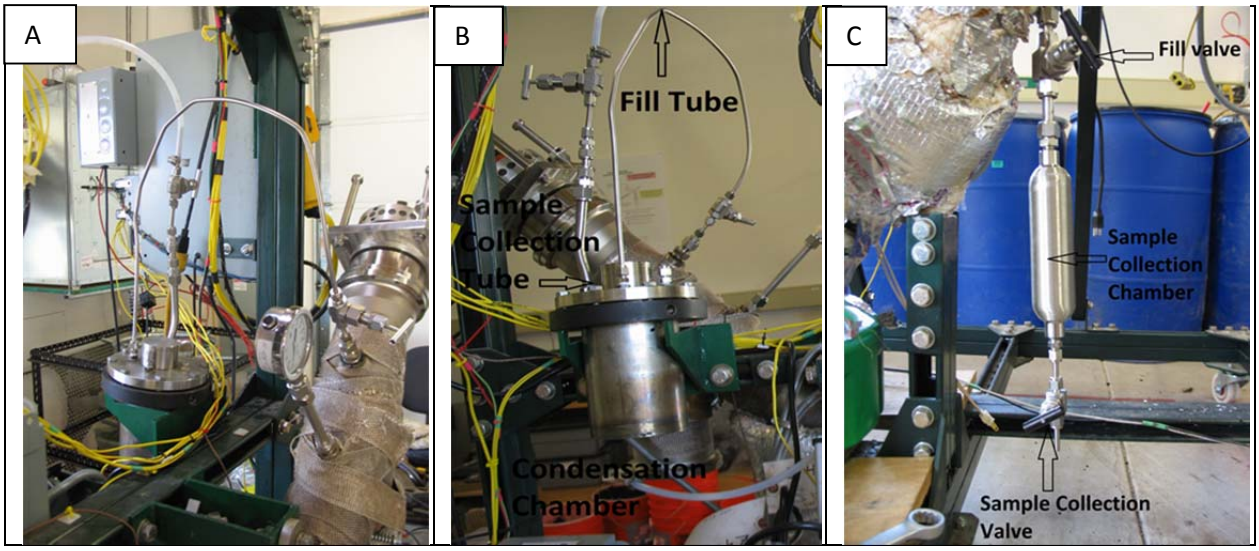

Figure 4. Photos of PDU gas sampling system (A) and (B) and liquid sampling system (C). Ancillary Equipment for Support of the PDU

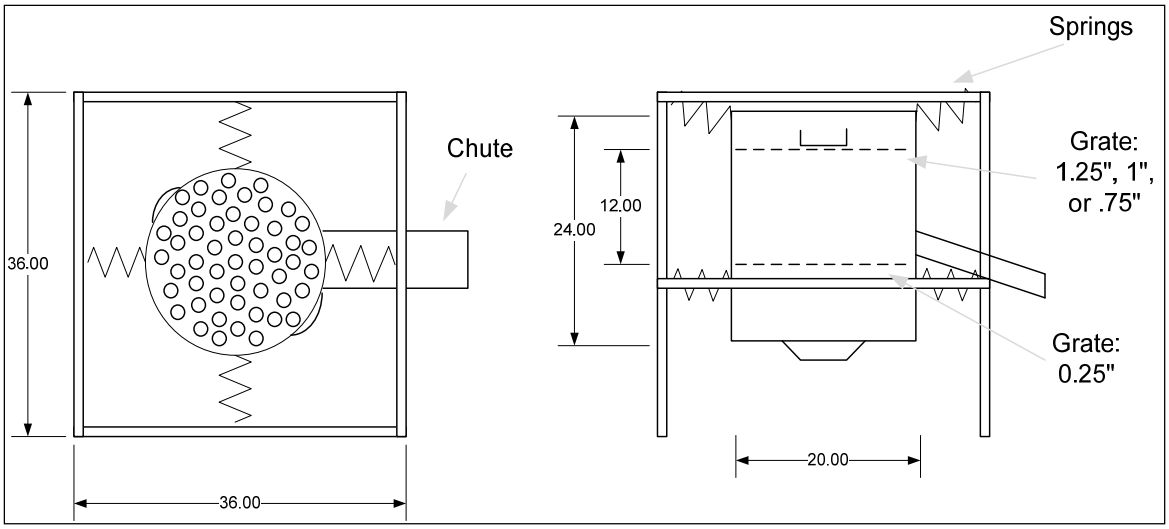

Figure 5. Top (left) and side (right) schematic views of wood chip sorter.

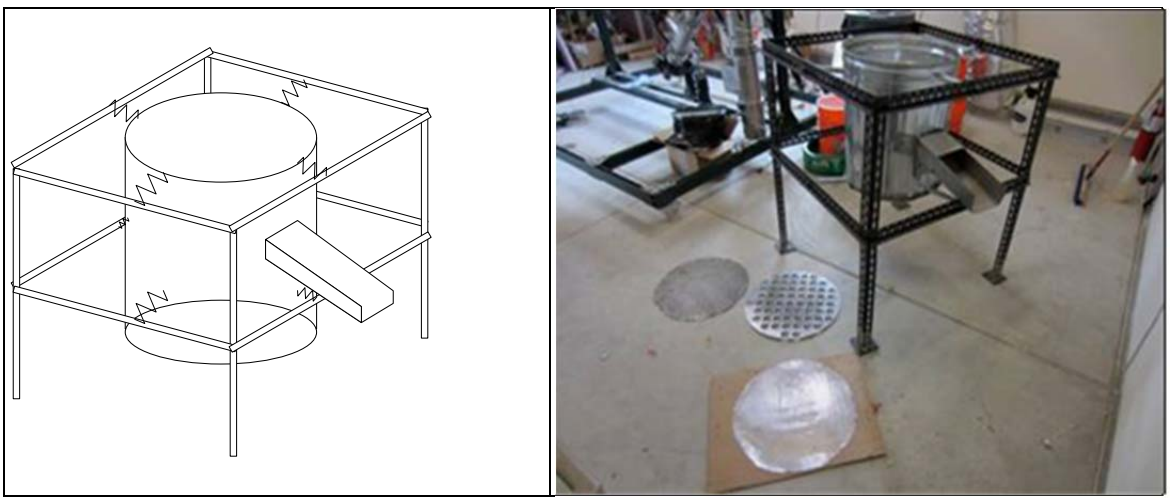

Figure 6. Schematic (left) and photograph (right) of wood chip sorter.

Water/Solid Separator: Following completion of an HTC experiment in the PDU, the produced hydrochar is retained in the collection vessel, along with condensed water. To isolate the hydrochar, the collection vessel (also called accumulator) is emptied into a strainer that allows the liquid to pass through, while retaining the hydrochar on a screen. A photo of this water/solid separator is provided in Figure 7.

Figure 7. Sieve for separating solid and liquid products.

Solar Oven for Drying Hydrochar: From each operation of the PDU, 1-2 kg of hydrochar is produced. To effectively dry this amount of product requires a sizable oven. For this purpose, we designed and built a solar oven to utilize hot air that is available within the REDD facility. Figure 8(A) provides a schematic of this indirectly heated

oven. The oven was permanently installed in a convenient location within the REDD, as shown in Figure 8(B). The performance of the oven was demonstrated by drying actual samples of hydro-char and by measuring temperature profiles over extended time periods. By these means, it was determined that over-night drying of the hydrochar is sufficient to produce a material that can be stored at room temperature without observable molding or other deterioration.

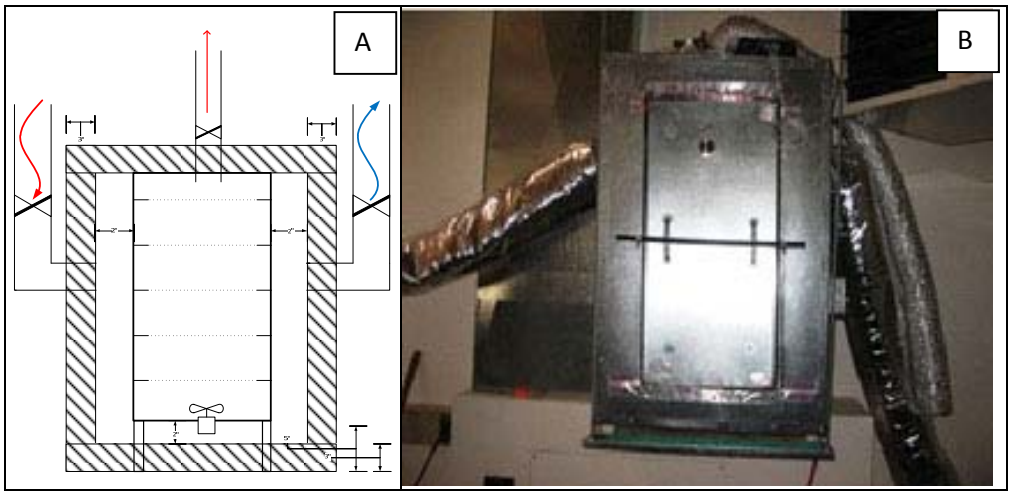

Figure 8. Solar oven for drying hydrochar produced in the PDU. (A) Schematic of indirectly-heated oven. (B) Photo of oven installed in the DRI REDD Facility.

Pellet Press and Die: A Carver bench top laboratory press Model M (Menomonee Falls, WI) was obtained and used to produce pellets from raw and hydrotreated biomass materials. Photographs of this press, located within a DRI laboratory, are shown in Figure 9. The photo on the right provides a close-up view of a pressure gauge that was installed on the press to provide more accurate determinations of hydraulic pressure (Wika Instruments Model 232.34, 0-5000 psi). Use of this pressure gauge provided better control of the pelletization process, thereby improving the uniformity of produced pellets.

Figure 9. Carver Laboratory Press Model M, with Wika Model 232.34 pressure gauge.

Production of satisfactory pellets requires that the solid material be heated while being compressed, so that the binder (either natural or added) becomes fluidized, causing more effective adhesion of the particles. To produce pellets in the DRI press, a 13-mm diameter, hardened steel heated die (Across International, Berkeley Heights, NJ) was purchased, along

with an Omega bench top temperature controller (Model CSC32J) and Omega thermocouple (type J iron-constantan). Photos of this equipment are shown in Figure 10

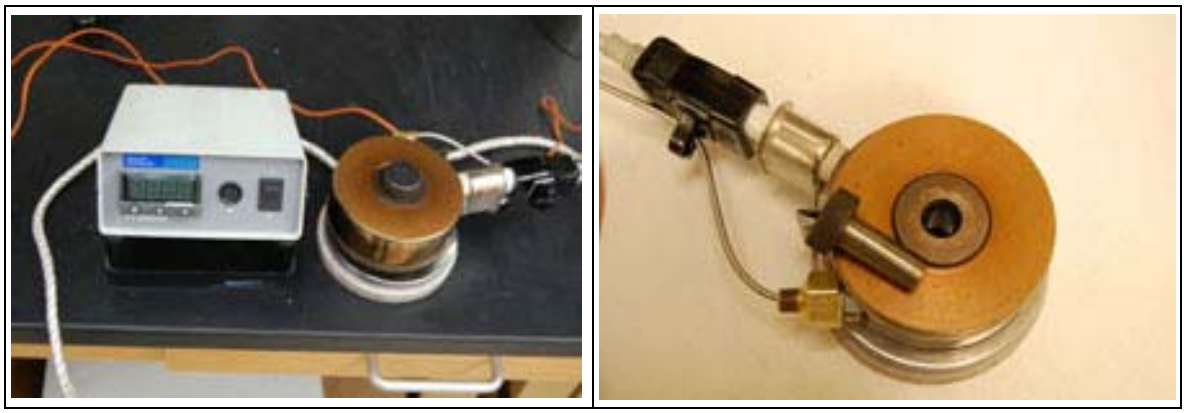

Figure 10. Across™ heated die with temperature controller.

The heated die system used to create pellets consists of a 13 mm diameter die with an electric heating element, support plate, core dies, thermal insulator plate, push rod, and pellet ejector. Schematics of this die system (taken from the Across™ website) are provided in Figure 11. To produce a pellet, the die is first heated to the desired temperature (usually 140°C). The die is placed on its support plate base, and a steel core die is inserted from the top. Approximately 1 g of hydrochar (or other material to be pelletized) is then added on top of the core die. The push rod is inserted and the die assembly is placed on the press. (A photo of the entire heated die assembly on the press is shown in Figure 12.)

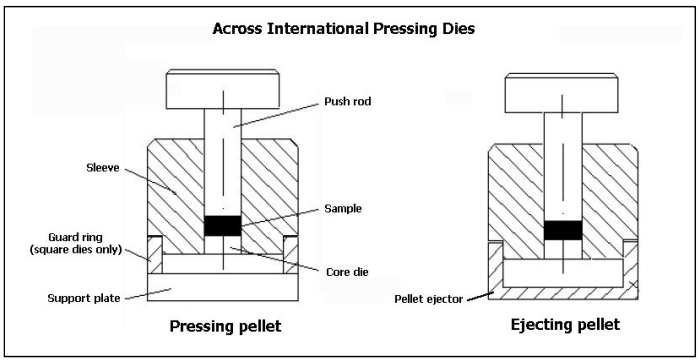

Figure 11. Schematic of Across™ heated die.

Figure12. Carver Pellet Press with heated die and controller.

Optimizing PDU Operating Conditions

The handle of the press is manually depressed while watching the pressure gauge. A hydraulic pressure of 20 MPa is attained and held for 60-seconds. (With a piston diameter of approximately 50 mm, and a pellet diameter of 13 mm, 20 MPa hydraulic pressure translates to approximately 295 MPa on the surface of the pellet.) The pressure is then released and the die assembly is removed from the press. The die body is removed from the support plate base and is placed on the pellet ejector base. This assembly is then placed back on the press, and gentle pressure is applied to the push rod until the pellet is ejected out the bottom. Raw, woody biomass that is chipped to approximately ¼ - ½ inch size is treated in a "batch-continuous" process using the custom-designed PDU described above. Before loading the unit with feedstock, the accumulator vessel is filled about ¾ full with approximately 10 kg of water. The starting biomass feedstock (of known mass and moisture content) is hand-fed into the feed port at the top (G-2, Feed Joint) of the unit. Approximately 2-3 kg of biomass is introduced while periodically activating the feed auger to completely fill the feed side of the PDU. Approximately 12 kg of hot water is added into the feed auger on top of the raw biomass, which mostly fills Zones 2, 3, and 4 of the PDU. The reactor is then sealed and the electric heating bands are activated.

Heating of the PDU is accomplished by individual control of 5 separate zones. The placement of all 14 heating bands is illustrated in Figure 13. Each heating zone is instrumented with an internal thermocouple whose output is continuously monitored using a National Instruments (NI) LabView® data acquisition program. Each zone is also instrumented with a band thermocouple to monitor and control the external wall temperature. An over-temperature set point is programmed for each heating zone to prevent excessive temperatures of the outer wall of the pressure vessel. The temperature setpoints for each of the five heated zones were determined by experience, with a desire to minimize the heat-up time of the reactor while avoiding over-heating in any zone. The Zone 4 setpoint was identical to the desired reaction temperature, Zone 1 was set at 275 °C, Zones 2 and 3 were set at 300 °C, and Zone 5 was set at 180 °C.

The reactor temperature is somewhat difficult to define. Within the PDU, temperature is measured at 5 different locations, identified as "TC-1" to "TC-5" in Figure 13. However, there is considerable variation among these 5 temperature measurements. Even the two thermocouples that are submerged within the reaction zone (TC-4A and TC-4B) indicate somewhat different temperatures. Consequently, reactor temperature is defined to be a calculated value, based upon measured pressure. A pressure transducer located in port 5A (just above the accumulator vessel) is used as the basis for the temperature calculation, according to the Antoine equation:

$$\log_{10} P = A - \frac{B}{C+T} \text{ , which solving for temperature gives: } T = \frac{B}{A - \log_{10} P} - C$$

In these equations, P = pressure; T = temperature; A, B, and C are component-specific constants. In calculating the PDU reaction temperature, specific constants for water are used for A, B, and C. However, in the HTC process, other gases (primarily CO_2) are produced. Consequently, the pressure at a given temperature is slightly higher than it would be without these gaseous products, and the calculated temperature is thus overestimated to a small extent. (With earlier HTC experiments using a 2-L Parr pressure reactor, we typically measured pressures that exceeded the calculated saturated steam pressure by 25-50 psi at reaction temperatures of 255°-

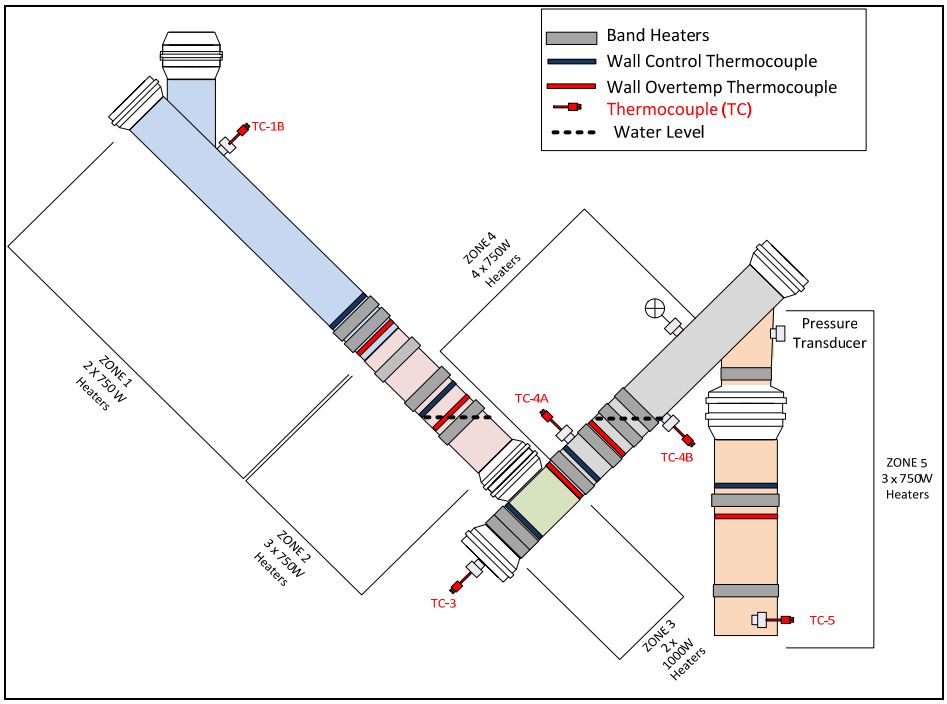

Figure. 13 PDU schematic showing locations of thermocouples, heaters, and water level. (Drawing not to scale.)

275°C.) However, given the non-homogeneity of temperature within the PDU, this method of calculating a reaction temperature is believed to be the most practical and repeatable approach.

Once the PDU internal temperature reaches the set point temperature (typically from 80-120 min., depending upon the desired temperature), the reactor and feed augers are activated. The biomass is moved through the reaction zone and into the accumulator, which is maintained at a cooler temperature to "quench" the reaction. The biomass residence time within the reaction zone (when the augers are running at full speed) was measured at approximately 6 minutes. After the augers have been running for 15 minutes, the heaters are turned off, and the system is allowed to cool overnight, with the augers still running for another 20 min.

Figure 14 shows a set of temperature traces from a typical PDU experiment. This illustrates the widely varying temperatures at different locations within the PDU. For example, temperatures measured by thermocouples 4A and 4B, both located in the reactor auger section of the PDU (Zone 4), increase rather quickly (black and grey lines in Figure 14). In contrast, the temperatures measured by thermocouple 3, located at the lowest point of the auger system (Zone 3; green line in Figure 14) increase very slowly. Heating at the top of the feed auger (Zone 1; thermocouple 1B; blue line) is intermediate between that of Zone 3 and Zone 4. The temperature at the bottom of the accumulator vessel (Zone 5; thermocouple 5; orange line) only increases slightly throughout the entire run. The calculated internal reactor temperature is shown by the red line in Figure 14. For this experiment, it took about 110 minutes to reach the desired reaction temperature. This temperature was then maintained for 15 min. before turning off the heaters, which was followed by a long cool-down period – typically overnight.

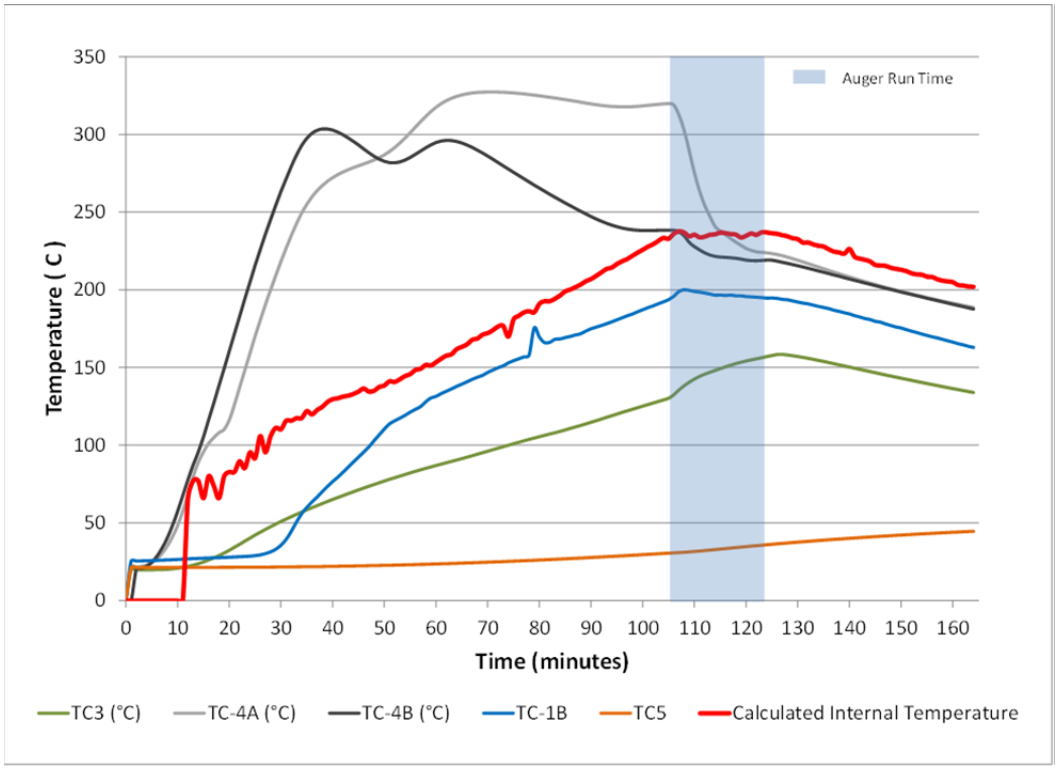

Figure14. Temperature monitoring and control of PDU (235 °C reaction temp. run).

2 x 2 Experimental Matrix: To demonstrate satisfactory operation of the PDU, a 2 x 2 matrix of HTC experiments was conducted using Slash Pine micro-chips as feedstock. (Micro-chips are approximately ¼ - ⅜ in. size.) In these experiments, the reactor temperature and auger speed were varied as shown in Table 1.

Table1. Matrix of PDU Experiments

Run No.	Feedstock Dry Mass, kg	Reactor Temp., °C	Auger Speed
1512	2.615	235	Slow
1513	1.787	235	Fast
1514	2.112	275	Slow
1515	1.371	275	Fast

Auger speed is related to reaction time, although it was not possible to define a precise reactor time that corresponds to a particular speed. Previous experiments were conducted to determine approximate transit time for wood chips to pass through the entire PDU and reach the accumulator vessel used to collect the hydrochar product. This showed that a "slow" auger speed corresponded to a transit time of about 12 minutes, while a "fast" auger speed corresponded to a transit time of about 6 minutes. The actual HTC reaction time would be somewhat shorter than this, because the feedstock is submerged in the hot, pressurized water for only a fraction of this total time.

After each of these 4 experiments, the PDU was allowed to cool overnight. The following day, the reactor was vented to release gaseous products. A port at the bottom of the unit (P-3A) was opened to drain out most of the water. Then the accumulator was removed, and its contents were filtered to recover the hydrochar product. Additional hydrochar was recovered by running the reactor auger in reverse, and collecting the solid material that fell out the bottom of the reactor. Following this, the feed auger was activated, and additional solids that fell out the bottom of the reactor were collected. The PDU was left in an open configuration for at least 24-hours, allowing the inside to completely dry out. This drying released a small amount of hydrochar that had adhered to the auger and reactor walls. Compressed air was used to blow this material out the bottom of the reactor. Thus, at the end of each experiment, the total hydrochar was collected in four fractions. Photos of these four fractions are provided in Figure 15. The mass recovery and the energy content of each fraction are shown in Table 2.

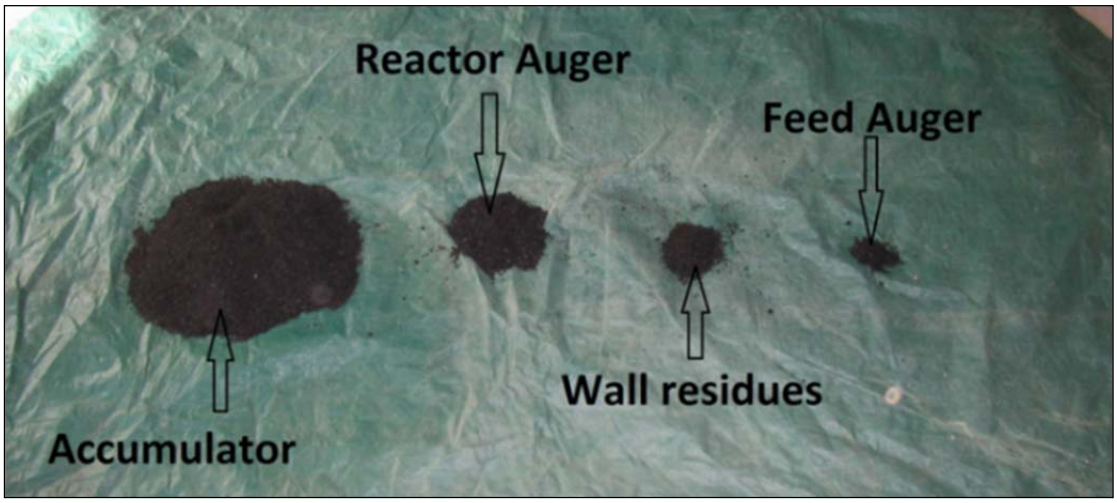

Figure 15. Four hydrochar fractions recovered from HTC experiment in PDU.

These results demonstrate that most of the recovered hydrochar was obtained from the accumulator, although a significant amount was also obtained from the reactor auger. Relatively little char was obtained from either the feed auger or the wall residues. Expected differences were seen between chars produced at low and high temperatures. At higher temperatures, total recovery of hydrochar was reduced, but the energy content of the hydrochar was increased.

Table 2. Hydrochar Recovery from PDU Experiments with Slash Pine Micro-Chips

Hydrochar Fractions	235° Reactor Temperature				275°C Reactor Temperature			
	Slow Augers		Fast Augers		Slow Augers		Fast Augers	
	Mass %	Energy , MJ/kg	Mass %	Energy, MJ/kg	Mass %	Energy, MJ/kg	Mass %	Energy, MJ/kg
Accumulator	52.50	22.79	49.00	22.28	40.10	28.43	35.40	28.67
Reactor auger	13.10	24.63	10.40	24.98	10.40	28.62	15.10	28.54
Feed auger	0.40	24.95	0.10	24.74	0.20	28.96	1.60	28.23
Wall residues	3.70	23.12	1.40	24.49	2.90	27.86	2.10	26.93
Total Recovery	69.70		60.90		53.60		54.20	

Note: Energy content of starting feedstock was 20.2 MJ/kg

These results demonstrate that most of the recovered hydrochar was obtained from the accumulator, although a significant amount was also obtained from the reactor auger. Relatively little char was obtained from either the feed auger or the wall residues. Expected differences were seen between chars produced at low and high temperatures. At higher temperatures, total recovery of hydrochar was reduced, but the energy content of the hydrochar was increased.

The total mass recoveries of 61-70% at 235°C and 53-54% at 275°C agree well with results obtained in earlier HTC experiments with woody biomass using a small (2-Liter) Parr pressure reactor. Similarly, the energy contents of 22-24 MJ/kg at 235°C and 27-29 MJ/kg at 275°C are in good agreement with values obtained in these previous Parr reactor experiments. This provides confidence that the PDU represents a realistic scale-up of the Parr reactor experiments, and that the HTC results obtained using other feedstocks in the Parr reactor are transferrable to the PDU.

No consistent effects of auger speed were observed in these reactions. Total hydrochar recovery was higher using the slow auger speed at 235°C, but not at 275°C. Also, the energy contents of each char fraction were very similar between the two speed conditions. Thus, it appears that the effects of auger speed (or biomass residence time) are small in comparison to the effects of reaction temperature.

The results in Table 2 show little variation in energy content among the four hydrochar fractions obtained from a single PDU experiment (especially at the higher temperature condition). Based upon this, it was concluded that all four hydrochar fractions from a single experiment within the PDU could simply be combined and characterized together. This greatly simplifies sample handling logistics and minimizes laboratory expenses.

Although the PDU was designed to enable collection of hot pressurized gases during operation, our initial attempts at gas sampling were largely unsuccessful. We attempted to collect hot gases immediately following the end of the PDU run by opening Port 4E, which is located near the top of the reactor auger (see Figure 1). High pressure tubing and valves were used to connect this port to a 1-L Parr pressure vessel that served to collect the pressurized gas sample. After cooling the gas sampling vessel, it was opened through another port, connected to a Tedlar bag, for collection of permanent gases.

Two problems with this gas sampling approach were encountered. First, in most cases, the Parr sampling vessel nearly completely filled with liquid, leaving very little permanent gas, but considerable water that entered the Tedlar bag. Second, significant amounts of tars were volatilized and/or solubilized in the steam that was vented from the PDU and collected in the 1-L Parr vessel. After cooling, these tars solidified, coating the surfaces of the Parr vessel, and presumably, the pressurized lines and valves between the PDU and the Parr vessel. These problems were addressed by re-locating the gas sampling port to a higher position that is well above the liquid water level within the PDU. Thus, later gas sampling was conducted from Port P-1A, which is located near the top of the feed auger section of the PDU. With this change in sampling location, we were successful in collecting hot, pressurized gas samples with the PDU. Gas chromatographic (GC) analyses were performed to confirm that the composition of this gas was approximately 90% CO_2, with most of the remainder being CO. This composition is very similar to what we observed in previous HTC experiments using a 2-L stirred Parr reactor.

Characterization of Hydrochar and Aqueous Products

The hydrochar and aqueous products from the 2 x 2 experimental matrix were characterized in a variety of ways. First, it was demonstrated that the extent of energy densification produced by HTC treatment of Slash Pine feedstock in the PDU was very similar to that observed previously during HTC treatment of other woody feedstocks in laboratory experiments with a stirred, 2-L Parr pressure reactor. This is illustrated in Figure 18, which shows the hydrochar energy densities from the 2 x 2 PDU matrix experiments as compared to hydrochars from many previous Parr reactor experiments. The PDU results, shown as star symbols, are very similar to the Parr results obtained using the woody feedstocks: Tahoe Mix (a mixture of woods obtained from thinning operations in the Tahoe, California National Forest, consisting primarily of Jeffrey Pine, with lesser amounts of White Fir), Loblolly Pine, and Pinyon-Juniper. This figure also illustrates the relative insensitivity of energy densification to reaction time, as compared to reaction temperature. Results from the two PDU runs at 235 °C (fast and slow auger speed) are shown as two partially overlapping stars in Figure 16; whereas the two stars symbols are completely overlapped for the 275 °C runs.

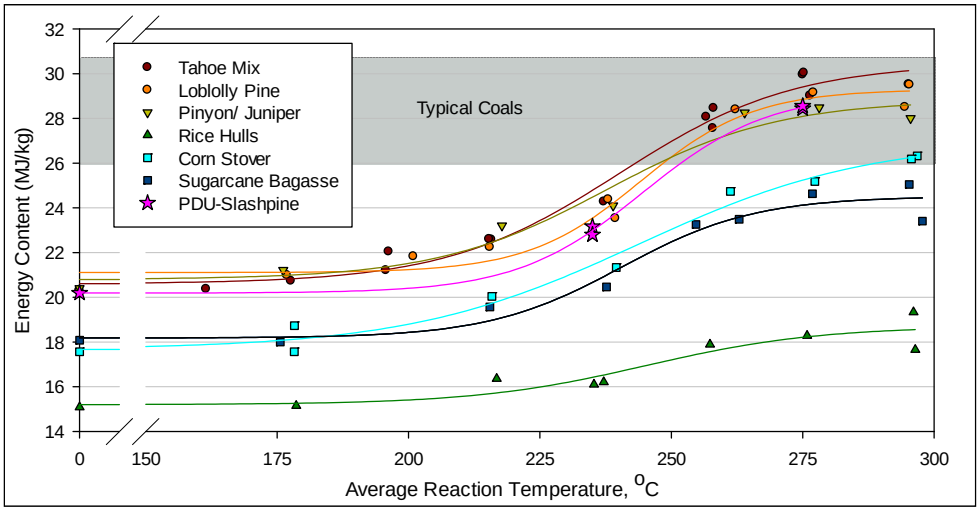

Figure 16. Effect of HTC reactor temperature on energy content of produced hydrochar. Star symbols represent PDU experiments with Slash Pine feedstock; all other experiments were conducted in a stirred, 2-L Parr reactor, with a 30-min. hold time.

Additional laboratory analyses were conducted to characterize both solid and aqueous products from these four PDU experiments. These results provide the basis for comparison of the PDU performance with the earlier 2-L Parr reactor experiments. Ultimate analyses of the four hydrochar products are summarized in Table 3, along with the energy content, mass yield, densification factor, and O/C ratios. (These values are all based upon analyses of the combined four hydrochar fractions obtained from each experiment, as explained above.) These results indicate that for most hydrochar measurements, there was very little difference between the slow and fast auger speeds. (The rather large difference shown for mass yield at 235 °C is likely due to an erroneous measurement.) The energy densification of the hydrochars at 235 °C and 275 °C were approximately 1.1 and 1.4, respectively. These values are in good agreement with energy densification values from other woody biomass feedstocks determined earlier using the 2-L Parr reactor. Also, the O/C ratios of the PDU-generated hydrochars are in good agreement with those observed from earlier Parr experiments, being approximately 0.5 at 235 °C and 0.3 at 275 °C.

Table 3. Properties of Solid Hydrochar from HTC Treatment of Slash Pine in the PDU

	Feedstock	235° C Reactor Temp.		275 °C Reactor Temp.	
Auger Speed		**Slow**	**Fast**	**Slow**	**Fast**
Energy Content, MJ.kg	20.19	23.17	22.80	28.44	28.56
Mass Yield		69.7%	60.8%	53.6%	54.2%
Energy Densification		1.15	1.13	1.41	1.41
Elemental Analysis, %					
C	49.35	57.08	56.53	69.34	67.05
H	6.21	5.83	5.81	5.10	4.88
N	0.01	0.09	0.10	0.18	0.17
S	-	-	-	-	-
O	45.98	37.37	39.54	25.49	23.63
O/C Ratio	0.70	0.49	0.52	0.28	0.26

Non-volatile residue (NVR), total organic carbon (TOC), and volatile organic analyses of the aqueous products from the PDU experiments are summarized in Table 4. In each experiment, three aqueous fractions were evaluated: (1) a small sample collected in a pressure vessel immediately after the heaters and reactor augers were shut off, but while the PDU was still hot and pressurized (this is called "in-situ" sample), (2) the contents of the accumulator (after cooling), and (3) the liquid that was drained from the bottom of the reactor (after cooling).

Table 4. Analysis of Aqueous Product Fractions from HTC Treatment of Slash Pine in the PDU. (NVR and TOC results expressed as percent of starting dry feedstock mass)

Target Temp, °C	Auger Speed	Collection Location	pH	NVR (%)	Volatiles* (%)	TOC (%)
235	Slow	In-situ	NM	0.11%	0.11%	0.11%
235	Slow	Accumulator	NM	1.82%	1.32%	1.43%
235	Slow	Reactor	NM	1.71%	2.08%	2.54%
235	Slow	Total Avg.	NM	**3.64%**	**3.52%**	**4.08%**
235	Fast	In-situ	NM	NM	0.00%	0.00%
235	Fast	Accumulator	NM	NM	3.42%	3.80%
235	Fast	Reactor	NM	NM	2.22%	2.22%
235	Fast	Total Avg.		-	**5.64%**	**6.02%**
275	Slow	In-situ	NM	0.01%	0.01%	0.01%
275	Slow	Accumulator	3.46	1.89%	1.14%	1.55%
275	Slow	Reactor	3.23	2.74%	2.47%	3.48%
275	Slow	Total Avg.		**4.65%**	**3.61%**	**5.04%**
275	Fast	In-situ	NM	0.01%	0.01%	0.02%
275	Fast	Accumulator	3.77	3.28%	1.62%	2.32%
275	Fast	Reactor	3.66	5.66%	2.74%	4.13%
275	Fast	Total Avg.		**8.95%**	**4.37%**	**6.47%**

*Volatiles = sum of 5-HMF, furfural, formic acid and acetic acid

The results in Table 4 are expressed as percent of starting dry Slash Pine feedstock. On this basis, the amounts measured for the in-situ samples are very small, because the total in-situ volume was only about 100-mL. Much larger aqueous sample volumes were collected from the accumulator and the reactor (6-10 L in each case). Therefore, it is expected that most of the NVR, TOC, and volatile organics would be found in the accumulator and reactor samples.

Sugars Analyses: Sugars were measured by HPLC/RI in each of the three aqueous product fractions collected from the 2x2 experiments: (1) in-situ, (2) accumulator, and (3) reactor. Figure 17 summarizes these results, with the sugar mass recoveries being expressed as percent of starting dry Slash Pine feedstock mass. Only a small amount of sugars was in the in-situ samples, while considerably larger amounts were in the accumulator and reactor samples.

The results shown in Figure 17 clearly illustrate that higher process temperatures result in lower sugar recoveries, which is consistent with our previous findings from HTC experiments conducted in a stirred, 2-L Parr reactor. These data also suggest that auger speed had a significant effect on the sugar results, with higher recoveries being observed at higher speeds (or shorter reaction times). This is expected, because many sugars are unstable at these elevated temperatures, and react further to produce furfurals, organic acids, and other degradation products.

The overall effects of auger speed and reaction temperature upon sugar yields are most clearly seen in the bar graphs on the right side of Figure 17. Here, total sugar results from all three sample locations are summed, and expressed as percent of starting dry feedstock mass. At both 235 °C and 275 °C, total sugar recoveries were noticeably higher with the fast auger speed

(shorter reaction time). Also, the compositional profiles of the sugars were quite different between the low and high temperatures. At 235 °C, furfural and 5-HMF were the major species present. At higher process temperature, these compounds were mostly degraded, while erythritol became more prominent. This same behavior was observed in earlier experiments with the 2-L Parr reactor when using woody biomass feedstocks.

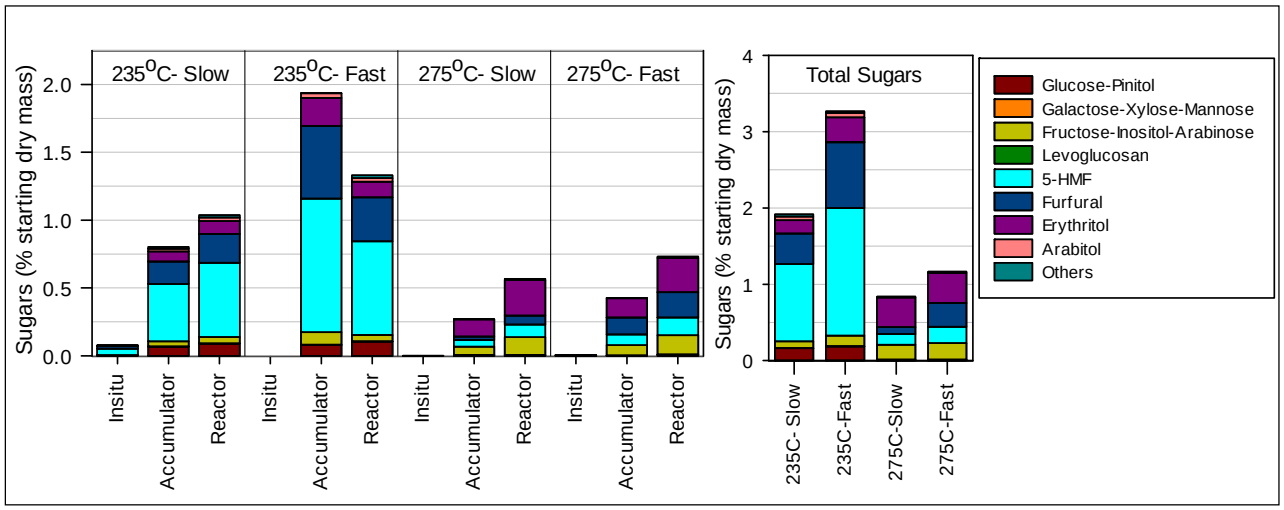

Figure 17. Sugar yields in aqueous PDU fractions from HTC treatment of Slash Pine.

One significant difference between the PDU results and the 2-L Parr results is that the total sugar yields were much higher from the Parr reactor. With woody feedstocks (Tahoe Mix and Loblolly Pine), total sugar yields from the Parr reactor at 235 °C were 6-8%; at 275 °C the yields were 1-2%. These yield values are approximately twice as large as observed here from the PDU experiments. A possible explanation for this is the long cool-down period in the PDU, compared to the rapid quenching (by immersion in an ice bath) with the Parr reactor. It is likely that degradation of sugars within the PDU occurs after the test run is complete -- during this long cool-down period. Evidence for this is provided in Figure 18, which shows that the sugar concentrations measured in the in-situ samples (which cooled much more quickly) were considerably higher than the concentrations measured in the accumulator or reactor samples.

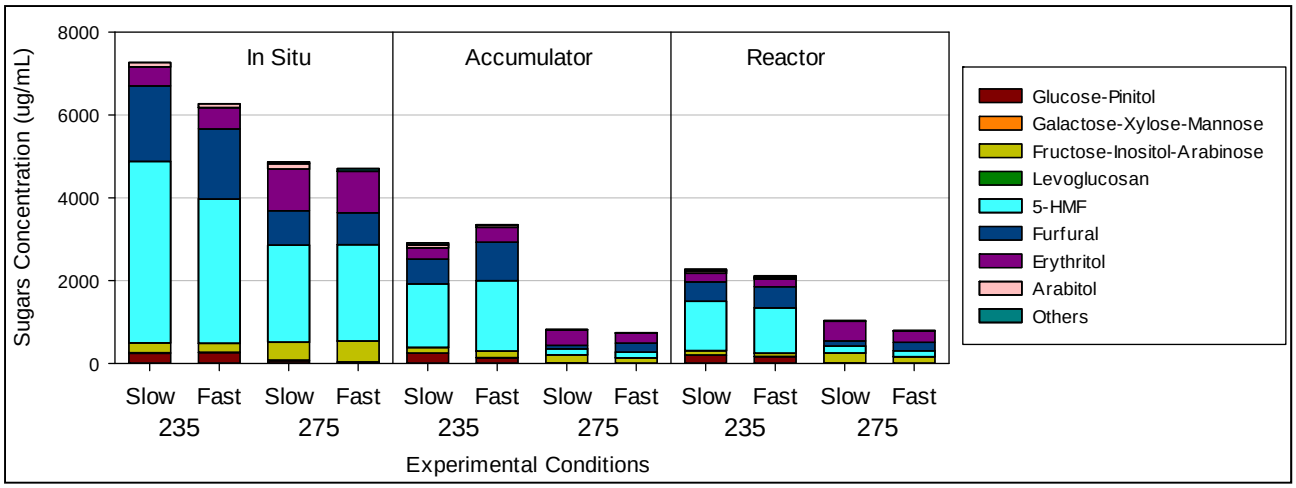

Figure 18. Sugar concentrations in aqueous PDU fractions from HTC treatment of Slash Pine.

Another consideration is that the sugar results shown in Figure 17 and Figure 18 were obtained from direct analysis of the "as is" aqueous samples, without any pre-treatment. Often, when interested in total sugars, samples are first subjected to acid hydrolysis to convert sugar oligomers into free sugars. (With our analytical methodology, only free sugars can be measured, not sugar oligomers.) This hydrolysis can result in much higher total sugar concentrations.

Overall, these PDU sugar results are consistent with the earlier results obtained using a 2-L Parr reactor. This gives further confidence that the simple Parr experiments provide a reliable indication of the HTC process and products when conducted on a larger scale. These results also confirm that a multi-temperature HTC process is necessary if both maximum sugar recovery and high energy density hydrochar production are desired.

Organic Acids: Organic acids were also measured in each of the three aqueous fractions collected from these PDU experiments. The results are shown graphically in Figure 19, using the same format as was used above for the sugars results. This figure shows that very little acids were recovered in the in-situ samples, while considerable amounts were recovered in both the accumulator and reactor samples.

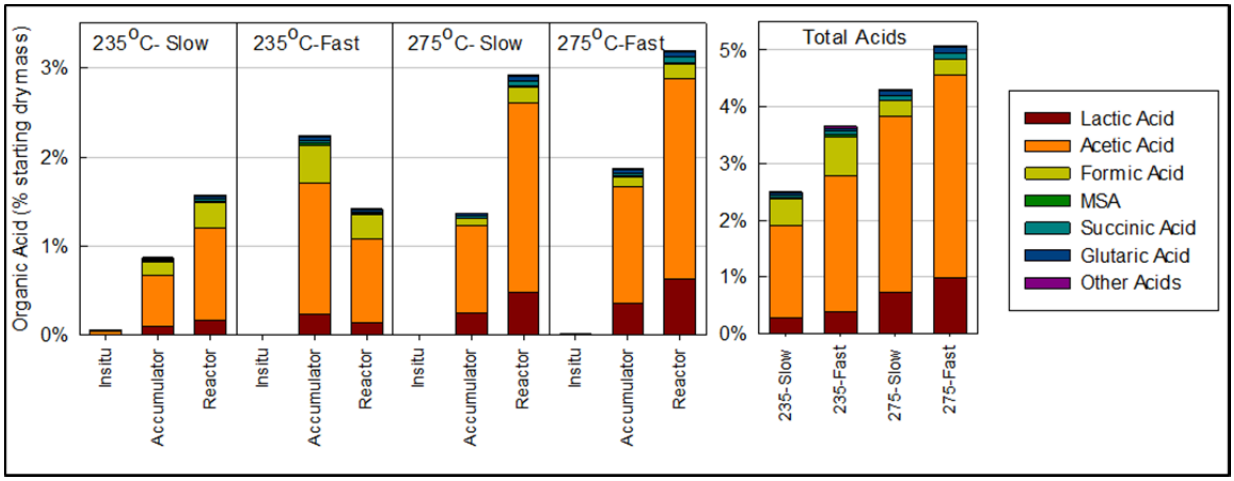

Figure 18. Organic acid yields in aqueous PDU fractions from HTC treatment of Slash Pine.

Reaction temperature clearly affected acid recoveries, with higher acid levels being seen at higher temperature. The effect of auger speed (reaction time) is not as clear. As shown in the total acid recoveries (right hand set of bar graphs in Figure 19), the faster auger speed appeared to give slightly higher recoveries at both temperatures. This is somewhat surprising, as slower auger speed might be expected to result in greater degradation of the lignocellulosic material, and hence greater acid yields. (This is the same argument used to explain the greater degradation of sugars at slow auger speed – as shown in Figure 17. Additional experiments, with better control of operating parameters, are necessary to accurately determine the true effects of reaction time in the PDU.

The total acid recoveries, and the compositional profiles of these acids, are quite similar to results obtained from earlier Parr reactor experiments. In all experiments, acetic acid was the dominant compound seen. (A small amount of levulinic acid was likely present as well, but could not be quantified easily, because it co-elutes with acetic acid under the chromatographic conditions used.) At the lower temperature, a significant amount of formic acid was seen, but this decreased at higher temperature. In contrast, lactic acid increased with reaction temperature. Similar changes in compositional profiles were seen in the earlier Parr experiments with woody feedstocks. The total acid yields in the Parr experiments were 4-6% at 235 °C and 6-8% at 275 °C, which are somewhat higher than the yields observed from these PDU experiments.
The acid concentrations measured directly from each aqueous sample are shown in Figure 20. Unlike the sugars, which showed large concentration differences among the samples (see Figure 18), the organic acids had more uniform levels – except for the two in-situ samples at 275 °C, which had higher acid concentrations than any other samples. Presently, there is no good explanation for this.

Other Batch PDU Experiments and Results

Following completion of the 2 x 2 experimental matrix with the PDU, as explained above, additional experiments were conducted using different feedstocks and temperature conditions. Because operation of the reactor augers was more stable at the fast speed, most of these additional experiments were conducted only while using the fast auger speed, which corresponds to a reaction time of approximately 6 minutes. The complete matrix of experiments performed with DRI's PDU is shown in Table 5.

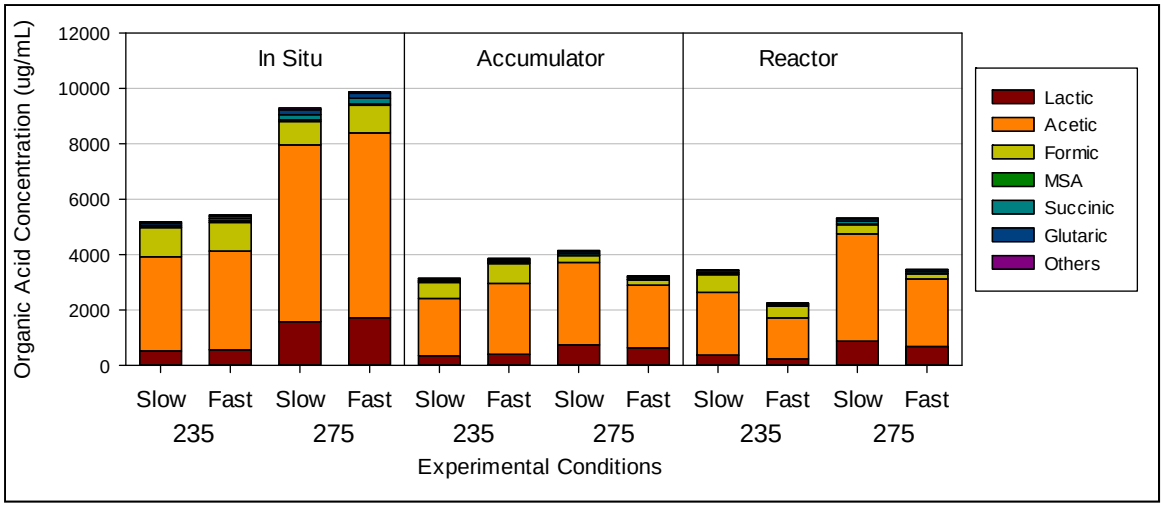

Figure 20. Organic acid concentrations in aqueous PDU fractions from HTC treatment of Slash Pine.

Table 5. Matrix of HTC Experiments Conducted in DRI's PDU

PDU Temperature	195 °C		235 °C		255 °C		275 °C		295 °C	
Auger Speed	Slow	Fast	Slow	Fast	Slow	Fast	Slow	Fast	Slow	Fast
Slash Pine		X	X	X		X	X	X		X
Loblolly Pine		X		X		X	X	X		
P-J		XX		X				X		
HTC Char from P/J-				X						

Hydrochar and Mass Balance: A partial summary of results from each PDU experiment is provided in Table 6. Besides the target temperatures, a calculated average temperature is also shown in some cases. These average temperatures were determined by averaging the second-by-second calculated temperatures (based upon pressure measurements as described above) over the entire period of time during which the augers were operated. As shown in Table 6, these average temperatures generally were in close agreement with the target temperatures.

For the 17 PDU experiments shown in Table 6, it was not possible to determine a complete mass balance. One reason for this is that total volumes of product gases were not measured. Additionally, the amount of water produced as an HTC product could not be determined in these experiments. Nevertheless, some relevant information pertaining to mass balance is available. For example, the yield of hydrochar was determined for each experiment, and is shown in Table 6, expressed as mass percent relative to starting dry feedstock mass. These results confirm the general trend of lower hydrochar yield at higher process temperature, for all three feedstocks.

Also shown in Table 6 are the non-volatile residue (NVR) contents of the aqueous products from each HTC experiment conducted in the PDU, expressed as mass percent of starting dry feedstock. Determining the total NVR content requires analysis of three aqueous fractions: (1) hot sample collected during operation of the PDU, (2) sample collected from the accumulator after cooling, and (3) sample collected from draining the reactor. In each case, the aqueous solution is filtered prior to determining the NVR content of the solution. The amount of solids removed by this filtration is small (typically <5% of the NVR content), but this amount is

Table 6. Mass Recovery and Energy Densification Results from HTC Experiments in PDU

Exp. #	Set Temp .(°C)	Avg. Temp. (°C)	Heat up Time (min)	Auger Speed	HTC Yield, % starting dry mass	NVR+filter mass, % starting dry mass	Energy Content, MJ/Kg	Energy Densification Factor	Water Recovery (%)	Total Recovery (%)
Slash pine							20.19			
525	195	196.1	103	Fast	96.9	9.4	21.46	1.06	102.0	95.7
512	235	-	130	Slow	69.7	3.2	23.17	1.15	101.8	95.8
513	235	-	126	Fast	61.0	NM	22.80	1.13	97.1	94.7
528	255	249.5	179	Fast	77.7	6.1	23.89	1.18	101.3	95.2
514	275	-	195	Slow	53.7	4.4	28.44	1.41	90.9	87.2
515	275	-	225	Fast	54.2	8.4	28.56	1.41	92.9	90.2
524	295	290.5	156	Fast	40.4	4.9	28.86	1.43	92.4	86.0
Loblolly							20.28			
526	195	195.6	85	Fast	76.6	8.8	21.10	1.04	105.7	96.8
527	235	236.3	111	Fast	67.9	3.4	22.79	1.12	103.0	95.0
522	255	255.2	111	Fast	63.3	4.3	24.20	1.19	118.4	105.5
529	275	277.0	122	Slow	39.3	6.2	27.68	1.36	102.2	93.1
523	275	276.7	144	Fast	30.8	5.3	27.50	1.36	105.9	92.9
P/J							20.25			
519	195	199.9	217	Fast	92.1	12.1	22.69	1.12	111.8	103.0
520	195	196.4	134	Fast	73.6	9.7	22.07	1.09	102.4	93.3
518	235	237.2	219	Fast	70.7	6.8	17.60	0.87	93.1	85.1
517	275	275.2	188	Fast	48.5	9.1	26.23	1.30	98.8	92.1
Recycled P/J (Exp. 519 & 520)							22.38			
521	235	238.3	289	Fast	72.3	3.9	25.11	1.12	98.0	91.3

combined with the NVR content of the filtered solution to generate the results shown in Table 6. These NVR results are similar to what we observed in previous 2-L Parr reactor experiments. As seen before, the highest NVR yields occurred at the mildest HTC process temperatures. The sum of the hydrochar and NVR yields from each PDU experiment are presented graphically in Figure 21. This clearly shows the overall reduction in yields with increasing process temperature, but with substantial variability in the results.

The energy contents of all feedstocks and hydrochar products are also given in Table 6. As expected, the mass energy content of hydrochar increased with process temperature. (An anomalously low energy content was measured for hydrochar produced from P-J feedstock at 235 °C.) The energy densification factors provided in Table 6 are quite similar to those observed from earlier 2-L Parr reactor experiments. This is further illustrated in Figure 22, which shows the energy contents of hydrochars produced in the PDU as star symbols overlaid on data from the 2-L Parr reactor. (The anomalous result for P-J at 235 °C is not included.) For the most part, these PDU star data points lie close to the curves representing the 2-L Parr results, although a few exceptions can be seen. For example, the Slash Pine and Loblolly Pine PDU data points at 250 °C show lower energy contents than expected based upon the earlier 2-L Parr results.

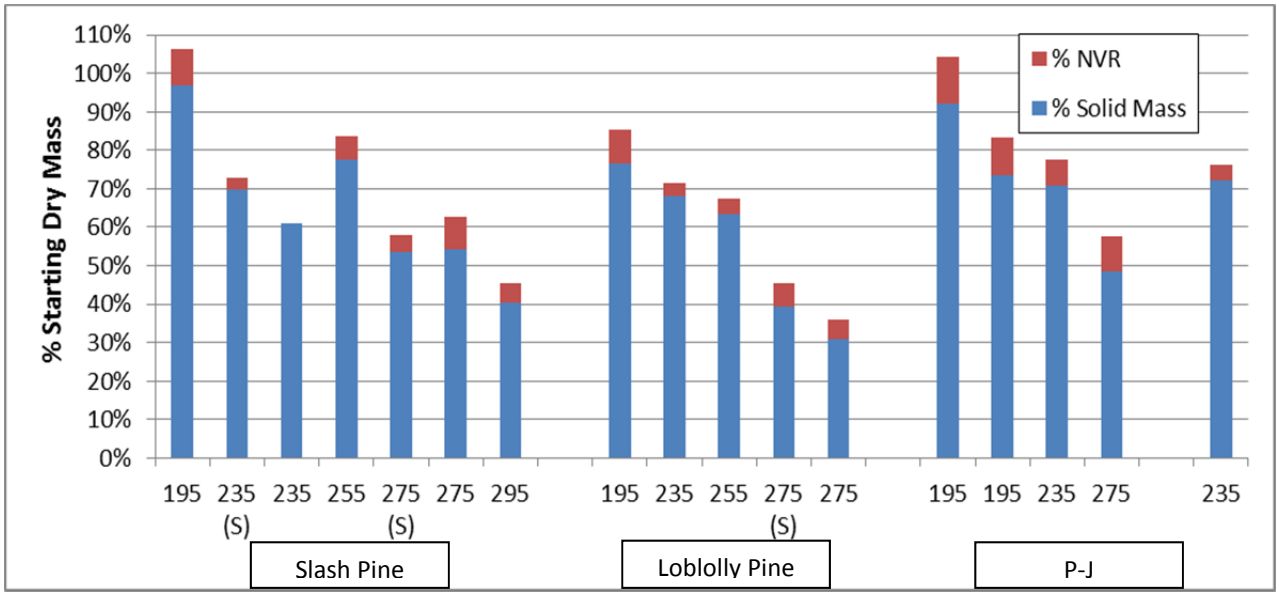

Figure 21. Mass recovery of hydrochar and NVR from PDU experiments. All experiments conducted with fast auger speed except those indicated by "(S)".

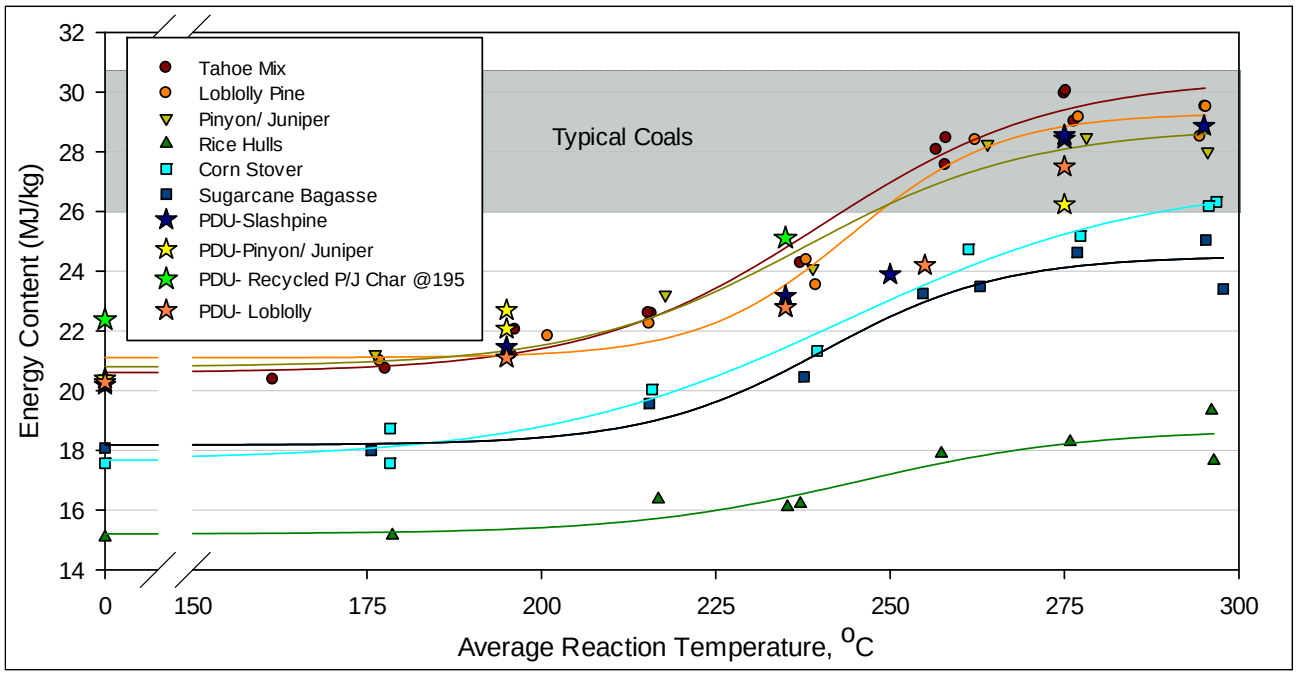

Figure 22. Effect of HTC reactor temperature on energy content of produced hydrochar. Star symbols represent PDU experiments; all other experiments were conducted in a stirred, 2-L Parr reactor, with a 30-min. hold time.

The "Water Recovery" results shown in Table 6 were computed as the total water out of the system (all water collected from the accumulator, reactor and moisture in the char) less the non-volatile residues and filtered mass from the liquids, divided by the total water into the unit (water added at the beginning, plus moisture of the feedstock, plus any rinse water added during product collection.) Lower water recovery can result from spills during product collection or other operational losses. For example, in Experiment #514, hot gases were sampled from the PDU,

and the collection vessel and Tedlar bags filled with water, thus reducing the amount of collected water. Reduced water recovery can also contribute to lower NVR results because the NVR content is measured on only a small aliquot, and is then used to calculate the NVR content for the entire amount of recovered water. This same problem results in under-estimation of other aqueous products that are measured from small aliquot samples, such as sugars and organic acids.

The "Total Recovery" results shown in Table 6 are computed as the sum of all solid and liquid products, divided by all solid and liquid inputs into the system. Low total mass recovery tends to correspond with low total water recovery. In addition, low total mass recovery may give an indication of the amount of gases produced. Although the data scatter is quite large, it is interesting to note that the average water recovery for the 17 PDU runs in Table 6 is 101%, while the average total recovery is 94%. These observations are consistent with the production of a small amount of gas from the PDU experiments -- perhaps 5-10% -- which is similar to the results obtained in earlier experiments with a 2-L Parr reactor. In addition, these 17 PDU experiments suggest that on average, the HTC process is in balance with respect to water, with inputs and outputs being nearly identical.

In this dataset, the variability appears to be larger than that observed in earlier experiments using a 2-L Parr reactor. This is expected, due to the greater complexity of the PDU operation, and the handling of larger and more numerous product fractions. One particular source of variability is the determination of moisture content of the hydrochar products. After air drying (or solar oven drying) this material, a small aliquot is taken for determination of moisture content by oven drying (at 105 °C). The measured moisture content is then applied to the entire mass of air-dried hydrochar. By this method, small errors in moisture determination become magnified upon application to the entire hydrochar mass. We believe that such errors may result from non-homogeneous mixtures of air-dried hydrochar, whereby a wetter than average or drier than average aliquot may be withdrawn for determination of moisture content. Evidence for this is suggested by the rather wide range of moisture levels determined from the PDU-generated hydrochar products we've characterized – from a low of 1.5% moisture (Loblolly Pine at 235 °C) to a high of 28.5% (Loblolly Pine at 275 °C). To minimize this problem, it is important to place the entire hydrochar product in a small mixing vessel, and to remove a representative sample after creating a homogeneous mixture.

Another indication of operational variability can be seen in the heat-up time reported in Table 6. Heat-up time is defined as the time between activating the electrical heating bands and when the target temperature is reached – at which point the augers are turned on. For higher target temperatures, longer heat-up times would be expected. However, in the course of these 17 PDU experiments, several changes were made in the placement of the heating bands, as well as changes to the insulation materials and placement – all in an effort to achieve more rapid and repeatable heating. In addition, for some of the later experimental runs, solar-heated water was used to fill the PDU, rather than tap water. Use of this warmer water (about 50 °C vs. 15 °C) resulted in a noticeable shortening of the heat-up time.

Characterization of Gaseous Products: As described above, relocating the gas sampling port from the top of the reactor auger (Port P-4E) to the top of the feed auger (Port P-1A) enabled satisfactory collection of gaseous products from the PDU, without the problems of tar contaminants and excessive water collection. With this improved arrangement, both hot gas

samples (while the PDU is in operation) and cold gas samples (after the PDU has cooled overnight) could be collected reliably. Hot samples are collected by manually opening a high pressure valve located between Port P-1A and a 1-L Parr pressure vessel. Once the pressure has equilibrated between the PDU and the Parr vessel, the valve is closed and the contents of both the PDU and the Parr vessel are allowed to cool to room temperature (generally overnight). The Parr vessel is then depressurized by opening a second valve to vent the contents into a Tedlar bag for subsequent GC analysis. Following this, the PDU is depressurized by venting through the same 1-L Parr vessel to determine the gas volume, and capture another Tedlar bag sample for analysis (if desired). A schematic showing details of this gas sampling system is provided in Figure 23.

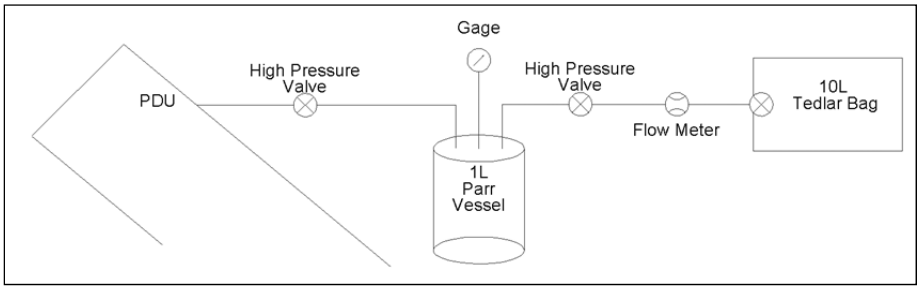

Figure 23. Schematic of sampling system for collecting hot, pressurized gaseous products from PDU.

This hot gas sampling technique, followed by GC analysis, was used to confirm that the gas composition is dominated by CO_2, with smaller amounts of CO also being present. As shown in the chromatogram of Figure 24, significant amounts of N_2 and O_2 are also seen, as the Parr collection vessel contained air before it was pressurized with hot PDU gas. (The PDU itself also contained air at the beginning of the experiment.) This is quite different from the chromatograms of gaseous products obtained from previous 2-L Parr reactor experiments, where the system was routinely flushed with helium prior to conducting the HTC treatment, leaving only trace levels of air.

To assess overall mass balance in the PDU, an experiment was conducted in which the total gas volume was determined, and the yields of CO and CO_2 were measured. This was done by HTC treatment of P-J feedstock at 235 °C. After the reaction was complete, the system was cooled overnight. The following day, the PDU was depressurized by venting into a series of ten 10-L Tedlar bags. Each bag was filled to a volume of approximately 8-L. There was sufficient pressure in the PDU to completely fill the first 3 bags. Following this, helium was used to sparge the PDU and drive out additional CO and CO_2. For Bags 4 and 5, the helium was introduced near the top of the reactor auger (Port P-4E); for Bags 6-10, the helium was introduced into the bottom of the accumulator vessel (Port P-5D). A schematic showing the design of this experiment is provided in Figure 25.

One objective of this 10-bag experiment was to demonstrate that although a significant amount of CO_2 remains dissolved in the water within the PDU at room temperature, it can be removed by helium sparging. All 10 bags were analyzed for gaseous products using the GC-TCD method that is routinely employed to characterize gases from 2-L Parr reactor experiments. The results shown

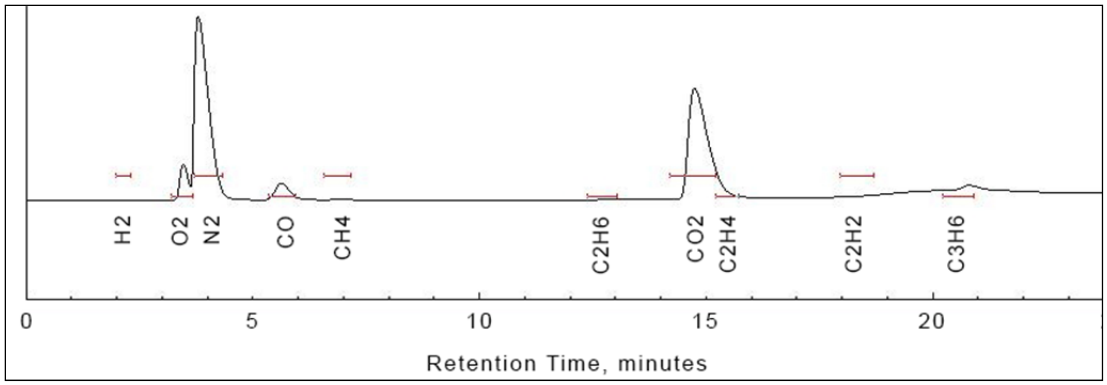

Figure 24. Gas chromatogram of headspace sample taken from PDU after HTC treatment of Loblolly Pine at 255 °C.

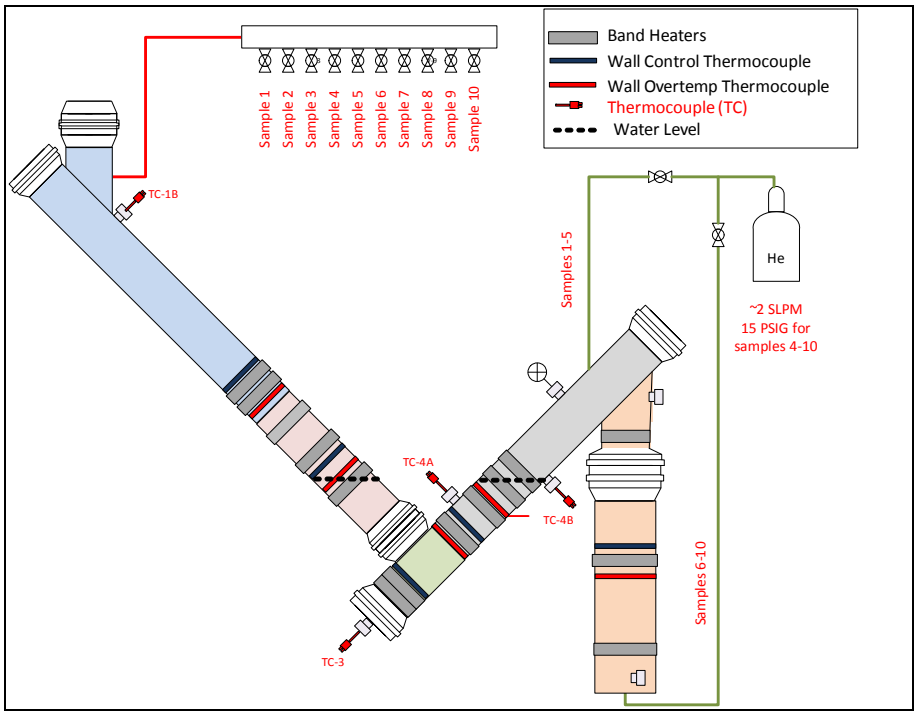

Figure 25. Schematic of 10-bag PDU sparging experiment to collect gaseous products from HTC treatment of P-J at 235 °C.

in Figure 26 clearly illustrate that CO_2 was the dominant gaseous product, with the first few bags consisting almost entirely of CO_2. After Bag 4, a nearly exponential decay in CO_2 was observed (the orange curve shown in Figure 26 is an exponential fit to the data).

These results illustrate that a considerable amount of CO_2 is dissolved in the aqueous solution within the PDU, and that it degasses rather slowly, making it difficult to remove and collect all

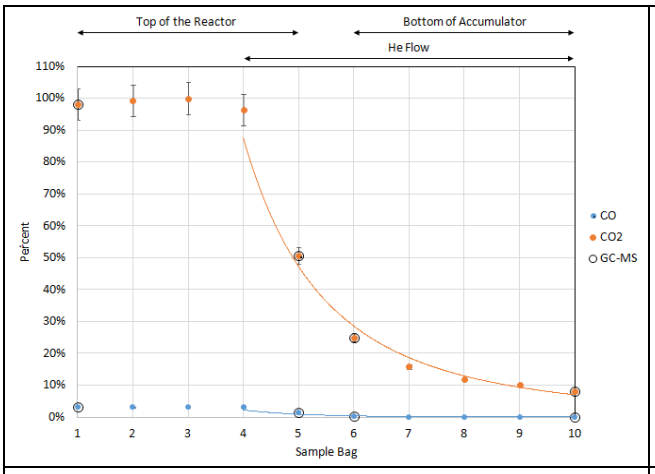

Figure 26. CO and CO_2 concentrations measured by GC in the PDU 10-bag experiment.

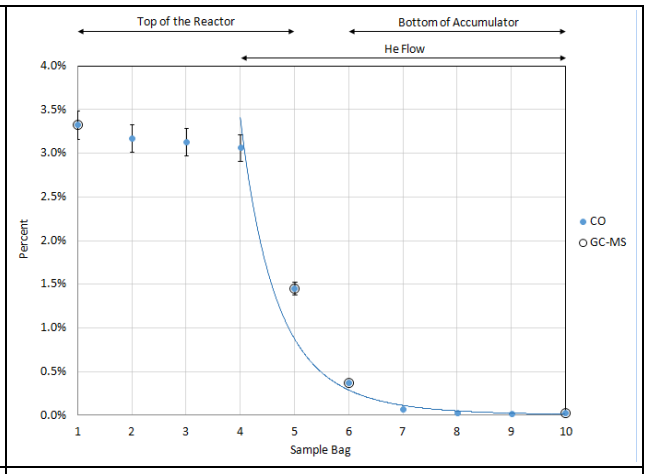

Figure 27. CO concentrations measured by GC in the PDU 10-bag experiment.

the CO_2. By using the exponential decay relationship shown in Figure 26, the amount of CO_2 remaining in the PDU after collection of Bag 10 was calculated to be 5.6% of the total CO_2. We also determined that 81.4% of the total CO_2 was collected in the first 5 bags. Thus, if desired, we could rather easily capture the majority of the CO_2 product from the PDU in a single 50-L Tedlar bag by simply venting the unit, along with a modest amount of helium sparging from the top of the reactor. The total CO_2 mass yield from this PDU was calculated to be 5.56%, relative to the mass of starting dry feedstock. This value is in excellent agreement with that determined previously using P-J feedstock in a 2-L Parr reactor under the same temperature conditions.

Carbon monoxide (CO) was also measured in these 10 Tedlar bags, with the results shown in Figure 26. Significant amounts were measured in the first few bags, but very little was seen after Bag 6. This is shown more clearly in Figure 27, which plots the measured concentrations of CO on an expanded scale. The more rapid decay in measured concentrations of CO compared to CO_2 is expected, because CO is much less soluble in water than is CO_2. The total CO mass yield from this PDU experiment was calculated to be 0.095% relative to the mass of starting feedstock. Approximately 96.5% of the total CO amount was captured in Bags 1-5.

To gain a better understanding of trace volatile organic compounds (VOCs) in the gaseous products from the PDU, several of the 10 Tedlar bag samples described above were analyzed by GC-MS. (This includes Bags 1, 5, 6, and 10 – as indicated by the open circles in Figure 27 and Figure 26.) Each bag sample was transferred to a 6-L stainless steel Summa canister and was diluted 17 x with ultra-high purity (UHP) nitrogen. The diluted sample was analyzed for VOCs using GC-MS according to EPA Method TO-15. The GC-FID/MS system used by DRI includes a Lotus Consulting Ultra-Trace Toxics sample pre-concentration system built into a Varian 3800 gas chromatograph with flame ionization detector (FID) coupled to a Varian Saturn 2000 ion trap mass spectrometer.

The Lotus pre-concentration system consists of three traps. Mid- and heavier weight hydrocarbons are trapped on the front trap consisting of 1/8” nickel tubing packed with multiple adsorbents. Trapping is performed at 55 °C and eluting is performed at 200 °C. The rear traps consist of empty 0.040” ID nickel tubing for trapping light hydrocarbons, and a cryo-focusing

trap for mid and higher weight hydrocarbons isolated in the front trap. The cryo-focusing trap is built from 6' x 1/8" nickel tubing filled with glass beads. Trapping of both rear traps occurs at -180 °C and eluting at 200 °C. Light hydrocarbons are deposited on a Varian CP-Sil5 column (15m x 0.32mm x 1µm) plumbed to a column-switching valve in the GC oven, then to a Chrompack Al_2O_3/KCl column (25m x 0.53mm x 10µm) leading to the flame ionization detector (FID) for quantitation of light hydrocarbons. The mid-range and heavier hydrocarbons cryo-focused in the rear trap are deposited on a J&W DB-1 column (60m x 0.32mm x 1µm) connected to the ion trap mass spectrometer. The GC initial temperature of 5 °C is held for approximately 9.5 minutes, then ramped at 3 °C/min to 200 °C for a total run time of 80 minutes. Calibration of the system is conducted with a mixture that containes commonly found hydrocarbons (75 compounds from ethane to n-undecane, purchased from Air Environmental) in the range of 0.2 to 10 ppbv.

Total ion current (TIC) chromatograms from four bag samples are shown in Figure 28. Overall, these chromatograms appear very similar, although the total VOC concentrations were quite different. For example, Bag 1 had higher total concentrations than Bag 10, and it required greater dilution prior to GC analysis. The major compounds in the bag samples are labeled by number on the chromatogram from Bag 1, and are identified in the title for Figure 28. Quantification of selected compounds is provided in Table 7.

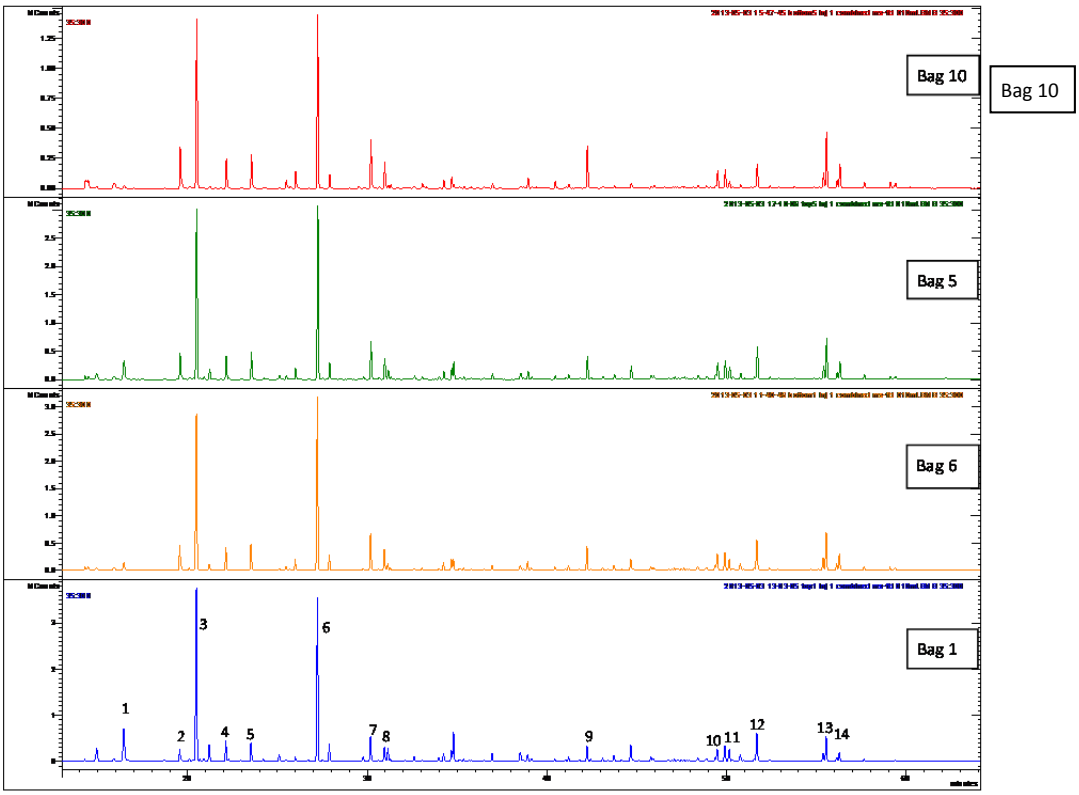

Figure 28. Chromatograms from GC-MS analysis of bag samples of gaseous products from the PDU after HTC treatment of P-J at 235 °C. Peaks: 1 – Butene-1 + isobutene; 2 – guanidine (?); 3 – furan; 4 – 2-methyl-2-butene; 5 – isobutylamine (?); 6 – 2-methylfuran; 7 – unknown; 8 - unknown; 9 – Furfural +?; 10 – isopropylbenzene; 11 – dimethylphenol; 12 – a-pinene; 13 – dimethylethylbenzene; 14 – unknown

Table 7. Molar Concentrations of Selected VOCs from GC/MS Analyses in the PDU 10-Bag Experiment, ppbv

Compound	RT (min)	Bag 1	Bag 5	Bag 6	Bag 10
1-butene + isobutene	16.45	12805.6	7576.2	3330.2	631.6
1,3-butadiene	16.53	1399.7	829.6	122.2	79.0
t-2-butene	17.00	653.3	395.7	181.5	49.5
c-2-butene	17.47	536.6	325.6	156.2	40.3
furan	20.48	99180.6	86963.3	81956.4	42887.7
isoprene	21.20	3038.3	1612.7	976.0	173.9
2-methyl-2-butene	22.12	1340.9	647.2	367.2	52.7
2-methyl-furan	27.23	46647.6	40040.1	40813.1	18602.1
benzene	31.28	282.5	289.0	294.5	177.3
2,5-dimethyl-furan	34.68	2766.9	2145.0	2321.9	1026.7
n-heptane	34.80	2309.7	1211.8	745.3	127.5
2-furfural	42.43	635.5	444.5	362.9	65.6
alpha-pinene	51.69	5120.9	4833.7	4856.9	1785.9

As shown in the chromatograms of Figure 28 and the data of Table 7, the two dominant VOCs measured in the gas-phase were furan and 2-methylfuran. All 13 compounds shown in Table 7 decrease in concentration from Bag 1 to Bag 10 – as would be expected due to increasing volumes of helium sparging – but not all compounds decrease at the same rate. Compounds that are reasonably soluble in water (such as benzene, alpha-pinene, and the furans) decrease in concentration at a slower rate than the non-soluble compounds. Although we don't have results from measurement of all 10 bags to display concentration decay curves like those shown in Figure 26 and Figure 27, it appears that these water-soluble VOCs behave similarly to CO_2, while the non-soluble VOCs behave similarly to CO.

For comparison purposes, we provide in Figure 29 a chromatogram from analysis of gaseous products collected from HTC treatment of loblolly pine conducted by Changing World Technologies (CWT) in late 2008. (This work was conducted as part of a previous DOE-funded project: DE-FG36-01GO11082.) Although the feedstock, process conditions, and gas sampling methodologies were all different from those used with DRI's PDU, compositional similarities are quite evident by comparing Figure 28 and Figure 29. (Note that the peak numbering schemes are slightly different between these two figures.) In both cases, furans are identified as the major constituents, with lesser amounts of hydrocarbons derived from degradation of the lignocellulosic feedstocks.

A more thorough analysis of the GC-MS data was conducted for the Bag 1 sample. A total ion current (TIC) chromatogram of this gaseous sample is provided in Figure 30. (Peaks 9 and 18 are shown as out of scale to reveal the less abundant components in this sample.) Clearly, this sample contained a complex mixture of VOCs. (The main constituents of CO and CO_2 do not appear in this analysis.) By a combination of spectral library matches and individual spectral analyses, 57 constituent species were identified, as shown in Table 8. In many cases, explicit identification of specific isomers was not possible. This is indicated by addition of a question mark to the compound name shown in Table 8.

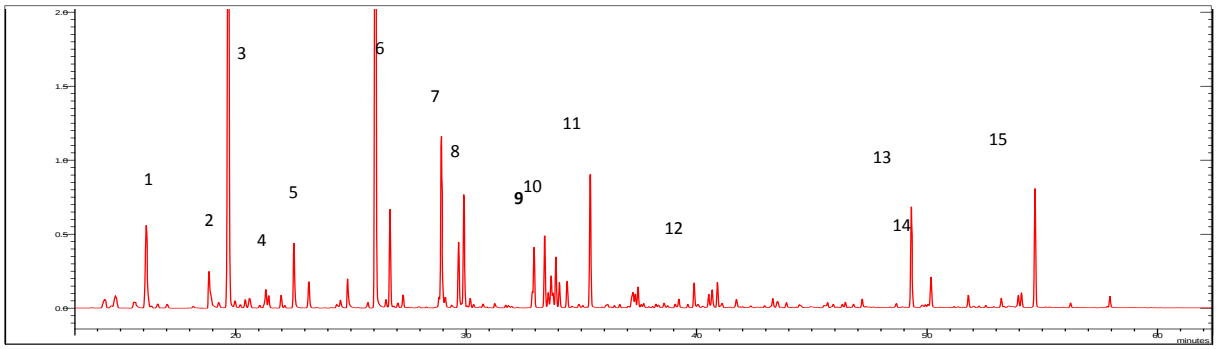

Figure 29. Chromatogram from GC-MS analysis of gaseous products from Changing World Technologies (CWT) HTC treatment of Loblolly Pine at 260 °C. Peaks: 1 – Butene-1 + isobutene; 2 – guanidine (?); 3 – furan; 4 – 2-methyl-2-butene; 5 – isobutylamine (?); 6 – 2-methylfuran; 7 – methylbutanal (?); 8 – 3-methylcyclopentene; 9 – 2-ethylfuran; 10 – 2,5-dimethylfuran; 11 – dimethyldisulfide; 12 – Furfural, 13 – unknown; 14– a-pinene; 15 – limonene (or camphene)

Accurate quantification of all identified VOCs was not possible, as no calibration standards were available for many compounds. However, to provide a qualitative estimate of relative concentrations, the size of each TIC peak is given in Table 8, expressed as percent of total peak size. Not surprisingly, many of the largest peaks are furan compounds (peaks 9, 18, 19, 21, 28, and 38). Furfural, which is of some concern due to its toxicity, was not seen in high concentration, although we believe it is present as a co-eluting compound under Peak 29. From HPLC analysis of the aqueous products, we know that furfural is a major product from HTC treatment of biomass feedstocks. However, it is also highly polar and water soluble, and therefore may not be sampled reliably by the Tedlar bag method used here. (It is also expected that much of the furfural would be adsorbed on the walls of the bag, or be dissolved in an aqueous film that may coat the walls.) Thus, alternative sampling methodologies – such as use of water-filled impingers – may be required to reliably sample furfural from the PDU gas-phase products. It is also recognized that if collected at higher temperatures (which is likely in commercial operation) the concentrations of all VOC species – including furfural – would be much higher.

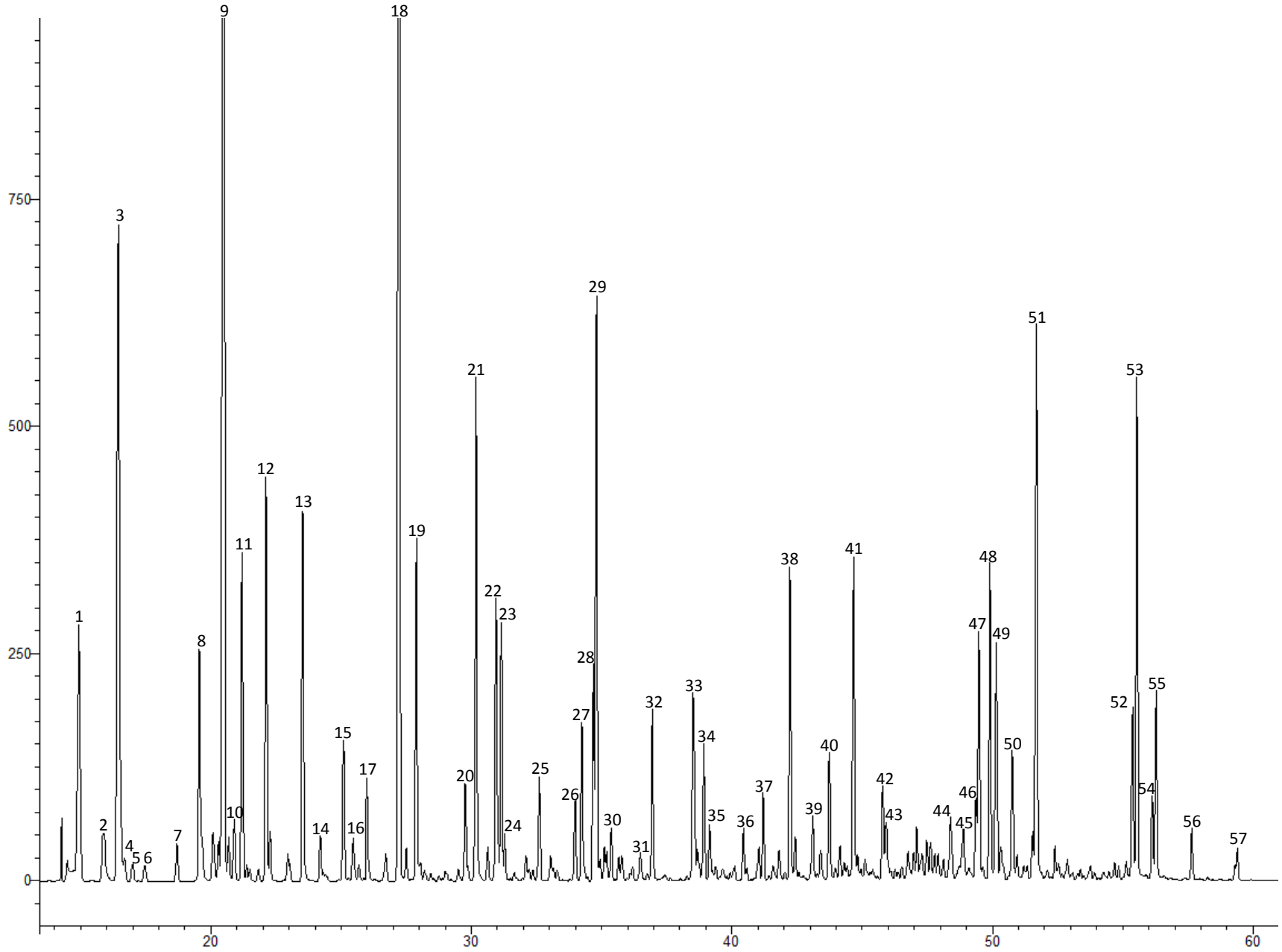

Figure 30. GC-MS TIC chromatogram of gaseous products from HTC treatment of Pinyon-Juniper in the PDU at 235 °C.

Table 8. GC-MS Analysis of Gaseous Products from HTC Treatment of P-J in the PDU at 235 °C

Peak No.	RT, Min.	% of Total Peak Area	Formula	Nominal MW	Compound Identity*
1	14.95	1.77	C_4H_6	54	butyne?
2	15.83	0.48	C_4H_{10}	58	isobutane
3	16.45	5.16	C_4H_8	56	1-butene + isobutylene
4	16.69	0.06	C_4H_{10}	58	n-butane
5	17.00	0.13	C_4H_8	56	t-2-butene
6	17.47	0.11	C_4H_8	56	c-2-butene
7	18.71	0.24	C_5H_{10}	70	3-methyl-1-butene
8	19.50	1.37	$C_4H_{10}O$	74	methyl isopropyl ether
9	20.48	18.92	C_4H_4O	68	furan
10	20.90	0.36	C_5H_8O	86	2-methyl tetrahydrofuran
11	21.20	1.85	C_5H_8	68	isoprene
12	22.12	2.02	C_5H_{10}	70	2-methyl-2-butene
13	23.52	1.94	$C_5H_{12}O$	88	methyl t-butyl ether
14	24.21	0.20	C_5H_{10}	70	cyclopentane
15	25.09	0.82	C_5H_8O	84	2,3-dihydro-3-methyl furan
16	25.47	0.26	$C_4H_6O_3$	102	acetic anhydride
17	26.00	0.50	$C_5H_{12}O$	88	ethyl isopropyl ether?
18	27.23	16.81	C_5H_6O	82	2-methyl furan
19	27.88	1.70	C_5H_6O	82	3-methyl furan
20	29.76	0.52	C_6H_{12}	84	2-methyl-2-pentene?
21	30.16	2.61	$C_6H_{12}O$	100	2-ethyl tetrahydrofuran?
22	30.93	1.59	$C_6H_{14}O$	102	ethyl t-butyl ether?
23	31.15	1.36	C_6H_{10}	82	1-methyl cyclopentene
24	31.28	0.22	C_6H_6	78	benzene
25	32.60	0.58	C_7H_{12}	96	di-methyl cyclopentane
26	33.99	0.45	C_7H_{14}	98	1-heptene
27	34.25	0.85	C_6H_8O	96	2-ethyl furan
28	34.69	0.98	C_6H_8O	96	2,5-dimethyl furan
29	34.80	3.02	C_7H_{16}	100	n-heptane? + furfural
30	35.35	0.25	C_6H_8O	96	2,4-dimethyl furan
31	36.48	0.17	C_8H_{12}	108	octatriene?
32	36.94	0.83	$C_2H_6S_2$	94	di-methyl-disulfide
33	38.51	1.30	C_8H_{14}	110	tri-methyl-cyclohexene?
34	38.92	0.72	C_7H_8	92	toluene
35	39.14	0.29	C_6H_{10}	94	1-methyl cyclohexadiene?
36	40.44	0.27	$C_8H_{16}O$	128	di-ethyl tetrahydrofuran?
37	41.20	0.40	$C_7H_{10}O$	110	2-ethyl-5-methyl furan
38	42.22	1.56	$C_7H_{10}O$	110	tri-methyl furan?
39	43.10	0.38	C_9H_{14}	122	di-methyl heptatriene?
40	43.73	0.69	C_9H_{14}	122	di-methyl heptatriene?
41	44.66	1.86	C_9H_{16}	124	tetra-methyl cyclopentene?
42	45.78	0.49	C_9H_{16}	124	tetra-methyl cyclopentene?
43	45.91	0.37	C_9H_{16}	124	tri-methyl cyclohexene?
44	48.39	0.45	C_9H_{14}	122	di-methyl heptatriene?
45	48.90	0.29	C_9H_{16}	124	tri-methyl hexadiene?
46	49.37	0.39	C_9H_{16}	124	tri-methyl cyclohexene?
47	49.48	1.42	C_9H_{12}	120	methyl ethyl benzene
48	49.90	1.66	$C_8H_{10}O$	122	dimethyl phenol?

Peak No.	RT, Min.	% of Total Peak Area	Formula	Nominal MW	Compound Identity*
49	50.15	1.41	$C_{10}H_{16}$	136	methyl isopropyl hexadiene?
50	50.76	0.74	$C_{10}H_{16}$	136	camphene?
51	51.69	3.30	$C_{10}H_{16}$	136	α-pinene
52	55.38	0.88	$C_9H_{12}O$	136	trimethyl phenol?
53	55.54	2.46	$C_{10}H_{14}$	134	ethyl-dimethyl-benzene
54	56.13	0.42	$C_{10}H_{16}$	136	methyl-isopropyl cyclohexene?
55	56.29	1.02	$C_8H_{10}O$	122	methyl methoxy benzene?
56	57.64	0.27	$C_{10}H_{16}$	136	methyl propyl cyclohexadiene?
57	59.39	0.17	$C_{10}H_{16}$	136	methyl propyl cyclohexadiene?

* Names followed by a question mark indicate compounds where specific isomeric identities are not known.

Hydrochar Characterization and Pelletization

Pelletization is commonly used to increase the mass and energy density of biomass. In addition, the uniform shape and size of pelletized biomass improves handling and storage, and reduces transportation costs. However, raw biomass pellets have relatively low energy content, as compared to coal, and very poor water tolerance. These problems can be partially overcome by a thermal pretreatment process known as torrefaction, which involves mild pyrolysis conducted in an inert atmosphere.[22-24] While torrefied biomass is somewhat hydrophobic, and has a higher energy density compared to raw biomass, it is quite friable and can create a dust hazard when handled. Torrefied biomass is also challenging to pelletize without the addition of an external binder material.[25-29]

Another biomass thermal pretreatment process that is gaining recognition, hydrothermal carbonization (HTC), is the subject of study in this project. As with torrefaction, a friable solid char product (hydrochar) is produced by the HTC process. Hydrochar has substantially increased energy content, compared to raw biomass.[9,21] However, hydrochar is strongly hydrophobic, and requires no binder to produce robust, water-resistant pellets.[30,31]

In this project, we systematically investigated the pelletization of hydrochar produced from woody biomass, and compared pelletized hydrochar with pellets made from raw and torrefied woods. Pelletization is known to be affected by numerous factors, including temperature, pressure, particle size, moisture content, pelletization equipment, and others.[33-37] Therefore, we developed and utilized standardized laboratory methodologies for producing pellets, in which many of these influential properties were held constant. This approach was successful in yielding highly repeatable results, and allowed us to explore the influence of other factors, such as the effects of HTC process temperature upon pellet properties, and the effects of blending hydrochar with other forms of biomass to improve the pelletization of these materials.

As described above, a Carver bench top laboratory hydraulic press, Model M (Menomonee Falls, WI) was used to produce pellets from raw and thermally treated woody biomass materials. This press was equipped with a Wika Instruments Model 232.34 pressure gauge, which enabled accurate determination of hydraulic pressure when making pellets.

Pellets were produced by placing approximately 1 g of ground biomass material into a 13-mm diameter, hardened steel heated die (Across International, Berkeley Heights, NJ, USA). By means of a bench top temperature controller (Omega Model CSC32J) and a thermocouple (Omega Type J iron-constantan), the material was heated to 140 °C. The press was manually

operated to apply a hydraulic pressure of 20 MPa that was held for 60 seconds. (20 MPa hydraulic pressure equates to approximately 295 MPa on the surface of a 13-mm diameter pellet.) After releasing the pressure, the die body was removed from the support plate base, and placed on the pellet ejector base to push out the formed pellet.

Pellet mass was determined using an Acculab Model ALC80.4 analytical balance, with a sensitivity of ± 0.0001 g. Pellet length was measured using a set of digital Vernier calipers, having a precision of ± 0.02 mm. A photo of these calipers is provided in Figure 31. When pelletizing approximately 1 g of biomass material, typical pellet lengths were 6-7 mm. Pellet diameters were 13 mm, having been produced in a 13-mm die, measured to confirm its internal diameter. Thus, pellets typically had L/D ratios of 0.5-0.6.

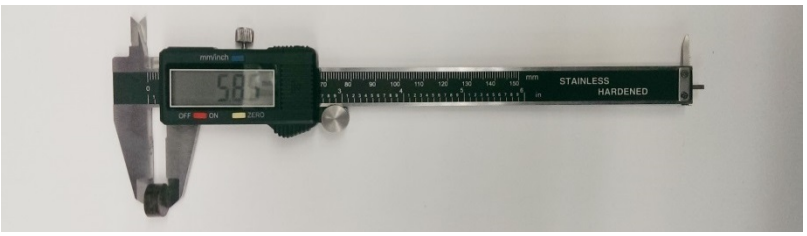

Figure 31. Measurement of pellet height by digital Vernier Calipers.

All feedstocks used to produce pellets were characterized on a dry basis. Moisture contents were determined by oven drying small samples at 105 °C for 18-24 hours. Calorific energy contents (HHV) of dried samples were measured with a Parr 6200 Calorimeter, equipped with a Parr 6510 water handling system (Parr Instrument Company, Moline, IL). Elemental compositions of the biomass materials (C, H, N, S, and O) were determined using a Thermo Scientific Flash EA 1112 Organic Elemental Analyzer (Thermo Electron Corp., Delft, The Netherlands) Further details of these analyses have been reported previously.[38,39] Energy content and compositional data for the feedstocks and pellets used in this work are summarized in Table 9.

Pellet Durability Tests: Several standard (and non-standard) tests are commonly employed to evaluate the quality of biomass pellets. These tests address properties such as mass density, energy density, compressive strength, durability, modulus of elasticity, equilibrium moisture content, and others. In this work, we established a laboratory protocol for assessing the durability of pellets produced in a heated die and hydraulic press, as described above. This protocol is shown schematically in Figure 32.

A simple, but very useful test of pellet durability involves rotary tumbling of pellets under conditions that simulate handling and transport. There are several commonly used tumbling tests, but in general, they all involve treatment of a large number of pellets, to assess mass loss due to abrasion of the pellets as they impact each other. In this project, pellet durability was determined using a tumbling test similar to that reported in the literature, [40,30,34] but modified to accommodate testing of a smaller number of pellets. The apparatus used was a Thumbler's Model A-R1 rotating tumbler, which includes a 4½ in. (11.4 cm) rubber barrel (Tru-Square Metal Products, Auburn, WA). In a standard test, 40 weighed pellets are placed in the barrel and rotated for 3000 revolutions at a speed of approximately 38 rpm (this requires 90-min. of tumbling). After tumbling, the pellets are removed from the barrel and re-weighed, while any attritted particles remain in the barrel. Durability is defined as the ratio of pellet weight after tumbling to the initial pellet weight. Photos of the tumbler and a sample of 40 pellets are shown in Figure 33.

Table 9. Characterization of Raw and Thermally Treated Feedstocks

Component	Raw Woods			Torrefied Woods		Hydrochar from Tahoe Mix					Pulverized Coal
	Tahoe Mix	Loblolly Pine	Mixed Hardwoods	Integro[1] (Tahoe Mix)	Astec[2] (Southern Pine)	HTC-175	HTC-215	HTC-235	HTC-255	HTC-275	Illinois Basin (Galatia)
Ultimate Analysis											
C, %	49.02	49.33	46.33	63.36	66.43	51.00	54.57	60.54	70.06	70.99	70.08
H, %	5.93	5.79	6.16	5.65	4.96	5.81	5.89	5.66	5.19	5.20	4.86
N,%	0.11	0.03	0.19	0.02	0.30	0.02	0.09	0.13	0.10	0.14	1.74
S,%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.57
O,%	43.26	44.92	42.77	29.70	26.37	42.60	34.89	31.59	23.42	21.35	12.87
Atomic O/C ratio	0.662	0.683	0.692	0.352	0.298	0.626	0.479	0.391	0.251	0.226	0.138
Pellet Properties											
Energy Content, MJ/kg	20.32	20.28	20.47	23.06	25.66	20.74	22.59	24.27	28.03	29.67	28.98
Mass Density, kg/m^3	1220.2	1217.8	1133.2	1064.6	1034.7	1182.4	1293.9	1313.9	1162.7	967.56	1300.7
Vol. Energy Density, GJ/m^3	24.61	24.33	23.20	25.51	26.55	24.52	29.24	31.89	29.18	28.07	37.70

1. Torrefaction of Tahoe Mix by Integro Earth Fuels, Inc., Arden, NC
2. Torrefaction of Southern Pine by Astec Inc., Chattanooga, TN.

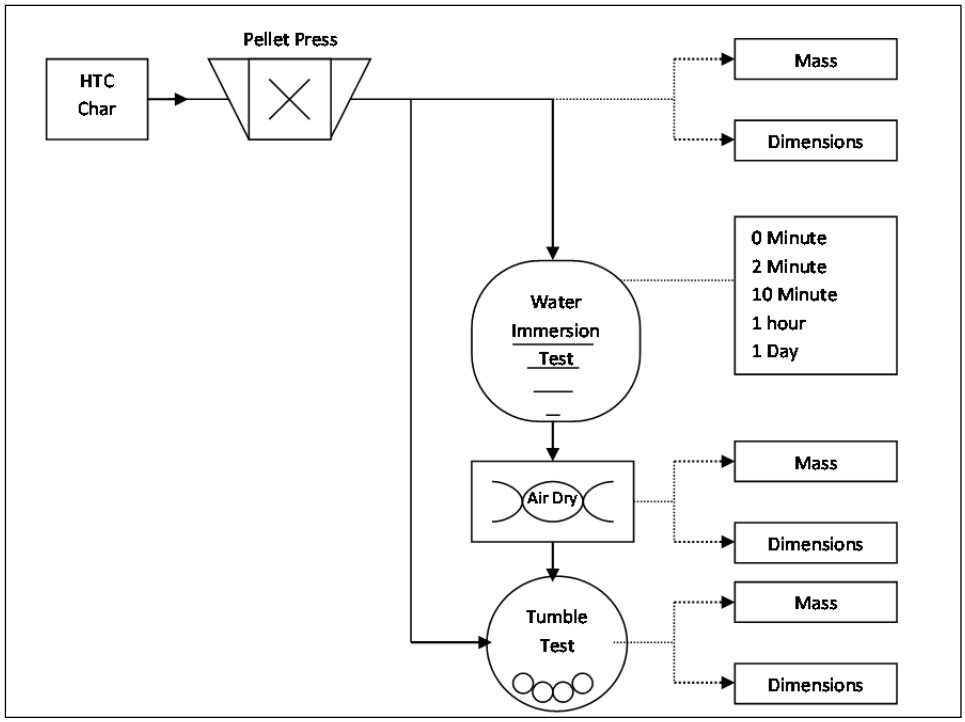

Figure 32. Laboratory protocol for assessing pellet durability.

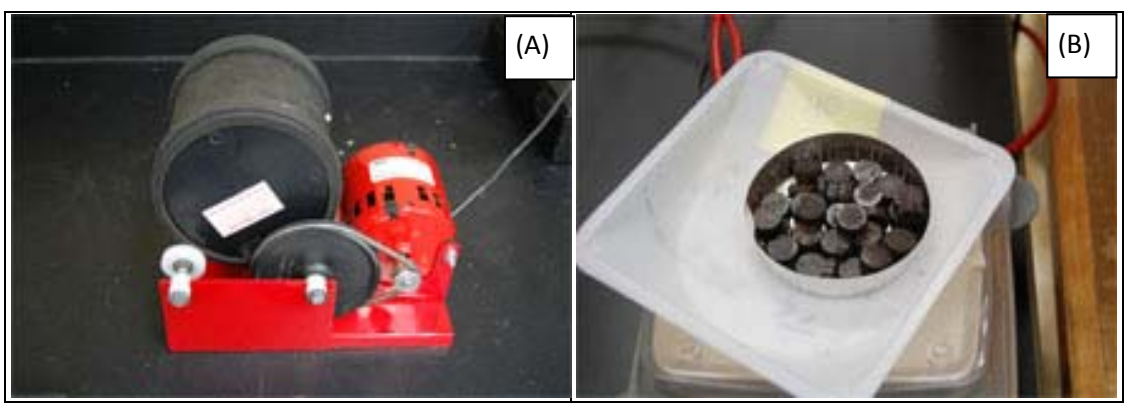

Figure 33. (A) Thumbler Model A-R1 tumbler used for pellet durability tests; (B) 40-hydrochar pellets on analytical balance.

The requirement of using 40 pellets in the durability test is a major limitation, as often, there is insufficient material available to produce this many pellets. In addition, considerable time and effort are required to produce such a large number of pellets when using a laboratory hand press. Consequently, experiments were conducted to determine whether similar durability test results could be obtained using a much smaller number of pellets. In these experiments, spherical objects were substituted as "filler" for most of the 40-pellets, and only a small number of actual test pellets were used. Three different filler materials were investigated – ½ in. diameter solid balls of maple wood, low-carbon steel, and plastic (HDPE). (All three of these filler types were obtained from McMaster-Carr). Figure 34(A) shows photos of raw and hydrochar pellets, along with the three types of artificial filler pellets. Figure 34(B) shows the tumbler barrel with wood filler pellets inside.

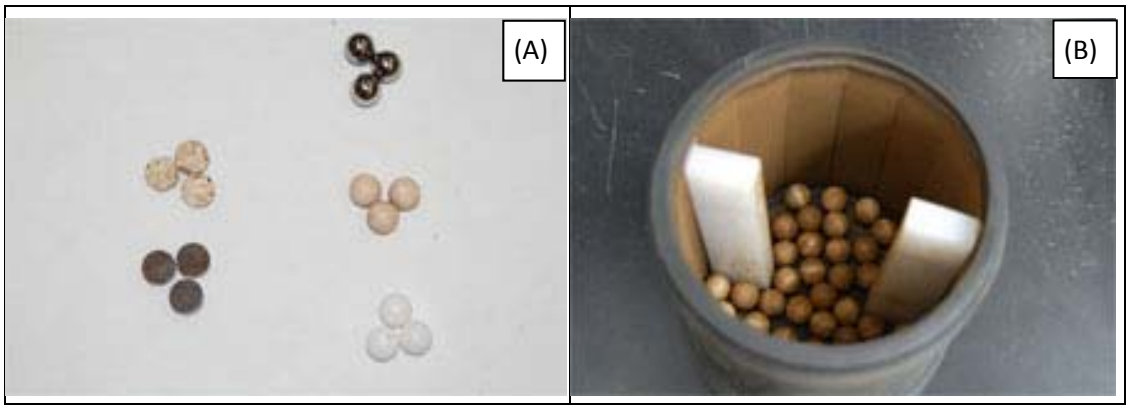

Figure 34 Pellets used in tumbler durability tests: (a) raw wood pellets, hydrochar pellets, and 3 "filler pellets": (steel, wood, and plastic; (b) tumbler drum containing wood filler pellets.

It was quickly discovered that hydrochar pellets were severely damaged when steel balls were used in the tumbler test, resulting in low values of pellet durability. The wood and plastic filler materials behaved similarly, and resulted in much less pellet damage. Because the wood balls are more similar to hydrochar pellets in material composition and density, we chose to use only these wood fillers in subsequent tumbler tests.

In an initial set of tests, pellets produced from hydrochar were used. The hydrochar was generated by hydrothermal carbonization (HTC) of Tahoe Mix wood at 255 °C for 30-min. The pellets were produced in a heated die (140 °C) using the Carver bench top laboratory hydraulic press, as described above, with 20 MPa of hydraulic pressure applied for 1-minute. First, 40 hydrochar pellets were tumbled together according to the standard test procedure (3000 revolutions in about 90 min.) As indicated by the results shown in Table 10, these pellets had extremely high durability (99.22%).

In the next set of experiments, a single hydrochar pellet was tumbled along with 39 fillers (all wood balls). This was repeated with 4 single hydrochar pellets. The average durability of these 4 tests was 99.14%, with a standard deviation of 0.21% (see Table 10). Finally, a set of 5 hydrochar pellets was tumbled along with 35 wood balls. Because the weights of these 5 pellets were different, it was possible to identify each individual pellet at the end of the tumbling. From this, a durability result was computed for each pellet. The results shown in Table 10 indicate that all 5 pellets had similar durability, with an average of 99.17% and a standard deviation of < 0.1%. Based upon the results from these three sets of experiments, it appears that the same durability value was obtained regardless of how many hydrochar pellets were tested.

However, because hydrochar is known to make very strong pellets, these tests alone may not provide adequate verification that use of a small number of pellets gives the same durability result as use of 40 pellets. Therefore, the entire set of experiments was repeated using pellets produced from torrefied Tahoe Mix wood, which is known to have poorer durability. These pellets were produced using the same method as described above. The results shown in Table 10 indicate that the durability of torrefied pellets was somewhat reduced compared to the hydrochar pellets (96% vs. 99%), but as before, the same durability results were obtained regardless of how many pellets were used.

Table 10. Pellet Durability Results from Tumbler Tests, % Mass Remaining

Bio-material	Pellet No.	40 Pellets 0 fillers	1 Pellet 39 fillers	5 Pellets 35 fillers
Tahoe Mix Hydrochar (255°C)	1		98.93	99.27
	2		99.12	99.15
	3		99.07	99.09
	4		99.42	99.22
	5			99.13
	Average	99.22	99.14	99.17
	Std.		0.21	0.07
Torrefied Tahoe Mix	1		95.86	96.20
	2		95.88	97.11
	3		96.07	96.31
	4		96.44	96.77
	5			96.11
	Average	96.13	96.06	96.50
	Std.		0.27	0.43
Raw Tahoe Mix	1		98.55	98.40
	2		98.98	98.97
	3		98.42	98.49
	4		98.73	98.26
	5			98.41
	Average	98.69	98.67	98.51
	Std.		0.24	0.27

Finally, this entire set of experiments was repeated a third time using pellets produced from raw Tahoe Mix wood. As before, similar durability results were obtained regardless of how many pellets were tested (see Table 10). Taken together, these multiple sets of tumbler experiments provide confidence that reliable durability measurements can be made when using a small number of test pellets. In most subsequent tumbler durability testing, three test pellets were used, which provides a reasonable measure of repeatability while minimizing the need for larger amounts of test materials.

All the pellets described above were produced – one at a time – in a Carver hydraulic hand press. However, as described by Shang et al., there can be important differences between pellets produced by a single pellet press and those produced by a larger-scale pelletizer.[41] It is of interest to compare the durability behavior of such "handmade" pellets with pellets produced commercially. For this purpose, two sets of commercially-produced, ¼ -in diameter pellets were obtained, along with the feedstocks used to produce them. The pellets were made from the same blend of mixed hardwoods, but with different levels of a proprietary pellet binder added. For comparison, 40 laboratory-produced pellets were made from each feedstock blend, using the heated die and hydraulic press described above. Standard tumbler tests were then conducted to determine the durability of these 40 laboratory- and 40 commercially-produced pellets. The results shown in Table 11 indicate that all these pellets were quite robust, easily tolerating three sequential tumbling tests. With both sets of pellets, the durability of the laboratory-produced pellets could not be distinguished from the durability of the commercially-produced pellets. These results confirm that laboratory-produced pellets behave similarly to commercially-produced pellets, with respect to tumbler durability measurements.

Table 11. Durability of Pellets from Mixed Hardwood, % mass remaining (Comparison of laboratory-produced and commercially-produced pellets)

Pellet Feedstock	90-Min. Tumbling	40 Commercial Pellets	40 Laboratory Pellets
Raw wood + 2% binder	1st Tumbling	98.41	98.82
	2nd Tumbling	98.53	98.94
	3rd Tumbling	98.67	99.11
	Average	**98.54**	**98.96**
	Std. Dev.	0.13	0.15
Raw wood + 4% binder	1st Tumbling	99.28	99.22
	2nd Tumbling	99.43	99.67
	3rd Tumbling	99.43	99.81
	Average	**99.38**	**99.57**
	Std. Dev.	0.09	0.31

Water Immersion Tests: When dry, raw wood pellets generally possess excellent durability (> 95% in tumbling test). However, exposure to water dramatically reduces pellet durability. This is illustrated in Figure 35, which shows photos of several pelletized woody biomass materials before and after the pellets had been immersed in water for 60-min. Also shown in this figure are photos of the same water-immersed pellets after they had undergone the tumbler durability test (1 pellet tested with 39 spherical wood filler pellets). Clearly, raw wood pellets cannot tolerate such aggressive testing conditions. Torrefied materials appear more stable, with these pellets maintaining their integrity during water immersion (albeit with significant swelling). However, the torrefied pellets completely disintegrated during tumbling. In contrast, pelletized HTC hydrochar showed very good stability, even with tumbling of the water-immersed pellet.

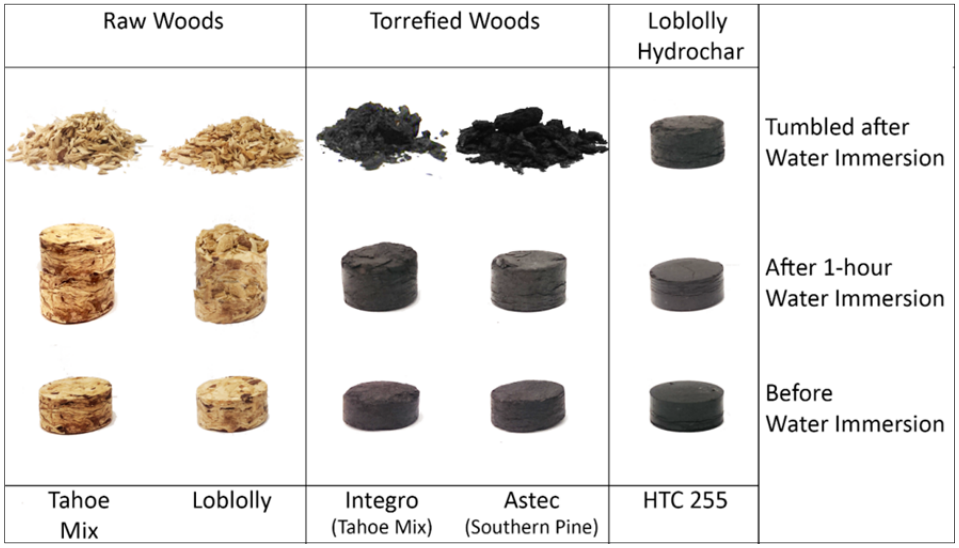

Figure 35. Effects of water immersion on stability of pelletized woody biomass materials. All pellets had diameters of 13 mm and heights of 6-7 mm prior to immersion.

To develop a standardized testing procedure for evaluating the water tolerance of pellets, a series of laboratory experiments was conducted, which systematically explored the effect of water immersion time. Three different pelletized materials were used: torrefied wood, hydrochar produced at 215 °C, and hydrochar produced at 275 °C. The feedstock for all three materials was the same Tahoe Mix wood. Pellets were immersed for 6 different lengths of time: 0 min. (control sample), 2 min., 10 min., 60 min., 1,440 min. (1-day), and 10,080 min. (1-week). These tests were conducted in triplicate. A photo showing a complete set of 18 pellets prepared to undergo these water immersion tests is shown in Figure 36.

Figure 36. Set of 18 pellets for water immersion tests.

Before immersion, each pellet was weighed and its dimensions were measured. From these measurements, pellet densities were calculated, expressed as kg/m^3. After water immersion, the pellets were allowed to air dry for 24 hours, and were then re-measured for weight and length. In addition, each pellet underwent a tumbler durability test, along with 39 spherical wood filler pellets as described above. Results of these tests are summarized graphically in Figure 37. Detailed tabular results are provided in Table 12.

Table Upon water immersion, changes in pellet weight and pellet diameter were small and insignificant for all the thermally treated materials. However, pellet length increased noticeably. Figure 37(A) shows the extent of pellet swelling as a function of immersion time. The pellets from hydrochar produced at 275°C (designated HTC-275) showed very little swelling, with less than 3% increase in length, even after 1-week of immersion. The more mildly treated hydrochar (HTC-215) exhibited modest swelling within the first 2-minutes of immersion, which increased to 18% after 1-week of immersion. However, swelling was much more extreme with the torrefied pellets. In this case, swelling of 40% was measured after just 2-minutes of immersion, increasing to 60% after 1-hour of immersion.

The effects of water immersion upon pellet density (kg/m^3) are shown in Figure 37(B). Density reductions were commensurate with dimensional changes associated with pellet swelling. Thus, pellets from severely treated hydrochar (HTC-275) remained nearly constant in density, while those from mildly treated hydrochar (HTC-215) showed slight reductions in density with increasing immersion time. In contrast, pellets of torrefied wood showed more significant

reductions in density upon water immersion. Interestingly, pellets produced from HTC-215 had higher density than those produced from HTC-275, at all immersion times.

The effects of water immersion on pellet durability (determined by tumbler tests) are shown in Figure 37(C). Only results from the two hydrochar materials are shown, because the torrefied

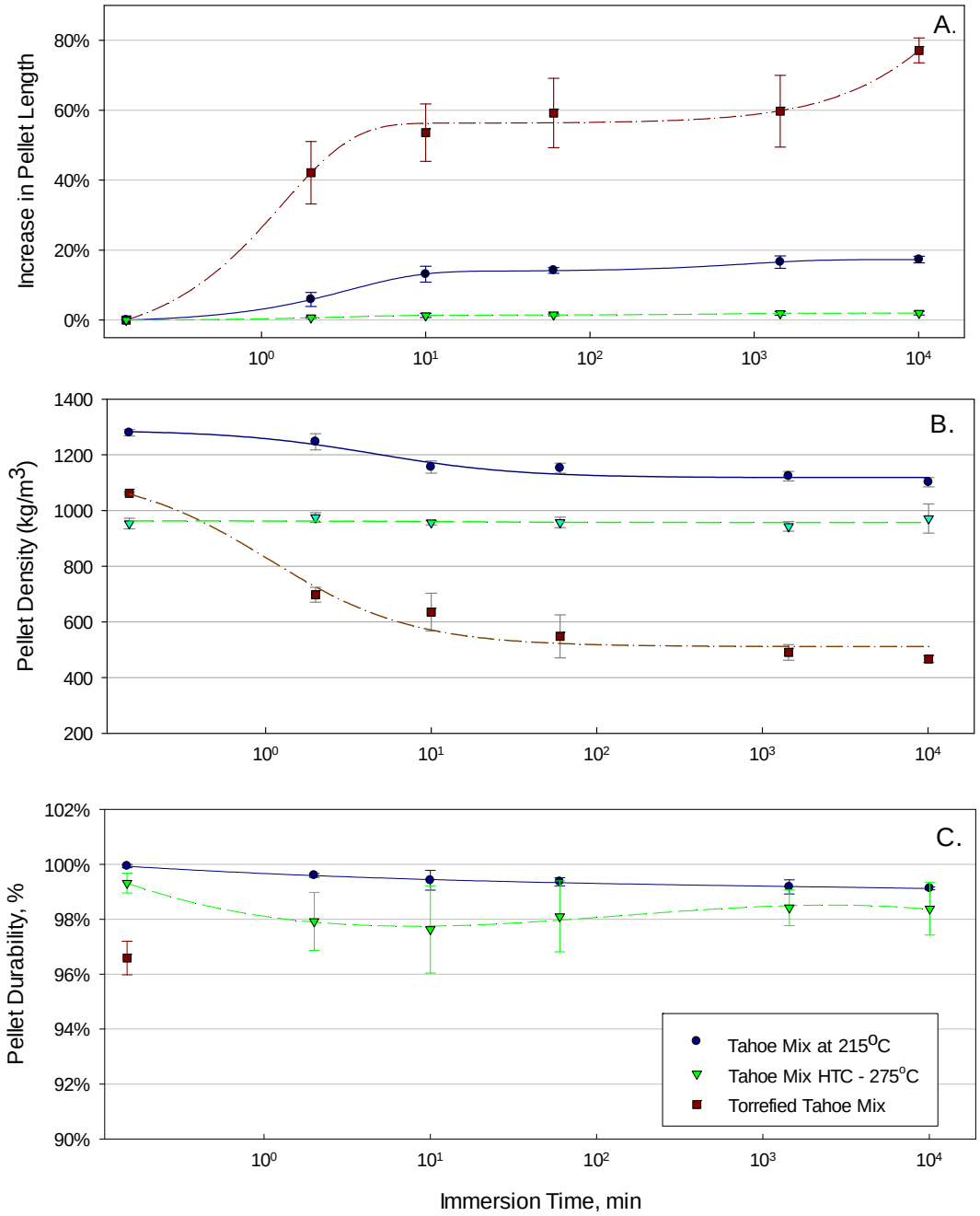

Figure 37. Effect of water immersion on the behavior of HTC and torrefied pellets. (A) Percent increase in pellet length; (B) pellet density; (C) pellet durability. Error bars represent standard deviations from triplicate experiments. (No durability results are shown for torrefied materials as these pellets did not survive tumbling.)

Table 12 (a). Pellet Water Immersion Test Results

Hydrochar from Tahoe Mix Treated at 215°C (HTC-215)

Immersion Time (min)	Pellet No.	Pellet Weight, (g)			Pellet Length, (mm)			Pellet Density, (kg/m^3)			Pellet Durability	
		Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion
0.0 (not immersed)	1	1.0791		1.0811	6.40		6.38	1270.3		1276.6	0.9998	
	2	1.1311		1.1337	6.60		6.58	1291.2		1298.1	0.9987	
	3	1.0539		1.0556	6.24		6.20	1272.4		1282.7	0.9994	
	Avg.							1278.0		1285.8	0.9993	
	SD							11.5		11.0	0.0006	
2	1	1.2121	1.2204	1.2161	7.00	7.28	7.20	1304.6	1264.8	1272.5		0.9965
	2	1.1148	1.1223	1.1169	6.48	7.00	6.90	1296.1	1213.4	1219.5		0.9952
	3	1.1940	1.2010	1.1965	6.78	7.18	7.10	1326.8	1262.1	1269.6		0.9963
	Avg.							1309.2	1246.8	1253.9		0.9960
	SD							15.8	28.9	29.8		0.0007
10	1	1.0914	1.0971	1.0928	6.40	7.26	7.00	1284.8	1146.7	1176.2		0.9961
	2	1.1006	1.1059	1.1019	6.42	7.10	6.90	1291.6	1181.1	1203.1		0.9964
	3	1.2298	1.2363	1.224	7.16	8.24	8.16	1294.0	1140.0	1130.1		0.9901
	Avg.							1290.1	1155.9	1169.8		0.9942
	SD							4.8	22.1	36.9		0.0036
60	1	1.1111	1.1164	1.1082	6.48	7.46	7.12	1291.8	1132.1	1172.6		0.9927
	2	1.1920	1.2085	1.2029	6.94	7.88	7.72	1294.0	1158.5	1173.9		0.9954
	3	1.1442	1.1554	1.1472	6.58	7.50	7.46	1310.1	1165.7	1158.6		0.9929
	Avg.							1298.6	1152.1	1168.4		0.9936
	SD							10.0	17.7	8.5		0.0015
1440 (1 Day)	1	1.1003	1.1198	1.1073	6.40	7.46	7.42	1295.3	1121.3	1124.3		0.9888
	2	1.1294	1.1448	1.1375	6.53	7.50	7.36	1303.0	1141.3	1164.4		0.9936
	3	1.0696	1.0863	1.0785	6.20	7.34	7.20	1299.7	1107.0	1128.6		0.9928
	Avg.							1299.3	1123.2	1139.1		0.9918
	SD							3.9	17.3	22.0		0.0026
10,080 (1 Week)	1	1.0185	1.0291	1.0202	6.00	7.10	6.98	1278.9	1084.5	1101.2		0.9914
	2	1.1053	1.1182	1.1078	6.48	7.56	7.36	1285.1	1102.5	1134.0		0.9907
	3	1.0873	1.1004	1.0913	6.30	7.36	7.16	1300.3	1117.5	1148.3		0.9917
	Avg.							1288.1	1101.5	1127.8		0.9913
	SD							11.0	16.5	24.2		0.0005

Table 12 (b). Pellet Water Immersion Test Results

Hydrochar from Tahoe Mix Treated at 275°C (HTC-275)

Immersion Time (min)	Pellet No.	Pellet Weight, (g)			Pellet Length, (mm)			Pellet Density, (kg/m^3)			Pellet Durability	
		Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion
0.0 (not immersed)	1	0.5544		0.5485	4.48		4.44	932.3		930.7	0.9894	
	2	0.5791		0.5771	4.50		4.48	969.5		970.5	0.9965	
	3	0.5772		0.5735	4.54		4.50	957.8		960.2	0.9936	
	Avg.							953.2		953.8	0.9932	
	SD							19.0		20.6	0.0036	
2	1	0.7626	0.7655	0.7563	5.78	5.82	5.70	994.0	990.9	999.6		0.9880
	2	0.5468	0.5486	0.5388	4.30	4.32	4.28	958.0	956.7	948.4		0.9821
	3	0.6029	0.6099	0.5901	4.66	4.70	4.66	974.7	977.7	954.0		0.9675
	Avg.							975.6	975.1	967.4		0.9792
	SD							18.0	17.2	28.1		0.0105
10	1	0.7367	0.7405	0.7094	5.74	5.78	5.42	966.9	965.2	986.1		0.9580
	2	0.5657	0.5669	0.5593	4.40	4.48	4.40	968.6	953.3	957.7		0.9866
	3	0.7973	0.7976	0.7851	6.22	6.32	6.16	965.7	950.8	960.2		0.9843
	Avg.							967.1	956.5	968.0		0.9763
	SD							1.5	7.7	15.7		0.0159
60	1	0.7101	0.7138	748.6101	5.60	5.70	5.64	955.3	943.5	933.2		0.9787
	2	0.4935	0.4936	493.7641	3.74	3.80	3.72	994.1	978.6	994.6		0.9949
	3	0.7972	0.8015	828.2495	6.28	6.36	6.24	956.4	949.4	938.1		0.9694
	Avg.							968.6	957.2	955.3		0.9810
	SD							22.1	18.8	34.1		0.0129
1440 (1 Day)	1	0.6954	0.7007	0.6852	5.58	5.72	5.62	938.9	922.9	918.5		0.9779
	2	0.7190	0.7213	0.7147	5.62	5.70	5.64	963.9	953.4	954.7		0.9908
	3	0.7159	0.7203	0.7087	5.60	5.70	5.62	963.1	952.1	950.1		0.9839
	Avg.							955.3	942.8	941.1		0.9842
	SD							14.2	17.2	19.7		0.0065
10,080 (1 Week)	1	0.9198	0.9247	0.9165	6.60	6.76	6.60	1050.0	1030.6	1046.2		0.9911
	2	0.7231	0.7294	0.7097	5.82	5.90	5.82	936.0	931.4	918.7		0.9730
	3	0.5889	0.5913	0.5838	4.58	4.68	4.60	968.7	951.9	956.2		0.9873
	Avg.							984.9	971.3	973.7		0.9838
	SD							58.7	52.3	65.5		0.0096

Table 12 (c). Pellet Water Immersion Test Results

Torrefied Tahoe Mix

Immersion Time (min)	Pellet No.	Pellet Weight, (g)			Pellet Length, (mm)			Pellet Density, (kg/m^3)			Pellet Durability	
		Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion
0.0 (not immersed)	1	0.8900		0.8745	6.34		6.44	1057.6		1023.1	0.9607	
	2	0.9739		0.9675	6.88		7.00	1066.5		1041.3	0.9726	
	3	0.9456		0.9308	6.68		6.80	1066.5		1031.3	0.9644	
	Avg.							1063.5		1031.9	0.9659	
	SD							5.1		9.1	0.0061	
2	1	0.9189	0.844	-	6.54	9.40	-	1058.6	676.5	-	-	
	2	1.0389	0.8792	-	7.26	9.62	-	1078.1	688.6	-	-	
	3	0.8682	0.8964	-	6.18	9.28	-	1058.4	727.7	-	-	
	Avg.							1065.0	697.6	-	-	
	SD							11.3	26.8	-	-	
10	1	0.9174	0.9504	-	6.48	10.28	-	1066.6	696.5	-	-	
	2	0.9242	0.7765	-	6.58	10.40	-	1058.2	562.5	-	-	
	3	1.0122	0.8781	-	7.10	10.23	-	1074.1	646.7	-	-	
	Avg.							1066.3	635.2	-	-	
	SD							7.9	67.7	-	-	
60	1	0.8992	0.6147	-	6.32	9.40	-	1071.9	492.7	-	-	
	2	0.9237	0.7268	-	6.62	10.62	-	1051.2	515.6	-	-	
	3	0.8726	0.8851	-	6.22	10.48	-	1056.9	636.3	-	-	
	Avg.							1060.0	548.2	-	-	
	SD							10.7	77.2	-	-	
1440 (1 Day)	1	0.9041	0.6778	-	6.44	11.0	-	1057.7	464.2	-	-	
	2	0.9770	0.6743	-	6.92	10.4	-	1063.7	487.5	-	-	
	3	0.9583	0.7387	-	6.78	10.7	-	1064.9	520.1	-	-	
	Avg.							1062.1	490.6	-	-	
	SD							3.9	28.1	-	-	
10,080 (1 Week)	1	0.9611	0.7425	-	6.86	12.2	-	1055.5	458.5	-	-	
	2	1.0136	0.7847	-	7.10	12.3	-	1075.6	480.6	-	-	
	3	0.9866	0.7593	-	6.88	12.4	-	1080.4	461.3	-	-	
	Avg.							1070.5	466.8	-	-	
	SD							13.2	12.0	-	-	

pellets were very weak after water immersion, and crumbled upon handling. Pellets from the mildly treated hydrochar (HTC-215) showed a small but steady loss of durability with increasing immersion time. HTC-275 pellets showed a more complex behavior, with greater loss of durability observed at relatively short immersion times, although the greatest loss of durability was less than 2%. To summarize, pellets from both HTC-215 and HTC-275 were very robust, and tolerated extended immersion times with minimal loss of durability, while torrefied pellets (and raw wood pellets) could not survive tumbling tests following even short immersion times.

These water immersion test results show a high degree of repeatability, and provide a means for readily distinguishing among pellets that exhibit different water-immersion behaviors. Based upon these results, 60-min. was selected as the standard immersion period for assessing water tolerance of pellets produced from woody biomass. Note that the water immersion and tumbling process is an extremely severe test of pellet durability, and that only very robust pellets can maintain their integrity when exposed to these conditions. In cases where the pellets are very

robust, it is preferable to use 3 test pellets and 37 spherical wood filler pellets in a single tumbler test, and to determine the individual weight loss from each pellet. However, low-stability pellets often lose a significant fraction of their weight, due to attrition of large fragments, making it difficult to identify the same pellet before and after tumbling if multiple pellets are used in a single tumbler test. Thus, for these weaker pellets, tumbler testing of a single pellet along with 39 filler pellets is preferred.

Effect of HTC Process Temperature upon Pellet Durability: The temperature under which HTC processing is conducted is known to have a strong effect upon many properties of the resulting hydrochar – including proximate analysis, ultimate analysis, moisture content, and energy content.[30,38,39] Here we explored the effect of HTC process temperature upon the durability of pellets produced from various hydrochar products derived from loblolly pine.

Hydrochars obtained from previous work were used in these experiments.[39] All materials were produced in a 2-L stirred Parr reactor, with a reaction hold time of 30-min. As shown in Figure 38, processing temperature has a significant effect on pellet behavior. At temperatures above 215 °C, the resulting pellets were extremely robust, showing very little swelling when immersed in water, and very little loss of durability upon tumbling of water-immersed pellets. However, at temperatures below 215 °C, the pellets began to swell significantly upon water immersion, reaching an increase of 140% at 175°C process temperature. The pellet durability, as measured by tumbling tests, showed a sharp reduction at low HTC processing temperature. While pellets made from hydrochar that was produced at an HTC temperature of 200 °C (HTC-200) were still quite stable, HTC-175 pellets could not survive the tumbling test following water immersion. Detailed numerical results from these water immersion tests are provided in Table 13.

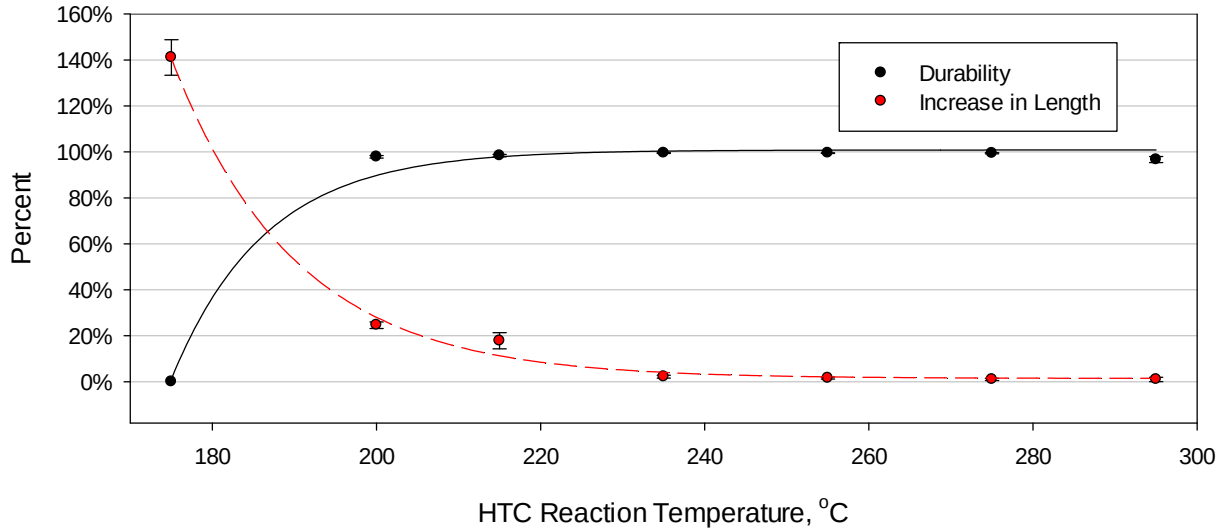

Figure 38. Effect of HTC process temperature upon behavior of hydrochar pellets after immersion in water for 60-min. Hydrochar was produced by treatment of Loblolly Pine at indicated temperature for 30-min. in a 2-L stirred Parr reactor. Error bars represent ± 1 std. dev. from measurement of 3 pellets produced from a single HTC experiment.

Table 13. Effect of HTC Process Temperature upon Properties of Loblolly Pine Pellets

HTC Reactor Temp, °C	Pellet No.	Pellet Weight, (g)			Pellet Length, (mm)			Pellet Density, (kg/m^3)			Pellet Durability	
		Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Pre Immersion	Post Immersion
Raw Loblolly (no HTC)	1	1.0267	1.0040	-	6.23	13.65	-	1241.6	-	-	0.9860	-
	2	1.0347	1.1225	-	6.32	13.67	-	1233.4	-	-	0.9896	-
	3	0.9460	0.7429	-	5.76	13.40	-	1237.3	-	-	0.9836	-
	Avg.							1237.5	-	-	0.9864	-
	SD							4.1	-	-	0.0030	-
175°	1	0.9418	0.9580	-	5.54	13.46	-	1280.8	536.2	-	0.9986	-
	2	0.9825	1.0001	-	5.75	13.38	-	1287.3	563.1	-	0.9980	-
	3	0.9460	0.9256	-	5.44	13.48	-	1310.1	517.3	-	0.9980	-
	Avg.							1292.7	538.9	-	0.9982	-
	SD							15.4	23.0	-	0.0004	-
200°	1	0.9388	0.9470	0.9313	5.43	6.74	6.58	1302.6	1058.6	1066.3	0.9982	0.9834
	2	0.9221	0.9336	0.9160	5.29	6.53	6.38	1313.2	1077.1	1081.7	0.9990	0.9811
	3	0.9990	1.0080	0.9804	5.80	7.32	7.06	1297.7	1037.5	1046.2	0.9992	0.9726
	Avg.							1304.5	1057.7	1064.7	0.9988	0.9791
	SD							8.0	19.9	17.8	0.0005	0.0057
215°	1	0.9362	0.9435	0.9313	5.35	6.39	6.32	1318.4	1112.4	1110.2	0.9976	0.9871
	2	0.9837	0.9932	0.9712	5.66	6.44	6.40	1309.4	1161.9	1143.3	0.9985	0.9778
	3	0.9763	0.9871	0.9743	5.59	6.72	6.68	1315.8	1106.7	1098.9	0.9983	0.9870
	Avg.							1314.5	1127.0	1117.4	0.9981	0.9840
	SD							4.6	30.4	23.1	0.0005	0.0053
235°	1	0.9554	0.9594	0.9533	5.63	5.79	5.79	1278.5	1248.4	1240.4	0.9985	0.9936
	2	1.0015	1.0066	1.0023	5.89	5.98	5.94	1281.0	1268.2	1271.3	0.9992	0.9957
	3	0.9453	0.9500	0.9465	5.57	5.69	5.69	1278.6	1257.9	1253.2	0.9966	0.9963
	Avg.							1279.4	1258.1	1255.0	0.9981	0.9952
	SD							1.4	9.9	15.5	0.0014	0.0014
255°	1	0.9855	0.9883	0.9832	6.02	6.15	6.10	1233.3	1211.7	1215.3	0.9945	0.9948
	2	0.9601	0.9667	0.9610	6.12	6.20	6.18	1181.9	1174.6	1171.5	0.9938	0.9941
	3	0.9238	0.9300	0.9260	5.84	5.91	5.91	1192.7	1185.5	1181.4	0.9967	0.9958
	Avg.							1202.6	1190.6	1189.4	0.9950	0.9949
	SD							27.1	19.1	23.0	0.0015	0.0008
275°	1	1.0156	1.0172	1.0131	6.41	6.50	6.40	1193.7	1179.0	1192.6	0.9904	0.9960
	2	0.9186	0.9267	0.9196	6.35	6.42	6.42	1089.9	1087.5	1079.2	0.9883	0.9923
	3	0.9022	0.9099	0.9055	6.10	6.13	6.12	1114.3	1118.3	1114.7	0.9968	0.9952
	Avg.							1132.6	1128.3	1128.8	0.9918	0.9945
	SD							54.3	46.6	58.0	0.0044	0.0019
295°	1	0.9854	1.0051	0.9718	6.93	7.07	7.02	1071.3	1071.1	1042.9	0.9813	0.9669
	2	0.9342	0.9553	0.9110	6.58	6.62	6.61	1069.6	1087.2	1038.3	0.9811	0.9536
	3	0.9336	0.9444	0.9260	6.53	6.55	6.52	1077.1	1086.3	1070.0	0.9928	0.9805
	Avg.							1072.7	1081.5	1050.4	0.9851	0.9670
	SD							3.9	9.1	17.1	0.0067	0.0134

The effects of HTC process temperature upon the mass density, energy content, and volumetric energy density of pellets are illustrated in Figure 39. As previously documented, the energy content of hydrochar (HHV; MJ/kg) increases with increasing process temperature – up to a point, then remains fairly constant with further increases in temperature.[39] Under the HTC conditions employed here (2-L stirred Parr reactor, 30-min. hold time), maximum energy content is reached at a process temperature of approximately 275 °C. At this point, the energy content is about 29 MJ/kg, which is 45% higher than that of the raw loblolly pine feedstock.

The mass density of raw wood pellets was approximately 1220 kg/m^3. For pellets of hydrochar materials, the mass density increased slightly as the HTC process temperature increased from 175 to 235 °C. Maximum density was achieved at process temperatures of approximately 200-215 °C, where it was about 5% higher than the density of raw loblolly wood pellets. At process temperatures near 250 °C, the pellet mass density was the same as for raw wood pellets; at 295 °C, the density was about 12% lower than the raw wood pellets. This decrease in pellet mass density with increasing process temperature is similar to that reported by Reza et al. for pellets of torrefied loblolly pine.[31]

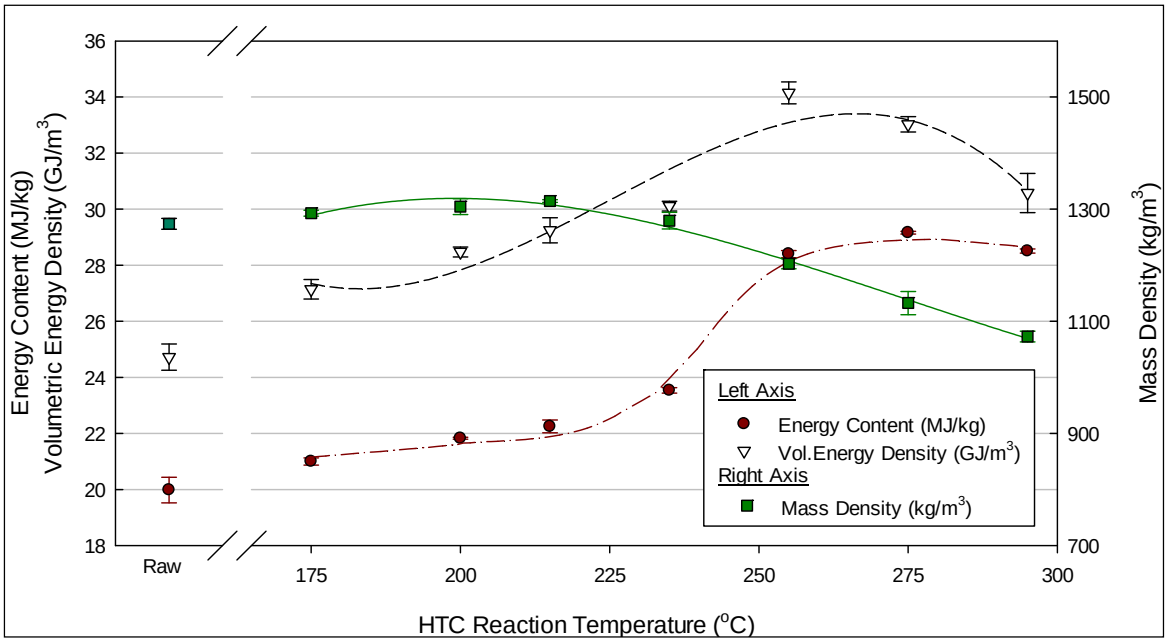

Figure 39. Effect of HTC process temperature upon mass and volumetric densities of pellets. Hydrochar was produced by treatment of Loblolly Pine at indicated temperatures for 30-min. in a 2-L stirred Parr reactor. All measurements were made prior to water immersion. Error bars represent ± 1 std. dev. from measurement of three pellets produced from a single HTC experiment.

The volumetric energy density (MJ/m^3) of a pellet is defined as the product of mass density (kg/m^3) and mass energy content (MJ/kg). Thus, the trend line shown in Figure 39 for the effect of process temperature upon volumetric energy density is the product of the other two trend lines. Raw loblolly pine pellets have an approximate volumetric energy density of 25 GJ/m^3. All pellets produced from hydrochar materials had higher energy densities. As HTC process temperature increased, the pellets' volumetric energy also increased – up to a maximum around 255 °C, where the value of 34 GJ/m^3 was 36% higher than that of raw pellets. As the process temperature was increased beyond 255 °C, the volumetric energy density declined slightly.

Extraction of Hydrochar: In an effort to understand what is responsible for the excellent binding ability of hydrochar, a series of extraction experiments was conducted using a Dionex Accelerated Solvent Extractor (ASE). Three solvents of differing polarity were used: hexane, acetone, and water. Hydrochar that was produced from treatment of Tahoe Mix wood at 255 °C for 30-min. was extracted, as well as the Integro (Integro Earth Fuels, Inc., Arden, NC) torrefied wood produced from the same feedstock. In each experiment, approximately 2.5 g of material

was extracted for 15 min. at a temperature of 80 °C and a pressure of 1500 psi. The extractable mass was determined gravimetrically, by weighing the dry samples before and after extraction.

The results shown in Table 14 indicate that very little material was extracted from the torrefied wood using any of the three solvents, although acetone was somewhat more effective than hexane or water. With HTC-255, hexane and water extracted slightly more total mass, while acetone extracted a much larger amount of material – accounting for 25.7% of the original hydrochar mass. Extraction of raw wood with acetone removed only 0.97% of the starting mass.

Table 14. Extractable Mass from Hydrochar and Torrefied Tahoe Mix Wood, %

Tahoe Mix- derived feedstocks	Extraction Solvent		
	Hexane	Acetone	Water
Hydrochar at 255 °C	0.5	25.7	2.1
Integro Torrefied	0.4	3.1	0.6
Raw Wood	-	1.0	-

This acetone extraction method was then applied to a set of archived hydrochar samples that had been produced by HTC treatment of Tahoe Mix wood over a wide range of process temperatures (all with reaction hold times of 30-min.). Results shown in Table 15 indicate that the mass of acetone extractables increases with increasing HTC process temperature, reaching a plateau at temperatures above 275 °C. This trend of increasing acetone-extractable fraction with process temperature is similar to the trend of hydrochar energy content shown in Figure 39, and inverse to the trend of pellet swelling with process temperature shown in Figure 38. These observations suggest that acetone extractable material within hydrochar has relatively high energy content, and may be partly responsible for the excellent binding properties of the hydrochar. Furthermore, the lack of acetone extractable material from raw wood, and particularly torrefied wood, may explain the relatively poor binding behavior of these materials.

Table 15. Acetone-Extractable Mass from Tahoe Mix Hydrochar
(All hydrochars produced in 2-L stirred Parr reactor, with 30-min. hold time)

HTC Temperature, °C	% Mass Extracted
155	3.0
175	5.0
195	6.0
215	12.7
235	16.4
255	21.9
275	31.8
295	29.4

To investigate further the effectiveness of acetone extracts as a pellet binder, a larger quantity (about 100 g) of hydrochar from Tahoe Mix HTC-275 was extracted using the ASE instrument. For this purpose, we combined Tahoe Mix hydrochar products obtained from several small scale (2-L Parr reactor) HTC experiments conducted at 255°C. A total of 99.0 g of this hydrochar was divided among 5 cellulose extraction thimbles for use with a Dionex Accelerated Solvent

Extractor (ASE-300) instrument. These samples were then extracted with acetone at 80°C and 1500 psi for 15 minutes. The acetone extract solutions from all thimble samples were combined and reduced to 100 mL.

The recovered solids from all thimbles were re-combined and weighed. It was determined that only 6.40 g (6.46%) of mass was lost by acetone extraction. This is much less than the 20-30% extractive loss we expected, based upon small-scale extractions of similar hydrochars we had conducted earlier. Upon further investigation, it was surmised that with these relatively large amounts of hydrochar (about 20 g per thimble), acetone was not able to penetrate effectively throughout the entire bed of char. In fact, a hard crust was observed to have formed on top of each thimble, perhaps providing a barrier to effective extraction.

To overcome this problem, we repeated the ASE extraction of this hydrochar material. (The same material that had previously been extracted was extracted again.) However, smaller samples of hydrochar were used (approximately 4 g in each of 10 thimbles) and a higher extraction temperature was applied (100°C rather than 80°C). In addition, each sample was extracted twice. After the first extraction, each thimble was removed and the hydrochar was manually agitated using a stirring rod, before placing it back into the ASE instrument for a second extraction. As shown in Table 16, this extraction procedure resulted in significantly greater loss of mass from the hydrochar. Considering the amount of acetone extracts from both of the first experiments (large thimbles and 80°C) and the second experiments (small thimbles and 100°C), the total acetone-extracted mass represented 22.0% of the starting hydrochar.

Table 16. Acetone Extraction of 255°C Hydrochar Produced from Tahoe Mix

Sample No.	Thimble wt., g	Thimble + Char before extract., g	Wt. of Char sample, g	Thimble + Char after extract., g	Extracted Mass, g	Percent Extracted
1	1.4106	5.7296	4.3190	5.1035	0.6261	14.50%
2	1.3578	5.4216	4.0638	4.7322	0.6894	16.96%
3	1.4596	5.6721	4.2125	5.1521	0.5200	12.34%
4	1.4937	5.5595	4.0658	4.8759	0.6836	16.81%
5	1.5522	5.6234	4.0712	4.7033	0.9201	22.60%
6	1.4203	5.5987	4.1784	4.6622	0.9365	22.41%
7	1.4136	5.3943	3.9807	4.8979	0.4964	12.47%
8	1.5231	5.4718	3.9487	4.8141	0.6577	16.66%
9	1.4018	5.4477	4.0459	4.9900	0.4577	11.31%
10	1.3809	5.5467	4.1658	4.6998	0.8469	20.33%
Avg.			4.1052			16.64%
S.D.						4.10%

An aliquot of these acetone extracts was evaporated to dryness, and its energy content was measured by calorimetry to be 29.85 MJ/kg (HHV), which is higher than any hydrochar products produced from this feedstock.

Effectiveness of Acetone Extracts as Pellet Binder: A series of experiments was conducted with the objective of determining whether addition of these acetone extracts could improve pelletization of biomass materials that otherwise do not form robust pellets (as determined by water immersion tests). For this purpose, samples of torrefied Tahoe Mix, raw loblolly pine, and

mildly-carbonized loblolly pine (HTC-200) were utilized. The acetone extracts from Tahoe Mix HTC-275 were diluted to 250 mL to create a stock solution that was then added to various biomass materials prior to pelletization. The amount of acetone extracts added to the biomass materials was 25%, 50%, and 100% of the amount that had been removed by extraction of the Tahoe Mix hydrochar. (In other words, the acetone extracts represented 5.5%, 11.0% and 22.0% of the final blends, by mass.) After adding the desired amount of acetone stock solution to weighed amounts of each biomass sample, the acetone was allowed to evaporate, and the remaining material was thoroughly mixed (with a mortar and pestle) to prepare homogeneous samples for pelletizing. The stability of the produced pellets was then assessed before and after immersion in water for 60-min. Figure 40 summarizes the results of pellet swelling and durability following water immersion. More detailed numerical results of all these tests are provided in Table 17.

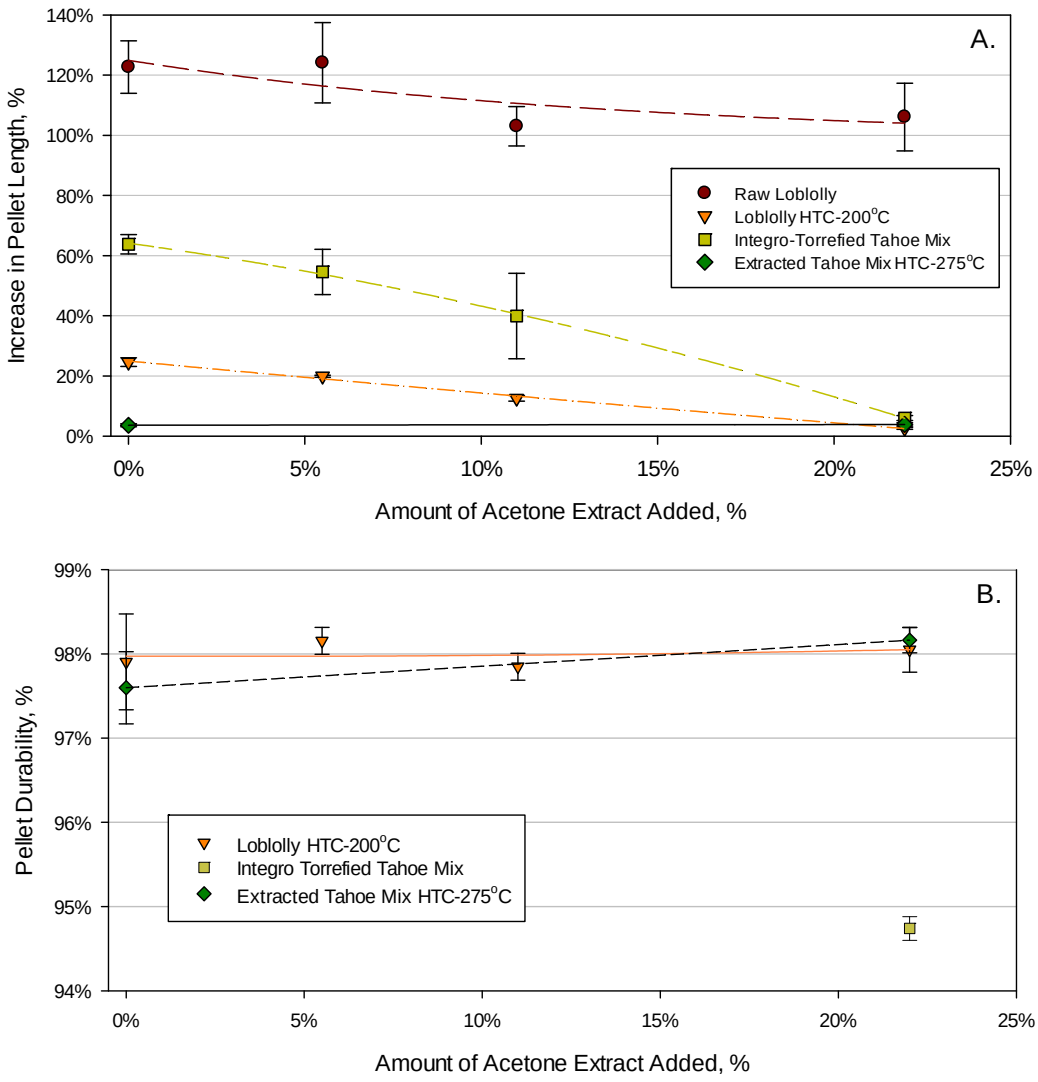

Figure 40. Effects of acetone extract addition upon pellet behavior after immersion in water for 60-min. (A) Increase in pellet length; (B) pellet durability. Error bars represent ± 1 std. dev. from triplicate experiments. (No durability results are shown for pellets made from raw loblolly as they did not survive a tumbling test.)

Table 17. Part 1. Effect of Acetone Extract Addition upon Pelletization Properties of Raw and HTC loblolly Pine

Biomass Material	Acetone Extracts, %	Pellet No.	Pellet Weight, g			Pellet Length, mm			Pellet Density, kg/m^3			Pellet Durability	
			Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion
Raw Loblolly	0%	1	1.0267	1.0040	-	6.23	13.65	-	1241.6	-	-	0.9860	-
		2	1.0347	1.1225	-	6.32	13.67	-	1233.4	-	-	0.9896	-
		3	0.9460	0.7429	-	5.76	13.40	-	1237.3	-	-	0.9836	-
		Avg.							1237.5	-	-	0.9864	-
		SD							4.1	-	-	0.0030	-
	5.5%	1	1.0317	1.0127	-	6.04	13.21	-	1241.6	1021.6	-	0.9750	-
		2	1.0207	0.9894	-	6.24	13.37	-	1233.4	1018.4	-	0.9706	-
		3	0.9647	0.7671	-	5.37	12.85	-	1237.3	1036.3	-	0.9863	-
		Avg.							1237.5	1025.5	-	0.9773	-
		SD							4.1	9.6	-	0.0081	-
	11.0%	1	1.0536	0.9771	-	6.14	12.51	-	1241.6	994.6	-	0.9805	-
		2	1.0616	1.0956	-	6.29	12.34	-	1233.4	996.4	-	0.9857	-
		3	0.9729	0.7160	-	5.83	12.19	-	1237.3	997.3	-	0.9767	-
		Avg.							1237.4	996.1	-	0.9810	-
		SD							4.1	1.4	-	0.0045	-
	22%	1	1.0538	0.9769	-	6.20	11.98	-	1241.6	1040.6	-	0.9889	-
		2	1.0618	1.0954	-	5.86	12.51	-	1233.4	1025.4	-	0.9806	-
		3	0.9731	0.7158	-	6.16	13.03	-	1237.3	1001.3	-	0.9783	-
		Avg.							1237.4	1022.4	-	0.9826	-
		SD							4.1	19.8	-	0.0056	-
Loblolly HTC-200	0%	1	0.9388	0.9470	0.9313	5.43	6.74	6.58	1302.6	1058.6	1066.3	0.9982	0.9834
		2	0.9221	0.9336	0.9160	5.29	6.53	6.38	1313.2	1077.1	1081.7	0.9990	0.9811
		3	0.9990	1.0080	0.9804	5.80	7.32	7.06	1297.7	1037.5	1046.2	0.9992	0.9726
		Avg.							1304.5	1057.7	1064.7	0.9988	0.9791
		SD							8.0	19.9	17.8	0.0005	0.0057
	5.5%	1	0.9525	0.9333	0.9450	5.15	6.18	6.16	1302.6	1058.6	1066.3	0.9819	0.9798
		2	0.9358	0.9199	0.9297	5.47	6.54	6.52	1313.3	1077.2	1081.7	0.9849	0.9830
		3	1.0127	0.9943	0.9941	5.09	6.12	6.09	1297.7	1037.5	1046.2	0.9794	0.9818
		Avg.							1304.5	1057.7	1064.8	0.9821	0.9816
		SD							8.0	19.9	17.8	0.0028	0.0016
	11.0%	1	0.9540	0.9318	0.9161	5.48	6.13	6.11	1302.5	1058.5	1066.3	0.9989	0.9767
		2	0.9373	0.9184	0.9008	5.12	5.82	6.80	1313.2	1077.1	1081.7	0.9811	0.9798
		3	1.0142	0.9928	0.9652	5.41	6.07	6.04	1297.6	1037.4	1046.2	0.9867	0.9789
		Avg.							1304.5	1057.7	1064.7	0.9889	0.9785
		SD							8.0	19.9	17.8	0.0091	0.0016
	22.0%	1	0.9472	0.9286	0.9303	5.84	6.00	5.99	1302.6	1058.6	1066.3	0.9869	0.9804
		2	0.9305	0.9152	0.9150	6.37	6.55	6.51	1313.2	1077.1	1081.7	0.9794	0.9836
		3	1.0274	1.0051	0.9794	6.27	6.41	6.36	1297.7	1037.5	1046.2	0.9897	0.9783
		Avg.							1304.5	1057.7	1064.7	0.9853	0.9807
		SD							8.0	19.9	17.8	0.0053	0.0027

Table 17. Part 2. Effect of Acetone Extract Addition upon Pelletization Properties of Torrefied and Raw Tahoe Mix Wood

Integro Torrefied	0%	1	0.7331	0.6984	-	5.40	9.00	-	1022.8	584.6	-	0.9745	-
		2	0.7838	0.7447	-	5.72	9.40	-	1032.4	596.9	-	0.9585	-
		3	1.0122	0.9834	-	6.30	10.10	-	1210.5	733.6	-	0.9737	-
		Avg.							1088.5	638.4	-	0.9689	-
		SD							105.7	82.7	-	0.0090	-
	5.5%	1	0.7166	0.7037	-	5.24	8.10	-	1030.3	654.5	-	0.9791	-
		2	0.7290	0.7223	-	5.48	8.06	-	1002.2	675.2	-	0.9812	-
		3	0.7812	0.7678	-	5.86	9.50	-	1004.4	608.9	-	0.9795	-
		Avg.							1012.3	646.2	-	0.9799	-
		SD							15.6	33.9	-	0.0011	-
	11.0%	1	0.6653	0.6608	-	4.96	7.40	-	1010.6	672.8	-	0.9805	-
		2	0.9415	0.9368	-	7.20	8.90	-	985.2	793.0	-	0.9811	-
		3	0.8005	0.7950	-	6.00	8.82	-	1005.2	679.1	-	0.9844	-
		Avg.							1000.3	715.0	-	0.9820	-
		SD							13.4	67.7	-	0.0021	-
	22.0%	1	0.4942	0.4905	0.4654	4.02	4.24	4.00	926.2	871.6	876.6	0.9842	0.9488
		2	0.6125	0.6113	0.5783	4.60	4.92	4.72	1003.2	936.1	923.1	0.9836	0.9460
		3	0.6267	0.6232	0.5904	5.00	5.28	5.02	944.3	889.2	886.1	0.9875	0.9474
		Avg.							957.9	899.0	895.2	0.9851	0.9474
		SD							40.2	33.3	24.6	0.0021	0.0014
Extracted Tahoe Mix HTC-275	0%	1	0.7425	0.7524	0.7306	5.20	5.36	5.30	1075.8	1057.6	1038.5	0.9995	0.9710
		2	0.7060	0.7151	0.6996	5.10	5.30	5.26	1042.9	1016.5	1002.0	0.9861	0.9783
		3	0.7106	0.7197	0.7043	5.12	5.32	5.28	1045.6	1019.2	1004.9	0.9899	0.9786
		Avg.							1054.8	1031.1	1015.2	0.9902	0.9760
		SD							18.2	23.0	20.3	0.0043	0.0043
	22.0%	1	0.6201	0.6318	0.6213	4.22	4.36	4.28	1107.1	1091.7	1093.7	0.9955	0.9834
		2	0.6521	0.6588	0.6461	4.52	4.70	4.62	1086.9	1056.0	1053.6	0.9995	0.9807
		3	0.6362	0.6458	0.6334	4.34	4.53	4.46	1104.4	1074.0	1070.0	0.9964	0.9808
		Avg.							1099.5	1073.9	1072.4	0.9971	0.9816
		SD							10.9	17.8	20.1	0.0021	0.0015

The results shown in Figure 40(A) suggest that in general, the addition of acetone extracts to biomass materials reduced swelling when pellets were immersed in water. This was seen most clearly with pellets made from the Integro torrefied Tahoe Mix wood. Without including acetone extracts, these pellets swelled by 60% upon immersion in water. The degree of swelling declined with increasing addition of extracts, reaching a minimum of 6% swelling upon addition of 22% extracts.

The beneficial effect of adding increased amounts of acetone extracts to the torrefied wood material is shown in Figure 41. This figure also illustrates the improved tumbling behavior of the torrefied pellets as increasing amounts of acetone extracts are added. With maximum extract addition (shown here as “100%”), a pellet could be recovered as a single piece; with 50% extract addition, a pellet typically broke into several large pieces that could be recovered; with less than 50% addition, a pellet crumbled into small pieces that could not easily be recovered. Addition of acetone extracts to the loblolly pine HTC-200 also reduced swelling of these pellets, although the change was not as large as with the torrefied pellets.

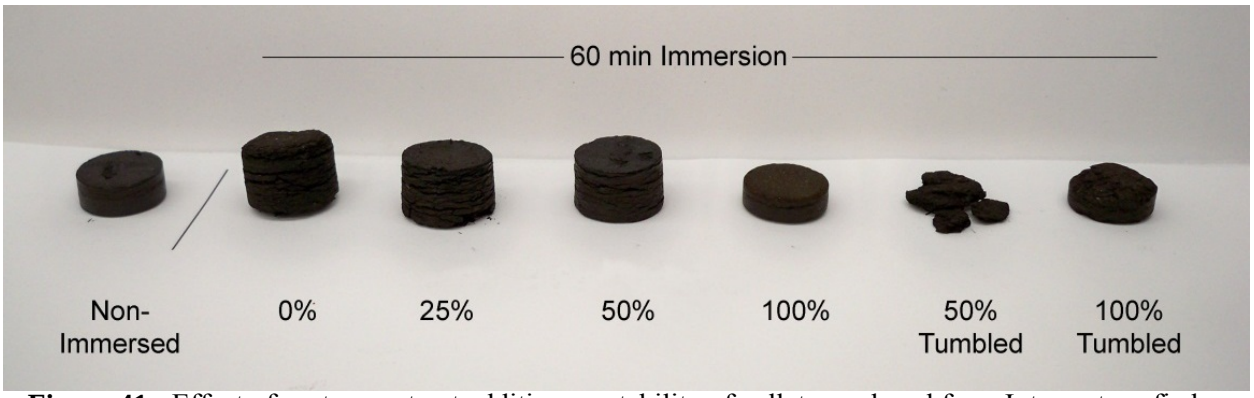

Figure 41. Effect of acetone extract addition on stability of pellets produced from Integro torrefied biomass. Percentage values indicate the amount of acetone extract added to the torrefied Tahoe Mix. "Tumbled" indicates pellet was tumbled for 3000 revolutions, after 60-min. immersion in water.

Figure 40(A) also shows that pellets produced from the HTC-275 that had been extracted with acetone remained very stable, exhibiting swelling of less than 2% upon water immersion. Thus, it appears that even when considerable mass was extracted from the Tahoe Mix HTC-275, this did not remove all of the inherent binder materials. Sufficient binder remained after extraction to enable production of very robust pellets. The strong stability of these HTC pellets – with or without addition of acetone extracts – is illustrated in the photographs of Figure.

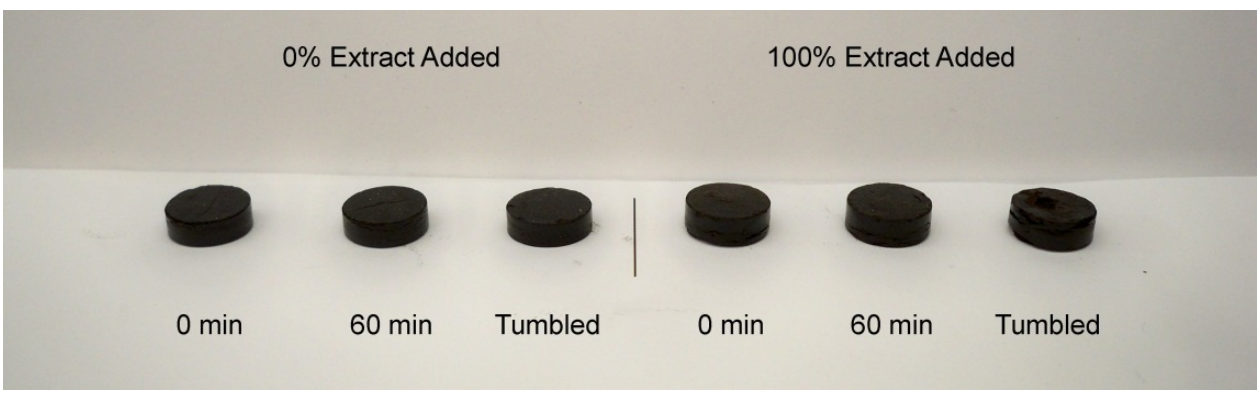

Figure 42. Effect of acetone extract addition on stability of pellets produced from extracted hydrochar. "60 min" indicates pellet was immersed in water for 60-minutes. "Tumbled" indicates pellet was tumbled for 3000 revolutions, after 60-min. immersion in water.

Figure 40(B) illustrates the effects of acetone extract addition on the tumbler durability results of pellets. *The loblolly HTC-200 material produced very durable pellets, regardless of the amount of acetone extracts added*. In contrast, pellets made from the torrefied Tahoe Mix had quite poor durability until acetone extracts were added at the 22% level, at which point the pellets were strong enough to survive the tumbling test. Pellets made from raw loblolly pine had very poor durability and could not survive the tumbling test, regardless of how much acetone extracts were added. As might be expected, pellets made from the extracted Tahoe Mix HTC-275 produced very durable pellets, even without addition of acetone extracts.

Characterization of Acetone Extracts: Based upon the pellet swelling and durability results discussed above, it appears that the materials extracted from hydrochar with acetone exhibit some degree of pellet binding behavior, even though they are not completely responsible for the

excellent durability observed with hydrochar pellets. To investigate this further, additional analyses were conducted to characterize the composition of these extracts. First, IR spectrometry was used to compare Tahoe Mix HTC-275 before and after acetone extraction. These spectra are shown in Figure 43, along with the spectrum of the acetone extracts themselves. All three of these spectra are quite similar, indicating that material remaining within the hydrochar after acetone extraction is similar in chemical composition to the material removed by extraction. All these spectra show rather weak absorptions at 3200-3600 cm^{-1} (associated with O-H bonds) and 900-1100 cm^{-1} (associated with C-O-C bonds in carbohydrates) as compared to the spectra of raw woods as reported in the literature.[31,42]

In contrast, IR spectra of the torrefied Tahoe Mix and the extracted torrefied char in Figure 44 exhibit considerable carbohydrate features in the 900-1100 cm^{-1} region. The acetone extracts obtained from the torrefied sample showed reduced absorption in this region, but enhanced aliphatic absorption bands at 2920 cm^{-1} and 2851 cm^{-1}. In general, the IR spectra reported here for samples derived from Tahoe Mix wood are consistent with those reported and interpreted by Reza et al. for samples derived from loblolly pine.[31]

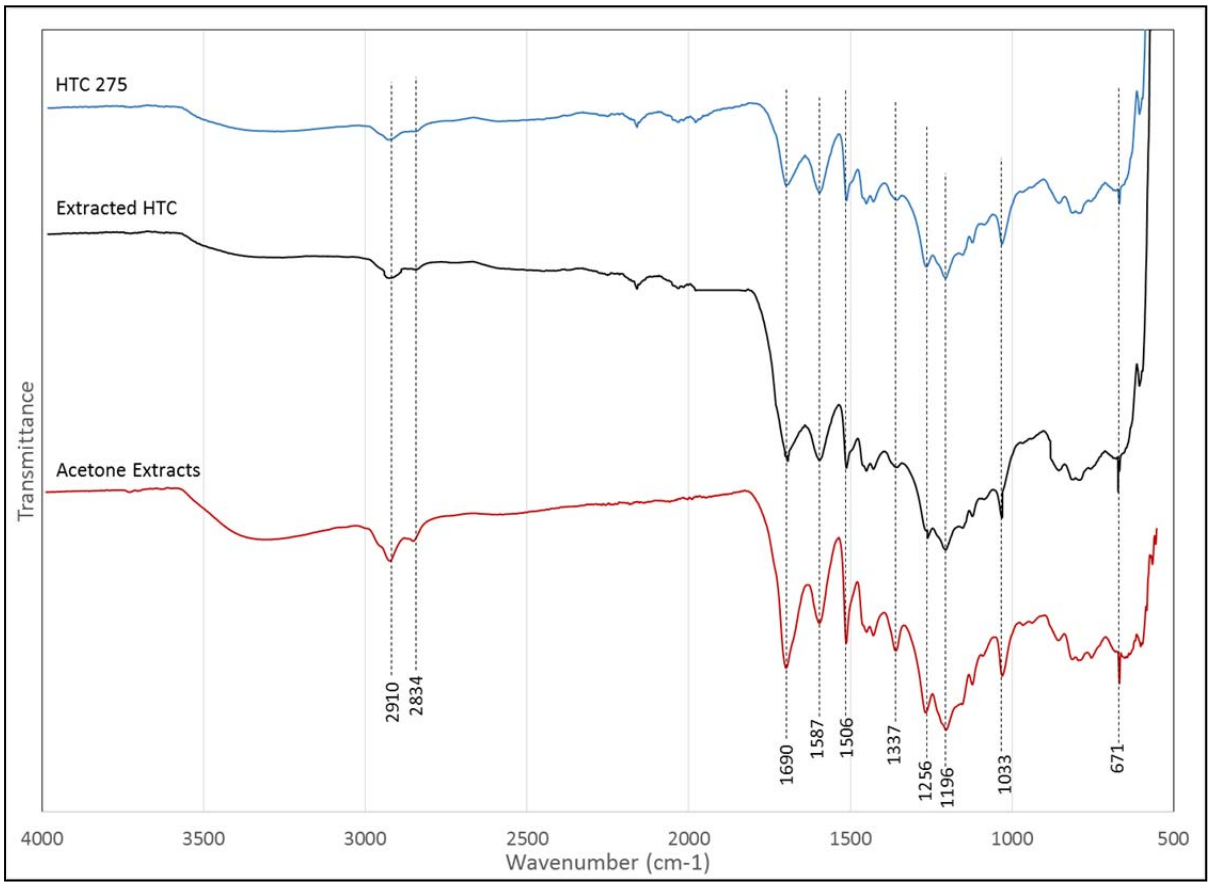

Figure 43. IR spectra of Tahoe Mix HTC-275 before acetone extraction, after extraction, and acetone extracts.

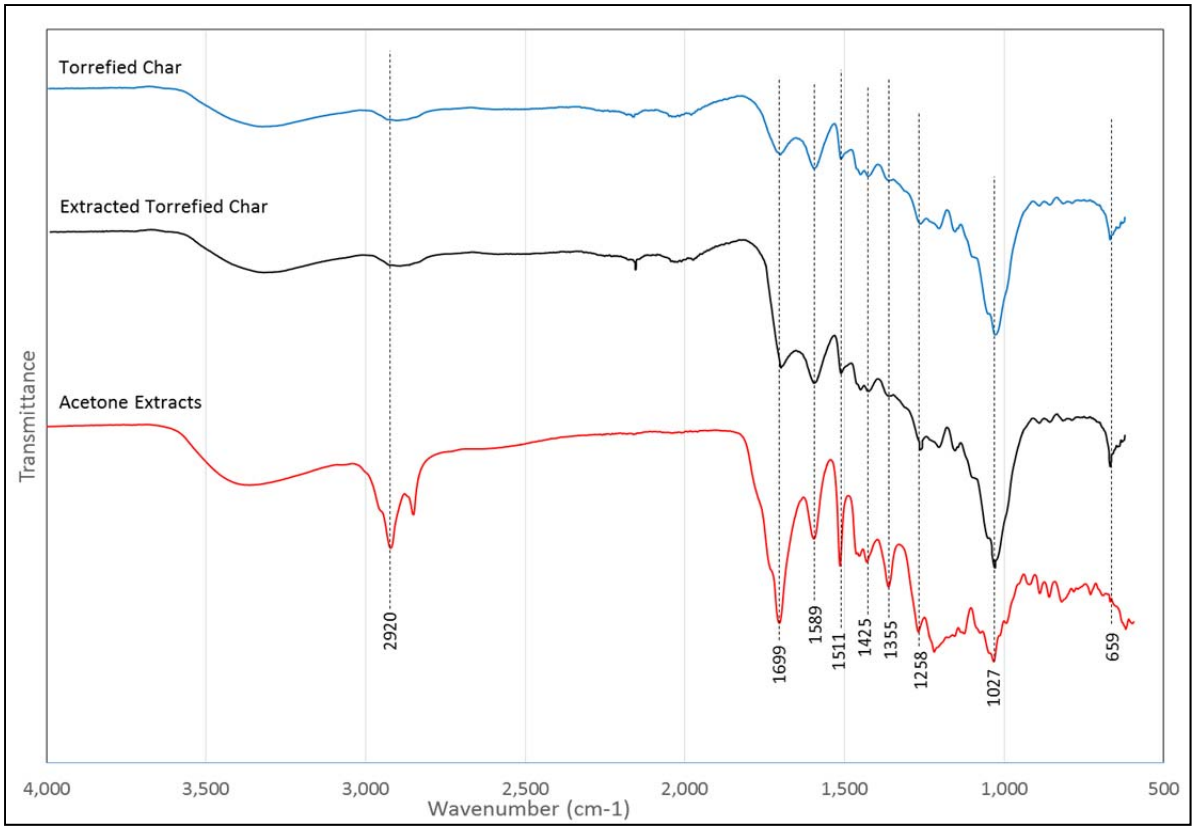

Figure 44. IR spectra of torrefied Tahoe Mix before acetone extraction, after extraction, and acetone extracts.

Additional spectroscopic data of the acetone extracts from both HTC-275 and torrefied Tahoe Mix are presented in Figure 45 and Figure 46. ^{1}H NMR spectra in Figure show that both materials contain a significant amount of aliphatic and aromatic functionality. However, compared to the torrefied extracts, the HTC extracts have greater aromatic character, and much greater concentrations of alkyl groups attached to carbonyl functionality. The ^{13}C NMR spectra, shown in Figure 46 are complex and difficult to interpret. However, consistent with the ^{1}H NMR spectra, it appears that the HTC extracts have greater aromatic and alkyl character as compared to the torrefied extracts. On the other hand, the torrefied extracts have a greater concentration of carbons directly attached to oxygen (chemical shifts of 50-80 ppm) as in alcohols and ethers. The ^{13}C spectrum of HTC-275 shown in Figure 46 is similar to those from several other biomass hydrochars, as reported by Wiedner et al.[43]

Gas chromatography/mass spectrometry (GC/MS) was also used to characterize the acetone extracts from Tahoe Mix HTC-275 and the torrefied Tahoe Mix wood. Results from these analyses are presented in Figure 47 and Table 18. Reconstructed total ion current (TIC) chromatograms shown in Figure 47 clearly indicate that the HTC and torrefied extracts have very different compositions. (It should be noted that the mass extracted from the HTC material was over 8-times that extracted from the torrefied material.) Quantitative results summarized in Table 18 indicate that levoglucosan was the largest single identified component in the torrefied biomass extract. Other major identified components include mannosan, vanillin, and vanillic acid. In contrast, dehydroabietic acid and 7-oxodehydroabietic acid were the two most dominant constituents identified in the HTC extracts. Abietic acids are major constituents of resin acids (or tall oil), which are obtained commercially from wood and used in various applications, including

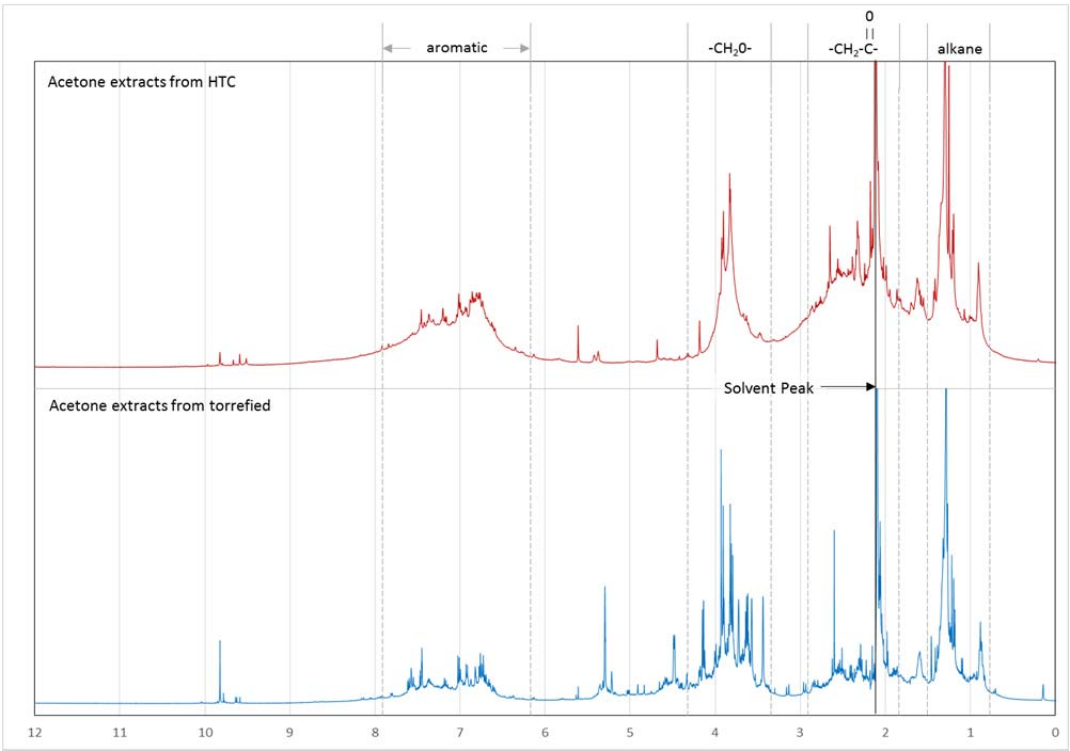

Figure 45. ^{1}H NMR spectra of acetone extracts from HTC-275 and torrefied Tahoe Mix wood.

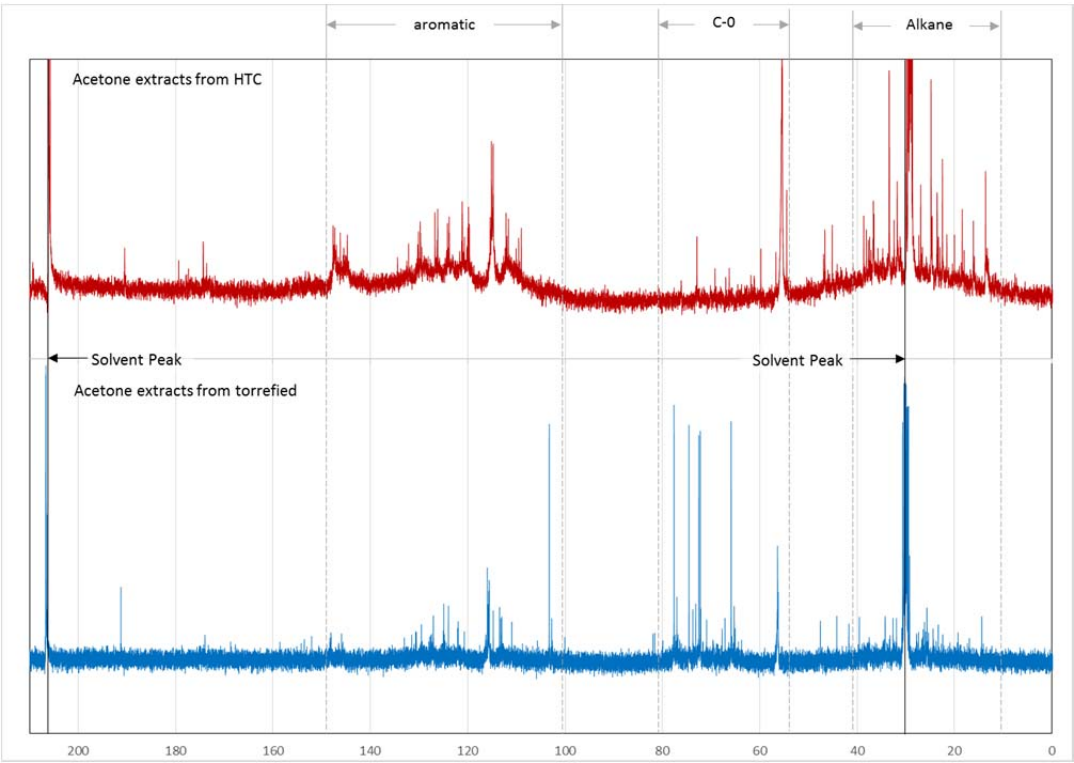

Figure 46. ^{13}C NMR spectra of acetone extracts from HTC-275 and torrefied Tahoe Mix wood.

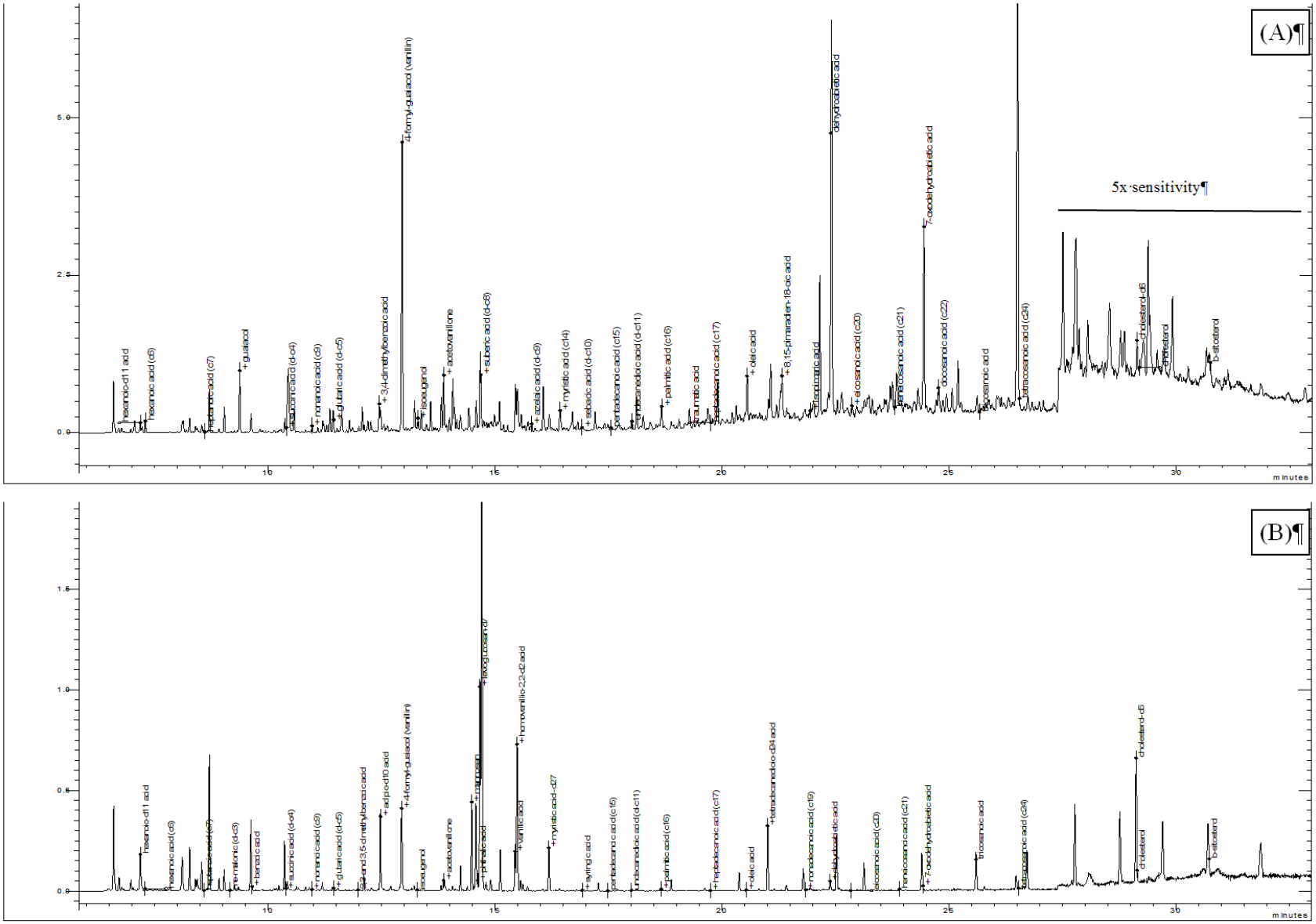

Figure 47. TIC from GC/MS analysis of acetone extracts from (A) Tahoe Mix HTC-275 and (B) torrefied Tahoe Mix.

Table 18. GC/MS Analysis of Acetone Extracts Obtained from Tahoe Mix HTC-275 and Torrefied Tahoe Mix

		Torrefied Tahoe Mix	Tahoe Mix HTC-275
	Starting amount of biomass, g	2.581	2.934
	Acetone extracted mass, g	0.081	0.755
	Percent of mass extracted,%	3.14	25.73
	Extracted fraction, mg/g	31.38	257.33
	Total identified by GC/MS, mg/g	3.400	36.132
	Percent of extracts mass identified	10.83	14.04
No.	Identified Compounds	mg/g	mg/g
1	hexanoic acid (c6)	0.000	0.073
2	heptanoic acid (c7)	0.000	0.064
3	guaiacol	0.000	0.781
4	benzoic acid	0.015	0.083
5	octanoic acid (c8)	0.000	0.306
6	maleic acid	0.000	0.006
7	succinic acid (d-c4)	0.032	0.174
8	me-succinic acid (d-c4)	0.004	0.089
9	4-me-guaiacol	0.001	0.078
10	o-toluic	0.001	0.006
11	m-toluic	0.001	0.018
12	nonanoic acid (c9)	0.002	0.352
13	p-toluic	0.000	0.004
14	2,6-dimethylbenzoic acid	0.003	0.000
15	4-ethyl-guaiacol	0.000	0.269
16	glutaric acid (d-c5)	0.014	0.101
17	syringol	0.000	0.004
18	2-methylglutaric (d-c5)	0.000	0.027
19	2,5-dimethylbenzoic acid	0.001	0.008
20	3-methylglutaric acid (d-c5)	0.000	0.004
21	2,4-dimethylbenzoic acid	0.003	0.012
22	decanoic acid (c10)	0.001	0.069
23	4-allyl-guaiacol (eugenol)	0.000	0.070
24	4-methyl-syringol	0.000	0.000
25	3,4-dimethylbenzoic acid	0.002	0.141
26	hexanedioic (adipic) acid (d-c6)	0.000	0.015
27	hexanedioic (adipic) acid (d-c6) un	0.000	0.001
28	salicylic acid	0.001	0.029
29	cis-pinonic acid	0.000	0.001
30	3-methyladipic acid (d-c6)	0.000	0.002
31	4-formyl-guaiacol (vanillin)	0.288	3.013
32	undecanoic acid (c11)	0.000	0.007
33	isoeugenol	0.000	0.199
34	2,3-dimethoxybenzoic acid	0.000	0.002
35	acetovanillone	0.041	0.759
36	2,6-dimethoxybenzoic acid	0.000	0.000
37	dodecanoic (lauric) acid (c12)	0.000	0.074
38	mannosan	0.334	0.003
39	phthalic acid	0.000	0.047

		Torrefied	HTC-275
	Top 5 Compounds		
	Next 5 Compounds		
No.	Identified Compounds	mg/g	mg/g
40	suberic acid (d-c8)	0.000	0.148
41	3,5-dimethoxybenzoic acid	0.000	0.010
42	levoglucosan	2.194	0.009
43	syringaldehyde	0.000	0.004
44	3,4-dimethoxybenzoic acid	0.000	0.001
45	2,4-dimethoxybenzoic acid	0.000	0.004
46	isophthalic acid	0.001	0.002
47	vanillic acid	0.135	0.554
48	homovanillic acid	0.010	0.087
49	azelaic acid (d-c9)	0.003	0.813
50	myristoleic acid	0.000	0.001
51	myristic acid (c14)	0.000	0.052
52	sebacic acid (d-c10)	0.000	0.093
53	syringic acid	0.000	0.000
54	pentadecanoic acid (c15)	0.000	0.054
55	undecanedioic acid (d-c11)	0.000	0.049
56	palmitoleic acid	0.000	0.006
57	palmitic acid (c16)	0.021	0.795
58	isostearic acid	0.000	0.001
59	dodecanedioic acid (d-c12)	0.000	0.004
60	heptadecanoic acid (c17)	0.001	0.109
61	traumatic acid	0.001	0.085
62	1,11-undecanedicarboxylic acid	0.000	0.006
63	oleic acid	0.031	2.637
64	elaidic acid	0.005	1.618
65	stearic acid (c18)	0.025	0.275
66	pimaric acid	0.000	0.057
67	sandaracopimaric acid	0.000	0.099
68	nonadecanoic acid (c19)	0.000	0.059
69	isopimaric acid	0.015	0.210
70	dehydroabietic acid	0.185	12.840
71	abietic acid	0.001	0.098
72	eicosanoic acid (c20)	0.000	0.487
73	heneicosanoic acid (c21)	0.000	0.011
74	7-oxodehydroabietic acid	0.024	6.250
75	docosanoic acid (c22)	0.007	0.708
76	tricosanoic acid	0.000	0.070
77	tetracosanoic acid (c24)	0.000	0.586
78	b-sitosterol	0.000	0.351

coatings and adhesives.[44,45] However, it should be stressed that only a small fraction of the total acetone extracts could be identified by GC/MS – about 11% of the torrefied extracts and 14% of the HTC extracts. Presumably, most of the extracted material was of sufficiently high molecular weight to prevent its analysis by GC/MS.

Considering the body of characterization information described above, it is postulated that the chemical processes which occur during HTC are similar to those that are deliberately undertaken during thermal treatments to produce and improve wood composite materials. Pelaez-Samaniego et al. have recently reviewed various wood pretreatment methods to produce particle board, fiberboard, strand board, and other wood composites. [46] Generally, these methods involve treatment with hot water or steam, which removes all hemicellulose, leaving behind a solid that has improved strength and water resistance compared to the raw wood feedstock.

Chemical mechanisms for the HTC process have been discussed in the literature.[7,8,6,47] In general, HTC involves hydrolysis, dehydration, decarboxylation, condensation, and aromatization processes. Major intermediate products resulting from these processes are derivatives of furans – particularly furfural and 5-hydroxymethyl furfural (5-HMF). These materials, and other similar chemicals, are capable of reacting to produce cross-linked oligomers and polymers, known as furan resins, which are commonly used as adhesives and strengtheners for engineered wood products. [48] Thus, it seems quite likely that when undergoing HTC processing, similar chemistry occurs to create furan resins, which contribute to the excellent binding behavior of the resulting hydrochar. In addition, spectroscopic characterization of hydrochar and its acetone extracts reveals considerable aromatic functionality, suggesting that phenolic resins may also be present.

Leaching of Organic Acids from Hydrochar: Another property of interest for hydrochar (and pellets made therefrom) is the leaching of organic acids, and other materials, when immersed in water. To assess this issue, we simply monitored the pH level of a water sample into which hydrochar was placed. This was done using the apparatus shown in Figure 48. A Hanna Instruments pH meter (Model HI 8314) and pH probe (Model HI 1217) were used. In these experiments, approximately 5 g of unpelletized hydrochar, or 5 pellets, were placed into 150 g of deionized water. The pH values were recorded at 5-min. intervals for the first 60-min, and less frequently thereafter. No stirring or agitation was used.

Figure 48. Measurement of pH during leaching of hydrochar.

Three different hydrochars produced by HTC treatment of Tahoe Mix feedstocks were used: HTC-215, HTC-255, and HTC-275. In addition, torrefied Tahoe Mix feedstocks (prepared by Integro) was used. Results from leaching of all four char samples are shown in Figure 49. In all four cases, leaching is more rapid for the non-pelletized form of the char compared to the pelletized form. These results indicate that leaching of acidic compounds from unpelletized chars was very rapid, with the pH level dropping from 7 to 4 (or lower) within a few minutes. (Due to instability of the pH probe, it is difficult to obtain an accurate measurement while the pH level is rapidly changing during the first few minutes of immersion.) Leaching from pellets is a slower process, requiring about 2-hours to reach a relatively stable level. Figure 49 also shows that as the HTC reaction severity

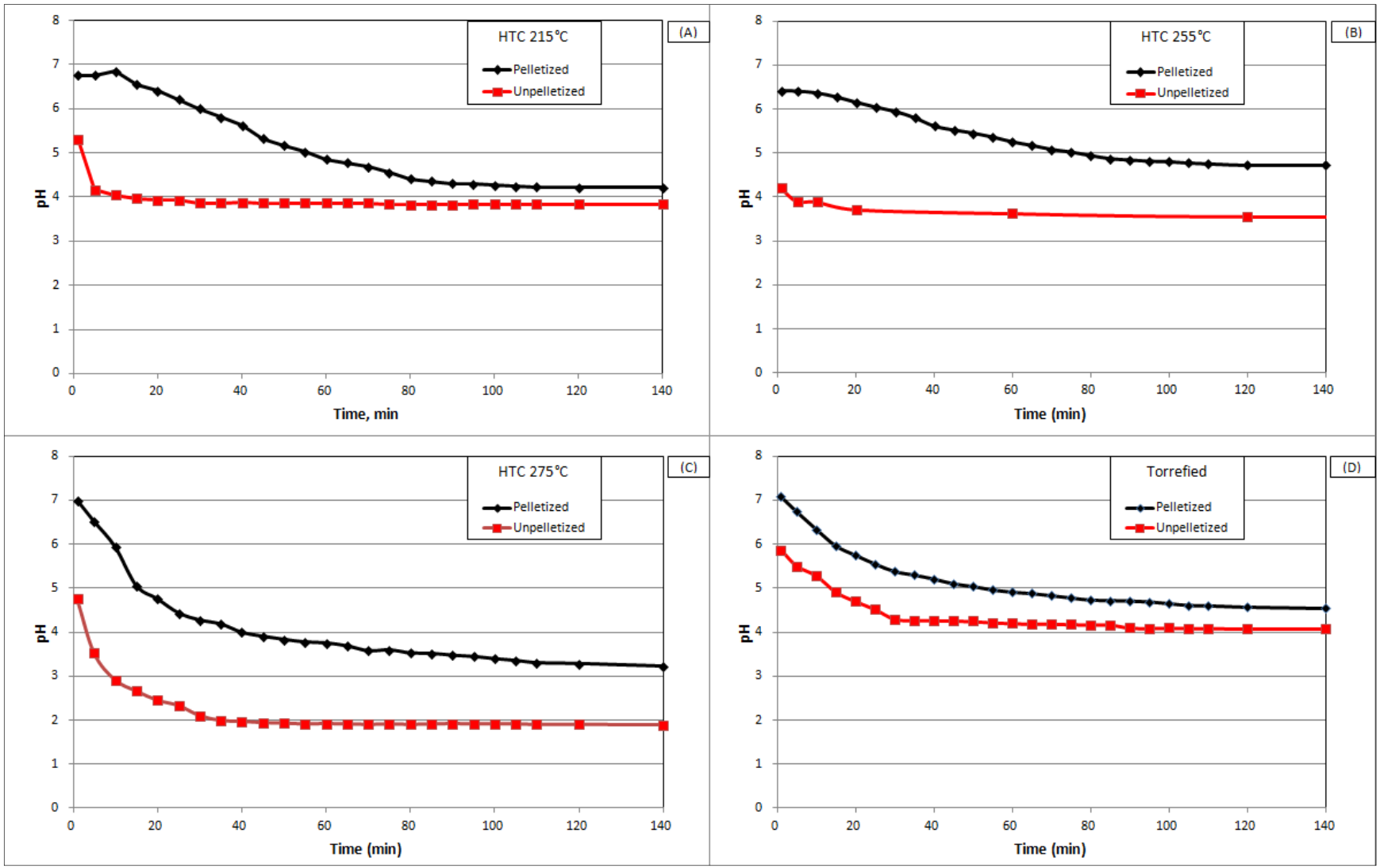

Figure 49. Leaching of acidic components from bio-chars into water. Monitoring of pH vs. time. (A) HTC-215°C, (B) HTC-255°C, (C) HTC-275°C, (D) Torrefied char.

increased, a greater degree of acid leaching occurred from the pellets. For instance, the observed pH levels after 2-hours of leaching were 3.9, 3.6, and 2.0 for HTC-215, HTC-255, and HTC-275, respectively. The torrefied samples did not leach as much acidic material as the severely treated hydrochar. In fact, the pH level of the torrefied material only reached a level of about 4.0, which was similar to HTC-215.

Effectiveness of Hydrochar as Pellet Binder: It is apparent that hydrochars produced from HTC processing of woody biomass at temperatures above 200 °C have excellent binding properties. To further explore the utility of this property, a series of experiments was conducted in which HTC hydrochar was used as a binder and mixed with other materials that by themselves do not form robust pellets. This concept of "engineered pellets" was recently discussed in a paper by Reza et al.[31] Varying amounts of Tahoe Mix HTC-275 were added to four different base materials: (1) raw Tahoe Mix wood, (2) Astec torrefied pine wood [Astec Inc., Chattanooga, TN], (3) Integro torrefied Tahoe Mix [Integro Earth Fuels, Inc., Arden, NC], and (4) pulverized Illinois Basin coal (Galatia coal). With each base material, a series of samples was prepared by blending 0, 10, 20, 30, and 50% of the Tahoe Mix HTC-275. Multiple pellets were prepared from each blend, and were characterized in terms of their dimension, density, and durability. Following immersion in water for 60-min., these properties were again measured. Results of pellet swelling are summarized graphically in Figure 50. Detailed tabular results of these tests are provided in Table 19.

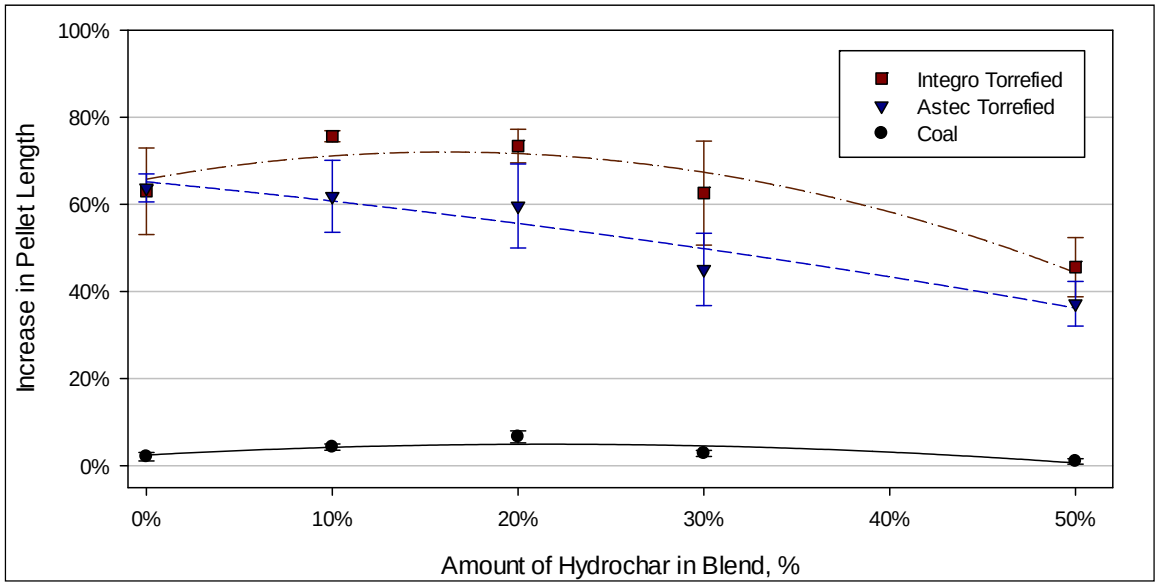

Figure 50. Effect of hydrochar blend amount on pellet swelling after water immersion for 60-min. Hydrochar was produced from HTC treatment of Tahoe Mix wood at 275 °C.

Pellets made from both raw and torrefied woody biomass swelled significantly upon immersion in water, while pellets made from pulverized coal did not. Raw wood pellets are extremely unstable when immersed in water, as illustrated in the photographs of Figure 51, completely disintegrating within 1-2 minutes. Addition of hydrochar improved the stability of raw wood pellets. As shown here, addition of 50% hydrochar resulted in pellets that somewhat maintained their integrity upon water immersion, although they swell dramatically. However, these water-immersed pellets are far too weak to survive a tumbling test.

Table 19. Effect of Hydrochar Blend Level upon Pellet Properties (Hydrochar was produced from Tahoe Mix Wood at 275 °C)

Material	Hydro-char,%	Pellet No.	Pellet Weight, g			Pellet Length, mm			Pellet Density, kg/m^3			Pellet Durability	
			Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion
Raw Tahoe Mix	0%	1	1.0267	1.0011	-	6.23	12.01	-	1241.6	628.0	-	0.9893	-
		2	1.0347	1.0122	-	6.32	12.13	-	1233.4	628.7	-	0.9845	-
		3	0.9460	0.9742	-	5.76	11.47	-	1237.3	639.9	-	0.9891	-
		Avg.							1237.5	632.2	-	0.9876	-
		SD							4.1	6.7	-	0.0027	-
	50%	1	0.7876	0.7956	-	5.00	11.50	-	1186.7	521.2	-	0.9989	-
		2	0.7649	0.7637	-	4.80	12.50	-	1200.6	460.3	-	0.9992	-
		3	0.6801	0.6685	-	4.32	11.50	-	1186.1	438.0	-	0.9965	-
		Avg.							1191.1	473.2	-	0.9982	-
		SD							8.2	43.1	-	0.0014	-
Astec Torrefied Pine	0%	1	0.7331	0.6984	-	5.40	9.00	-	1022.8	584.6	-	0.9745	-
		2	0.7838	0.7447	-	5.72	9.40	-	1032.4	596.9	-	0.9585	-
		3	1.0122	0.9834	-	6.30	10.10	-	1210.5	733.6	-	0.9737	-
		Avg.							1088.5	638.4	-	0.9689	-
		SD							105.7	82.7	-	0.0090	-
	10%	1	0.6792	0.6614	-	5.20	8.70	-	984.1	572.8	-	0.9869	-
		2	0.7306	0.715	-	5.40	8.96	-	1019.3	601.2	-	0.9984	-
		3	0.8963	0.8804	-	6.50	9.90	-	1038.9	670.0	-	0.9849	-
		Avg.							1014.1	614.6	-	0.9901	-
		SD							27.8	50.0	-	0.0073	-
	20%	1	0.0000	0.7062	-	4.96	7.60	-	0.0	700.1	-	0.9854	-
		2	0.0000	0.747	-	4.84	7.50	-	0.0	750.4	-	0.9860	-
		3	0.0000	0.5636	-	3.76	6.42	-	0.0	661.4	-	0.9864	-
		Avg.							0.0	703.9	-	0.9859	-
		SD							0.0	44.6	-	0.0005	-
	30%	1	0.6935	0.6904	-	5.24	7.70	-	997.1	675.5	-	0.9982	-
		2	0.6613	0.6595	-	4.90	7.46	-	1016.8	666.0	-	0.9872	-
		3	0.6995	0.6979	-	5.00	6.80	-	1054.0	773.2	-	0.9864	-
		Avg.							1022.6	704.9	-	0.9906	-
		SD							28.9	59.3	-	0.0066	-
	50%	1	0.6293	0.6287	-	4.52	6.38	-	1048.9	742.4	-	0.9979	-
		2	0.5808	0.5806	-	4.10	5.70	-	1067.3	767.4	-	0.9962	-
		3	0.6897	0.6892	-	4.90	6.44	-	1060.4	806.3	-	0.9952	-
		Avg.							1058.9	772.0	-	0.9964	-
		SD							9.3	32.2	-	0.0014	-
Integro Torrefied Tahoe Mix	0%	1	0.8992	0.6147	-	6.32	9.40	-	1071.9	492.7	-	0.9606	-
		2	0.9237	0.7268	-	6.62	10.62	-	1051.2	515.6	-	0.9725	-
		3	0.8726	0.8851	-	6.22	10.48	-	1056.9	636.3	-	0.9643	-
		Avg.							1060.0	548.2	-	0.9659	-
		SD							10.7	77.2	-	0.0061	-
	10%	1	0.6370	0.585	-	4.70	8.32	-	1021.1	529.7	-	0.9727	-
		2	0.6528	0.6561	-	4.78	8.34	-	1028.9	592.7	-	0.9740	-
		3	0.6593	0.5581	-	4.80	8.42	-	1034.8	499.4	-	0.9743	-
		Avg.							1028.3	540.6	-	0.9737	-
		SD							6.9	47.6	-	0.0008	-
	20%	1	0.6468	0.6447	-	4.60	7.80	-	1059.3	622.7	-	0.9721	-
		2	0.6263	0.629	-	4.42	7.66	-	1067.5	618.7	-	0.9609	-
		3	0.6056	0.6053	-	4.22	7.48	-	1081.2	609.7	-	0.9810	-
		Avg.							1069.4	617.0	-	0.9714	-
		SD							11.0	6.7	-	0.0010	-

Table 19 Continued.

Integro Torrefied Tahoe Mix	30%	1	0.6877	0.6631	-	5.00	8.40	-	1036.2	594.7	-	0.9835	-
		2	0.6659	0.6687	-	4.70	7.00	-	1067.4	719.7	-	0.9966	-
		3	0.6709	0.6725	-	4.88	8.34	-	1035.8	607.5	-	0.9880	-
		Avg.							1046.5	640.6	-	0.9893	-
		SD							18.1	68.8	-	0.0067	-
	50%	1	0.7356	0.7368	-	4.90	7.50	-	1131.0	740.1	-	0.9890	-
		2	0.6793	0.6803	-	4.72	6.60	-	1084.3	776.6	-	0.9901	-
		3	0.6812	0.672	-	4.74	6.82	-	1082.7	742.3	-	0.9891	-
		Avg.							1099.3	753.0	-	0.9894	-
		SD							27.4	20.4	-	0.0006	-
Coal	0%	1	1.1687	1.1665	-	7.50	7.74	-	1174.0	1135.4	-	0.9997	-
		2	1.2028	1.2013	-	7.70	7.80	-	1176.9	1160.3	-	0.9861	-
		3	1.1328	1.1311	-	7.30	7.43	-	1169.1	1146.9	-	0.9939	-
		Avg.							1173.3	1147.6	-	0.9932	-
		SD							3.9	12.5	-	0.0068	-
	10%	1	1.3090	1.3046	1000.801	8.19	8.60	7.54	1204.1	1142.9	1002.5	0.9873	0.7690
		2	1.1211	1.116	805.685	7.05	7.35	6.07	1198.1	1143.9	825.3	0.9470	0.5958
		3	1.3104	1.3038	992.8375	8.11	8.40	7.48	1217.3	1169.4	982.7	0.9095	0.7484
		Avg.							1206.5	1152.1	936.8	0.9479	0.7044
		SD							9.8	15.0	97.1	0.0389	0.0946
	20%	1	1.1957	1.194	0.6515	7.44	7.82	5.70	1210.8	1150.3	861.1	0.9910	0.5456
		2	1.1264	1.1218	0.9729	6.96	7.45	7.31	1219.3	1134.4	1002.7	0.9944	0.8673
		3	1.1863	0.9056	0.728	7.34	7.91	5.77	1217.6	862.5	950.6	0.9935	0.8039
		Avg.							1215.9	1142.4	976.6	0.9929	0.8356
		SD							4.5	161.8	71.6	0.0018	0.1704
	30%	1	1.0694	1.0559	955.6725	7.05	7.20	7.20	1142.8	1104.9	1083.2	0.9939	0.9804
		2	1.0366	1.0232	891.961	6.51	6.74	6.72	1199.6	1143.7	1109.9	0.9903	0.9676
		3	1.0761	1.0588	853.4686	6.72	6.91	6.43	1206.4	1154.4	943.7	0.9904	0.7607
		Avg.							1183.0	1134.3	1045.6	0.9915	0.9029
		SD							34.9	26.1	89.3	0.0021	0.1233
	50%	1	0.9076	0.8959	784.4478	5.86	5.91	5.91	1166.9	1142.1	1134.0	0.9634	0.9930
		2	0.8955	0.8842	807.0123	5.98	6.08	6.08	1128.2	1095.6	1072.0	0.9858	0.9784
		3	0.6512	0.6418	610.5685	4.60	4.62	4.60	1066.5	1046.6	1039.2	0.9951	0.9886
		Avg.							1120.5	1094.8	1081.7	0.9814	0.9867
		SD							50.6	47.7	48.2	0.0116	0.0075

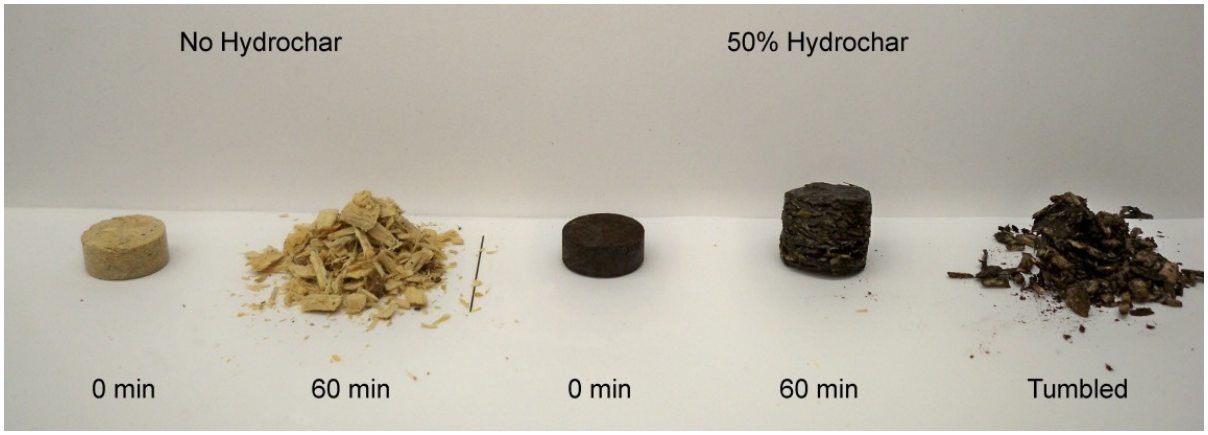

Figure 51. Effect of hydrochar blending on stability of pellets produced from Tahoe Mix wood.

Hydrochar was produced from Tahoe Mix wood at 275°C. “60-min.” indicates the pellet was immersed in water for 60-minutes. “Tumbled” indicates the pellet was tumbled for 3000 revolutions, after 60-min. of immersion in water.

Addition of increasing amounts of hydrochar to the torrefied biomass materials reduced the extent of pellet swelling by a small, but noticeable degree. Without any hydrochar addition, torrefied pellets swelled 60-80%; adding 50% hydrochar reduced this swelling to 40-50%. This reduced swelling with increasing amounts of hydrochar is shown in the photographs of Figure 52.

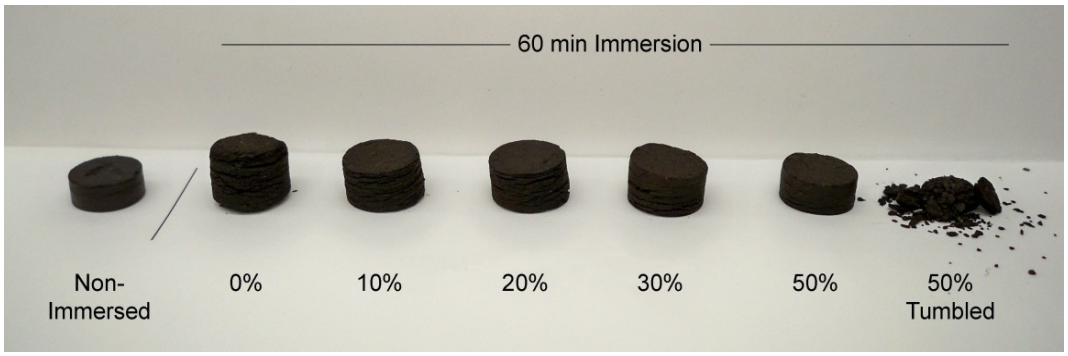

Figure 52. Effect of hydrochar blending on stability of pellets produced from Astec torrefied biomass. Percentage values indicate the fraction of Tahoe Mix hydrochar included in the blend. “50% Tumbled” indicates a pellet that was tumbled for 3000 revolutions, after immersion in water for 60-min.

The reduced pellet swelling upon addition of 50% hydrochar is similar to that observed with addition of 50% acetone extracts (compare Figure 50 and Figure 40(A)). Although addition of hydrochar reduced the extent of swelling after water immersion, these water-immersed pellets were still too unstable to survive a tumbler durability test.

The effects of hydrochar addition upon stability of pellets are further shown in the series of photos in Figure 53, where each column of 3 photos represents one of 5 base biomass materials with which the Tahoe Mix HTC-275 was blended. The bottom row of photos shows pellets made from the base materials, without any other treatment. (No photo is provided for the Earth Care torrefied material because this could not be pelletized.) The middle row of photos in Figure 53 shows pellets after 60-min. of immersion in water. The raw Tahoe Mix pellet was very unstable under these conditions, while pellets made from the Astec torrefied, Integro torrefied, and coal all held together, but with modest swelling. The top row of photos shows pellets made from blends of 50% hydrochar and 50% base material, after these pellets had been immersed in water for 60-min. Addition of hydrochar enabled the Earth Care material to be pelletized. In the case of the Astec torrefied, Integro torrefied, and coal pellets, addition of hydrochar improved the pellet stability, as noted by reduced swelling upon immersion in water. However, of all the hydrochar blends investigated here, only those made from coal were sufficiently stable to survive the tumbler test.

3.2.2 Task 2: Characterization of Pelletized HTC Process Solids/Extractables with Coal

One of the main objectives of this project is to demonstrate that a satisfactory solid fuel can be produced by blending coal with HTC biomass. To investigate this, DRI prepared blends of pulverized Galatia coal with HTC-275 derived from both loblolly pine and Tahoe Mix woods.

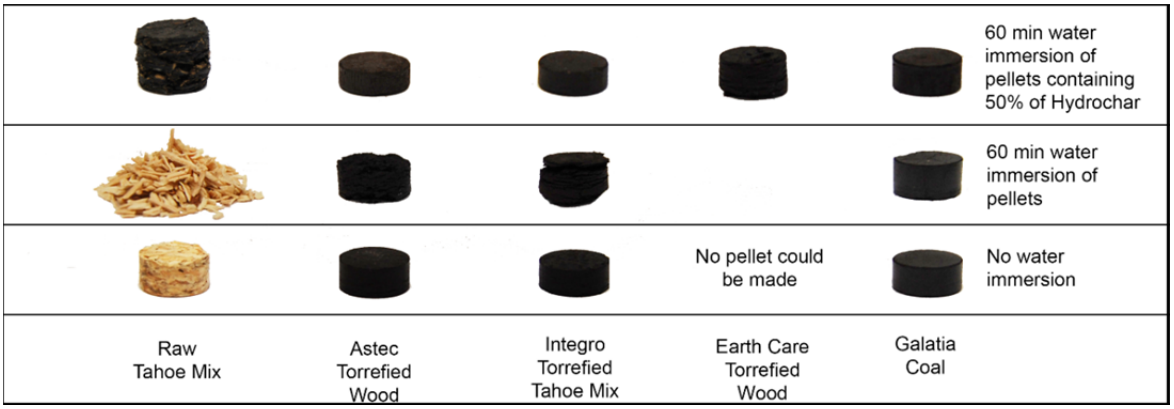

Figure 53. Effect of hydrochar blending upon stability of pellets produced from various solid biomass materials. The hydrochar was produced from treatment of Tahoe Mixed woods at 275°C for 30-min.

Both hydrochars were prepared in batch-based 2-L Parr experiments, with a hold time of 30-min. Blends containing from 10% to 50% of the hydrochars were prepared. In addition, coal blends containing 10% and 30% raw loblolly pine were prepared for reference. Photographs illustrating the effects of increasing Tahoe Mix HTC-275 concentrations upon the stability of the mixed hydrochar/coal pellets are provided in Figure 54. All the pellet blends were quite stable, showing very little swelling upon water immersion. However, this immersion clearly weakened the pellets, as they did not all maintain their integrity upon tumbling.

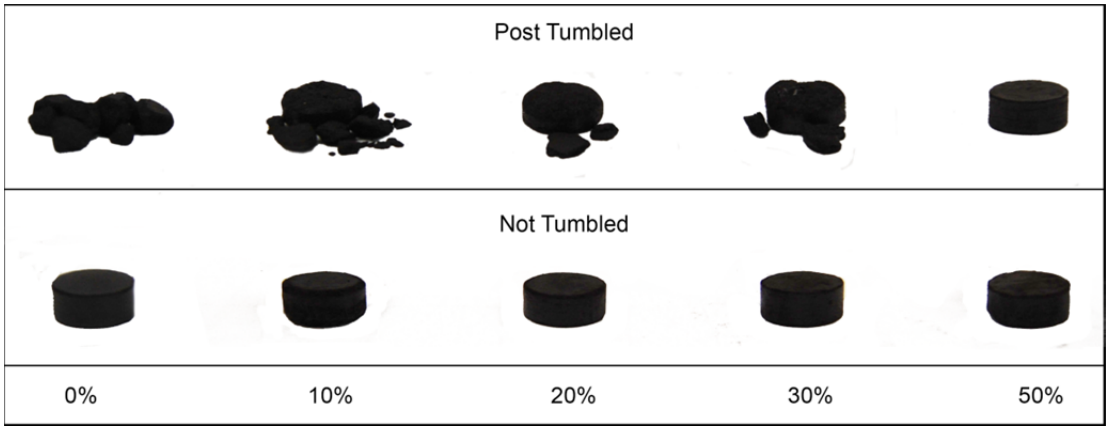

Figure 54. Effect of hydrochar blending on stability of pellets produced from pulverized Galatia coal. Percentage values indicate the fraction of Tahoe Mix hydrochar included in the blend. All pellets were immersed in water for 60-min.

Numerical results demonstrating the water tolerance of these blended pellets are summarized in Figure 55. The top panel shows the extent of swelling that occurred when the pellets were immersed in water for 60-min. Pellets of 100% coal are quite stable, and do not swell to a measureable extent, although they do develop cracks when immersed in water. When either

loblolly HTC-275 or Tahoe Mix HTC-275 was blended with the coal (at various blend ratios), very slight swelling of the pellets was noted (<5%). However, when raw loblolly was mixed with the coal, the resulting pellets swelled considerably – by about 55% with a 10% biomass blend and 100% with a 30% blend.

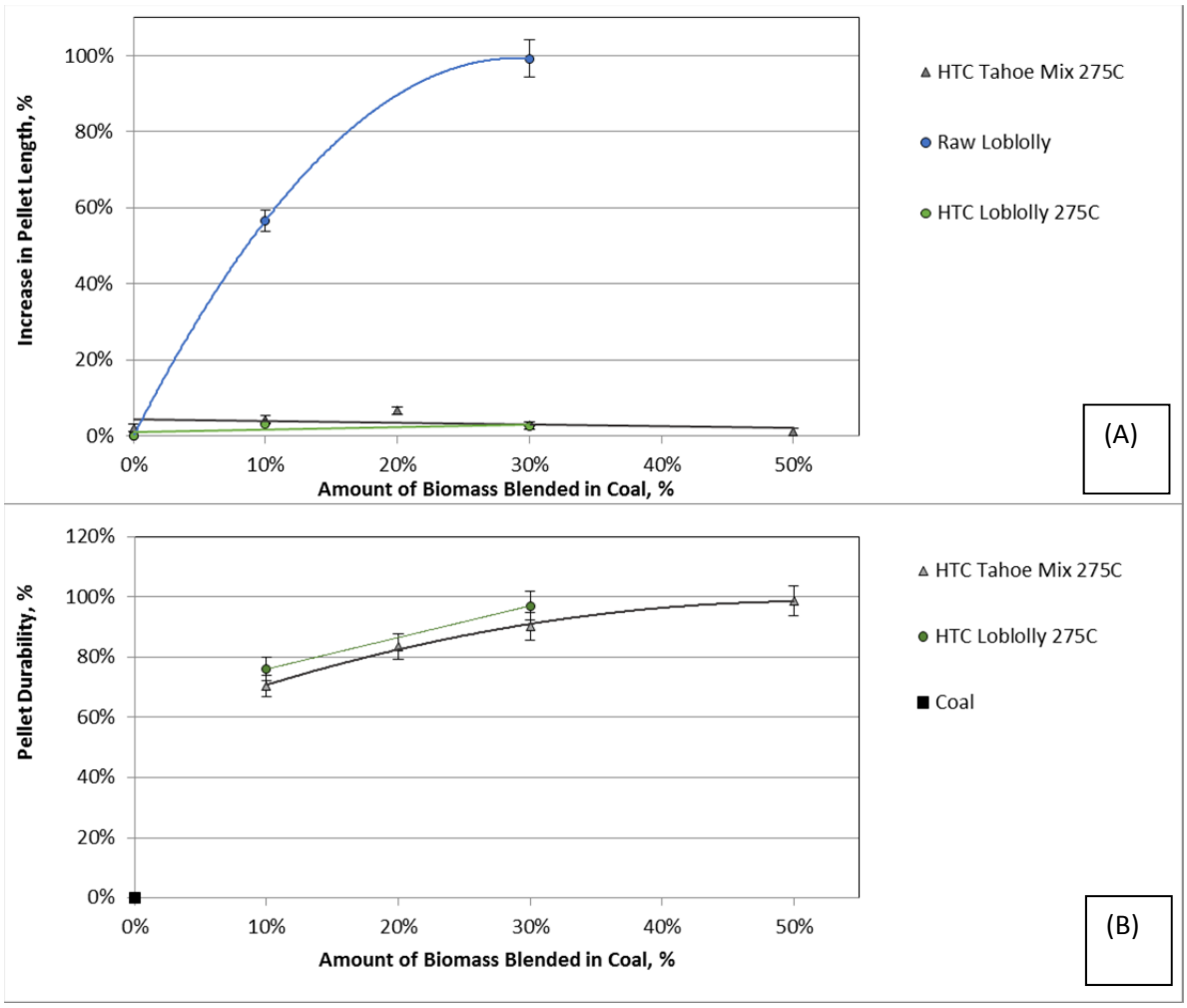

Figure 55. Behavior of pellets produced from blends of biomass and Galatia coal. Effects of blending ratio upon pellet behavior after immersion in water for 60-min. (A) pellet swelling; (B) pellet durability. Data points are averages of three pellets from a single HTC experiment; error bars represent ± 1 std. dev.

Results of tumbler durability tests performed on these pellets (after 60-min. of water immersion) are shown in the bottom panel of Figure 55. Upon tumbling, pellets produced from 100% coal broke apart into several large pieces, but they did not disintegrate to a powder. Addition of 10% hydrochar to the coal greatly improved the pellet integrity, although the measured durability values were still quite low, at less than 80%. However, the pellet durability consistently increased as larger fractions of hydrochar were used in the coal blends. With 30% hydrochar in the blend, the measured pellet durability exceeded 90%; with a 50% blend, the durability exceeded 98%. (Only one of the two hydrochars was tested at a 50% blend.) No durability data are shown in Figure 55 for blends of raw loblolly and coal, because these pellets did not survive the tumbling test.

Photographic results of these water immersion and tumbler durability tests are shown in Figure 56 for pellets made from blends of coal with raw loblolly pine and with loblolly HTC-275. The blends with raw biomass were clearly unstable when immersed in water, and disintegrated completely upon tumbling. However, pellets made with blends of loblolly HTC-275 were much more stable, as evidenced by their lack of swelling in water, and good retention of integrity upon tumbling.

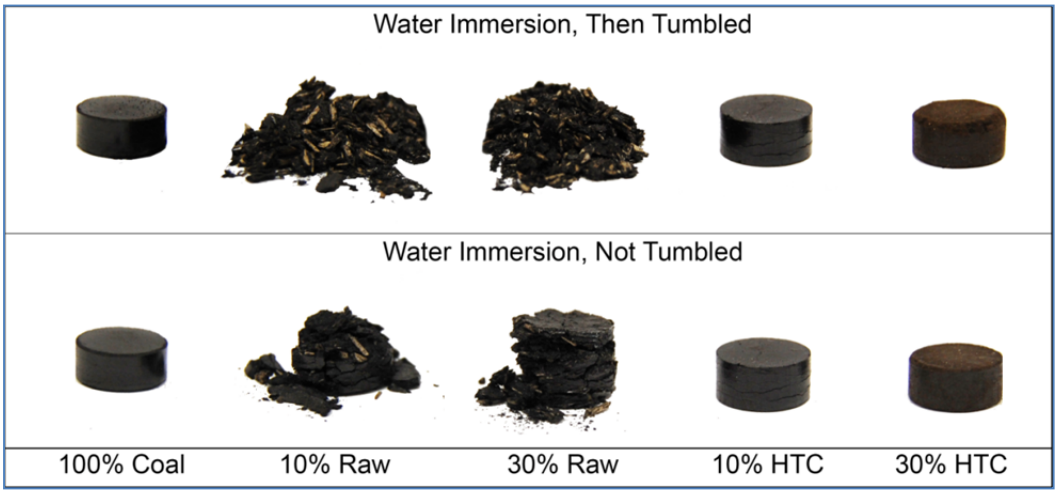

Figure 56. Effect of biomass blending upon stability of pellets produced from pulverized Galatia coal. "Raw" indicates untreated loblolly pine; "HTC" indicates hydrochar from loblolly pine at 275 °C.

Finally, we also conducted experiments involving co-processing of pulverized coal and raw loblolly pine biomass. This was done to explore the eventual possibility of treating coal fine slurries with biomass under HTC conditions, thereby producing a solid fuel consisting of a homogeneous mixture of coal and hydrochar. This could also be a useful way to address environmental concerns associated with of growing stockpiles of coal fines in certain locations.

To demonstrate co-processing, we prepared a mixture of 20% ground loblolly pine and 80% pulverized Galatia coal. A laboratory blender was used to ensure a homogenous blend. An initial experiment was conducted in DRI's small, 2-chamber reactor, which has recently been described in the literature.[49] A 5.0 g sample of the 80/20 coal/loblolly blend was placed in a cylindrically-shaped sample holder (0.5-in diameter) made of 320 mesh steel screen with the bottom being twisted closed. Once the sample was loaded, the top of the screen holder was also twisted closed, and the entire holder was placed in the upper chamber of the 2-chamber reactor. Deionized water (40-mL) was placed in the bottom chamber, and was heated to the desired temperature of 250 °C. The sample holder was then dropped from the top chamber to the bottom chamber by opening a ball valve that separates the two chambers. After 30-minutes of reaction, the reactor was removed from the heater and was rapidly cooled by placing it in a cold bath. Once cool, the reactor was opened and the sample holder was removed.

In all previous HTC experiments with the 2-chamber reactor, woody biomass was used as the only feedstock. In these cases, the solid hydrochar product was always retained in the steel mesh sample holder. However, when co-processing the coal/biomass mixture, it was observed that most of the coal had fallen through the fine mesh, and was located in the bottom of the reactor. This separation of materials is shown in the photos of Figure 57. Of the 5.0 g of starting material,

0.7 g was retained in the sample screen and 3.9 g was located at the bottom of the reactor. (These weights were determined after drying the materials collected by filtration.) The color and texture of these materials also suggested that the mesh screen contained hydrochar, while the bottom of the reactor held unreacted, pulverized coal.

A second co-processing experiment was conducted using a 2-L stirred Parr reactor. In this case, 100.0 g of the coal/loblolly (80/20) mixture was combined with 1000 g of deionized water. While stirring, the mixture was heated to 250 °C, and held for 30-min. After cooling, the Parr vessel was opened and the solid products (89.7 g) were recovered by filtration. The solid product was a homogenous mixture of coal and hydrochar, as shown in the photo of Figure 57.

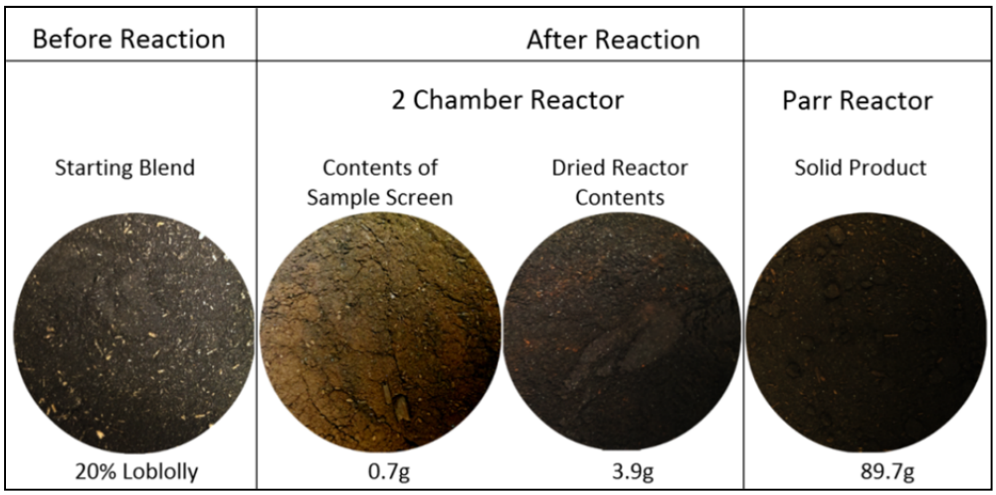

Figure 57. Photos of starting feedstock blends and products from HTC co-processing experiments.

The homogeneous coal/hydrochar product from this co-processing experiment was readily pelletized. Upon immersion in water, these pellets exhibited very little swelling, although the measured durability dropped to about 80%. This durability value is what would be expected, based upon the data shown in Figure 55 for other pellets made of coal/hydrochar blends.

Clearly, *robust pellets of hydrochar and finely-divided coal can be easily prepared and these pellets exhibit acceptable durability under tumbling and immersion in water*. The next project activity by DRI was to assess the behavior of pelletized hydrochar and hydrochar/coal blends with HCT loblolly pine produced by the GTI FHTC PDU. The FHTC PDU, and its use to prepare hydrochar from loblolly pine crumbles is discussed next. After that discussion, we will return to the assessment of pellets and briquettes made from FHTC hydrochar and FHTC hydrochar/coal blends.

The GTI Continuous, Fast Hydrothermal Carbonization (FHTC) PDU

The GTI continuous fast hydrothermal carbonization (FHTC) PDU was developed under DOE Cooperative Agreements DE-FG36-02GO12011 and DE-FG36-01GO11082. The GTI FHTC PDU utilizes a twin-screw extruder (TSE) as a platform to rapidly transform lignocellulosic biomass to a wet HTC solid.[50] The TSE utilized in this work is a refurbished Clextral 25mm BC-21 unit with reversible co-rotating screw segments positioned along dual splined shafts with an integrated hydraulic ram for screw extraction and maintenance. The TSE enables the overall PDU to maintain a continuously fed, high-pressure reaction zone operating at the temperature

levels required to promote the HTC of biomass. Operation of the TSE is managed with Clextral's FITSYS V2.6 control and operating system.

The Clextral 25mm BC-21 TSE includes easily accessed actuators for emergency shutoff if warranted. A general schematic cross-section drawing of this device is shown in Figure 9.

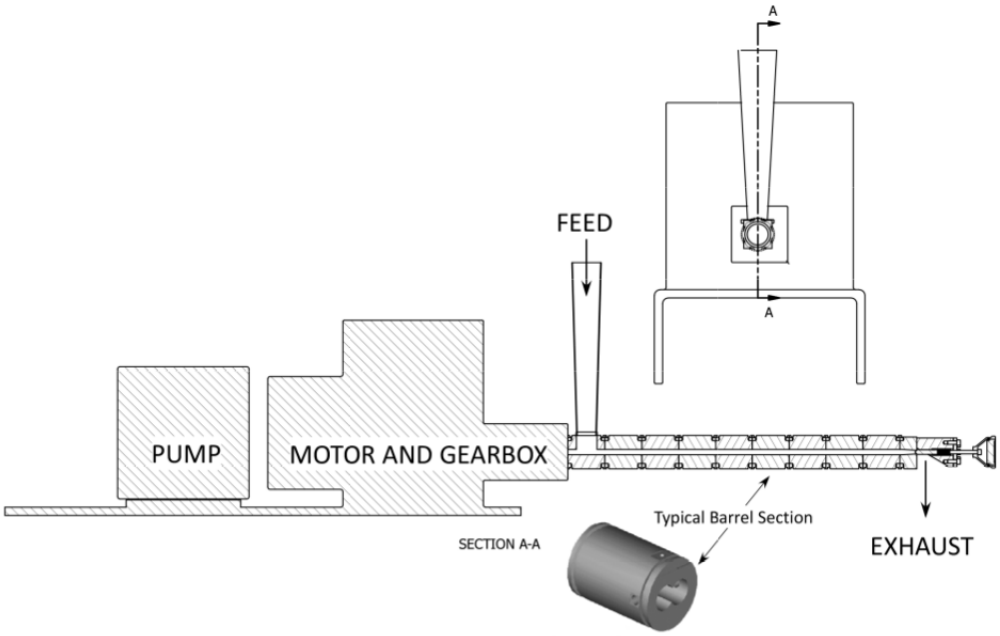

Figure 58. Cross-section view of the Clextral BC-21 twin-screw extruder obtained to prepare FHTC biomass. A separate volumetric feeder and water heater are not shown.

A more detailed cross-section view of the BC-21 is shown in Figure 59. In this figure, barrel sections of the BC-21 are numbered and a side view of one of the twin splined shafts is shown with screw sections arranged in the configuration employed during shakedown testing. In this figure, locations of major system components are noted, and in particular, the left and right boundaries of the HTC reaction zone. Note that reversed screw sections define the left pressure boundary while downstream; the same reversed screw sections serve to mix and impede flow of the paste-like HTC material to increase residence time in the reaction section. The adjustable flow restriction located at the exhaust of the PDU serves as the downstream pressure boundary that defines the end of the HTC reaction zone while providing a permeable dynamic barrier that allows the HTC product to be exhausted from the PDU. A photograph of representative screw sections is presented in Figure 60. As shown in Figure 59, the BC-21 is configured with nine barrel sections. Barrel 1 is set up to be a feed inlet port, and barrels 2, 3, 5, 6, 7, 8, and 9 are rated for 250 bar (3,625 psi) at temperatures up to 300 °C (572 °F) continuous operation with brief excursions up to 400 °C (752 °F). A photograph of a typical barrel section is shown in Figure 61.

Barrel 4 serves as a dedicated vent to exhaust steam and water released when incoming biomass is compressed into the dynamic plug that comprises the first pressure boundary. All nine barrel sections are equipped with K-type thermocouples that measure barrel temperature via integrated thermowells. Barrels 5-9 each are fitted with pressure transducers to measure the pressure inside the channel housing the screw assembly. Barrels 3, 5, 6, 7, 8, and 9 also include internal cooling

channels for cold water throughput as well as externally mounted band heaters to maintain each of these barrel sections at temperatures and pressures required for the production of FHTC biomass. In this way, each barrel section of the extruder can function as a localized transport reactor. Biomass is fed into Barrel 1 of the BC-21 using an integrated K-Tron KS-60 volumetric feeder fitted configured for wood chips. Barrel 5 of the TSE provides the location for injection

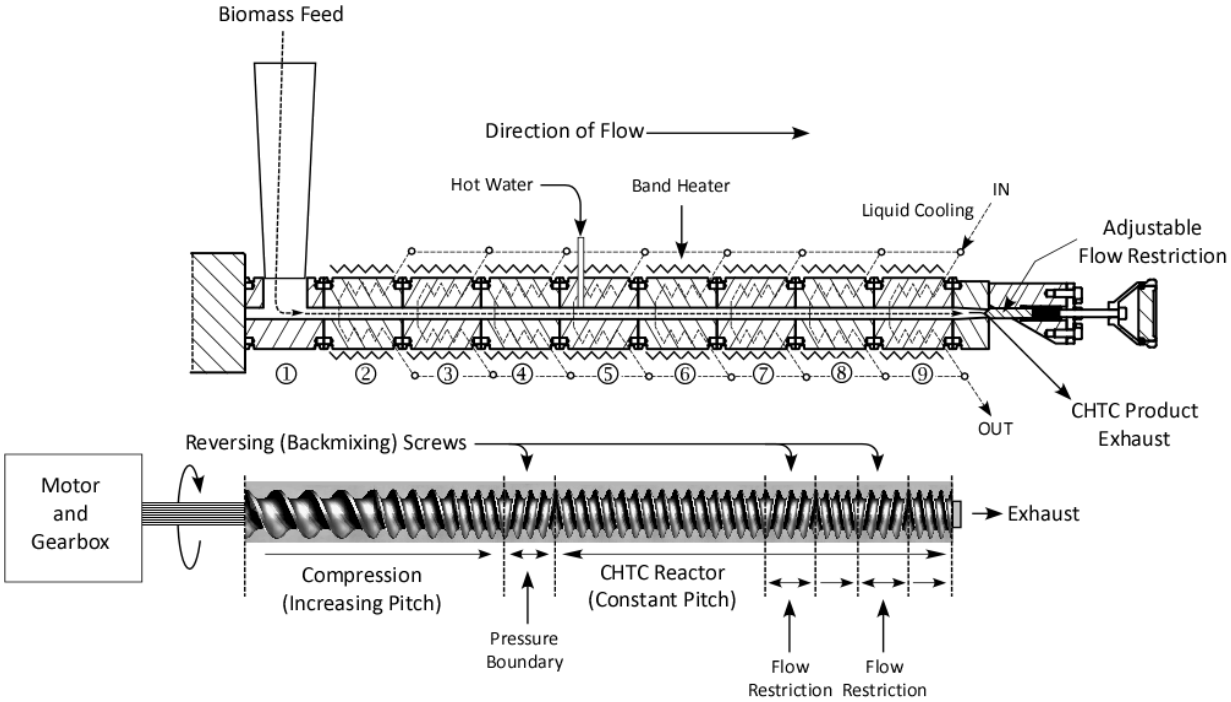

Figure 59. Schematic cross-section drawing of the BC-21 TSE (top) and (bottom) the configuration of one of the two intermeshing screw sets configured along splined shafts that moved particulate biomass introduced at the left to the right as the CHTC reaction proceeded and was completed with the ejection of the CHTC product.

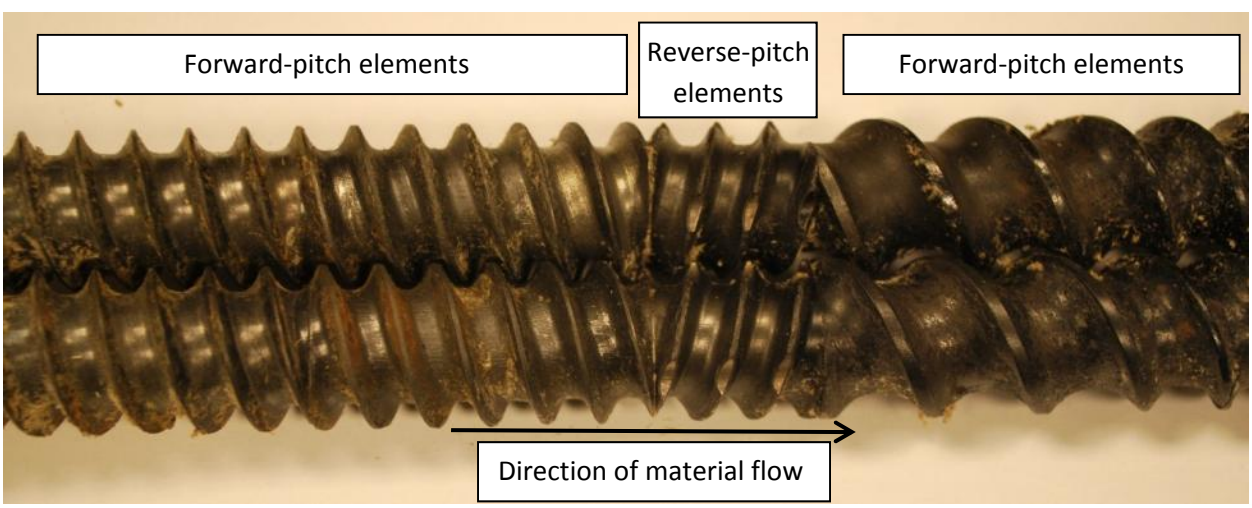

Figure 60. Segment of the two co-rotating TSE shafts illustrating the appearance of forward-pitch, and reverse-pitch screw elements.

Figure 61. End View of a Typical TSE Barrel Section Removed from the BC-21.

of high pressure, high temperature (HPHT) water into the FHTC reaction zone. The BC-21 TSE is equipped with a dedicated data logger that records process parameters at one-second intervals. These parameters include material pressure in each zone, zone temperatures, screw rpm, biomass feed rate, water feed rate, overall BC-21 torque level, and BC-21 power consumption. In addition, the PDU was designed so that GTI could also record the weight of biomass fed, weight of HTC product formed, volume of condensate collected, as well as other temperatures and pressures characteristic of PDU operation.

In the BC-21, individual short screw sections within the extruder can be configured to convey particulate biomass from the point where it enters the extruder through a series of internal reactor sections to a point where the HTC product and associated liquids are delivered across the dual-function, variable-restriction pressure boundary ("Exhaust" in Figure 59). Each small screw section can be of a different pitch so that when placed in sequence on the splined shafts, the rate at which material is conveyed through the TSE can vary while the rotational speed of the shafts upon which the screw sections are deployed is kept constant. By interspersing short, specialized reversing screw elements, robust pressure boundaries are able to be maintained that create separate sections at much higher or lower internal pressures than preceding or succeeding sections.

Reverse-pitch screw elements tend to recirculate the transported material in place, allowing this material to collect and compress at the point of recirculation. Thus, biomass fed into the TSE can compress to the extent that a dynamic pressure seal, or boundary, can be formed at the point where the reverse-pitch screw elements are located. As shown in Figure 59, the TSE is configured with screw sections arranged to create a first recirculating pressure boundary after biomass fed into the TSE has been masticated and compressed in the compression section.

Masticated biomass is defibered as it recirculates within, and eventually passes through the first pressure boundary (which is maintained at a moderate temperature, ~ 110 – 130 °C, to facilitate the decomposition of hemicellulose). The defibered biomass is then passed into the section of the TSE that serves as the FHTC Reactor, shown as a section of constant pitch screws in Figure 60 (although screw sections of various pitches could be utilized). The pressure boundary was found to be quite robust, easily maintaining continuous material pressures of 40 to 60 bar with

typical downstream internal CHTC Reactor pressures of 55 to 85 bar at 230 – 300 °C. In these experiments, a hot water injection port was located in the BC-21 TSE immediately after the dynamic pressure boundary. The injection of high temperature water (typically at 230 °C or above so that liquid water enters the reaction section to mix with the defibered and decomposing biomass) was chosen to provide a surfeit of water required for the FHTC reaction to proceed in a rapid manner. At these temperatures and pressures, water is known to have a pH of ~3, making it a strong acid that is capable of carrying out acid hydrolysis of biomass by itself. Thus, under the conditions described above, no acid needed to be added to cause or improve hydrolysis. Also, no copolymerizing or other chemical agents were required to create the FHTC product.

Screw speeds of 200 to 400 revolutions per minute are employed to transport biomass rapidly through the reactor section. In the FHTC reactor, cellulose in biomass tends to decompose and along with the previously decomposed hemicellulose, create a mixture of water, FHTC biochar, acids (acetic, formic), furan resins (from the condensation and polymerization of decomposed cellulose and hemicellulose), phenolic polymers from lignin, and gases, primarily CO_2. It is important to note that a significant portion of the solids in the biomass that entered the TSE are decomposed into liquids and gases in the CHTC Reactor. In addition, the physical characteristics of the biomass remaining in the solid phase changes during the HTC reaction, behaving more like a flowing viscous liquid. Consequently, the solids, liquids, and gases that passed from the CHTC Reactor to the second and third sets of reversing elements do not form dynamic pressure boundaries. However, these reverse-pitch elements induce a recirculation of biomass material within the CHTC Reactor, which serves to increase the residence time of biomass within the reactor. Based on observations during PDU testing, the residence time of biomass in the CHTC Reactor was estimated to be in the range of 10 to 30 seconds.

To define a downstream pressure boundary for the FHTC reactor, a special dual-function, variable-restriction pressure-sustaining valve (VRPSV) was designed and located at the discharge of the process so that the FHTC Reactor could be maintained at the desired pressure, and the HTC product could be exhausted from the TSE into a receiving container maintained at near ambient pressure. The VRPSV enabled proper process functionality as it permits a quasi-steady-state process to be carried out within the FHTC reaction section while controlling the delivery of a FHTC product to a much lower pressure (ambient pressure and temperature) or a pressure and temperature between that of the extruder outlet and ambient. Figures 62 and 63 show an early version of this valve design that was manually operated and discussed in our patent application.[50] Subsequently, the manually operated valve shown in these figures was replaced with an automated system and this system was employed to manage the production of FHTC biomass produced for this project. The design of these automatic systems is the subject of ongoing development and due to the proprietary nature of this effort it will not be described in more detail here. However, results will be presented that show the level of control that was achieved was sufficient to permit the steady, continuous production of FHTC loblolly pine.

Figure 63, shows the manually operated VRPSV installed on the TSE central feed die plate at the exhaust of the BC-21. This valve incorporates a spring-loaded valve plunger that is preloaded by tightening the calibrated hand wheel to a predetermined setting (first function). In practice, the valve was first set to provide a low level of resistance. As FHTC production commenced, tension (resistance) on the valve plunger was increased until FHTC product and liquids were released every 2-5 s, preferably in a regular, controlled manner (second function). This controlled release of FHTC solids, liquids, and vaporized liquids was observed to continue

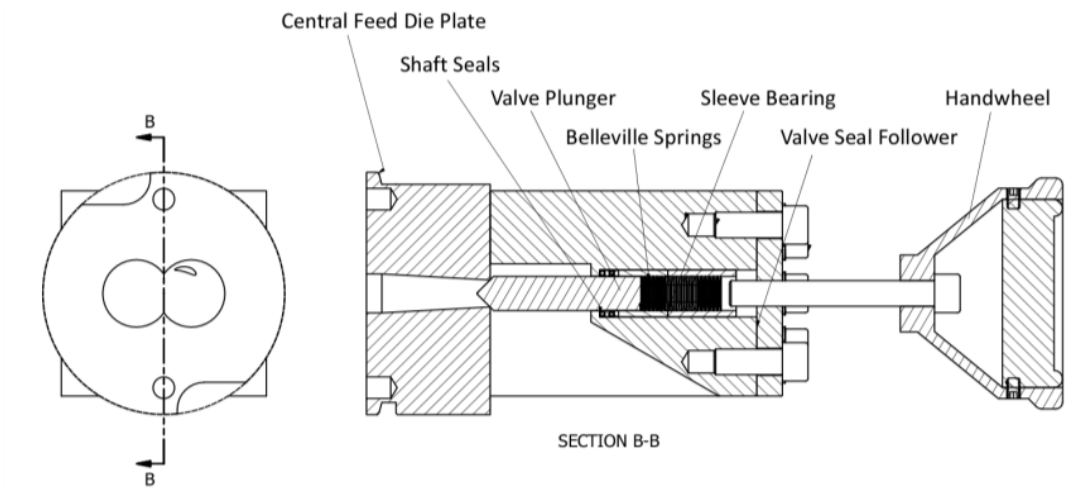

Figure 62. Manually-operated, dual-function variable restriction pressure-sustaining valve.

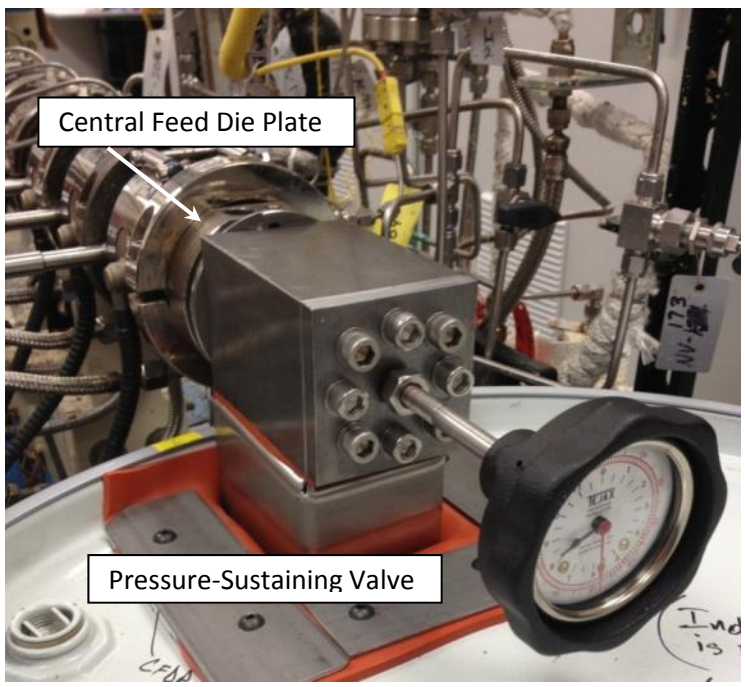

Figure 63. Custom-Built manual valve located at the exit of the BC-21 TSE.

every 2-5 s for as long as the TSE was operated at a constant input feed rate of biomass and level of hot water injection (constant, uneventful operation for up to four hours was documented in these shakedown tests).

HPHT water is supplied to the FHTC reaction zone by a custom-built, on-demand, water heating and injection system that utilizes a DKM Super K piston pump and novel pressure regulation to control water pressure in the heater independently of water temperature. Within this on-demand system, pressurized water passes through a series of external and internal heaters to heat the water to a predetermined injection temperature. Because this system is the subject of an ongoing patent application, it will not be described in further detail in this report.

Other key components of the FHTC PDU design include:

- A circulating chilled water system to provide up to seven gallons per minute of 3 °C water to the BC-21 chilled water supply line at a pressure of 50 psig to limit the upper temperatures in individual barrel sections,
- A sealed collection vessel to collect discharged FHTC biomass product and vent excess gas and moisture,
- A central ventilation system to maintain a negative pressure in the sealed collection vessel,
- Condensing coils to dry vented process gases,
- Activated charcoal canisters to remove any remaining volatile organic compounds (VOC's) from the process gas prior to discharge to the atmosphere,
- A condensate pump to transport process condensate collected during the gas drying process to collection vessels,
- A compressed nitrogen manifold which was used to aid in the control and operation of the HTHP water system,
- Portable gas sampling devices (Draeger gas detector tubes, continuous CO_2 and O_2 analyzers) to measure fugitive emissions of furfural and acetic acid, and other gases,
- Gas sampling ports located upstream and downstream of the sorbent collection canisters.

Continuous Production of FHTC Biomass: The Continuous FHTC PDU was operated for extended times in from January, 2013 through July, 2014, producing ~250 lbs. of FHTC biomass from loblolly pine. During this time, three generations of the VRPSV were developed and tested. While each generation of the VRPSV permitted production of FHTC loblolly pine, the third-generation VRPSV permitted the most continuous, stable production of FHTC biomass, required for stable FHTC product generation.

Figures 64 through 66 show how process behavior and stability consistently improved for tests carried out with the first-generation, manual, spring-loaded control valve (April 21, 2013), a second-generation, semi-automatic valve (March 21, 2014), and the-third generation, completely automated valve (July,15, 2014). In each figure, TSE motor amperage and internal pressure in each TSE barrel segment are shown. Note that the pressure traces in these figures are displaced from one another, particularly for the results from July, 2014. This displacement is more due to offsets among pressure transducer output than actual differences in pressure in the various TSE barrel segments from the July test series as several of the transducers had failed and were replaced before the July tests. These results do reveal, particularly for TSE motor amperage and internal barrel pressures, that the third-generation, completely automated FHTC exhaust control valve did permit the FHTC PDU to operate with much less variation than was observed in any of the earlier testing.

Table 20 quantifies the improvements in TSE reactor performance for tests conducted in April, 2013, March, 2014, and July, 2014. These data for locations near the reactor exhaust and include median reactor pressure and temperature, sample standard deviations of reactor pressure and temperature, and coefficient of variation of pressure for stable periods for three tests covering the three generations of HTC exhaust valves. Reductions in the coefficient of variation for successive data sets along with increasing median pressure and zone 9 reactor temperature indicates a clear trend of improvement in process stability and severity as greater levels of process control were reached with later-generation control valves.

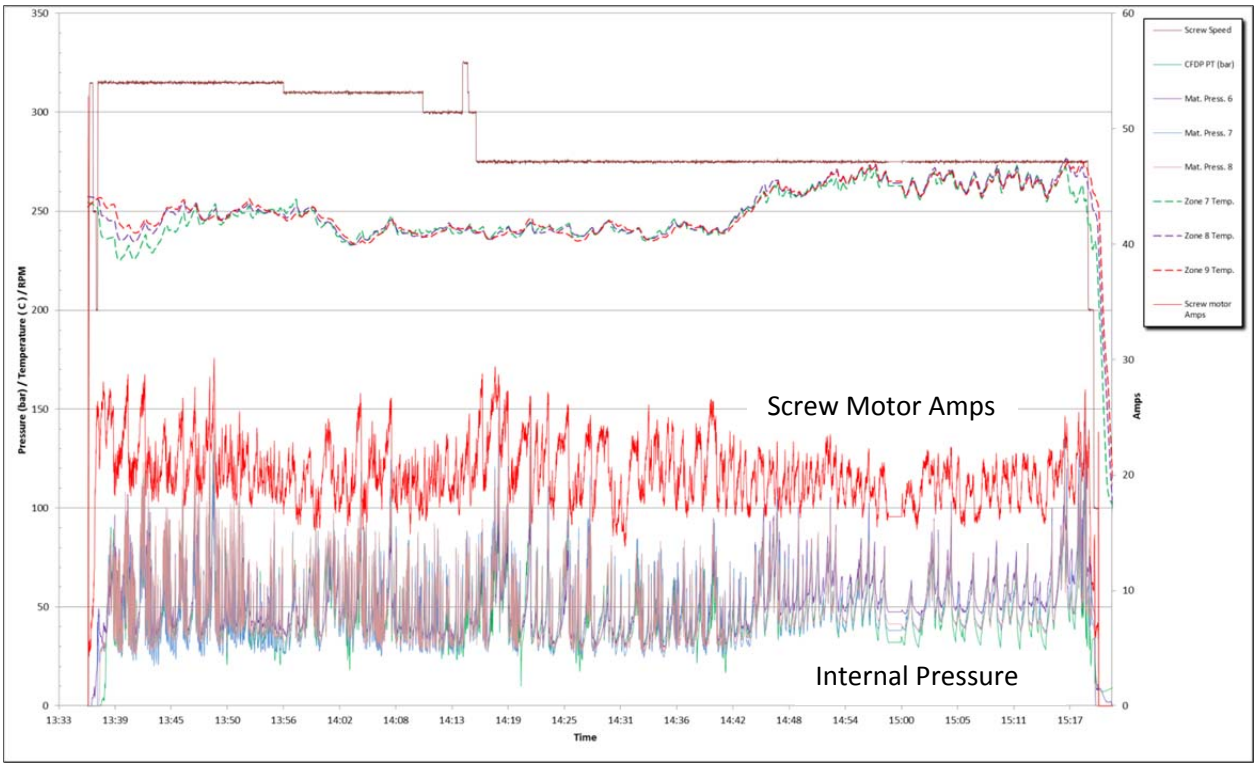

Figure 64. Process charts for first-generation HTC exhaust VRPSV, April 21, 2013.

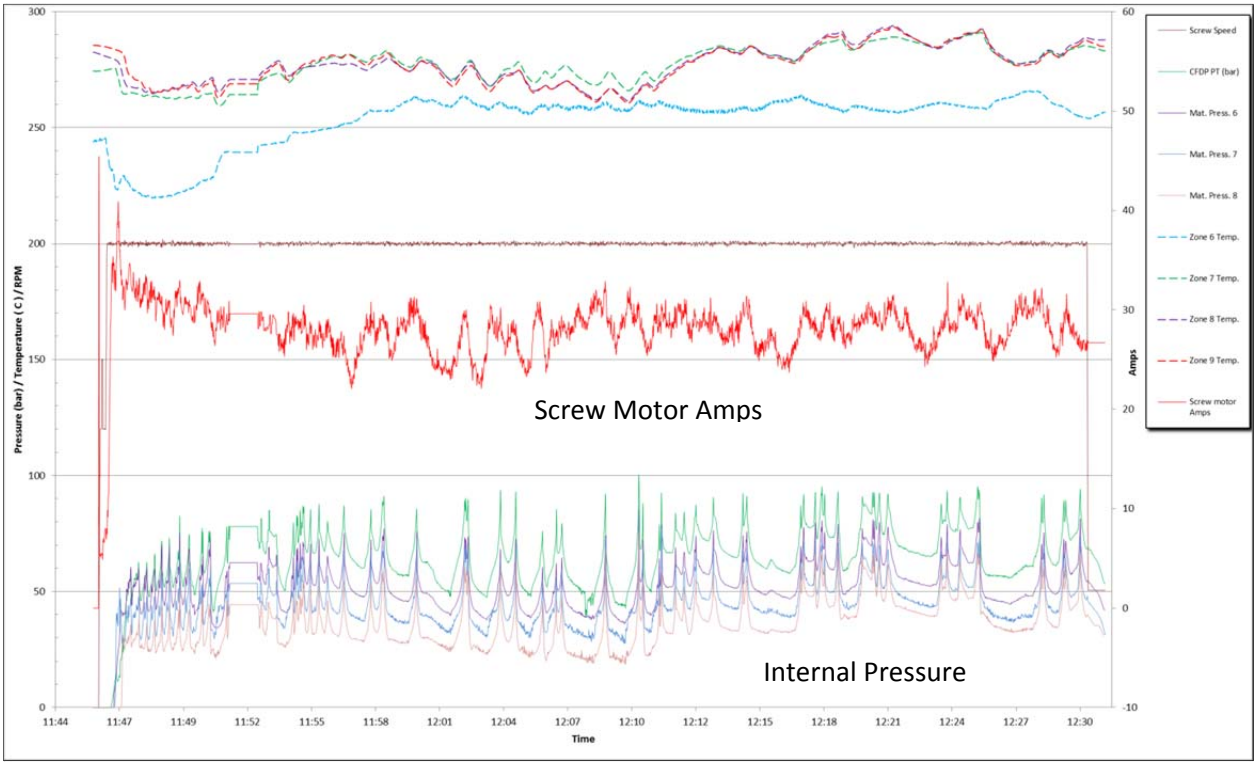

Figure 65. Process charts for second-generation FHTC exhaust VRPSV, March 21, 2014.

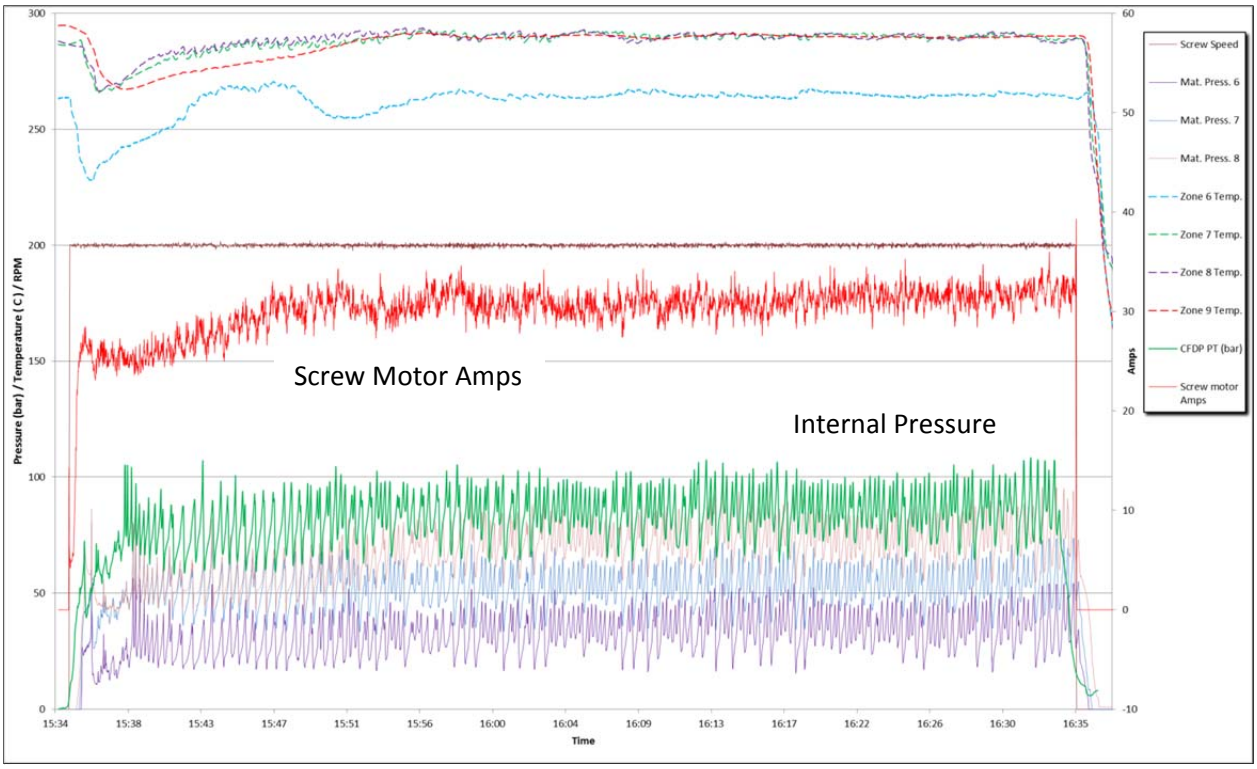

Figure 66. Process charts for third-generation FHTC exhaust VRPSV, July 15, 2014.

Table 20. Improvements in FHTC reactor stability over three generations of the VRPSV

Test	Exhaust VRPSV	Zone 9[1] Median Temp. (°C)	Zone 9[1] Temp. SSD[2] (°C)	Zone 9[1] Temp. COV[3]	CFDP[1] Median Pressure (psig)	CFDP[1] Pressure SSD[2] (psig)	CFDP[1] Pressure COV[3]
4/21/13	GEN-1. Manual Control	240	2.9	1.2%	581	230	39.6%
3/21/14	GEN-2. Semi-automatic Control	280	3.4	1.2%	1,052	257	24.4%
7/15/14	GEN-3. Automatic Control	**290**	**0.8**	**0.03%**	**1,334**	**43**	**3.2%**

1. CFDP – Central Feed Die Plate – at the TSE reactor exhaust, directly downstream from TSE Zone 9
2. SSD – Sample Standard Deviation
3. COV – Coefficient of Variation (ratio of the standard deviation to the mean)

Assessment of FHTC Products from the GTI TSE-Based PDU: While DRI was developing and optimizing the operation of its PDU, and characterizing the resulting products as described above, GTI proceeded with the optimization of a fast HTC (FHTC) PDU in their laboratory in Birmingham, AL. As described above, this PDU was developed under DOE Cooperative Agreements DE-FG36-02GO12011 and DE-FG36-01GO11082. Under this project, the operation pf the FHTC PDU was optimized and interfaced with a mixing, conveying, and drying system that mixed pulverized coal and fresh FHTC biomass that was subsequently briquetted.

Heretofore, DRI had characterized HTC produced in laboratory and pilot-scale batch-based systems and determined that HTC produced in batch processes was a superior material for pelletizing with itself and with coal. However, FHTC produced in the GTI PDU needed to be

subjected to a similar assessment to determine if it possessed the same characteristics as HTC biomass produced in batch processes. This is a reasonable question because batch-based HTC processes are carried out over long times (up to hours) and a continuous HTC biomass processes, such as the GTI FHTC PDU produces HTC biomass in an inherently rapid process, requiring less than one minute.

Within a TSE, the biomass feedstock (Loblolly pine) and hot water are masticated, intimately mixed, forced through a dynamic seal, and subjected to rapid acid hydrolysis. Due to the rapid transit through the TSE system, the HTC reaction time is short (~ 20-30 sec.). Because these operating conditions are so different from those employed in DRI's reactor systems (2-chamber reactor, 2-L stirred Parr reactor, and auger-driven PDU) it is of considerable interest to characterize the products from the FHTC system, and to compare these results with those obtained from DRI's reactor systems. In the following sections, we describe the HTC product characterization from three different experimental operating campaigns of GTI's FHTC system.

FHTC Experiments in February, 2013: The first operation of GTI's FHTC system that included product collection and characterization occurred in February of 2013. Over a 1-week period, three different sampling episodes were conducted. (The feedstock for all experiments was Loblolly pine.) In each case, the operating temperature within the FHTC was believed to be 250-260 °C. The thick slurry products extruded from the FHTC PDU were sent to DRI for characterization, along with one sample called "exhaust." This exhaust sample was not collected at the end of the PDU, but was exhausted out of a port near the inlet of the system. The exhaust sample resembled starting feedstock in its appearance, although it had a sweet, sugary odor.

FHTC Product Characterization by DRI: All hydrochar products from the February, 2013 experiments were received in a wet form. Aliquots of each material were oven dried to determine the moisture content. As shown in Table 21, these samples contained about 65-75% water, as received. Portions of the wet hydrochar samples were washed with deionized (DI) water to remove water-soluble products, and were then dried to obtain solid materials for characterization and pelletization.

The mass energy contents (MJ/kg) of the GTI hydrochar materials are also given inTable 21. The starting feedstock (Loblolly pine) has an energy content of 20.3 MJ/kg (see Table 9). Thus, very little energy densification was observed in the hydrochars produced in GTI's FHTC PDU, although the sample collected on 2/21/13 showed a slight increase to 21.1 MJ/kg. Also, this sample gave a further increase in energy density upon water washing (to 23.6 MJ/kg), suggesting that the water soluble products that were removed had lower energy contents than the solids remaining behind.

The proximate and ultimate analyses of these washed and unwashed hydrochar products from the FHTC system are also provided in Table 21. These results suggest that the degree of carbonization that occurred in all experiments was quite small. For example, the carbon contents of all four washed samples were in the range of 52.2% - 53.9%, as compared to the raw Loblolly pine feedstock which has 49.3% carbon (see Table 9). This degree of carbonization was slightly less than what we've observed in standard 2-L Parr reactor experiments at 215 °C. As shown in Table 9, the carbon content of HTC-215 produced in the Parr reactor was 54.6%, while the carbon content of HTC-175 was 51.0%.

Table 21. Characterization of Solid Products from the GTI FHTC Process – Feb. 2013

Solids and Energy Contents

Treatment	GTI Sample Date/ID	Solids Content, % of delivered sample	Mass Energy Content of Solids, MJ/kg	Vol. Energy Content of Pellets, GJ/m^3
Unwashed	2/19/2013	24.92	20.247	27.772
	2/21/2013	36.84	21.089	29.190
	2/26/2013	25.33	20.094	27.796
	2/26/13 Exhaust	27.11	19.764	24.881
Washed	2/19/2013	22.81	20.352	27.195
	2/21/2013	31.83	23.646	32.312
	2/26/2013	19.64	20.666	28.041
	2/26/13 Exhaust	26.29	20.032	24.446

Proximate Analysis

Treatment	GTI Sample Date/ID	% Moisture Content	% Volatile Matter (db)	% Ash (db)	% Fixed Carbon (db)
Unwashed	2/19/2013	1.69	96.57	0.29	3.14
	2/21/2013	1.13	81.10	0.42	18.48
	2/26/2013	1.37	85.84	0.38	13.78
	2/26/13 Exhaust	3.77	88.60	0.40	11.00
Washed	2/19/2013	2.14	94.49	0.17	5.34
	2/21/2013	1.66	86.36	0.11	13.53
	2/26/2013	1.53	86.88	0.06	13.05
	2/26/13 Exhaust	3.61	90.19	0.18	9.63

Ultimate Analysis

Treatment	GTI Sample Date/ID	%C	%H	%N	%O	Sum
Unwashed	2/19/2013	51.5324	6.3022	0.0436	43.1164	100.99
	2/21/2013	53.7378	6.1906	0.0365	41.7345	101.70
	2/26/2013	52.2714	6.2268	0.0583	42.8897	101.45
	2/26/13 Exhaust	49.6120	6.0585	0.2872	40.9630	96.92
Washed	2/19/2013	52.1973	6.2433	0.3308	42.3387	101.11
	2/21/2013	53.9029	6.0679	0.2835	40.9666	101.22
	2/26/2013	52.6072	6.0433	0.1313	38.4939	97.28
	2/26/13 Exhaust	53.0633	6.0606	0.2059	41.4190	100.75

Besides hydrochar, GTI's FHTC PDU produced gaseous and condensed liquid products. The gaseous products were simply vented, but the condensed liquids were captured and analyzed for sugar content, using an HPLC-RI procedure described previously. In addition, the water washings (also called rinsate) from the hydrochar samples described above were analyzed for sugars. The sugar concentrations in two liquid condensate samples and four hydrochar washings are presented graphically in Figure 67. Figure 67(A) shows concentration values expressed as

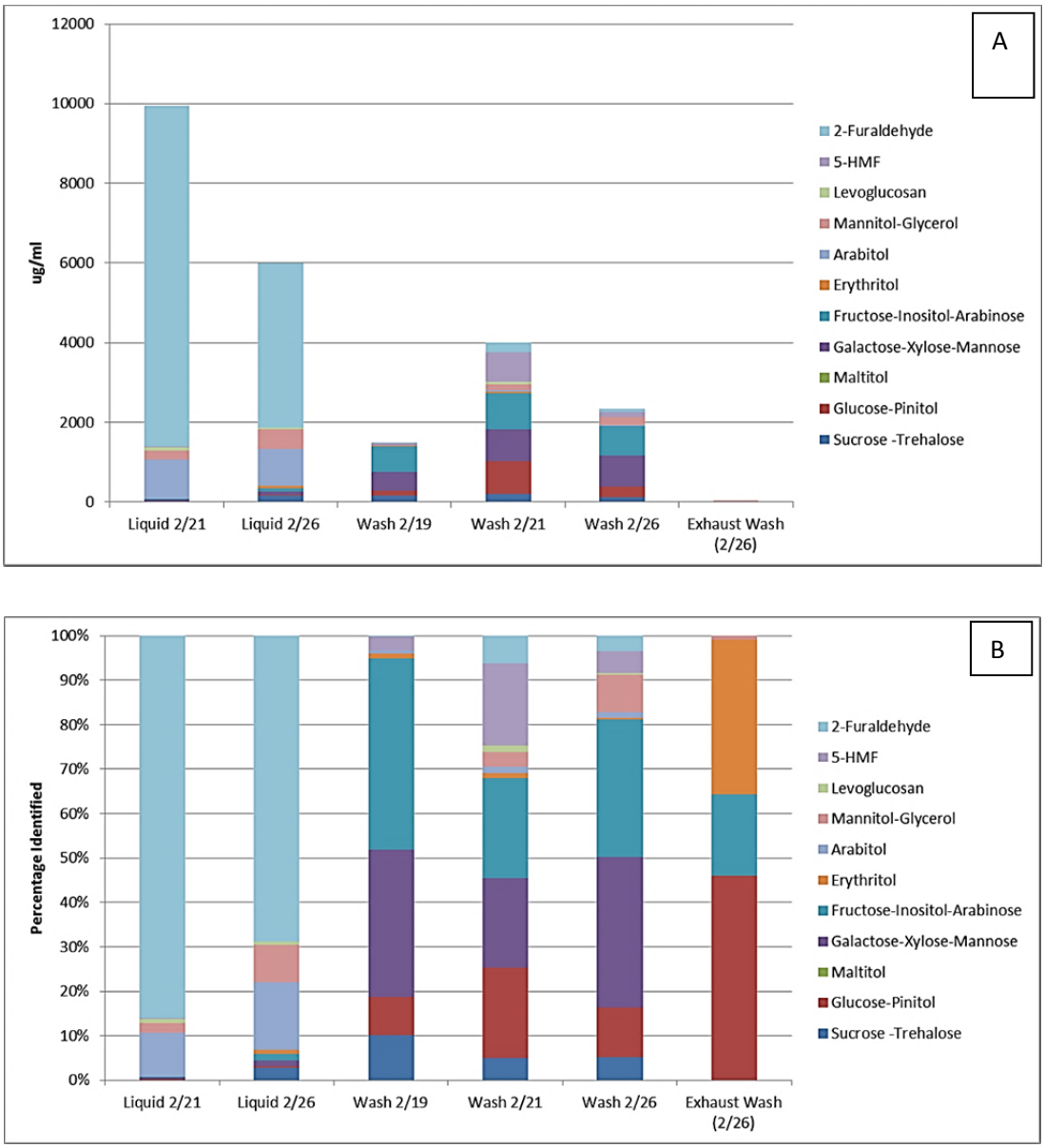

Figure 67. Analysis of sugars in aqueous products from HTC treatment of Loblolly Pine in GTI's FHTC PDU: (A) concentrations in liquid samples, (B) normalized distribution of identified constituents – Feb. 2013.

µg/ml; Figure 67**Figure** (B) shows these concentrations normalized to 100%. The condensed liquid product streams from GTI's FHTC system on 2/21/13 and 2/26/13 were dominated by furfural, with lesser amounts of arabitol and mannitol-glycerol. The total yields of these sugars (i.e. g sugar/kg feedstock) are unknown, as we do not know the total volume of the condensed liquid, or the mass of loblolly pine feedstock that was processed to produce this condensate.

The relative sugar compositions in the three hydrochar washes from February 19, 21, and 26 were similar, but not identical. As shown in Figure 67(B), these washes contained primarily 5-HMF, fructose, galactose-xylose, glucose, and sucrose; but very little furfural. These

compositions are very different from the compositions of the liquid product stream from the PDU. This is expected, since the liquid product stream is obtained by condensing gaseous material that is flashed from the PDU. Thus, volatile organic compounds (VOCs) that exit the reactor in the gas phase, but are condensed to a liquid phase (such as furfural) would be expected in these liquid samples. However, non-volatile organics (such as most sugars) would not be vaporized, but would exit the PDU in the liquid and/or solid phase.

The GTI sample identified as "exhaust" contained very little water-soluble sugars. Furthermore, the sugars that were present had a very different composition than all the other samples, consisting primarily of glucose-pinitol and erythritol. This information, along with the solids characterization data of Table 20, suggest that this "exhaust" sample underwent very little (if any) hydrothermal carbonization.

Because the water washing of these GTI-generated hydrochar samples was conducted in DRI's laboratories, the amounts of water and hydrochar used in each case are known. With this information, we calculated the sugar concentrations in each water wash sample as a percentage of the starting dry hydrochar. These results, shown in Figure 68, indicate that the overall amounts of sugars removed from the hydrochars were not very large – ranging from about 0.3% to 0.8% for the three samples that were analyzed. The amount of sugars washed from the exhaust sample represented less than 0.01% of the solid mass.

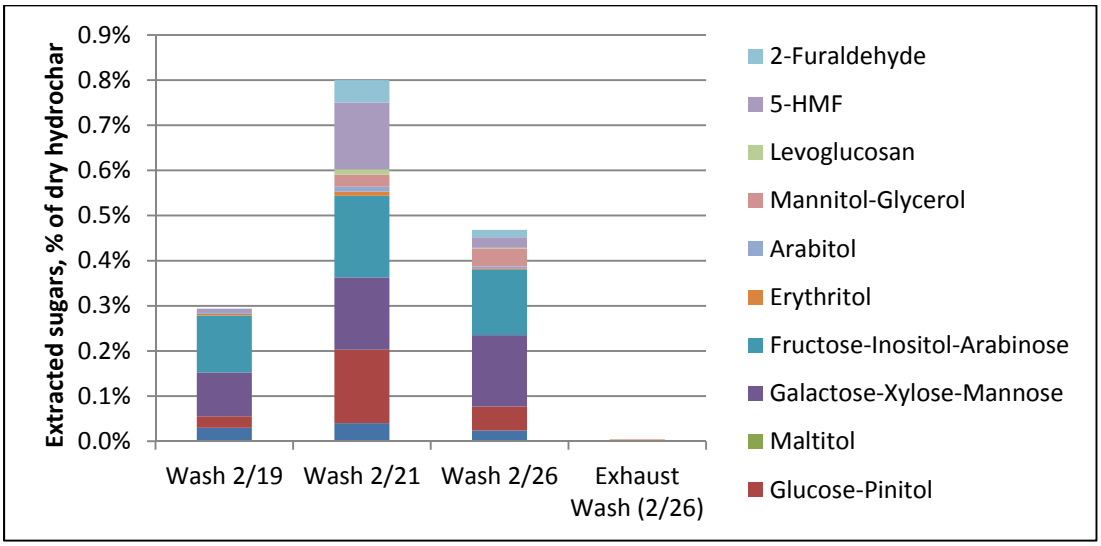

Figure 68. Amount of sugars removed by water washing of hydrochar produced from HTC treatment of Loblolly Pine in GTI's FHTC PDU – February, 2013.

Pelletization of FHTC hydrochar: Pelletization of all three hydrochar materials produced by the FHTC PDU was explored, using the pellet production and evaluation processes described above. Both washed and unwashed hydrochar samples were pelletized. The results of water immersion tests of these pellets are provided in Figure 69. It is clear that the hydrochar produced on 2/19/13 behaved differently from the other two materials. While pellets from all three original materials showed very little swelling upon water immersion, pellets made from water-washed hydrochar or 2/19/13 swelled considerably. This swelling can also be seen in the photos ofFigure 70. However, despite this swelling, the pellets produced from the water-washed hydrochar of 2/19/13 (as well as all the other pellets) were extremely durable. As shown in the

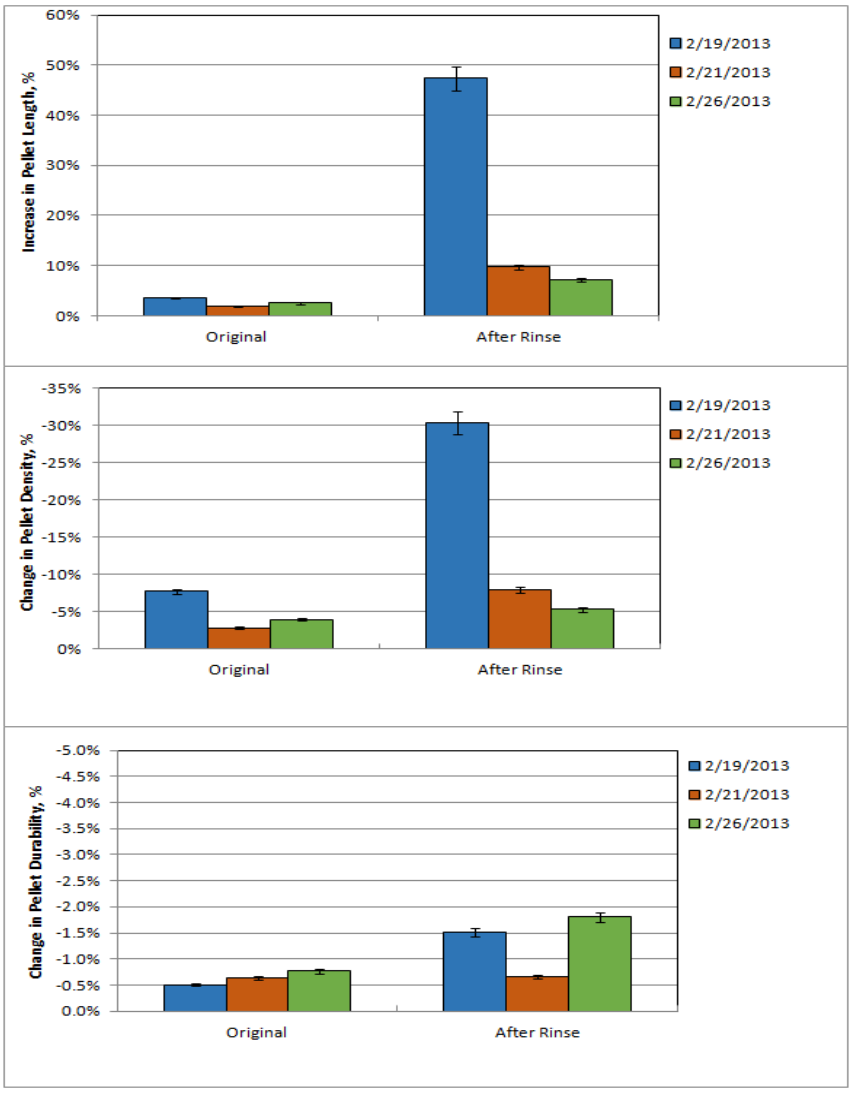

Figure 69. Effects of water immersion (60-min.) upon characteristics of pellets produced from FHTC hydrochar from Loblolly pine – February, 2013. All results expressed as % change from behavior of pellets that did not undergo water immersion.

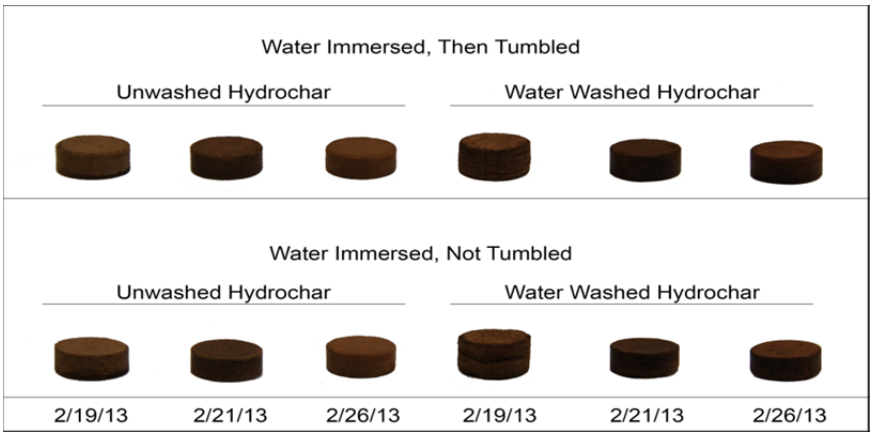

Figure 70. Effect of water washing upon behavior of pellets produced from FHTC hydrochar of Loblolly Pine.

bottom panel of Figure 69 , even in the worst case, the reduction in tumbler durability of water-immersed pellets was less than 2%.

Comparisons between FHTC hydrochar and raw Loblolly pine are further shown in Figure 71. These photos also illustrate the rusty-brown color of the hydrochar from the FHTC, which contrasts with the darker brown-black color typically seen in hydrochar produced in a stirred Parr reactor at temperatures > 250°C. Pellets made from these materials were unaffected by immersion in water, or by subsequent tumbling. All three of the FHTC hydrochar samples behaved similarly, producing very stable pellets. For comparison, photos of raw loblolly pine, and pellets made from it, are also shown in Figure 71. While not shown here, the "Exhaust" sample from 2/26/13 behaved very similarly to raw loblolly pine, exhibiting extreme swelling upon immersion in water.

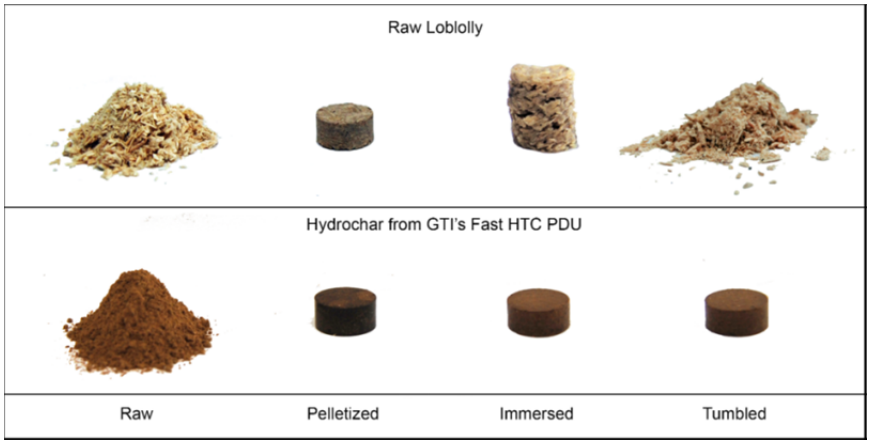

Figure 71. Comparison of raw Loblolly Pine and hydrochar produced 2/21/13 in GTI's FHTC PDU. "Immersed" indicates the pellet was immersed in water for 60-minutes. "Tumbled" indicates the pellet was tumbled for 3000 revolutions, after 60-min. of immersion in water.

Volumetric energy contents (GJ/m^3) of the pelletized hydrochar materials are given in Table 20. These values (27.7 – 29.2 GJ/m^3) were computed from the mass energy content of the hydrochar, and the measured volume and mass of the pellets. For reference, the volumetric energy content of raw loblolly pine pellets is approximately 24.6 GJ/m^3. Therefore, the three FHTC hydrochar samples all showed significant increases in volumetric energy content compared to raw loblolly pine. The pelletized sample produced from the 2/21/13 material showed a substantial further increase in volumetric energy density after water washing the HTC product, to 32.3 GJ/m^3.

These mass and volumetric energy density results of the FHTC hydrochars are illustrated graphically in Figure 72. Also shown here are energy density values of hydrochars produced previously by DRI using a 2-L stirred Parr reactor. (Loblolly pine was the feedstock for both DRI-generated and GTI-generated hydrochar products.) As shown in this figure, the mass energy density of hydrochar increased with HTC temperature within the Parr reactor. Similar behavior has been shown with HTC treatment of many other biomass feedstocks in the 2-L Parr reactor. On a pellet volumetric energy basis, a different behavior is seen, where a maximum is reached at an intermediate process temperature of 255 °C. (These 2-L Parr data are also shown in Figure 39.) Reasons for this behavior are not yet completely understood. However, there are indications from the literature that at high HTC process temperature, the hydrochar product becomes more porous, and thus may pack with lower density when pelletized.

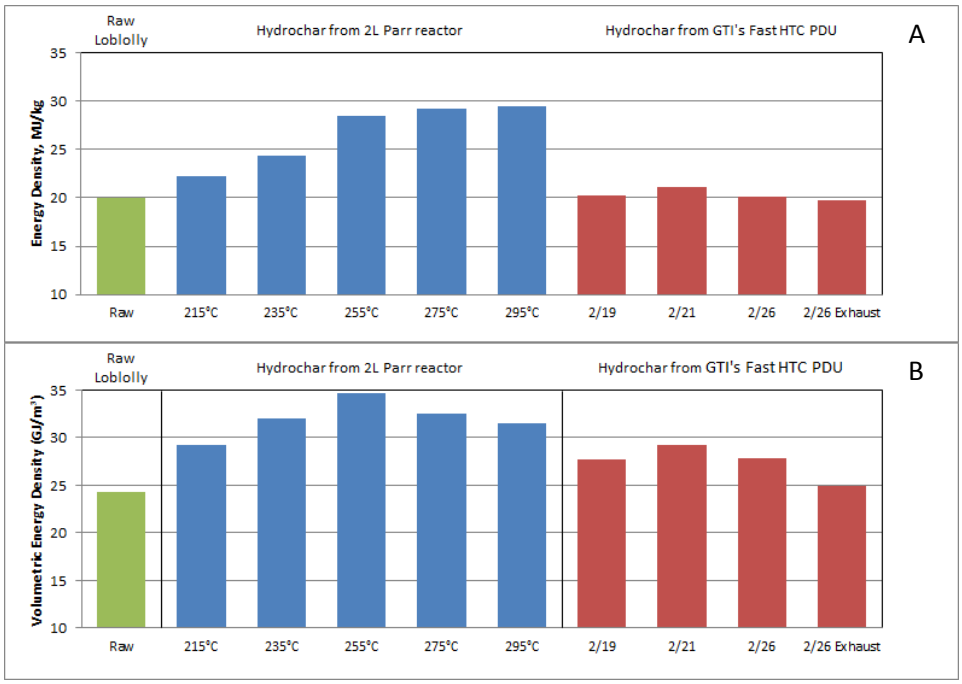

Figure 72. Energy densities of hydrochar produced from loblolly pine using DRI's 2-L Parr reactor and GTI's FHTC PDU:(A) mass energy density of powders, (B) volumetric energy density of pellets. (All hydrochar samples from GTI were used as received, without water washing.)

The results shown in Figure 72 indicate that of the three FHTC hydrochar materials investigated, that produced on 2/21/13 had the highest mass energy density and produced pellets having the highest volumetric energy density. This suggests that the FHTC reaction severity was slightly higher during operation on this day compared to the two other days. By comparing with the 2-L Parr reactor data also shown in Figure 72, it appears that the FHTC hydrochar from 2/21/13 corresponded most closely with HTC-215 from the Parr batch reactor. Although the energy densification of Parr-derived HTC-215 was quite modest, this material was also found to produce very robust pellets (see Figure 38).

FHTC PDU Experiments in May, 2013: On May 24, 2013, GTI conducted another series of experiments using Loblolly Pine in the FHTC PDU. Operational parameters of the PDU were varied (particularly water feed rate and biomass feed rate) to produce different product mixtures. When using a relatively high ratio of water/feedstock, the hydrochar product still had a fibrous appearance; at a lower water/feedstock ratio, the hydrochar had a paste-like appearance. Small samples of both hydrochar and the accompanying aqueous product stream (obtained by condensation of vapors) were collected while operating the PDU under these low and high water/feedstock ratio conditions. The wet hydrochar products were vacuum filtered to remove most of the water in a "filtrate" fraction. The filter cake remaining after this water removal was rinsed with fresh water to obtain a "rinsate" fraction. Thus, each experimental condition produced three aqueous samples (condensate, filtrate, and rinsate) which were then sent to DRI for analysis of sugars and organic acids. A schematic showing the collection and identification of these three aqueous samples is provided in Figure 73. In addition, a "bulk" sample of hydrochar and condensate were collected at the end of this series of experiments. These represented composite products that had been generated over the range of experimental conditions employed during the entire day.

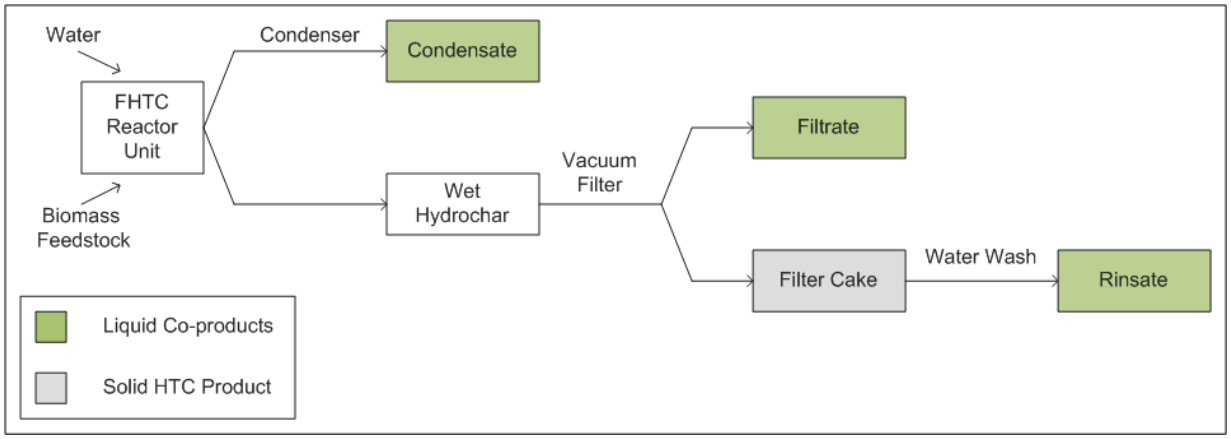

Figure 73. Sampling schematic for the GTI FHTC PDU.

DRI's standard HPLC-RI method was utilized to quantify sugars present in the three aqueous process streams from the FHTC experiments: condensate, filtrate, and rinsate. Because the total volumes of these aqueous materials (and the amount of loblolly pine that was treated to produce them) were unknown, we could not express the results in the usual terms of mass of sugars per mass of feedstock. Instead, we simply determined the sugar concentrations in the aqueous samples as supplied, and then expressed the concentration results as normalized to 100%. The sugar results from all nine aqueous samples from the FHTC experiments conducted on 5/24/13 are presented in Figure 74. Figure 74A gives concentrations in units of µg/ml; Figure 74B shows these concentrations normalized to 100%. These graphical results reveal several interesting features:

1. In all three sample types (condensate, filtrate, and rinsate) the bulk sample had sugar concentrations intermediate between the fiber and paste samples. This is expected, since the bulk samples represent a composite of all operating conditions throughout the experimental period.
2. Sugar concentrations in the filtrate samples were higher than in the rinsate samples. This is also expected, since the filtrate samples were collected without any dilution, while the rinsate samples were diluted with water.
3. The compositions of all filtrate and rinsate samples were quite similar, consisting mainly of 5-HMF, levoglucosan, fructose, galactose-xylose, glucose, and sucrose.
4. The compositions of the three condensate samples were also quite similar, but were very different from the filtrate and rinsate compositions. The condensate samples were dominated by furfural, with lesser amounts of levoglucosan and arabitol. This is expected, because furfural is the most volatile of these sugar species, and hence, is most likely to exit the reactor in the gas phase and be captured in the condensate. Because of its occurrence in relatively pure form in the condensate, it may be useful to explore ways of isolating furfural for commercial purposes.
5. Comparing Figure 67 and Figure 74 shows that in general, the compositions of the condensate samples were very similar to the liquid samples analyzed from the previous FHTC runs in February of 2013. The filtrate and rinsate compositions were very similar to the "wash" samples from the previous FHTC runs.

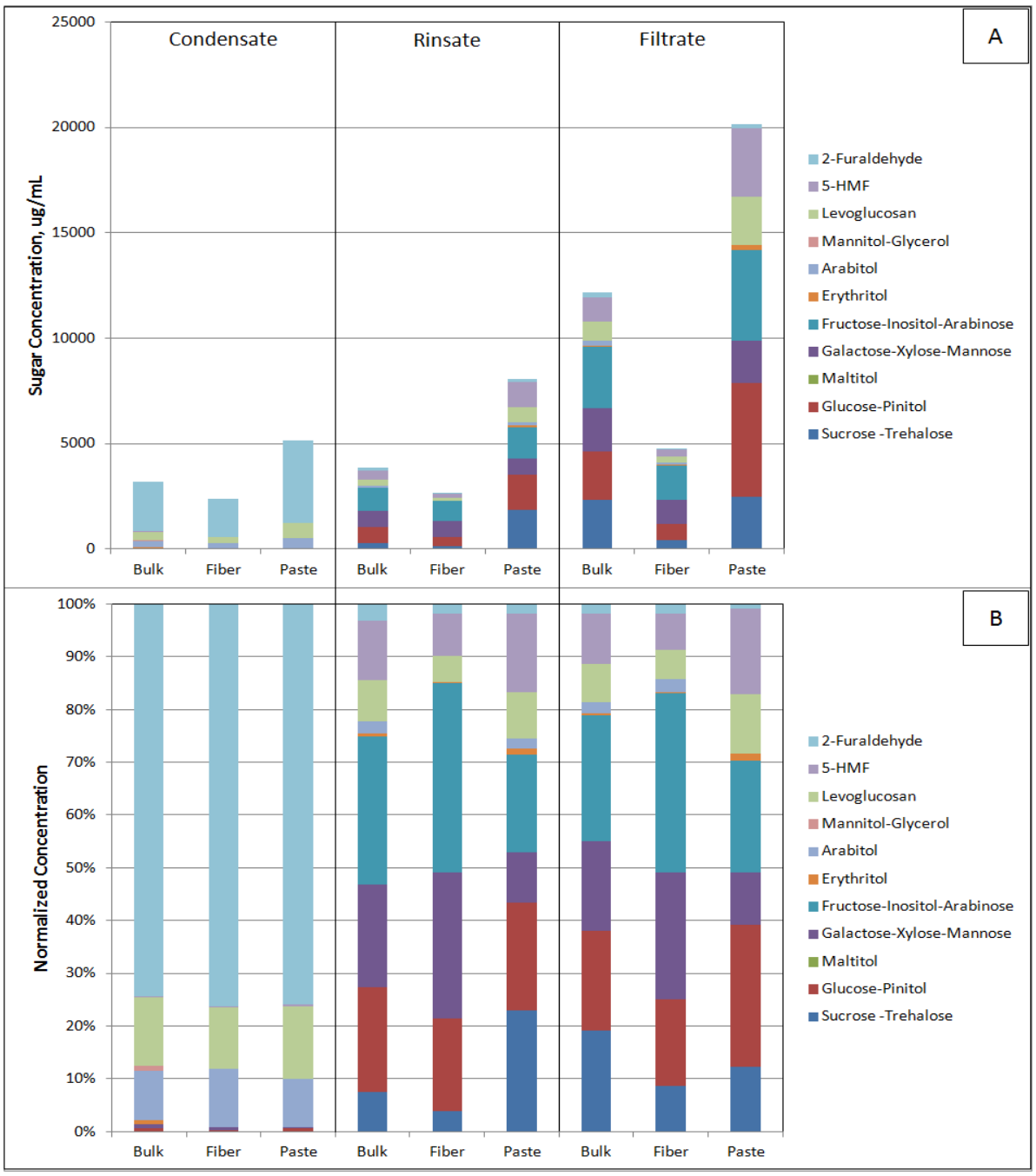

Figure 74. Analysis of sugars in aqueous products from treatment of Loblolly in the GTI FHTC PDU – May, 2013. (A) concentrations in units of µg/ml; (B) concentrations normalized to 100%.

The aqueous product streams from the GTI FHTC reactor experiments in May of 2013 were analyzed for organic acids using an ion chromatography method described previously. The earlier aqueous products collected during operation of the FHTC PDU in February of 2013 were also analyzed for organic acids at the same time. Results from all these samples are shown graphically in Figure 75.

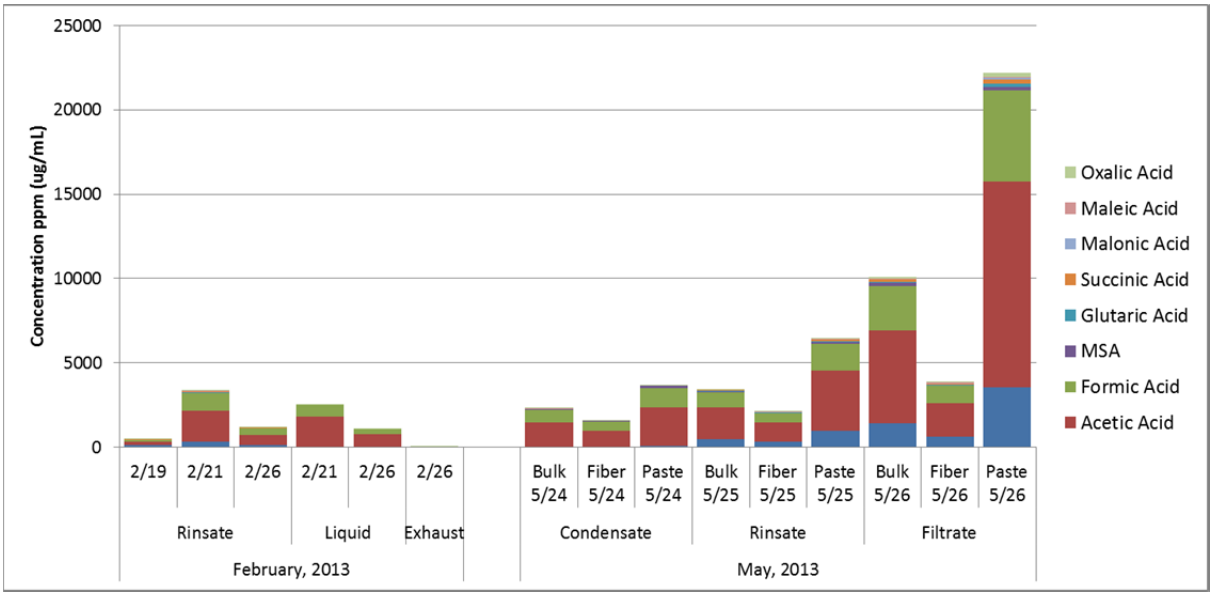

Figure 75. Concentration of organic acids in aqueous products from treatment of Loblolly pine in the GTI FHTC PDU.

As was discussed above, the total volumes of these aqueous products or the amount of Loblolly pine that was processed to produce them are not known. Therefore, these acid results cannot be expressed as mass of product per mass of feedstock. In Figure , the organic acid results are shown as normalized to 100%. These results indicate that acetic acid is the dominant organic acid species present in all samples.

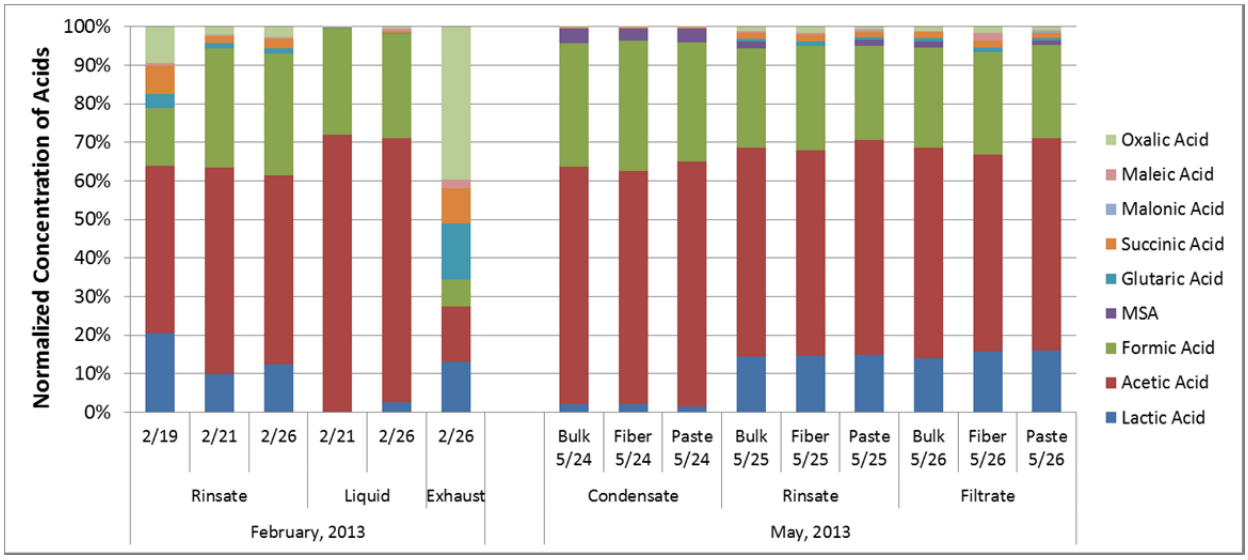

Figure 76. Normalized concentrations of organic acids in aqueous products from treatment of Loblolly pine in GTI's FHTC PDU.

The "liquid" samples from February, 2013 are very similar to the "condensate" samples of May, 2013. (In fact, these may be considered two different terms for the same product stream.) They are dominated by acetic acid, but also contain a significant amount of formic acid and a trace of lactic acid. The rinsate samples from February, 2013 are considered the same product stream as the rinsate from May, 2013. These samples are also dominated by acetic acid, but compared to

the condensate samples, they have relatively larger amounts of lactic acid. They also contain small amounts of several other acids, including glutaric acid, succinic acid, and oxalic acid.

The "exhaust" sample from February, 2013 had a very different composition of organic acids compared to all other samples. This is consistent with our previous observations based upon sugars analysis (see Figure 67) and energy content measurements (see Figure 72) that the "exhaust" material did not undergo a significant degree of carbonization. No solid hydrochar products were obtained from the FHTC experiments conducted in May of 2013.

Assessment of Process Severity: Throughout the course of this project, we have produced and characterized HTC products that were generated in a variety of process equipment, operated under a range of conditions. At DRI, we have utilized both a stirred 2-L Parr reactor, a small 2-chamber reactor system (which enables very short reaction times) and a larger semi-continuous process development unit (PDU; which enables production of large quantities of hydrochar product).

Having such diversity in reactor configurations and conditions makes it difficult to compare all the results together. This is illustrated in Figure 77, which shows the energy content values (MJ/kg) of hydrochars from all HTC experiments we've conducted using Loblolly pine and Tahoe Mix wood feedstocks in all three reactor systems. While the energy contents clearly increase with process temperature in each reactor system, it is not possible to explain all the results using a single relationship. In particular, results from the 2-chamber reactor and the PDU lie quite far off the trend lines shown for the 2-L stirred Parr reactor results.

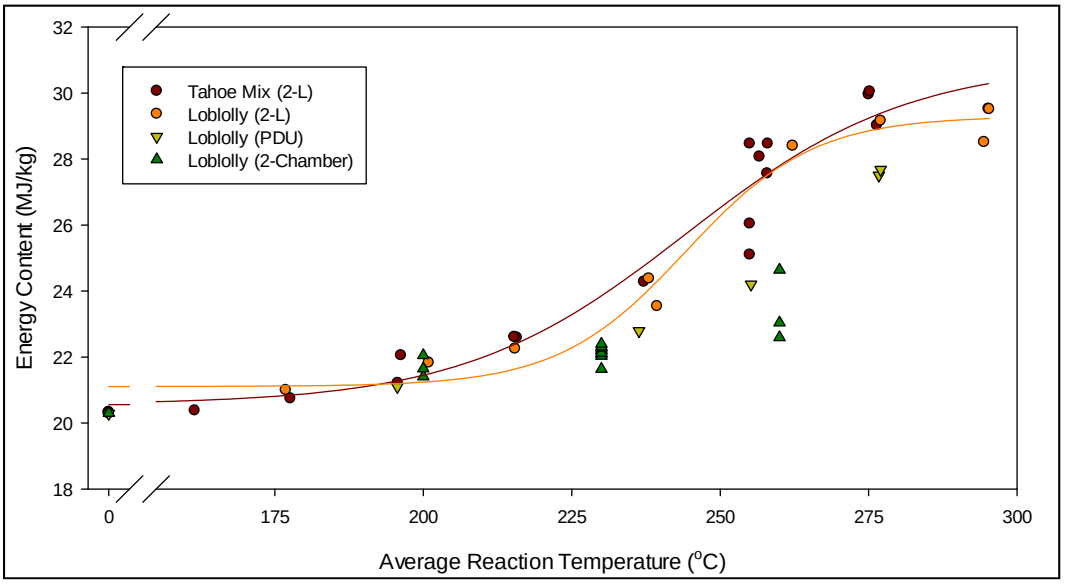

Figure 77. Relationship between HTC reaction temperature and hydrochar energy content. Experiments with Loblolly pine and Tahoe Mix feedstocks were conducted in different reactor systems under various conditions. Trend lines are shown for 2-L Parr reactor experiments.

When dealing with thermochemical processes in which temperature and time are both important parameters, it is sometimes useful to combine these parameters into a single factor for evaluating the overall process severity. Several different predictive equations for reaction severity have been developed and applied to aqueous-phase hydrolysis processes occurring during wood

pulping and similar operations. [51] The equation for severity that we have investigated was used by Kim et al. for HTC treatment of Tulip tree sawdust, [52] and is defined as follows:

$$R_0 = t * e^{[(T-100)/14.75]} \qquad \text{(Eq. 1)}$$

In this expression, R_0 (also called the reaction ordinate) has units of time (min.). The variable "t" is the experimental reaction time (min.); the variable "T" is the reaction temperature (°C). This expression assumes the HTC process involves first-order reactions having an Arrhenius dependence upon temperature. A reference temperature of 100 °C is used. When graphically portraying experimental data in terms of process severity, it is common to plot the logarithm of the reaction ordinate (log R_0), which is called the "severity factor."

The same set of energy content data from HTC experiments of loblolly pine and Tahoe Mix as shown in Figure 76 was analyzed using severity factor as a reaction parameter, rather than temperature. The results shown in Figure 78 indicate that this analysis draws the data much closer together to a single relationship that can explain the energy content of hydrochars produced from a wide variety of process equipment and conditions. The data fit is especially improved for experiments conducted with short reaction times in the 2-chamber reactor and in DRI's PDU.

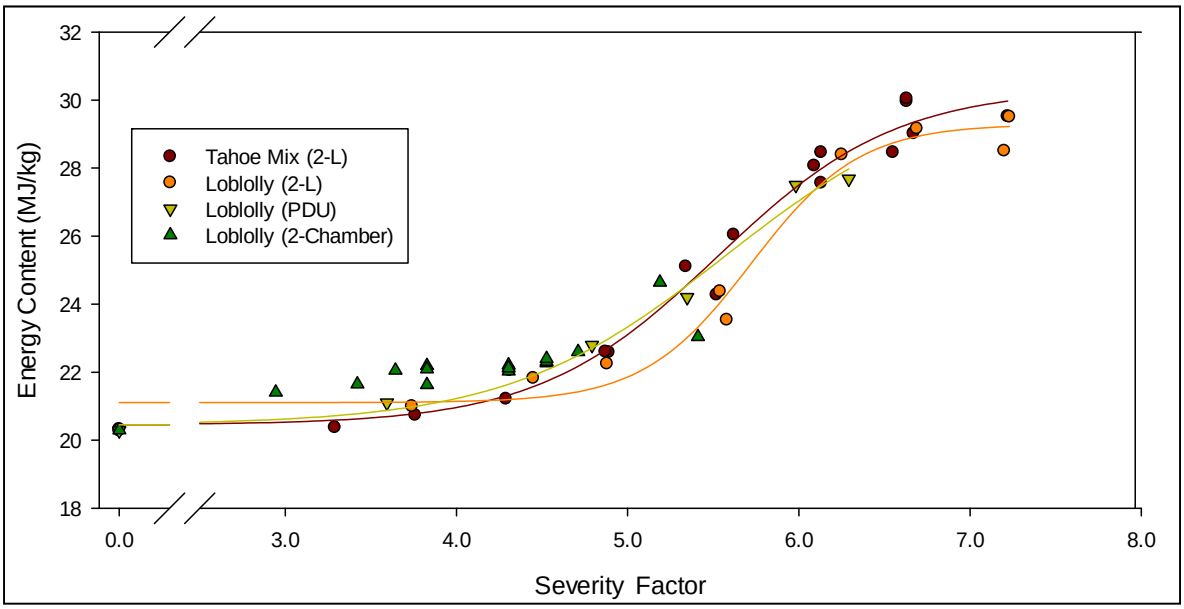

Figure 78. Relationship between reaction severity factor and hydrochar energy content. Experiments with Loblolly pine and Tahoe Mix feedstocks were conducted in different reactor systems under various conditions. Trend lines are shown for 2-L Parr reactor experiments and PDU experiments.

We also wished to apply this concept of reaction severity factor to the operation of GTI's FHTC PDU. However, using energy content of the hydrochar product as the dependent variable (as was done in Figure 77 and Figure 78) was not possible, because all the hydrochars produced to-date in the FHTC unit had nearly the same energy content – showing very little energy densification compared to the starting feedstock (see Figure 72A). Instead, we examined the sugar and organic acid profiles from the HTC aqueous product streams, and compared them to similar aqueous stream profiles obtained previously from experiments conducted in the stirred, 2-L Parr reactor.

Sugar profiles obtained from the Parr experiments when using Loblolly pine feedstock over a range of process temperatures are shown in Figure 79. In this figure, the profiles have been normalized to 100%. Clearly, these profiles change drastically as the HTC process temperature changes. At low temperatures, galactose-xylose-mannose and fructose-inositol-arabinose dominate. (These sugar groups probably contain mainly xylose and fructose, although the HPLC-RI method utilized for analysis cannot resolve the named compounds.) At moderate temperatures, these sugar groups decrease, while furfural and 5-HMF become more dominant. At the highest temperatures, the simple sugars are completely gone, while sugar alcohols (erythritol, arabitol, mannitol, glycerol) and levoglucosan become more prevalent.

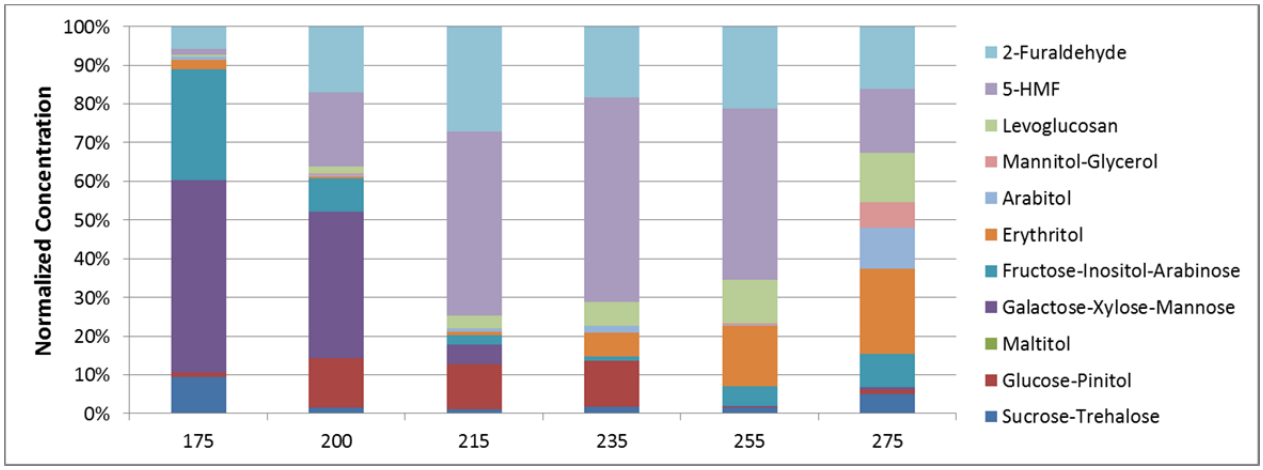

Figure 79. Sugar profiles from HTC treatment of Loblolly Pine at different temperatures in DRI's 2-L stirred Parr reactor. All experiments had 30-min. hold times.

The sugar profiles from GTI's FHTC experiments (Figure 74B) do not match closely any of the Parr reactor profiles shown in Figure 79. Thus, it is not possible to definitively state that the FHTC conditions (at a nominal reactor temperature of 260 °C) are of the same severity as the Parr conditions at a specific temperature. Nevertheless, some interesting insights can be obtained by further graphical analyses.

Figure 80 shows the same sugar profiles as in Figure 79, but now plotted as a function of severity factor in the 2-L Parr experiments. [Furfural was excluded from these normalized profiles to enable comparisons with the sugar profiles in the rinsate and filtrate samples from the GTI FHTC experiments. (Due to its high volatility, most furfural from the GTI experiments was collected in the condensate samples, not in the rinsate or filtrate samples.)] This figure illustrates that as the HTC reaction severity is increased from 3.5 to 5.5, increases are seen in the relative amounts of glucose-pinitol (red squares), 5-HMF (purple circles), and levoglucosan (green squares); while decreases are seen in the relative amounts of galactose-xylose-mannose (purple diamonds) and fructose-inositol-arabinose (blue circles). These same changes are seen in relative sugar concentrations when comparing the sugar profiles from the FHTC "fiber" and "paste" samples, suggesting that the reaction severity was slightly higher when the paste sample was produced.

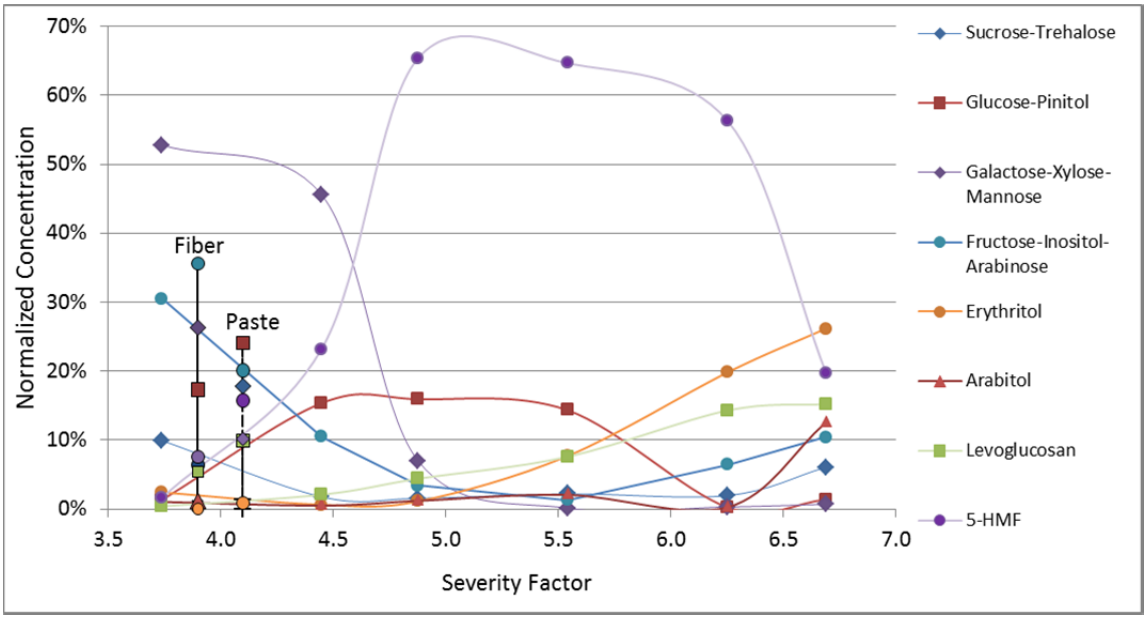

Figure 80. Effect of reaction severity upon sugar profiles from HTC treatment of Loblolly pine. Data points connected with trend lines are from DRI's 2-L Parr reactor with 30-min. hold times. Data points at a severity factor of 3.9 represent the average profile of rinsate and filtrate from GTI's "fiber" samples. Data points at a severity of 4.1 represent the average profile of rinsate and filtrate from GTI's "paste" samples.

The FHTC sugar profiles are included in Figure 80, positioned at severity factors of 3.9 and 4.1 for the fiber and paste samples, respectively. (These profiles are averages of the rinsate and filtrate samples shown in Figure 73) While far from conclusive, comparing these FHTC sugar profiles with DRI's 2-L Parr reactor-derived profiles suggests that the FHTC process severity was at a value of approximately 4.0, with slightly higher severity for the "paste" condition compared to the "fiber" condition. Applying this same approach to the sugar profiles from the FHTC products obtained in February of 2013 (see Figure 67) leads to the same conclusion that the severity factor of the FHTC process at this earlier time was also about 4.0.

As with the sugar data described above, we also evaluated the organic acids data with respect to severity factor. To do this, we first normalized the organic acid profiles determined from HTC experiments with Loblolly pine conducted in DRI's 2-L stirred Parr reactor over a range of temperatures. These normalized profiles, shown in Figure 81, were then expressed as a function of reaction severity in Figure 82.

In comparing Figure 80 and Figure 82, it is clear that the organic acid profiles are not as variable as the sugar profiles over this range of severity. Upon increasing the severity factor from 3.5 to 5.5, the main trends observed in Figure 82 are increases in acetic acid and lactic acid, but decreases in all other acids. (Note that only formic, acetic and lactic acids are shown on the left axis. All other acids are present in much smaller amounts, and are shown on the expanded right axis.)

The organic acid profiles determined for the FHTC fiber and paste samples are also shown in Figure 82. Their placement at severity factors of 3.9 and 4.1 matches the Parr reactor profiles reasonably well, especially for acetic acid and formic acid. This adds further strength to our belief that the severity factor for the FHTC reactor system was approximately 4, and that the "paste" condition was somewhat more severe than the "fiber" condition.

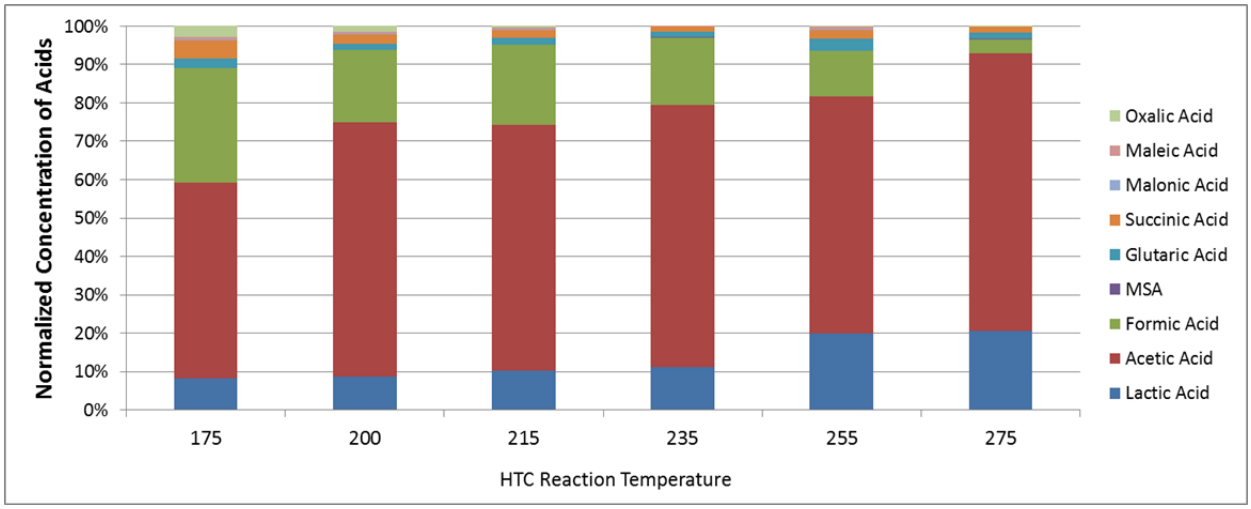

Figure 81. Organic acid profiles from HTC treatment of Loblolly Pine at different temperatures in the DRI 2-L stirred Parr reactor. All experiments had 30-min. hold times.

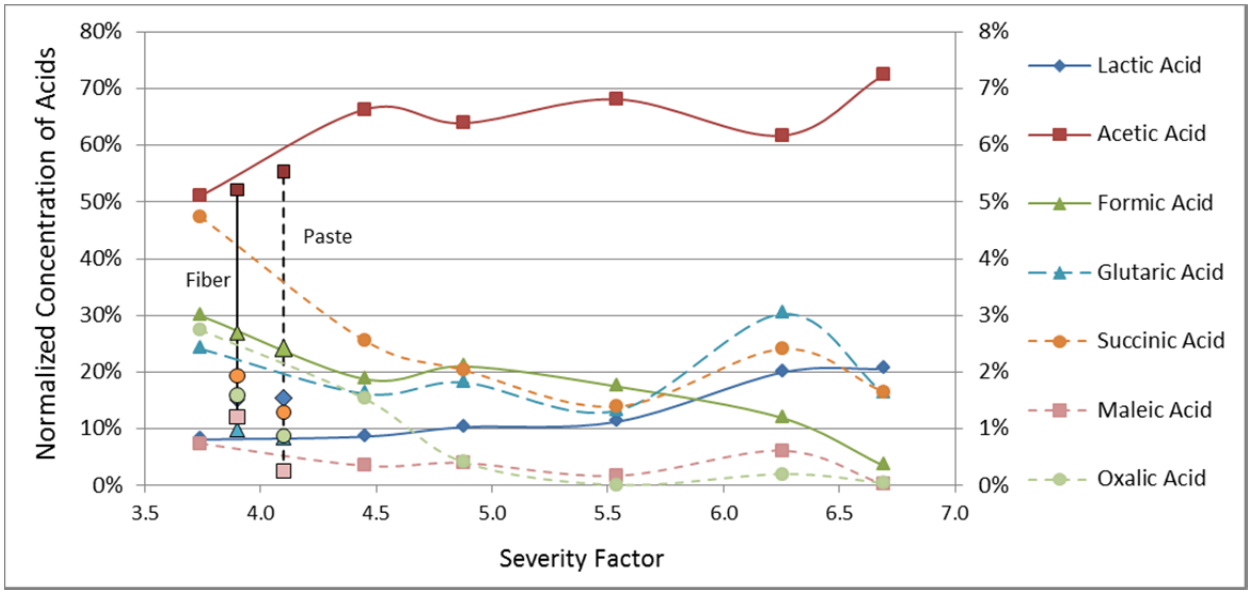

Figure 82. Effect of reaction severity upon organic acid profiles from HTC treatment of Loblolly pine. Data points connected with trend lines are from the DRI 2-L Parr reactor with 30-min. hold times. Solid lines (lactic, acetic, and formic acids) are on left axis; dashed lines are on right axis. Data points at a severity factor of 3.9 represent the average profile of rinsate and filtrate from GTI's "fiber" samples. Data points at a severity of 4.1 represent the average profile of rinsate and filtrate from GTI's "paste" samples.

FHTC Experiments in July, 2014: To conclude the experimental phase of this project, DRI visited the GTI laboratory in Birmingham, AL, and conducted sampling of gaseous, liquid, and solid product streams during operation of the FHTC PDU under several different conditions, all while using Loblolly pine as feedstock. Before this visit, a set of operating plans and procedures was developed to define how the sampling would be performed. These plans and procedures are included as Appendix I to this report.

Sampling at GTI's laboratory was conducted over a two day period. On the first day (July 15, 2014), relatively stable operating conditions were maintained over a one-hour long period, and

three sets of samples were collected under these steady operating conditions. On the second day of sampling (July 16, 2014), operating conditions were varied (primarily the water and biomass feed rates) to change the severity of the reaction. Two minute "snapshots" of each product stream were collected simultaneously, with the exception of the "cold" gas sample, which was collected on a 30-second delay compared to the rest of the samples.

The same basic sampling scheme shown in Figure 73 was used for these experiments, with the additional collection of gaseous products before the condenser (called hot gas) and after the condenser (called cold gas). The wet hydrochar product (called slurry) was collected from the TK-100 vessel in GTI's FHTC unit. Photos of the hot and cold gas sampling systems, and collected slurry samples, are shown in Figure 83.

The liquid condensate from these FHTC experiments was collected from the TK-107 vessel. In addition, a sample of mixed solids and liquids exiting Zone 4 of the FHTC reactor unit was collected. This Zone 4 material (previously called exhaust) was ejected from the FHTC unit at a location just upstream of the high pressure reactor zone. These 5 samples from each run (hot gas, cold gas, slurry, condensate, and Zone 4) were shipped back to DRI for further analysis.

On July 15, 2014, "standard operating conditions" for the FHTC unit included a Loblolly pine feed rate of 7.5 kg/hr (wet basis), a hot water injection rate of 8.5 kg/hr, and a reactor zone temperature of 290 °C. Two-minute samples of the slurry and "hot gases" were collected simultaneously, while 5-min. samples of condensate were collected. Two-minute "cold gas" samples were collected starting about one minute after conclusion of the "hot gas" samples. During the entire operating period, three sets of samples were collected in approximately 10-minute intervals. A single sample of the Zone 4 "exhaust" was taken from the homogenized material collected over the entire day's run. These samples and corresponding run conditions are identified in Table 21. To estimate the mass balance from the full day's run, all slurry, condensate, and Zone 4 products were weighed at the completion of the run.

On the second day of sampling (July 16), three distinct operating conditions were set by varying the feedstock and water input rates in an attempt to affect the severity of each run. Table 22 shows the different operating conditions for each run, and identifies the samples collected. To estimate a mass balance from each run, all five samples (hot gas, cold gas, slurry, condensate, and zone 4) were collected in simultaneous two minute increments, with a 30 second delay to collect the cold gas (this was done to clear head space of air in the sampling system). To estimate the mass balance for each condition, the loblolly feed rate, collected sample masses, and gas flow rates over each 2-minute period were used.

Sample Preparation: Samples collected from each of the experimental runs in Alabama were shipped back to DRI for processing and analysis. A flow chart of the sample processing is shown in Figure 84.

The product collected from Zone 4, which was (80-90%) water, was rinsed and filtered to remove the water into a separate liquid "filtrate." The solid cake remaining was dried and its energy content was measured. A similar filtering procedure was attempted on the wet slurry of hydrochar collected from each experimental run, although most samples had little or no free liquid that could be removed. Some preliminary analyses were performed on an aliquot of each slurry sample prior to washing and filtering, including moisture content, calorimetry, and pelletization characterization. Rinse water was added to the remaining slurry and mixed

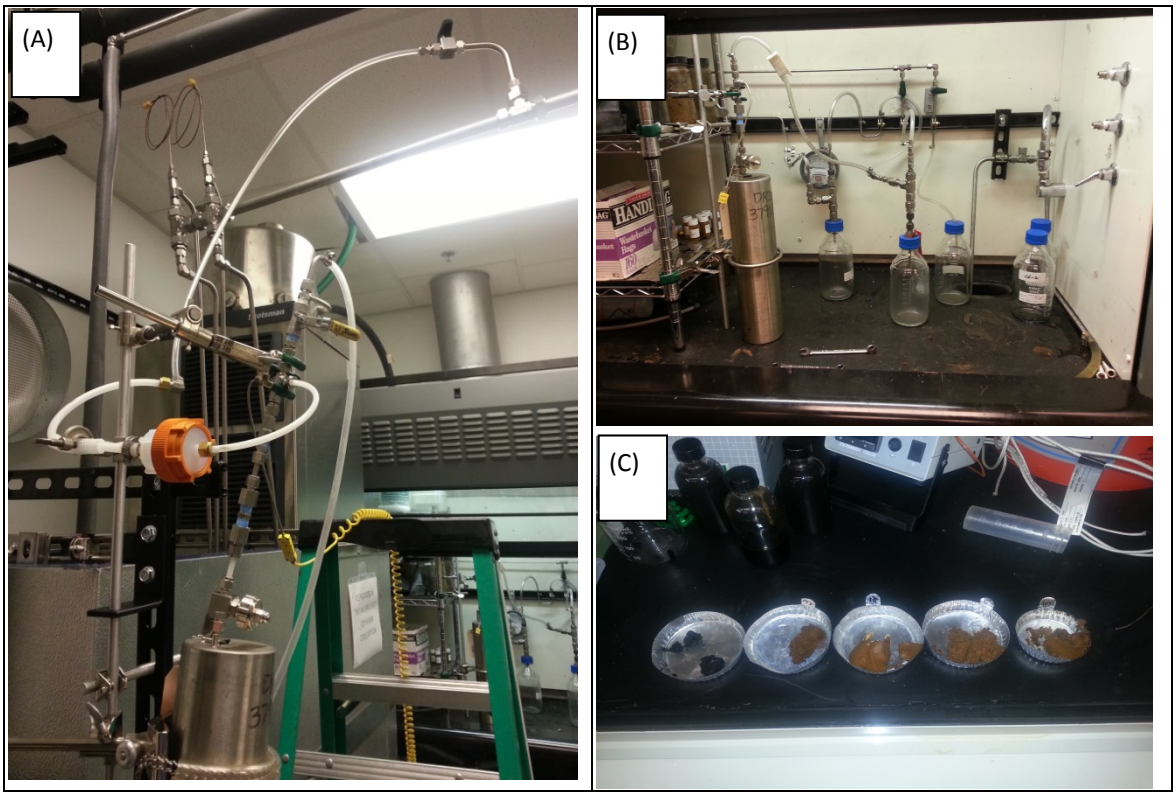

Figure 83. Sampling setup at GTI's FHTC Laboratory: (A) hot gas sampling; (B) cold gas sampling; (C) hydrochar slurry samples.

Table 22. Operating Conditions and Sample ID for July 2014 Runs of GTI's FHTC PDU

Experimental Parameters							Sample ID No.				
Exp. No.	Date	Temp., °C	Loblolly Feed rate, kg/hr	Water Rate, kg/hr	Time Stamp	Sample Duration (min.)*	Slurry	Hot Gas	Cold Gas	Condensed Liquid	Zone 4
1-3	7/15/2014	290	7.5	8.3	15:35:24	59.7	-	-	-	-	I001
1	7/15/2014	290	7.5	8.3	15:57:00	2.0	I001	I015	I004	I001	N/A
2	7/15/2014	290	7.5	8.3	16:10:00	2.0	I002	I003	I016	I002	
3	7/15/2014	290	7.5	8.3	16:20:00	2.0	I003	I013	I014	I003	
4	7/16/2014	290	7.5	8.3	12:43:00	2.0	I004	I010	I012	I004	I004
5	7/16/2014	290	9.4	9.0	13:17:00	2.0	I005	I009	I008	I005	I005
6	7/16/2014	290	6.5	6.5	13:45:00	2.0	I006	I011	I007	I006	I006

* 2-min. samples for slurry and gas samples; condensate was sampled 5-min. on July 15, and 2-min. on July 16.

thoroughly to wash it from the storage container into the vacuum filtration unit. The water/slurry mix was difficult to filter, and took several hours under vacuum to draw the free liquid from the solid. The remaining solid was subsequently air dried for additional analysis including moisture content, calorimetry, CHNSO, and pelletization characterization.

This series of rinsing the solid samples, generated a total of three liquid samples from each experimental run: (1) condensate, (2) filtrate from filtering and rinsing of the Zone 4 material, and (3) rinsate from rinsing and washing of the solid hydrochar slurry. Each of the aqueous samples was analyzed for NVR, TOC, sugars by HPLC-RI, and organic acids by IC. The

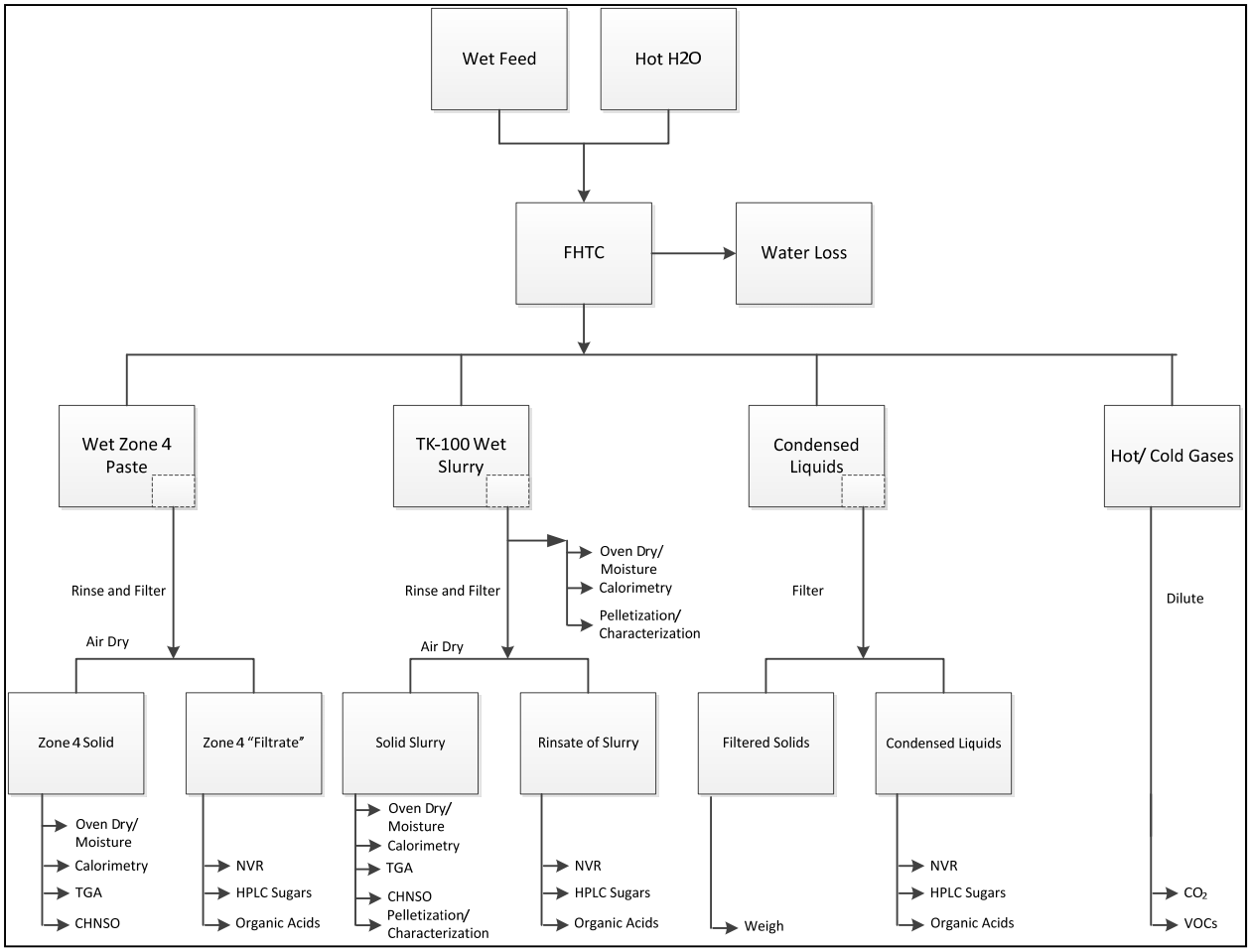

Figure 84. Schematic of collection, processing and analysis of samples collected from GTI's FHTC in July, 2014.

washed, solid slurries were also analyzed for CHNSO, proximate analysis by TGA, energy content by calorimetry, and pelletization behaviors.

Hot and cold gas samples were collected at GTI using evacuated 3-Liter canisters, which were subsequently shipped back to DRI for analysis. To improve storage stability of the gases prior to analysis, the canisters were pressurized with helium (after return to DRI) to a level just above atmospheric pressure. Each canister was then analyzed for CO_2 and CO using an SRI Model 8610C GC, equipped with a thermal conductivity detector (TCD). This analysis indicated that some of the canisters may have had leaks before or after sample collection, as they were dominated by peaks due to air (N_2 and O_2), with very little evidence of CO_2 being present. Even in cases where a CO_2 peak was clearly seen, the size of the peak was so small as to be near the instrumental detection limit. Consequently, this GC-TCD method was not able to reliably determine CO_2 levels in the gaseous samples. Due to the high expense of GC-MS analysis for VOCs, only four canisters were selected for this analysis: hot and cold gases from experiment numbers 3 and 5.

Characterization of FHTC Solid Products: A small aliquot of each slurry sample obtained from the TK-100 vessel was analyzed for moisture and energy content before rinsing with de-ionized water, as shown in the schematic of Figure 73. The remainder of each slurry sample (and

the Zone 4 samples) was washed with de-ionized water to obtain rinsate samples and washed slurry samples. The washed slurries were dried and analyzed by calorimetry, ultimate and proximate analysis.

Table 23 shows the solids content and energy content of these FHTC products. In contrast to the hydrochars produced previously in GTI's FHTC PDU, these solid products generated in July of 2014 indicated that substantial carbonization had occurred, as evidenced by a significant increase in energy content. Raw Loblolly pine was determined previously to have an energy content of 20.28 MJ/kg (see Table 9). All the slurry products analyzed here – whether water-washed or not – had significantly higher energy contents than the feedstock. The unwashed hydrochar samples had energy contents in the range of 23.8 – 25.0 MJ/kg, while the washed hydrochar samples were somewhat lower at 21.8 – 23.3 MJ/kg. In every case, the washed hydrochar had slightly lower energy content than the unwashed hydrochar, indicating that the water-soluble materials that were removed by washing had higher energy content than the remaining char. [Note: this is opposite of what was found in February of 2013, with HTC processing under less severe conditions, where the water-soluble materials removed by washing had lower energy content than the remaining char.]

Table 23. Solids and Energy Contents of Products from GTI's FHTC PDU in July, 2014

Solid Sample	Date	Experiment No.	Solids Content (%)	Energy Content, MJ/kg	
				Unwashed	Washed
Slurry (Hydrochar)	7/15/14	1	47.2%	24.87	23.32
		2	45.8%	24.23	22.18
		3	46.5%	24.41	22.67
	7/16/14	4	38.0%	25.02	22.06
		5	43.3%	24.12	21.99
		6	43.1%	23.80	21.75
Zone 4 (Exhaust)	7/15/14	1-3	16.8%	-	-
	7/16/14	4	13.2%	-	-
		5	7.0%	-	18.91
		6	17.5%	-	-

On average, the six unwashed slurry samples produced in July of 2014 had 20.4% higher energy content than the loblolly feedstock; the six washed samples had 10.1% higher energy contents. These energy densification results are in contrast to those obtained from hydrochar produced in GTI's FHTC PDU in February of 2013, which showed almost no increase in energy content compared to the loblolly feedstock (see Figure 72). The increased energy content measured in these recent experiments is comparable to that observed in earlier experiments with a 2-L Parr pressure vessel (with 30-min. hold time) at process temperatures of about 230-240 °C (see Figure 77).

Another way to compare HTC experiments in GTI's FHTC PDU with previous experiments conducted at DRI is on the basis of process severity. As described above (Section 3.3.3), calculation of a severity factor is a way to express HTC process conditions as a function of both reaction temperature and time. For the FHTC reactor, reaction time was estimated to be 30 seconds under normal operating conditions of 7.5 kg/hr feed rate and 8.5 kg/hr water injection rate. (Slightly different reaction times were calculated when other FHTC operating conditions

were used.) Using this time, along with the reactor temperature of approximately 290°C, gives calculated severity factors of approximately 5.2 – 5.4.

Measured hydrochar energy content values are plotted against severity factor in Figure 85. The data from the FHTC PDU are seen to fit well with the rest of the data obtained from DRI's HTC experiments conducted in three different reactors: 2-L Parr reactor, 2-chamber reactor, and PDU. *These data suggest that calculated severity factor may be a useful predictor of hydrochar energy content, regardless of the reactor vessel used.*

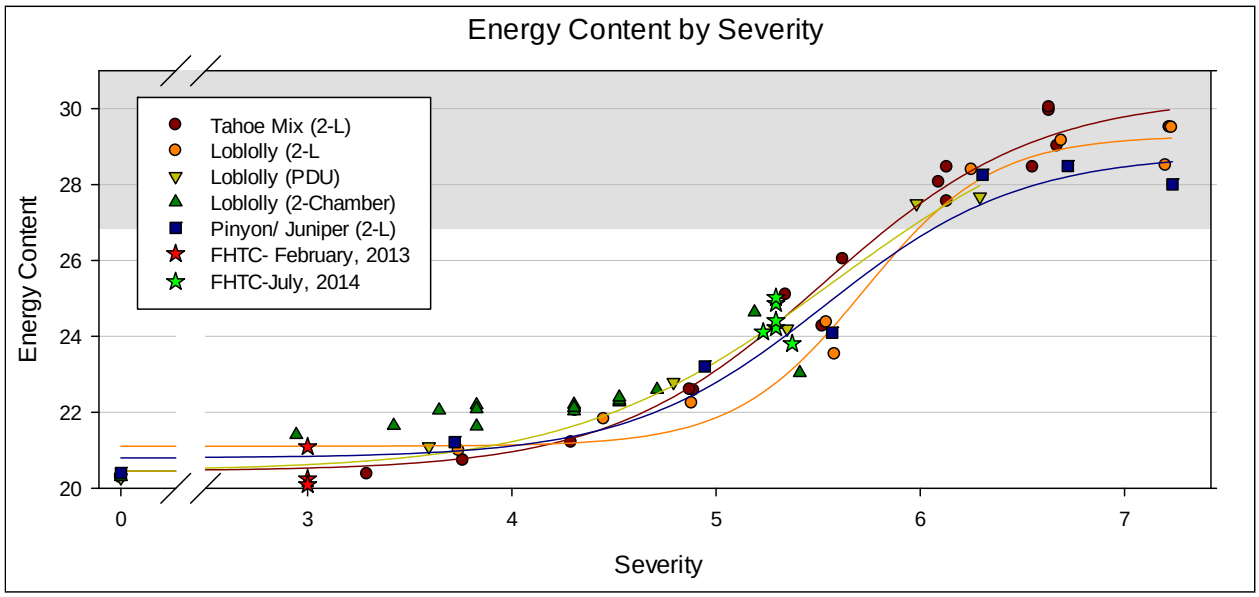

Figure 85. Relationship between severity factor and hydrochar energy content (MJ/kg).

Proximate and ultimate analyses of the solid products from the six FHTC experiments conducted in July, 2014 are provided in Table 24 and Table 25, respectively. These analyses were performed on the washed slurry samples only (not the unwashed slurries), in addition to the solids recovered from Zone 4. The proximate analysis results show virtually no difference between the Zone 4 solids and raw loblolly pine feedstock, indicating that very little carbonization had occurred. However, the six hydrochar slurry samples all showed significant increases in fixed carbon and decreases in volatiles, indicating that carbonization had occurred. In addition, it appears that about one-half of the ash in the starting feedstock was removed in the washed hydrochar samples, while little ash was removed from the Zone 4 solids – although these results are quite variable. Comparing these proximate analyses with those obtained from hydrochar slurries produced in February of 2013 (see Table 21) show that a higher degree of carbonization occurred with these more recent FHTC experiments.

The ultimate analysis results also indicate that considerably greater carbonization occurred during the July 2014 FHTC experiments compared to the February 2013 experiments (compare Table 25 with Table 21). This is further illustrated in the Van Krevelen diagram of Figure 86. The atomic O/C ratios of the July 2014 samples are clustered near a value of 0.48, whereas the February 2013 samples are clustered near 0.57 (all from washed slurries). The calculated severity factors for the 2-L Parr reactor experiments are indicated on this Van Krevelen diagram. Based upon these values, and the relative placement of the data points from the July 2014 samples, we estimate that the severity of these recent FHTC PDU experiments was between 5.0 and 5.5.

Table 24. Proximate Analysis of Solid Products Produced by GTI's FHTC PDU in July, 2014

Sample Type	Expt. No.	% Moisture Content	% Volatiles (db)	% Fixed Carbon (db)	% Ash
Loblolly Feedstock	-	5.63	90.07	9.35	0.59
Washed slurry (Hydrochar)	1	2.98	79.16	20.47	0.38
	2	3.03	78.02	21.62	0.37
	3	2.68	80.01	19.73	0.26
	4	2.73	77.59	21.99	0.23
	5	2.84	81.43	18.29	0.28
	6	3.03	77.73	22.07	0.20
Zone 4 (Exhaust)	1-3	5.51	93.40	5.96	0.64
	4	5.68	89.77	9.69	0.54
	5	5.17	91.75	7.95	0.30
	6	5.04	91.19	8.70	0.11

Table 25. Ultimate Analysis of Solid Products Produced by GTI's FHTC PDU in July, 2014

Sample Type	Expt. No.	% C	% H	% N	% O	Sum	Atomic O/C
Loblolly Feedstock	-	49.33	5.79	0.03	44.92	100.07	0.68
Washed slurry (Hydrochar)	1	56.91	5.80	0.30	36.79	99.80	0.48
	2	56.19	5.70	0.29	35.83	98.00	0.48
	3	55.84	5.80	0.32	36.18	98.13	0.49
	4	55.57	5.81	0.31	35.33	97.02	0.48
	5	55.08	5.83	0.22	36.57	97.70	0.50
	6	56.59	5.80	0.28	35.72	98.39	0.47
Zone 4 (Exhaust)	1-3	50.76	5.96	0.31	40.22	97.26	0.59
	4	50.66	5.98	0.31	40.69	97.64	0.60
	5	51.26	6.00	0.36	39.74	97.37	0.58
	6	50.18	6.00	0.31	41.68	98.19	0.62

Further support for this is provided in Figure 87, in which the relationship between O/C ratios and severity factor for Loblolly-derived hydrochar is shown.

Samples of the hydrochar slurry (both washed and unwashed) were also examined with respect to their pelletization behavior. The same pelletization procedures as described earlier were utilized with these materials. Due to limited amounts of some materials, only one or two pellets of each type were prepared. As before, the pellets were characterized with respect to their weight, length, density, and durability – both before and after immersion in water for 60 minutes. Numeric results from all these measurements are provided in Table 26.

Overall, these pellets were very stable, exhibiting virtually no swelling upon water immersion, and having high tumbler durability values. This is similar to what was observed with pellets made from previous runs of the FHTC PDU in 2013 (see Figure 69 and Figure 70). However, closer examination reveals some differences in these recent pellets as compared to previous ones. For example, the physical appearance of the recent pellets is slightly different in having a somewhat darker color, which is consistent with the higher process severity of the FHTC PDU.

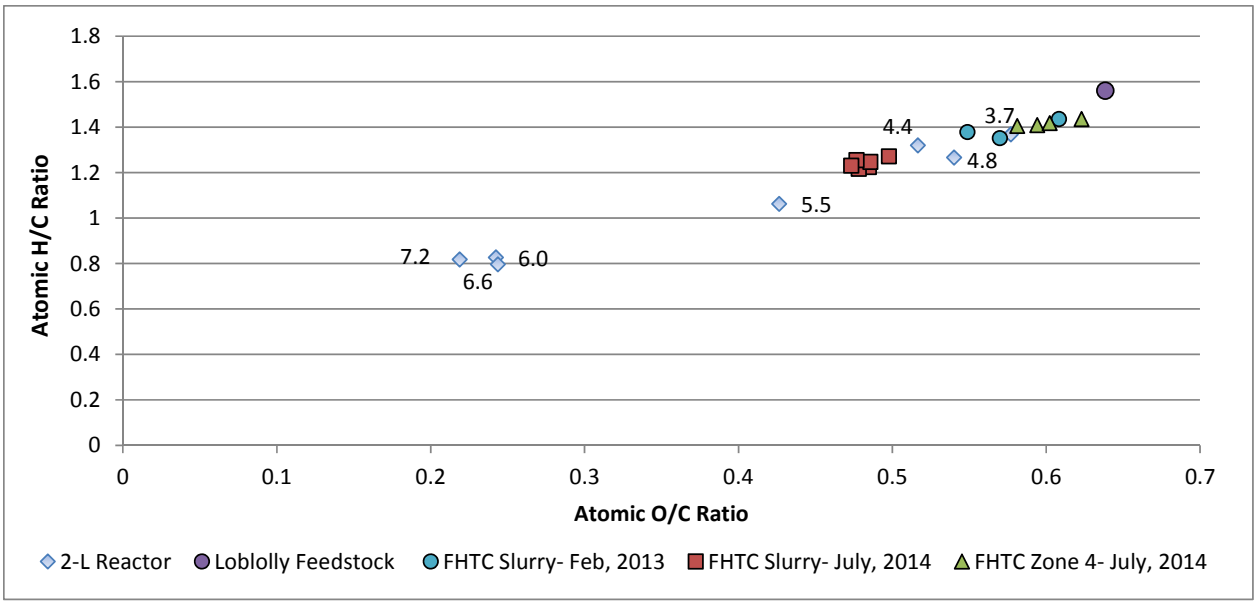

Figure 86. Van Krevelen diagram of hydrochar products from different reactors/conditions. Severity factors noted are for 2-L Parr reactor experiments.

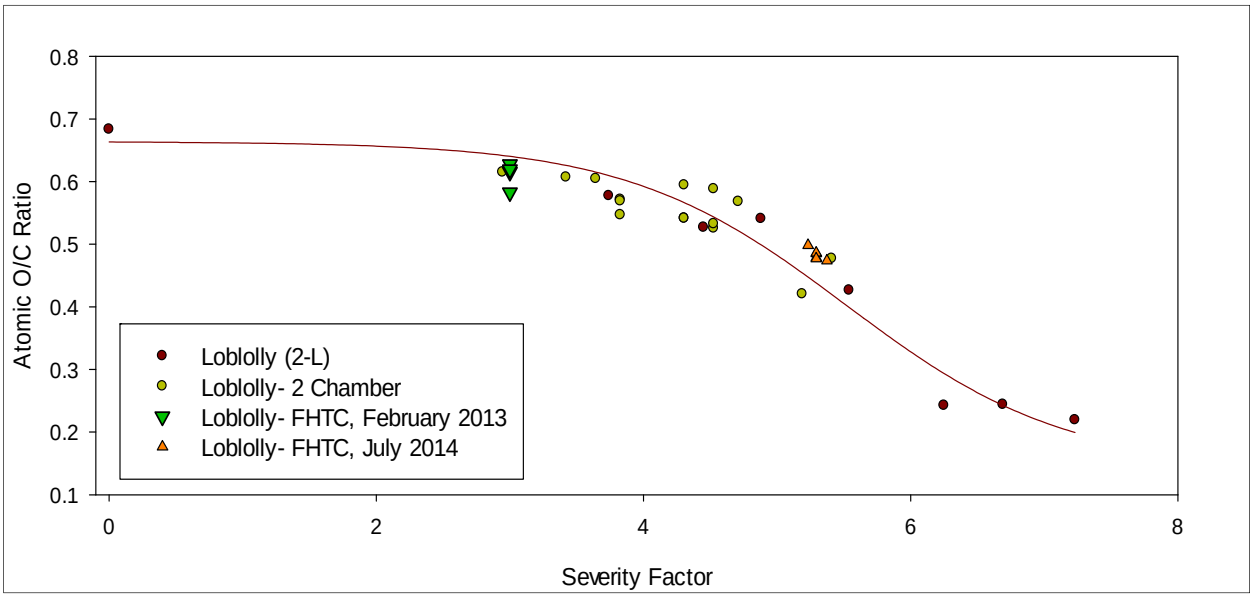

Figure 87. Relationship between O/C ratios and severity factor for hydrochar produced from Loblolly pine. Curve shown is fitted to the 2-L Parr reactor data.

Also, the recent pellets have somewhat uneven flat surfaces (top and bottom of pellets), whereas previous pellets had smooth surfaces. This uneven surface can be seen in the photos of Figure 88. The reasons for these rough surfaces are not known, but could be related to evolution of gases during the pelletization process.

Water immersion also gave somewhat different results with these recent pellets as compared to pellets produced in 2013. Upon immersion, slight flaking and separation of the pellets was observed, although this did not result in significant pellet swelling. Some of this flaky material

Table 26. Water Immersion Tests of Pellets from Hydrochar Produced in the GTI FHTC PDU (July, 2014)

Immersion Time (min)	Expt. No.	Pellet Weight (g)			Pellet Length (mm)			Pellet Density (kg/m^3)			Pellet Durability	
		Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion	Post Tumble	Initial	Post Immersion
0	1	1.0664	-	1.0627	6.15	-	6.11	1306.4	-	1310.4	99.65%	
	2	1.0027	-	0.9935	6.07	-	6.06	1244.5	-	1235.1	99.08%	
	3	1.2522	-	1.2474	7.03	-	7.01	1342.0	-	1340.6	99.62%	
	4	0.9370	-	0.9344	5.28	-	5.21	1337.0	-	1351.2	99.72%	
	5	1.1092	-	1.1088	6.16	-	6.08	1356.6	-	1374.0	99.96%	
	6	1.5606	-	1.5178	8.74	-	8.74	1345.3	-	1308.4	97.26%	
60	1	1.1426	1.1226	1.0205	6.52	6.53	6.51	1320.3	1295.2	1181.0		90.91%
	2	1.0977	1.0889	0.9833	6.30	6.30	6.21	1312.7	1302.2	1192.9		90.30%
	3	1.0318	1.0251	0.9663	5.82	5.83	5.72	1335.7	1324.7	1272.7		94.26%
	4	1.2713	1.2673	1.2341	7.10	7.10	7.00	1349.0	1344.8	1328.2		97.38%
	5	1.1677	1.1389	1.1062	6.45	6.47	6.45	1363.9	1326.2	1292.1		97.13%
	6	1.1488	1.1327	1.1009	6.36	6.37	6.35	1360.9	1339.7	1306.2		97.19%
0	1 wash	1.0705	-	1.0521	5.90	-	5.89	1367.0	-	1345.8	98.28%	
	2 wash	1.0938	-	1.0738	6.06	-	6.05	1359.8	-	1337.2	98.17%	
	3 wash	1.1590	-	1.1271	6.47	-	6.45	1349.6	-	1316.5	97.25%	
	4 wash	1.0876	-	1.0518	6.07	-	6.07	1349.9	-	1305.5	96.71%	
	5 wash	1.0227	-	0.9985	5.48	-	5.48	1406.0	-	1372.7	97.63%	
	6 wash	1.0687	-	1.0308	5.91	-	5.90	1362.4	-	1316.3	96.45%	
60	1 wash	1.2077	1.1000	1.0705	6.60	6.65	6.59	1378.6	1246.2	1223.8		97.32%
	2 wash	1.1184	1.1119	1.0755	6.14	6.21	6.13	1372.3	1349.0	1321.8		96.73%
	3 wash	1.1937	1.1390	1.0842	6.60	6.74	6.40	1362.6	1273.2	1276.3		95.19%
	4 wash	1.1541	1.1432	1.0301	6.38	6.40	6.12	1362.8	1345.8	1268.1		90.11%
	5 wash	1.1153	1.1164	1.0132	6.02	6.05	6.01	1395.8	1390.2	1270.1		90.76%
	6 wash	1.0538	0.9828	0.8827	5.81	5.97	6.64	1366.5	1240.3	1115.8		89.81%

Figure 88. Pellets from hydrochar produced in GTI's FHTC PDU in July, 2014.

was lost during tumbling tests, resulting in about 5-10% reduction in durability values. Slightly smaller durability losses occurred with pellets produced from washed hydrochar as compared to the unwashed hydrochar for experiments 1-3, while the opposite was observed for experiments

4-6 (see Figure 89). Reasons for these differences are not known, but it should be emphasized that all results were derived from testing of single pellets, so the uncertainty may be rather high. Overall, these results suggest that washing of the hydrochar slurry removes some materials that act as effective binders. Nevertheless, both the washed and unwashed pellets are very robust in comparison to raw wood pellets or torrefied pellets.

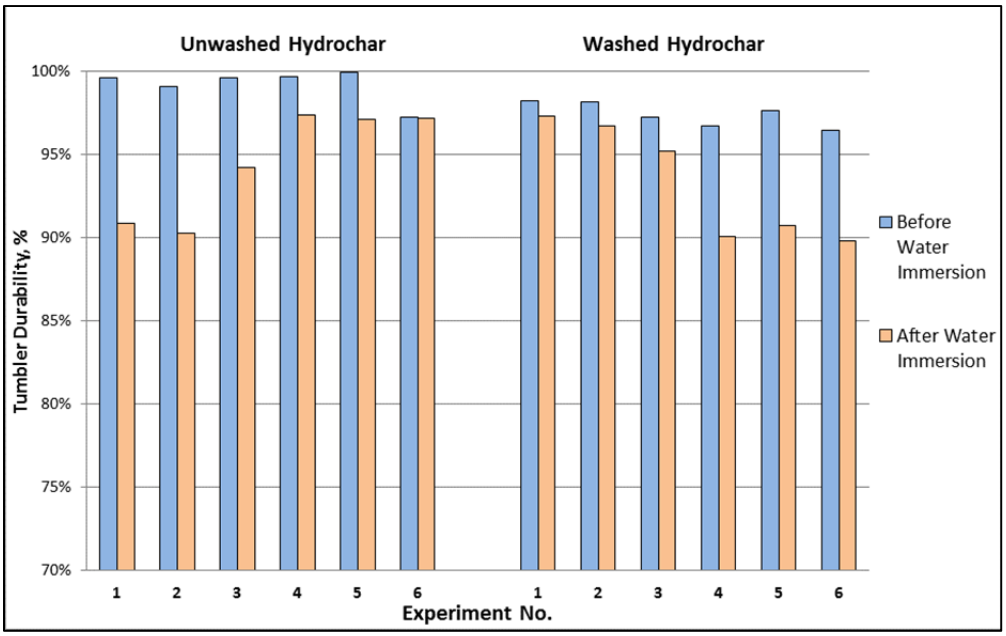

Figure 89. Durability of pellets from hydrochar slurries produced by the GTI FHTC PDU (July, 2014).

Characterization of FHTC Aqueous Products: Three aqueous samples were characterized from each experimental run of the FHTC PDU during July, 2014: (1) condensate, (2) filtrate/rinsate from the hydrochar slurries, and (3) filtrate from Zone 4. Non-volatile residue (NVR) and total organic carbon (TOC) results from each sample are presented in Table 27, where they are expressed on the basis of mass percent of starting dry feedstock. The NVR results show very little mass recovery in either the condensate or Zone 4 filtrate, but significant amounts in the slurry rinsate. However, it should be pointed out that the NVR test is quite aggressive in removing not only highly volatile material, but also semi-volatiles. As discussed below, the condensate sample contained significant concentrations of semi-volatile materials, which were lost during the NVR test procedure.

The NVR material in the slurry rinsate was somewhat higher on the 2nd day of FHTC runs (experiments 4-6) than the 1st day (experiments 1-3), while the TOC results were more similar between the two days. The NVR and TOC results from experiments 1-6 shown in Table 27 were calculated based upon the mass of each slurry sample that was collected during the 2-min. sampling period, the amount of feedstock processed through the FHTC reactor during this time, and the moisture contents of the slurries. The composite results were calculated by a different method. In this case, the total mass of accumulated condensate, slurry, and Zone 4 material collected over the entire 60-min. run were used, along with the total mass of loblolly feedstock processed over this 60-min. period.

Table 27. NVR and TOC of Aqueous Products from GTI's FHTC PDU (July, 2014). Results expressed as percentage of starting dry feedstock

	Expt. No.	Condensate	Slurry Rinsate	Zone 4 Filtrate
NVR, %	Composite Run 1-3*	0.12	11.67	0.16
	1	0.10	10.50	N/A
	2	0.14	7.29	
	3	0.12	10.92	
	4	0.14	15.65	0.23
	5	0.15	16.94	0.31
	6	0.15	16.43	0.18
TOC, %	Composite Run 1-3*	0.30	3.43	0.07
	1	0.33	2.59	N/A
	2	0.29	2.75	
	3	0.26	3.08	
	4	0.32	2.37	0.10
	5	0.35	1.83	0.10
	6	0.32	3.16	0.04

* Results for the composite samples were calculated from the average concentrations measured in individual samples 1-3, which were then applied to the entire mass of liquid and slurry collected throughout the duration of the day's run. The moisture content of the composite slurry sample was taken as 62.3%, as measured by GTI.

Sugars were quantified in the three aqueous products using the same HPLC-RI method used previously. The results given in Figure 90A are presented as mass percent of starting dry loblolly feedstock. To permit comparison with previous FHTC experiments, these results are also expressed in concentration units (µg/mL) and as normalized concentration in Figure 90B and Figure 90C, respectively.

Sugar yields were highest in the slurry rinsate and lowest in the Zone 4 filtrate. As was seen with the NVR results, average sugar yields in the slurry samples were somewhat higher on the 2nd day of runs (experiments 4-6) than on the 1st day (experiments 1-3). A wide variety of sugars was seen in these slurry samples, with the sugar profiles being nearly the same in all six samples. These profiles are similar, but not identical to what was observed from the FHTC experiments in May of 2013 (compare Figure 74 with Figure 90). In particular, samples from the recent experiments – conducted under higher severity – contained somewhat higher fractions of erythritol and mannitol-glycerol, and lower fractions of fructose-arabinose and sucrose-trehalose.

The six condensate samples also had very consistent sugar profiles, although these profiles were much simpler – consisting mostly of furfural, with lesser amounts of levoglucosan, mannitol-glycerol, and arabitol. Of these materials, furfural is the most volatile, which accounts for its near complete absence in the slurry samples. Apparently, "flashing" of the hot product stream from the FHTC reactor transfers nearly all the furfural into the vapor stream that is subsequently collected as condensate.

The sugar results from the FHTC experiments in July of 2014 were compared with sugar results obtained earlier from 2-L Parr reactor experiments under a range of process temperatures. These comparisons are shown in Figure 91, where they are expressed as both percentage of dry

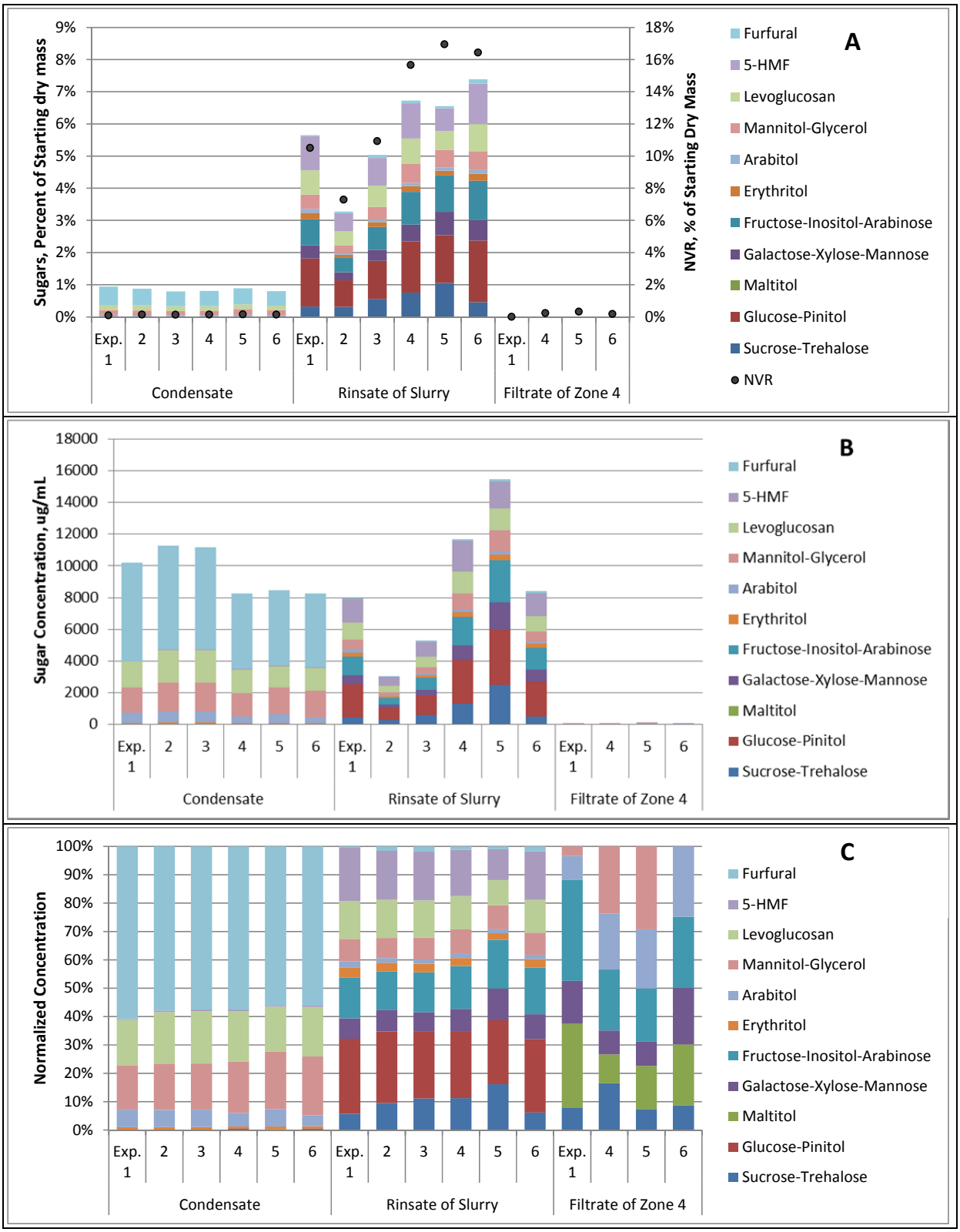

Figure 90: Analysis of sugars in aqueous products from July 2014 HTC treatment of Loblolly Pine in the GTI FHTC. Shown as (A) percentage of starting dry mass, (B) measured concentration (µg/mL), and (C), concentration normalized to 100%.

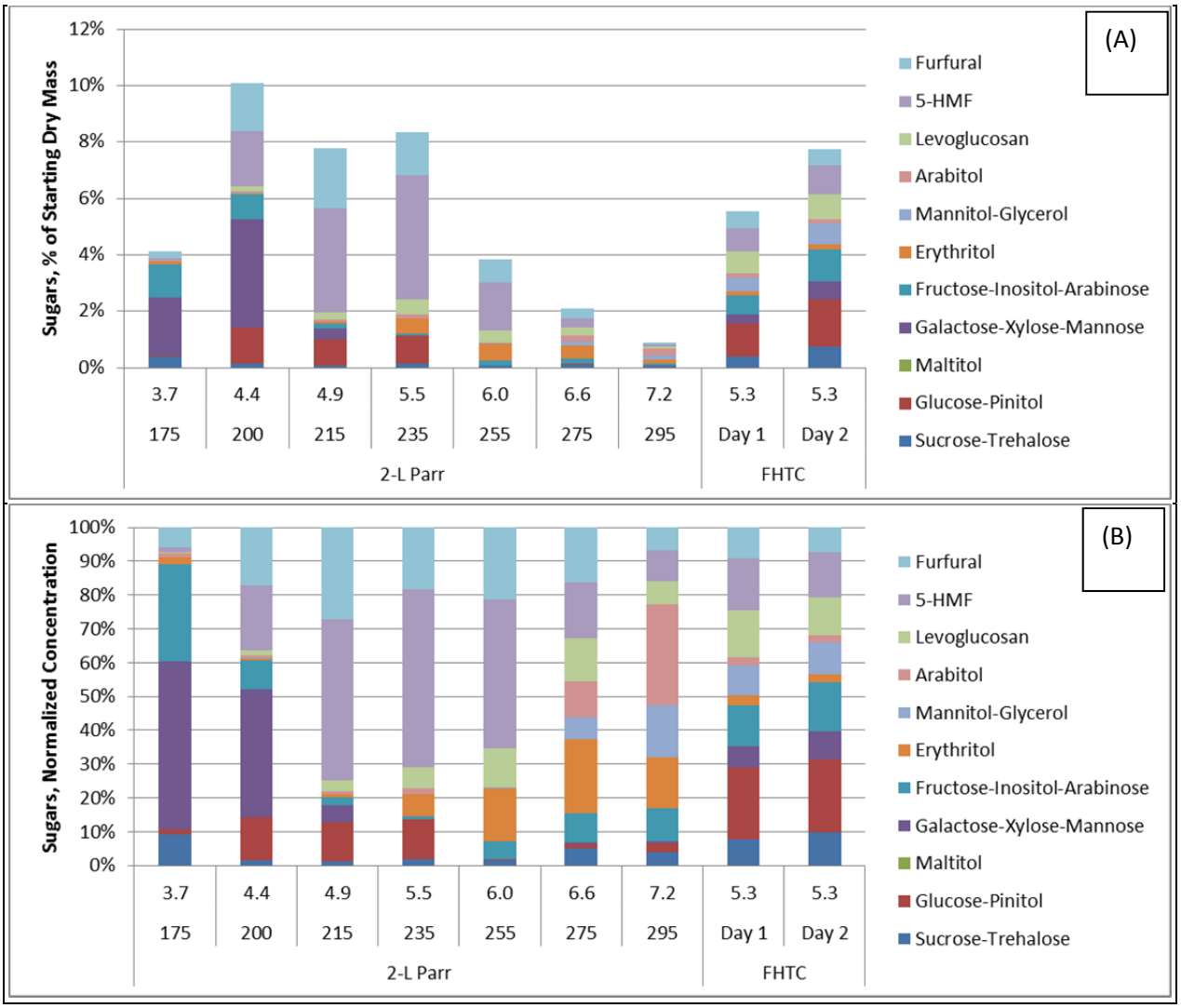

Figure 91. Comparison of sugar results between the GTI FHTC and DRI 2-L Parr treatment of loblolly pine. The numbers directly beneath each bar are calculated reaction severity factors. FHTC results are the sum of sugars from slurry and condensate.

feedstock (Loblolly pine in all cases) and as normalized concentrations. Two profiles are shown for the FHTC samples – one being the average from the first day of experiments (July 15), the other being the average from the second day (July 16). These profiles include the sugars measured in both the slurry rinsate and the condensate samples.

Another comparison of sugar profiles is shown in Figure 92. In this figure, furfural has been eliminated and the remaining sugars were re-normalized to 100%. (Figure 92 is identical to Figure 80, with addition of the average sugar profiles of the recent FHTC experiments now being shown at a severity factor of 5.3.) This portrayal further highlights the difference between the Parr reactor and the FHTC reactor sugar profiles. The difference in 5-HMF is particularly large, with considerably smaller amounts of this compound being measured in the FHTC-derived samples. *We speculate that this may be due to the extremely short residence time in the FHTC reactor.* As 5-HMF is a secondary product of cellulose degradation, its formation may be kinetically limited in the FHTC reactor, while it has adequate time to form in the Parr reactor.

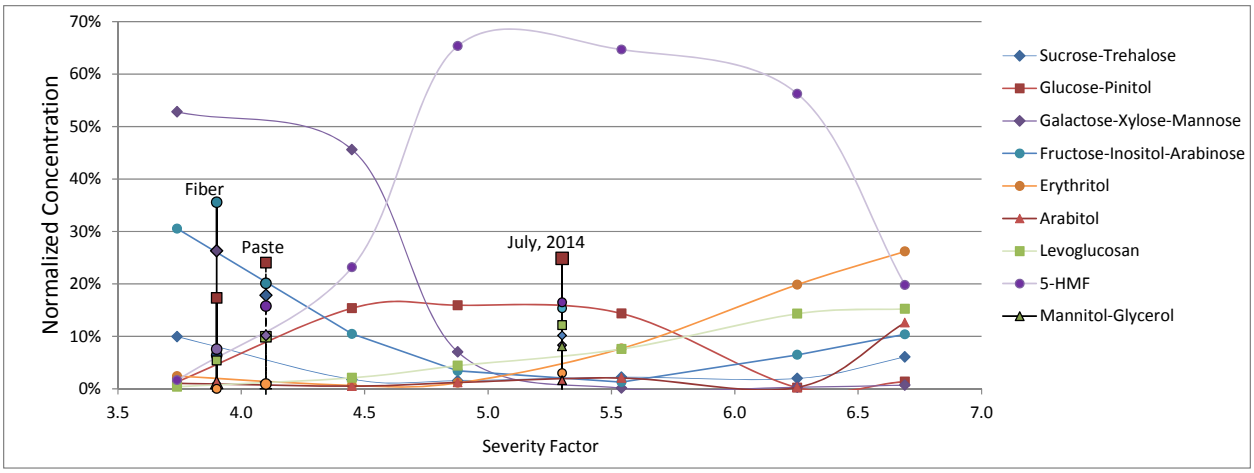

Figure 92. Effect of reaction severity upon sugar profiles from HTC treatment of Loblolly Pine. Data points connected with trendlines are from the DRI 2-L Parr reactor with 30-minute hold times. Data points at severity factors of 3.9 and 4.1 represent the average profiles of rinsate/filtrate from GTI's "fiber" and "paste" samples, respectively from May, 2013. The average profile of the FHTC slurry rinsate from the July, 2014 sampling campaign is shown at a severity of 5.3.

Kinetic limitations may also explain other differences between HTC experiments conducted in the FHTC reactor and the Parr reactor.

Organic acids were measured in the aqueous products from the FHTC using an ion chromatography (IC) method. Results are presented in Figure 93, where they are portrayed on three bases: (A) percentage of starting dry feedstock, (B) concentration in water, and (C) normalized concentrations. Similar to the sugar results described above, the organic acid yields shown in Figure 93(A) were highest in the slurry rinsate and lowest in Zone 4, with intermediate yields seen in the condensate. As expected, only relatively volatile acids were seen in the condensate – primarily acetic acid and formic acid. The slurry rinsate samples also had large amounts of acetic and formic acids, but contained less volatile acids as well – such as lactic acid, methane sulfonic acid (MSA), succinic acid, glutaric acid, and others.

These organic acid results from the FHTC experiments in July of 2014 were compared with organic acid results obtained earlier from Parr reactor experiments conducted over a range of process temperatures. These comparisons are shown in Figure 94, where they are expressed as percentage of dry feedstock (Figure 94A) and as normalized concentrations (Figure 94B). As with the sugar profiles described above, two organic acid profiles were used to represent the FHTC experiments: one being the average of runs on the first day (July 15), the other being the average of runs on the second day (July 16). These profiles include the sum of organic acids measured in the slurry rinsate and the condensate.

Figure 94shows similar, but not identical profiles between the FHTC and the Parr reactor experiments. As with the sugars, the FHTC organic acid profiles most closely match the Parr reactor profiles at severity factors between 4.9 and 5.5 (temperatures between 215 and 255 °C). The total yields of organic acids in this range of operating conditions were 3-5% for both the FHTC and the Parr experiments, expressed as percentage of starting feedstock.

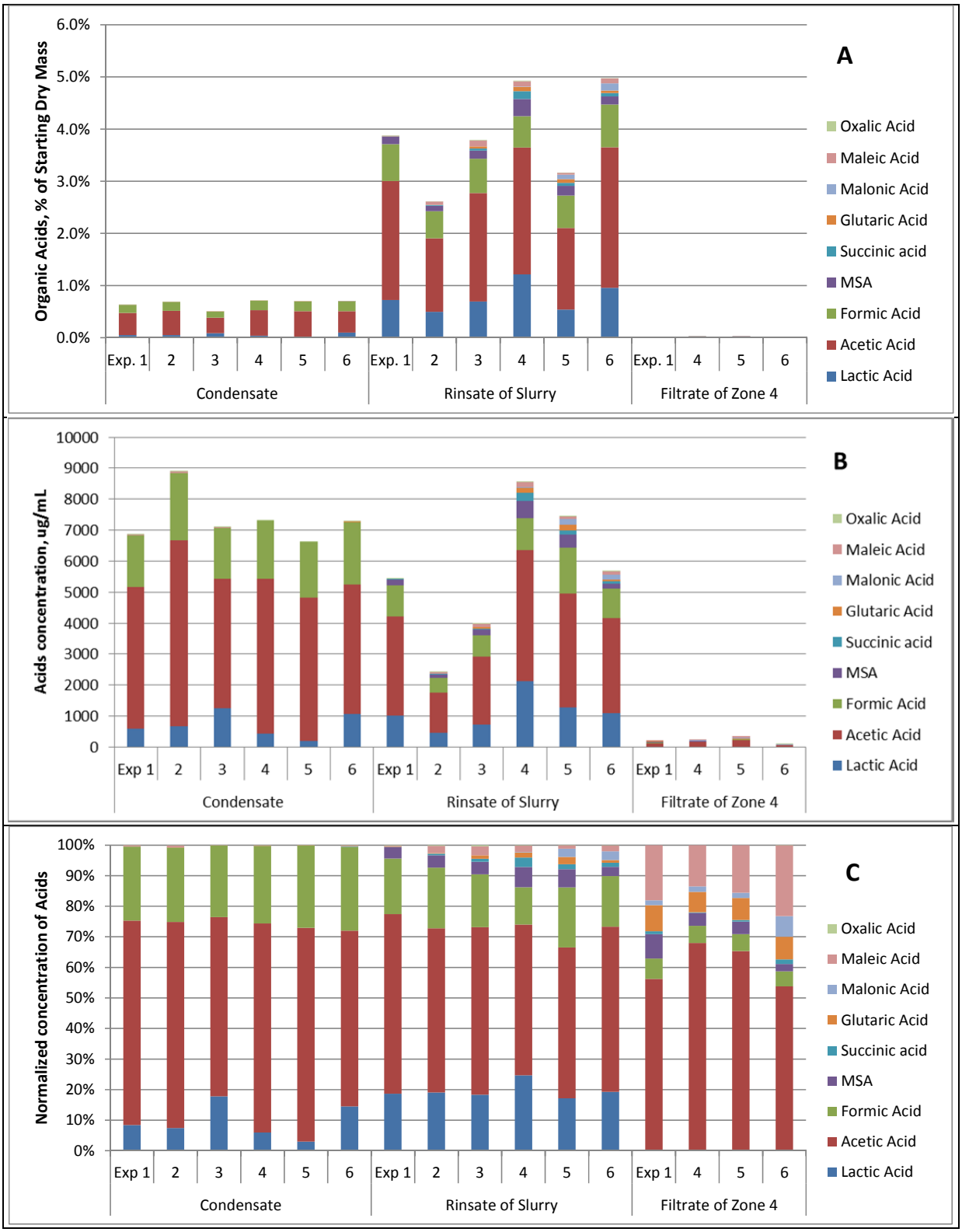

Figure 93. Organic acids measured in aqueous products from operation of GTI's FHTC PDU with Loblolly pine in July, 2014.

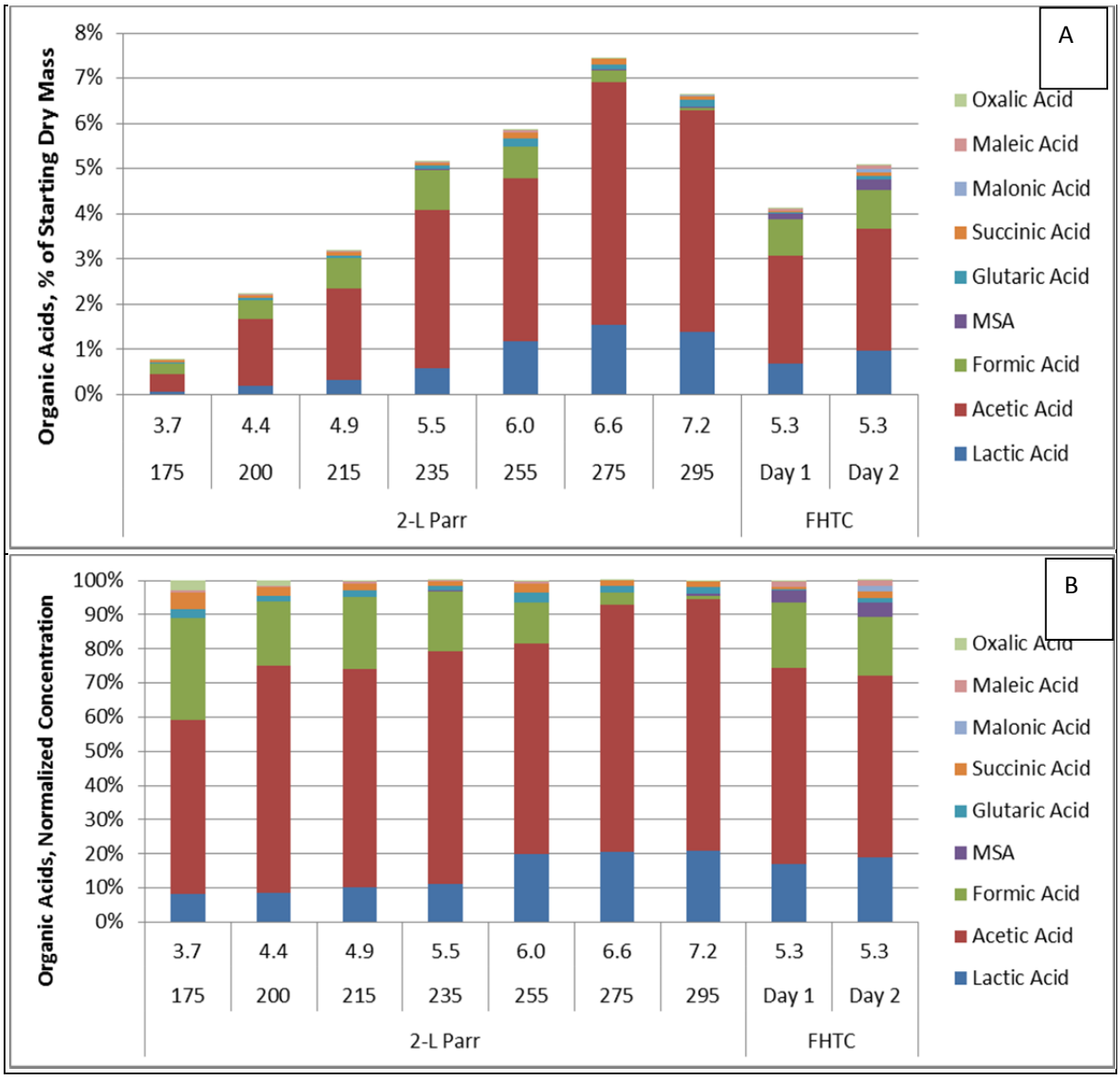

Figure 94. Comparison of organic acid results between GTI's FHTC and DRI's 2-L Parr treatment of Loblolly pine. (A) Percentage of starting dry mass; (B) concentrations normalized to 100%.

All the organic acid profiles are dominated by acetic acid, although the FHTC samples appear to have slightly lesser amounts of acetic acid and slightly greater amounts of lactic acid. These differences are illustrated more clearly in Figure 95, in which the organic acid profiles are displayed as a function of severity factor. (Figure 95 is identical to Figure 82 with addition of the average organic acid profile of the recent FHTC experiments now being shown at a severity factor of 5.3.) *Again, we speculate that the differences in profiles between the two reactor systems may be due (in part) to kinetic limitations.*

Characterization of FHTC Gaseous Products: As described above, both hot gas and cold gas samples were collected from each of the six experimental runs of the FHTC reactor (see Table 22 for sample ID). Based upon operational parameters, and the relative stability of the runs, it was decided to analyze only the gas samples from Experiment No. 3 (July 15) and Experiment No. 5(July 16). It was subsequently learned that the hot gas sample from Experiment No. 3 was

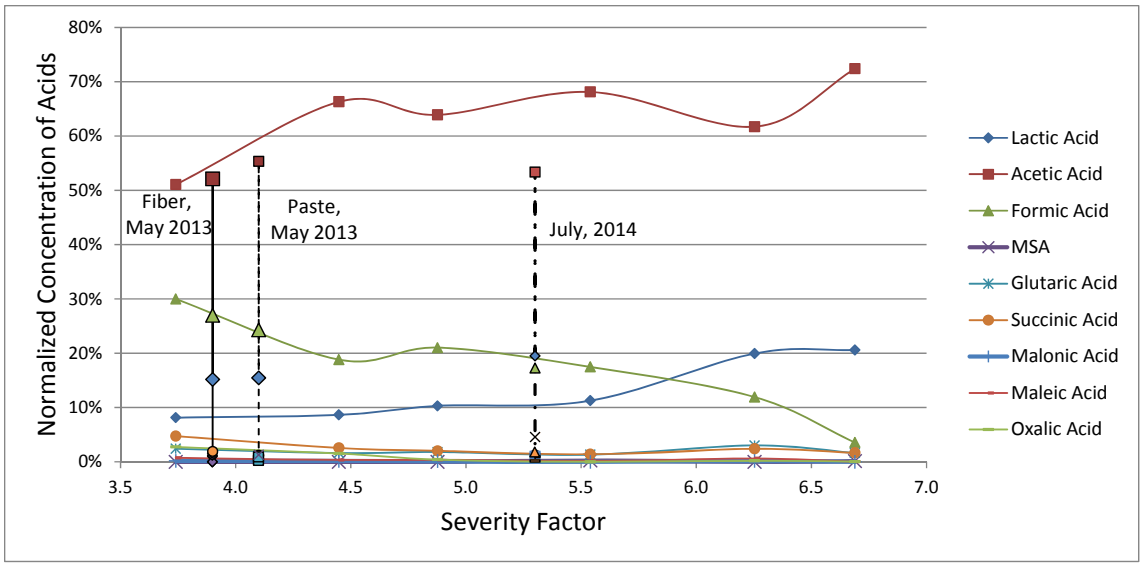

Figure 95. Effect of reaction severity upon organic acid profiles from HTC treatment of Loblolly Pine. Data points connected with trendlines are from DRI's 2-L Parr reactor with 30-minute hold times. Data points at severity factors of 3.9 and 4.1 represent the average profiles of rinsate/filtrate from GTI's "fiber" and "paste" samples, respectively from May, 2013. The average profile of the FHTC slurry rinsate from the July, 2014 sampling campaign is shown at a severity of 5.3.

compromised by leaking air into the evacuated sampling canister. Consequently, only three samples were thoroughly analyzed by GC-MS.

The same GC-MS methodology was used for these analyses as was used earlier to characterize gaseous products collected from operation of DRI's PDU (see Section 3.1.4.2). Detailed chromatograms of these FHTC samples are presented in Figure 96 (Experiment No. 3, cold gas), Figure 97 (Experiment No. 5, cold gas), and Figure 98 (Experiment No. 5, hot gas). Peak identities and relative sizes of the peaks are presented in Table 28. The 55 compound identities shown in Table 28 were assigned based upon a combination of spectral library matches and individual spectral analyses. This list of compounds can be compared with the earlier list derived by analysis of the gaseous products from DRI's PDU, as shown in Table. (Note that the peak ID numbers differ between Table 8 and Table 28.)

Many of the compounds on these two lists are the same. In both cases, furans are dominant species. However, significant differences are also observed. For instance, the FHTC gas samples contained significant levels of acetamide (C_2H_5NO), acetic anhydride, and furfural (in the hot gas sample), which were not seen in the gas samples from DRI's PDU. However, there are several major differences in sample generation and collection procedures between the FHTC and the PDU cases that should be recognized. First, different biomass feedstocks were use: loblolly pine was treated in the FHTC reactor, while pinyon-juniper (P-J) was treated in the PDU. Second, samples were collected directly from the FHTC gaseous product stream while the unit was operating. At the point of sampling, this product stream is hot (about 80°C), and thus contains significant amounts of steam and volatile organic compounds (VOCs). (The FHTC "cold" gas samples were collected after passing through an ice/water condenser, and thus

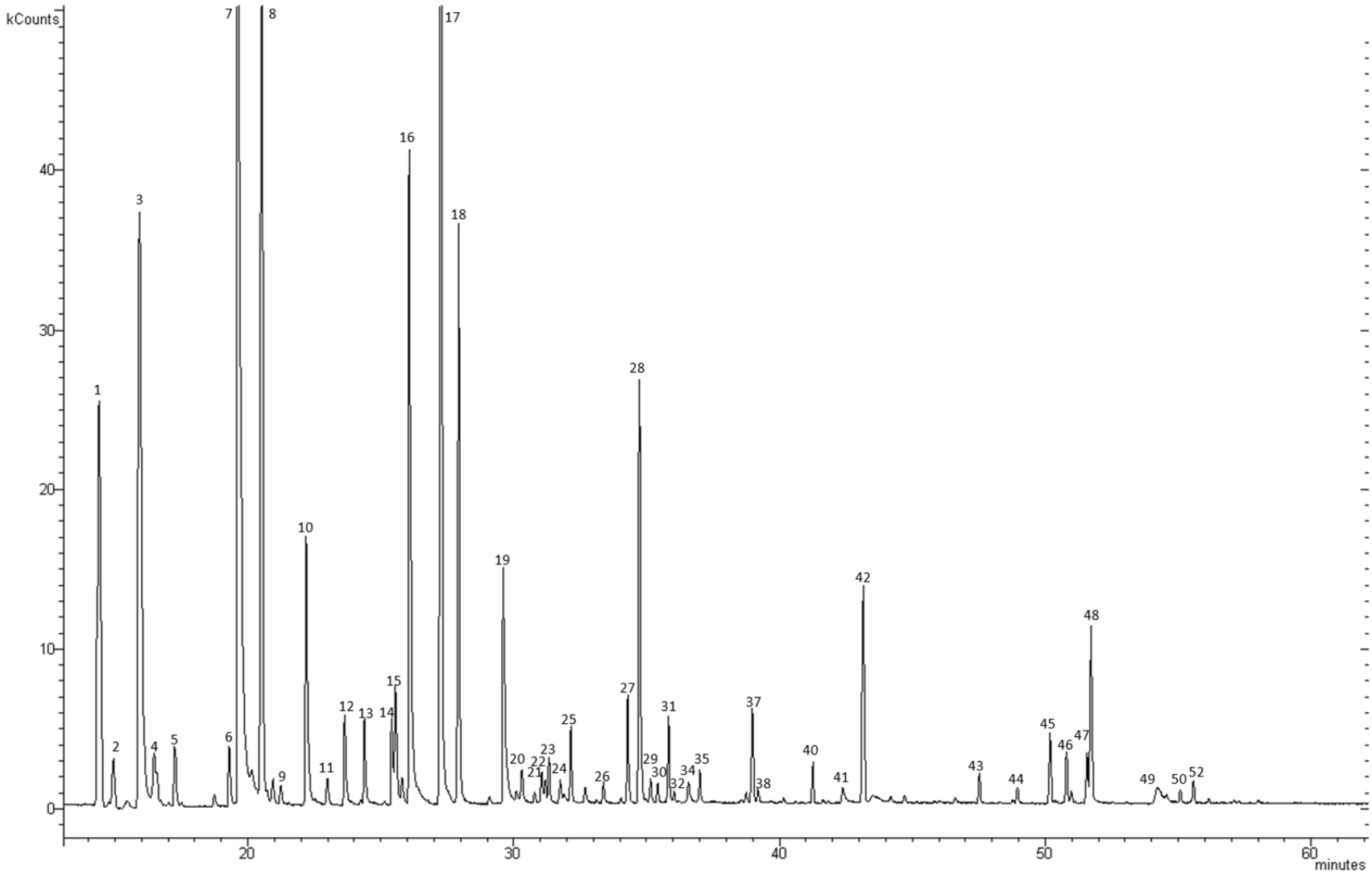

Figure 96. GC-MS TIC chromatogram of cold gas sample I014 from FHTC experiment No. 3, July 15, 2014.

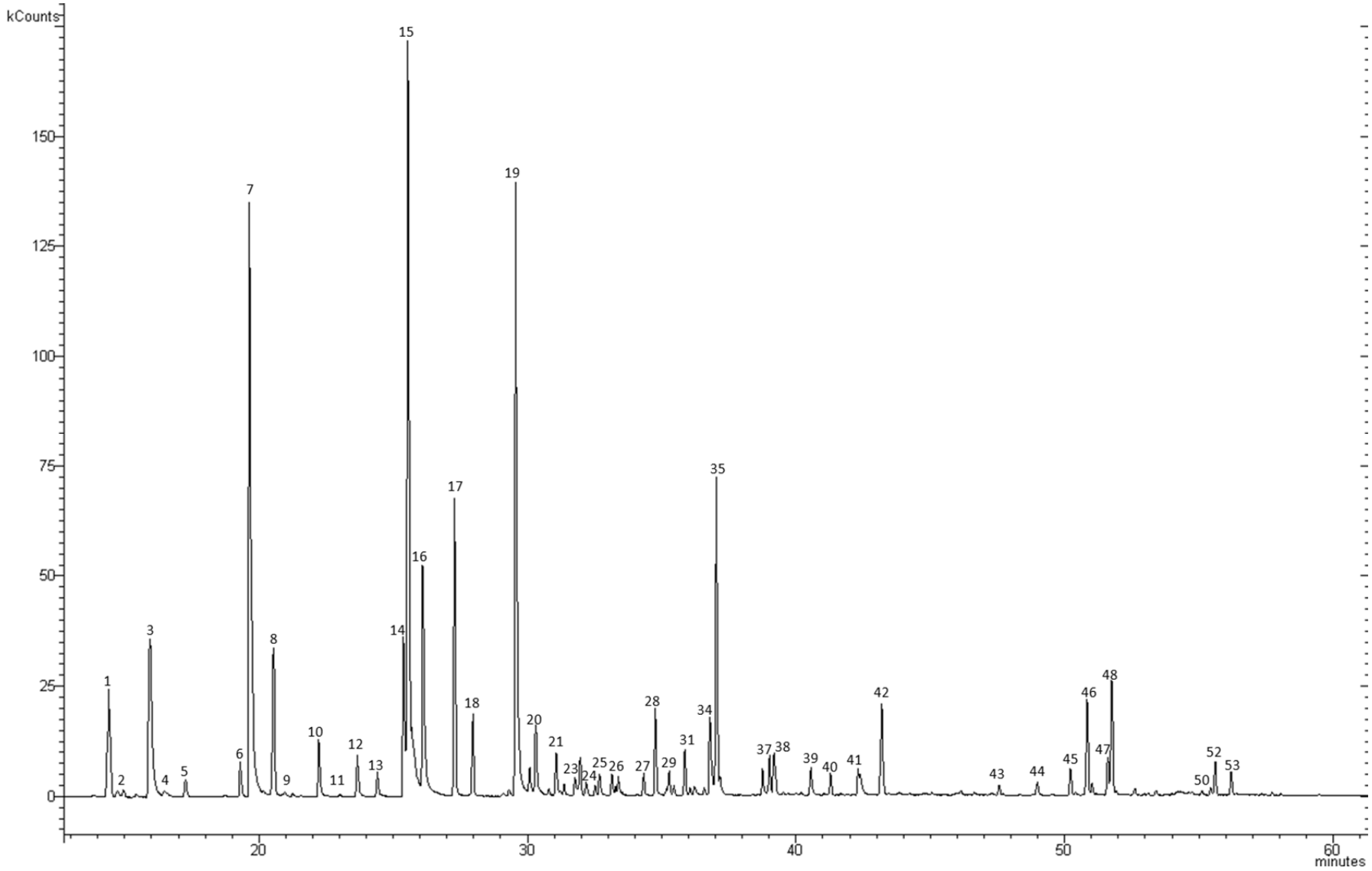

Figure 97. GC-MS TIC chromatogram of cold gas sample I008 from FHTC experiment No. 5, July 16, 2014.

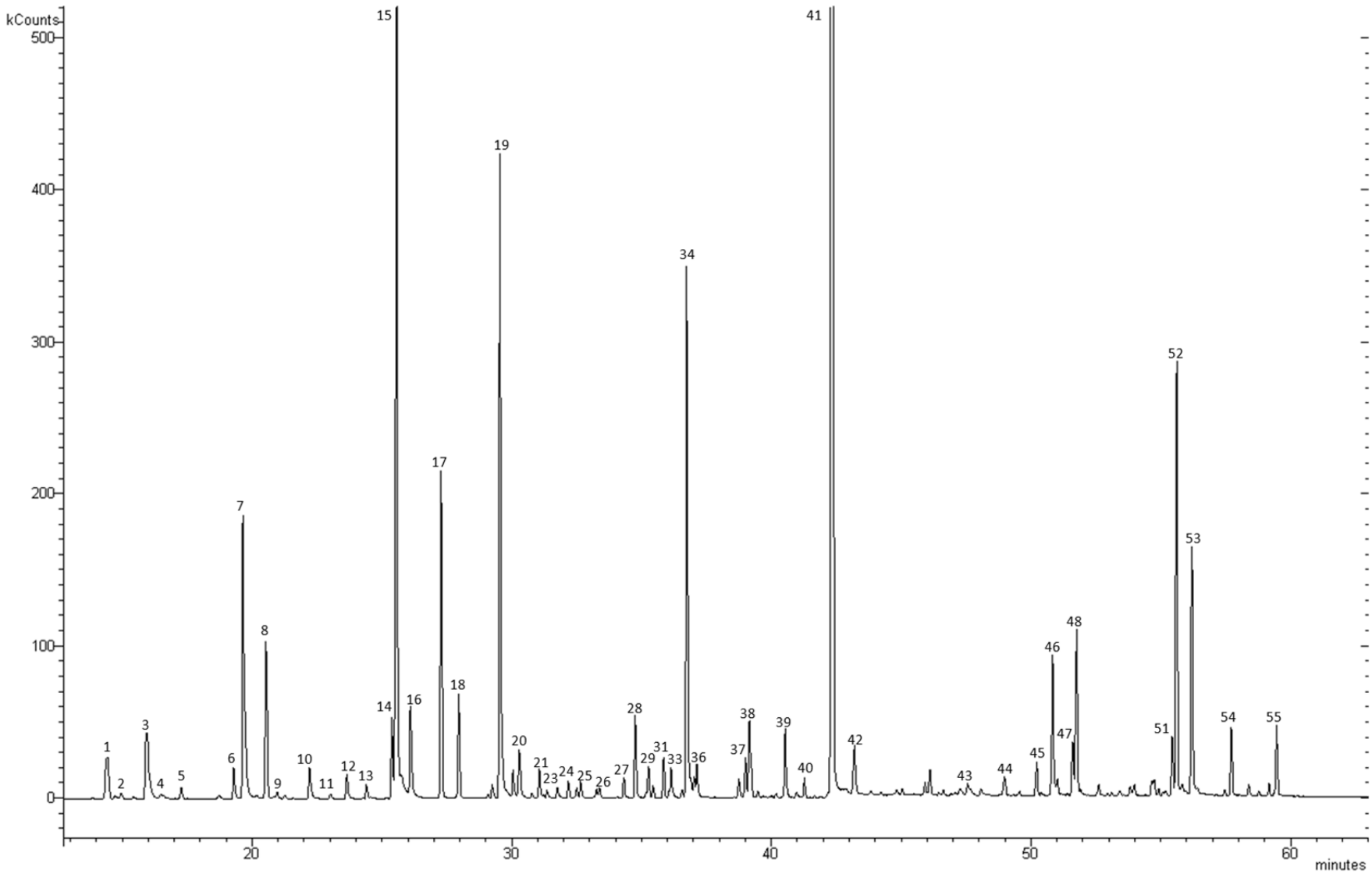

Figure 98. GC-MS TIC chromatogram of hot gas sample I009 from FHTC experiment No. 5, July 16, 2014.

Table 28. GC-MS Analysis of Gaseous Products from the GTI FHTC Treatment of Loblolly Pine at 290 °C. Top 5 Compounds Highlighted in Yellow; Next 5 Highlighted in Green

Peak No.	RT, Min.	% of Total Peak Area			Formula	Nominal MW	Compound Identity*
		Sample 1 I014 (cold)	Sample 2 I008 (cold)	Sample 3 I009 (hot)			
1	14.36	5.72	3.18	0.95	CO_2	44	carbon dioxide
2	14.95	0.52	0.18	0.05	$C_2H_4O_2$	60	acetic acid
3	15.92	9.52	5.58	1.57	C_4H_{10}	58	i-butane
4	16.45	0.52	0.18	0.04	C_4H_8	56	i-butene
5	17.28	0.65	0.40	0.15	C_3H_8O	60	methyl ethyl ether
6	19.29	0.54	0.75	0.37	C_5H_{10}	70	3-methyl-1-butene
7	19.63	18.51	14.02	3.93	C_2H_5NO	59	acetamide
8	20.52	9.77	3.33	1.85	C_4H_4O	68	furan
9	21.24	0.16	0.09	0.04	C_5H_8	68	pentadiene?
10	22.19	2.44	1.19	0.40	$C_3H_6O_2$	74	methyl acetate
11	23.00	0.25	0.09	0.04	C_5H_6	66	cyclopentadiene
12	23.64	0.79	0.87	0.31	C_4H_8O	72	2-methyl propanal?
13	24.37	0.72	0.45	0.14	C_4H_6O	70	dihydrofuran
14	25.41	0.68	2.63	0.68	C_4H_6O	70	methyl vinyl ketone?
15	25.55	1.19	16.75	9.39	$C_4H_6O_3$	102	acetic anhydride
16	26.07	6.22	4.90	1.01	C_3H_7NO	73	N-methyl-acetamide
17	27.21	19.36	5.49	3.35	C_5H_6O	82	2-methyl furan
18	27.93	4.58	1.48	1.11	C_5H_6O	82	3-methyl furan
19	29.61	2.70	12.29	6.72	C_4H_6O	70	2-butenal?
20	30.29	0.28	1.59	0.63	$C_5H_{10}O$	86	3-methyl-butenal?
21	31.05	0.27	0.76	0.32	$C_5H_{10}O$	86	2-methyl-butenal?
22	31.19	0.19	0.09	0.04	$C_6H_{10}O$	82	1-methyl cyclopentene
23	31.34	0.39	0.13	0.07	C_6H_6	78	benzene
24	31.76	0.15	0.88	0.14	C_5H_8O	84	3-pentene-2-one?
25	32.16	0.58	0.40	0.16	C_6H_8	80	methyl cyclopentadiene?
26	33.37	0.18	0.42	0.11	$C_5H_{10}O$	86	3-pentanone
27	34.28	0.85	0.41	0.20	C_6H_8O	96	2-ethyl furan?
28	34.74	3.43	1.54	0.88	C_6H_8O	96	2,5-dimethyl furan
29	35.16	0.20	0.32	0.26	C_6H_8O	96	3-ethyl furan?
30	35.42	0.15	0.09	0.04	C_6H_8O	96	2,4-dimethyl furan
31	35.83	0.62	0.80	0.41	C_6H_6O	94	phenol
32	36.01	0.11	0.00	0.00	C_6H_6O	94	vinyl furan
33	36.14	0.00	0.05	0.25	C_5H_8O	84	3-pentene-2-one?
34	36.58	0.18	1.54	4.97	C_5H_8O	84	3-methyl-2-butenal?
35	37.01	0.25	5.39	0.13	$C_2H_6S_2$	94	dimethyl disulfide
36	37.13	0.00	0.00	0.32	C_5H_8O	84	2-pentanal?
37	38.99	0.80	0.52	0.48	C_7H_8	92	toluene
38	39.19	0.12	1.04	1.15	C_6H_{10}	94	1-me-cyclohexadiene?
39	40.54	0.05	0.57	0.77	$C_6H_{12}O$	100	hexanal?
40	41.26	0.28	0.37	0.20	$C_7H_{10}O$	110	2-ethyl-5-methyl furan?
41	42.38	0.19	0.17	41.72	$C_5H_4O_2$	96	furfural
42	43.16	2.07	2.19	0.68	$C_6H_{18}O_3Si_3$	222	D3 siloxane
43	47.52	0.24	0.13	0.11	$C_{10}H_{16}$	136	bicycloterpene?
44	48.96	0.13	0.18	0.18	$C_{10}H_{16}$	136	bicycloterpene?
45	50.18	0.58	0.53	0.40	$C_{10}H_{16}$	136	bicycloterpene?
46	50.81	0.40	1.88	1.51	$C_{10}H_{16}$	136	camphene?
47	51.57	0.38	0.71	0.58	$C_{10}H_{16}$	136	bicycloterpene?
48	51.72	1.60	2.33	1.93	$C_{10}H_{16}$	136	α-pinene
49	54.27	0.27	0.00	0.00	$C_8H_{24}O_4Si_4$	296	D4 siloxane
50	55.07	0.05	0.09	0.04	$C_{12}H_{24}$	168	pentamethyl heptane?
51	55.46	0.00	0.00	0.60	$C_{10}H_{16}$	136	mono-cyclo-terpene?
52	55.58	0.16	0.60	4.49	$C_{10}H_{14}$	134	methyl-i-propyl benzene?
53	56.19	0.00	0.43	2.64	$C_{10}H_{16}$	136	mono-cyclo-terpene?
54	57.74	0.00	0.00	0.73	$C_{10}H_{16}$	136	mono-cyclo-terpene?
55	59.47	0.00	0.00	0.75	$C_{10}H_{16}$	136	mono-cyclo-terpene?

* Names followed by a question mark indicate compounds where specific isomeric identities are not known.

contained much less vaporized water and VOCs). In contrast, gases analyzed from the PDU were room temperature headspace samples, collected a day after the PDU run was conducted. Finally, the FHTC gas samples were collected in evacuated summa canisters, while the PDU gas samples were collected in Tedlar bags.

The major gas species observed, and their approximate concentrations in the headspace of DRI's PDU, are shown in Table 7. In Table 29, the highest concentration sample from the PDU headspace (Bag 1) is compared with the three summa canister samples collected from the GTI FHTC reactor in July of 2014. It should be emphasized that the quantification of some VOCs is quite uncertain – particularly for many of the oxygenated species. This is both because of uncertain compound identifications (as indicated by "?" in Table 28) and because many of the identified species were not included in the calibration gas standard. Therefore, quantification of many oxygenated species is based upon TIC peak areas, using the assumption that they all have the same response factor as furan.

Table 29. Molar Concentrations of Selected VOCs from GC-MS Analysis of Gaseous Products from DRI's PDU and GTI's FHTC Reactor, ppm

Compound	DRI's PDU, ppm	GTI's FHTC Reactor, ppm		
	Bag 1 Headspace Sample	Expt. 3 Sample I014 (cold gas)	Expt. 5 Sample I008 (cold gas)	Expt. 5 Sample I009 (hot gas)
1-butene + isobutene	12.81	0.45	0.04	0.19
1,3-butadiene	1.40	0.35	0.04	0.17
t-2-butene	0.65	0.03	0.00	0.01
c-2-butene	0.54	0.03	0.00	0.01
acetamide	-	2.69	0.97	1.59
furan	99.18	1.42	0.23	0.75
isoprene	3.04	0.07	0.01	0.05
2-methyl-2-butene	1.34	0.00	0.01	0.00
acetic anhydride*	-	0.17	1.16	3.81
2-methyl-furan*	46.65	1.63	0.20	0.86
benzene	0.28	0.07	0.02	0.05
2,5-dimethyl-furan*	2.77	0.27	0.06	0.20
n-heptane	2.31	-	-	-
furfural	0.64	0.02	0.03	9.72
alpha-pinene	5.12	0.41	0.31	1.74
other terpenes*		0.48	0.59	6.76
Approximate Total †	**195**	**9.3**	**4.2**	**29.8**

Notes: - indicates the VOC species was not a major constituent in this sample
* indicates uncertain quantification, as this species was not included in the calibration standard
† Total includes all identified VOCs, not only the species named in this table

Mass Balance for July, 2014 FHTC Testing: Efforts were made to compute a mass balance for the six experimental runs of the FHTC reactor conducted in July of 2014. Mass inputs of the loblolly feedstock were taken from the experimental parameters shown in Table 22. Mass outputs were computed as the sum of four product masses: condensate, Zone 4, slurry, and gases.

On the first day of experiments (July 15), a single, integrated sample of Zone 4 product was collected and analyzed, while three individual samples of gases, condensate, and slurry were collected and analyzed. The gas samples collected in evacuated canisters were too dilute for DRI to reliably measure CO_2 concentrations. (Individual VOCs measured from the canisters had very low concentrations, which were ignored in determining mass balances.) However, CO_2 concentrations were measured by GTI using a continuous monitor throughout the entire sampling period. The CO_2 values used in the mass balance determinations were based upon integrated concentrations coinciding with the 2-minute sampling periods. The mass yields of condensate and slurry were determined for each sample, based on the mass collected over the 2-min. sampling period and the known loblolly feed rate. On the second day of experiments (July 16), the total amount of slurry, condensate, and Zone 4 materials produced over each 2-minute sampling period were collected, thus enabling calculation of individual product yields for each sample.

The hydrochar mass recoveries for each of the 6 experiment shown in Table 30 were computed in two ways: (1) simply oven drying a small aliquot of the raw (unwashed) slurry, and (2) washing the slurry and determining the mass of material washed out in the form of NVR and volatiles in the filtrate. (Volatiles include furfural, 5-HMF, acetic acid, and formic acid – all of which were measured by chromatographic methods.) These two methods gave similar total mass recovery results, although the simple oven-drying-derived mass recovery was consistently lower (by 2-5%). This is expected, because oven drying would also remove the volatile products. Thus, the alternative method of determining hydrochar masses – which includes the volatiles – may be a more accurate way to determine mass balance.

Because Zone 4 samples were not collected for the individual experiments 1-3, these mass balance results include a composite value, which was determined from the total amount of Zone 4 material collected over the entire 60-min. run time. Similarly, a composite value of hydrochar was determined for the July 15 samples. This was based on the total amount of wet slurry collected throughout the 60-min. run, adjusted for the moisture content of the slurry. For this adjustment, a moisture content of 62.3% was used, as measured by GTI for this composite slurry.

Determination of accurate moisture contents is critical to calculating product yields and mass balances. In Table 29, all mass balance values are expressed as percentage of starting dry feedstock. To determine moisture contents of feedstock and slurry products, DRI oven-dried small samples in weighing tins at 105 °C for 24 hours. For feedstocks, this drying procedure is suitable, but for the hydrochar slurry, it probably overestimates the true moisture content because volatile products in the slurry (besides water) are also driven off in the oven.

Another factor is the difference in moisture content of hydrochar slurry when collected during a short, 2-min. sampling period, as compared to a composite sample from the collection vessel at the conclusion of an extended run period. A composite slurry sample is expected to have higher moisture content because additional water from steam is condensed and captured in the collection vessel throughout the run period. Evidence of this can be seen in Table 31 which shows moisture contents of various samples as measured by both DRI and GTI. For the

Table 30. Mass Balance for FHTC Experiments Conducted in July, 2014. All results expressed as a percentage of starting dry feedstock (Loblolly pine). All moisture contents used in mass calculations are based on measurements taken at DRI

FHTC Product Stream	July 15, 2014					July 16, 2014			
	Composite	Expt. 1	Expt. 2	Expt. 3	Avg.	Expt. 4	Expt. 5	Expt. 6	Avg.
Condensate									
Solids in condensate	0.1%	0.0%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%
NVR in condensate	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.2%	0.1%	0.1%
Volatiles in condensate (5-HMF, furfural, acetic and lactic acids)	1.1%	1.2%	1.1%	1.0%	1.0%	1.0%	1.0%	1.0%	1.0%
Zone 4									
Solids from Zone 4	4.0%	-	-	-	4.0%	4.2%	3.4%	4.6%	4.1%
NVR from Zone 4 filtrate/rinsate	0.2%	-	-	-	0.2%	0.2%	0.3%	0.2%	0.2%
Volatiles in Zone 4 filtrate/rinsate (5-HMF, furfural, acetic and lactic acids)	0.0%	-	-	-	0.0%	0.0%	0.0%	0.0%	0.0%
Hydrochar									
Oven dried slurry (not washed/filtered)	78.8%	91.0%	79.9%	71.3%	80.8%	77.7%	84.3%	76.8%	79.6%
Including filtrate volatiles (sum of three rows below)		(92.9%)	(83.2%)	(74.5%)	(83.5%)	(81.2%)	(86.9%)	(82.4%)	(83.5%)
Dried slurry after washing	-	78.3%	73.4%	59.9%	70.5%	60.7%	67.1%	61.0%	62.9%
NVR of slurry filtrate/rinsate	11.7%	10.5%	7.3%	10.9%	9.6%	15.7%	16.9%	16.4%	16.3%
Volatiles in filtrate/rinsate of slurry	3.4%	4.1%	2.5%	3.7%	3.4%	4.8%	2.9%	5.0%	4.2%
Gases									
CO_2	2.3%	-	-	-	2.3%	3.2%	2.2%	2.7%	2.7%
Total mass recovery									
Based on oven dried whole slurry	86.6%	92.3%	81.3%	72.4%	88.5%	86.6%	91.6%	85.5%	87.9%
Based on washed slurry + NVR + volatiles	-	94.2%	84.5%	75.6%	91.3%	90.0%	94.2%	91.1%	91.8%

Notes:

- Composite results were calculated by taking the average concentrations of individual samples 1-3 and applying them to the entire product mass that was generated during one hour of operation. The composite slurry moisture was taken to be 62.3%, as measured by GTI.
- Avg. results for slurry and condensate were calculated as means of samples 1-3 and 4-6.
- Total mass recoveries from Exp. 1-3 do not include gases or Zone 4 masses, whereas the Avg. and Composite total mass recoveries do.

experiments conducted on July 15, GTI only measured the moisture content of the composite slurry collected over the entire day, while DRI measured three discrete samples, each collected over a 2-min. period. It is clear that the composite sample had considerably higher moisture content than that from the discrete samples. On July 16, however, both DRI and GTI measured moisture contents of samples collected over the same discrete, 2-min. periods. In this case, the DRI and GTI values are in close agreement.

Overall, the results shown in Table 31 indicate acceptable mass balances for the FHTC experiments conducted in July of 2014. Using hydrochar recoveries based upon washed slurries + NVR + volatiles, the average total mass recoveries were 91.3% and 91.8% on July 15 and 16, respectively. In addition, it is known that water is also produced in the HTC process. Based upon previous HTC experiments conducted in a 2-L stirred Parr reactor, we would expect a water

yield of about 10% at a reaction severity of 5.2 - 5.4. Including this water yield with the results in Table gives total mass yield results near 100%.

Table 31. Moisture content comparisons from samples measured at GTI and at DRI

Sample	Experiment No.	DRI	GTI
Feedstock	-	52.7%	55.0%
July 15 Hydrochar Slurries	1	52.8%	62.3%*
	2	54.2%	
	3	53.5%	
July 16 Hydrochar Slurries	4	62.0%	60.0%
	5	56.7%	-
	6	56.9%	58.3%

* composite of entire day's run

Summary and Conclusions: Use of an auger-based process development unit (PDU) installed at DRI was explored, and operating conditions were optimized to produce a high energy density hydrochar from HTC treatment of woody biomass. *Over the range of conditions employed, it was demonstrated that product yields and compositions (gaseous, aqueous, and solid hydrochar) from this PDU agreed well with earlier results obtained using a small, 2-L stirred Parr reactor.* These findings suggest that Parr reactor experiments are reliable predictors of how the PDU would function over a wider range of feedstocks and operating conditions.

Mass balance assessments of HTC experiments within the PDU showed that over 90% of starting feedstock mass could be recovered. Assuming that a small amount of water was also produced (as has been demonstrated previously with Parr reactor experiments) the total mass recovery was near 100%, although there is significant variability in this assessment. As with earlier Parr reactor experiments, it was shown that maximum sugar recovery in the aqueous product stream occurred at relatively low temperatures (<235 °C) while maximum hydrochar energy densification occurred at somewhat higher temperatures (>250 °C). The principal gaseous product of HTC reactions was CO_2, although trace levels of numerous VOCs have also been detected – particularly furans.

Standardized and highly repeatable methods were developed to prepare pellets of raw and thermally-treated woods, and to evaluate their durability. Laboratory-produced pellets were shown to behave similarly to commercially-produced pellets, based upon tumbler durability tests. A standardized laboratory test was developed to assess the stability of pellets before and after immersion in water at room temperature. Such immersion, followed by a tumbler test, is an extremely severe test of a pellet's durability. Only very robust pellets – such as those produced from HTC hydrochar – can survive these extreme conditions.

HTC process temperature was found to have a significant effect on the durability of resulting pellets. At very low process temperatures (<175 °C), pellets were quite unstable upon immersion in water. Increasing the process temperature to 200 °C dramatically improved the pellet stability, even though very little energy densification of the hydrochar occurred until the temperatures were raised further to 235 °C and beyond.

Mass and volumetric energy densities of hydrochar pellets increased with HTC process temperature until reaching a maximum at 250-275 °C. Based upon HTC experiments with Loblolly pine in a 2-L stirred Parr reactor, the mass energy density increased from about 20 MJ/kg (raw feedstock) to 29 MJ/kg (HTC-275). Volumetric energy density of pellets increased from about 25 GJ/m^3 (raw feedstock) to 34 GJ/m^3 (HTC-275). Mass density of hydrochar pellets increased with process temperature up to about 235 °C, then decreased with a further temperature increase. Mass densities of individual pellets were measured as approximately 1220 kg/m^3, 1315 kg/m^3, and 970 kg/m^3 for raw Loblolly, HTC-235, and HTC-275, respectively.

In contrast to torrefied wood, hydrochar contains significant levels of solvent extractable organics. For example, hydrochar produced from HTC treatment of Tahoe Mix wood at 255 °C contained approximately 25% acetone-extractable material. Torrefied wood from the same feedstock contained only 3% of acetone-extractable material. These acetone-extractable materials are believed to be partially responsible for the excellent binding properties of hydrochar. The lack of extractable material from torrefied wood (and raw wood) may explain the relatively poor binding behaviors of these materials. The acetone-extractable material from hydrochar was found to have high energy content (nearly 30 MJ/kg), which also contributes to the energy densification that occurs during the HTC process.

Chromatographic and spectroscopic techniques were used to characterize the acetone extracts obtained from hydrochar and torrefied wood. Levoglucosan and other carbohydrates were identified by GC/MS analysis of extracts from torrefied wood. In contrast, abietic acids, which are known for their adhesive properties, were detected in the extracts from hydrochar. It is believed that the HTC process involves hydrolysis, dehydration, decarboxylation, condensation, and aromatization mechanisms, which lead to formation of furan resins. These resins are commonly used as adhesives and strengtheners for engineered wood products.

Laboratory experiments were conducted to show that hydrochar acts as an effective binder when added to other woody biomass materials that by themselves do not form robust pellets. It was demonstrated that improved pellet durability resulted from increasing blend levels of hydrochar when mixed with raw wood and with torrefied woods. However, even with blends containing up to 50% hydrochar, these pellets were generally not able to survive the extreme conditions of water immersion followed by tumbling.

Blends of pulverized Galatia coal with 10% and 30% hydrochar were shown to produce robust pellets that maintained their shape even when immersed in water. It was also demonstrated that co-processing of coal with 20% raw wood under HTC conditions at 250 °C produced a homogeneous mixture of hydrochar and coal, which could readily be formed into robust pellets. *These results suggest that HTC processing of wet coal fines with small amounts of woody biomass may provide an effective way to productively utilize the growing stockpiles of coal fines that exist in certain locations.*

Operation of GTI's fast HTC (FHTC) PDU was shown to be effective in rapidly producing hydrochar from Loblolly pine. This PDU utilizes a twin-screw extruder (TSE), as well as a specially designed hot water handling system and a computer controlled valve at the extruder exit. The process reaction time within the TSE is estimated to be 20-30 sec. Upon exiting the TSE, products are flashed into a large collection vessel, where a wet, paste-like slurry of hydrochar is collected. Excess water and volatile organic products pass through this collection

vessel to a condenser, where they are obtained as liquids. Non-condensable gases are vented out of the product collection system.

Operation of the FHTC PDU in February of 2013 was conducted with a process temperature of approximately 260 °C. The hydrochar produced under these conditions had excellent binding properties, but showed very little energy densification. The extent of energy densification was comparable to that observed in previous experiments with a 2-L stirred Parr reactor at 215 °C. Subsequent operation of the FHTC PDU in July of 2014 was conducted at a higher temperature of 290 °C. Under these more severe conditions, a greater degree of hydrochar energy densification occurred, comparable to what was observed at 230-240 °C in the stirred Parr reactor. This FHTC-produced hydrochar also exhibited excellent binding behavior.

The concept of "reaction severity" is a useful way to express the HTC reaction conditions as a single parameter that accounts for both reaction time and reaction temperature. Reaction "severity factor" was shown to be a good predictor of hydrochar energy content across a wide range of HTC conditions and reactor vessels. *Plotting hydrochar energy content against severity factor revealed a reasonably consistent behavior across four different reactor systems: (1) DRI's small 2-chamber reactor, (2) a 2-L stirred Parr reactor, (3) DRI's auger-driven PDU, and (4) GTI's TSE-based FHTC PDU.* This analysis showed that hydrochars having good binding behavior can be produced at a severity factor as low as 4. However, to achieve substantial energy densification of the hydrochar requires a severity factor of 5-6. The estimated severity factor of GTI's FHTC PDU when operated in July of 2014 was 5.2 – 5.4.

Due to its continuous operating behavior, it was more difficult to determine a mass balance from the FHTC PDU, as compared to earlier stirred Parr reactor experiments. Nevertheless, *based upon a series of 2-minute product collection experiments, we believe the total mass balance is close to 100%, and the distribution of products is similar to previously observed distributions from Parr experiments conducted at similar levels of severity. From these 2-min. collection experiments, 80-90% of the starting dry Loblolly feedstock was recovered as hydrochar slurry, with about 20% of this mass being water-soluble organics that could be washed out of the slurry.*

While the HTC products from GTI's FHTC PDU were similar to those observed in earlier experiments with DRI's Parr reactor and auger-driven PDU, they were not identical. For example, a much larger fraction of 5-HMF was produced in the 2-L Parr reactor than in the FHTC reactor. This may be due to kinetic limitations of the FHTC system. With short reaction times of only 20-30 seconds, there may be insufficient time to produce secondary degradation products, such as 5-HMF.

Considerable levels of furfural were produced in all the HTC reactor systems that were utilized. However, the unique product flashing step with the FHTC PDU system allows for effective separation of this valuable product, as most of it passes through the hydrochar collection vessel and is obtained in the condensed liquid phase. Commercial production of furfural would still require separation from water (perhaps by distillation) and purification.

Thus, hydrochar produced in the GTI FHTC PDU should be representative of hydrochar produced in batch-based systems, with the proviso that lover levels of 5-HMF are produced due to reaction kinetics. Otherwise, the hydrochar produced by batch-based or continuous FHTC TSE-based reactors should be considered to be the same for equal levels of process severity.

3.2.3 Task 3: PDU Modification for Online Coal/FHTC Biomass Fuel Production

Modifications to Accommodate On-Line Mixing of Coal and FHTC Biomass: The second major component for the continuous online production of a blended coal/FHTC product is a heated twin-auger, cut-flight blender/conveyor designed specifically for mixing, conveying, and drying a mixture of pulverized coal and fresh FHTC biomass. The online blender/conveyor connects directly to the discharge of the FHTC PDU and accepts a continuous feed of coal and fresh FHTC biomass. The blender/conveyor thoroughly blends the coal/FHTC biomass mixture and transports it to a centralized collection vessel. Residence time is varied by adjusting the rotational speed of the intermeshed twin augers and the unit incorporates heating and venting to enable drying of the coal/FHTC mixture to a required moisture level for optimal product consistency and briquetting. Figure 99 shows an isometric view of this device as connected to the BC-21 TSE, and Figure 100 shows top and side views of this arrangement.

Following consultations with GTI, the design of twin-auger, cut-flight blender/conveyor was completed by Thomas & Muller Systems, Ltd. in mid-February 2014. The system was ordered late that month after a final design review. After unexpected delays were encountered in manufacture, the system was delivered in early June, 2014. Figure 101 shows a photograph of the blender/conveyor, as delivered.

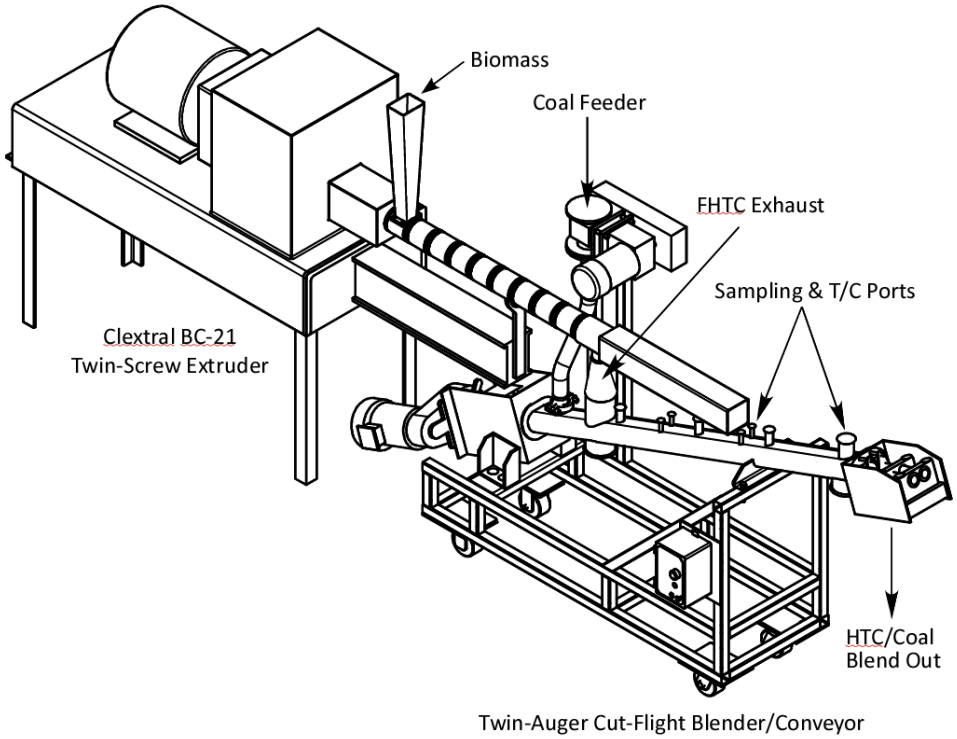

Figure 99. Isometric view of the twin-auger, cut-flight blender/conveyor as configured with the Clextral BC-21 TSE.

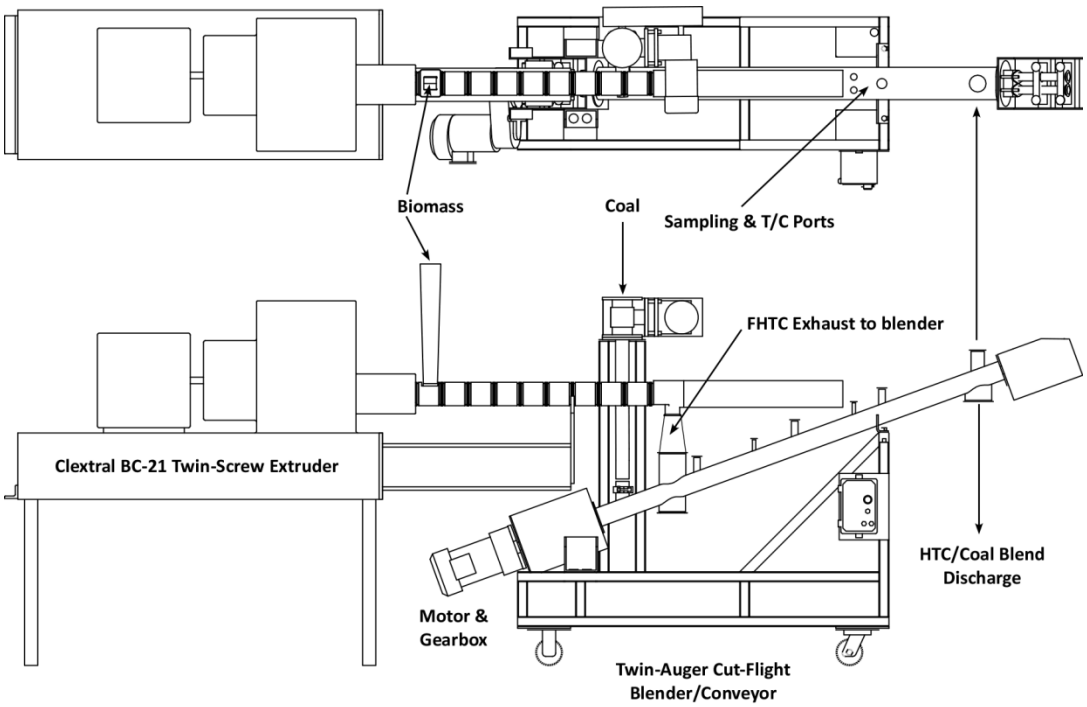

Figure 100. Top and side views of the twin-auger, cut-flight blender/conveyor as configured with the Clextral BC-21 TSE.

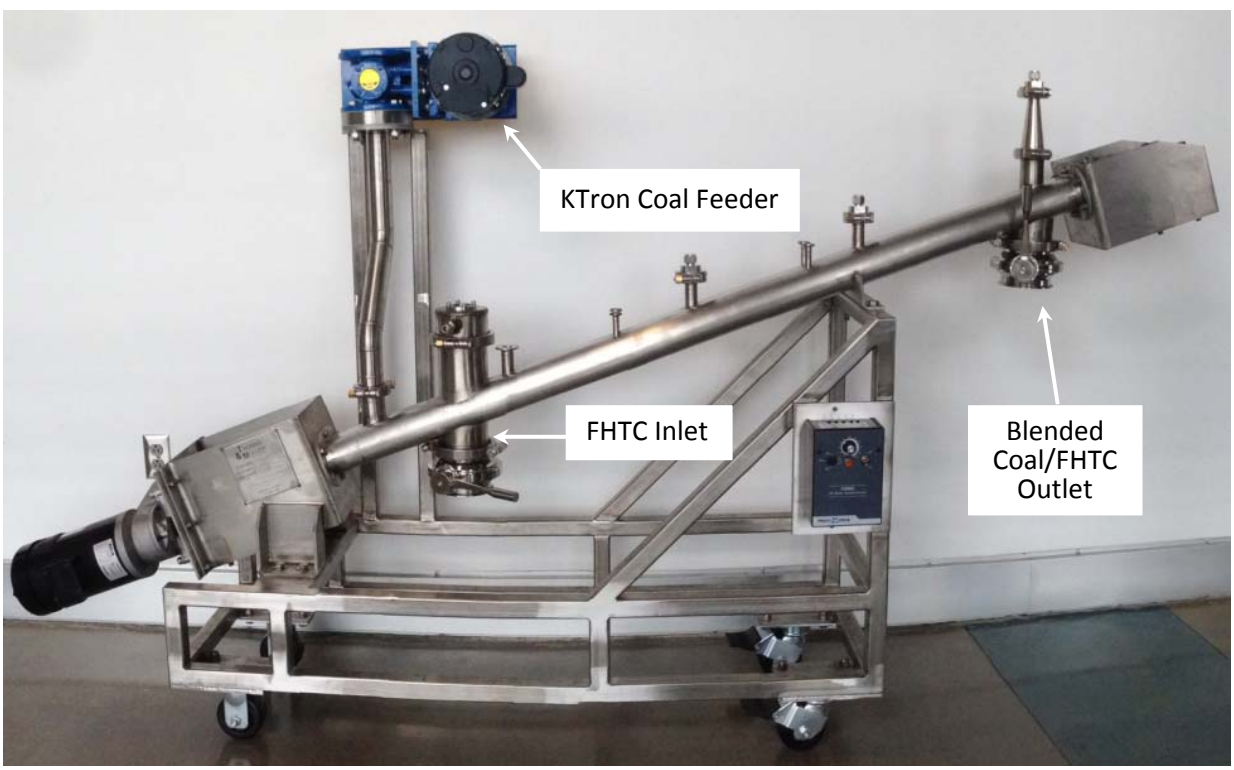

Figure 101: The blender/conveyor unit as delivered.

After receipt of the blender/conveyor unit installation began for the installation of external drying heaters and the framework to support the K-Tron coal feeder. Figure 102 shows the assembled mixer with vent lines, coal feeder support frame, insulation, collection vessel and the upgraded control valve and Figure 103 shows a detail of the assembled and insulated blender/conveyor installed with the BC-21 TSE.

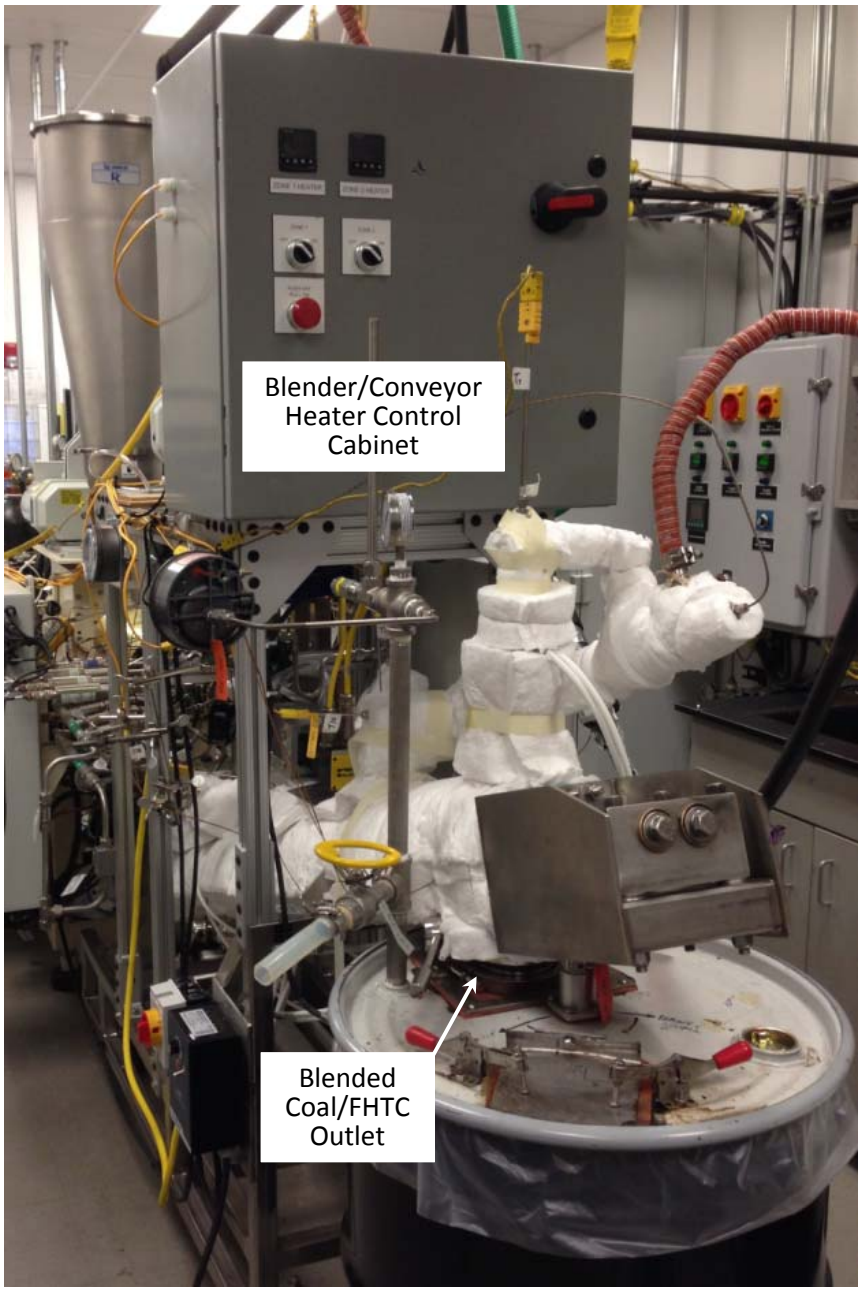

Figure 102: Overview of assembled and insulated blender/conveyor unit installed with the Clextral BC-21 TSE.

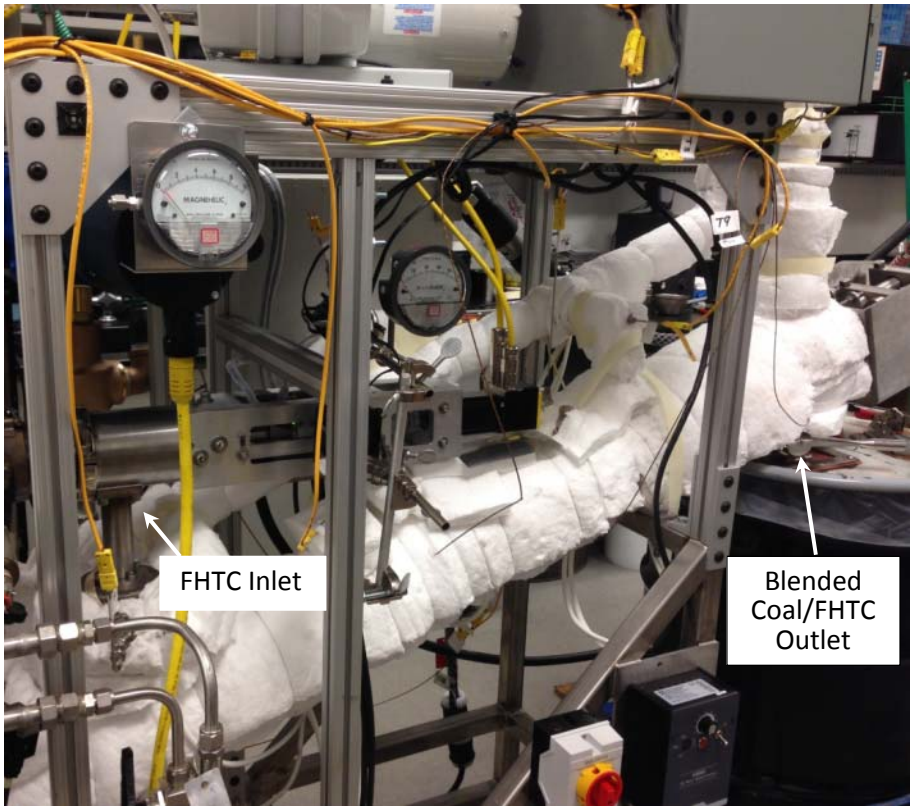

Figure 103: Detail of the assembled and insulated blender/conveyor unit installed with the Clextral BC-21 TSE.

3.2.4 Task 4: Forming & Characterization of Coal/HTC Biomass Briquettes

Briquette Forming: GTI leased a Komarek, Inc. B100QC briquetting machine for this task. The briquetter uses two roller press heads which have been indexed to each other to produce compressed formed products, as shown schematically in Figure 103, below. Each roller press incorporates multiple cupped indentations that come together as the synchronized heads rotate. As the synchronized cups are pressed together, a briquette is formed by a squeezing process. A photograph of the briquetter is shown in Figure 104. Photographs of the Komarek, Inc. B100QC briquetting machine are shown in Figures 105 and 106.

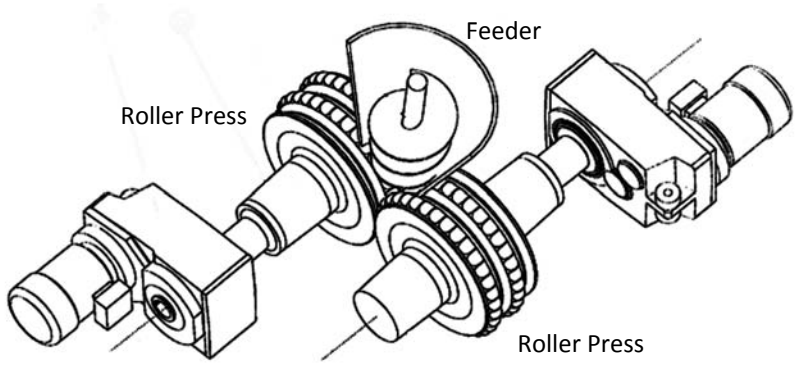

Figure 104. Schematic representation of a roller-press briquetter.

Figure 105. Komarek, Inc. Model B100QC briquetting machine used in laboratory trials.

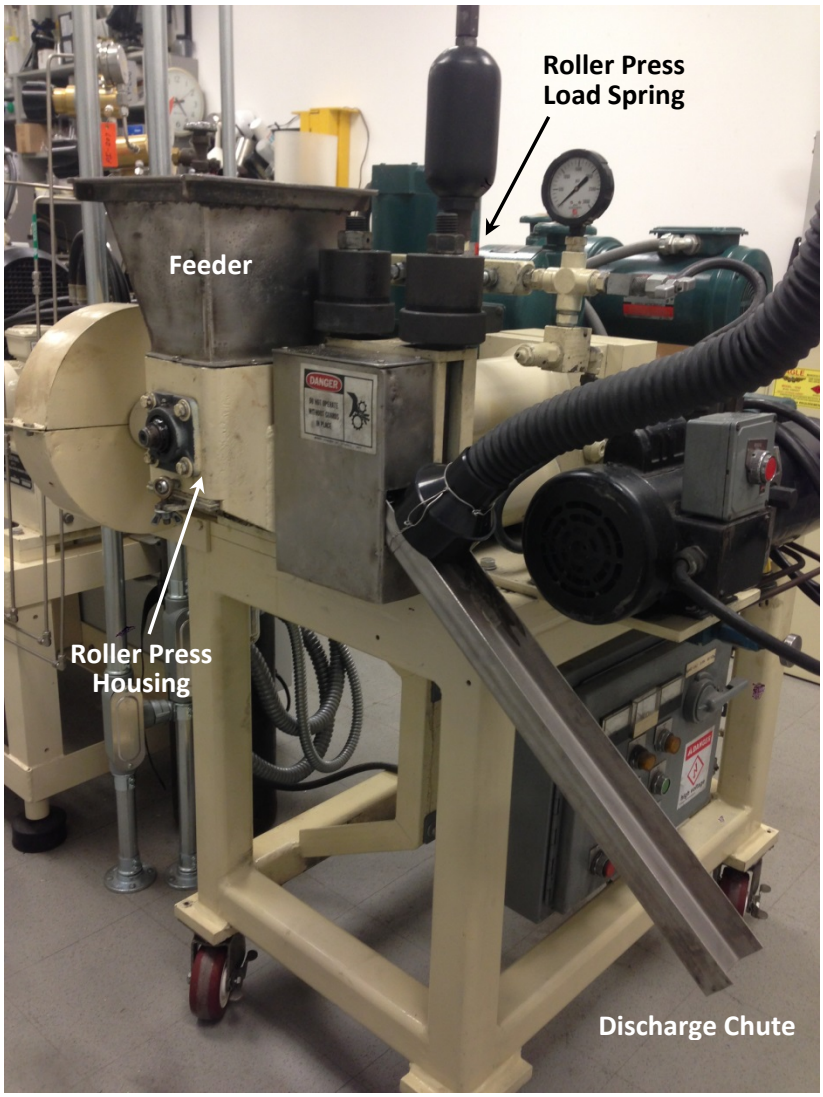

Figure 106. Overview from briquetting head side with vent line installed.

Briquette Characterization: Briquettes made by the Komarek, Inc. B100QC briquetting machine were characterized by several methods, as described in Sections 3.2.5 and 3.2.6 that discuss the separate tasks devoted to offline and online briquetting and characterization of two specified blends of pulverized coal and FHTC loblolly pine to meet project deliverable requirements. The two required blends were 90 wt. % coal/10 wt. % FHTC biomass and 70 wt. % coal/30 wt. % FHTC biomass. For both tasks, the Komarek briquetting machine was used to prepare briquettes from the two required blends.

3.2.5 Task 5: HTC Biomass and Offline Briquetting/Characterization

Offline Production of Coal/FHTC Biomass Blends: In order to form and evaluate briquettes made from mixtures of coal and FHTC loblolly pine (hereafter, FHTC loblolly pine will be referred to as "FHTC" or "FHTC biomass" with "loblolly pine" understood, except where clarification would be appropriate), two basic approaches for creating these mixtures were tested. In the first approach, wet FHTC paste produced during the February 25, 2013 run of the FHTC PDU was mixed with pulverized bituminous coal (Illinois Basin Galatia coal). The mixture resulted in a 74% pulverized coal/26% FHTC blend (dry basis weight). Because of the stickiness and viscosity of the FHTC paste, and also because of the powder-like nature of the pulverized coal, extensive mixing of these two materials left numerous small coal-covered balls of FHTC paste (approx. 0.125" diameter) in the mixture. The non-homogeneity of this mixture was not ideal, and adversely affected the quality of the briquettes made from it, as discussed under Briquetting Operation, below.

Drying the HTC Prior to Mixing with Pulverized Coal: Because mixing FHTC paste directly with coal resulted in a product that was non-homogeneous, the decision was made to pursue an alternative method: drying the FHTC paste and mechanically reducing its size to a fine powder before mixing it with the pulverized coal. This approach was intended to allow the FHTC biomass and the pulverized coal to become fully blended, producing a homogeneous mixture before the briquetting process. The procedure for drying and reducing the FHTC to produce a powder for mixing is explained in Table 32.

Mixing of Dried HTC with Coal: The procedure for mixing dry FHTC paste powder with pulverized coal is shown in Table 33. To maximize the flexibility of testing the blends of pulverized coal and dry FHTC powder, FHTC from PDU runs on May 16, 2013 and May 24, 2013 were dried and mechanically processed to reduce the dry FHTC to a powder, before mixing with pulverized coal. Two blends of pulverized coal and FHTC powder were produced with the procedure described in Table 33 (90% pulverized coal/10% FHTC, and 70% pulverized coal/30% FHTC). Photographs of those two blends, and the two source powders used to produce them, are shown in Figure 107. The bulk densities of these materials are presented in Table 34.

In three subsequent operating cycles of a Komarek, Inc. B100QC briquetting machine (discussed below), briquettes comprising 100 % pulverized coal were produced, as well as briquettes from the 90% pulverized coal/10% FHTC blend, and the 70% pulverized coal/30% FHTC blend.

Briquette Production: As described above, GTI leased a Komarek, Inc. B100QC briquetting machine to use for this task. Photographs of the briquetter are shown in Figures 104 and 105. The briquetter uses two roller press heads which have been indexed to each other to produce compressed formed products. Each roller press incorporates multiple cupped indentations that come together as the synchronized heads rotate. As the synchronized cups are pressed together, a briquette is formed by a squeezing process.

Briquetter Operating Trials: The blends produced from pulverized coal mixed with the wet FHTC produced on February 25, 2013 yielded briquettes that easily fragmented. Subsequently, briquettes were produced from blends of pulverized coal and dried, powdered FHTC material (as described above), and also from 100% pulverized coal. Briquettes formed from the blends of pulverized coal and FHTC powder exhibited improved strength when compared to 100% coal, and were therefore selected for the additional analyses described below.

Table 32. HTC Drying and Reducing Procedures

Step	Procedure
1	Assemble all the source containers of the FHTC biomass to be dried and treated for size reduction.
2	Gently suction the free-standing liquid off the surface of the solid FHTC biomass that has collected at the bottom of the container(s) the using the laboratory vacuum line, an Erlenmeyer flask, and clear tubing. (Safely store the free-standing liquid for future studies, if desired.)
3	Spread the "dewatered" FHTC biomass onto shallow pans for passive drying in the laboratory hood. Smooth the material into a layer about 3/8" thick over the surface of each pan. Place the pans onto the drying rack in the hood.
4	Let the FHTC biomass dry for one to three days (the time required depends on the progress of the drying process). The dryness of the material is indicated by the coolness of the FHTC (or the pan) and also by the color and consistency of the HTC cake. To speed the drying process, manually break up the partially or fully dried cakes into small pieces to expose them to as much airflow as possible for any remaining drying that is required. ,
5	When all the HTC cake material has driedsubject the dry HTC material to mechanical size reduction. (A rapidly rotating blade was used to convert the dried HTC cake into a fine powder.) Combine all the powdered HTC into a large bucket and mix it thoroughly.

Table 33. Procedure for Mixing Pulverized Coal and Dried, Chopped FHTC Powder

Step	Procedure
1	Measure the moisture content of the FHTC powder.
2	Measure the moisture content of the pulverized coal.
3	Based on the moisture content of the HTC powder, the moisture content of the pulverized coal, the dry basis ratio of the mixture desired for briquetter testing, and the amount of total mixed material needed to operate the briquetter, calculate the amounts of HTC and coal that should be blended.
4	Blend the HTC with the coal by hand (using a spatula in a large bucket). Stir the material thoroughly (at least until the black swirls from the pulverized coal, and the brown swirls from the dried, HTC powder are no longer detectable). Measure the moisture content of the mixture.

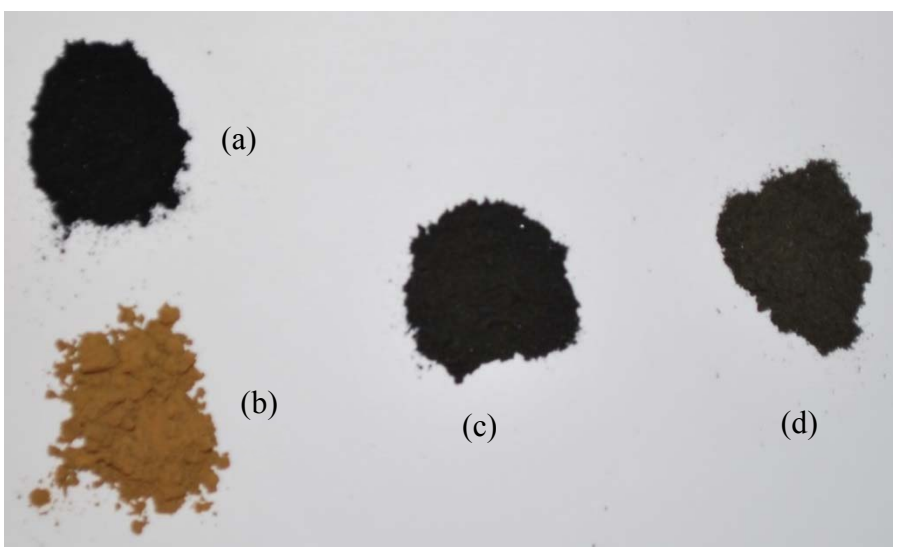

Figure 107. Photographs of (a): the pulverized coal, (b): dried FHTC powder, and the two blends produced from them (c): 90% pulverized coal/10% FHTC, and (d): 70% pulverized coal/30% FHTC.

Table 34. Bulk Densities of Source Powders and Pulverized Coal/FHTC Blends

Material	Moisture Content, % wt.	Bulk Density, g/cm^3
100% pulverized coal	7.8	0.57
90% pulverized coal/10% HTC	7.7	0.55
70% pulverized coal/30% HTC	7.3	0.46
Source FHTC (May 16 & May 24, 2013)	6.0	0.27

Operation of the briquetting machine produced briquettes that often had small tabs or flakes that extended out from the center seam between the two halves of the briquette, as shown in Figure 108. Before strength analyses were performed on any of the briquettes formed on February 17, 2014, tabs on the briquettes were removed by rolling the briquettes in a mixing drum as described below. The mixing drum is commercially available under the trade name ODJOB™.

Each group of briquettes formed on February 17, 2014, was loaded into a commercially available mixing barrel (ODJOB™ concrete mixing barrel) and hand-rolled 25 linear feet across the floor (approx. 7 rotations) to break off the friable tabs from the briquettes. For each of these three samples, the briquettes were then removed from the mixing barrel by hand and shaken lightly to segregate the tabs and flakes from the briquettes. Approximately 12 lb. of each sample were treated this way to create the samples of the briquettes GTI sent to CONSOL for testing. The rest of each sample rolled in the mixing barrel was also segregated ("cleaned" briquettes vs. the tabs and flakes) and weighed and saved for future laboratory use. The weights of these sample portions are summarized below in Table 35. These briquettes, and the tabs and flakes were stored for possible future analyses. Also, the three samples identified in Table 35 were shipped to CONSOL for analysis. In addition, a drop test evaluation of these three briquette samples was performed, as described below.

Drop Test Evaluation of Briquettes: Briquettes from the three briquetter production runs on February 17, 2014, were evaluated by a technique designed to rank their resistance to damage when subjected to repeated impacts. Figures 109 through 111 show the briquettes that were used in these drop test evaluations.

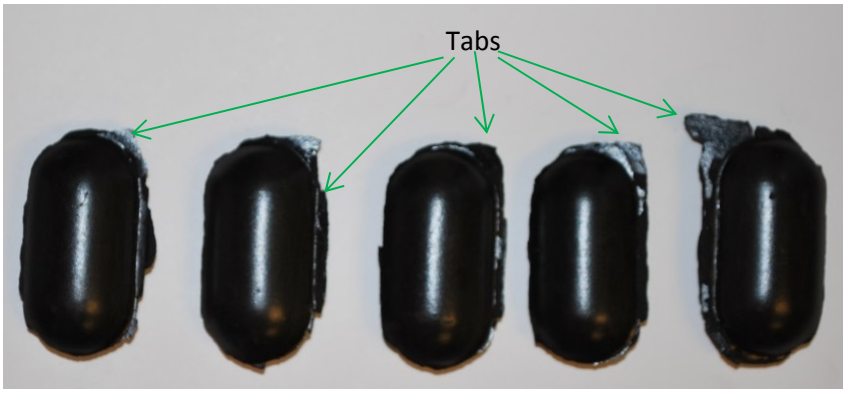

Figure 108. Photograph of briquettes with tabs formed around the center seam of the briquettes.

Table 35. Summary of Off-Line Briquette Production for Subsequent Analysis

Briquette Blend	Initial wt.,lb.	Briquettes sent to CONSOL for analysis, lb.	Briquettes for lab. use, lb	Tabs and flakes removed from briquettes, lb.	Portion of formed briquettes contained in tabs and flakes, %
100% pulverized coal	17.48	11.995	3.305	2.145	12.2
90% pulverized coal/10% FHTC	26.20	12.000	12.095	2.115	8.1
70% pulverized coal/30% FHTC	21.10	12.000	7.735	1.165	5.5

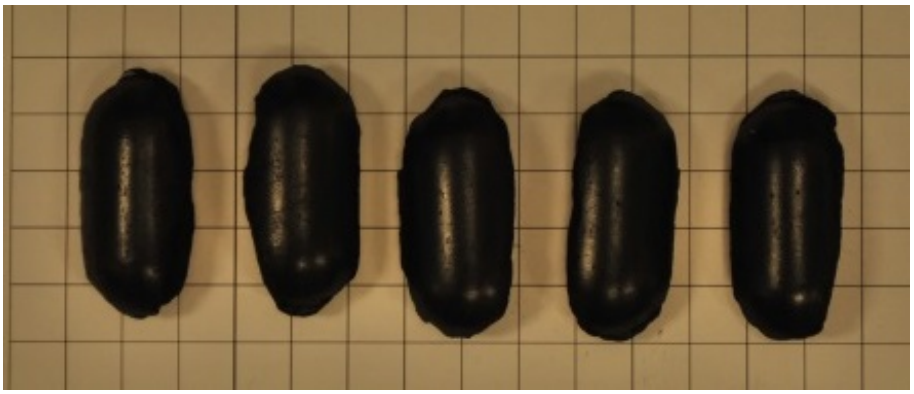

Figure 109. Briquettes formed from 100% pulverized coal prior to the drop tests.

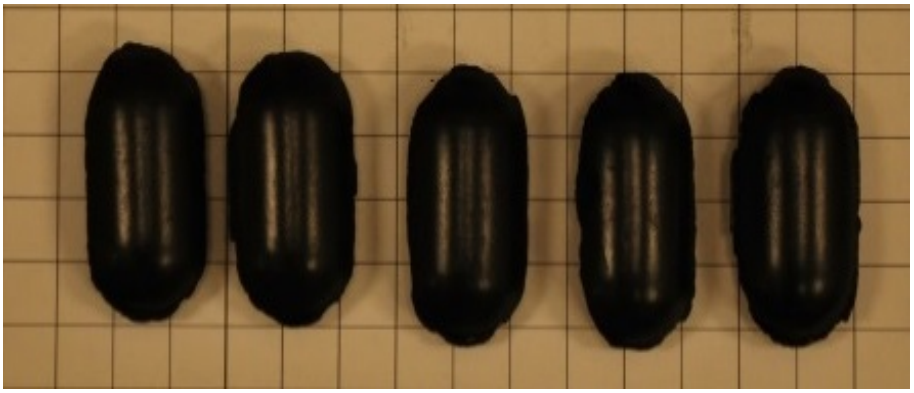

Figure 110. Briquettes formed from 90% pulverized coal/10% HTC prior to the drop tests.

Figure 111. Briquettes formed from 70% pulverized coal/30% HTC prior to the drop tests.

The test used for the evaluation comprised dropping a preweighed briquette 72 inches onto a thick glass plate striking surface, and collecting the significant pieces of the briquette following the drop. All pieces having weights greater than 20% of the original briquette were collected and weighed, and then dropped again onto the glass plate striking surface. This process was repeated for a maximum of four drop cycles, or until no pieces contained over 20% of the original mass of the briquette. Photographs were taken of the result of each drop cycle. The complete procedure used for these evaluations is presented in Table 36.

The relative strengths of the briquettes were established by 1) comparing the original weight of each briquette (before any drops) to the sum of the weights of all pieces of that briquette that each had weights > 20% of the original briquette's mass, and 2) noting how many drops each briquette endured while still yielding pieces having > 20% of its original mass. The results of these drop test evaluations are summarized in Figure 112, which shows that the resistance of the briquettes to disintegration on impact was significantly improved by the addition of FHTC to the material comprising the briquette. These data also show that the briquettes formed with 30 % FHTC by weight were more resistant to fragmentation than the briquettes formed with 10 % FHTC by weight. The 100 % coal briquettes were the weakest of the briquettes evaluated with this procedure.

Figures 113 and 114 provide a visual comparison of how representative briquettes formed from 100% coal and from 70% coal/30% HTC appeared after being subjected to the drop test.

Table 36. Briquette Drop Test Procedures

Step #	Procedure
1	Prepare and clean the striking surface (12" x 12" x 3/8" glass plate) and place it on top of the white paper background for photographs). Position the 6" diameter, 24" long PVC tube over the center of the strike zone to prevent pieces of the briquette from bouncing out of the collection zone after hitting the strike plate.
2	Select five intact briquettes for drop test evaluation. Take a single photograph of all briquettes assembled together.
3	Weigh each of the five briquettes and lay them out in the order in which they will be dropped.
4	Hold the first (or next) briquette horizontally (with the seam parallel to the striking surface) and release it from the drop release location (72 inches above the striking surface.) The briquette will hit the striking surface. Examine and photograph the result.
5	Collect each of the pieces of the briquette that appear to represent over 20% of the original mass. Note how many pieces are collected. (If no single pieces represent more than 20% of the starting mass of the briquette, discontinue the test and record the discontinuation.) Weigh each of the individual pieces with weights over 20% of the original mass and record their weights. Sum the weight of the total of these pieces. (Leave any smaller fragments on the glass surface in the drop zone where they ended up after the drop.)
6	Gather all the piece(s) that each represent over 20% of the original mass, and drop them individually onto the glass plate in the drop zone. These pieces will hit the striking surface. Examine and photograph the result.
7	If less than four drops have been completed for the briquette and/or its pieces, return to Step 5.
8	The test is completed if four drops have been achieved. Photograph the material in the drop zone after the last drop.

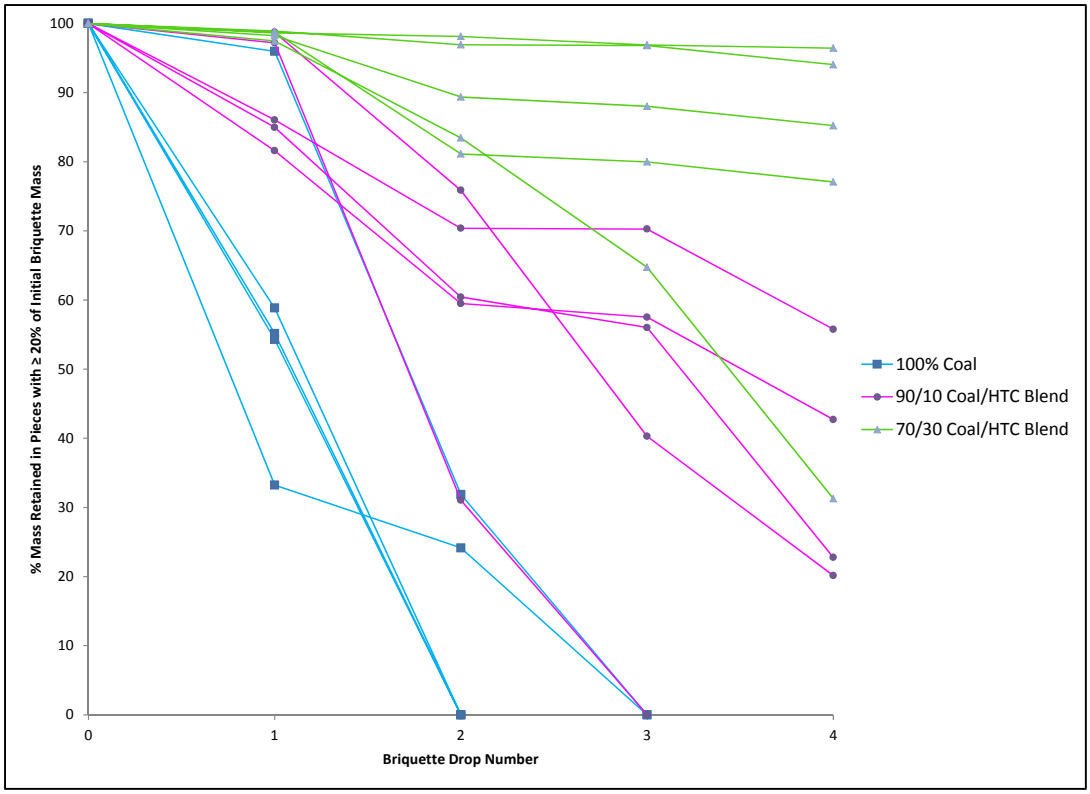

Figure 112. Results of the drop test evaluations of the briquettes formed from 100% pulverized coal, 90% pulverized coal/10% HTC, and 70% pulverized coal/30% HTC.

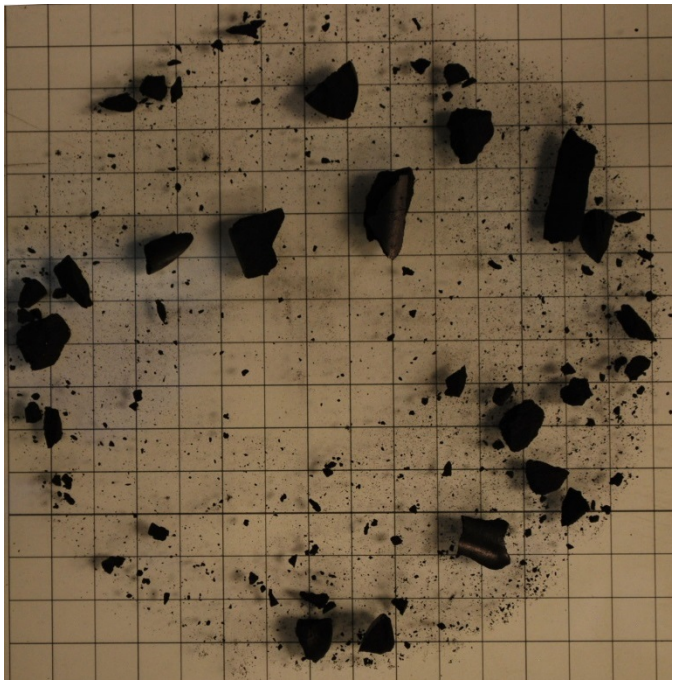

Figure 113. Briquette fragments (each having a mass <20% of the original mass) from a 100% coal briquette after two drops. A 1 cm x 1 cm grid is shown under the striking plate.

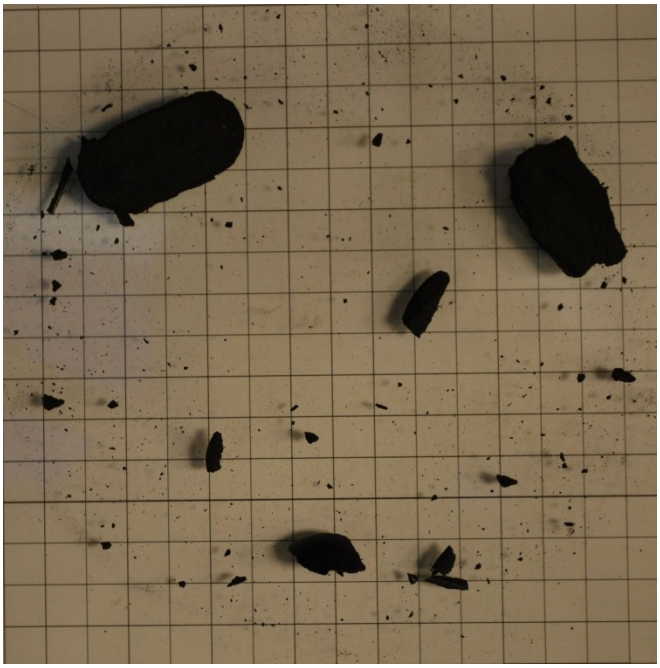

Figure 114. After four drops, 85% of the original briquette mass was contained in the two major pieces of this briquette formed from 70% coal/30% FHTC. A 1 cm x 1 cm grid is shown under the striking plate.

Evaluation of Offline Briquettes by CONSOL: Approximate 12 lb. portions of the off-line briquettes formed from 100% pulverized coal, 90% pulverized coal/10% FHTC, and 70% pulverized coal/30% FHTC were shipped to CONSOL ENERGY, Inc. for a range of analyses. The chemical data measured by CONSOL are summarized in Table 37. CONSOL also subjected the briquettes to a Rotap™ tumbler test. After passing through the Rotap tumbler, CONSOL measured the size distribution of the resulting briquette fragments with a screening analysis. The results of these measurements is shown in Table 38. In their summary of results, CONSOL stated "*The data suggests that the addition of biomass to the briquettes results in increased stability of the product during handling*".

Table 37. Chemical Analyses of Off-Line Briquettes

Description	100% coal	90% coal/10% HTC	70% coal/30 % HTC
Residual Moisture (Wt. %, AD Basis)	7.00	6.94	6.60
Volatile Matter (Wt. %, Dry Basis)	37.54	42.45	52.03
Ash (Wt. %, Dry Basis)	8.24	6.43	5.45
Fixed Carbon (diff.) (Wt. %, Dry Basis)	54.22	51.12	42.52
Carbon (Wt. %, Dry Basis)	72.42	71.47	67.48
Hydrogen (Wt. %, Dry Basis)	4.51	4.82	5.01
Nitrogen (Wt. %, Dry Basis)	1.74	1.57	1.32
Oxygen (diff.) (Wt. %, Dry Basis)	11.42	14.55	19.82
Sulfur (Wt. %, Dry Basis)	1.30	1.16	0.92
Chlorine (Wt. %, Dry Basis)	0.3715	--	--
Heating Value (Btu/lb) Dry Basis	12671	12502	11809
Hardgrove Grindability Index	200	162	133

Table 38. Size Analyses of Off-Line Briquette Fragments by Screening

Coal/Biomass Blend	**100% coal**	**90% coal/10% HTC**	**70% coal/30% HTC**
Size (inches or Tyler mesh)			
+5/8”	0%	1%	11%
5/8” x 3/8”	**33%**	**62%**	**67%**
3/8” x 1/4”	17%	7%	1%
1/4” x 6 mesh	8%	4%	3%
6 mesh x 10 mesh	3%	3%	3%
10 mesh x 16 mesh	3%	3%	3%
- 16 mesh (including dust)	**37%**	**21%**	**11%**
Total	100%	100%	100%

3.2.6 Task 6: HTC Biomass and Online Mixed Fuel Production/Characterization

Online Production of Coal/FHTC Briquettes – The unexpected delivery delay for the online blender/conveyor unit extended several project deliverables because it was a critical path item with a promised zero lag time. However, this delay did not affect the July, 2014 tests. During testing conducted in July, 134.8 lb. of FHTC loblolly pine was produced which was processed with the online blender/conveyor unit and Komarek BK-100 briquetter permitted the production of 45.1 lb. of 90 wt. % coal/10 wt. % FHTC biomass briquettes and 53.2 lb. of 70 wt. % coal/30 wt. % FHTC biomass briquettes by July 30, 2014.

90/10 coal/FHTC biomass briquettes were prepared by mixing and drying FHTC biomass with pulverized Galatia coal in the online blender/conveyor unit while it was maintained at approximately 100°C. The mixture was delivered to a holding barrel and then fed at 12-13% moisture into the Komarek BK-100 briquetter and formed into briquettes. Qualitative drop-shatter tests of these briquettes showed their strength to be poor, as was separately verified by testing by Consol Energy. It was ultimately determined that the poor strength of these briquettes was due to moisture levels greater than 8% because the online blender/conveyor unit was not adequately vented. Therefore, when the 70/30 FHTC biomass briquettes were produced, the online mixer was heated as before but the precaution was taken to separately air-dry the mixture delivered by the online mixer to ~3-4% moisture before briquetting was attempted. This level of moisture was found to be too low as briquettes made from the 3-4% moisture mixture appeared to not be fully compressed in the forming head and tended to fragment when ejected from the briquetter,. This mixture was then rehydrated to 7-8% moisture content and delivered to the Komarek briquetter. It was found that this level of moisture content was sufficient to produce a strong briquette.

It was found that at ~2-3% moisture content, the air-dried 70/30 coal/FHTC biomass mixture became quite hard and difficult to break apart. Because these fragments were so hard, samples of the air-dried ~1 in. fragments were included in the material conveyed to Consol Energy and in the samples subjected to drop tests conducted by GTI. Photographs of samples of the 90/10 coal/HTC and 70/30 coal/FHTC biomass briquettes produced **Briquette Analyses**: GTI submitted samples of the briquettes prepared in July to Consol Energy, Inc for evaluation and in mid-September received a report of Consol's analyses. GTI also performed drop tests with coal briquettes and fragments of the air-dried and crushed 70/30 coal/biomass mixture produced in July, 2014. GTI's research partner carried out post-testing activities that included thorough chemical and physical characterization of HTC solids, liquids, and gases produced during the July testing.

Evaluation of Online Briquettes by CONSOL: Consol Energy conducted tests on samples of coal/FHTC biomass briquettes produced in April, and July, 2014. Also, because they were difficult to break, fragments of the air-dried and crushed 70/30 coal/FHTC biomass mixture produced in July, 2014 were included in the samples sent to Consol. To promote understanding, we have compared the analyses reported by Consol for the offline briquettes produced in April, 2014 with the online briquettes and air-dried mixture produced in July, 2014. The reports submitted by Consol Energy are reproduced below in Figures 117 and 118. Graphs which show

Figure 115. Online coal/HTC biomass briquettes produced in July, 2014.

Figure 116. Fragments of ~1 in. air-dried 70/30 coal/HTC biomass produced in July, 2014.

CONSOL ENERGY

Company: GTI
Date: 4/2/2014
General Description: Offline Coal/biomass blend samples

Analysis Results		Wt %, AD Basis	Wt %, Dry Basis									BTU/lb, Dry Basis	
Lab Sample Number	Description	Residual Moisture	Volatile Matter	Ash	Fixed Carbon (by diff.)	Carbon	Hydrogen	Nitrogen	Oxygen (by diff.)	Sulfur	Chlorine	Heating Value	HGI
20145558	GTI 100% COAL	7.00	37.54	8.87	53.59	72.42	4.51	1.74	10.79	1.30	0.3715	12671	200
20145559	GTI 90/10 COAL/BIOMASS	6.94	42.45	6.91	50.64	71.47	4.82	1.57	14.07	1.16		12502	162
20145560	GTI 70/30 COAL/BIOMASS	6.60	52.03	5.84	42.13	67.48	5.01	1.32	19.43	0.92		11809	133

Tumbler Test Results	20145558	20145559	20145560
Average results of paired tests at 100 revolutions			
Coal/Biomass Blend	100%/0%	90%/10%	70%/30%
Size (inches or Tyler mesh)			
+5/8	0%	1%	11%
5/8 x 3/8	33%	62%	67%
3/8 x 1/4	17%	7%	1%
1/4 x 6 mesh	8%	4%	3%
6 mesh x 10 mesh	3%	3%	3%
10 mesh x 16 mesh	3%	3%	3%
- 16 mesh (including dust)	37%	21%	11%
Total	100%	100%	100%

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Figure 117. Consol Energy, Inc. test report for offline coal/FHTC briquettes produced in April, 2014.

CONSOL ENERGY

Company: GTI
Date: 9/12/2014
General Description: Online Coal/biomass blend samples

Analysis Results		Wt %, AD Basis	Wt %, Dry Basis								BTU/lb, Dry Basis	
Lab Sample Number	Description	Residual Moisture	Volatile Matter	Ash	Fixed Carbon (by diff.)	Carbon	Hydrogen	Nitrogen	Oxygen (by diff.)	Sulfur	Heating Value	HGI
20150253	90% COAL + 10% HTC BIOMASS BRIQUETTES	9.22	39.20	6.26	54.54	71.67	4.88	1.64	14.39	1.16	12545	202
20150254	70% COAL + 30% HTC BIOMASS BRIQUETTES	6.17	45.47	5.52	49.01	67.29	5.13	1.28	19.82	0.96	11757	104
20150255	70% COAL + 30% HTC BIOMASS AIR DRIED SAMPLE											163

Tumbler Test Results - Briquettes	20150253	20150254
Average results of paired tests at 100 revolutions		
Coal/Biomass Blend	90/10	70/30
Size (inches or Tyler mesh)		
+5/8	0%	73%
5/8 x 3/8	15%	13%
3/8 x 1/4	26%	1%
1/4 x 6 mesh	14%	2%
6 mesh x 10 mesh	6%	2%
10 mesh x 16 mesh	7%	2%
- 16 mesh (including dust)	32%	7%
Total	100%	100%

Description of Tumbler Tests

The 90/10 coal/biomass pellets were rather broken up when we received them. In order to get a better idea of degradation during handling, we prescreened the material to exclude any material less than ½". The remaining +1/2" material was then divided evenly between the two tumbler chambers.

The 70/30 coal/biomass pellets were split and tumbled as received.

The 70/30 coal/biomass irregular material was screened before and after a single tumbler run in order to show the change in the size distribution due to tumbling

Tumbler Test Results - 70% Coal + 30% HTC Biomass Air Dried Sample	20150255	
Before and After Results (see "Description of Tumbler Tests")		
	Before	After
Size (inches or Tyler mesh)		
+5/8	70%	32%
5/8 x 3/8	29%	47%
3/8 x 1/4	0%	5%
1/4 x 6 mesh	0%	4%
6 mesh x 10 mesh	0%	2%
10 mesh x 16 mesh	0%	2%
- 16 mesh (including dust)	1%	8%
Total	100%	100%

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Figure 118. Consol Energy, Inc. test report for online coal/FHTC briquettes produced in July, 2014.

similarities and differences in the briquettes produced in April and July, 2014 follow in Figures 8 through 11. The analyses were performed according to ASTM D2013, D5142, D5865, D4239, D5373, D6721, and D409 (grindability) for coal and D3402 (tumbler attrition) for coke.

Figure 119 compares the proximate and ultimate analyses carried out on samples of briquettes from April and July, 2014 and the air-dried 70/30 coal/FHTC mixture prepared in July, 2014. The analyses carried out and reported above by DRI of FHTC biomass produced in July, 2014 suggest that the FHTC biomass produced then was made under more severe conditions than earlier FHTC materials. This observation also tends to agree with the results shown in Figure 119. Inspection of this figure also shows that the 90/10 coal/FHTC biomass material has a constituency more like coal than the 70/30 coal/FHTC biomass mixtures.

Figure 120 compares tumbler tests carried out by Consol on the April, 2014 and July 2014 samples. Several observations can be made. First, the 90/10 coal/FHTC biomass briquettes made in April, 2014 appear much more robust than similar briquettes made in July, 2014. This can be attributed to the problems discussed above with regard to excessive moisture content in the 90/10 coal/FHTC biomass mixtures prepared in July, 2014 which resulted in weaker briquettes. Clearly briquettes of coal/FHTC biomass need to be maintained at ~7-8% moisture when briquetting takes place. The drop tests discussed below also support these observations. With regard to the 70/30 coal/FHTC biomass briquettes, it is also apparent that the briquettes made in July, 2014 appear to be much more robust that those prepared from FHTC biomass produced in February-April, 2013 and processed into briquettes in April, 2014. This also tends to confirm the observations that HFTC biomass produced in July 2014 was processed under greater severity (and exhibited higher strength when pelletized or briquetted) than FHTC biomass prepared in February-April, 2013. Finally, the air-dried 70/30 coal/FHTC biomass fragments also appear to be quite strong under tumbling and given that they are shards, and not smooth like briquettes, this material may offer promise as a coal substitute that would require minimal (or much simpler) preparation for use.

Figure 121 compares Hargrove grindability index (HGI) measurements for coal/FHTC biomass briquettes prepared in April, 2014 and July, 2014, along with the air-dried coal/FHTC biomass mixture prepared in July, 2014 and described above. First, as in the discussion of Figure 120, online briquettes prepared from the 90/10 coal/FHTC biomass mixture prepared in July, 2014 suffer in comparison to similar offline briquettes prepared in April, 2014 from FHTC biomass (from February-April, 2013) known to be of a lower severity than FHTC biomass prepared in July, 2014. The reasons for this apparent disparity have been discussed above. What is of more interest is that the 70/30 coal/FHTC biomass briquettes prepared in July, 2014 have a HGI value near 100 which is not far from some coals. Also, the air-dried 70/30 coal/FHTC biomass fragments appear to confirm the observations made above with respect to HGI.

Finally, Figure 122 shows high heating value (HHV) measurements for the briquettes and air dried coal/FHTC biomass blends submitted to Consol. As expected, the 90/10 coal/FHTC biomass briquettes contain ~98-99% of the energy of briquetted 100% Galatia coal. Also expected, the 70/30 coal/HTC biomass briquettes and air-dried material has less energy than coal, at about 93% of the HHV for 100% Galatia coal briquettes which suggests that the HHV of the FHTC biomass from July, 2014 (from 10,232 to 10,692 Btu/lb as reported by DRI, above), being significantly greater than that of raw loblolly pine (8,719 Btu/lb as reported by DRI, above) introduces a lesser energy penalty when mixed with coal than would be otherwise imagined.

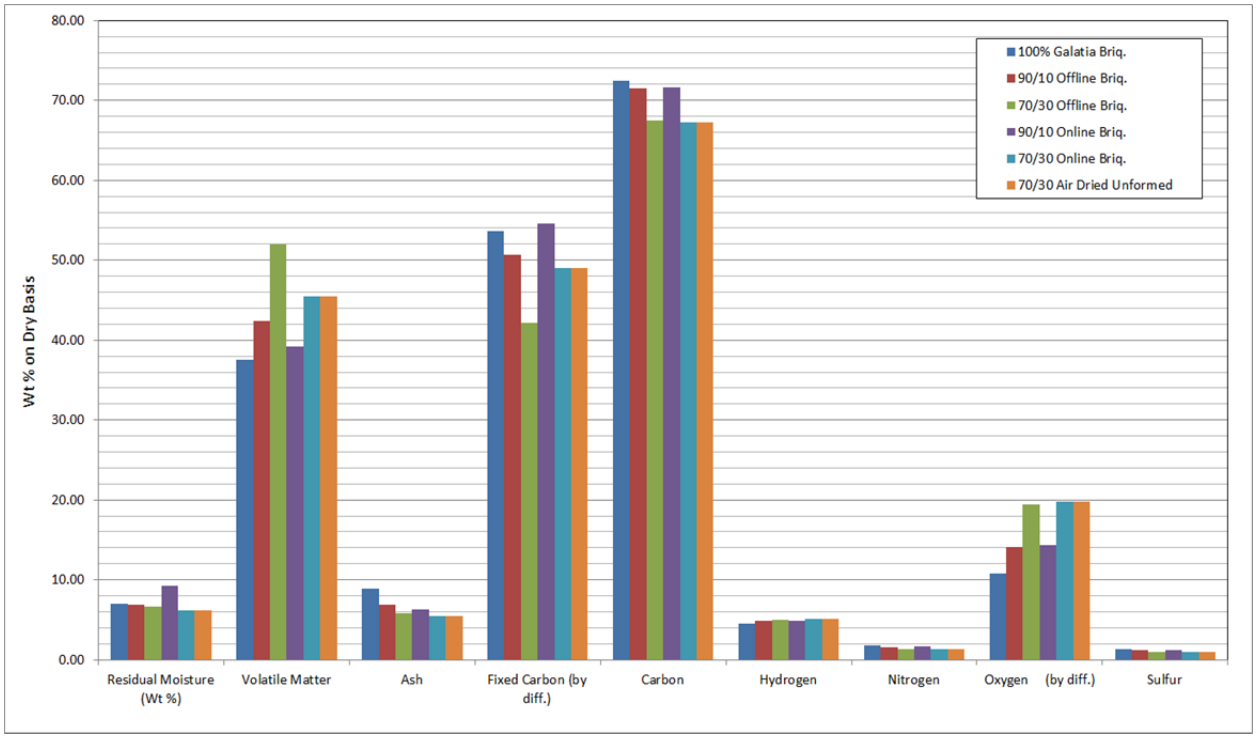


Figure 119. Comparison of proximate and ultimate analyses of coal/HTC briquettes and fragments of air-dried wet 70/30 coal/biomass mixture as reported in Figures 4 and 5.

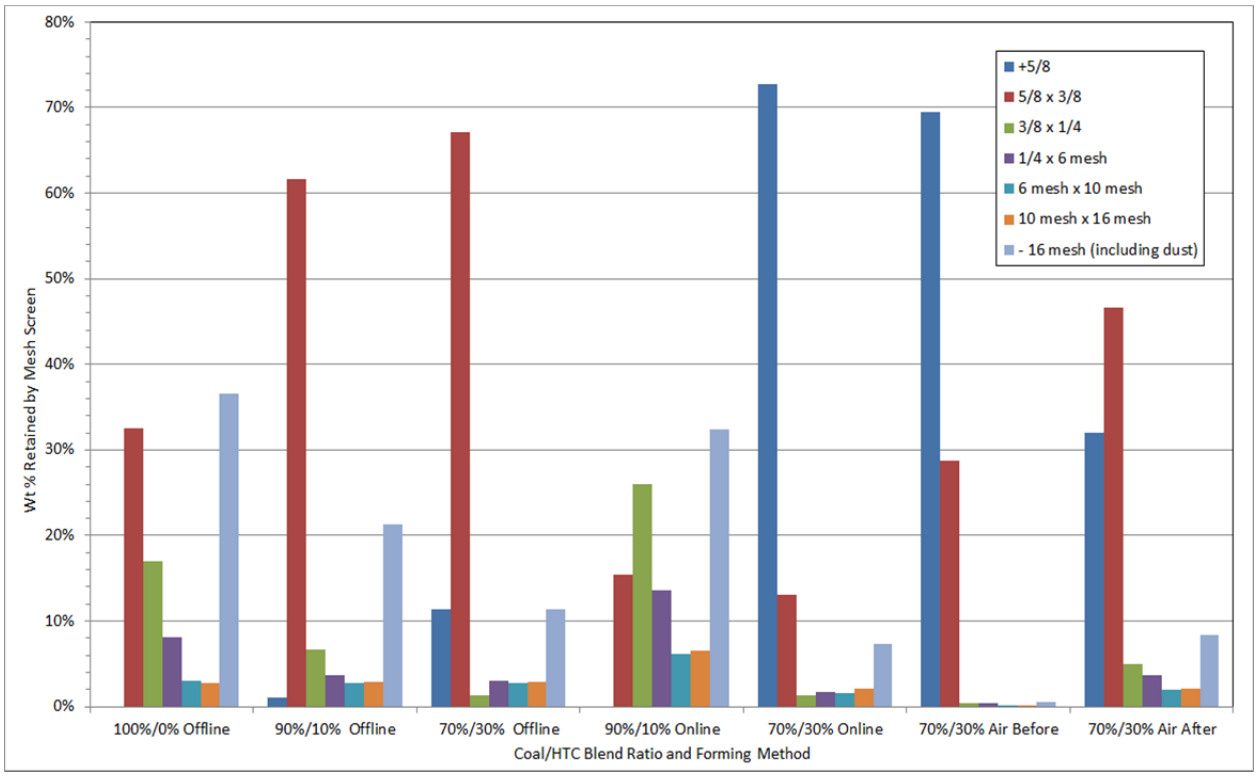


Figure 120. Comparison of sieve analyses of tumbled coal/HTC briquettes and fragments of air-dried wet 70/30 coal/biomass mixture as reported in Figures 4 and 5.

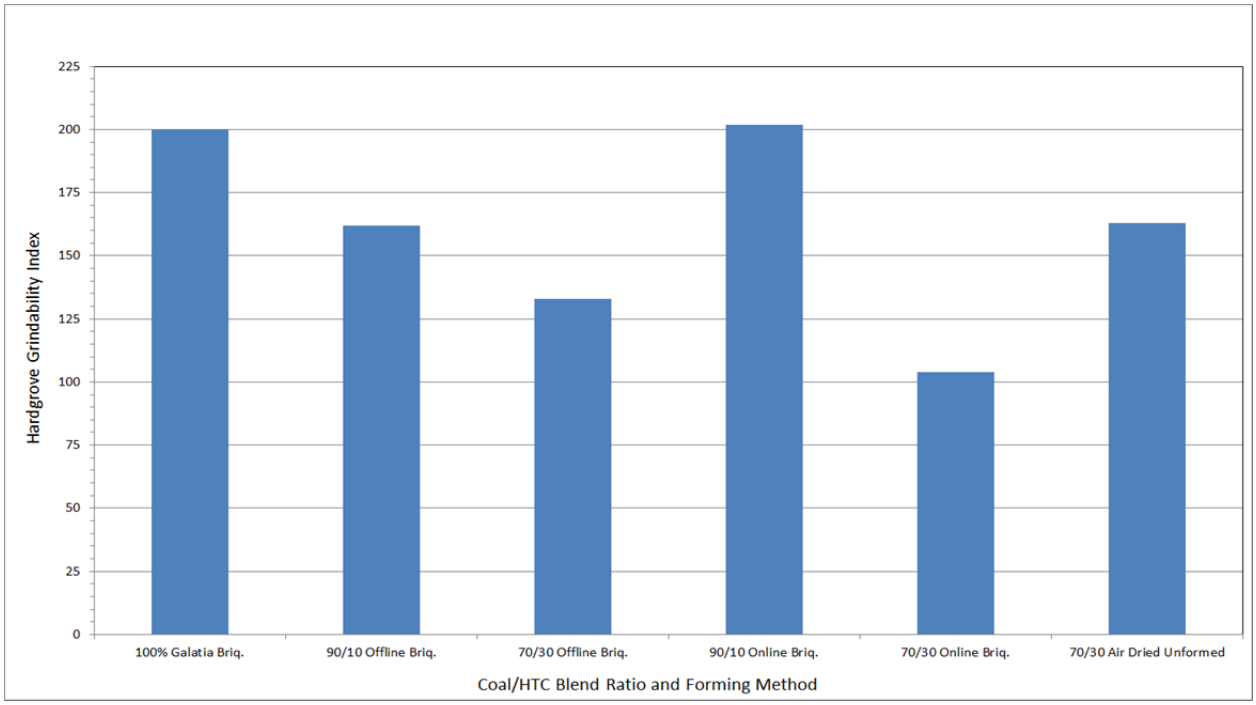


Figure 121. Hardgrove grindability index measurements for offline and online coal/HTC briquettes and fragments of air-dried wet 70/30 coal/biomass mixture.

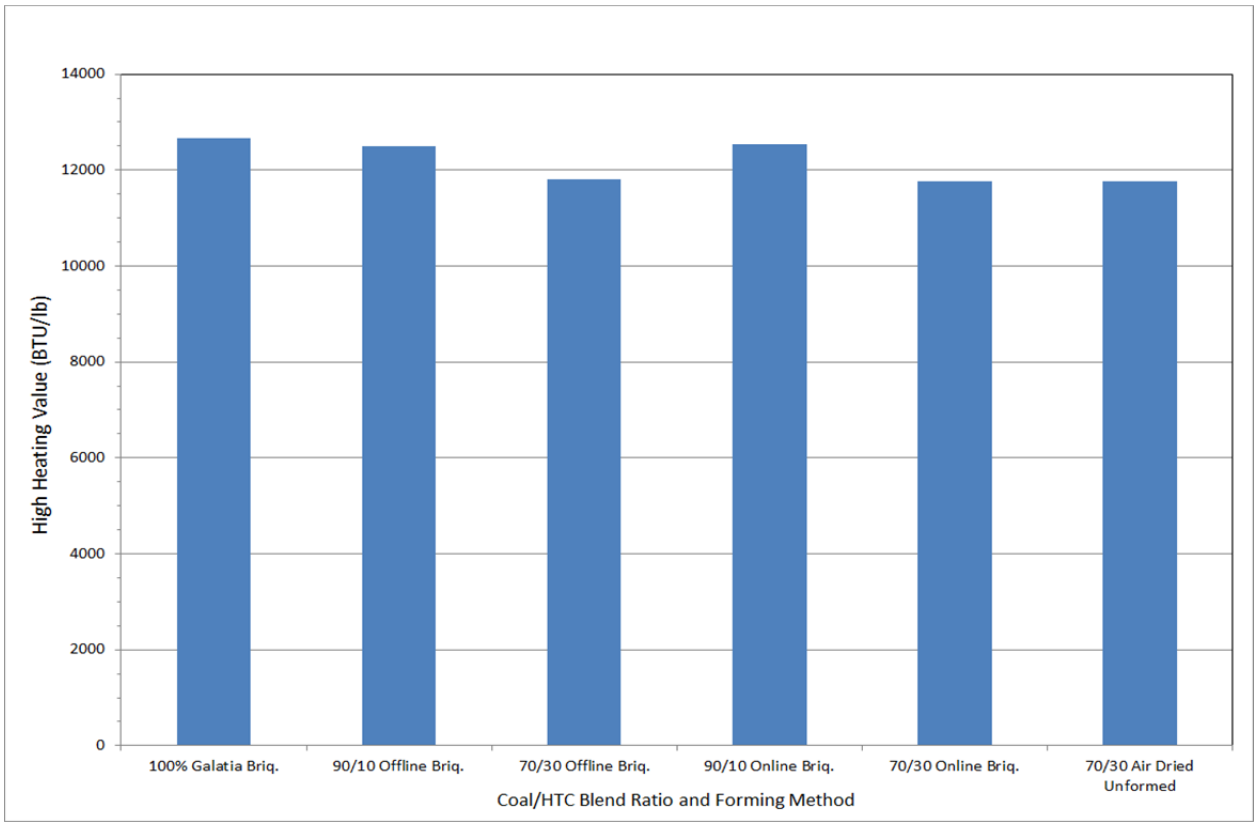


Figure 122. High heating value determinations for offline and online coal/HTC briquettes and fragments of air-dried wet 70/30 coal/biomass mixture.

Drop-Shatter Testing of Briquettes – Tests were performed by GTI using a modified version of ASTM D3038 for briquettes. Similar tests are available from Consol the ASTM standard requires a 150-lb sample, which is greater than this project could supply. In each test, 5 briquettes were individually dropped from a 72-inch height onto a glass plate. Each drop was repeated 3 times, noting fragments created after each drop. A fragment was defined as 20% of the original briquette mass while smaller pieces were removed. Results and procedural details for similar tests carried out on briquettes produced in the offline tests carried out before development of the third-generation variable-resistance, pressure-sustaining valve (VRPSV), which permitted operation of the FHTC PDU at higher levels of process severity.

As expected, briquettes made from the 70/30 online coal/FHTC biomass mix were the most rugged. After 4 drops, all five briquettes retained at least 99% of their original mass, and showed no sign of breakage. A comparison of drop-shatter results for 70/30 briquettes produced in the offline and online tests is shown in Table 39. As with the Consol tumbler tests results reported above, the ruggedness of these briquettes was substantially increased from the offline to online test series (by improvement of the FHTC PDU stability accomplished with the third-generation VRPSV and improved mixing accomplished with the automated blender/conveyor unit). In this online test series there was no breakage of 70/30 briquettes and essentially no attrition. Also, nodules resulting from drying of the 70/30 blend were subjected to this drop-shatter evaluation. With no further processing than drying, these nodules were also found to be quite rugged. Nodule mass ranged from 4 to 8 g. Only 20% the nodules experienced breakage and 98.7% of the original mass remained in useful fragments.

Table 39. Comparison of drop-shatter test results for online and offline test series. (breakage of a briquette is defined as multiple pieces containing 20% or more of the original briquette mass.)

Component	Online Test Series	Offline Test Series
Percent of Briquettes Broken	0.0%	80%
Average No. Fragments*	0.0	1
Fraction Retained of Original Mass	99.2%	76.8%

*Largest piece not included as a fragment.

As indicated above, the moisture level of 90/10 coal/FHTC biomass mix was too high (over 12%) for forming strong briquettes. Comparison of drop-shatter results for briquettes from the online tests to the offline test (carried out at 7-8% moisture) reflects the importance of maintaining optimum moisture for briquetting. For example, in the offline tests an average of 28.3% of the original briquette mass remained after 4 drops in fragments larger than 20% of its original mass while essentially no fragments were created for 90/10 coal/FHTC biomass briquettes created in the online tests.

3.2.7 Task 7: Economic Feasibility and Assessment of Environmental Impacts

Summary: Techno-economic analysis is a methodology that been widely used to provide an economic perspective for the research and development of biofuel production processes based on lignocellulosic biomass. The purpose of this study is to develop a techno-economic model for assessing the costs of mixing (co-forming) coal fines with hydrochar produced by GTI's fast hydrothermal carbonization (FHTC) process and briquetting the co-formed mixture. The briquetted product can be used as a drop-in replacement for coal in thermal applications such as a coal-fired power plant. The economic analysis presented in this report includes total capital investment, operating expenses, and minimum selling price (MSP) of a co-formed and briquetted product produced from coal fines with FHTC hydrochar. Furthermore, sensitivity analysis was also performed to discern the effect of plant size, feedstock cost, and mixing ratio of coal fines and FHTC hydrochar on the minimum selling price of the co-formed and briquetted product. Finally, we include the results of calculations that formed the basis of this TEA.

Process Overview: GTI has developed a novel fast hydrothermal carbonization process (FHTC) to convert lignocellulosic biomass into an energy-dense, solid hydrochar product that also serves as an enhanced binder for hydrochar, biomass, and coal.[53-58] The FHTC process employs a specially-modified twin screw extrusion (TSE) reactor for masticating and transporting biomass feedstocks across a robust internal pressure boundary to a downstream reactor section of the TSE to carry out reactions of HTC. Mass and energy balances of the hydrothermal carbonization reaction have been developed based on experimental findings in both batch and continuous modes of operation.[53-58] Mass and energy balances for FHTC product separation and briquetting with coal fines were modeled utilizing Aspen Plus® simulation. GTI has also consulted with knowledgeable industrial partners to develop appropriate financial estimates for known feedstocks and TSE-based HTC reactors.

The co-forming process that is the focus of this techno-economic analysis was the subject of this project (DOE Award No. DE-FE0005349) and utilizes technologies developed and validated under U.S. DOE Cooperative Agreements DE-FG36-02GO12011 and DE-FG36-01GO11082. For the development of the TSE-based FHTC process, we refer the reader to the final reports for the U.S. DOE Cooperative Agreements referred to above (DE-FG36-02GO12011 and DE-FG36-01GO11082) as well as a recently published US Patent Application.[59]

A schematic representation of fast hydrothermal carbonization process is shown in Figure 123. This reaction is carried out in a TSE reactor, which serves as both a feeder that conveys biomass across a pressure boundary, and a high-temperature, high-pressure FHTC reactor. The FHTC product comprises gases, aqueous liquids, and solid HTC biomass. Typical liquid by-products include water, acetic acid, formic acid, furfural, 5-hydroxymethyl furfural (5-HMF), along with sugars that could be further purified and become a product or suite of products in some variation of the envisioned process. Compared to the parent biomass, solid FHTC hydrochar exhibits higher energy density, hydrophobicity, and appears to be an effective binding agent.[54-58]

Techno-economic Analysis (TEA): In process economic analysis, the first step is to determine total equipment costs based on process information (mass and energy balances) resulting from Aspen Plus® simulations. The total capital investment (TCI) is then determined, based on total equipment cost.[60, 61]

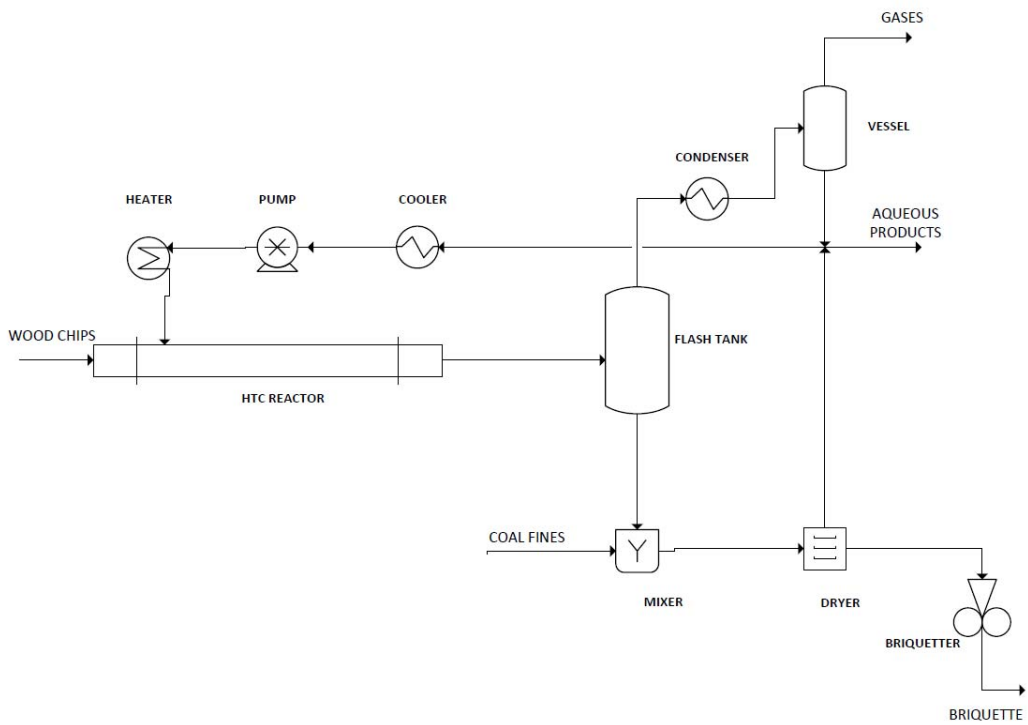


Figure 123. Process flow diagram of co-forming of coal fines with FHTC hydrochar.

In this study, the baseline plant is presumed to have the capability of processing 120 metric tons (MT) per day of woody biomass (as standard wood chips with nominal 50% moisture). This scale is chosen based on an existing commercially-available TSE reactor. The TSE reactor is capable of transporting wood chips and about half of the moisture (bound within dry biomass) across the pressure boundary that precedes the pressurized reactor. The HTC of woody biomass is carried out in the pressurized reaction zone, where a temperature of 290 °C and appropriate saturation pressure to maintain liquid water (>~1100 psia) is maintained [2-4]. At the exit of the TSE reactor, products pass through a dynamic flow restriction into the flash tank, where the discharged HTC product becomes a mixed vapor, condensate and slurry stream at ambient pressure. The vapor stream exiting the flash tank is cooled to form a non-condensable gas stream and a condensate stream predominantly water. A large percentage of this condensate is recycled to maintain HTC reactions in the TSE and the remaining portion is taken as aqueous products. Condensate that remains in the flash tank combines with solids to form an HTC slurry product. The HTC slurry stream is mixed with a coal fines stream at a desirable ratio (a ratio of coal fines to hydrochar of 90/10 or 70/30, on a dry mass basis). Then the mixed stream is dried to a moisture level appropriate for forming robust briquettes (7-9%). The coal fines/FHTC hydrochar stream exiting the dryer is fed to a briquetter to form a high-quality briquetted product. Further processing of the aqueous product stream is not addressed in this study.

In the FHTC of loblolly pine, it is found that water is produced as a co-product. In addition, biomass feedstocks contain substantial moisture. Thus, after startup, there is no need to add make-up water into the process.[56] In this analysis, product mass yield (on a dry basis of woody biomass), hydrochar, acetic acid, formic acid, lactic acid, furfural, 5-hydroxymethyl furfural,

sugar-derivatives, carbon dioxide, and water were considered to account for 71.5%, 3.3%, 1.2%, 1.5%, 1.0%, 1.5%, 14.0%, 1.5%, and 4.5%, respectively.[54-56]

The process scheme for this TEA presumes that all process solids and liquid products are consumed in producing binder for preparing coal-biomass briquettes. Gaseous emissions include renewable CO_2 (from biomass) and water vapor from drying the coal fines/HTC mixture prior to briquetting. Therefore, the environmental impacts are considered inconsequential and inherently minimized by this technology.

Total Capital Investment: All costs are projected in 2014 dollars (presuming an inflation index factor based on the Consumer Price Index, as published by the US Bureau of Labor Statistics). Equipment costs for some common equipment items (e.g. pumps, heat exchanger, direct-fired heater, vessel, mixer, dryer) are based on a variety of sources.[60-61] For specially-designed equipment items (e.g. the TSE reactor, biomass feeder, coal fines feeder, and briquetter), equipment costs were obtained from preliminary manufacturers' quotes. A typical biomass processing facility also includes biomass unloading, short-term storage, conveying, biomass drying and size reduction. The equipment cost for the feedstock handling area is greatly reduced in this process, since this process is designed to handle standard wood chips as delivered from a conventional wood pulp chipping facility. The TSE reactor includes the solids pumping device to transport feedstock across pressure boundary into the pressurized reactor zones. As a result, there is no need for a traditional high pressure feeding system (e.g. with multiple lock hoppers and inert venting or a slurry pump of powderized biomass), and biomass drying or biomass size reduction from standard chips.

The cost of equipment is usually expressed in terms of free-on-board (*f.o.b*). In this study, the economy of scale sizing exponent is applied to estimate equipment cost, depending on the kind of equipment and sometimes the size range of the equipment. Both material costs and labor costs for equipment installation are also estimated based on materials module factors and labor module factors available in Aspen Plus®. Table 40 summarizes the installed equipment costs for a plant processing 120 MT/day of standard wood chips. Other cost estimates are presented, including freight, insurance, taxes, construction overhead, and engineering expenses.

Table 40. Installed Equipment Costs (Coal Fines/Hydrochar: 90/10, on a Dry Mass Basis)

Installed Equipment	Installed Cost in 2014$
Heat exchangers	101,164
Pumps & motors	46,001
Direct-fire heater	46,031
Vessels (flash, separator)	39,709
Mixer (blender)	25,743
Dryer (rotary, direct)	43,469
HTC reactor	450,000
Coal fines feeder	100,000
Biomass feeder	100,000
Briquetter	100,000
Total	**1,052,117**

Equipment costs were developed assuming a minimum of sparing. In general, each pump has a spare, but other unit operations are designed without redundancy. To account for any miscellaneous equipment left out of the analysis, i.e. uncertainty due to the early stage of development, as well as the conceptual nature of the analysis, a contingency factor of 18% [60, 61]

is applied in the analysis for total equipment costs. Furthermore, the costs for auxiliary facilities (e.g. for brief storage of feedstock and product) are also included in total capital costs. The sum of costs described above is grassroots fixed capital costs.

Once the grassroots fixed capital cost is determined, the next step is to add working capital costs to obtain an estimate of total capital investments (TCI). Working capital costs are usually about 10% of grassroots fixed capital costs.[60,61] Table 41 summarizes each category of costs for determining the total capital investments.

Table 41. Total Capital Investments (TCI), (Coal Fines/Hydrochar: 90/10, on a Dry Mass Basis)

Categories in TCI	Cost in 2014$
Direct Costs	1,052,117
Equipment (f.o.b)	894,673
Materials for installation	78,178
Labor for installation	79,266
Indirect Costs	272,988
Freight, insurance, taxes	55,574
Construction overhead	55,486
Engineering expenses	115,928
Contingency & Fee	238,519
Auxiliary Facilities	78,181
Working Capital	164,181
Total Capital Investment	**1,805,986**

Annual Operating Expenses: In this study, operating expenses are broken into direct operating expenses, indirect operating expenses, and general expenses. Direct operating expenses are determined from feedstock expenses, operating and supervisory labor, utilities, maintenance expenses, patents and royalties.

The 2014 cost of woody feedstock used in this study is $35/MT on a wet basis (with 50% moisture), which was provided in consultation with the industrial partners in this project. For optimum reliability at the commercial-scale, the use of process pulpwood chips, sometimes described as clean chips including debarking, is planned.[62-65] A well-known market publication lists average cost in 2011 across the Southeast US for loblolly pulpwood chips from chip mills as $36 /MT with a variation of over 20% during the preceding 5 years[66] which supports the feedstock estimate assumed in this analysis of $35/MT.

Chips with 50% moisture can be used in this process and require no drying. As described above for equipment costs, the TSE reactor consumes standard wood chips, as delivered. The cost of coal fines cost used in this study is $10/MT (on a dry basis), which is estimated from the open literature.[67] Labor includes a plant manager and 9 shift operators (3 shift operators per shift). Utilities include electricity, cooling water, and natural gas. Maintenance expenses and the costs associated with patents and royalties are estimated. Indirect and general expenses are also estimated for expenses such as overhead, local taxes, insurances, and general expenses. Hence, as shown in Table 42, the total sum of expenses described above is the annual operating expense.

Table 42. Annual Operating Expenses (Coal Fines/Hydrochar: 90/10, on a Dry Mass Basis)

Categories in Annual Operating Expenses	Cost in 2014$
Direct Expenses	4,564,734
Feedstock (microchips)	1,147,680
Feedstock (coal fines)	1,674,562
By-product credits	0
Operating labor	576,000
Supervisory labor	57,600
Utilities (electricity, water, natural gas)	635,793
Maintenance & repairs	32,836
Operating supplies	3,283
Laboratory charges	28,800
Patent & royalties	84,180
Indirect & General Expenses	488,251
Overhead	332,218
Local taxes	16,418
Insurance	6,567
General expenses	132,047
Annual Operating Expenses	**5,052,985**

Minimum Selling Price of Briquettes of Blended Hydrochar & Coal Fines: In this analysis, the economic assumptions are 80% equity financing, 7% interest rate, and 15-year plant life. Annual capital charges are calculated as $158,630. Annual operating hours are 8410, and annual production costs (the sum of annual operating expenses and annual capital charges) is $5,052,985. The annual 5% profit assumed in this analysis is calculated from annual production costs.[53] Hence, the minimum selling price (MSP) of briquette is calculated and shown in Table 4. Annual briquette production is 186,062 MT (ratio of coal fines to hydrochar: 90/10, on a dry mass basis) and the annual overall cost is $ 5,472,196. The resulting minimum selling price of these briquettes is $29.4/MT, as shown in Table 43.

Table 43. Parameters for Determining Minimum Selling Price of Char (Coal Fines/Hydrochar :90/10, on a Dry Mass Basis)

Plant life	15 years
Financing	80% equity
Interest rate	7.0%
Annual capital charges	$158,630.00
Annual operating expenses	$5,052,985.00
Annual production costs	$5,211,615.00
Profit (5% on annual production costs)	$260,581.00
Annual overall costs	$5,472,196.00
Annual briquetter production	186,062 MT
Minimum selling price of char	$29.4/MT

Sensitivity Analysis of Plant Size on MSP of Coal Fines Briquettes: The overall effect of TSE reactor capacity on the minimum selling price of coal fines briquetted with FHTC hydrochar was investigated. In this study, the analysis is also performed on a plant with two large TSE reactors with a processing capacity of 360 MT/day and 2400 MT/day of standard wood chips. For briquetting, a ratio of coal fines to hydrochar is 90/10, on a dry mass basis.

Case 1: The plant is designed to process 360 MT/day of standard wood chips (at 50% moisture). A TSE reactor is installed to produce the FHTC product and all by-products are separated in a separation system. Total installed equipment costs are $1,542,967. Total capital investments are calculated as $2,670,200. Annual operating expenses are determined as $12,857,244. In this analysis, the economic assumptions are 80% equity financing, a 7% interest rate, and 15-year plant life. Annual capital charges are calculated as $234,539. Annual operating hours are 8410. The sum of annual operating expenses and annual capital charges are the annual production costs, which are $13,091,783. Annual 5% profit is presumed in this analysis and is calculated from annual production costs. Hence, the minimum selling price (MSP) of char is calculated and shown below. The annual briquette production is 558,187 MT (with the ratio of coal fines to hydrochar: 90/10, on a dry mass basis). Annual overall costs are $+13,746,372. The minimum selling price of briquette is $24.6/MT.

Case 2: The plant is designed to process 2,400 MT/day standard wood chips (at 50% moisture). A TSE reactor is installed to produce the FHTC product and all by-products are separated in a separation system. Total installed equipment costs are $3,880,076. Total capital investments are calculated as $6,788,745. Annual operating expenses are determined to be $77,727,296. In this analysis, the economic assumptions are 80% equity financing, a 7% interest rate, and 15-year plant life. Annual capital charges are calculated to be $596,294. Annual operating hours are 8410. The sum of annual operating expenses and annual capital charges comprise the annual production costs, which are $79,652,181. Annual 5% profit is presumed in this analysis and is calculated from annual production costs. Hence, the minimum selling price (MSP) of char is calculated and shown below. The annual briquette production is 3,721,248 MT (coal fines/hydrochar: 90/10, on a dry mass basis). Annual overall costs are $83,634,700. The minimum selling price of briquette is $22.5/MT.

Sensitivity Analysis of Wood Chips Cost on MSP of Briquette: Wood chips cost is a significant component of operating expenses while also being the component with greatest variability with geographical location, type of wood, type of harvesting, as well as market conditions. In this study also includes the effect of feedstock cost on the minimum selling price of briquette (coal fines/hydrochar: 90/10 and 70/30, on a dry mass basis). By consulting with industrial partner for standard wood chips cost and reviewing literature, it is reasonable to estimate the cost of standard wood chips ranging from $30/MT to $40/MT on a wet basis (with 50% moisture). Table 44 and Table 45 summarize the minimum selling price of briquette based on three wood chips costs.

Sensitivity Analysis of Coal Fines Cost on MSP of Briquette: The cost of coal fines is another significant component of operating expense and is the component with greatest variability over geographical location, type of coal mine, type of harvesting, as well as market conditions. In this study we also include the effect of coal fine cost on the minimum selling price of briquettes (the ratio of coal fines to hydrochar: 90/10 and 70/30, on a dry mass basis). By consulting with industrial partner for coal fines and reviewing pertinent literature, it is reasonable to estimate the cost of coal fines cost ranging from $10/MT to $30/MT on a dry basis. Table 46 and Table 47 summarize the minimum selling price of briquette based on three coal fines costs.

Table 44. Minimum Selling Price[1] (MSP/MT) of Briquettes Based on Various Feedstock Costs (Coal Fines @ $10/MT, on a Dry Basis, Mixing Ratio: 90% Coal Fines/10% Hydrochar)

Wood chips[2] cost/MT	MSP/MT of briquette 120 MT/day	MSP/MT of briquette 360 MT/day	MSP/MT of briquette 2,400 ton/day
$30	$28.2	$23.4	$21.2
$35	$29.4	$24.6	$22.5
$40	$30.6	$25.9	$23.7

1. 2014 $
2. 50% moisture

Table 45. Minimum Selling Price[1] (MSP/MT) of Briquettes Based on Various Feedstock Costs (Coal Fines @ $10/MT, on a Dry Basis, Mixing Ratio: 70% Coal Fines/30% Hydrochar)

Wood chips[2] cost/MT	MSP/MT of briquette 120 MT/day	MSP/MT of briquette 360 MT/day	MSP/MT of briquette 2,400 ton/day
$30	$63.2	$48.9	$42.4
$35	$66.9	$52.6	$46.1
$40	$70.6	$56.3	$49.8

1. 2014 $
2. 50% moisture

Table 46. Minimum Selling Price [1] (MSP/MT) of Briquettes Based on Three Coal Fines Costs (Wood Chips[2] @ $35/MT, Mixing Ratio: 90% Coal Fines/10% Hydrochar)

Coal fines cost/MT (dry basis)	MSP/MT of briquette 120 MT/day	MSP/MT of briquette 360 MT/day	MSP/MT of briquette 2,400 MT/day
$10	$29.4	$24.6	$22.5
$20	$40.2	$34.2	$32.0
$30	$49.7	$43.7	$41.6

1. 2014 $
2. 50% moisture

Table 47. Minimum Selling Price [1] (MSP/MT) of Briquettes Based on Three Coal Fines Costs (Wood Chips[2] @ $35/MT, Mixing Ratio: 70% Coal Fines/30% Hydrochar)

Coal fines cost/MT (dry basis)	MSP/MT of briquette 120 MT/day	MSP/MT of briquette 360 MT/day	MSP/MT of briquette 2,400 MT/day
$10	$66.9	$52.6	$46.1
$20	$74.3	$60.0	$53.6
$30	$81.8	$67.4	$61.0

1. 2014 $
2. 50% moisture

Sensitivity Analysis of Mixing Ratio on MSP of Briquettes: Hydrochar cost is another significant component of operating expense and capital investment. Thus, mixing ratio of coal fines and hydrochar from FHTC process can have a great impact on the minimum selling price of briquette. Table 48 summarizes the minimum selling price of briquette based on two mixing ratio of coal fines and FHTC hydrochar.

Table 48. Minimum Selling Price[1] (MSP/MT) of Briquettes Based on Two Mixing Ratios of Coal Fines and FHTC hydrochar (Wood Chips[2] @ $35/MT, Coal Fines @ $10/MT, Dry Basis)

Mixing ratio (coal fines/hydrochar)	MSP/MT of briquette 120 MT/day	MSP/MT of briquette 360 MT/day	MSP/MT of briquette 2,400 MT/day
90/10	$29.4	$24.6	$22.5
70/30	$66.9	$52.6	$46.1

1. 2014 $
2. 50% moisture

Energy Costs (MSP/GJ): **S**tandard ASTM measurements of heating values for blend briquettes from Galatia coal yield a HHV of 29.2 (90/10 blend) and 27.3 (70/30 blend) MJ/kg (see CONSOL data for July, 2014 Galatia coal analyses, Figure 117). Costs of coal fine/FHTC hydrochar briquetted fuels in terms of heating values (MSP/GJ) from Table 48 are presented in Table 49 adjusted based on the assumption that the heating value of coal fines are 75% of Galatia heating value.

Table 49. Minimum Selling Price[1] (MSP/GJ) of Briquettes Based on Two Mixing Ratios of coal fines and FHTC hydrochar (wood chips[2] @ $35/MT, coal fines @ $10/MT, dry basis)

Mixing ratio (coal fines/hydrochar)	MSP/GJ of briquettes 120 MT/day	MSP/GJ of briquettes 360 MT/day	MSP/GJ of briquettes 2,400 MT/day
90/10	$1.34	$1.12	$1.03
70/30	$3.26	$2.56	$2.25

1. 2014 $
2. 50% moisture

TEA - Conclusions: This techno-economic study estimates the cost of producing briquettes of coal fines and FHTC hydrochar and is based on a single plant processing 120 MT/day of standard wood chips, into FHTC hydrochar which is mixed with coal fines and briquetted (coal fines/hydrochar mixing at 90/10 at a dry mass basis). This produces briquettes at a minimum selling price (MSP) of $29.4/MT. The annual briquette production is 186,062 MT and the total capital investments are estimated to be $1.8 million (2014 dollars).

If a larger HTC reactor system is installed to process 2,400 MT/day standard wood chips, briquettes can be produced using coal fines and FHTC hydrochar mixture (coal fines/hydrochar mixing at 90/10 on a dry mass basis) at a MSP of $22.5/MT. Likewise, for coal fines/hydrochar mixing at 70/30 on a dry mass basis, the MSP is $46.1/MT. In this case, the annual briquette production is 3,721,248 MT. The total capital investments are estimated to be $6.8 million.

At this price, the benefits of CO_2, SO_2, and NO_X reductions gained by choosing this blend must be factored in to process economics and the decision would be made more clear if there was a legislative incentive for utilizing biomass renewable energy and a similar legislative incentive for reducing CO_2 emissions.

Before the first commercial plant is built, various technical challenges are likely. Future techno-economic studies could shed light on advantages and disadvantages of different process design and assumptions. Results provided in this study can serve as the baseline for future comparison.

Calculations: In process economic analysis, the first step is to determine total equipment costs based on process information (mass and energy balances) resulting from Aspen Plus® simulations. The mass and energy balances used for calculations in this TEA are derived from the mass and energy balances determined from testing of the GTI FHTC PDU carried out in July, 2104. This approach forms the best possible information base we can provide as it is derived from measurements made on a FHTC process carried out with an instrumented TSE. In the Appendix, the process scheme for this simulation is presented with baseline values shown for each parameter of the process. Then, in the pages that follow, discrete process values for a 120 Metric Ton/day Aspen Plus® simulation for a 90% coal fines, 10% FHTC biomass, plant processing nominal 50% moisture Loblolly Pine Wood into briquettes.

3.5 Conclusions and Recommendations

The overall goal of the work performed in this project is to demonstrate and assess the technical and economic viability of continuous fast, hydrothermal carbonization (FHTC) for transforming lignocellulosic biomass into a densified, friable fuel that gasifies like lignite coal but that can be easily blended with ground coal and/or coal fines and formed and into robust, weather-resistant pellets and briquettes without the need of an external binding agent. For this work, FHTC biomass (loblolly pine) specifically refers to biomass that has been subjected to continuous, rapid hydrothermal carbonization in a specially-modified twin-screw extruder with internal processing times of less than 1 minute. This novel method of hydrothermally carbonizing biomass is the subject of ongoing patent applications, one of which has been published.[50]

When a woody biomass such as loblolly pine is hydrothermally carbonized in a batch process (e.g., a Parr reactor), the resulting energy-dense product has been found to form durable, waterproof pellets.[68-70] When HTC biomass is mixed with finely-divided coal, it has also been found to be easily pelletized and form durable, waterproof pellets, as shown in Section 3.2.2 of this report. However, for this project it was necessary to establish that FHTC biomass possesses the same propensity for forming durable, water-resistant pellets as HTC biomass because it is not obvious that a rapid process (< 1 min.) produces a product that is equivalent to that produced in a much longer batch process (hours, for HTC biomass from a Parr reactor). Table 26 and Figure 88 of this report show that pelletized FHTC loblolly pine hydrochar is essentially indistinguishable from pelletized HTC loblolly pine hydrochar and that the concept of process severity permits a direct comparison of HTC and FHTC biomass. Indeed, there are only two discernable differences between FHTC and HTC processes which are most likely due to differences in process kinetics. First, the FHTC process tends to produce significantly more 5-HMF than furfural whereas the HTC process produces much more furfural than 5-HMF. Process kinetics are thought to be responsible because furfural is a decomposition product of 5-HMF and in the rapid FHTC process, 5-HMF may not have time to decompose into furfural. Second, the organic acid profiles of HTC biomass are dominated by acetic acid, although the FHTC liquids appear to have slightly lesser amounts of acetic acid and slightly greater amounts of lactic acid. While these findings were not pursued in this project as the focus was on briquetting, 5-HMF is a valuable chemical byproduct that is easily recovered by fractional distillation. The authors suspect that a techno-economic analysis of an FHTC process that included the production of 5-HMF would benefit from including 5-HMF production.

With the determination that HTC and FHTC biomass are equivalent as far as pelletization (or briquetting) are concerned, subsequent project activities focused on briquetting and characterizing briquettes prepared from two blends of pulverized coal and FHTC biomass. One blend was composed of 90% coal and 10% FHTC biomass ("90/10 blend") and a second blend was composed of 70% coal and 30% FHTC biomass ("70/30 blend"). Two sets of the two blends were prepared. One ("offline") set was prepared from pulverized Galatia coal and FHTC that had been stored after production. The offline set therefore represents a case where FHTC biomass is generated and stored before being mixed with coal. The second ("online) set was prepared from fresh FHTC biomass that was produced and mixed with pulverized Galatia coal in a heated blender/conveyor that was specifically designed to be interfaced with the FHTC PDU. Both sets of blends were briquetted using a Komarek, Inc. B100QC briquetting machine leased for this purpose and characterized for composition, strength, and fracture resistance by CONSOL ENERGY, Inc. and for fracture resistance by drop tests at GTI's Birmingham, AL facilities.

The primary result of the briquetting effort (with either set of blends) was that moisture level of any coal/FHTC biomass blend directly affected briquette strength and durability. Moisture levels of ~7% appear to be optimal for making robust coal/FHTC briquettes. As might be expected, the second most important result is that a 90/10 blend (of either set) is more fragile than a 70/30 blend (of either set). In fact, the 70/30 blend of FHTC produced in July 2014 was found to be quite robust, resisting fracture when dropped from a height of 72 in. onto a thick glass plate multiple times. This suggests that an 80/20 blend (of either set) would be sufficiently robust to withstand the rigors of shipping and handling. Also, all of these briquettes were prepared in small batches (~50 lb./batch maximum). With extended operation, the briquetter tended to become very hot (~150°F) and while because of cost constraints large amounts of briquettes could not be prepared with a hot briquetter, we believe that higher briquetting temperatures would increase briquette strength and durability due to better bonding of the polymers in FHTC with finely-divided coal.

Finally, because the FHTC process densifies biomass and renders it into a readily pelletizable, coal-like fuel, the thermal energy available in briquettes made of mixtures of coal and FHTC biomass was found to approach that of 100% coal. For example, briquetted Galatia coal was measured to have a thermal energy of 12,671 Btu/lb. (dry basis), whereas, for briquetted blends of Galatia coal and FHTC loblolly pine, briquettes of 90wt. % Galatia coal and 10% FHTC loblolly pine contained 12,545 Btu/lb. (dry basis) or *99% of the energy available in coal* and briquettes of 70wt. % Galatia coal and 30% FHTC loblolly pine contained 11,757 Btu/lb. (dry basis) or *93% of the energy available in coal*.

With respect to process economics, an Aspen Plus® simulation was carried out that provided a minimum selling price (MSP) for both conservative and aggressive cases. In the conservative case, the MSP was determined for producing briquettes of coal fines and FHTC hydrochar based on a single plant processing 120 metric tons (MT)/day of standard wood chips into FHTC hydrochar which is then mixed with coal fines and briquetted (coal fines/hydrochar mixing at 90/10 at a dry mass basis). This case produces briquettes at a MSP of $29.4/MT with an annual briquette production of 186,062 MT and the total capital investments are estimated to be $1.8 million (2014 dollars). Likewise, for coal fines/hydrochar mixed at 70/30 on a dry mass basis, at this level of production, the MSP is $66.9/MT, at too high a price .

In the aggressive case, a large HTC reactor system is installed to process 2,400 MT/day standard wood chips, and at this level, briquettes can be produced using coal fines and FHTC hydrochar mixture (coal fines/hydrochar mixing at 90/10 on a dry mass basis) at a MSP of $22.5/MT. Likewise, for coal fines/hydrochar mixed at 70/30 on a dry mass basis, the MSP is $46.1/MT. In this case, the annual briquette production is 3,721,248 MT. The total capital investments are estimated to be $6.8 million.

At these prices, the benefits of CO_2, SO_2, and NO_X reductions gained by choosing this blend must be factored in to process economics and the decision would be made clearer if there was a legislative incentive for utilizing biomass renewable energy and a similar legislative incentive for reducing CO_2 emissions.

In summary, the primary goals of this project have been achieved. Technically, FHTC biomass is an infrastructure compatible approach for integrating a renewable component into fossil-fuel power generation. Process economics would be aided, however by a legislative requirement for reducing fossil CO_2 emissions and introducing a renewable component into coal-based power.

Recommendations for Future Work: As with any complex R&D effort, the work carried out under this project, and the findings that were obtained lead to several suggestions for further work. Among the most significant findings were that many similarities were observed in the HTC processing of woody biomass over a range of four different reactor systems: (1) DRI's small 2-chamber reactor, (2) a 2-L stirred Parr reactor, (3) DRI's auger-driven PDU, and (4) GTI's TSE-based FHTC PDU. Yet, some differences were found, such as lower yields of 5-HMF from the FHTC PDU, perhaps due to the much shorter reaction time in this system. Within the limits of satisfactory FHTC operation, it would be useful to vary reaction time, and to optimize this parameter with respect to product yields and characteristics.

Additional work should be undertaken to assess the mass balance of the FHTC operation. In this project, higher mass balances were calculated when using composite slurry mass accumulated over an entire day's run, as compared to calculations based upon short (2-min.) sample collection periods. It is believed that these differences are due in part to different slurry moisture levels measured in the different samples. However, this issue should be investigated in greater detail.

The product flashing step that occurs during operation of the FHTC PDU presents an opportunity to recover valuable volatile organic products that are condensed along with water. Two particular products of interest are furfural and acetic acid. With the aid of techno-economic analysis (TEA), further work should be undertaken to assess the feasibility of recovering these volatile organic products in sufficient yield and acceptable purity, and to estimate the economic impact of such recovery.

The issue of water recycling within the FHTC PDU requires further study. In this project, all water inputs to the PDU were "once through." However, in commercial operations, it would be desirable to capture and recycle at least some of the produced water. Further work is required to determine whether the condensate from the FHTC process could be recycled directly, or require some level of clean-up before it is acceptable. Similarly, additional work is needed to determine the degree to which the process water (condensate) must be cleaned up before it can be safely disposed.

The FHTC work conducted in this project utilized a single woody feedstock, Loblolly Pine. Further work should be done to demonstrate the applicability of this system for other feedstocks – including agricultural residues, organic fractions from MSW, wastewater sludge, and algae. In addition, mixtures of feedstocks are of interest.

Additional work is needed to investigate the fuel properties of the hydrochar products, and blends of these products with coal, torrefied woods, and other materials. While some useful information can be derived from analytical techniques such as thermal gravimetric analysis (TGA), larger scale experiments in instrumented combustion and gasification testing systems should be conducted. Such evaluations may require production of large quantities of test materials.

The potential use of hydrochar as a carbon sequestering soil amendment continues to be of interest. With use of the FHTC PDU, sufficient quantities of hydrochar could be produced to investigate this at a meaningful scale. Both directly-produced hydrochar slurry and water-washed slurry are of interest. These two char materials may be quite different in soil applications, as up to 20% of the total slurry mass can be removed by water washing.

Finally, there are two recommendations for improvements in analytical methodologies used for analysis of sugars. First, the HPCL-RI method currently being used should be modified to improve the resolution of certain sugar species of interest that co-elute. Efforts are underway to explore different HPCL columns and operating conditions to affect this improvement. Second, the current sugar analysis method is only applicable to "free sugars," not "potential sugars" that exist in the form of oligosaccharides. It is known that considerable amounts of water-soluble oligosaccharides are produced by HTC treatment, particularly under mild conditions – as evidenced by high NVR content. To determine the potential sugar content of these materials requires an additional analytical step whereby the oligosaccharides are hydrolyzed to produce free sugars prior to HPCL-RI analysis.

3.5 Publications and Presentations

Throughout the course of this project, two manuscripts were prepared for publication. There are also plans to prepare one or two additional manuscripts. The first manuscript describes the design, fabrication, and operation of DRI's PDU. A citation for this paper is as follows:

S.K. Hoekman, A. Broch, C. Robbins, R. Purcell, B. Zielinska, L. Felix, and J. Irvin. *Process development unit (PDU) for hydrothermal carbonization (HTC) of lignocellulosic biomass*. Waste Biomass Valor. 5, 669-678 (2014). Doi: 10.1007/s12649-013-9277-0.[32]

A second manuscript has been prepared and submitted, and is now accepted for publication. This paper, which describes the procedures and results from laboratory pelletization of hydrochar. A citation for this paper is as follows:

S.K. Hoekman, A. Broch, A. Warren, L. Felix, and J. Irvin. *Laboratory pelletization of hydrochar from woody biomass*. Biofuels, in press (2015). [68]

In addition, several presentations of this research have been made at technical conferences. Three of these are listed below:

- S.K. Hoekman, A. Broch, A. Warren, L. Felix, and G. Coble, *Waterproof Wood Pellets via Hydrothermal Carbonization (HTC)*. Energy, Utility and Environment Conference, Phoenix, AZ, February 3-5, 2014.[69]
- S.K. Hoekman, A. Broch, U. Jena, C. Robbins, L. Felix, and W. Yan, *Hydrothermal Carbonization (HTC) of Agricultural Residues and Other Biomass*, 247th American Chemical Society National Meeting, Dallas, TX, March 16-20, 2014.
- A. Broch, S.K. Hoekman, A. Warren, L. Felix, and G. Coble, *Waterproof Wood Pellets via Hydrothermal Carbonization (HTC)*, International Biomass Conference, Orlando, FL, March 25-26, 2014. [70]

The latest presentation at the International Biomass Conference in Orlando, FL, was also the basis of a webinar presentation given by Amber Broch of DRI as part of a live webinar organized by BBI International. This webinar, which occurred on July 31, 2014, had approximately 350 participants.

3.6 References

1. Agar, D. and M. Wihersaari; Torrefaction Technology for Solid Fuel Production. *Global Change Biology,* 1-4. 2011.
2. Uslu, A., A. P. C. Faaij, and P. C. A. Bergman; Pre-Treatment Technologies, and Their Effect on International Bioenergy Supply Chain Logistics. Techno-Economic Evaluation of Torrefaction, Fast Pyrolysis and Pelletisation. *Energy,* 33, 1206-1223. 2008.
3. Acharya, B., I. Sule, and A. Dutta; A Review on Advances of Torrefaction Technologies for Biomass Processing. *Biomass Conversion and Biorefinery,* 2, 349-369. 2012.
4. Bobleter, O.; Hydrothermal Degradation of Polymers Derived From Plants. *Progress in Polymer Science,* 19, (5), 797-841. 1994.
5. Funke, A. and F. Ziegler; Hydrothermal Carbonization of Biomass: A Literature Survey Focussing on its Technical Application and Prospects. *Proceedings of the 17th European Biomass Conference, Technische Universitat Berlin, Institute of Energy Engineering, Hamburg, Germany, 29 June - 3 July, 2009*, 17th European Biomass Conference and Exhibition, Hamburg, Germany 2009.
6. Funke, A. and F. Ziegler; Hydrothermal Carbonization of Biomass: A Summary and Discussion of Chemical Mechanisms for Process Engineering. *Biofuels Bioproducts & Biorefining,* 4, 160-177. 2010.
7. Peterson, A. A., F. Vogel, R. P. Lachance, M. Froling, M. J. Antal, and J. W. Tester; Thermochemical Biofuel Production in Hydrothermal Media: A Review of Sub- and Supercritical Water Technologies. *Energy Environ.Sci.,* 1, 32-65. 2008.
8. Yu, Y., X. Lou, and H. Wu; Some Recent Advances in Hydrolysis of Biomass in Hot-Compressed Water and Its Comparisons With Other Hydrolysis Methods. *Energy & Fuels,* 22, 46-60. 2008.
9. Yan, W., T. C. Acharjee, C. J. Coronella, and V. R. Vasquez; Thermal Pretreatment of Lignocellulosic Biomass. *Environ.Progress & Sustainable Energy,* 28, (3), 435-440. 2009.
10. Yan, W., J. T. Hastings, T. C. Acharjee, C. J. Coronella, and V. R. Vasquez; Mass and Energy Balances of Wet Torrefaction of Lignocellulosic Biomass. *Energy & Fuels,* 24, (9), 4738-4742. 2010.
11. Libra, J. A., K. S. Ro, C. Kammann, A. Funke, N. D. Berge, Y. Neubauer, M.-M. Titirici, C. Fuhner, O. Bens, K. Jurgen, and B. Emonts; Hydrothermal Carbonization of Biomass Residuals: A Comparative Review of the Chemistry, Processes and Applications of Wet and Dry Pyrolysis. *Biofuels,* 2, (1), 89-124. 2011.
12. Titirici, M. M. and M. Antonietti; Chemistry and Materials Options of Sustainable Carbon Materials Made by Hydrothermal Carbonization. *Chemical Society Reviews,* 39, 103-116. 2010.
13. Hu, B., K. Wang, L. Wu, S.-H. Yu, M. Antonietti, and M.-M. Titirici; Engineering Carbon Materials From the Hydrothermal Carbonization Process of Biomass. *Advanced Materials,* 22, 813-828. 2010.
14. Liu, Z. and F.-S. Zhang; Removal of Lead From Water Using Biochars Prepared From Hydrothermal Liquefaction of Biomass. *J.Hazardous Materials,* 167, 933-939. 2009.
15. Mochidzuki, K., N. Sato, and A. Sakoda; Production and Characterization of Carbonaceous Adsorbents From Biomass Wastes by Aqueous Phase Carbonization. *Adsorption,* 11, 669-673. 2005.
16. Titirici, M.-M., A. Thomas, and M. Antonietti; Back in the Black: Hydrothermal Carbonization of Plant Material As an Efficient Chemical Process to Treat the CO2 Problem? *New Journal of Chemistry,* 31, 787-789. 2007.

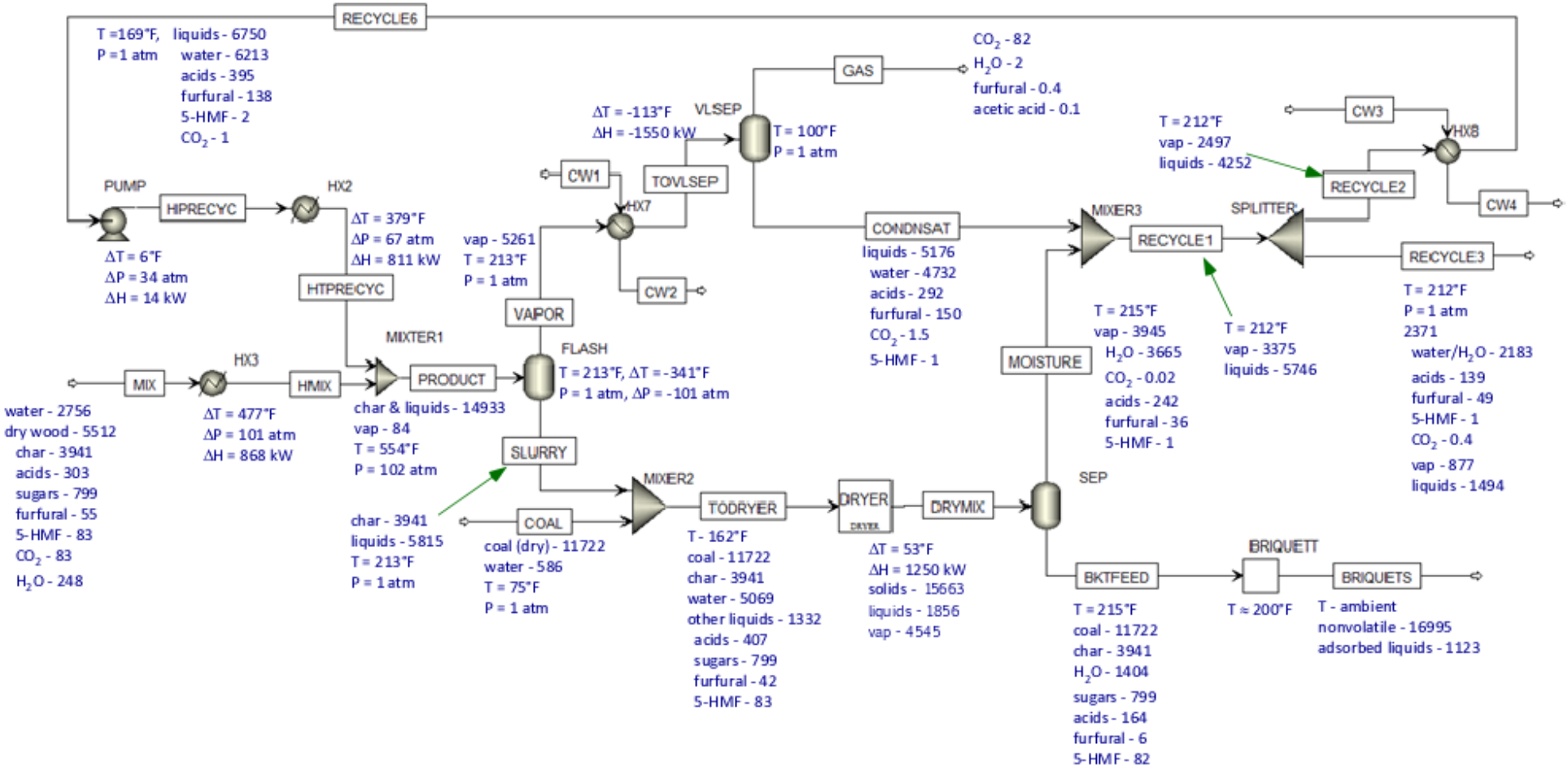
17. Lehmann, J., J. Gaunt, and M. Rondon; Bio-Char Sequestration in Terrestrial Ecosystems - A Review. *Mitigation and Adaptation Strategies for Global Change,* 11, 403-427. 2006.
18. Fowles, M.; Black Carbon Sequestration As an Alternative to Bioenergy. *Biomass & Bioenergy,* 31, 426-432. 2007.
19. Glaser, B., J. Lehmann, and W. Zech; Ameliorating Physical and Chemical Properties of Highly Weathered Soils in the Tropics With Charcoal - a Review. *Biol Fertil Soils,* 35, 219-230. 2002.
20. Kleinert, M. and T. Wittman; Carbonisation of Biomass Using a Hydrothermal Approach: State-of-the-Art and Recent Developments. *Proceedings of the 17th European Biomass Conference*, 17th European Biomass Conference and Exhibition, Hamburg, Germany 1683-1687. 2009.
21. Kobayashi, N., N. Okada, A. Hirakawa, T. Sato, J. Kobayashi, S. Hatano, Y. Itaya, and S. Mori; Characteristics of Solid Residues Obtained From Hot-Compressed-Water Treatment of Woody Biomass. *Industrial & Engineering Chemistry Research,* 48, (1), 373-379. 2009.
22. Agar, D. and M. Wihersaari; Torrefaction Technology for Solid Fuel Production. *Global Change Biology,* 1-4. 2011.
23. Acharya, B., I. Sule, and A. Dutta; A Review on Advances of Torrefaction Technologies for Biomass Processing. *Biomass Conversion and Biorefinery,* 2, 349-369. 2012.
24. Uslu, A., A. P. C. Faaij, and P. C. A. Bergman; Pre-Treatment Technologies, and Their Effect on International Bioenergy Supply Chain Logistics. Techno-Economic Evaluation of Torrefaction, Fast Pyrolysis and Pelletisation. *Energy,* 33, 1206-1223. 2008.
25. Ciolkosz, D. and R. Wallace; A Review of Torrefaction for Bioenergy Feedstock Production. *Biofuels Bioproducts & Biorefining,* 5, 317-329. 2011.
26. Tumuluru, J.S., C.T. Wright, K.L. Kenney, and J.R. Hess; A Technical Review on Biomass Processing: Densification, Preprocessing, Modeling, and Optimization. 2010 ASABE Annual International Meeting 2010.
27. Tumuluru, J., S. Sokhansanj, C. Wright, J. Hess, and R. Boardman; A Review on Biomass Torrefaction Process and Product Properties. INL/CON-11-22634, Idaho National Laboratory, 2011.
28. Stelte, W., J. K. Holm, A. R. Sanadi, S. Barsberg, J. Ahrenfeldt, and U. B. Henriksen; A Study of Bonding and Failure Mechanisms in Fuel Pellets From Different Biomass Resources. *Biomass & Bioenergy,* 35, (2), 910-918. 2011.
29. Shang, L., N. P. Nielsen, J. Dahl, W. Stelte, J. Ahrenfeldt, J. K. Holm, T. Thomsen, and U. B. Henriksen; Quality Effects Caused by Torrefaction of Pellets Made From Scots Pine. *Fuel Processing Technology,* 101, 23-28. 2012.
30. Reza, M. T., J. G. Lynam, V. R. Vasquez, and C. J. Coronella; Pelletization of Biochar From Hydrothermally Carbonized Wood. *Environmental Progress & Sustainable Energy,* 31, 225-234. 2012.
31. Reza, M. T., M. H. Uddin, J. G. Lynam, and C. J. Coronella; Engineered Pellets From Dry Torrefied and HTC Biochar Blends. *Biomass and Bioenergy,* 63, 229-238. 2014.
32. Hoekman, S. K., A. Broch, C. Robbins, R. Purcell, B. Zielinska, L. Felix, and J. Irvin; Process Development Unit (PDU) for Hydrothermal Carbonization (HTC) of Lignocellulosic Biomass. *Waste Biomass Valor,* 5, 669-678. 2014.
33. Kaliyan, N. and R. V. Morey; Factors Affecting Strength and Durability of Densified Biomass Products. *Biomass & Bioenergy,* 33, (3), 337-359. 2009.
34. Obernberger, I. and G. Thek; The Pellet Handbook. The Production and Thermal Utilization of Pellets. Earthscan, 2010.

35. Gilbert, P., C. Ryu, V. Sharifi, and J. Swithenbank; Effect of Process Parameters on Pelletisation of Herbaceous Crops. *Fuel,* 88, (8), 1491-1497. 2009.
36. Stelte, W., A. R. Sanadi, L. Shang, J. K. Holm, J. Ahrenfeldt, and U. B. Henriksen; Recent Developments in Biomass Pelletization - A Review. *BioResources,* 7, (3), 4451-4490. 2012.
37. Misljenovic, N., QV. Bach, K.-Q. Tran, C. Salas-Bringas, and O. Skreiberg; Torrefaction Influence on Pelletability and Pellet Quality of Norwegian Forest Residues. *Energy & Fuels,* 28, 2554-2561. 2014.
38. Hoekman, S. K., A. Broch, and C. Robbins; Hydrothermal Carbonization (HTC) of Lignocellulosic Biomass. *Energy & Fuels,* 25, 1802-1810. 2011.
39. Hoekman, S. K., A. Broch, C. Robbins, B. Zielinska, and L. G. Felix; Hydrothermal Carbonization (HTC) of Selected Woody and Herbaceous Biomass Feedstocks. *Biomass Conversion and Biorefinery,* 3, 113-126. 2013.
40. Gil, M. V., P. Oulego, M. D. Casal, C. Pevida, J. J. Pis, and F. Rubiera; Mechanical Durability and Combustion Characteristics of Pellets From Biomass Blends. *Bioresource Technology,* 101, (22), 8859-8867. 2010.
41. Shang, L., N. P. K. Nielsen, W. Stelte, J. Dahl, J. Ahrenfeldt, J. K. Kolm, M. P. Arnavat, L. S. Bach, and U. B. Henriksen; Lab and Bench-Scale Pelletization of Torrefied Wood Chips-Process Optimization and Pellet Quality. *Bioenergy Res.,* 7, 87-94. 2014.
42. Stelte, W., C. Clemons, J. K. Holm, A. R. Sanadi, J. Ahrenfeldt, L. Shang, and U. B. Henriksen; Pelletizing Properties of Torrefied Spruce. *Biomass & Bioenergy,* 35, 4690-4698. 2011.
43. Wiedner, K., C. Naisse, C. Rumpel, A. Pozzi, P. Wieczorek, and B. Glaser; Chemical Modification of Biomass Residues During Hydrothermal Carbonization - What Makes the Difference, Temperature of Feedstock? *Organic Geochemistry,* 54, 91-100. 2013.
44. Coll, R., S. Udas, and W. A. Jacoby; Conversion of the Rosin Acid Fraction of Crude Tall Oil into Fuels and Chemicals. *Energy & Fuels,* 15, (5), 1166-1172. 2001.
45. Axelsson, S., K. Eriksson, and U. Nilsson; Determination of Resin Acids During Production of Wood Pellets-a Comparison of HPLC/ESI-MS With the GC/FID MDHS 83/2 Method. *Journal of Environmental Monitoring,* 13, (10), 2940-2945. 2011.
46. Pelaez-Samaniego, M. R., V. Yadama, E. Lowell, and R. Espinoza-Herrera; A Review of Wood Thermal Pretreatments to Improve Wood Composite Properties. *Wood Sci.Technol.,* 47, 1285-1319. 2013.
47. Reza, M. T., J. Andert, B. Wirth, D. Busch, J. Pielert, J. G. Lynam, and J. Mumme; Hydrothermal Carbonization of Biomass for Energy and Crop Production. *Applied Bioenergy,* 1, (1), 2300-3553. 2014.
48. Pfriem, A., T. Dietrich, and B. Buchelt; Furfuryl Alcohol Impregnation for Improved Plasticization and Fixation During the Densification of Wood. *Holzforschung,* 66, (2), 215-218. 2012.
49. Yan, W., S. K. Hoekman, A. Broch, and C. J. Coronella; Effect of Hydrothermal Carbonization Reaction Parameters on the Properties of Hydrochar and Pellets. *Environmental Progress & Sustainable Energy,* 33, (3), 676-680. 2014.
50. U.S. Patent application, US 2014/0262727 Al, Application #14/216,028, Rapid Production of Hydrothermally Carbonized Biomass Via Reactive Twin-Screw Extrusion, Filed March 17, 2013.
51. Overend, R. P. and E. Chornet; Fractionation of Lignocellulosics by Steam-Aqueous Pretreatments. *Phil.Trans.R.Soc.Lond.,* A 321, 523-536. 1987.

52. Kim, D. S., A. A. Myint, H. W. Lee, J. Yoon, and Y.-W. Lee; Evaluation of Hot Compressed Water Pretreatment and Enzymatic Saccharification of Tulip Tree Sawdust Using Severity Factors. *Bioresource Technology,* 144, 460-466. 2013.
53. Final report "Developing Thermal Conversion Options for Biorefinery Residues", DE-FG36-01GO11082, Gas Technology Institute, December 2014.
54. Yan, W., Acharjee, T.C., Coronella, C.J., and Vasquez, V.R. "Thermal pretreatment of lignocellulosic biomass," Environ. Prog. Sustainable Energy, 28, 435-440 (2009).
55. Yan, W., Hastings, J.T., Acharjee, T.C., Coronella, C.J., and Vasquez, V. "Mass and energy balances of wet torrefaction of lignocellulosic biomass," Energy and Fuels 24, 4738-4742 (2010).
56. Hoekman, S.K, Broch, A., and Robbins, C., "Hydrothermal carbonization (HTC) of lignocellulosic biomass," Energy and Fuels 25, 1802-1810 (2011).
57. Acharjee, T.C., Coronella, C.J., and Vasquez, V.R. "Effect of thermal pretreatment on equilibrium moisture content of lignocellulosic biomass," Bioresource Technology 102, 4849-4854 (2011).
58. Lynam, J. G., Coronella, C. J., Yan, W., Reza, M. T., Vasquez, V. R. "Acetic acid and lithium chloride effects on hydrothermal carbonization of lignocellulosic biomass," Bioresource Technology 102, 6192-6199 (2011).
59. United States Patent Application: Rapid Production of HTC Biomass by Reactive Twin-Screw Extrusion, US 2014/0262727 A1 - Serial No. 14/216,028, March 17, 2014.
60. Brown, R. C., Biorenewable Resources: Engineering New Products from Agriculture, Iowa State Press, Ames, IA, April 2003.
61. Guthrie K.M., Process Plant Estimating, Evaluation, and Control. Solano Beach, California: Craftman, 1974.
62. Hein T. Small Is Beautiful: Microchipping Woody Biomass, Canadian Biomass Mag., http://www.canadianbiomassmagazine.ca Nov.-Dec. 2011 (6)
63. Peterson D. R. Real Cost of Extracting Logging Residue", http://dnr.wi.gov/topic/ForestBusinesses, Lumberjack RC&D Council, Sept. 2005. pp 17.
64. Texas Comptroller Public Accounts, The Energy Report 2008 Chapter 15: Wood" http://www.window.state.tx.us/specialrpt/energy/pdf/15-Wood.pdf
65. Ward J. E., Mackes K.H., Lynch D.L. Wood Wastes and Residues Generated Along the Colorado Front Range as a Potential Fuel Source, USDA, Research Paper RMRS-RP-50, August 2004, pp14.
66. Timber Mart-South, Inc. Timber Mart-South Market News, 2nd Quarterly vol. 16 (2) 2011. pp 48.
67. Harrison C.D., Alkers D.J. Coal Fines: Resource of the Future. http://www.netl.doe.gov/publications/proceedings/97/97cl/harrison.pdf
68. S.K. Hoekman, A. Broch, A. Warren, L. Felix, and J. Irvin. "Laboratory pelletization of hydrochar from woody biomass." Biofuels, in press (2015).
69. S.K. Hoekman, A. Broch, A. Warren, L. Felix, and G. Coble, "Waterproof Wood Pellets via Hydrothermal Carbonization (HTC)." Energy, Utility and Environment Conference, Phoenix, AZ, February 3-5, 2014.
70. S.K. Hoekman, A. Broch, A. Warren, L. Felix, and G. Coble, "Waterproof Wood Pellets via Hydrothermal Carbonization (HTC)." Energy, Utility and Environment Conference, Phoenix, AZ, February 3-5, 2014.

Appendix: Simulation of Briquetting Coal Fines with FHTC Hydrochar in Aspen Plus®

Process Values for 120 MT of dry wood/day[1,2]



1. Acids are organic acids; where omitted units are lb/hr; "water "denotes liquid while "H_2O" denotes vapor or adsorbed; "ΔH" denotes energy input/output (kW)
2. 2204.6 lb/MT

90% Coal, 10% Biomass, 120 tons/day of wet Loblolly Pine Wood.

Component		**BKTFEED**	**COAL**	**CONDNSAT**	**CW1**	**CW2**	**CW3**
From		**SEP**		**VLSEP**		**HX7**	
To			**MIXER2**	**MIXER3**	**HX7**		**HX8**
Substream: ALL	**Units**						
Mass Flow	LB/HR	18118.72`	12308.00	5176.18	176370.00	176370.00	99208.02
Mass Enthalpy	KW	-6090.57	-2642.46	-9768.77	-352830.00	-351280.00	-198470.00
MASSFLOW							
WATER	LB/HR	1404.41	586.00	4731.58	176370.00	176370.00	99208.02
CO_2	LB/HR	0.00	0.00	1.50	0.00	0.00	0.00
C_2H_4O-01	LB/HR	74.27	0.00	235.11	0.00	0.00	0.00
FURFURAL	LB/HR	6.17	0.00	150.46	0.00	0.00	0.00
DEXTROSE	LB/HR	799.18	0.00	0.00	0.00	0.00	0.00
FORMI-01	LB/HR	35.22	0.00	55.93	0.00	0.00	0.00
LACTI-01	LB/HR	54.69	0.00	0.53	0.00	0.00	0.00
HMF	LB/HR	82.01	0.00	1.07	0.00	0.00	0.00
O_2	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00
N_2	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00
CHAR	LB/HR	3940.76	0.00	0.00	0.00	0.00	0.00
COAL	LB/HR	11722.00	11722.00	0.00	0.00	0.00	0.00
VOLFLMX	CUM/MIN	0.11	0.07	0.05	1.77	1.79	1.00
MASSVFRA		0.00	0.00	0.00	0.00	0.00	0.00
MASSSFRA		0.86	0.95	0.00	0.00	0.00	0.00
RHOMX	LB/CUFT	79.74	84.08	46.60	47.05	46.50	47.05
TEMP	F	214.78	75.00	100.00	75.00	104.33	75.00
PRES	KPA	101.35	101.35	101.35	101.35	101.35	101.35
Substream: MIXED							
Phase:		**Liquid**	**Liquid**	**Liquid**	**Liquid**	**Liquid**	**Liquid**
Component Mole Flow							
WATER	LBMOL/HR	77.96	32.53	262.64	9790.01	9790.01	5506.88
CO_2	LBMOL/HR	0.00	0.00	0.03	0.00	0.00	0.00
C_2H_4O-01	LBMOL/HR	1.24	0.00	3.92	0.00	0.00	0.00
FURFURAL	LBMOL/HR	0.06	0.00	1.57	0.00	0.00	0.00
DEXTROSE	LBMOL/HR	4.44	0.00	0.00	0.00	0.00	0.00
FORMI-01	LBMOL/HR	0.77	0.00	1.22	0.00	0.00	0.00

LACTI-01	LBMOL/HR	0.61	0.00	0.01	0.00	0.00	0.00
HMF	LBMOL/HR	0.65	0.00	0.01	0.00	0.00	0.00
O_2	LBMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00
N_2	LBMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00
Component Mass Flow							
WATER	LB/HR	1404.41	586.00	4731.58	176370.00	176370.00	99208.02
CO_2	LB/HR	0.00	0.00	1.50	0.00	0.00	0.00
C_2H_4O-01	LB/HR	74.27	0.00	235.11	0.00	0.00	0.00
FURFURAL	LB/HR	6.17	0.00	150.46	0.00	0.00	0.00
DEXTROSE	LB/HR	799.18	0.00	0.00	0.00	0.00	0.00
FORMI-01	LB/HR	35.22	0.00	55.93	0.00	0.00	0.00
LACTI-01	LB/HR	54.69	0.00	0.53	0.00	0.00	0.00
HMF	LB/HR	82.01	0.00	1.07	0.00	0.00	0.00
O_2	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00
N_2	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00
Mole Flow	LBMOL/HR	85.72	32.53	269.39	9790.01	9790.01	5506.88
Mass Flow	LB/HR	2455.96	586.00	5176.18	176370.00	176370.00	99208.02
Volume Flow	CUFT/HR	45.79	12.46	111.08	3748.86	3792.78	2108.74
Temperature	F	214.78	75.00	100.00	75.00	104.33	75.00
Pressure	PSIA	14.70	14.70	14.70	14.70	14.70	14.70
Vapor Fraction		0.00	0.00	0.00	0.00	0.00	0.00
Liquid Fraction		1.00	1.00	1.00	1.00	1.00	1.00
Solid Fraction		0.00	0.00	0.00	0.00	0.00	0.00
Molar Enthalpy	BTU/LBMOL	-143780.00	-122970.00	-123730.00	-122970.00	-122430.00	-122970.00
Mass Enthalpy	BTU/LB	-5018.19	-6826.09	-6439.58	-6826.09	-6796.09	-6826.09
Enthalpy Flow	BTU/HR	-12324000.00	-4000100.00	-33332000.00	-1203900000.00	-1198600000.00	-677200000.00
Molar Entropy	BTU/LBMOL-R	-46.05	-39.14	-38.74	-39.14	-38.16	-39.14
Mass Entropy	BTU/LB-R	-1.61	-2.17	-2.02	-2.17	-2.12	-2.17
Molar Density	LBMOL/CUFT	1.87	2.61	2.43	2.61	2.58	2.61
Mass Density	LB/CUFT	53.63	47.05	46.60	47.05	46.50	47.05
Average Molecular Wt.		28.65	18.02	19.21	18.02	18.02	18.02
Substream: NCPSD							
Component Mass Flow							
CHAR	LB/HR	3940.76	0.00	0.00	0.00	0.00	0.00

COAL	LB/HR	11722.00	11722.00	0.00	0.00	0.00	0.00
Mass Flow	LB/HR	15662.76	11722.00	0.00	0.00	0.00	0.00
Temperature	F	214.78	75.00				
Pressure	PSIA	14.70	14.70	14.70	14.70	14.70	14.70
Vapor Fraction		0.00	0.00				
Liquid Fraction		0.00	0.00				
Solid Fraction		1.00	1.00				
Mass Enthalpy	BTU/LB	-539.97	-427.94				
Enthalpy Flow	BTU/HR	-8457400.00	-5016400.00				
Mass Entropy	BTU/LB-R						
Mass Density	LB/CUFT	86.33	87.52				
Average Molecular Wt.		1.00	1.00	1.00	1.00	1.00	1.00

Component		CW4	DRYMIX	GAS	HMIX	HPRECYC	HTPRECYC	MIX	MOISTURE
From		**HX8**	**DRYER**	**VLSEP**	**HX3**	**PUMP**	**HX2**		**SEP**
To			**SEP**		**MIXTER1**	**HX2**	**MIXTER1**	**HX3**	**MIXER3**
Substream: ALL	**Units**								
Mass Flow	LB/HR	99208.02	22063.54	85.15	8267.34	6749.53	6749.53	8267.34	3944.82
Mass Enthalpy	KW	-197720.00	-12456.49	-96.70	-7513.04	-12677.15	-11866.13	-8380.58	-6365.93
MASSFLOW									
WATER	LB/HR	99208.02	5069.27	2.31	3003.80	6213.36	6213.36	3003.80	3664.86
CO_2	LB/HR	0.00	0.02	82.28	82.67	1.12	1.12	82.67	0.02
C_2H_4O-01	LB/HR	0.00	252.65	0.10	181.88	305.98	305.98	181.88	178.38
FURFURAL	LB/HR	0.00	42.29	0.43	55.12	138.06	138.06	55.12	36.11
DEXTROSE	LB/HR	0.00	799.18	0.00	799.18	0.00	0.00	799.18	0.00
FORMI-01	LB/HR	0.00	98.12	0.02	66.14	87.93	87.93	66.14	62.89
LACTI-01	LB/HR	0.00	55.78	0.00	55.12	1.20	1.20	55.12	1.08
HMF	LB/HR	0.00	83.48	0.00	82.67	1.88	1.88	82.67	1.47
O_2	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N_2	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CHAR	LB/HR	0.00	3940.76	0.00	3940.76	0.00	0.00	3940.76	0.00
COAL	LB/HR	0.00	11722.00	0.00	0.00	0.00	0.00	0.00	0.00
VOLFLMX	CUM/MIN	1.01	48.06	0.38	0.08	0.07	0.10	0.41	47.95
MASSVFRA		0.00	0.18	1.00	0.00	0.00	0.00	0.01	1.00
MASSSFRA		0.00	0.71	0.00	0.48	0.00	0.00	0.48	0.00
RHOMX	LB/CUFT	46.58	0.22	0.10	48.92	44.98	31.78	9.50	0.04
TEMP	F	100.25	214.78	100.00	554.00	174.78	554.00	77.00	214.78
PRES	KPA	101.35	101.35	101.35	10342.14	3550.80	10342.14	101.35	101.35
Substream: MIXED									
Phase:		**Liquid**	**Mixed**	**Vapor**	**Liquid**	**Liquid**	**Liquid**	**Mixed**	**Vapor**
Component Mole Flow									
WATER	LBMOL/HR	5506.88	281.39	0.13	166.74	344.89	344.89	166.74	203.43
CO_2	LBMOL/HR	0.00	0.00	1.87	1.88	0.03	0.03	1.88	0.00
C_2H_4O-01	LBMOL/HR	0.00	4.21	0.00	3.03	5.10	5.10	3.03	2.97
FURFURAL	LBMOL/HR	0.00	0.44	0.00	0.57	1.44	1.44	0.57	0.38
DEXTROSE	LBMOL/HR	0.00	4.44	0.00	4.44	0.00	0.00	4.44	0.00
FORMI-01	LBMOL/HR	0.00	2.13	0.00	1.44	1.91	1.91	1.44	1.37

LACTI-01	LBMOL/HR	0.00	0.62	0.00	0.61	0.01	0.01	0.61	0.01
HMF	LBMOL/HR	0.00	0.66	0.00	0.66	0.01	0.01	0.66	0.01
O_2	LBMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N_2	LBMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Component Mass Flow									
WATER	LB/HR	99208.02	5069.27	2.31	3003.80	6213.36	6213.36	3003.80	3664.86
CO_2	LB/HR	0.00	0.02	82.28	82.67	1.12	1.12	82.67	0.02
C_2H_4O-01	LB/HR	0.00	252.65	0.10	181.88	305.98	305.98	181.88	178.38
FURFURAL	LB/HR	0.00	42.29	0.43	55.12	138.06	138.06	55.12	36.11
DEXTROSE	LB/HR	0.00	799.18	0.00	799.18	0.00	0.00	799.18	0.00
FORMI-01	LB/HR	0.00	98.12	0.02	66.14	87.93	87.93	66.14	62.89
LACTI-01	LB/HR	0.00	55.78	0.00	55.12	1.20	1.20	55.12	1.08
HMF	LB/HR	0.00	83.48	0.00	82.67	1.88	1.88	82.67	1.47
O_2	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N_2	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mole Flow	LBMOL/HR	5506.88	293.88	2.00	179.36	353.39	353.39	179.36	208.17
Mass Flow	LB/HR	99208.02	6400.78	85.15	4326.57	6749.53	6749.53	4326.57	3944.82
Volume Flow	CUFT/HR	2129.89	101651.00	815.02	121.50	150.07	212.41	822.88	101605.00
Temperature	F	100.25	214.78	100.00	554.00	174.78	554.00	77.00	214.78
Pressure	PSIA	14.70	14.70	14.70	1500.00	515.00	1500.00	14.70	14.70
Vapor Fraction		0.00	0.71	1.00	0.00	0.00	0.00	0.01	1.00
Liquid Fraction		1.00	0.29	0.00	1.00	1.00	1.00	0.99	0.00
Solid Fraction		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Molar Enthalpy	BTU/LBMOL	-122510.00	-115850.00	-164590.00	-124590.00	-122400.00	-114570.00	-136060.00	-104350.00
Mass Enthalpy	BTU/LB	-6800.25	-5319.03	-3875.01	-5164.71	-6408.78	-5998.78	-5640.38	-5506.32
Enthalpy Flow	BTU/HR	-674640000.00	-34046000.00	-329940.00	-22345000.00	-43256000.00	-40489000.00	-24404000.00	-21721000.00
Molar Entropy	BTU/LBMOL-R	-38.29	-19.90	0.71	-30.28	-36.35	-26.91	-45.16	-9.13
Mass Entropy	BTU/LB-R	-2.13	-0.91	0.02	-1.26	-1.90	-1.41	-1.87	-0.48
Molar Density	LBMOL/CUFT	2.59	0.00	0.00	1.48	2.35	1.66	0.22	0.00
Mass Density	LB/CUFT	46.58	0.06	0.10	35.61	44.98	31.78	5.26	0.04
Average Molecular Wt.		18.02	21.78	42.48	24.12	19.10	19.10	24.12	18.95
Substream: NCPSD									
Component Mass Flow									
CHAR	LB/HR	0.00	3940.76	0.00	3940.76	0.00	0.00	3940.76	0.00

COAL	LB/HR	0.00	11722.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass Flow	LB/HR	0.00	15662.76	0.00	3940.76	0.00	0.00	3940.76	0.00
Temperature	F		214.78		554.00			77.00	
Pressure	PSIA	14.70	14.70	14.70	1500.00	515.00	1500.00	14.70	14.70
Vapor Fraction			0.00		0.00			0.00	
Liquid Fraction			0.00		0.00			0.00	
Solid Fraction			1.00		1.00			1.00	
Mass Enthalpy	BTU/LB		-539.97		-834.89			-1063.81	
Enthalpy Flow	BTU/HR		-8457400.00		-3290100.00			-4192200.00	
Mass Entropy	BTU/LB-R								
Mass Density	LB/CUFT		86.33		82.97			82.97	
Average Molecular Wt.		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Component		PRODUCT	RECYCLE	RECYCLE1	RECYCLE2	RECYCLE3	RECYCLE6	SLURRY	TODRYER
From		**MIXTER1**		**MIXER3**	**SPLITTER**	**SPLITTER**	**HX8**	**FLASH**	**MIXER2**
To		**FLASH**		**SPLITTER**	**HX8**		**PUMP**	**MIXER2**	**DRYER**
Substream: ALL	**Units**								
Mass Flow	LB/HR	15016.86	5263.54	9120.99	6749.53	2371.46	6749.53	9755.54	22063.54
Mass Enthalpy	KW	-19379.18	-10529.86	-16134.73	-11939.70	-4195.03	-12690.90	-11064.03	-13706.49
MASSFLOW									
WATER	LB/HR	9217.16	5263.54	8396.43	6213.36	2183.07	6213.36	4483.27	5069.27
CO_2	LB/HR	83.80	0.00	1.52	1.12	0.39	1.12	0.02	0.02
C_2H_4O-01	LB/HR	487.86	0.00	413.49	305.98	107.51	305.98	252.65	252.65
FURFURAL	LB/HR	193.17	0.00	186.57	138.06	48.51	138.06	42.29	42.29
DEXTROSE	LB/HR	799.18	0.00	0.00	0.00	0.00	0.00	799.18	799.18
FORMI-01	LB/HR	154.07	0.00	118.82	87.93	30.89	87.93	98.12	98.12
LACTI-01	LB/HR	56.31	0.00	1.62	1.20	0.42	1.20	55.78	55.78
HMF	LB/HR	84.55	0.00	2.54	1.88	0.66	1.88	83.48	83.48
O_2	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N_2	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CHAR	LB/HR	3940.76	0.00	0.00	0.00	0.00	0.00	3940.76	3940.76
COAL	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11722.00
VOLFLMX	CUM/MIN	0.18	0.05	40.45	29.93	10.52	0.07	0.08	0.15
MASSVFRA		0.00	0.00	0.37	0.37	0.37	0.00	0.00	0.00
MASSSFRA		0.26	0.00	0.00	0.00	0.00	0.00	0.40	0.71
RHOMX	LB/CUFT	39.36	47.05	0.11	0.11	0.11	45.06	57.42	70.33
TEMP	F	553.68	75.00	211.80	211.80	211.80	169.15	212.60	161.67
PRES	KPA	10342.14	101.35	101.35	101.35	101.35	101.35	101.35	101.35
Substream: MIXED									
Phase:		**Liquid**	**Liquid**	**Mixed**	**Mixed**	**Mixed**	**Liquid**	**Liquid**	**Liquid**
Component Mole Flow									
WATER	LBMOL/HR	511.63	292.17	466.07	344.89	121.18	344.89	248.86	281.39
CO_2	LBMOL/HR	1.90	0.00	0.03	0.03	0.01	0.03	0.00	0.00
C_2H_4O-01	LBMOL/HR	8.12	0.00	6.89	5.10	1.79	5.10	4.21	4.21
FURFURAL	LBMOL/HR	2.01	0.00	1.94	1.44	0.50	1.44	0.44	0.44
DEXTROSE	LBMOL/HR	4.44	0.00	0.00	0.00	0.00	0.00	4.44	4.44
FORMI-01	LBMOL/HR	3.35	0.00	2.58	1.91	0.67	1.91	2.13	2.13

LACTI-01	LBMOL/HR	0.63	0.00	0.02	0.01	0.00	0.01	0.62	0.62
HMF	LBMOL/HR	0.67	0.00	0.02	0.01	0.01	0.01	0.66	0.66
O_2	LBMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N_2	LBMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Component Mass Flow									
WATER	LB/HR	9217.16	5263.54	8396.43	6213.36	2183.07	6213.36	4483.27	5069.27
CO_2	LB/HR	83.80	0.00	1.52	1.12	0.39	1.12	0.02	0.02
C_2H_4O-01	LB/HR	487.86	0.00	413.49	305.98	107.51	305.98	252.65	252.65
FURFURAL	LB/HR	193.17	0.00	186.56	138.06	48.51	138.06	42.29	42.29
DEXTROSE	LB/HR	799.18	0.00	0.00	0.00	0.00	0.00	799.18	799.18
FORMI-01	LB/HR	154.07	0.00	118.82	87.93	30.89	87.93	98.12	98.12
LACTI-01	LB/HR	56.31	0.00	1.62	1.20	0.42	1.20	55.78	55.78
HMF	LB/HR	84.55	0.00	2.54	1.88	0.66	1.88	83.48	83.48
O_2	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N_2	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mole Flow	LBMOL/HR	532.75	292.17	477.55	353.39	124.16	353.39	261.36	293.88
Mass Flow	LB/HR	11076.10	5263.54	9120.99	6749.53	2371.46	6749.53	5814.78	6400.78
Volume Flow	CUFT/HR	334.03	111.88	85712.65	63424.16	22284.16	149.80	122.40	132.29
Temperature	F	553.68	75.00	211.80	211.80	211.80	169.15	212.60	161.67
Pressure	PSIA	1500.00	14.70	14.70	14.70	14.70	14.70	14.70	14.70
Vapor Fraction		0.00	0.00	0.37	0.37	0.37	0.00	0.00	0.00
Liquid Fraction		1.00	1.00	0.63	0.63	0.63	1.00	1.00	1.00
Solid Fraction		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Molar Enthalpy	BTU/LBMOL	-117940.00	-122970.00	-115280.00	-115280.00	-115280.00	-122540.00	-129250.00	-129340.00
Mass Enthalpy	BTU/LB	-5672.91	-6826.09	-6035.97	-6035.97	-6035.97	-6415.73	-5809.29	-5938.55
Enthalpy Flow	BTU/HR	-62834000.00	-35929000.00	-55054000.00	-40740000.00	-14314000.00	-43303000.00	-33780000.00	-38011000.00
Molar Entropy	BTU/LBMOL-R	-28.01	-39.14	-25.66	-25.66	-25.66	-36.50	-38.79	-40.01
Mass Entropy	BTU/LB-R	-1.35	-2.17	-1.34	-1.34	-1.34	-1.91	-1.74	-1.84
Molar Density	LBMOL/CUFT	1.59	2.61	0.01	0.01	0.01	2.36	2.14	2.22
Mass Density	LB/CUFT	33.16	47.05	0.11	0.11	0.11	45.06	47.51	48.38
Average Molecular Wt.		20.79	18.02	19.10	19.10	19.10	19.10	22.25	21.78
Substream: NCPSD									
Component Mass Flow									
CHAR	LB/HR	3940.76	0.00	0.00	0.00	0.00	0.00	3940.76	3940.76

COAL	LB/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11722.00
Mass Flow	LB/HR	3940.76	0.00	0.00	0.00	0.00	0.00	3940.76	15662.76
Temperature	F	553.68						212.60	161.67
Pressure	PSIA	1500.00	14.70		14.70	14.70	14.70	14.70	14.70
Vapor Fraction		0.00						0.00	0.00
Liquid Fraction		0.00						0.00	0.00
Solid Fraction		1.00						1.00	1.00
Mass Enthalpy	BTU/LB	-835.07						-1008.01	-559.11
Enthalpy Flow	BTU/HR	-3290800.00						-3972300.00	-8757200.00
Mass Entropy	BTU/LB-R								
Mass Density	LB/CUFT	82.97						82.97	86.33
Average Molecular Wt.		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Component		TOVLSEP	VAPOR
From:		**HX7**	**FLASH**
To:		**VLSEP**	**HX7**
Substream: ALL	**Units**		
Mass Flow	LB/HR	5261.325	5261.325
Mass Enthalpy	KW	-9865.461	-8315.147
MASSFLOW			
WATER	LB/HR	4733.893	4733.893
CO_2	LB/HR	83.78156	83.78156
C_2H_4O-01	LB/HR	235.212	235.212
FURFURAL	LB/HR	150.8867	150.8867
DEXTROSE	LB/HR	3.09E-05	3.09E-05
FORMI-01	LB/HR	55.94716	55.94716
LACTI-01	LB/HR	0.5344978	0.5344978
HMF	LB/HR	1.070408	1.070408
O_2	LB/HR	0	0
N_2	LB/HR	0	0
CHAR	LB/HR	0	0
COAL	LB/HR	0	0
VOLFLMX	CUM/MIN	0.4370703	62.3099
MASSVFRA		0.0161834	1
MASSSFRA		0	0
RHOMX	LB/CUFT	5.681165	0.0398503
TEMPERATURE	°F	100	212.5998
PRES	KPA	101.3529	101.3529
Substream: MIXED			
Phase:		**Mixed**	**Vapor**
Component Mole Flow			
WATER	LBMOL/HR	262.771	262.771
CO_2	LBMOL/HR	1.903702	1.903702
C_2H_4O-01	LBMOL/HR	3.91677	3.91677
FURFURAL	LBMOL/HR	1.570337	1.570337
DEXTROSE	LBMOL/HR	1.72E-07	1.72E-07
FORMI-01	LBMOL/HR	1.215564	1.215564

LACTI-01	LBMOL/HR	0.00593367	0.00593367
HMF	LBMOL/HR	0.0084953	0.0084953
O_2	LBMOL/HR	0	0
N_2	LBMOL/HR	0	0
Component Mass Flow			
WATER	LB/HR	4733.893	4733.893
CO_2	LB/HR	83.78156	83.78156
C_2H_4O-01	LB/HR	235.212	235.212
FURFURAL	LB/HR	150.8867	150.8867
DEXTROSE	LB/HR	3.09E-05	3.09E-05
FORMI-01	LB/HR	55.94716	55.94716
LACTI-01	LB/HR	0.5344978	0.5344978
HMF	LB/HR	1.070408	1.070408
O_2	LB/HR	0	0
N_2	LB/HR	0	0
Mole Flow	LBMOL/HR	271.3918	271.3918
Mass Flow	LB/HR	5261.325	5261.325
Volume Flow	CUFT/HR	926.0996	132027
Temperature	F	100	212.5998
Pressure	PSIA	14.7	14.7
Vapor Fraction		0.00738641	1
Liquid Fraction		0.9926136	0
Solid Fraction		0	0
Molar Enthalpy	BTU/LBMOL	-124040	-104540
Mass Enthalpy	BTU/LB	-6398.075	-5392.645
Enthalpy Flow	BTU/HR	-33662000	-28372000
Molar Entropy	BTU/LBMOL-R	-38.45184	-9.044322
Mass Entropy	BTU/LB-R	-1.983438	-0.4665278
Molar Density	LBMOL/CUFT	0.2930481	0.00205558
Mass Density	LB/CUFT	5.681165	0.0398503
Average Molecular Wt.		19.38646	19.38646
Substream: NCPSD			
Component Mass Flow			
CHAR	LB/HR	0	0

COAL	LB/HR	0	0
Mass Flow	LB/HR	0	0
Temperature	F		
Pressure	PSIA	14.7	14.7
Vapor Fraction			
Liquid Fraction			
Solid Fraction			
Mass Enthalpy	BTU/LB		
Enthalpy Flow	BTU/HR		
Mass Entropy	BTU/LB-R		
Mass Density	LB/CUFT		
Average Molecular Wt.		1	1