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DEVELOPMENT AND CHARACTERIZATION OF DENSIFIED BIOMASS-PLASTIC BLEND FOR ENTRAINED FLOW GASIFICATION

Final Technical Report

Report Period
August 1, 2021 to April 30, 2024

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Report Issued
May 7, 2024

Work Performed Under Award Number
DE-FE0032043

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ACKNOWLEDGEMENT: University of Kentucky is grateful to the U.S. Department of Energy National Energy Technology Laboratory for the support of this project. The project team is also grateful to the many UK CAER research personnel for assistance with the project, as listed below (alphabetical order).

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ABSTRACT: Supported by the U.S. DOE NETL Award DE-FE0032043, this project was a collaborative effort. Project participants included the University of Kentucky Institute for Decarbonization and Energy Advancement (UK IDEA), Biosystems and Agricultural Engineering department (UK BAE), and Wabash Valley Resources, LLC.

The goal of this final technical project report is to comprehensively summarize the work conducted on project DE-FE0032043. In accordance with the Statement of Project Objectives (SOPO), the University of Kentucky (UK) (Project Prime Recipient) has developed and studied a biomass/plastic fuel with a hydrophobic surface area less than 10 m^2/gram that is suitable for oxygen-blown entrained flow gasification with slurry feed. The project involved the utilization of an existing thermogravimetric analysis (TGA)-mass spectrometer (MS), 1.5” drop tube furnace, 1 ton per day (TPD) coal gasifier, and high-pressure extruder operated at UK. The pilot-scale production of blended material was done at the Polymers Technology Center in Charlotte, North Carolina. Parametric testing and solid fuel blend slurry performance validation was completed using the UK entrained flow gasifier with multiple opposed burners to narrow the major near-term technical gaps that impede gasification of biomass and carbonaceous mixed wastes such as plastics in order to achieve net-negative CO_2 emissions.

Project results validated the UK approach to address the major technical challenges on the biomass/plastic pretreatment and gasification. Previously, this has been limited in application to fluidized-type or moving bed-type gasifiers due to the high-water uptake of porous biomass containing hydroxyl groups during the conventional slurry preparation, resulting in a highly viscous, un-pumpable slurry. The biomass pretreatment with plastic developed for this project demonstrates advantages in cost and flexibility, which include: 1) the development of a blended solid fuel slurry with 55-60 wt% solids and comparable heating value to 100% coal-based water slurry; 2) the collection of gasification kinetic data and identification of preliminary operating conditions by performing thermogravimetric analysis, gasification experiments by using a 1.5” drop tube furnace; and finally 3) the demonstrated gasification of the blended solid fuel in the UK entrained flow gasifier with a long-lasting stable solid fuel blend slurry, dataset detailing operating conditions, and characterization of slag phase formation and solidification. The lab-scale data and experience obtained during this project encourages the development of technologies and commercial approaches to enable a hydrogen-based energy economy while achieving net-negative CO_2 emissions through gasification of coal, biomass, and carbonaceous mixed wastes such as plastics.

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1) EXECUTIVE SUMMARY

1.1 Overview

To meet the US Department of Energy (DOE) strategic goal on enabling existing commercial matured entrained flow gasification technologies to utilize coal, biomass, and waste plastics, the proposed work, in collaboration with the Wabash Valley Resources, LLC, focused on biomass pre-processing with plastic for densification and encapsulation of the hydroxyl groups at a lab-scale by using hydraulic press and by extrusion co-processing for gasification. This study included the fuel characterization (e.g. proximate, ultimate, heating value, chemical composition, ash fusion temperatures, surface area, porosity, and size distribution). Simulation work in FactSage [1] was used to calculate slag viscosity, liquidus temperature, mineral, and crystalline composition. The impact of the biomass/plastic ratio on fuel grindability was analyzed as well as the impact of solid particle distribution on slurry stability and pumpability of the blended fuel.

The proposed research accomplished the following three goals: (1) Demonstration of hydrophobic layer encapsulated biomass production that is suitable for slurry with solid content ≥ 60 wt% of blended of coal/biomass and plastic; (2) Completion of lab-scale kinetic and gasification studies on the blended biomass/plastic fuel; and (3) Demonstration of practical operations in the commercially relevant, UK 1 ton per day (TPD) entrained flow gasifier.

The large-scale slurry production process and operating parameters were identified, and approximately 200 kg of co-extruded torrefied pine wood and high-density polyethylene (HPDE) plastic fuel were prepared for lab-scale studies on grindability, slurryability, and stability while giving considerations to different gasification kinetics between plastic/biomass and coal. Finally, testing was conducted with an acceptable coal/biomass/plastic slurry in the UK 1 TPD opposed multi-burner entrained flow gasifier for investigation on carbon conversion, syngas composition, and practical operations/ troubleshooting. This study aims at reaching a higher flexibility and variability of fuel feed and to improve fuel conversion and gasification efficiency by providing a better flow pattern and mixing through the opposed burner arrangement.

The UK 1 TPD (dry basis) opposed multi-burner (OMB) gasifier was modified to allow for staged gasification with a four-burner configuration, an in-situ camera for real-time monitoring of the gasification process and was operated to demonstrate the flexibility in fuel feed and load while maintaining operational stability and reliability through parametric experiments. Overall, the lab-scale data and experience obtained from this project further encourage the development of technologies and commercial approaches to enable a hydrogen-based energy economy while achieving net-negative CO_2 emissions through gasification of coal, biomass, and carbonaceous mixed wastes such as plastics.

2) BACKGROUND AND TECHNOLOGY DESCRIPTION

2.1 Project Objectives

The main objective of the proposed work is to utilize the existing thermogravimetric analysis (TGA)-mass spectrometer (MS), 1.5” drop tube furnace, 1 TPD coal gasifier and high pressure extruder operated at UK to develop and study a coal/biomass/plastic fuel with a surface area less than 10 m^2/gram that is suitable for oxygen-blown entrained flow gasification with slurry feed. Conventional biomass pretreatment has been

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[1] C. W. Bale, E. Bélisle, P. Chartrand, S. A. Decterov, G. Eriksson, A.E. Gheribi, K. Hack, I. H. Jung, Y. B. Kang, J. Melançon, A. D. Pelton, S. Petersen, C. Robelin. J. Sangster, P. Spencer and M-A. Van Ende, *FactSage Thermochemical Software and Databases* - 2010 - 2016, Calphad, vol. 54, pp 35-53, 2016 <www.factsage.com>

limited in application to fluidized-type or moving bed-type gasifiers due to the high-water uptake by porous biomass containing hydroxyl groups during the conventional slurry preparation resulting in a highly viscous, unpumpable slurry. To address this issue, while satisfying the objective of the Funding Opportunity Announcement (FOA), biomass was processed with plastic for densification and to encapsulate the surface hydroxyl groups at the lab-scale using a press pelletizer and by extrusion co-processing. Upon a preferable production process and operating parameters being identified, approximately 200 kg pine wood-plastic fuel were prepared for lab-scale studies on grindability, slurryability, and stability while considering different gasification kinetics between plastic/biomass and coal. Finally, testing was conducted with an acceptable coal/biomass/plastic slurry in the UK 1 TPD opposed multi-burner entrained flow gasifier for investigation on burner atomization, carbon conversion, syngas composition, slag characterization, and practical operations. The lab-scale data and experience obtained from this project further encourage the development of technologies and commercial approaches to enable a hydrogen-based energy economy while achieving net-negative CO_2 emissions through gasification of coal, biomass, and carbonaceous mixed wastes such as plastics.

All Project Success Criteria were satisfied and are shown in **Exhibit 1**.

Exhibit 1. Project Success Criteria.

Completion Date	**Success Criteria**
FY21 and FY22	**Demonstration of blended solid fuel slurry with 55-60 wt% solids and comparable heat value to 100% coal water slurry.** Ultimate, proximate, heating value, and major ash analysis completed for HDPE/biomass, 37:63 (higher heating value (HHV) basis). Ash fusion temperature evaluated for 70 wt% coal and 30 wt% HDPE:torrefied wood (TW), 37:63 HHV ratio. Determined to be not significantly different than coal by itself due to negligible ash content in the biomass and plastic blend. Volatized species from polyethylene terephthalate (PET), polystyrene (PS), HDPE, and biomass/plastic blends quantified at 550, 700, and 900 °C using flame ionization detector (FID). Slurryability test completed with 60 wt% solid fuel at HDPE/biomass:coal ratio of 30:70 by mass (37:63 HHV ratio). The viscosity was measured to be lower than a 55 wt% coal slurry. The HDPE/biomass ratio is 1:4 with 70 wt% of particles sized between 420 µm and 1.18 mm and 30 wt% of particles between 75 µm and 420 µm. Slurry prepared with extruded material was confirmed to have a lower viscosity at 60 solid wt% than a 55 solid wt% coal only slurry.
FY22 and FY23	**Collection of gasification kinetic data and identification of preliminary operating conditions.** TGA measurements completed using HDPE:TW, 37:63 HHV ratio, extruded material from 110 °C to 900 °C in the gas environments 100% argon and 80% argon with 20% CO. The measurements were extended from 110 °C to 1100 °C in the gas environments: 80% argon with 20% water vapor and 80% argon with 10% CO and 10% water vapor. The results indicate that extrusion does not impact the gasification characterization – the blended fuel still maintains the individual characters of biomass and plastic. FactSage[1] simulations determined two slag formations during gasification. One from coal that is similar to what occurs during gasification of only coal. Another from the biomass and plastic blend, but of a significantly smaller quantity. Slag viscosities were calculated. The viscosity is lowered with the inclusion of 30 wt% of HDPE:TW (37:63 HHV ratio), but not to a significant degree.

	The drop tube furnace and reactor were rebuilt to have a dedicated solid input with nitrogen as carrier gas. Gas analyzers calibrated and set up with condensation trap and silica beads. Testing was completed with HDPE:TW (61:39 HHV ratio) material produced in large quantity in increasing concentrations of water vapor. Data analysis of drop tube reactor experiments completed with no unexpected results.
FY23	**Demonstrated gasification of the blended solid fuel in the UK entrained flow gasifier with dataset detailing optimum operating conditions and characterization of slag phase formation and solidification.** Gasifier unit prepared for operation with coal water slurry as a baseline. Pumpability tests using the extruded material from the Polymers Center was conducted. The HDPE:TW (61:39 HHV ratio) pellets were ground to less than 0.5 mm with coal in the hydromill. The solid content of the slurry was 70% dried coal-water slurry and 30% of the ground extruded material. The specific gravity of the 55 solid wt% was 1.3 g/cm^3. The specific gravity of the 50 solid wt% was 1.13 g/cm^3. Detailed protocol developed to complete 8 hours of 40 solid wt% coal-water slurry as a baseline and 8 hours of 40 solid wt% slurry with 70% coal and 30% HDPE:TW (61:39 HHV ratio). A total of 9 hours of testing was conducted with 40 solid wt% coal-water slurry. The gasifier was prepared to conduct the testing of coal biomass slurry at 40 solid wt% slurry with 70% coal and 30% HDPE:TW (61:39 HHV). Slurry was prepared for the 40 solid wt% slurry with solids containing 70 wt% coal and 30 wt% 61:39 HHV ratio HDPE:TW. Operation of the gasifier was attempted with this slurry on the same day but had to be aborted after 25 minutes due to clogs developing in both slurry burners. Slag samples were collected and analyzed by X-ray diffraction (XRD), carbon content analysis, and scanning electron microscopy (SEM). Material was extracted from the clogged burners and from the blended fuel slurry, washed and examined under an imaging microscope for further understanding as to why the burner clogged. Biomass particles that were too big to pass through the tip of the UK pilot scale gasifier were found, indicating that commercial scale gasification with larger burner tip spacing and proper solid blend material processing unit operation will allow for successful gasification of the 70% coal and 30% HDPE:TW material.

Knowledge gained from the execution of this project includes addressing a current technological gap regarding the lack of a blended fuel solid slurry of acceptable biomass content resulting in carbon-neutral or net negative CO_2 emissions for entrained flow gasification. The present study proved the fuel flexibility, variability, and process efficiency as well as the syngas composition that could be obtained by gasifying a blended coal/biomass/plastic fuel at the 1 TPD scale. The obtained results and datasets provide valuable insight on slurry preparation, burner atomization, carbon conversion, syngas composition and slag behavior, as well as practical system operability. With these findings the upper limit of biomass and waste plastic utilization for co-gasification in an entrained flow gasifier are better defined. Findings made regarding the gasification of plastic/biomass and its impact on the initial gasification of coal particles; char conversion, slag formation, flow and discharge, and interaction with the refractory material; and the internal temperature profile support continued technology development and feasibility for application to a commercial scale entrained flow gasifier. In addition to the specific goals and success criteria for this project, the UK broader objective was to contribute to building a base of knowledge, techniques, and infrastructure that will accelerate beneficial technology developments emerging from this project toward commercialization.

These objectives have the potential to benefit the economy and society by providing cost-efficient and sustainable environmental protection related to power generation from municipal plastic waste, biomass, coal, and other fuels.

2.2 Biomass/Plastic Blended Fuel Description

The UK team used its suite of existing instruments, equipment, and facilities to develop and investigate the blended solid water slurry with coal, biomass, and plastic. This included the fuel characterization (e.g. Proximate; Ultimate; heating value; chemical composition; ash fusion temperatures; surface area, porosity, and size distribution; and slag viscosity, liquidus temperature, and mineral and crystalline composition); the impact of solid particle distribution on slurryability, stability, and pumpability of the blended fuel; and gasification characterization. As shown in **Exhibit 1**, primary existing equipment included the following:
(1) a Buskirk PM605 pellet mill to produce a small-quantity in batch-mode of TW with plastic for a surface modified and densified fuel blend; (2) a Davis-Standard high-temperature and pressure extruder to co-process biomass and plastic to continuously produce a large quantity of hydrophobic product material in which the biomass is encapsulated in plastic; (3) a ThermoFisher Scientific Fourier transform infrared (FTIR) spectrometer for biomass surface functional group identification both before and after treatment;
(4) LECO carbon hydrogen nitrogen analyzer (CHN), TGA and calorimeter to determine the fuel proximate and ultimate analysis and heating value, a PANalytical X-ray fluorescence spectrometer (XRF) for ash composition and LECO Ash Fusion Determinator to study the ash characteristics and flowability; (5) a Micromeritics Brunauer-Emmet-Teller (BET) analyzer for determination of surface area, pore volume and size distribution; (6) a Biolin Scientific Optical tensiometer for surface hydrophobicity; (7) Rolling mills and grinders to study the crushability of produced densified biomass and extruded fuel blends and the impact of coal/biomass ratio and particle size distribution on slurryability; (8) A Lovis microviscometer to determine slurry pumpability (e.g. viscosity); (9) A Netzsch wet-furnace thermogravimetric, quadrupole mass spectrometry with differential scanning calorimetry (TGA/MS/DSC), and Frontier Lab Multi-Shot Pyrolyzer (EGA/PY-3030D) for gasification kinetics and operating parameter pre-selection; (10) A 1.5" inside diameter (ID) pressurized, drop tube reactor for gasification condition determination, syngas composition and solid residual (slag) characterization; (11) a Rigaku X-ray diffraction (XRD) for slag characterization and verification of the predicted phases generated from FactSage22 simulation; (12) a 1 TPD oxygen-blown, slurry-fed and molten slag discharge entrained flow gasifier for large quantity slurry preparation, burner atomization, feed-ability via progressive cavity pumps, gasification operating parameter verification, and slag formation and discharge behavior determination.

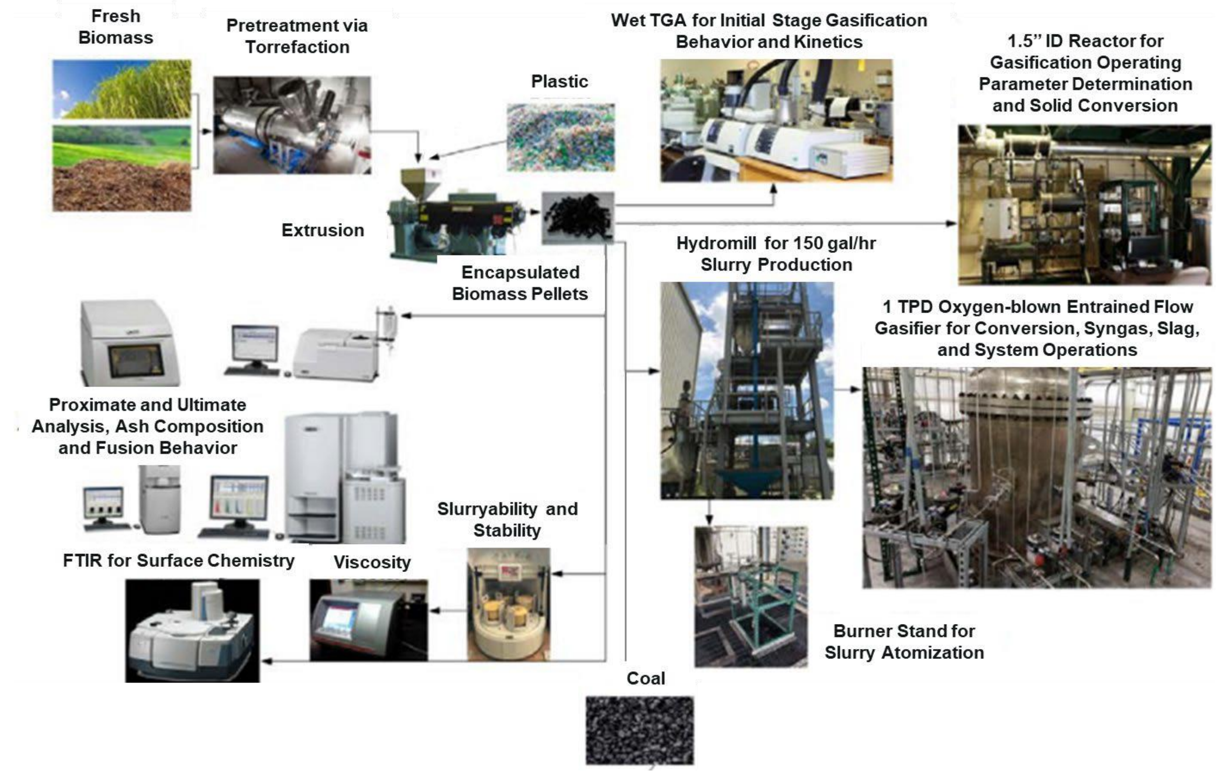

Exhibit 1. UK Approach to Co-utilize Biomass and Plastic for CO_2 Emissions Reduction.

As part of previous DOE funded research and development (R&D) projects (DE-NT0005988 and DE-FE0010482), an entrained-flow OMB gasifier has been fabricated, installed, and operated at UK with four burners, as shown in **Exhibit 2**. The entire facility consists of three systems. (a) The coal water slurry preparation and supply system has a normal handling capacity of ~200 kg coal per hour. The mill is generally used to produce the coal water slurry as ~60 wt% coal and ~40 wt% water, with a suspension additive Tamol SN. The coal is ground with a water-fed ball mill that uses the rotation of stainless-steel balls to reduce the particle size. (b) The gasifier, which is 4 ft. in outside diameter and ~20 ft. in height, is constructed of a refractory and stainless-steel outer wall and is divided into two sections with the gasification chamber at the top and the quench chamber at the bottom. (c) The control and safety systems consist of a DeltaV Distributed Control System (DCS) from Emerson Company that is used to control the unit startup, operation, and shutdown including emergency cut-off. Upon entering the gasification chamber, the coal/biomass water slurry and oxygen react to produce crude syngas and molten ash, which then passes to the quench chamber through a crossflow water spray and subsequent water bath. This acts as a first wash for the raw syngas and removes large ash particles while also quickly removing heat. After the washed syngas leaves the quench chamber, it proceeds to a water scrubber which removes about 80% of the solid fines that escaped from the water quenching chamber. This existing four-burner OMB gasifier was operated along with the supporting systems during this project.

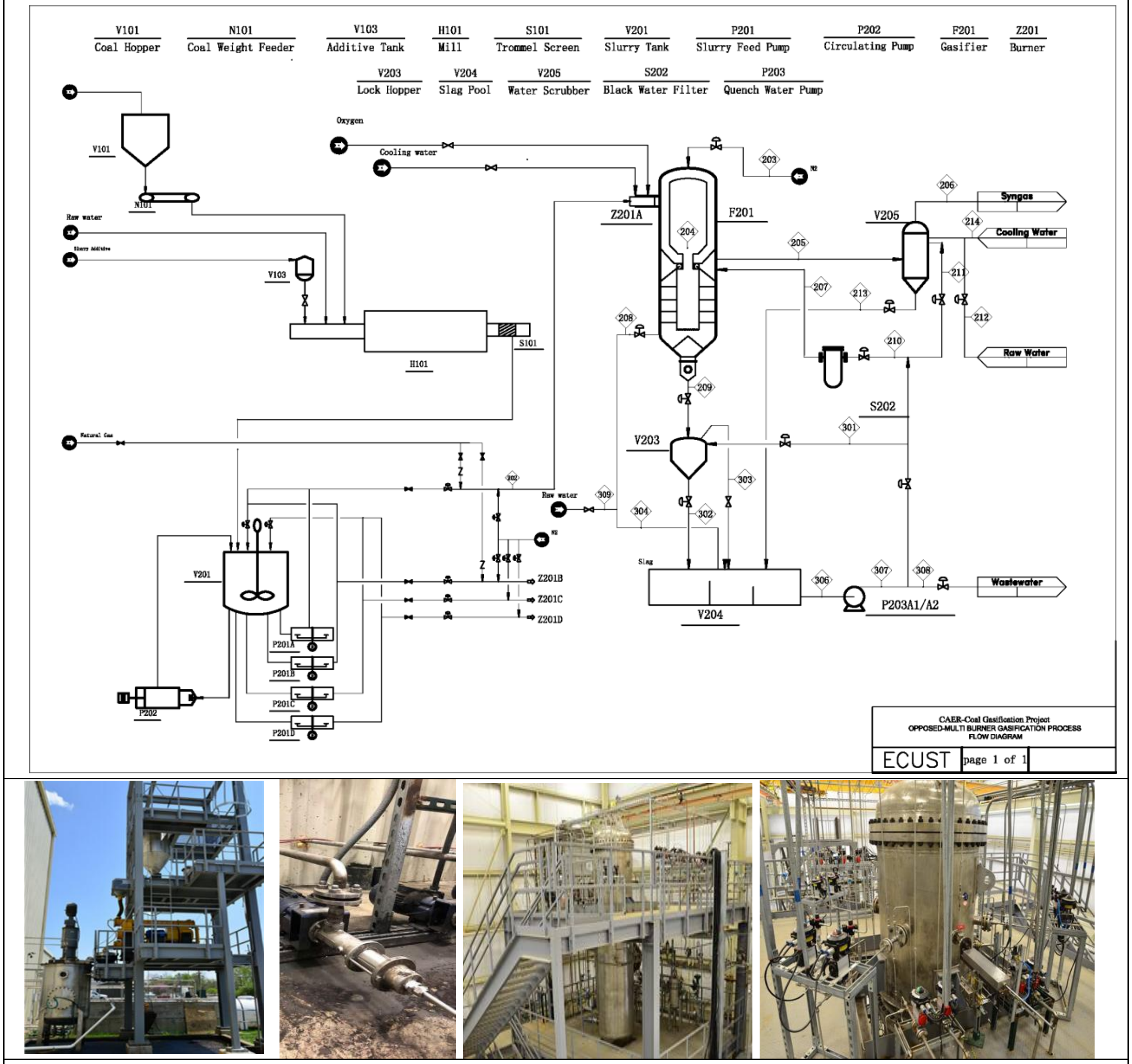

Exhibit 2. Process flow diagram, the slurry preparation unit, the slurry pumps, and the OMB gasifier operated at UK.

3) PROJECT TECHNICAL RESULTS

3.1 Biomass Property Control Using Plastic

Seven plastics in bead form – PET, HDPE, polyvinyl chloride (PVC), low density polyethylene (LDPE), polypropylene (PP), PS, and Nylon-66 – were purchased from a plastic distributor in the amount of 20 lbs. each. Grinding and screening procedures were established for both plastic and TW samples. The municipal waste plastic (MWP) blend was prepared according to DE-FOA-0002376, Appendix G, Table 4 with Nylon 66 used as the "other" category. The composition used for the MWP blend is shown below.

Component	Percentage	Heat Content (dry basis) (Btu/lb)
#1 Polyethylene terephthalate (PET)	40.0	10,250
#2 High density polyethylene (HDPE)	18.0	19,000
#3 Polyvinyl chloride (PVC)	5.9	8,250
#4 Low density polyethylene (LDPE)	18.0	12,050
#5 Polypropylene (PP)	2.0	19,000
#6 Polystyrene (PS)	12.0	17,800
#7 Other*	4.1	13,332
Average Mixed Waste Plastic	100	13,240

Specifically, as shown in **Exhibits 3-5** the MWP blend was ground to sizes of 2-0.5 mm and <0.5 mm. 5 lb of MWP blend was prepared, as shown in **Exhibit 3**. The biomass was ground to sizes of 1/8 to 1/16 inch and <1/16 inch. To prepare the biomass samples, a large quantity (~150 lbs.) of TW was obtained and mixed. From this large quantity, a smaller quantity (~20 lbs.) was taken and pre-dried at 50 ^{0}C overnight to avoid sample variation. The dried material was then ground and sieved for future experimentation. The best method for grinding the plastic was found to be submerging plastic beads in liquid nitrogen before grinding with a professional grade blender. This proved to be an effective way of reducing the plastic particle size for lab scale production of plastic-biomass coprocessing by pelletization. The pelletizing of these two materials was performed by heating the MWP plastic and biomass. Use of two pelletizing apparatus was evaluated during the process.

1. A Buehler SimpliMet 1000 Pelletizer with a 1-inch mold was used with 1.5 g ± 0.002 g of biomass/plastic blend. The coprocessing included 5 minutes of heat time at 350 ºF followed by 5 minutes of cooling time at a pressure of 1200 psi.
2. A Dake 10-ton hydraulic press with a 0.25-inch (6.35 mm) diameter pellet pressing die was also used to prepare pellets. Pellets were formed with 0.3 g plastic-wood blend sample in the die set preheated to 260 ºC for the PET blend or 150 ºC for HDPE blend at 2239 psi pressure for 1 minute.

Representative pellets are shown in **Exhibit 5**. Due to different melting points of the MWP components, the pellets show heterogenous distribution of plastic particles, demonstrated by different colors in the discs.

	
Exhibit 3. MWP as received (right), ground to 2-0.5 mm (left), and ground to <0.5 mm (top).	**Exhibit 4.** TW ground to 1/8-1/16 inch (left) and <1/16 inch (right).

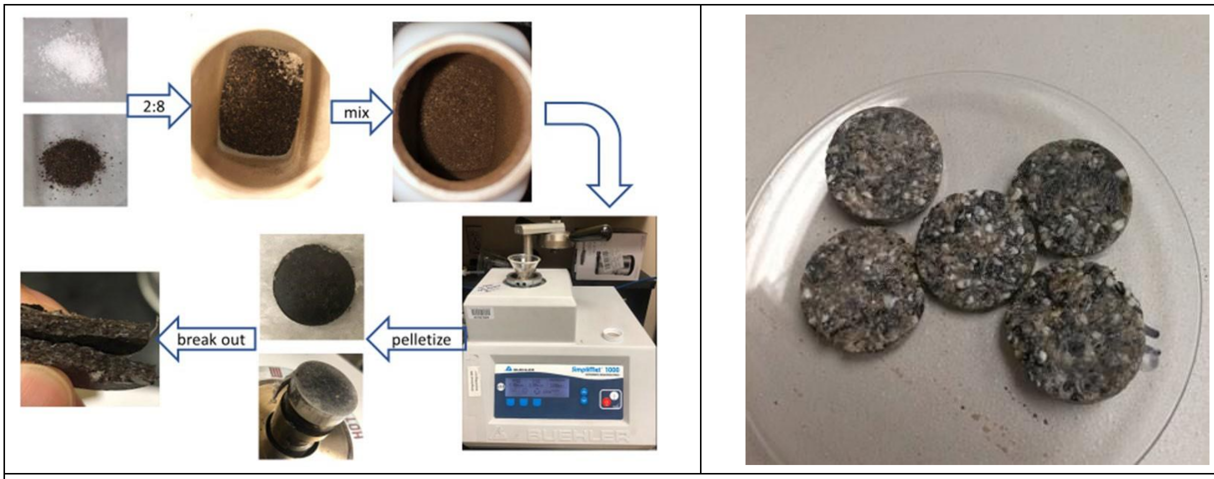

Exhibit 5. Pelletizing Process using Buehler SimpliMet 1000 Lab Scale Apparatus (left), initial MWP/biomass blend with 50:50 weight ratio (right).

The physical properties of the pelletized materials were analyzed by measuring the water uptake, density, porosity by BET, surface hydrophobicity (contact angle) and the presence of surface hydroxyl groups by FTIR as a function of pelletizing parameters, particle size distribution and coal/biomass ratio. This pretreatment method was used to obtain blend fuels with water uptake of <10% and a surface area less than 10 m^2/g.

A. Water Uptake Measurements

Water uptake was measured from the biomass/plastic blend pellets, as shown in **Exhibit 6.** Pellets of the biomass/plastic blends were submerged in water and weighed incrementally through a 24-hour period. It should be noted that when preparing a solid fuel slurry for entrained flow gasification, during normal operation the fuel material will not be exposed to water for more than 8 hours. For better understanding of the material performance, observations were made for 24 hours which is beyond the range of solid fuel slurry processing before gasification.

Exhibit 6. Typical plastic/biomass blend pellets prepared with the Buehler Pelletizer, in the form of plastic energy input to blend fuels.

When the pellets were removed from the water for weighing, they were patted with a paper towel to remove standing water. Assuming zero water uptake of pure plastics, the water uptake is calculated as per **Equations 1 and 2**.

$$Water\ Uptake\ (T)(\%) = \left(\frac{mass\ of\ sample\ pellet\ after\ immersion\ in\ water}{initial\ mass\ of\ pellet} - 1\right) \cdot 100$$ **Equation 1.**

$$Water\ Uptake\ (Biomass)(\%) = \left(\frac{mass\ of\ sample\ pellet\ after\ immersion\ in\ water}{(initial\ mass\ of\ pellet)\cdot(mass\ fraction\ of\ torrefied\ wood)} - 1\right) \cdot 100$$ **Equation 2.**

Exhibit 7. Water Uptake (%) for Biomass/Plastic Blend Pellets Prepared with Buehler Pelletizer. Values are the average of two measurements. Top Value is the Percent of the Total Sample Mass (**Equation 1**) and Bottom Value is the Percent of the Biomass Mass (**Equation 2**).

				Immersion Time (h)				
Sample	**Particle Size**	**Composition (HHV %)**	**Composition (wt %)**	**2**	**4**	**6**	**8**	**24**
TW		100	100	113	115	120	125	148
MWP Blend	1/16 to 1/8-inch	100	100	1.2	1.8	2.2	2.3	3.0
HDPE/Biomass	1/16 to 1/8-inch	15:85	12:88	3.2 3.6	5.4 6.1	5.3 6.1	5.6 6.4	8.7 9.9
PET/Biomass	1/16 to 1/8-inch	15:85	12:88	-	-	-	-	-
MWP/Biomass	1/16 to 1/8-inch	30:70	25:75	3.9 5.2	5.1 6.8	5.9 7.9	6.1 8.1	6.1 9.2
MWP/Biomass	1/16 to 1/8-inch	50:50	45:55	3.3 6.0	4.8 8.7	5.8 10.6	6.5 11.8	8.1 14.7
MWP/Biomass	1/16 to 1/8-inch	70:30	65:35	1.9 5.4	2.7 7.7	3.3 9.4	3.4 9.7	5.5 15.7
HDPE/Biomass	<1/16-inch	15:85	12:88	1.7 2.0	4.0 4.6	3.5 4.0	4.3 4.9	5.6 6.3
PET/Biomass	<1/16-inch	15:85	12:88	4.9 5.6	5.8 6.6	5.5 6.3	5.1 5.8	6.2 7.1
MWP/Biomass	<1/16-inch	30:70	25:75	1.5 2.0	2.1 2.8	2.6 3.5	3.4 4.6	4.3 5.7
MWP/Biomass	<1/16-inch	50:50	45:55	1.3 2.3	2.2 4.0	2.9 5.3	3.4 6.2	7.3 13.3
MWP/Biomass	<1/16-inch	70:30	65:35	1.0 2.7	1.7 5.0	2.6 7.3	3.3 9.5	4.4 12.7

The first point to note is that the water uptake of the biomass without any plastic component is more than 100% even after only 2 hours. This is consistent with earlier UK findings where less than 10 wt% TW was able to be added to a solid fuel (coal) slurry as all the free water was absorbed. This resulted in a thick paste that could not be pumped or tested with the viscometer.

The next point is that ≤10% water uptake was observed in all MWP blend/biomass samples through 8 hours of immersion. Even after 24 hours of immersion the water uptake was only approaching 10%, when considered on total mass basis. The exception to this is for the 15:85 HHV% PET/biomass sample, highlighted in gray, in **Exhibit 7**. In this case the pellet disintegrated in the water before 2 hours and subsequent masses could not be measured. It is worth mentioning that the data for the 15:85 HHV% HDPE/biomass and 15:85 HHV% PET/biomass samples, highlighted in gray in **Exhibit 7**, were uncertain. Between 4 and 8 hours separated particles were visually observed in the water, indicating slight disintegration of the sample disk. This is reflected in the decreased masses between 4 and 8 hours.

Overall, to achieve minimum CO_2 emissions during gasification, the maximum amount of biomass in the solid fuel blend is desired. Based on these results, the optimal biomass content is 80-85 HHV% and the optimal plastic content is 15-20 HHV%.

As shown in **Exhibit 8,** the water uptake increased over immersion time.

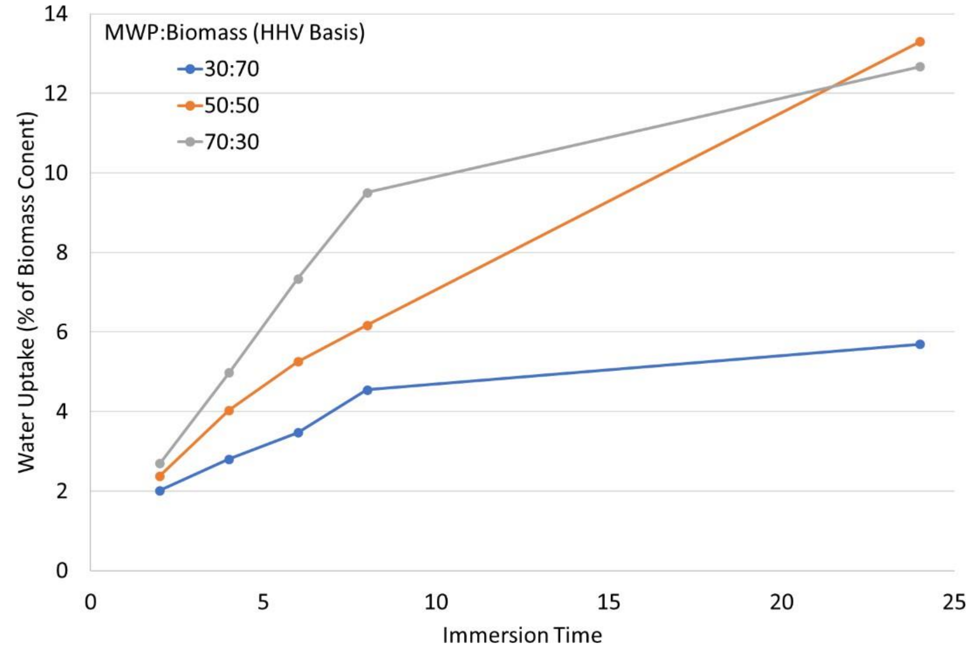

Exhibit 8. Water Uptake of MWP/Biomass Blend Pellets with <1/16-inch Particles over Time.

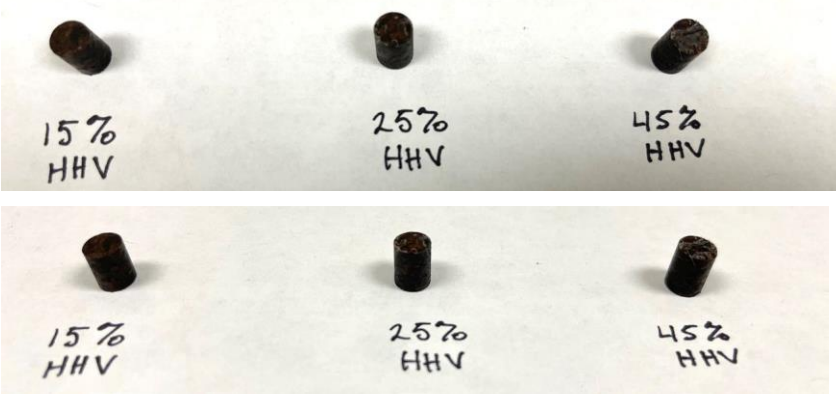

Exhibit 9. Typical Plastic/Biomass Blend Pellets Prepared with the Dake Hydraulic Press with 0.25-inch Die.

Water uptake was also measured from pellets prepared with the Dake hydraulic press with a 0.25-inch die, **Exhibit 9**. Since the die set doesn't have forced cooling, the pellets were taken out when the die set was cooled to around 100 ºC. The surface of the pellet is coarse, compared to the pellets made from the Buehler Pelletizer. **Exhibit 10** shows that the water uptake decreased significantly when the ratio of plastic increased from 15% to 45%. Three pellets of each blend were evaluated with the average water uptake values shown. Error bars represent the range between the maximum and minimum values. The dip observed with the 15% HDPE sample is due to degradation of the pellets causing a slight weight decrease. However, overall, the water uptake of these small pellets appeared to be higher compared to the pellets made from the Buehler Pelletizer. These results suggest that the pelletization holding time and the cooling rate of pellets after pelletization might play an important role in forming a strong hydrophobic surface. Thus, these parameters must be controlled for future large-scale extrusion tests.

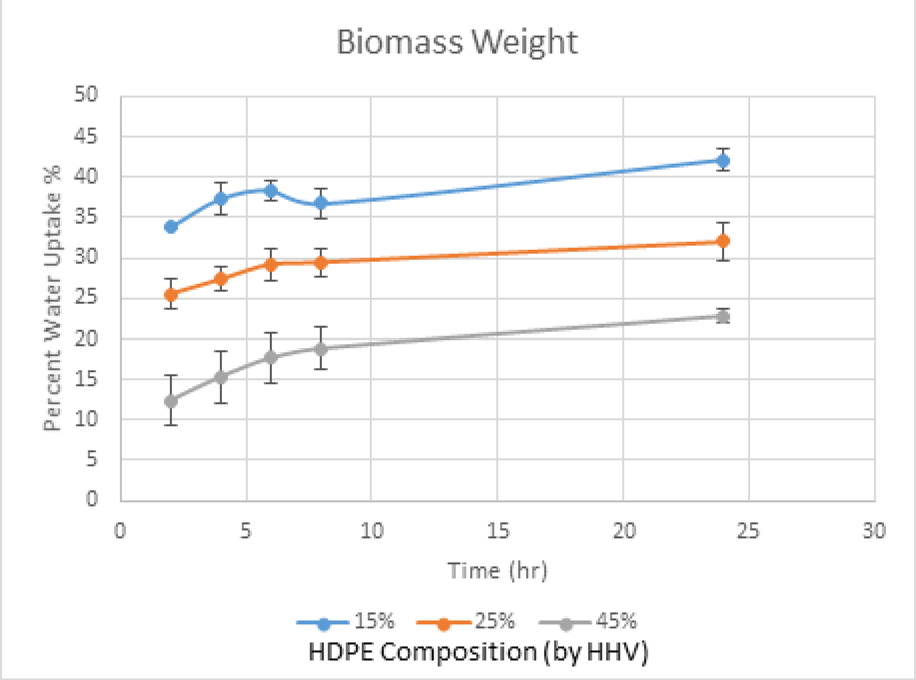

Exhibit 10. Water Uptake of MWP/Biomass Pellets with 1/8-inch Particles Blended with HDPE over Time.

B. Contact Angle

Contact angles of various plastic/biomass blend pellets made with the Buehler pelletizer were measured with an optical tensiometer (Attention Theta-lite). The results are presented in **Exhibit 11**. Consistent with water uptake data, a hydrophobic surface was observed on most samples with a contact angle >90°. The exception to this is the 15:85% HDPE/biomass sample where the contact angle approached 90°. The contact angle was not measured for the biomass sample due to its unavailability of smooth biomass surface. However, one published study reported a contact angle in the range of 103-113° for TW during torrefaction between 200-300 °C[2]. It should also be noted that during the contact angle experiments with 15:85 ratios of plastic/biomass blends, the water drop was observed to slowly decrease in size as it penetrated the sample pellet.

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[2] Wei-Hsin Chen, Bo-Jhih Lin, Baptiste Colin, Anelie Petrissans, Mathiew Petrissans. A Study of Hygroscopic Property of Biomass Pretreated by Torrefaction. Energy Procedia. Volume 158. February 2019. Pages 32-36.

Exhibit 11. Contact Angle (^{0}) of Plastic/Biomass Blend Pellets Made with the Buehler Pelletizer.

Samples	**Size**	**Composition (HHV %)**	**Contact Angle (^{0})**
MWP Blend	1/16 to 1/8-inch	100	131.3
HDPE/Biomass	1/16 to 1/8-inch	15:85	88.9
MWP/Biomass	1/16 to 1/8-inch	15:85	109.2
MWP/Biomass	1/16 to 1/8-inch	30:70	98.0
MWP/Biomass	1/16 to 1/8-inch	50:50	106.7
MWP/Biomass	1/16 to 1/8-inch	70:30	112.3
HDPE/Biomass	<1/16-inch	15:85	94.4
MWP/Biomass	<1/16-inch	15:85	99.7
MWP/Biomass	<1/16-inch	30:70	110.4
MWP/Biomass	<1/16-inch	50:50	108.3
MWP/Biomass	<1/16-inch	70:30	109.6

Contact angles were not able to be measured from the pellets prepared with the Dake hydraulic press with 0.25-inch die due to an uneven surface, which was possibly caused by the slower cooling rate of pellets after pelletization.

C. Density

As shown in **Exhibit 12**, the bulk density of the pellets prepared with the Buheler pelletizer range from 0.88 to 1.23 g/cm^3 for all MWP/biomass blends. The density increases with an increasing plastic composition. Taken together with the contact angle measurements, Project Milestone 3 is met as the density and hydrophobicity are increased by >20%.

Exhibit 12. Bulk Density of Various MWP/Biomass Blends.

Samples	**Size**	**Composition (HHV%)**	**Bulk Density (g/cm^3)**
MWP	1/16 to 1/8-inch	100	1.45
Biomass (TW)	1/2 to 2-inch	100	0.52
HDPE/biomass	1/16 to 1/8-inch	15:85	0.88
PET/biomass	1/16 to 1/8-inch	15:85	0.95
MWP/biomass	1/16 to 1/8-inch	30:70	0.96
MWP/biomass	1/16 to 1/8-inch	50:50	0.96
MWP/biomass	1/16 to 1/8-inch	70:30	1.23
HDPE/biomass	<1/16-inch	15:85	0.81
PET/biomass	<1/16-inch	15:85	0.90
MWP/biomass	<1/16-inch	30:70	0.91
MWP/biomass	<1/16-inch	50:50	1.01
MWP/biomass	<1/16-inch	70:30	1.15

D. FTIR Characterization

FTIR characterization was performed on the plastic/biomass pellets prepared with the Buehler pelletizer using a ThermoFisher Scientific iS10 Nicolet instrument with an attenuated total reflection (ATR) accessory. The spectra collected are presented in **Exhibit 13.** The background was collected from a pure biomass sample. All spectra were recorded in absorption mode under ambient conditions with a collection time of 40 s. Biomass adsorption peaks include:

1. O-H (water) stretch: 3338 cm^{-1},
2. C-O stretch: 1028cm^{-1}
3. Aliphatic symmetric and asymmetric $-CH_2-$ stretching: 2906-2850 cm^{-1}

The FTIR characterization clearly demonstrated the decrease of biomass adsorption with the decrease of biomass composition. This is consistent with the water uptake and contact angle data and verifies that the plastic encapsulates the biomass, meeting Project Milestone 4.

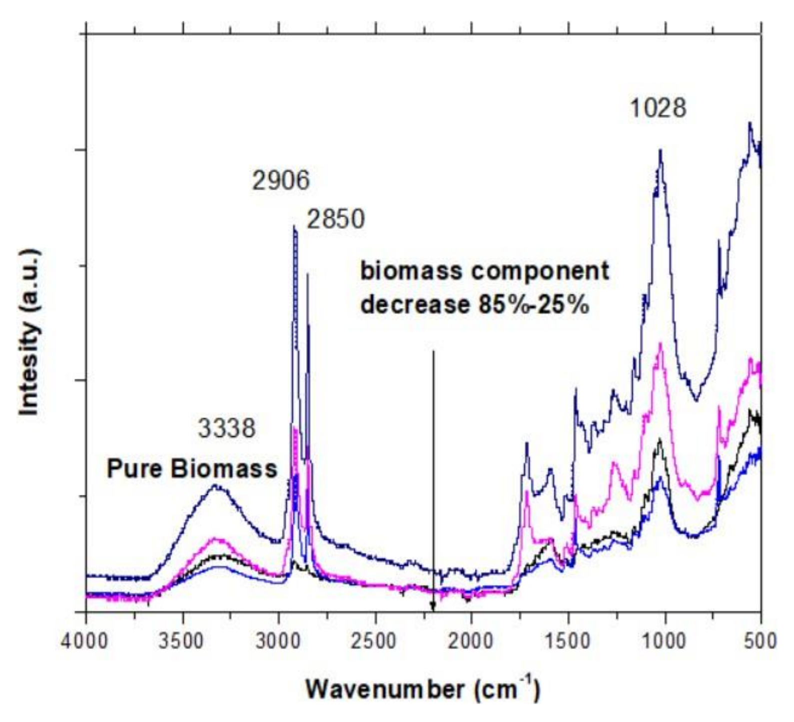


Exhibit 13. FTIR Spectra Collected from MWP/Biomass Blend Pellets made with the Buehler Pelletizer.

E. Porosity

The BET surface area measurements were investigated using MWP:biomass blend pellets prepared with a 15:85 (HHV basis) blend and particles of 1/16 to 1/8-inch in size, with results shown in **Exhibit 14**. A reduced surface area was found for both the solid pellet surface, ~55%, and the reground pellet material, ~25%.

Exhibit 14. BET Surface Area Measurements.

Sample	**BET Surface Area (m^2/g)**	
Biomass	0.5401	1/8-inch Particles
Blended Pellet	0.2452	MWP/Biomass, 15% Biomass (HHV Basis), Pellet made with 1/8-inch Particles
Reground Pellet	0.4068	Pellet Reground with Mortar and Pestle, MWP/Biomass, 15% Biomass (HHV Basis), Pellet made with 1/8-inch Particles

Notes:
System error of BET method is 10 m^2/g.
Degassing at 104 °C for 600 min.
BET surface area calculated at relative pressure of 0.23.

3.2 Biomass/Plastic Co-Extrusion for Blended Fuel Production

By applying the methods described earlier from Project Task 3, extrudable plastic pellets were prepared. Torrefied pinewood was blended with the MWP and then co-extruded for larger quantity production. Initially, the extruder was tested without the die using mixtures of plastic and biomass material. A picture of the extruder is shown in **Exhibit 15**.

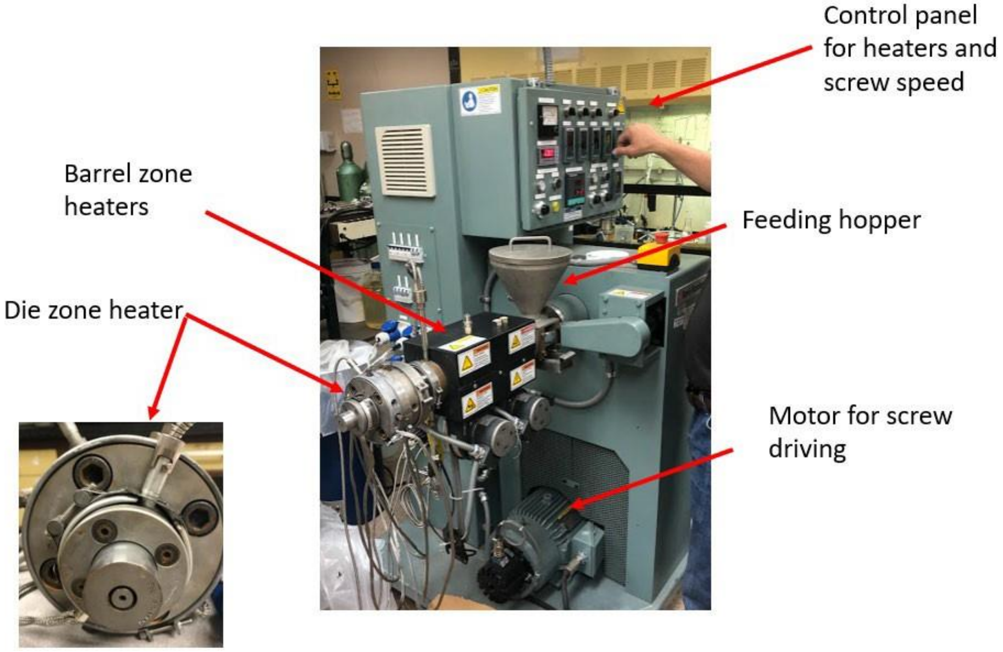


Exhibit 15. Extruder for Plastic/Biomass Blend Fuel Production.

Three different HDPE:TW mass ratios were tested for extrusion. The HHV ratio is calculated based on the estimated heating value of HDPE (19,000 Btu/lb) and the measured heating value of TW (8,421 Btu/lb). The test matrix and conditions are shown in **Exhibit 16**. The barrel zone temperatures were set as 370 °F and 420 °F.

Exhibit 16. Test Matrix and Conditions for Extrusion Without Die.

Mass Ratio (HDPE:TW)	HHV Ratio (HDPE:TW)	Total Mass (g)	Residence Time (min)	Feed Rate (g/min)
1:1	69:31	100	8~11	2.1
1:2	53:47	100	12~14	2.7
1:4	36:64	100	8~11	2.6

The feed materials were premixed from ground HDPE and TW, as shown in **Exhibit 17**.

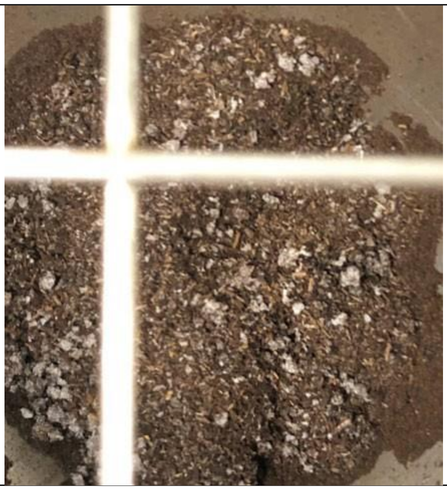


Exhibit 17. Premixed Plastic/Biomass Mixture for Extrusion

The extrusion results for three different plastic/biomass ratios are shown in **Exhibits 18-20**. The result shows extruded material is bonded together with higher HDPE contents. The extruded material is one continuous piece with mass ratio of HDPE:TW = 1:1, while separated short pieces with mass ratio of HDPE:TW = 1:4. Considering no pressure has been placed on to the extrusion material yet, a better result is expected when the die is installed.

Exhibit 18. Extruder Testing Result (without die) with Mass Ratio of HDPE:TW = 1:1

Exhibit 19. Extruder Testing Result (without die) with Mass Ratio of HDPE:TW = 1:2

Exhibit 20. Extruder Testing Result (without die) with Mass Ratio of HDPE:TW = 1:4

After optimizing the operational parameters and gaining experience on the co-extrusion process, the extruder was tested with the die using the 1:4 mass ratio of HDPE:TW, which performed the best in slurryability testing. The HHV ratio was calculated based on measured heating values of HDPE (19,871 Btu/lb) and TW (8,421 Btu/lb). The testing matrix and conditions are shown in **Exhibit 21**. The barrel zone temperatures were set to 330 ºF.

Exhibit 21. Test Matrix and Conditions for Extrusion with Die.

Mass Ratio (HDPE:TW)	HHV Ratio (HDPE:TW)	Total Mass (g)	Residence time (min)	Feed rate (g/min)
1:4	37:63	250	24	5.8

The extrusion results for the 1:4 mass ratio of HDPE/biomass are shown in **Exhibits 22** to **25**. As expected, the results show that the extruded materials are bonded together better with the die than without as a result of compacting force, **Exhibit 22**. The following extruder parameters were used to produce additional material for further testing. All zone temperatures were set to 330 °F and screw speed at 3 rpm. The die and screw were allowed to preheat for 30 minutes, and the screw and feed roller were turned on and allowed to heat for another hour. The material was then loaded up to 250 g. Once extrusion ceased, the material remaining in the die was left to cool and extruded with the next batch. Trial 1 was done with an empty die and barrel. **Exhibit 24** illustrates how the Trial 1 results in **Exhibit 23** are defined. There is a lag between when the material reaches the die and extrusion begins. This also creates three different feeding rates over the course of the extrusion. Trial 2 was separated into three stages due to extruder troubleshooting. These runs were done with the die full of material from the previous run. Trial 2.1 and 2.2 started with an empty barrel and Trial 2.3 started with a full barrel. **Exhibit 25** illustrates how the Trial 2 results in **Exhibit 23** are defined. With the die full of material from a previous trial, the extrusion begins once the material reaches the die. This reduces the feeding rates to just two over the course of the extrusion process.

Exhibit 22. Extruder Testing Result (with Die) with Mass Ratio of HDPE:TW = 1:4.

Exhibit 23. Extrusion with Die Trial 1 Details.

Trial	Mass Ratio (HDPE:TW)	HHV Ratio (HDPE:TW)	Mass Loaded (g)	Mass Extruded (g)	Residence Time (min)	Feed Rate (g/min)	Output Rate (g/min)	Temperature Set Point (°F)
1	1:4	37:63	250	65.5	24	5.8	1.8	330
2.1	1:4	37:63	500	157.1	17		4.8	330
2.2	1:4	37:63	500	82	7		3.2	330
2.3	1:4	37:63	500	28	12		1.8	330

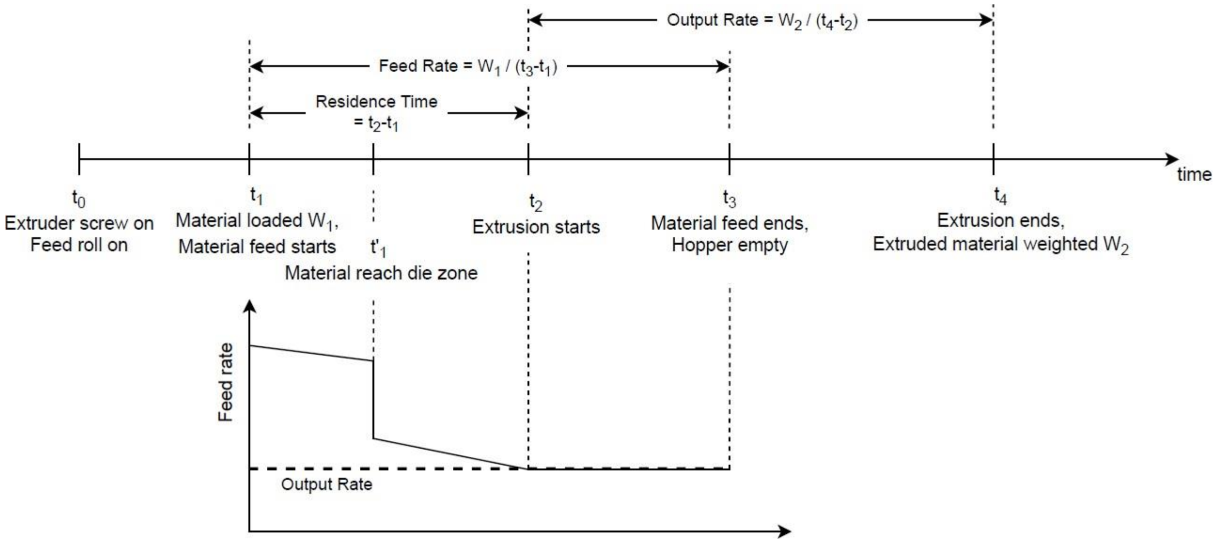


Exhibit 24. Extrusion Diagram with Empty Die.

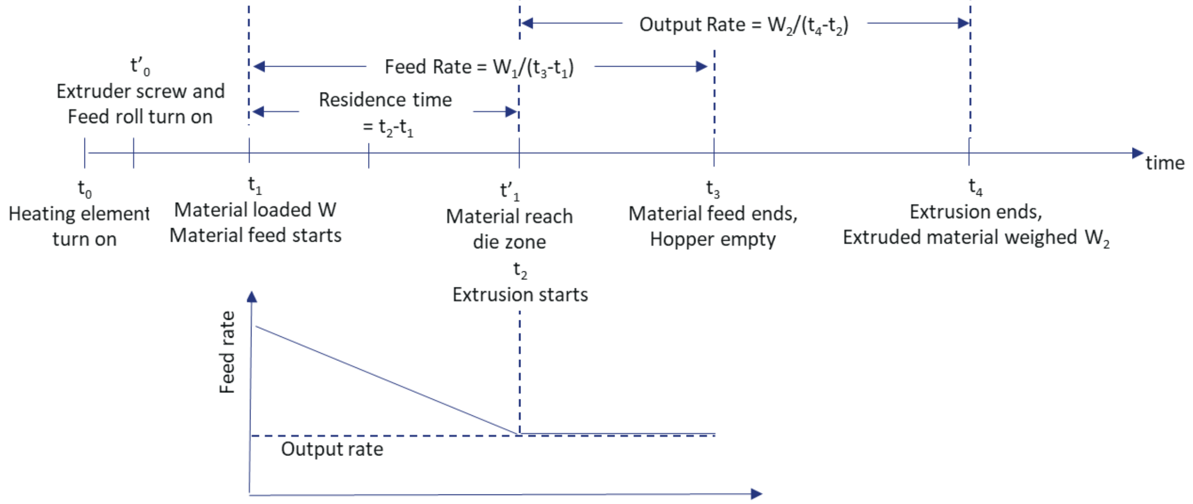


Exhibit 25. Extrusion Diagram with Full Die.

The lesson learned from the abovementioned study was that the material produced from the UK extruder, was determined to be well mixed, but the process too slow to produce the amount of material needed for a gasification demonstration. To produce the material required for Project Task 10 it would take longer than the allotted time. The extruder die vendor, Davis Standard, was contacted about a replacement die that could produce material faster and it was suggested that the Polymers Center in Charlotte, North Carolina may be able to produce the material needed. The Polymers Center is a non-profit organization supported by North Carolina State University that works with companies to advance polymer and extrusion processes. They have also worked with furniture manufacturers in the past to blend sawdust and plastic making them an ideal resource to produce the amounts of blended material needed for Project Task 10.

The Polymers Center requires processed wood particles no larger than 500 microns. To ensure that our materials will work with their equipment, 100 lbs of milled TW less than 500 microns was prepared along with 30 lbs. of HDPE for shipment. TW that was purchased a few years ago for coal/biomass to liquid chemicals research was used, as shown in **Exhibit 26**.

Exhibit 26. Wet TW in Storage Bag (Left). Blower Used to Create Airflow Over Spread Material (Center). A portion of the Dried TW after Two Days of Drying (Right).

A hammer mill with a 2 mm screen was used to break down the wood chips. The resulting material was sieved using a 500 micron sieve tray and the material that didn't pass through the sieve was further broken down using a blade mill with a 1 mm screen. This material was then sieved again. Approximately 100 lbs. of material, **Exhibit 27**, was milled and sieved and shipped to the Polymers Center.

Exhibit 27. Milled Torrefied Wood Sieved to < 500 µm.

A 25 kg trial test was conducted at the Polymers Center in Charlotte, NC. Due to torque limitations of the extruders, the weight ratio of 1:4 HDPE:TW (37:63 HHV ratio) was changed to 2:3 weight ratio of HDPE: TW (61:39 HHV ratio). Please note that our previous investigation indicated that including only 20% plastic in the fuel blend is enough to meet the target water uptake, heating value and slurryability. A higher amount of HDPE will result in a better output on heating value and water uptake. To ensure enough material for 1 TPD gasifier operation, additional TW was dried and ground, and an additional 50 kg of HDPE was purchased. A picture of the extruded material as produced by the Polymers Center is presented in **Exhibit 28**.

Exhibit 28. Extruded Material Produced by the Polymers Center with 2:3 weight ratio of HDPE:TW (61:39 HHV). It was produced in pellets and reground for gasification testing (Project Task 10).

3.3 Slurry Preparation and Characterization

Blends of solid fuels were prepared by blending the coal and extruded biomass/plastic fuels from Project Task 4. Slurryability tests were completed with 60 wt% solid fuel at HDPE/biomass:coal ratio of 30:70 by mass. The viscosity was measured to be lower than a 55 wt% coal only slurry. The HDPE/biomass ratio was 1:4 by mass with 70 wt% of particles sized between 420 µm and 1.18 mm and 30 wt% of particles between 75 µm and 420 µm.

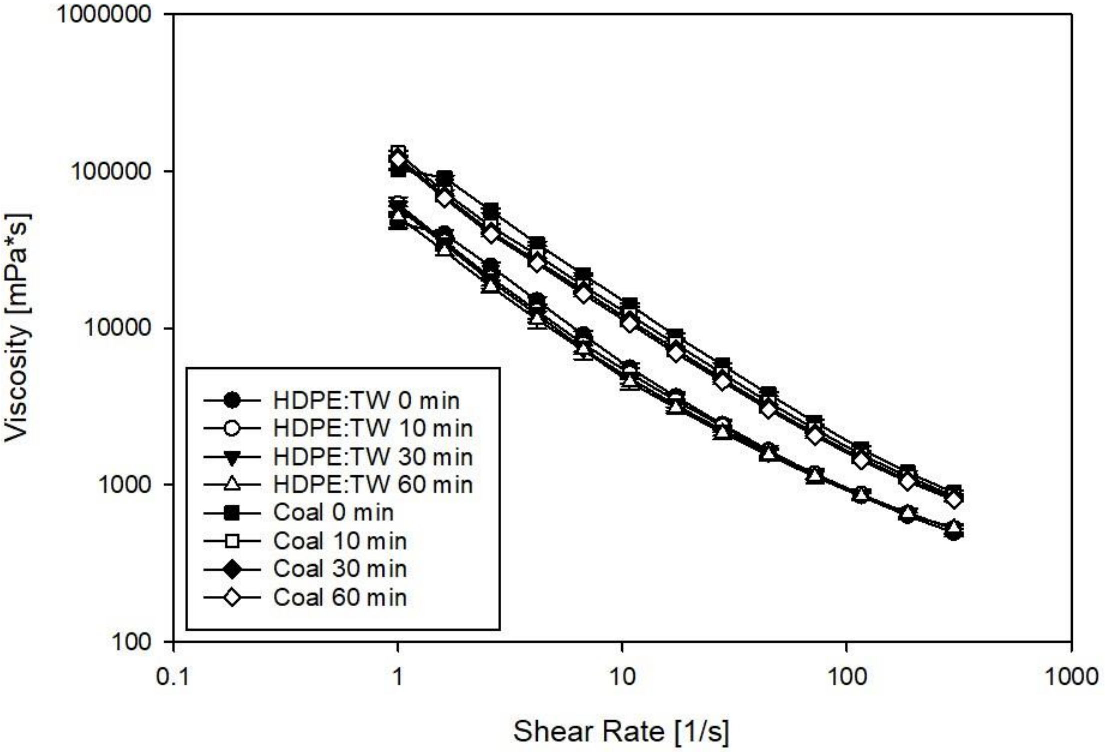


Exhibit 29. Measured Viscosities from 55 wt% Coal Only Slurry (Top Set) and From the HDPE:TW Blend at a 1:4 Mass Ratio (Bottom Set).

Results are presented in **Exhibits 29** and **30** and images of the slurries in **Exhibit 31**. In **Exhibit 29**, the top set of curves are from the 55 wt% coal only slurry. The bottom set are from the HDPE:TW blend.

Exhibit 30. Slurry Evaluation Parameters.

Case	HDPE % in Blend	TW % in Blend	Blend % in Solids	Coal % in Solids	Solid % in Total	Water % in Total	Coarse % in Blend	Fine % in Blend	µ (cp) @ 100 -s	wt% (HDPE)	wt% (TW)	wt% (Coal)	HHV% (HDPE)	HHV% (TW)	HHV% (Coal)	Mixing Speed (RPM)
1	20%	80%	30%	70%	60%	40%	70%	30%	942	6%	24%	70%	9.3%	16.5%	74.2%	1000
2	-	-	0%	100%	55%	45%	-	-	1731	-	-	100%	-	-	100%	1000

Exhibit 31. 60 wt% Solid Slurry Containing HDPE:TW 1:4 Mass Ratio (Left) and 55 wt% Solid Coal Only Slurry (Right).

Further tests were conducted to determine the impact of the particle size and the total viscosity measurement time on the slurryability. The slurry tested contains 60 solid wt% of which 70 wt% is coal and 30 wt% is extruded material of HDPE:TW. Two different particle size ranges were used for the extruded material, less than 1 mm and less than 2 mm. The slurry for each particle size was made two times and the viscosity was measured at 0, 10, 30, and 60 minutes. The data points for each were averaged with error bars.

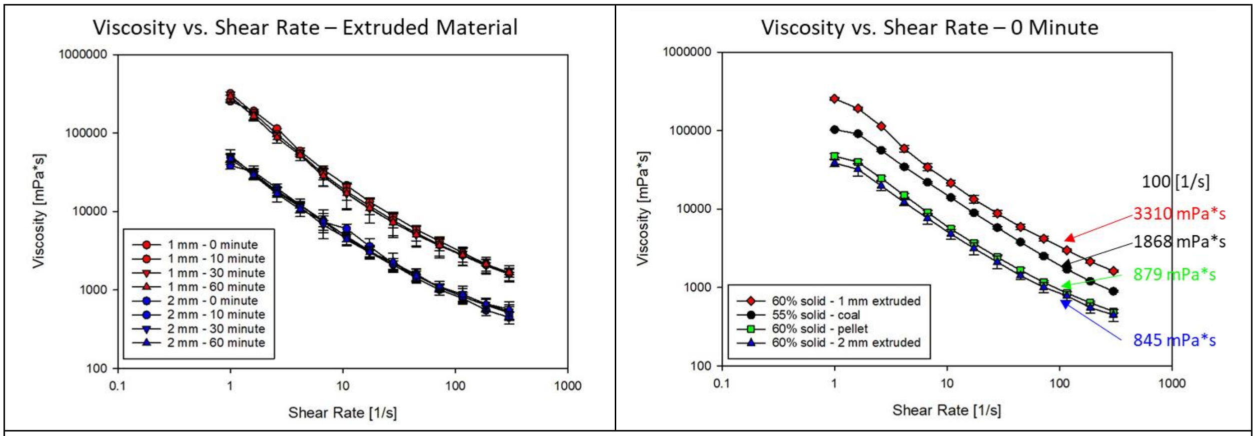


Exhibit 32. The Viscosity vs. Shear rate as a Function of Particle Size (Left). Initial Viscosity vs. Shear Rate of Slurries Prepared with the Extruded Material slurries, the Pellets, and Coal Only (Right).

Slurry prepared with extruded material particles of <2 mm and the slurry made from the pelletized material have similar viscosities. Slurry prepared with extruded material particles of <1 mm had a higher viscosity than the coal water slurry, however, the solid wt% of the coal slurry was 55 and not 60, illustrated in **Exhibit 32**. To conclude, the slurryability study shows a decreased viscosity of a TW-plastic-coal-water slurry using a 1:4 HDPE:TW weight ratio (37:63 HHV ratio) at 60 wt% solids when 70 wt% of the solids is coal and 30 wt% of the solids is the extruded material compared to a coal-water slurry with solids of only coal.

3.4 Solid Fuel Characterization

The coal/biomass/plastic solid fuel blend and the coal identified in Project Task 5 were characterized by proximate, ultimate, heating value, major and minor ash mineral content, and ash fusion temperatures as per ASTM standards.

The ultimate analysis was performed for TW and the HHV was determined with results shown in **Exhibit 33**.

Exhibit 33. Ultimate Analysis and HHV of Ground TW.

%Ash	3.05
%Moisture	8.95
%Carbon	49.59
%Hydrogen	5.88
%Nitrogen	0.2
%Total Sulfur	0.03
%Oxygen	41.25
%Volatile Matter	69.73
%Fixed Carbon	18.28
BTU/lb Gross Calorific Value	8421

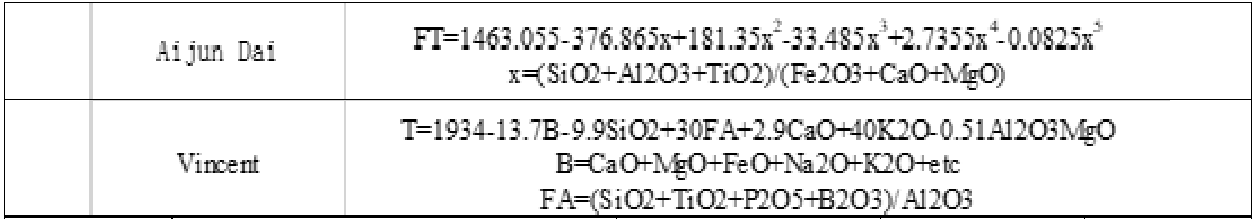
The major ash analysis was conducted via XRF on ash produced by the blended material of HDPE:TW, listed in **Exhibit 34**.

Sample	%SiO$_2$	%Al$_2$O$_3$	%Fe$_2$O$_3$	%CaO	%MgO	%Na$_2$O	%K$_2$O	%P$_2$O$_5$	%TiO$_2$	%SO$_3$
HDPE1 TW4 ash	39.5	9.54	11.5	17.77	4.16	1.76	3.36	1.87	3.48	1.09

Sample	%Ash	%Moisture	ppm Mn	ppm Cu	ppm Zn	ppm Ba
HDPE1 TW4 ash	63.15	4.91	7055	731	1938	1349

Exhibit 34. Major Ash Analysis Results Showing the Percent of Oxides (Top) and the Percent of Ash, Moisture, and Mineral Content (Bottom).

The results from the major ash analysis for the blended material as well as results from a previous major ash analysis on the coal were used to approximate the ash fusion temperature using two different methods.



Aijun Dai	$FT=1463.055-376.865x+181.35x^2-33.485x^3+2.7355x^4-0.0825x^5$ $x=(SiO_2+Al_2O_3+TiO_2)/(Fe_2O_3+CaO+MgO)$
Vincent	$T=1934-13.7B-9.9SiO_2+30FA+2.9CaO+40K_2O-0.51Al_2O_3MgO$ $B=CaO+MgO+FeO+Na_2O+K_2O+etc$ $FA=(SiO_2+TiO_2+P_2O_5+B_2O_3)/Al_2O_3$

Fuel	**FT (Aijun Dai)**	**FT (Vincent)**
Coal	1229.97 °C	1257.46 °C
70 wt% Coal with 30 wt% 1:4 HDPE:TW	1213.18 °C	1275.88 °C

Exhibit 35. Ash Fusion Temperature Approximation Methods by Aijun Dai (Top) and Vincent (Middle) use the Oxide Contents in Calculations. The results show a difference of less than 20 °C between coal only and the coal/blended material (bottom).

The ash fusion approximation, **Exhibit 35**, shows a difference of less than 20 °C between each method. This is close enough to the results of coal alone, for no major issues or differences to be expected during the gasification.

TGA was conducted using a MWP:biomass blended pellet prepared with a 15:85 (HHV basis) blend and particles of <1/16-inch, with profiles shown in **Exhibit 36**. The TGA heating rate was 20 ºC and a helium flow of 100 scfm was used. Major mass loss is observed at ~347 ºC due to pyrolysis with minor mass loss at ~71 ºC due to water loss. A single pyrolysis peak accounting for most of the mass loss, 72.1%, suggests co-pyrolysis of the blended material.

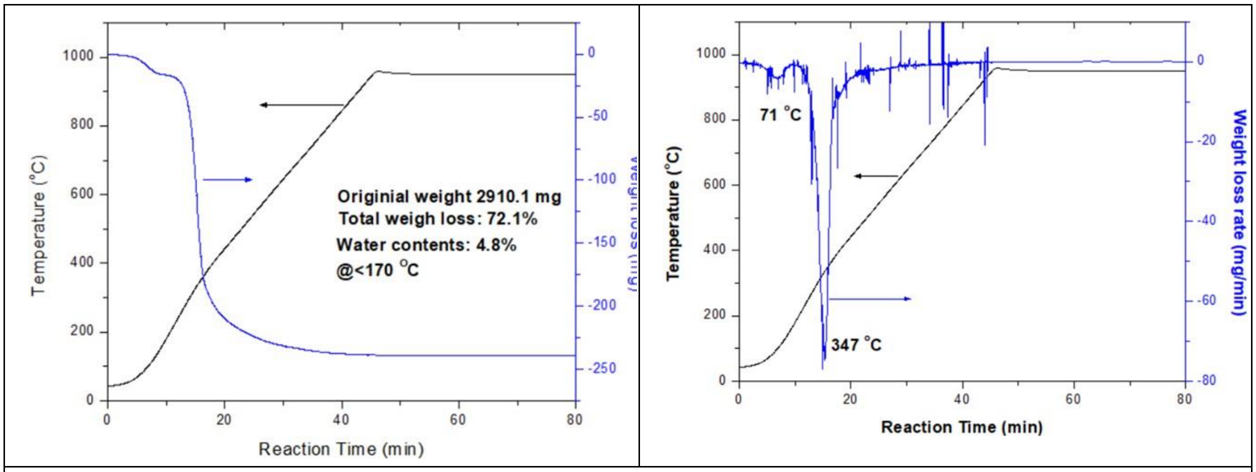


Exhibit 36. TGA profiles. Left: Temperature and Mass Loss as a Function of Time. Right: Temperature and Mass Loss Rate as a Function of Time.

Evolved gas analysis (EGA) was performed with a Frontier Lab Multi-Shot Pyrolyzer (EGA/PY-3030D) with gas chromatography-mass spectrometry (GC-MS) on individual components and 50:50 or 30:70 (HHV basis) blends of PS, PET, and HDPE with torrefied wood. The total sample mass was ~0.2 mg. Results are shown in **Exhibit 37** through **40**. Overall, the torrefied wood started to decompose at 370 ºC and showed a broad thermal decomposition temperature range up to 500 ºC. However, the peak intensity was smaller than the plastics, suggesting that a large portion of the volatile compounds in wood has been released during the torrefaction process. The plastics showed higher thermal decomposition temperatures with HDPE peaked at 497 ºC, PET peaked at 447 ºC, and PS peaked at 430 ºC, respectively. Two distinct peaks were observed from the blended materials, corresponding to the individual components, plastic and wood. Peaks of the

PET:wood blend occurred at 432 ºC, 15 ºC lower than for individual PET, and at 377 ºC, 2 ºC lower than for individual wood. Blending of PS and wood however caused a small shift (to higher temperature) in thermal decomposition; while blending HDPE and wood didn't show significant changes to thermal decomposition temperatures.

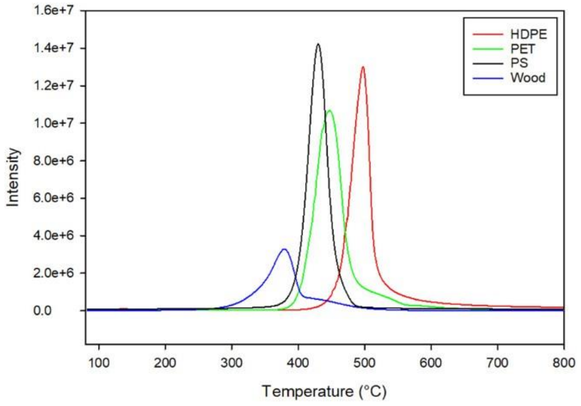


Exhibit 37. EGA of Individual Components. HDPE Peak at 497 ºC and Intensity of 1.30x10^{7}. PET Peak at 447 ºC and Intensity of 1.06x10^{7}. PS Peak at 430 ºC and Intensity of 1.42x10^{7}. Torrefied Wood Peak at 379 ºC and Intensity of 3.29x10^{6}.

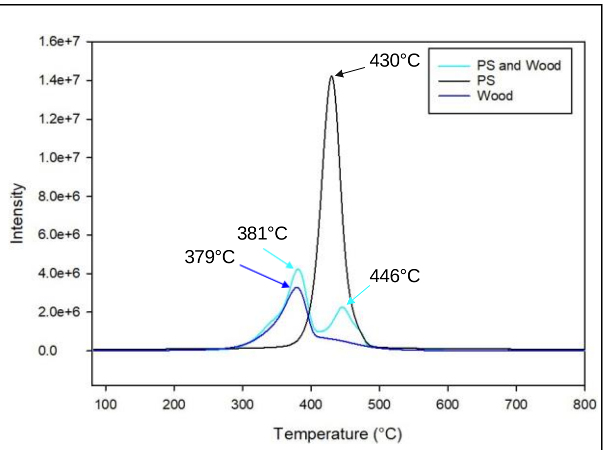


Exhibit 38. EGA of PS, Wood and PS:Wood Blend. PS and Wood Blend (30:70)
Peak 1 at 381 ºC and Intensity of 4.23x10^{6}.
Peak 2 at 446 ºC and Intensity of 2.27x10^{6}.

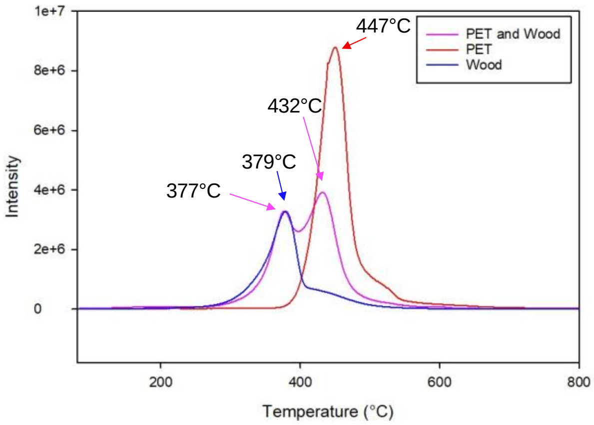


Exhibit 39. EGA of PET, Wood and PET:Wood Blend. PET and Wood Blend (50:50)
Peak 1 at 377 ºC and Intensity of 3.29x10^{6}.
Peak 2 at 432 ºC and Intensity of 3.92x10^{6}.

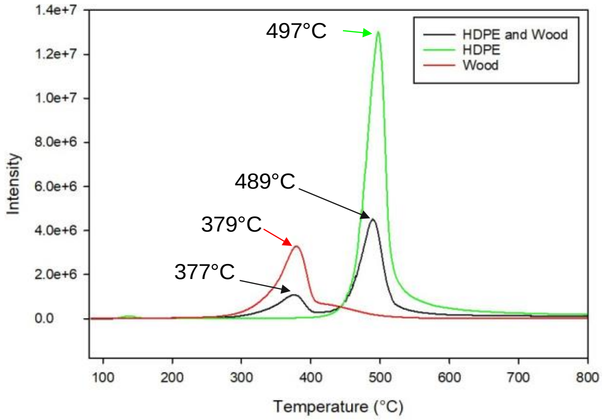


Exhibit 40. EGA of HDPE, Wood and HDPE:Wood Blend.
HDPE and Wood Blend (50:50)
Peak 1 at 377 ºC and Intensity of 1.04x10^{6}.
Peak 2 at 489 ºC and Intensity of 4.12x10^{6}.

Baseline TGA measurements from ground extruded material (1:4 by mass ratio of HDPE:torrefied wood) were collected. These measurements were done in a 100% argon gas environment at a 100 mL/min flowrate with a heat range of 110-900 °C. As shown in **Exhibits 41** and **42**, there were two distinct peaks of mass loss, the first at 330 °C and the second at 450 °C. Literature indicates the 330 °C peak is for the torrefied wood and the 450 °C peak for the HDPE. A baseline measurement for torrefied wood and HDPE were done separately to confirm peak correlation. There was little difference between the mass loss at the different heating rates, but the rate of mass lost increased with the heating rate.

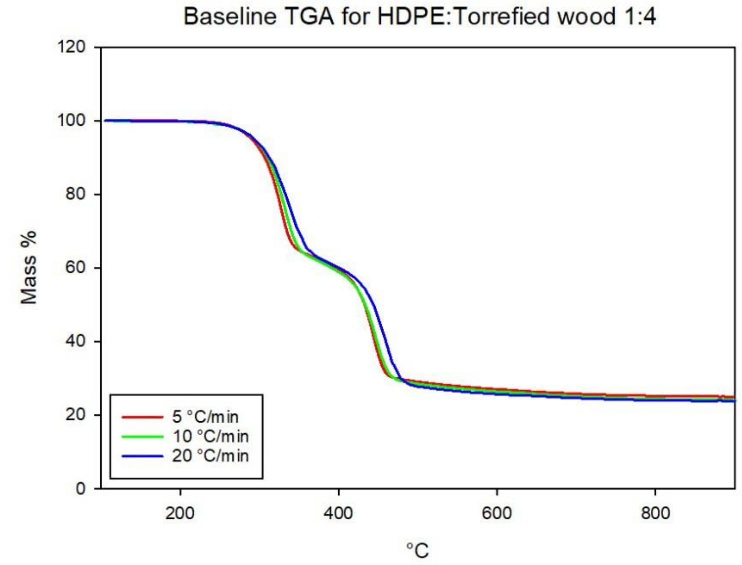


Exhibit 41. Baseline in Pure Argon Gas Environment for Percent of Mass Loss for Co-Extruded HDPE and Torrefied Wood.

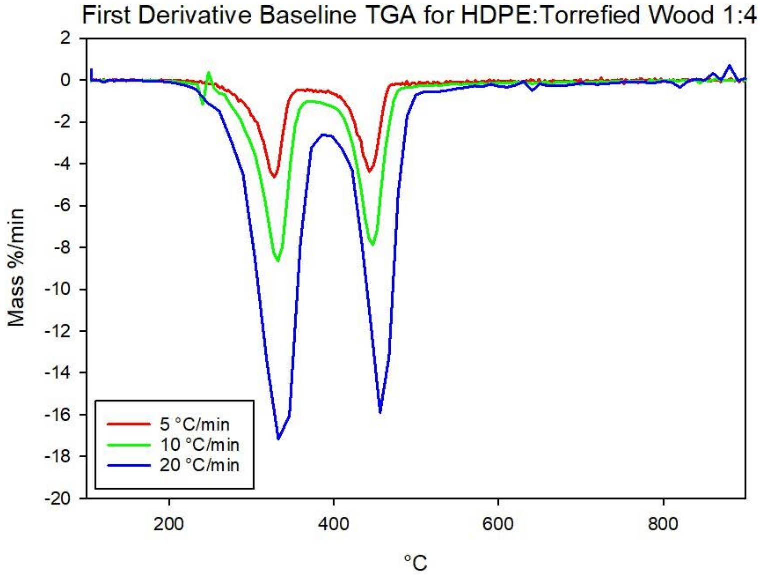


Exhibit 42. Baseline in Pure Argon Gas Environment for the Rate of the Percent of Mass Loss Per Minute for Co-Extruded HDPE and Torrefied Wood at a 1:4 Mass Ratio.

In addition to TGA, fast pyrolysis with GC-MS analysis was also performed at 550 ºC for biomass, PET, PS, HDPE and biomass/plastic blends with identification of volatilized species by FID+MS detectors with results shown in **Exhibits 43** to **49**. Partial breakdown of the tested feedstocks was observed with several signature volatile compounds identified for each feedstock. Blending torrefied wood and plastics produces a mixture of volatiles matching the compounds identified for individual feedstock. This is likely due to the low pyrolysis temperature (550 ºC).

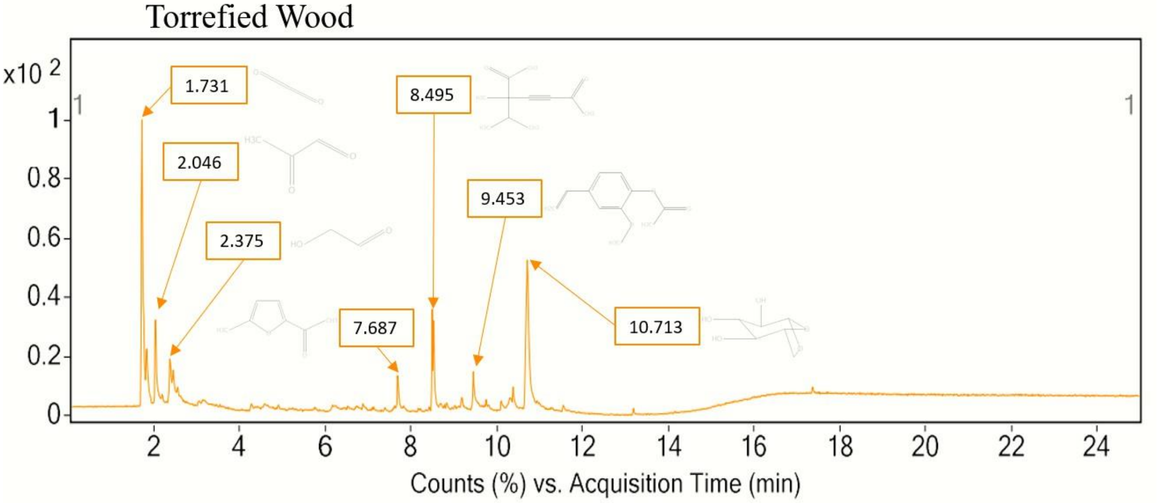


Exhibit 43. Fast Pyrolysis GC-MS analysis at 550 ºC for Torrefied Wood with Evolved Constituents Identified as:
1.731: Carbon Dioxide
2.046: Methyl glyoxal
2.375: Acetaldehyde
7.687: Acetyl-5-methylfuran
8.495: 3-Heptyne-2,6-dione, 5-methyl-5-(1-methylethyl)-
9.453: 4-Acetyoxy-3-methoxystyrene
10.713: Beta-D-Glucopyranose

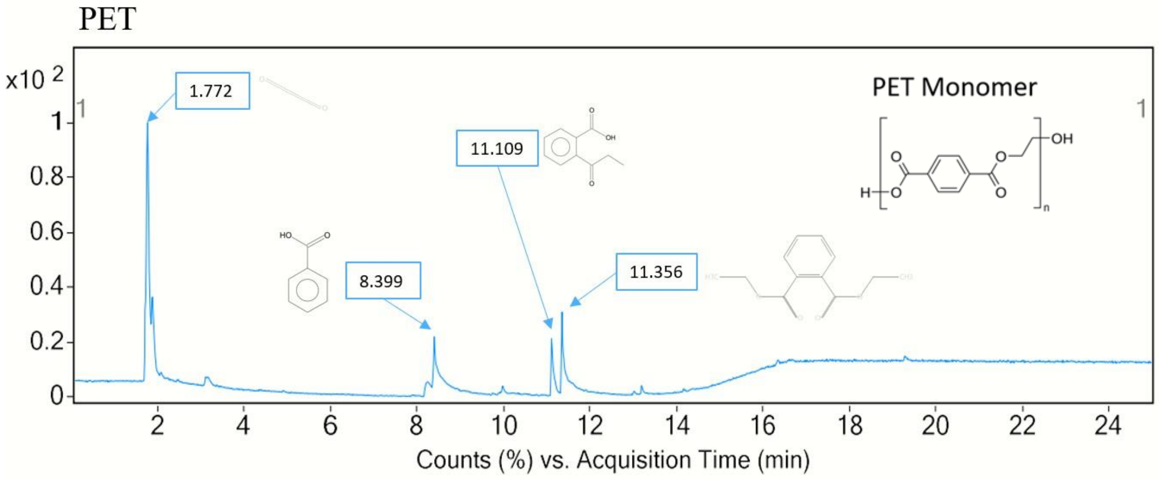


Exhibit 44. Fast Pyrolysis GC-MS analysis at 550 ºC for PET with Evolved Constituents Identified as:
1.772: Carbon Dioxide
8.399: Benzoic acid
11.109: Benzoic acid, 2-(1-oxopropyl)-
11.356: Di-ethyl Phthalate

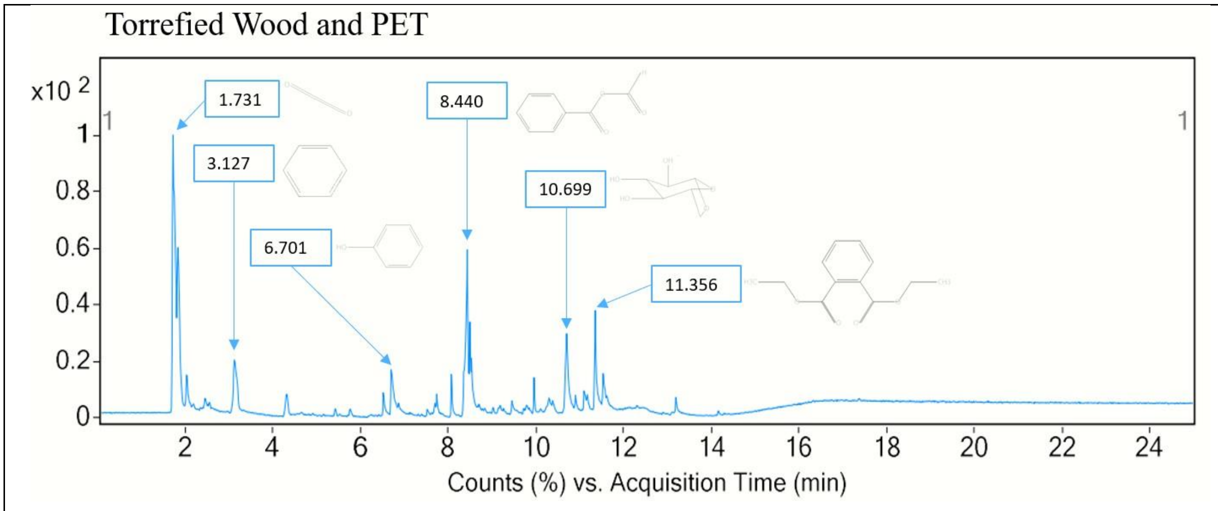


Exhibit 45. Fast Pyrolysis GC-MS analysis at 550 ºC for Torrefied Wood:PET 50:50 (mass ratio) Blend with Evolved Constituents Identified as:
1.731: Carbon Dioxide
3.127: Benzene
6.701: Phenol
8.440: Methanol, oxo-, benzoate
10.699: beta-D-Glucopyranose → found in torrefied wood
11.356: Diethyl Phthalate → found in PET

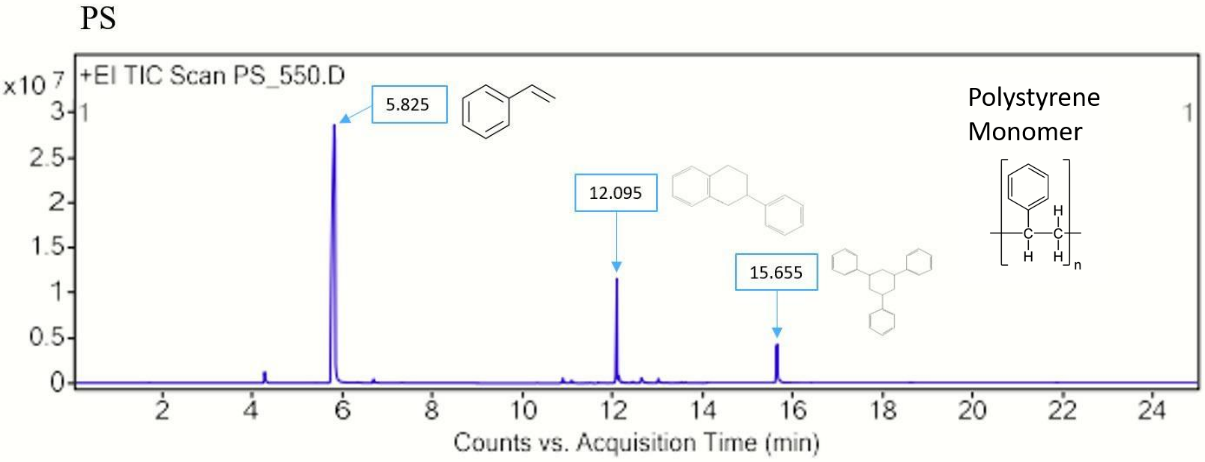


Exhibit 46. Fast Pyrolysis GC-MS analysis at 550 ºC for PS with Evolved Constituents Identified as:
5.825: Styrene
12.095: Napthalene, 1,2,3,4-tetrahydro-2-phenyl-
15.655: Cyclohexane, 1,3,5-triphenyl-

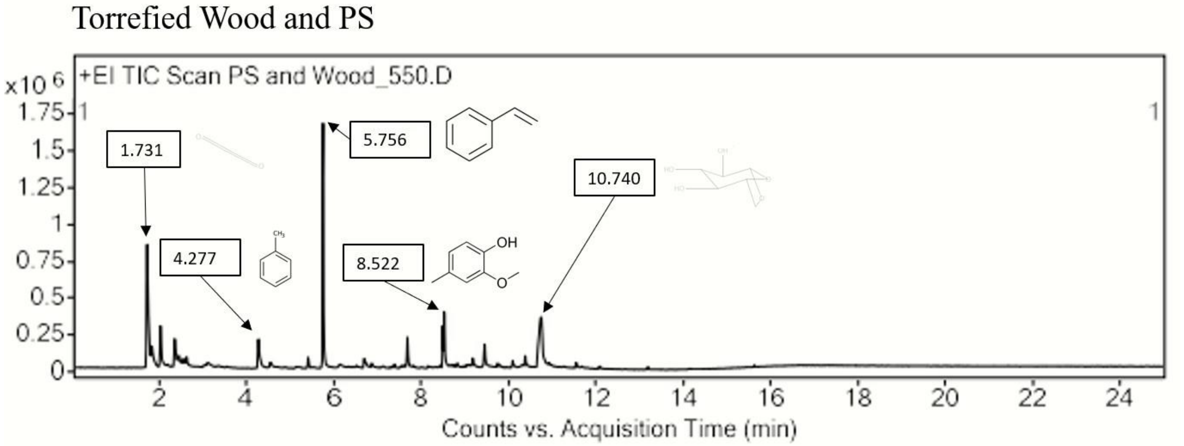


Exhibit 47. Fast Pyrolysis GC-MS analysis at 550 ºC for Torrefied Wood:PS 70:30 (mass ratio) Blend with Evolved Constituents Identified as:
1.731: Carbon Dioxide
4.277: Toluene
5.756: Styrene → found in PS
8.522: Creosol
10.740: beta-D-Glucopyranose → found in torrefied wood

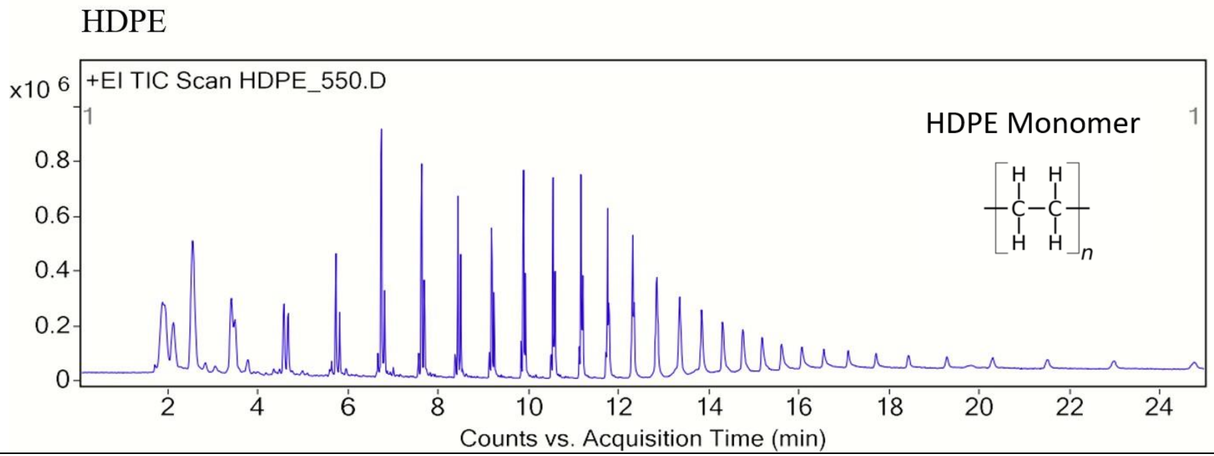


Exhibit 48. Fast Pyrolysis GC-MS analysis at 550 ºC for HDPE with Evolved Constituents Identified. HDPE is structurally a chain of hydrocarbons and the peaks mostly show the different lengths of hydrocarbons that resulted from pyrolysis. Many of the peaks have another peak close-by which show alkanes and alkenes for the same length.

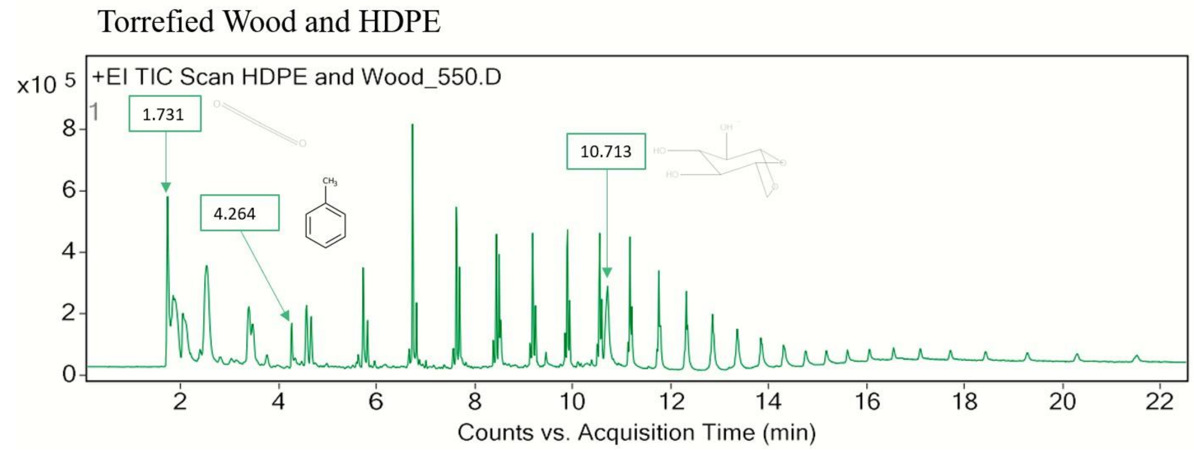

Torrefied Wood and HDPE

Exhibit 49. Fast Pyrolysis GC-MS analysis at 550 ºC for Torrefied Wood: HDPE 50:50 (mass ratio) Blend with Evolved Constituents Identified as:
1.731: Carbon Dioxide
4.264: Toluene → found in torrefied wood and PS
10.713: beta-D-Glucopyranose → found in torrefied wood

Overall, proximate, ultimate, heating value, and major and minor ash mineral content analyses were measured for the individual components of the fuel (coal, HDPE, and torrefied wood) as well as for the 1:4 weight ratio of HDPE:torrefied wood (37:63 HHV ratio) blended material. The ash fusion temperatures were calculated using the results from the previously mentioned analyses for each component and was found to show a less than 20 °C difference from the coal-only ash fusion temperature.

3.5 Blended Fuel Gasification Kinetic Study

Kinetics were evaluated for the solid fuels by pyro-gas GC-MS and TGA. The weight loss and evolved gas composition were measured as a function of temperature from 100 to 1200 °C, and gasification reaction kinetics and reaction activation energies were also determined. The impact of the surrounding gas environment ($CO/H_2/H_2O$) on the reaction kinetics was determined too. The TGA measurements were completed using extruded material from 110 °C to 1100 °C in the following gas environments and were used for the determination of the thermal kinetic and thermodynamics analysis:
1. 100% Argon,
2. 80% Argon with 20% CO,
3. 80% Argon with 20% water vapor,
4. 80% Argon with 10% CO and 10% water vapor.

The ending temperatures were set at a point in which the material would no longer lose mass. A few additional studies were repeated to reach the upper temperature of 1200 °C.

Fast pyrolysis experiments at higher temperatures (700 and 900 ºC) were also studied. Fast pyrolysis with GC-MS analysis was completed at 550, 700, and 900 °C for biomass, PET, PS, HDPE, and biomass/plastic blends with identification of volatized species by FID+MS detectors. As the temperature increased, the ratio of smaller molecular weight compounds to larger compounds increased as well. These results can be seen in **Exhibits 50** to **55.** For these materials, 900 °C was a high enough temperature to break the bonds in many of the compounds and reduce them to more simple ones. This finding could be beneficial due to smaller compounds requiring less energy to form the main products of gasification, CO and H_2.

Monomer:Dimer Ratios		
550 °C	700 °C	900 °C
0.45	3.44	4.26

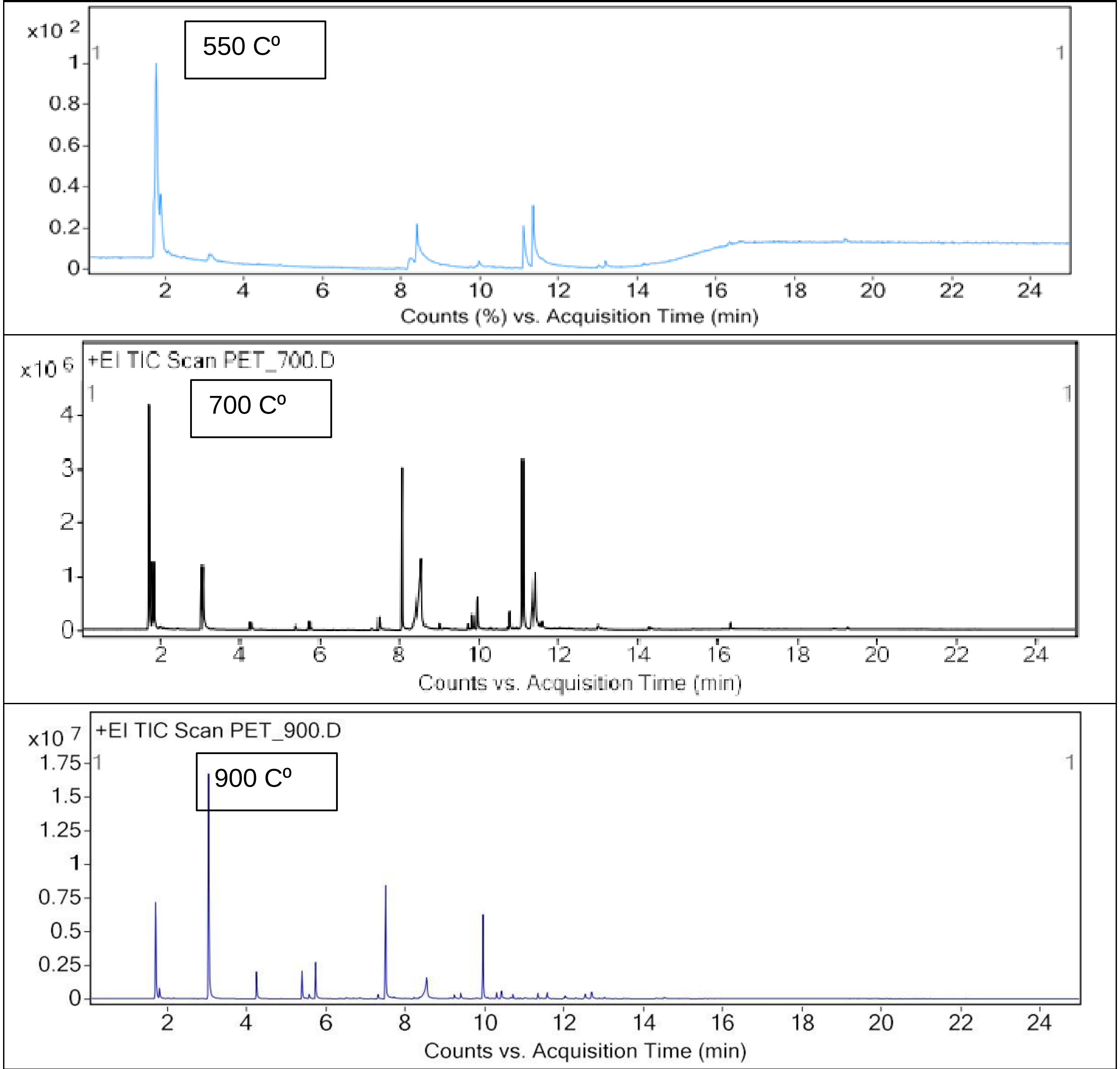


Exhibit 50. Fast Pyrolysis Results for PET without Wood and the Ratios of Monomer to Dimer.

Monomer:Dimer Ratios		
550°C	700°C	900°C
0.62	3.36	11.31

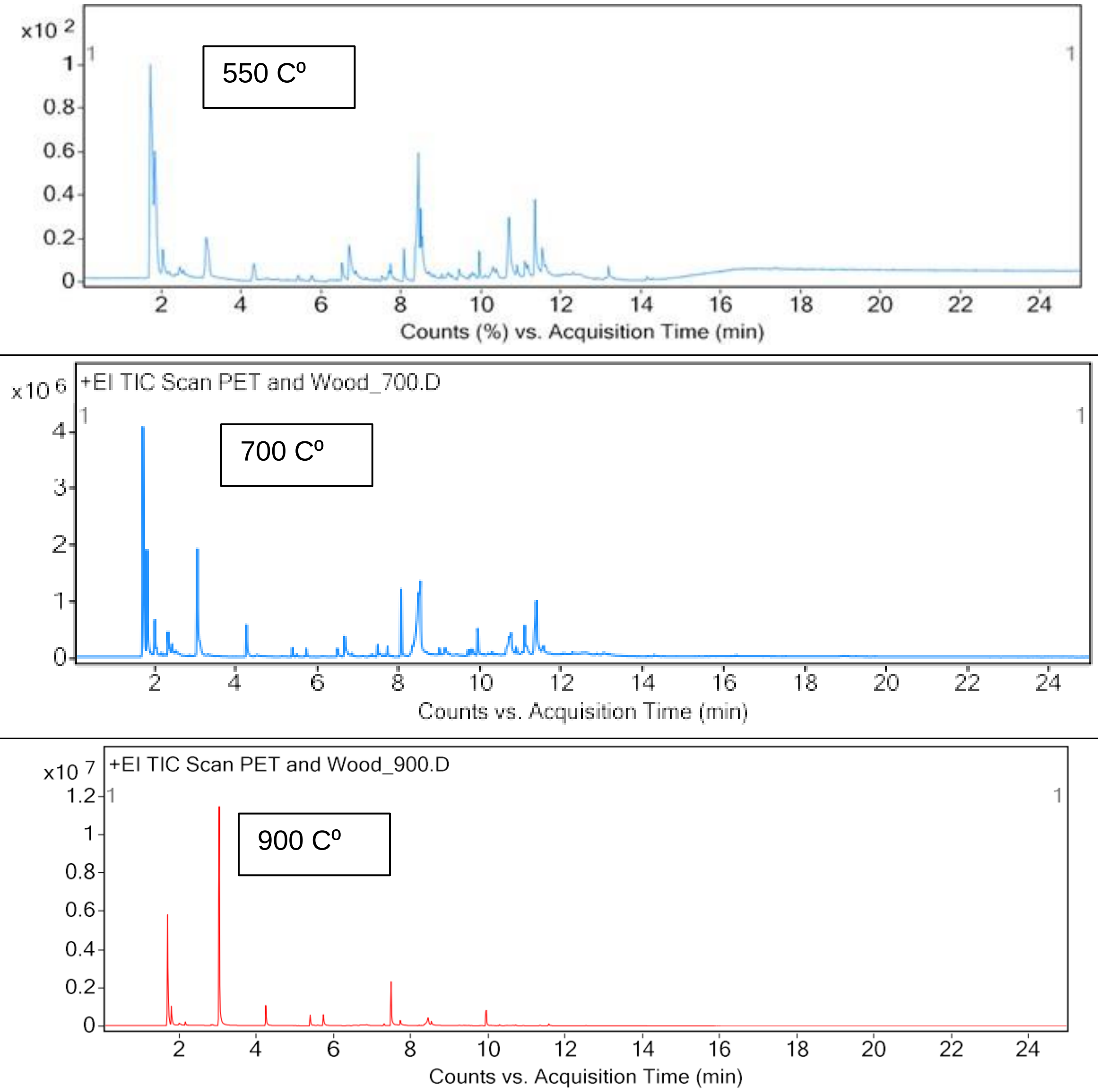


Exhibit 51. Fast Pyrolysis Results for PET with Wood and the Ratios of Monomer to Dimer.

Monomer:Dimer Ratios		
550°C	700°C	900°C
4.82	11.11	13.79

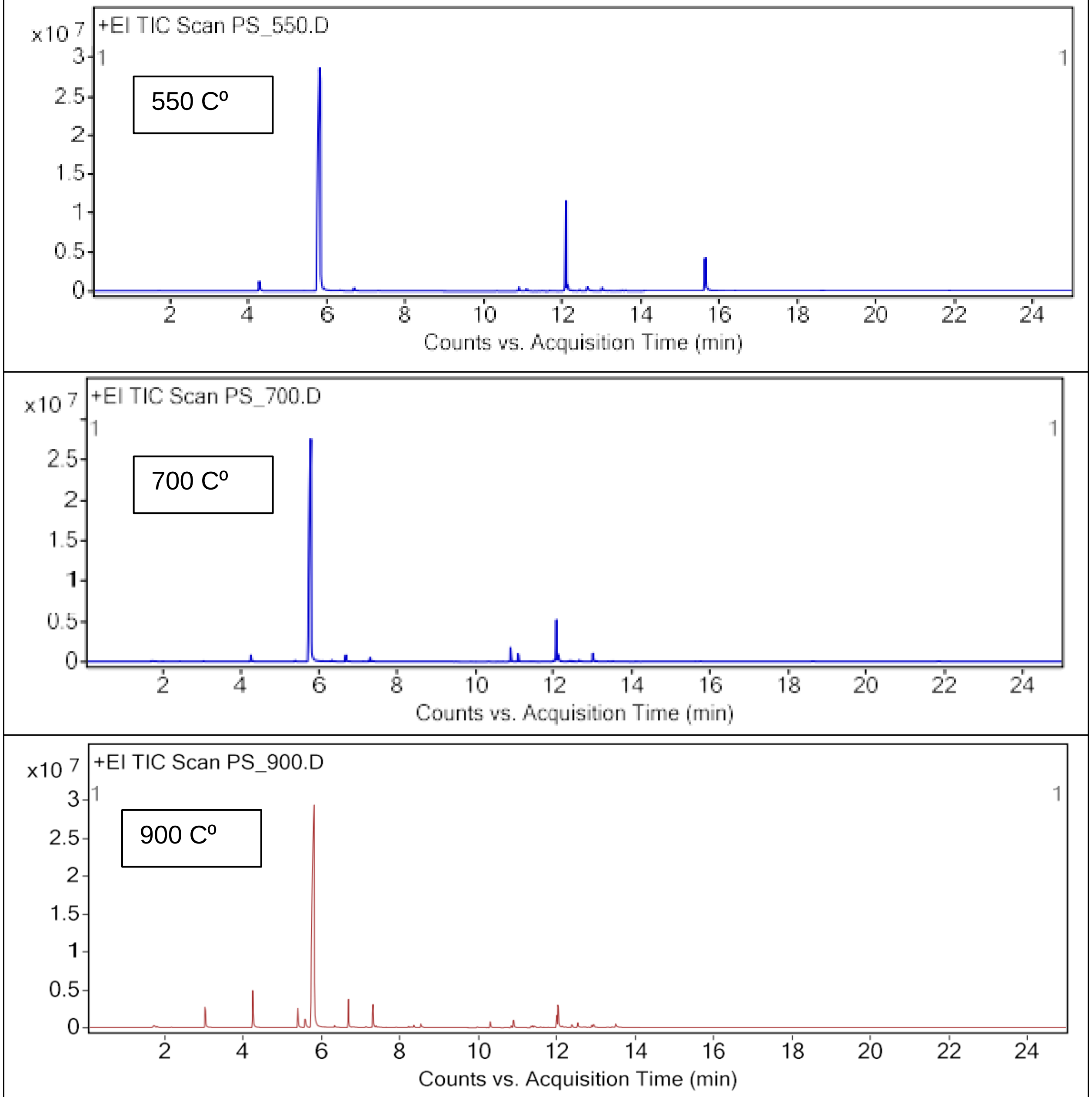
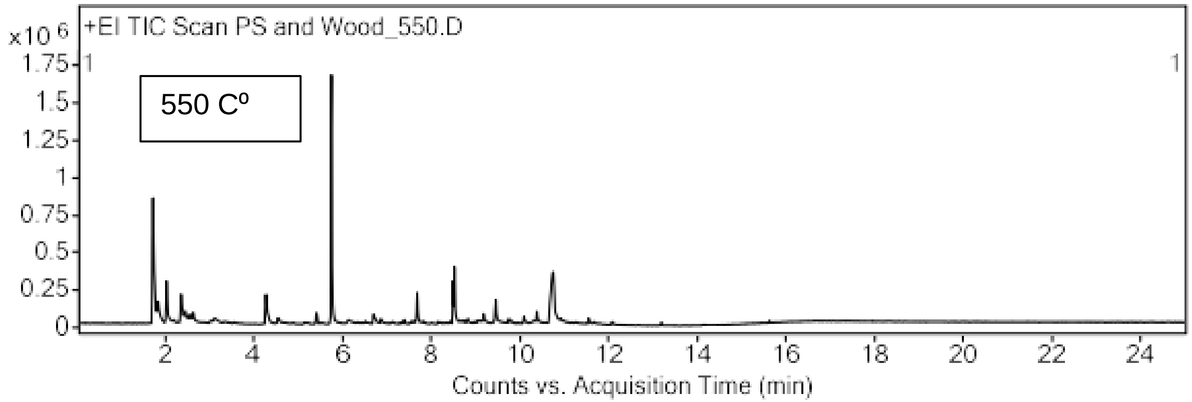
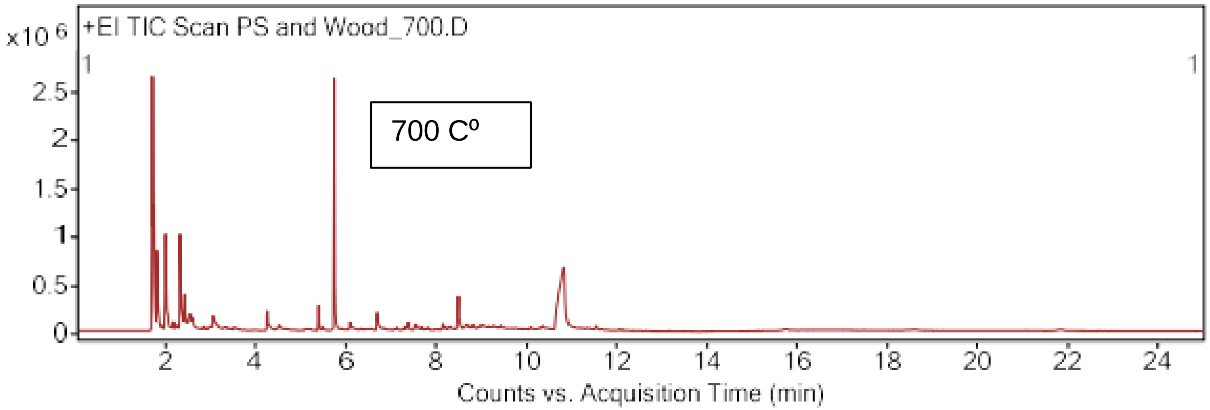


Exhibit 52. Fast Pyrolysis Results for PS Without Wood and the Ratios of Monomer to Dimer.

Monomer:Dimer Ratios		
550°C	700°C	900°C
2.07	49.82	46.67





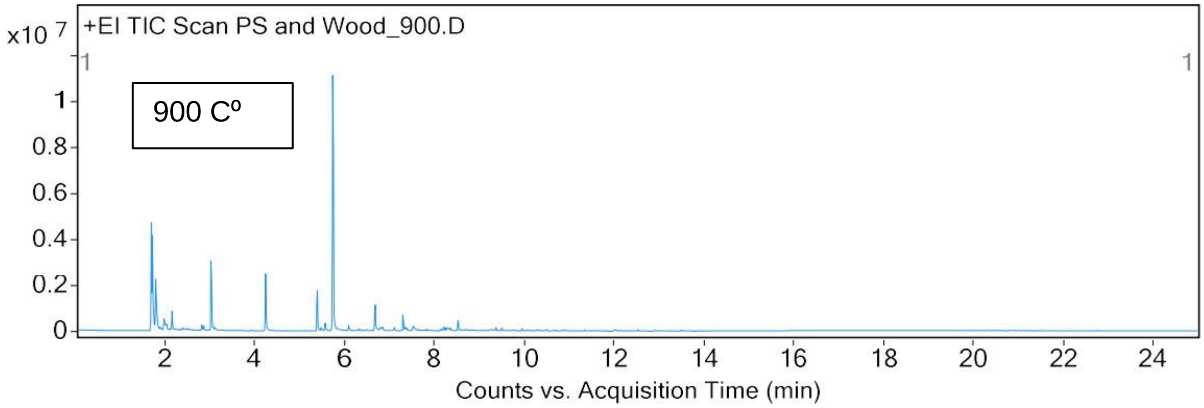


Exhibit 53. Fast Pyrolysis Results for PS with wood and the Ratios of Monomer to Dimer.

Low:High Length of Carbon Chain Ratios		
550°C	700°C	900°C
0.39	0.96	-

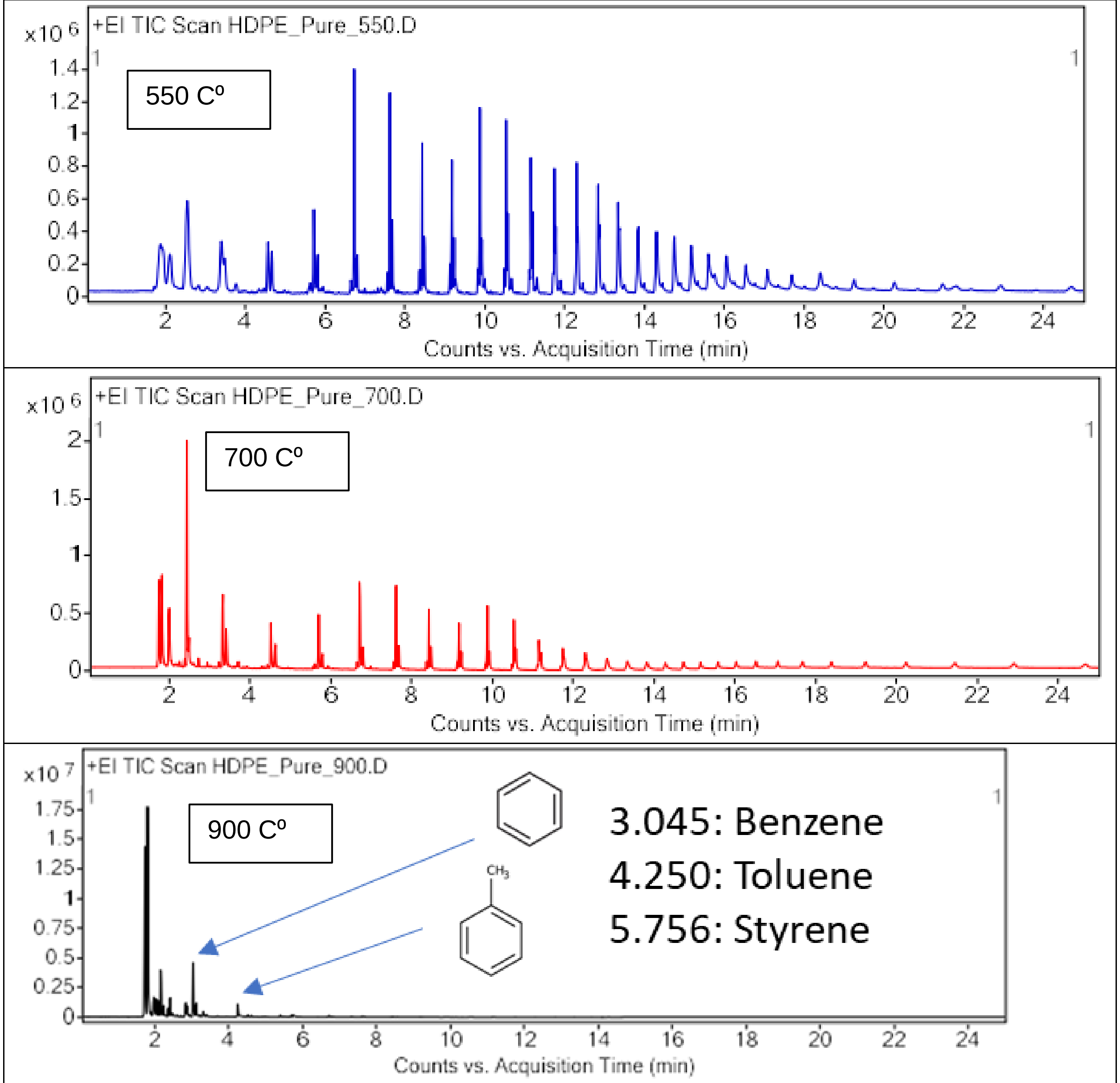


Exhibit 54. Fast Pyrolysis Results for HDPE without Wood. Low carbon chain length = less than ten. High carbon chain length = ten and higher. Aromatic hydrocarbons found at 900 °C with none present in HDPE before pyrolysis.

Low:High Length of Carbon Chain Ratios		
550°C	700°C	900°C
0.73	0.92	-

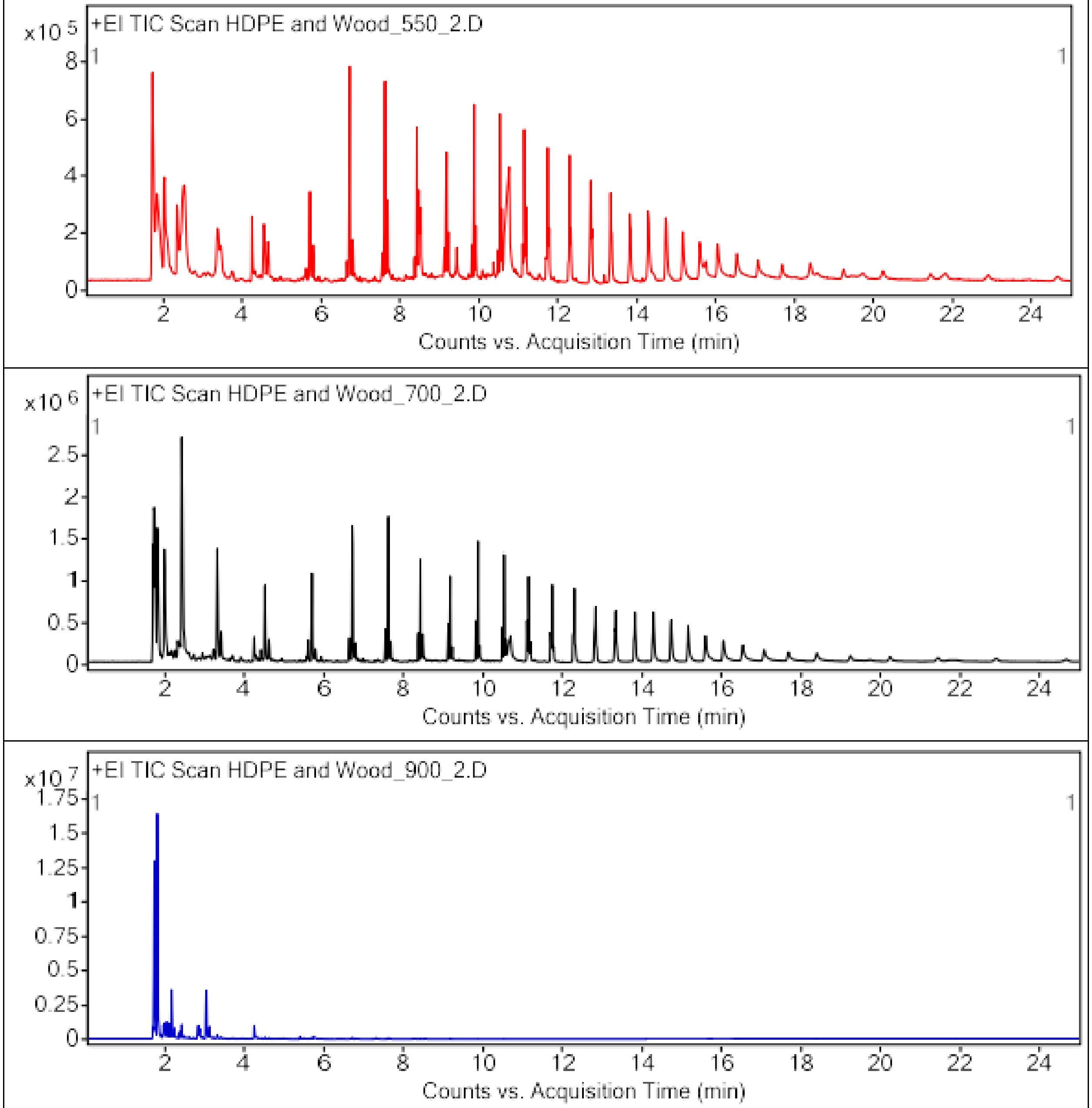


Exhibit 55. Fast Pyrolysis Results for HDPE with Wood. Low carbon chain length = less than ten. High carbon chain length = ten and higher.

The thermo-kinetic parameters including the activation energy and frequency factor under pyrolysis, CO, water vapor and oxidation were obtained by applying the model integral fitting of the Coats-Redfern method, which is a non-isothermal model fitting method to determine the kinetic parameters of solid-state materials. It was found that the change in Gibbs free energy of the blend was lower than that of torrefied wood and HDPE separately, implying that the spontaneity of the reaction is higher in the case of the blend than parent components, resulting in an increased reaction rate and a significant reduction in the energy required for the decomposition process. The Coats-Redfern approach, which was applied on both temperature zones, revealed that the heating rate and the different gas environments had a considerable impact on the thermo-kinetic characteristics of the biomass/plastic blend. Diffusion controls the thermo-kinetic process for both the first and second temperature stages of the blend's pyrolysis from the low to the higher heating rates, **Exhibit 56** and **57**. The diffusion model is also the most prominent and represents the thermal decomposition of the mix fuel under oxygen environment well, as demonstrated by both model-free and model-fitting approaches. The densified and extruded nature of the blend enhances closeness and interfacial reactions during the heating process, which drives interactions and synergistic effects between the blend's components. The diffusion mechanism of the kinetic analysis also accounts for the two zones of the biomass pyrolysis, whereas a first order chemical reaction, **Exhibit 56,** adequately characterizes the thermal decomposition of the blend in a water vapor environment and HDPE in an inert atmosphere.

Exhibit 56. Thermo-kinetic and thermodynamic parameters of TW, HDPE and HDPE:TW 1:4 material at heating rates 5, 10, 20 °C/min and under various environments (Ar/O_2/CO/H_2O) by applying a first-order chemical reaction model.

Heating rates (°C/min)	Range A						Range B					
	Kinetics			Thermodynamics			Kinetics			Thermodynamics		
HDPE&TW (Pyrolysis)	E_a	R^2	A	ΔH	ΔG	ΔS	E_a	R^2	A	ΔH	ΔG	ΔS
5	165.86	0.9895	3.38E+13	160.88	471.77	-0.52	271.73	0.9906	9.872E+18	265.77	712.75	-0.62
10	124.21	0.997	5507538489	119.22	386.60	-0.45	244.67	0.9948	1.185E+17	238.33	686.98	-0.59
20	94.381	0.9969	8913124.30	89.35	326.67	-0.39	191.50	0.9789	1.197E+13	185.44	558.06	-0.51
TW (Ar) 20°C/min	95.90	0.9931	16562097.13	90.73	338.06	-0.40	N/A	N/A	N/A	N/A	N/A	N/A
HDPE (Ar) 20°C/min	N/A	N/A	N/A	N/A	N/A	N/A	435.60	0.9981	1.847E+30	429.39	1057.20	-0.84
HDPE&TW (CO) 20°C/min	113.49	0.9988	290831385.10	108.31	370.90	-0.42	176.18	0.9422	5.045E+11	169.96	532.75	-0.48
HDPE&TW (H_2O) 20°C/min	102.76	0.9996	35346392.61	98.36	311.34	-0.40	230.46	0.9954	5.102E+15	224.30	639.89	-0.56
HDPE&TW (O_2) 20°C/min	81.23	0.9902	649351.57	76.24	298.49	-0.37	91.23	0.9612	221721.9	85.15	350.58	-0.36

Exhibit 57. Thermo-kinetic and thermodynamic parameters of TW, HDPE and HDPE:TW 1:4 material at heating rates 5, 10, 20 °C/min and under various environments (Ar/O_2/CO/H_2O) by using the diffusion-driven parabolic reaction model.

Heating rates (°C/min)	Range A						Range B					
	Kinetics			Thermodynamics			Kinetics			Thermodynamics		
HDPE&TW (Pyrolysis)	E_a	R^2	A	ΔH	ΔG	ΔS	E_a	R^2	A	ΔH	ΔG	ΔS
5	329.58	0.9914	1.42534E+27	324.58	792.02	-0.78	534.97	0.9922	3.82E+37	529.01	1230.81	-0.97
10	246.99	0.9973	5.80435E+19	241.99	624.53	-0.64	465.47	0.9928	4.16E+32	459.13	1134.89	-0.88
20	195.09	0.9972	1.03367E+15	190.06	520.81	-0.55	358.49	0.9851	4.64E+24	352.43	886.806	-0.73
TW (Ar) 20°C/min	194.11	0.9962	1.79872E+15	188.94	531.98	-0.55	N/A	N/A	N/A	N/A	N/A	N/A
HDPE (Ar) 20°C/min	N/A	N/A	N/A	N/A	N/A	N/A	807.62	0.9936	8.58E+55	801.41	1796.34	-1.33
HDPE&TW (CO) 20°C/min	230.27	0.9992	4.91E+17	225.09	5.98E+02	-5.98E-01	329.21	0.9526	1.19E+22	322.98	8.34E+02	-6.84E-01
HDPE&TW (H_2O) 20°C/min	210.68	0.9997	1.17164E+16	206.28	505.58	-0.57	410.14	0.9931	1.01E+28	403.98	993.80	-0.79

HDPE&TW (O_2) 20°C/min	168.69	0.9904	6.14998E+12	163.70	466.09	-0.50	183.88	0.9692	3.08E+11	177.80	529.21	-0.48

3.6 Bench Scale Gasification Study Using 1.5” ID Drop Tube Reactor

A 1.5” drop tube reactor was operated under gasification conditions in order to simulate the gasification process of the coal/biomass/plastic blend identified in Project Task 5. The surrounding gas environment ($CO/H_2/H_2O$) was replicated with bottled gas at the gasification temperature determined in Project Task 7.

The drop tube reactor setup had gone through several iterations to achieve accurate and consistent results. Specifically, the reactor was initially setup to have the sample drop from the vibration feeder into the reactor through tubing that was shared with the exhaust gas that connected to a flask located under the fume pump. Water vapor is controlled by a Harvard Apparatus PHD 4400 water pump, **Exhibit 58**. This caused an inconsistent amount of solids to reach the reactor due to gas moving against the particles and the particles pyrolyzing and sticking to the tubing before reaching the reactor.

Exhibit 58. Initial Setup of the Reactor. Solid inlet and gas exhaust share the opening into the reactor. The flask located under the fume hood pump captures gas from the reactor or from the mass flow controllers directly for gas analyzer calibration. The input of the gas analyzer is in the flask situated above the others (left). Harvard Apparatus PHD 4400 water pump (right).

Two X-stream gas analyzers were setup to extract exhaust gas from the flask and pump it through a condensation trap and silica beads to remove water content from the gas as shown in **Exhibit 59**.

Exhibit 59. X-stream Gas Analyzer System including Two Analyzers, Vacuum Pump, Condensation Trap, and Silica Beads.

The initial results were inconsistent due to variation of fuel fed and subsequent alterations were made to the reactor setup. The exhaust line was moved to the line containing the pressure sensor to allow a dedicated solids inlet into the reactor. Nitrogen was connected to the vibration feeder to act as a carrier gas to ensure the entire solid sample reaches the reactor, **Exhibit 60**.

Exhibit 60. Modified Reactor Setup with a Dedicated Solid Inlet (left). Nitrogen Line Connected to the Vibration Feeder with a Quick Connection Cap to Pressurize the Container (right).

Consistency tests were conducted to ensure the setup was reliable, with results shown in **Exhibit 61.** Four tests were conducted, three using HDPE:torrefied wood at 1:4 weight ratio (37:63 HHV ratio) and one using HDPE:torrefied wood at 2:3 weight ratio (61:39 HHV ratio). The first test, results shown with the black line, used the vibration feeder pressurized between 2 and 3 psi with no continuous flow of nitrogen, the results for this test were off due to some obvious clogging in the fuel feeding line during the test. The other three tests, results shown with cyan, blue and red lines, used a continuous flow of nitrogen carrier gas during the two minutes that the sample valve is open. The results for these tests are consistent with each other, showing that this modified reactor setup and method were acceptable.

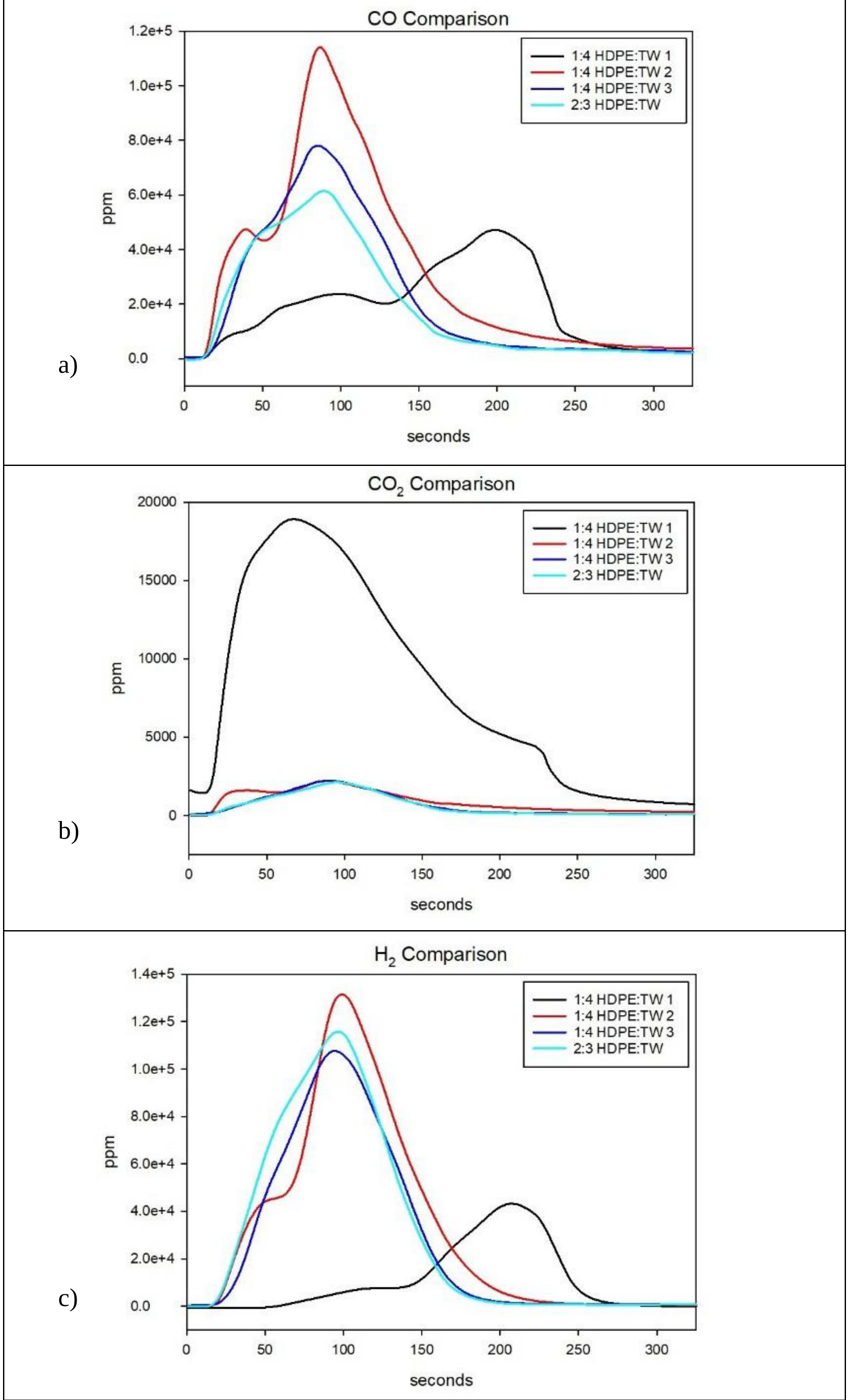


Exhibit 61. Gas Concentration Levels of a) CO, b) CO_2, and c) H_2 during Sample Reaction of 1:4 weight ratio of HDPE:torrefied wood (37:63 HHV ratio) and 2:3 weight ratio of HDPE:torrefied wood (61:39 HHV ratio) in a 100% N_2 environment.

To simulate gasification at the bench scale, a test plan was developed. The furnace and reactor temperature were held at 1100 °C, a total flow rate of 3 L/min of gas flowed through the reactor, and 2 g of HDPE:torrefied wood at 2:3 weight ratio (61:39 HHV ratio) were used for each gas condition listed below:

1. 100% N_2, 0% water vapor
2. 95% N_2, 5% water vapor
3. 90% N_2, 10% water vapor
4. 85% N_2, 15% water vapor
5. 80% N_2, 20% water vapor
6. [35% N_2, 35% CO_2, 30% CO]x1 and 0% water vapor
7. [35% N_2, 35% CO_2, 30% CO]x0.9 and 10% water vapor
8. [35% N_2, 35% CO_2, 30% CO]x0.8 and 20% water vapor

Testing was completed for the eight gas conditions listed above and the results are shown in **Exhibits 62-65.**

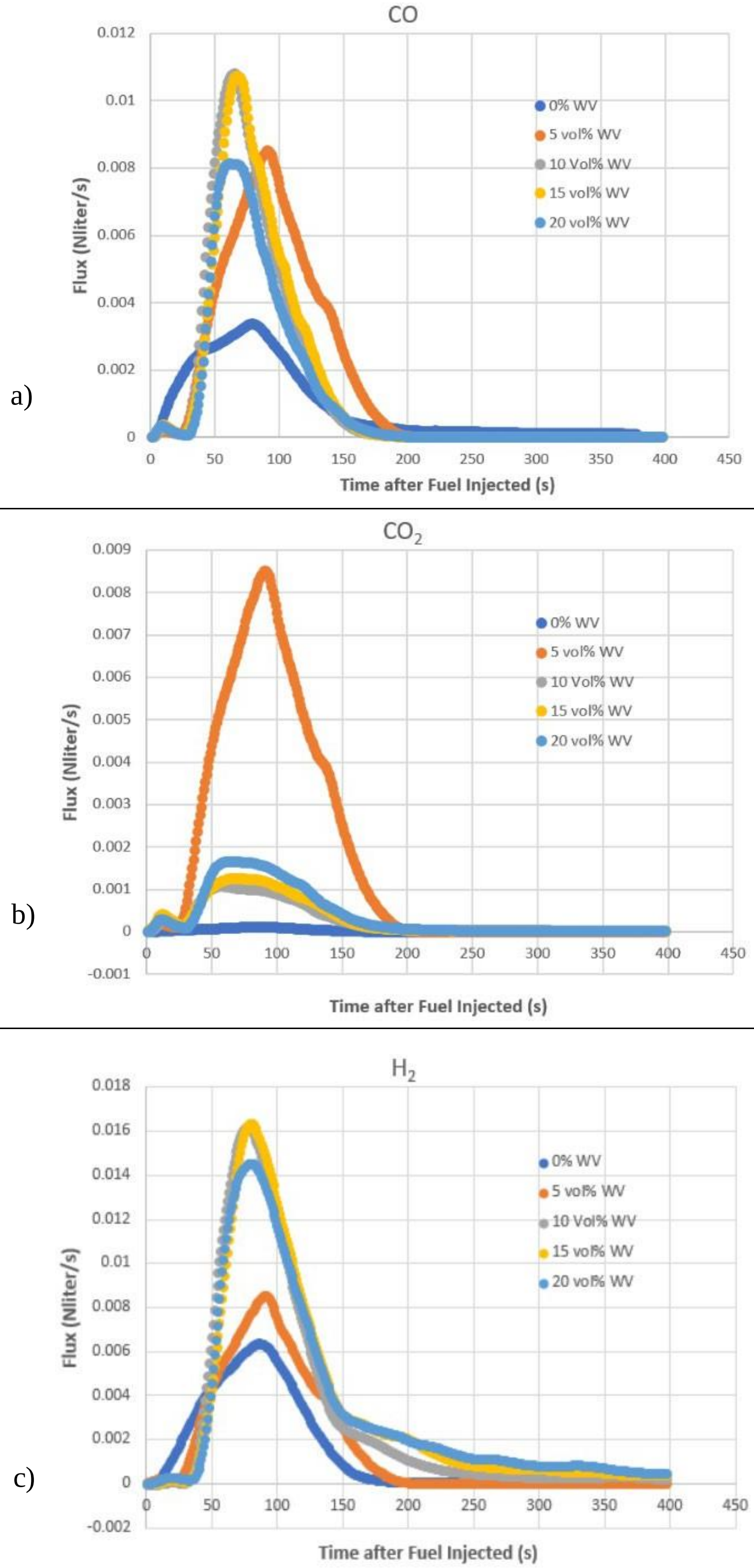


Exhibit 62. Gas Concentration Levels of a) CO, b) CO_2, and c) H_2 During Sample Reaction of 2:3 weight ratio HDPE:Torrefied Wood (61:39 HHV Ratio) with 0, 5, 10, 15, and 20% Water Vapor (WV).

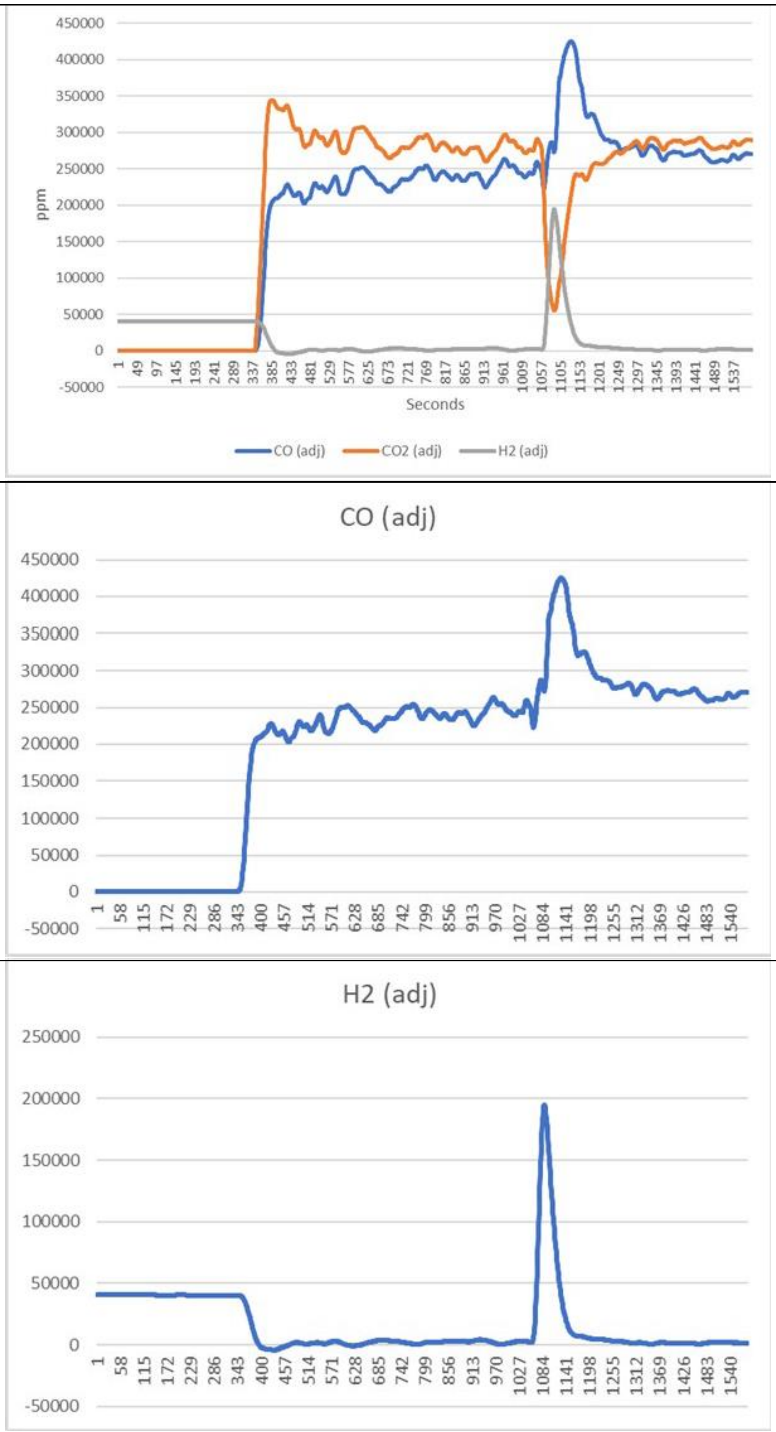
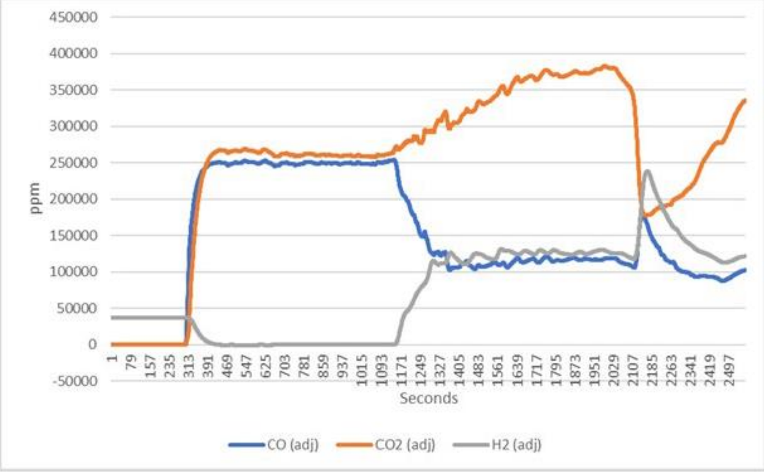
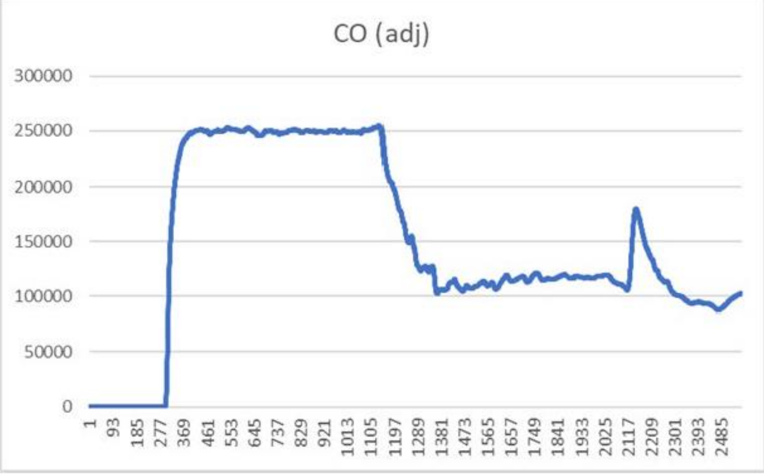


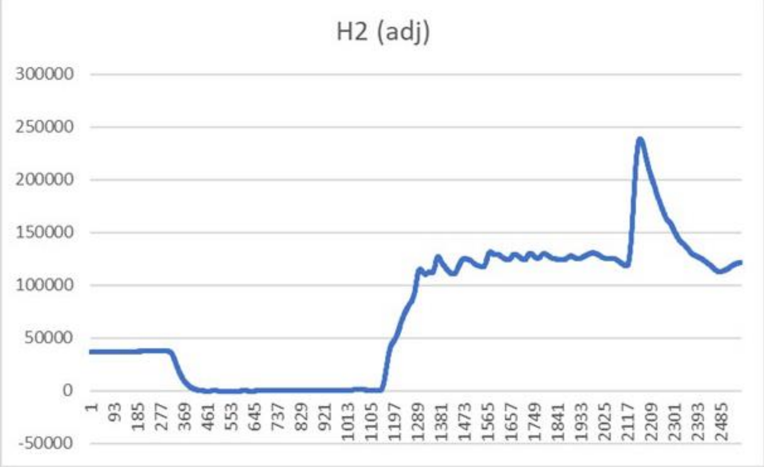
Exhibit 63. Gas Concentration Levels of a) CO, CO_2, & H_2, b) CO, and c) H_2 During Sample Reaction of 2:3 weight ratio HDPE:Torrefied Wood (61:39 HHV ratio) in a [30% CO, 35% CO_2, and 35% N_2]x1 with 0% WV Gas Environment.



a)



b)



c)

Exhibit 64. Gas Concentration Levels of a) CO, CO_2, & H_2, b) CO, and c) H_2 During Sample Reaction Of 2:3 weight ratio HDPE:Torrefied Wood (61:39 HHV ratio) in a [30% CO, 35% CO_2, and 35% N_2]x0.9 with 10% WV Gas Environment.

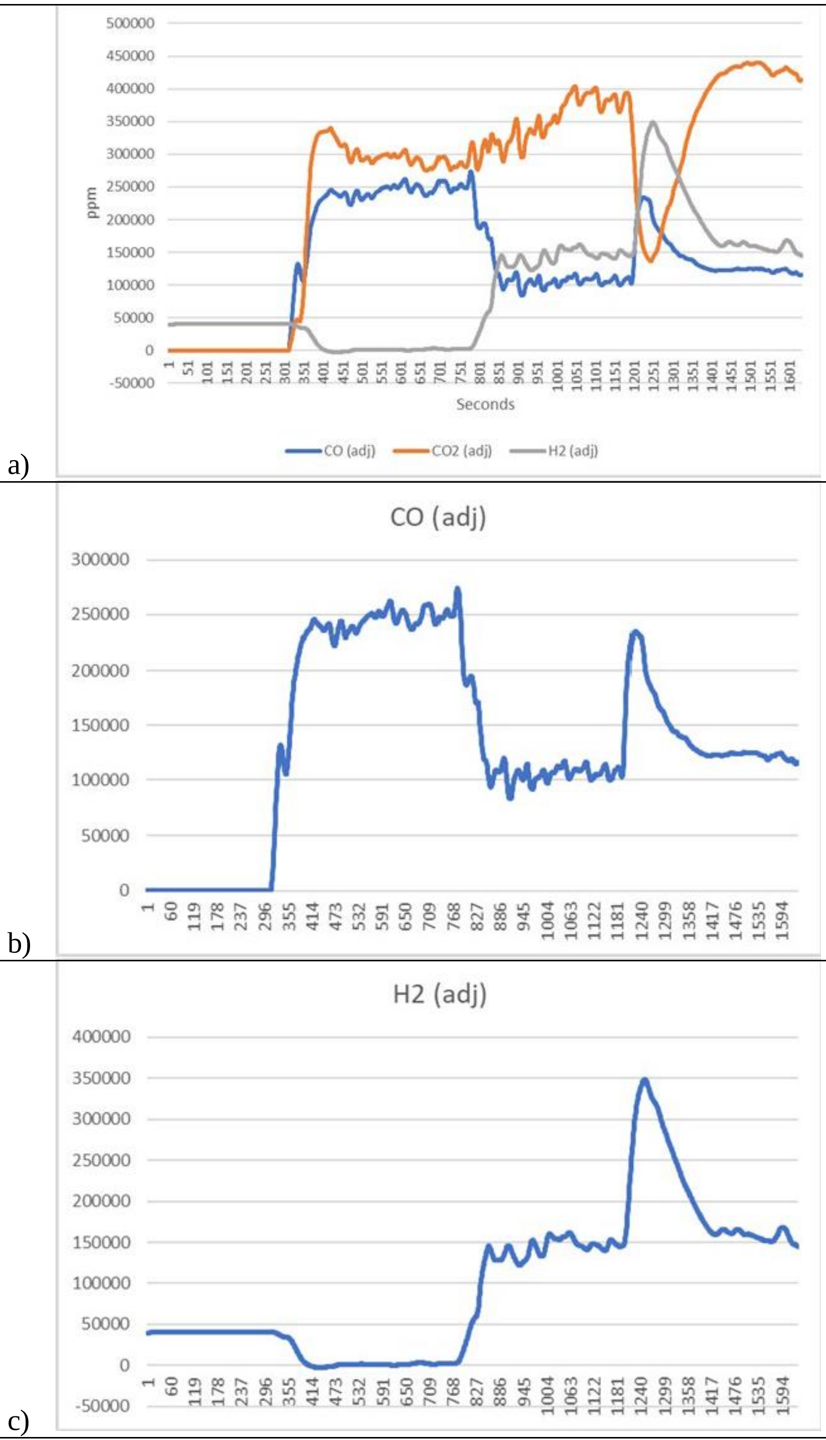
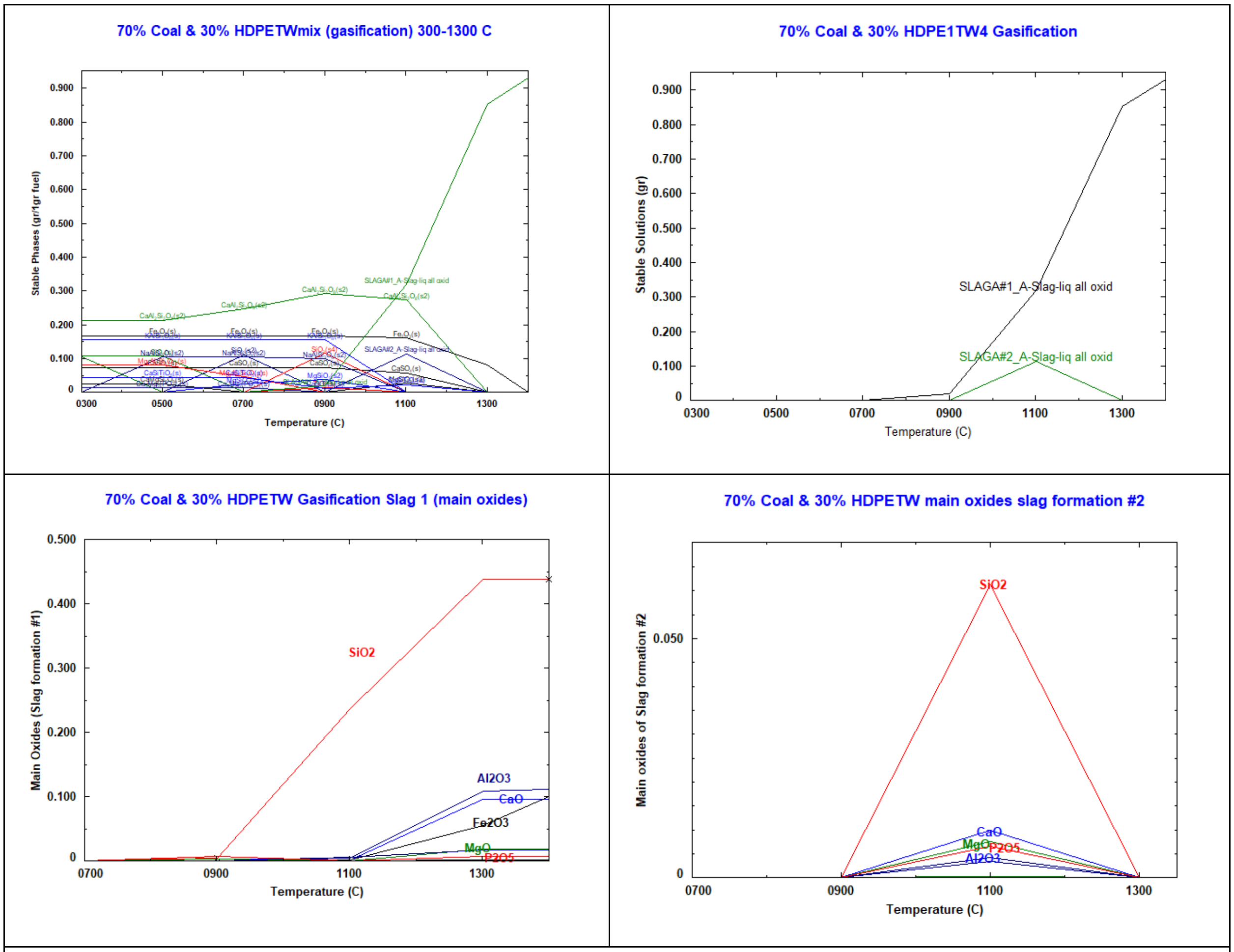


Exhibit 65. Gas Concentration Levels of a) CO, CO_2, & H_2, b) CO, and c) H_2 During Sample Reaction of 2:3 weight ratio HDPE:Torrefied Wood (61:39 HHV ratio) in a [30% CO, 35% CO_2, and 35% N_2]x0.8 with 20% WV Gas Environment.

The abovementioned gasification data and syngas compositions show an increase in CO and H_2 at 10, 15, and 20% WV concentrations when compared to the 0 and 5% WV concentrations.

3.7 FactSage Simulation

FactSage[1] simulations were conducted to predict slag formation during the gasification of 70 wt% coal and 30 wt% HDPE:torrefied wood (1:4 weight ratio; 37:63 HHV ratio). The simulations, **Exhibit 66**, show that two distinct slags are formed during the gasification of these materials. The first slag is what we expect to see from the gasification of coal and the second slag is from the HDPE:torrefied wood blend. Due to the significantly lower amount of slag produced from HDPE:torrefied wood, we don't expect any issues from this during the gasification testing. The viscosities determined in the simulation show that the blend of HDPE:torrefied wood is lower than that of coal and the inclusion of the blend with coal lowers its viscosity as well. The difference between the 100% coal and coal with 30% blend is small enough that problems during gasification are not expected.



70% Coal & 30% HDPETWmix (gasification) 300-1300 C

70% Coal & 30% HDPE1TW4 Gasification

70% Coal & 30% HDPETW Gasification Slag 1 (main oxides)

70% Coal & 30% HDPETW main oxides slag formation #2

Exhibit 66. Total Oxides and Slag Produced During the Gasification of 70 wt% Coal and 30 wt% HDPE:Torrefied Wood are Shown (Top Left). Taking the oxides out of the figure, two distinct slags form (top right). The first is associated with coal and begins formation at 700 °C and continues past the 1400 °C endpoint of the simulation (bottom left). The slag associated with the HDPE:torrefied wood blend begins at 900 °C and ends formation by 1300 °C (bottom plots).

Factsage[1] simulations were also done on the slag viscosities of the slags formed, **Exhibit 67**. The viscosities determined in the simulation show that the blend of HDPE:torrefied wood is lower than that of coal and the inclusion of the blend with coal lowers its viscosity as well. The difference between the 100% coal and coal with 30% blend is small enough that problems during gasification are not expected.

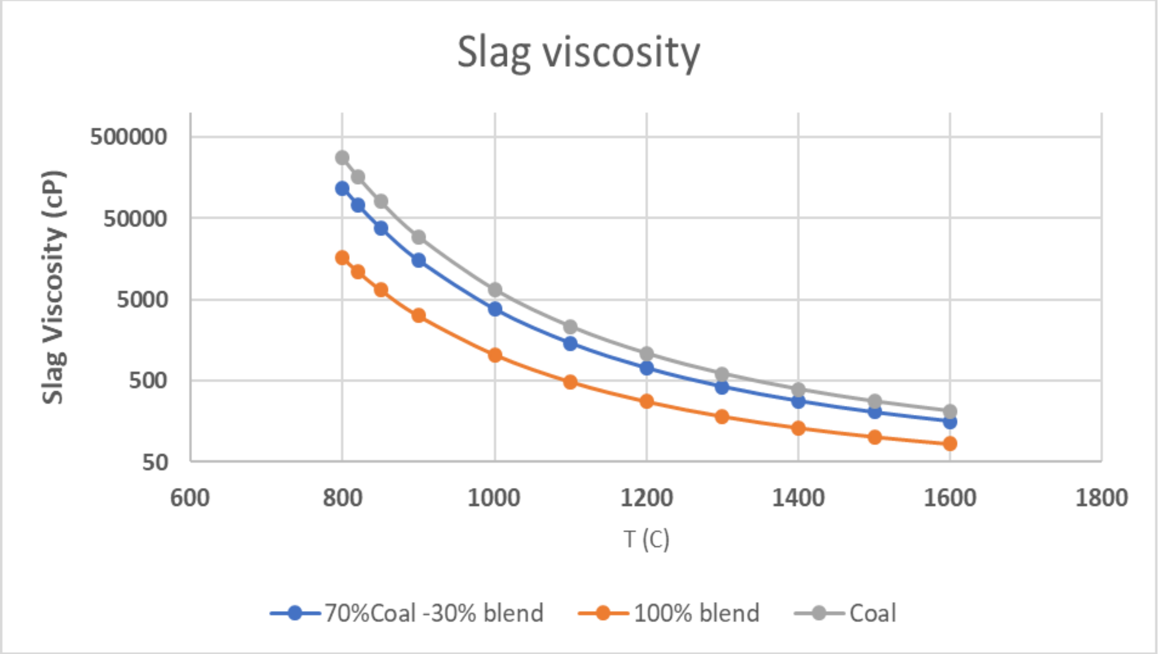


Exhibit 67. Viscosity of Each Slag Decreases as Temperature Increases. The inclusion of HDPE:torrefied wood reduces the overall viscosity of the slag produced.

3.8 Gasification on 1 TPD Gasifier

Operation of the 1 TPD gasifier was planned using the 2:3 weight ratio (61:39 HHV ratio) of HDPE:torrefied wood extruded material from the Polymers Technology Center. Four subtasks were set within this task. These subtasks were to develop an operation plan, conduct slurry preparation, operate the gasifier, and analyze the data from operation. Each of these subtasks relied on each other and needed to be conducted simultaneously to effectively test the material.

The slurry containing the 1:4 weight ratio (37:63 HHV ratio) of HDPE:torrefied wood material had been tested and was shown to have a lower viscosity than the 100% coal slurry at a higher solid wt%. This result was confirmed with the 2:3 weight ratio (61:39 HHV ratio) of HDPE:torrefied wood from the Polymers Technology Center. The slurry preparation for the 1 TPD gasifier uses a water-fed ball mill, shown in **Exhibit 68**, to crush coal to a size appropriate for the feeding of the gasifier, which is typically close to 50 μm. An initial test was conducted using a portion of the extruded 2:3 weight ratio (61:39 HHV ratio) of HDPE:torrefied wood material and coal to make a 55 solids wt% and a 50 solids wt% slurry with solids consisting of 70 wt% coal and 30 wt% of the 2:3 weight ratio (61:39 HHV ratio) HDPE:torrefied wood. These slurry concentrations were first tested on a lab scale and then were scaled up to the full attempt on the slurry preparation unit.

Exhibit 68. UK 4-Level Slurry Preparation Unit (Ball Mill, Weight Belt, Coal Hopper) was Operated (Left). The water intake of the produced pellets was tested for 2 hrs (upper right). Two slurries of coal/biomass-plastic blend 55 wt% and 50 wt% were produced (bottom right).

During the operation of the ball mill, the machine experienced a malfunction when the exit screen broke. The resulting material in the ball mill showed the coal and extruded material had separated. The top part of the ball mill had significantly more extruded material and it had not been broken down nearly as much as was expected, due to a lighter density. The bottom section was mostly coal, and it was in the form of a very thick paste. This led us to conclude that the solid wt% of the slurry was too high and the operation of the ball mill needed to be adjusted. The results of this test are shown in **Exhibit 69**. This is an issue that is unique to the UK system as it is a pilot scale research setup that is equipped to handle primarily coal. Commercial scale units wouldn't need to reduce the size of the blended fuel pellets to utilize them during gasification.

Exhibit 69. During Operation of the Ball Mill the Outlet Screen Broke (Top). The lower section, on the other hand, had mostly coal slurry, and the presence of biomass may have absorbed most of the water, resulting in a thick paste-like slurry (bottom).

The operation plan was adjusted to conduct two gasification tests with slurries at 40 wt%, one with solids containing 100 wt% coal as a baseline and the other with solids containing 70 wt% coal and 30 wt% of 2:3 weight ratio (61:39 HHV ratio) HDPE:torrefied wood. The ball mill was repaired and the size composition of the steel balls within the mill were changed from one uniform size to an assortment of sizes to keep the

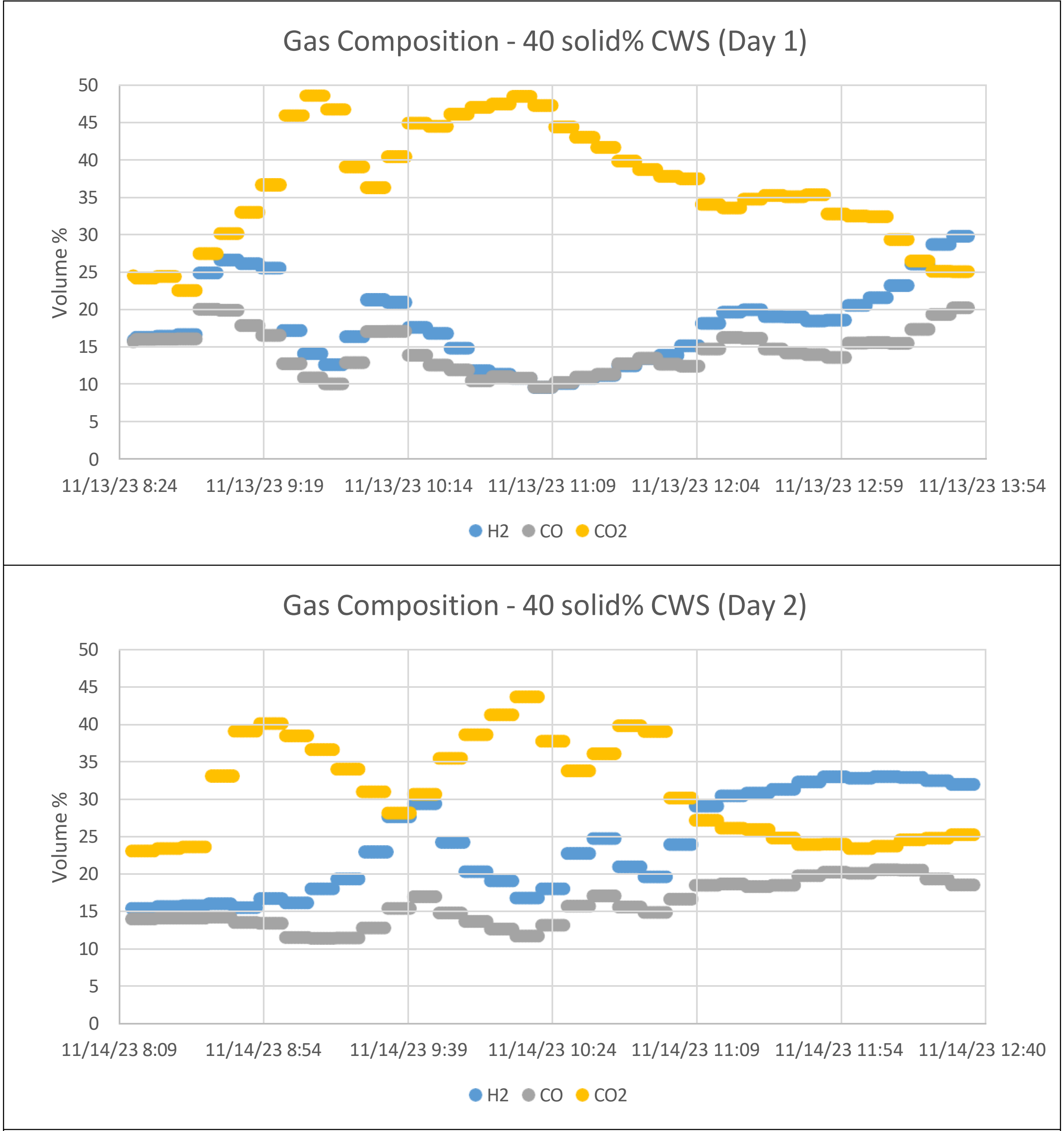


Exhibit 70. UK 1 TPD Gasifier Product Gas Composition by Online GC.

extruded material from filling the voids between the steel balls and not being crushed, which can be seen in the bottom right image in **Exhibit 69**.

The new operation plan required a baseline test of a 40 solid wt% slurry with 100 wt% of solids as coal due to no previous gasification tests being conducted with this slurry composition. The slurry for this baseline test was made using the new ball mill setup on November 6, 2023. The solid wt% was measured to be 40 wt% and the slurry density was 1.13 g/mL, which is within the acceptable range for the slurry pumps. Both of these metrics were checked again after water adjustment due to evaporation the day before operation in the gasifier.

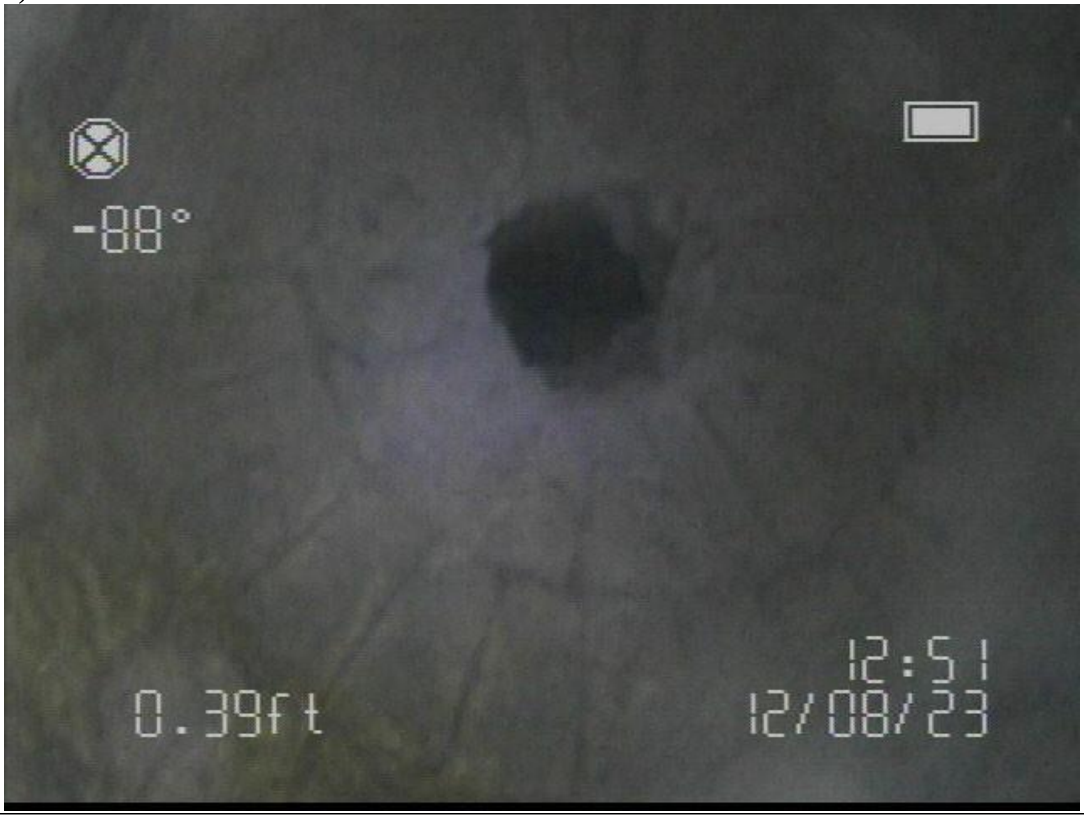
Operation of the gasifier for the baseline 40 wt% coal slurry testing was conducted over two days on November 13 and 14, 2023 for a total of 9 hours of operation. The gas composition results are shown in **Exhibit 70**.

The GC gas composition of the product gas is expressed in two graphs to show the results of both days of testing. Because the UK 1 TPD gasifier utilizes natural gas and oxygen to maintain gasifier temperatures, the levels of H_2, CO, and CO_2 will naturally vary as adjustments to the gas inputs are made. Day one of the baseline testing (11/13/2023) of 40 solid wt% coal water slurry has two spikes of CO_2 owing to the input gas being adjusted to increase the heat of the gasification chamber to prevent clogging. Day two (11/14/2023) had three smaller spikes of CO_2 for the same reason. However, during the last hour and a half of testing the input gas was not adjusted and the H_2 concentration increased and surpassed the CO_2 concentration. The data from the baseline testing was analyzed for the hydrogen to carbon (H/C) ratio (carbon in CO only). The overall H/C weight ratio was 1.05 across all 9 hours of testing, which is expected with a slurry with a low solid content, as we are using (40 solid wt%).

The UK gasifier experiences a high rate of clogging at the bottom of the gasification chamber during operation due to relatively a low syngas exhaust velocity and high unburned carbon content and after the 40 solid wt% coal-water slurry testing, the gasification chamber required unclogging. The process for unclogging includes breaking through the initial clog, washing away loose ash and slag, and then widening the gap through drill powered chisel tools. The progress of widening the gap is shown in **Exhibit 71**. Other maintenance on the gasifier was required before the blended fuel test could be conducted. A small leak developed near burner C which required the burner to be pulled out for resealing and two of the three large thermocouples used to monitor the temperature at different points in the gasification chamber failed during cooldown. The thermocouples were removed and replaced and the gasifier was ready for operation again.

a)

b)



c)

d)

Exhibit 71. Progress of Breaking Through the Slag Buildup in the Gasification Chamber. a) initial breakthrough, b) after initial chiseling, c) continued progress, d) final result with opening clearly shown.

Testing of the 40 solid wt% slurry with solids consisting of 70 wt% coal and 30 wt% of 2:3 weight ratio (61:39 HHV ratio) HDPE:torrefied wood was conducted on January 9, 2024. The material was loaded into the hopper the week prior and on the morning of 1/9/2024 the weigh belt, hopper, and slurry tank were turned on and the slurry was made over two hours with a Tamol additive being added every 30 minutes. A sample of the slurry was taken and measured to be 1.1 g/mL, which is lower than the typical 1.13 g/mL that has been targeted in the past. During the ball mill operation, a portion of the blended fuel did not get broken down enough to go through the screen between the mill and the slurry tank. The material that remained on the screen was later dried and weighed and came out to be about 10 wt% of the total solids that were input into the hopper. As a result, the solid content of the slurry was reduced to 37.5 solid wt%.

The slurry was injected for 25 minutes before a clog in burner D occurred and burner C clogged within another few minutes. The gasifier was shut down to cool to a temperature where an attempt could be made to unblock the burners without removing them in a few days. During the cool down days, a sample of the slurry was taken each day and tested for density to establish the viability of the slurry over time. Prior to the testing, it was assumed the slurry would only remain viable for about eight hours due to uncertainty with how effective the plastic encapsulation would be after the material was broken down in the ball mill and the biomass absorbing water and thickening the slurry. The results are shown in **Exhibit 72,** and it was found that the slurry remained viable for at least 72 hours as it was still within density ranges that would be pumpable. After that period, however, the density suddenly lowers and this is likely due to the larger extruded material particles falling out of the slurry due to a lack of enough agitation.

Exhibit 72. Slurry Density (g/mL) of the blended fuel slurry over four days.

1/9/2024	1/10/2024	1/11/2024	1/12/2024
1.10	1.12	1.13	1.11

After the gasifier cooled down to 500 °C on 1/12/2024, the injectors were pulled off the burners and an attempt was made to manually push the clog through, but they were not able to be cleared. It was determined that the gasifier would not be able to be restarted without removing the burners and a severe winter storm was set to occur over the next week, so the gasifier was completely shut down and winter proofed. The slurry remaining in the tank was discarded, and three samples were taken periodically during the process.

The gas composition results from the blended fuel slurry test are shown in **Exhibit 73**, no notable difference is seen compared to the coal-only slurry, except H/C ratio.

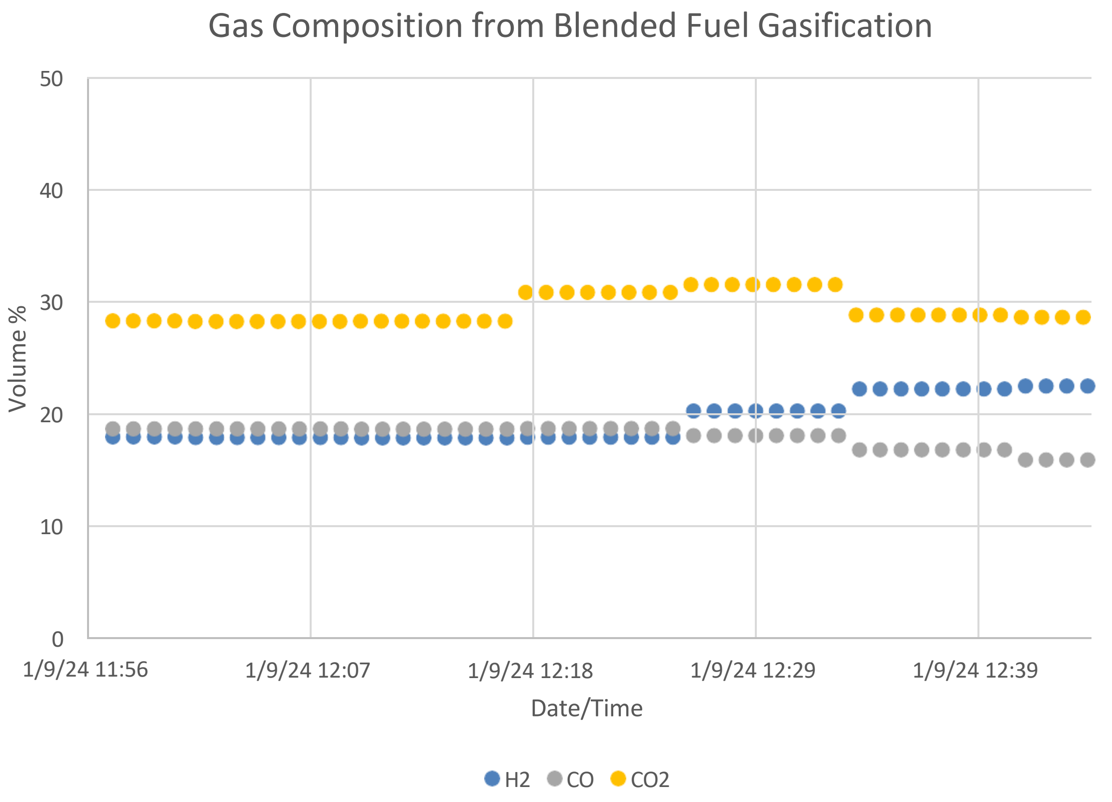


Exhibit 73. Gas Composition for Operation of the 40 solid wt% with Solids Consisting of 70 wt% Coal and 30 wt% 2:3 HHV ratio HDPE:Torrefied Wood.

Slag samples from the baseline and blended fuel tests were collected and analyzed using XRD, carbon content, and SEM. XRD is a nondestructive technique that provides details about the crystallographic structure, chemical composition, and physical properties of a material. The XRD results are shown in **Exhibit 74**. The major oxides that were predicted in the FactSage[1] simulations were present in both samples except CaO was missing from the blended fuel slag.

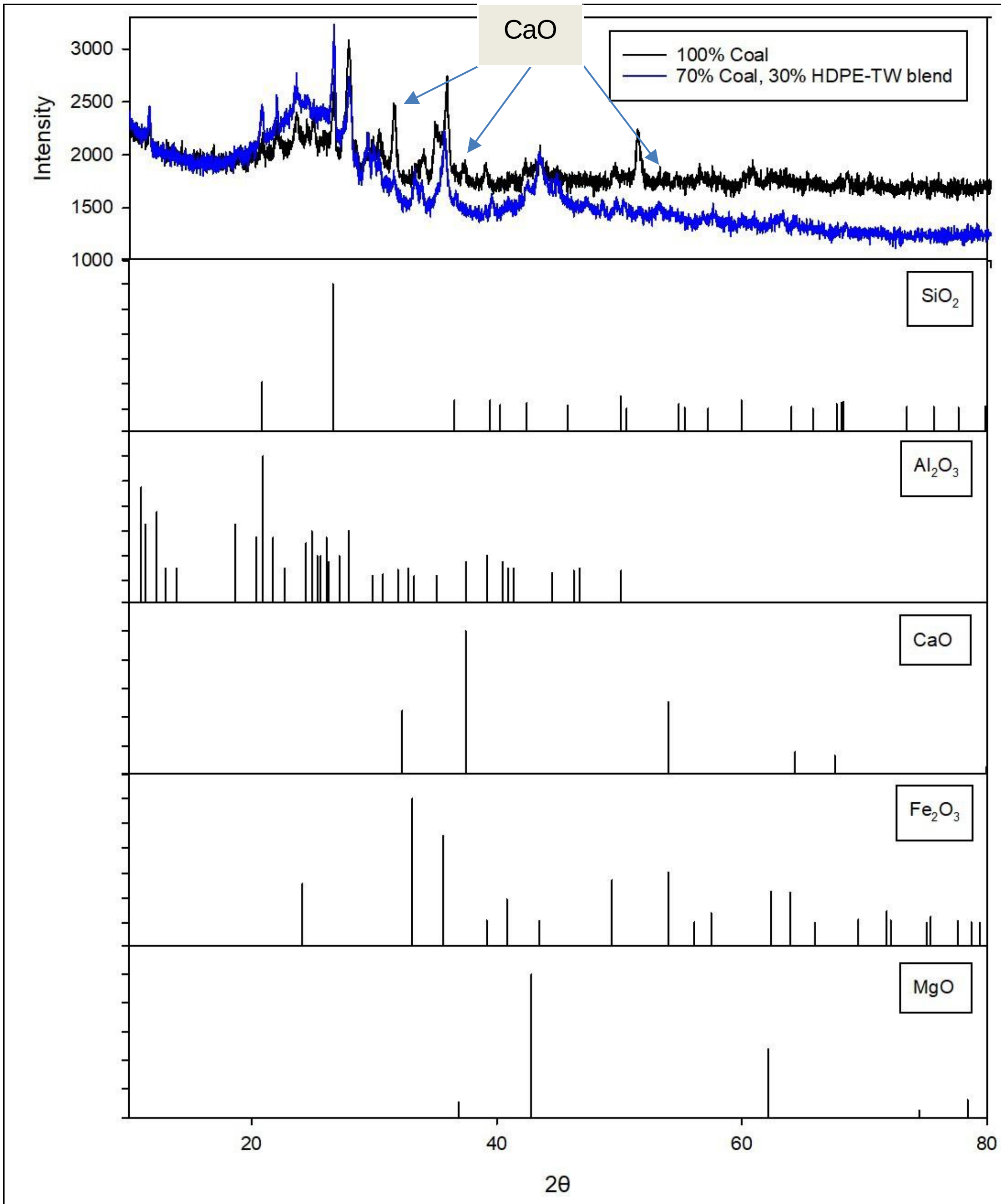
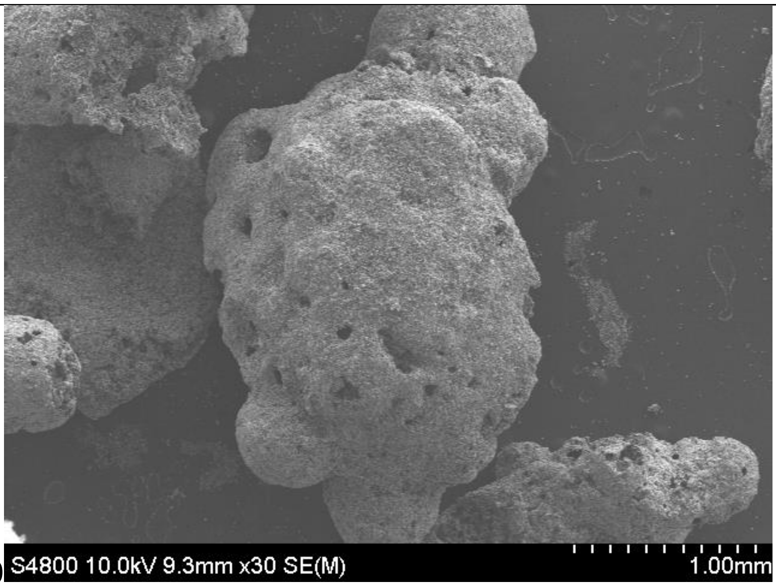


Exhibit 74. XRD Analysis Results of the Coal Baseline and Blended Fuel Slags. The top graph shows the output from the XRD on these slags. Each of the other charts are standards for each oxide used to identify if that compound was present in the slag.

The SEM images of the slag samples are shown in **Exhibit 75**. The SEM image reveals a difference in the morphologies of the two sets of slag. The coal baseline slag is porous while the blended fuel slag shows little to no pores. On the x500 images we see that the coal baseline slag has uniform, granular surface. The blended fuel slag has two distinct morphologies on the surface. One is the same as the coal baseline, but the other is smoother and larger. This was predicted in the FactSage[1] simulation as we expected the coal and biomass-plastic to produce separate slags.

a)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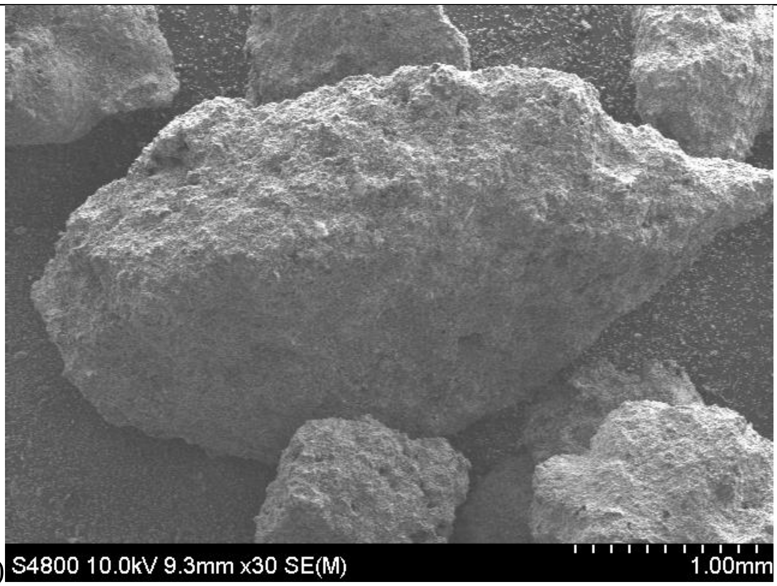
1.00mm

b)


S4800 10.0kV 9.3mm x30 SE(M)
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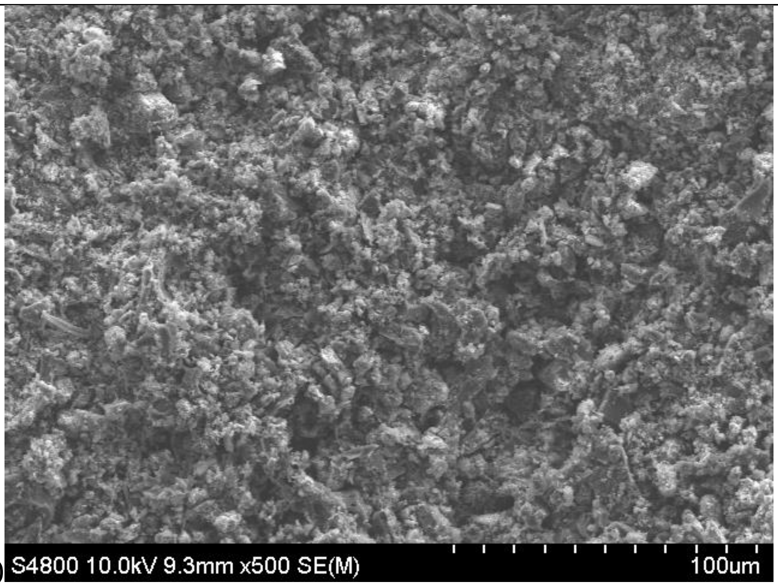
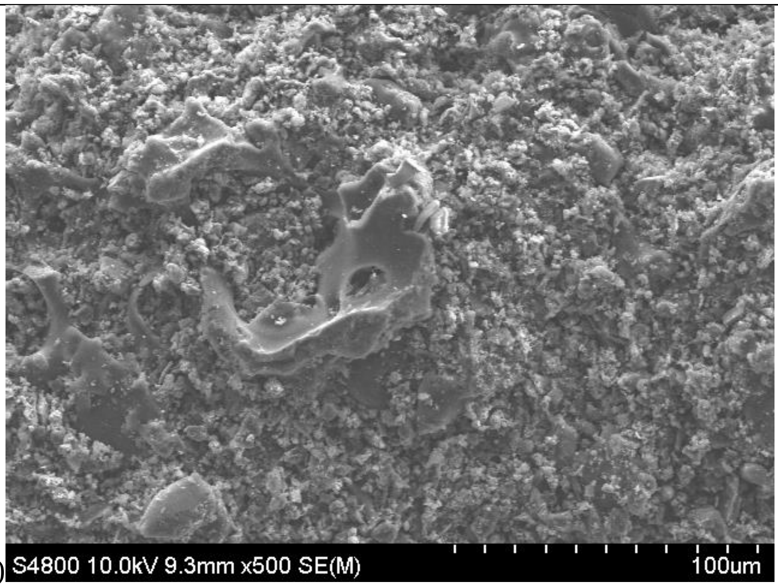


c)



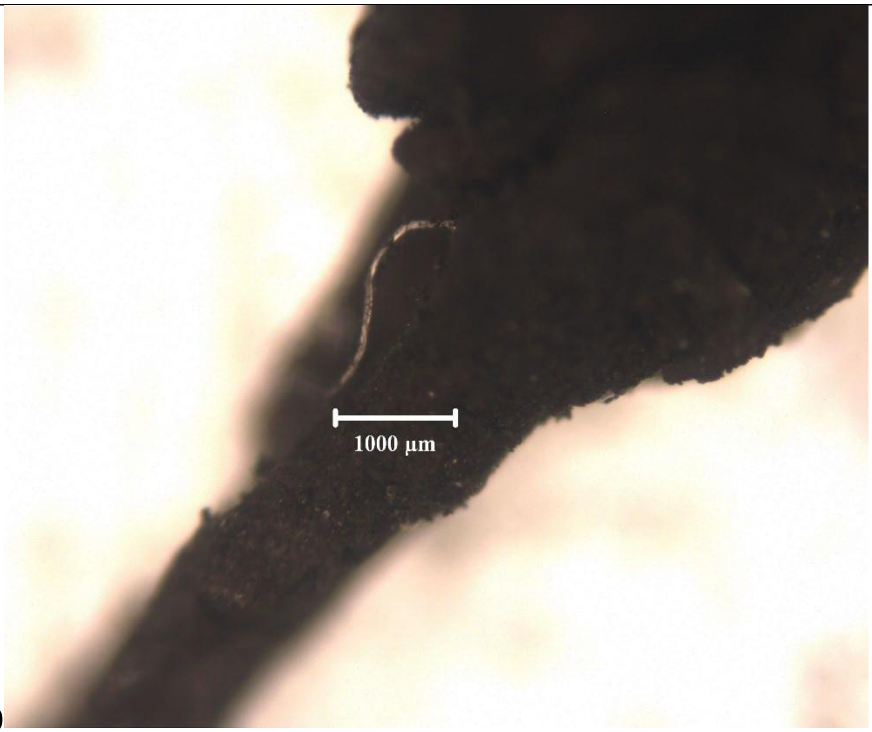
d)

Exhibit 75. SEM Images from Coal Baseline and Blended Fuel Slags. a) Coal baseline x30 image, b) blended fuel x30 image, c) coal baseline x500 image, d) blended fuel x500 image.

Material removed from the clogged burner was compared to the large particles found in the slurry using an imaging microscope. The burners that clogged during the blended fuel operation were removed and cleaned and the particles clogging the burner were saved for microscope imaging. Large particles were found in the blended fuel slurry samples that were collected when the blended fuel slurry was disposed. The large particles from the burner and the slurry were washed with water three times and dried in an oven at 80 °C before being analyzed on an imaging microscope.

The clogging that occurred during the blended fuel gasification testing happened in both slurry burners within a few minutes of each other and the reason for this was uncertain until we could analyze the material that was in the burners. The theorized causes were 1) the particle size of the torrefied wood not being decreased enough in the UK pilot size ball mill or 2) the plastic in the blend causing multiple particles of wood to agglomerate and creating a larger particle than would be allowed through the sieve after the ball mill. Either of these might cause a blockage in the burner, especially at the tip where the diameter decreases from 10 mm to 3 mm. The particles removed from the burner were mostly uniform and small in particle size, but there were a couple larger pieces, >3 mm in size, and one that stood out especially. That is the particle that was used for microscope imaging to determine if it was one solid piece of wood or multiple pieces adhered together by the plastic. The images are laid out in **Exhibit 76**.

The images show that the particle is one piece of wood that has had most of the plastic removed from the surface. The coal particles are relatively close to uniform at 50 μm and are found along most of the surface of the particle. There are obvious translucent particles along the surface as well that are pieces of the HDPE plastic, with a long strand that of HDPE that stands out on the 5x magnification image. The underlying structure of the particle, the uniformity of the coal particles on the surface, and the lack of a significant presence of plastic are enough to conclude that the particle is a piece of torrefied wood that was small enough to get through the sieve, but too large to reliably pass through the burner.



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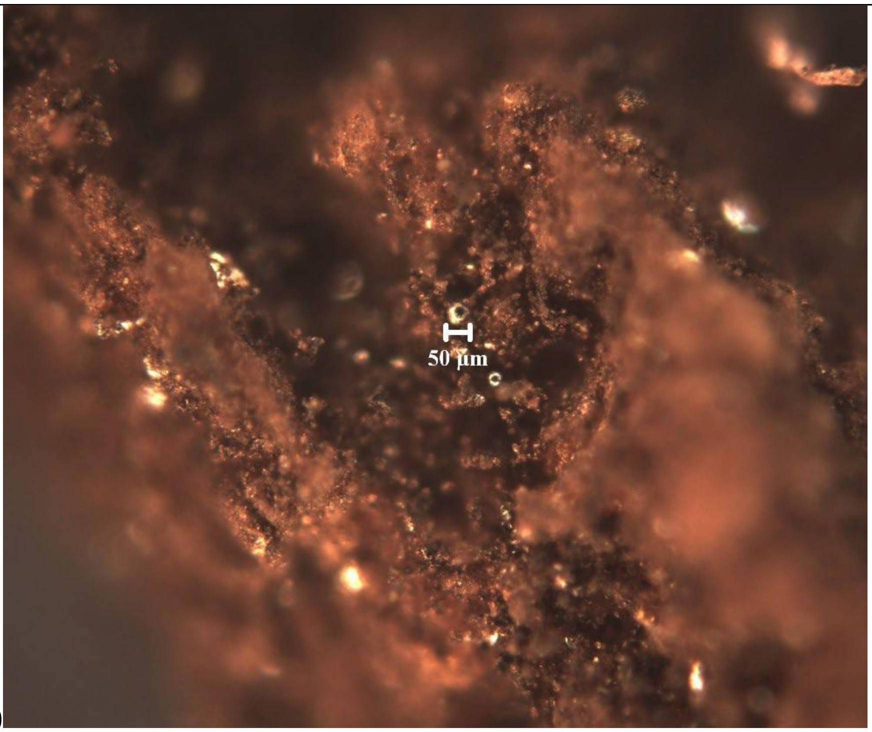

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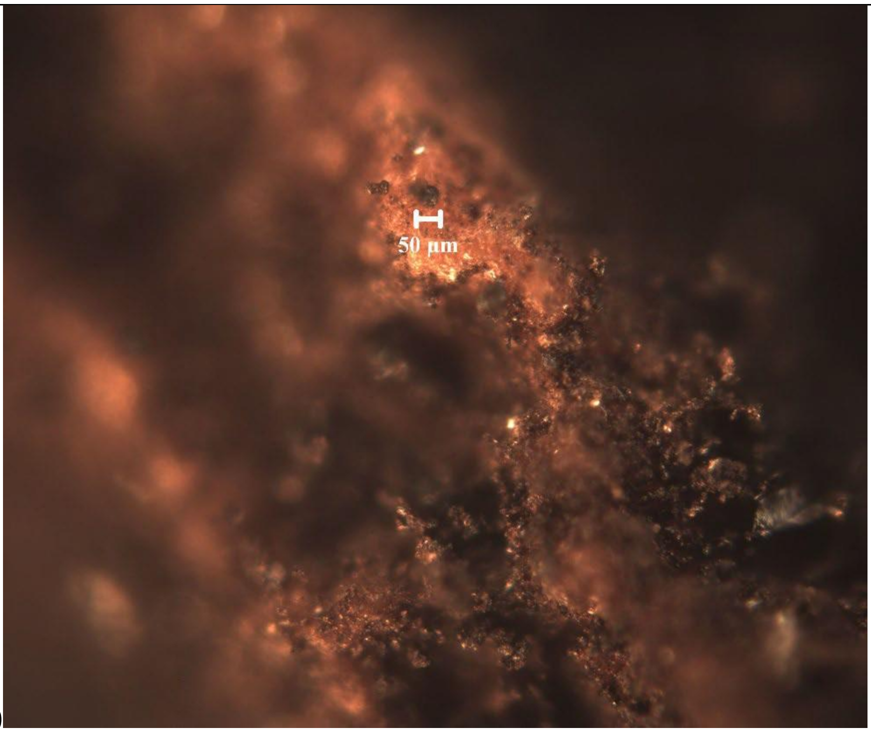


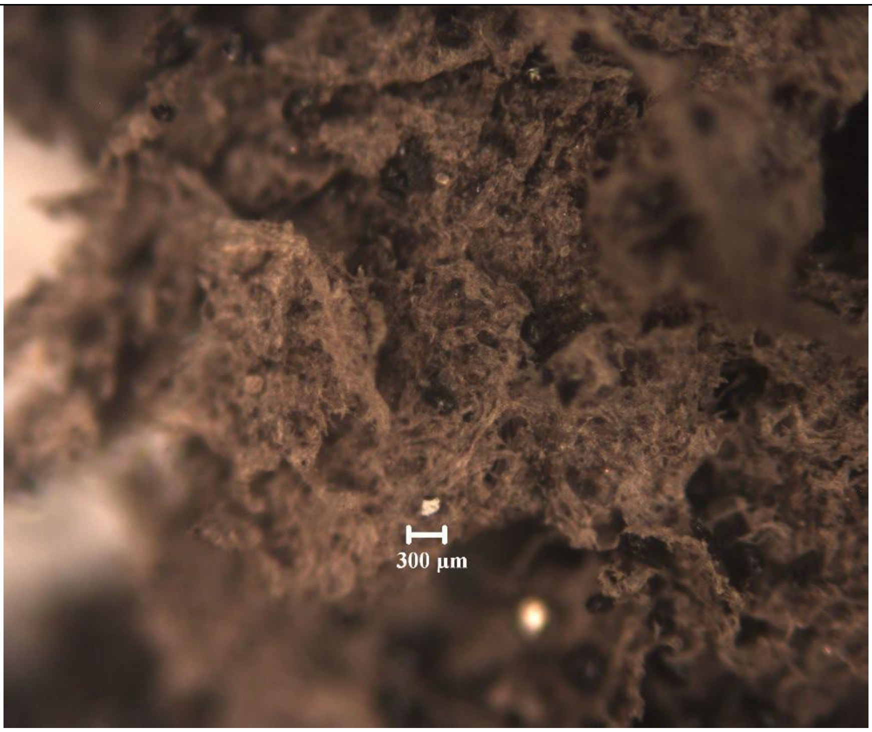
d)

Exhibit 76. Images of the Larger Particle Extracted from the Burner after Blended Fuel Testing. a) The washed and dried particle observed, b) The same particle at 5x magnification, c) The same particle at 20x magnification, d) 20x magnification of a different place on the particle.

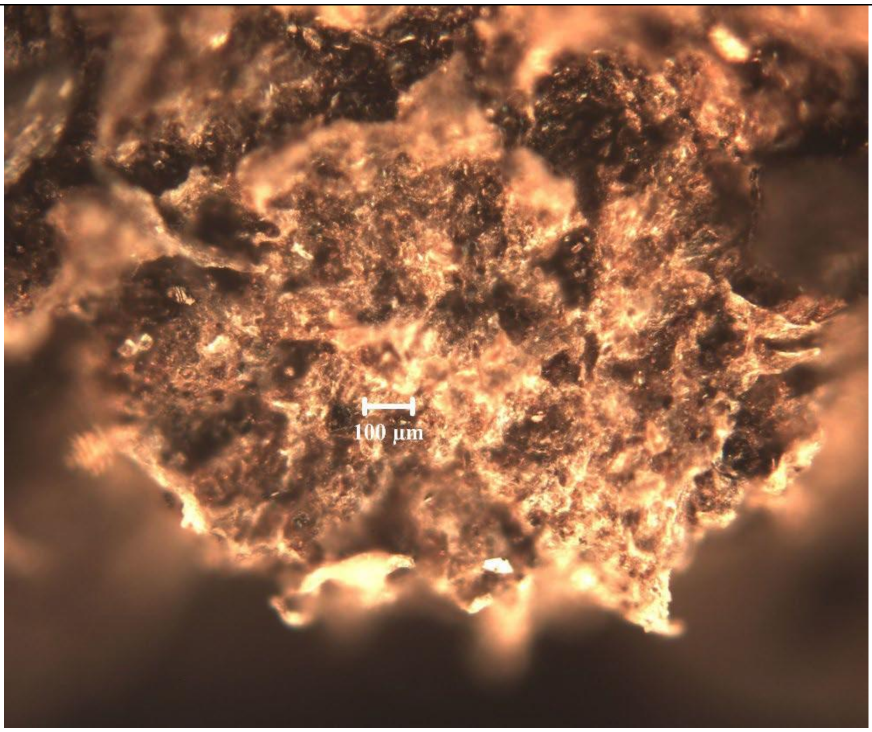
The microscope images for the larger particles found in the slurry samples are presented in **Exhibit 77**. These particles were relatively flat, likely due to the plastic flattening in the ball mill. At 5X magnification, the particles appeared to be coated with coal that couldn't be washed away, but when going to 20X magnification, the surface has a large presence of plastic coating the particles. This shows the efficacy of the co-extrusion method in coating the biomass particles to make them hydrophobic.

a)

b)



c)



d)

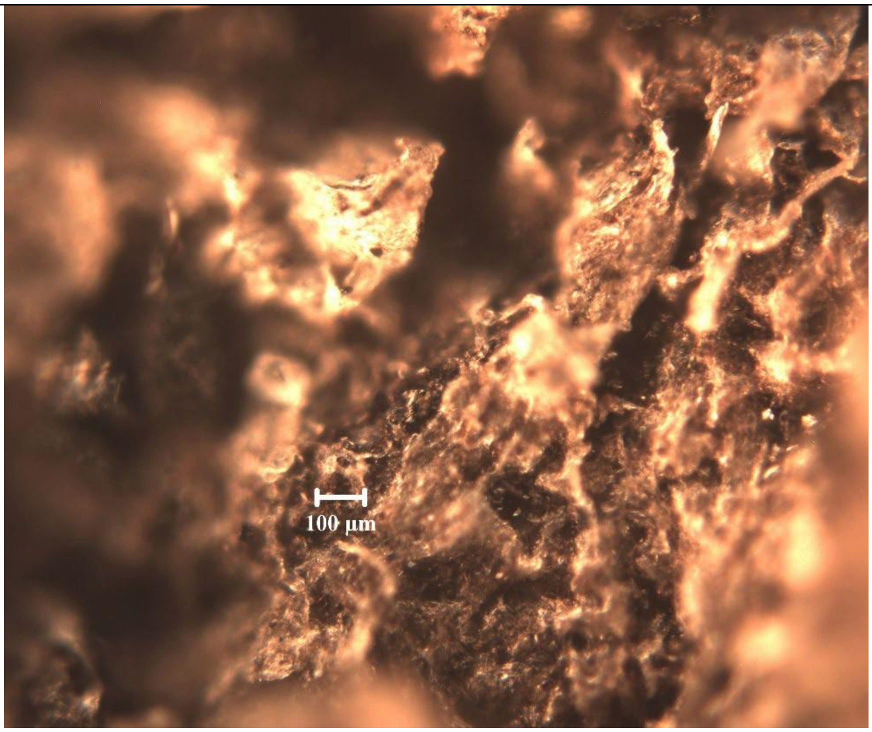


Exhibit 77. Images of Particles Extracted from the Slurry Sample that Remained after the Blended Fuel Gasification Test. a) The washed and dried particles with no magnification, b) The same particles at 5x magnification, c) The same particles at 20x magnification, d) 20x magnification of a different place on the particles.

4) CONCLUSIONS

4.1 Lessons Learned

There were several challenges faced through the completion of this project, predominantly due to the pilot scale of testing that will not be challenges at a commercial scale. Plastic requires certain equipment to break down into fine particles once it has been formed, and the resources available in the UK lab were not compatible. These issues, however, would be significantly reduced when scaled up to a commercial level. There would be no need to pre-process plastic pellets for co-extrusion or for co-gasification as the piping size on a commercial entrained flow gasifier would be capable of pumping full sized pellets, less than ¼ inch. For the pilot scale testing on the 1TPD UK gasifier, co-gasification testing may have been more successful with an alternative size reduction method for the blended fuel pellets. A ball mill is suitable for brittle material, such as coal, but will only flatten plastic material. Processing the blended fuel pellets separately in a knife mill or a cryo mill would have reduced the particle size lower and more evenly than the ball mill, reducing the risk of clogging in the slurry lines and burner tips of the gasifier.

Throughout the project there were three significant outcomes that we found. 1) Gasification of biomass with slurry-fed entrained flow gasifiers is possible when co-processed with plastic and could lead to carbon-neutral or –negative carbon emission operations. 2) Co-extrusion of HDPE and torrefied wood produces a blended fuel that is surface-encapsulated in plastic, is hydrophobic, and has significantly decreased water uptake compared to biomass alone. 3) The HDPE-torrefied wood blended fuel is compatible with slurry preparation and remains stable within the slurry for roughly 72 hours, longer than previously expected.

4.2 Technology Benefits and Shortcomings

The main benefit of this technology, and the goal of the project itself, was the introduction of biomass to entrained flow coal gasification to reduce the carbon impact to net-zero or, potentially, to net-negative emissions. To achieve net-zero carbon emission coal gasification, approximately 30 HHV% of the coal must be replaced with biomass. Although a lower replacement HHV% was evaluated due to constraints imposed by the size of slurry feed pipe, it has been shown that it is possible to introduce a significant amount of biomass to entrained flow gasification using plastic surface encapsulation through co-extrusion when the slurry is used in commercial scale applications that don't require the blended fuel to be grinded to less than 500 microns.

One of the shortcomings of co-gasifying biomass is the increase in volume of the slurry to make up for the decrease in total heating value due to the inclusion of biomass. This is slightly offset by the higher heating value of plastic, but it does not completely make up for the loss. A second shortcoming is in the testing of pre-processed biomass – torrefied wood. Ideally, green biomass would be co-extruded with plastic at a temperature that would volatilize the biomass to a point that is suitable for gasification.

4.3 Future Development

Wabash Valley Resources, LLC, provided support, including financial support, for this project and further collaboration is planned to continue scale up and commercial demonstration of this technology.

A future development to be made is to utilize an alternative source of biomass other than torrefied wood. Sawdust is a green biomass that has no heat treatment and is the primary source of wood utilized in plastic-wood co-extrusions at facilities such as the Polymers Technology Center.