



Delivering the Right Results

# Rapid Determination of Ultimate Analysis and Gross Calorific Value in Biomass-Derived Fuels

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## INTRODUCTION

Increased attention has been focused on biomass-derived fuels due to the rise of traditional energy feedstock prices and the concerns associated with global warming. Fuels are commonly characterized by ultimate analysis and the gross calorific value. The determination of Carbon, Hydrogen, Nitrogen, Sulfur, and Oxygen in fuel is commonly referred to as Ultimate Analysis. Ultimate Analysis can be used to calculate combustion efficiency, material balance, emission potential, reactivity, and yield of products in fuel conversion processes such as gasification or liquefaction. Gross Calorific value of a fuel is often considered the most important attribute of the fuel as it is used to calculate the heating potential of the fuel.

Carbon, hydrogen, and nitrogen in the biomass-derived fuel samples were determined concurrently with a combustion instrument using a pure oxygen combustion furnace and infrared (IR) detection for the carbon and hydrogen; and a thermal conductivity cell for nitrogen detection resulting in an analysis time of four minutes. Sulfur was determined using high-temperature tube furnace combustion with IR detection resulting in an analysis time of ~2 minute, while oxygen was determined using a pyrolysis furnace followed by IR detection resulting in a 1 minute analysis. The gross calorific values of the biomass samples were determined using an isoperibol oxygen combustion calorimeter with an analysis time of 5 minutes.

This poster presents rapid analytical techniques for the determination of ultimate and gross calorific value in biomass fuel materials used or produced in a wood-based fast pyrolysis process.

## METHODOLOGY

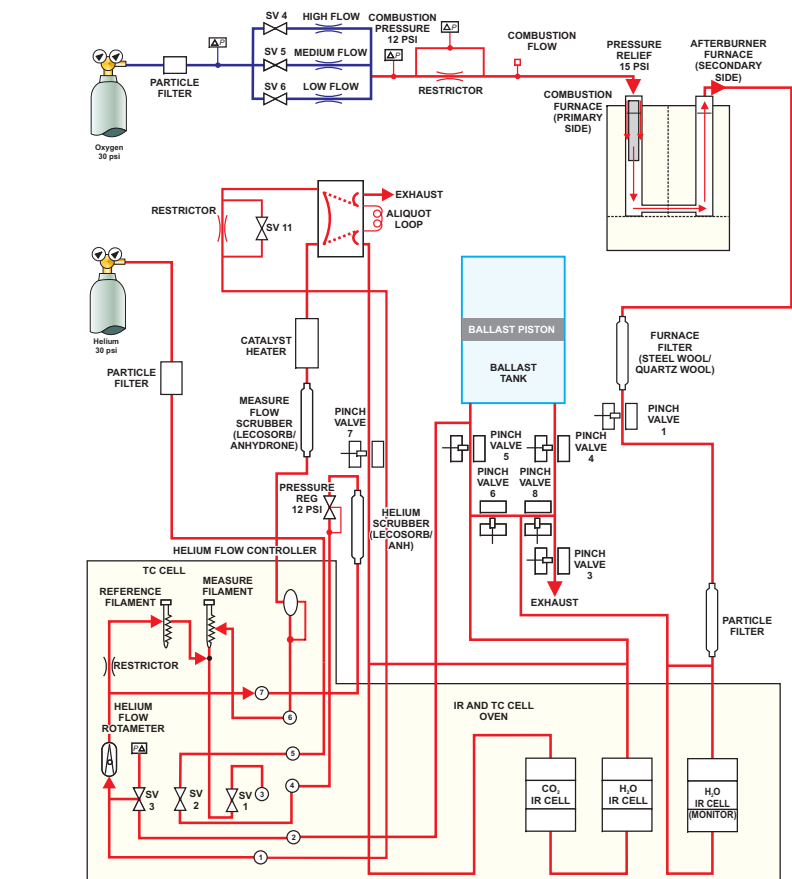


- LECO TruSpec® CHN
- LECO TruSpec Sulfur Module
- LECO TruSpec Micro Oxygen Module
- LECO AC600 Isoperibol Calorimeter

### Procedure

#### Carbon, Hydrogen and Nitrogen Determination

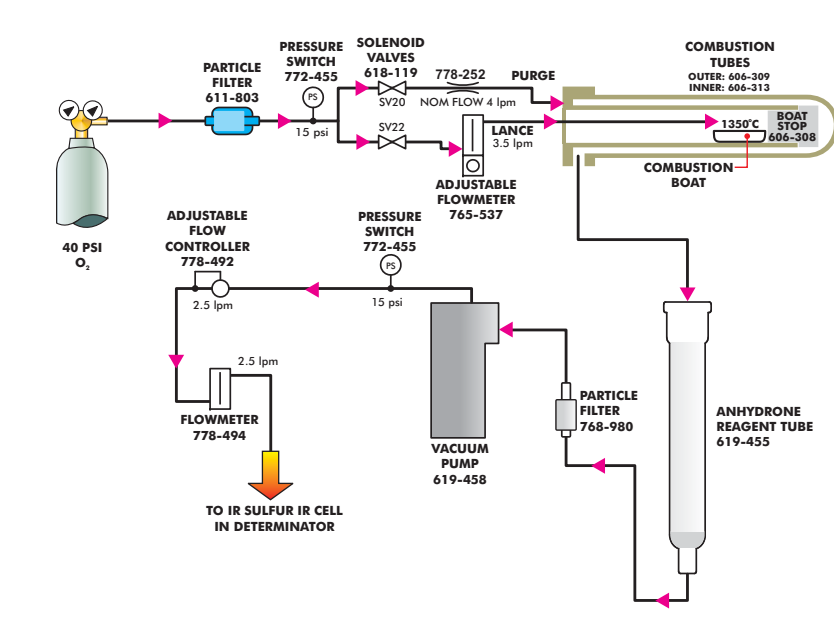
- Weigh ~100 to 150 mg of sample into tin foil wrapper or tin capsule
- Load sample into autoloader



Sample combusted in a resistance furnace (950°C) using pure oxygen. Combustion gas collected in a ballast where an aliquot is collected for Nitrogen determination via a thermal conductivity cell. Carbon and Hydrogen are detected using infrared detection. Carbon, Hydrogen, and Nitrogen are all measured concurrently with a total analysis time of 4 minutes.

#### Sulfur Determination

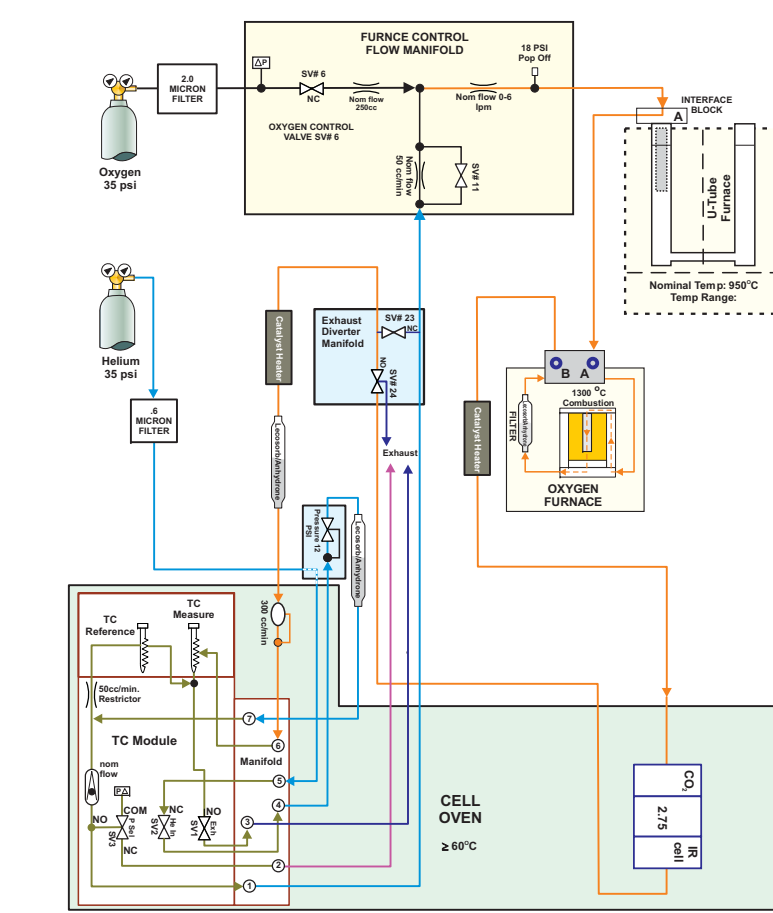
- Weigh ~100 to 200 mg of sample into ceramic combustion boat
- Cover sample with ~1 g combustion accelerator (LECO COM-CAT #502-321)
- Mix the COM-CAT and sample with weighing spatula
- Place the sample into the high-temperature tube furnace



The sample is combusted in the furnace at 1350°C with pure oxygen causing all sulfur to be oxidized to SO<sub>2</sub>. Combustion gases pass through anhydrous, removing moisture and on to the Infrared Detection Cell. The analysis time is approximately 2 minute.

#### Oxygen Determination

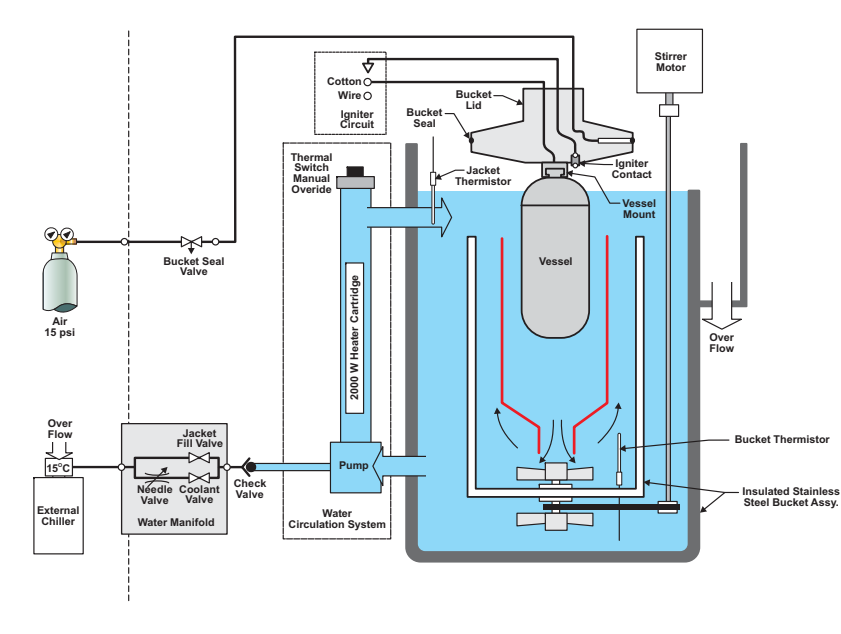
- Weigh ~1 to 2 mg of sample into tin capsule
- Load sample into autoloader



The sample is dropped into a 1300°C pyrolysis furnace. The oxygen released during pyrolysis of the sample reacts with a carbon-rich environment in the furnace to form CO. The CO is swept from the furnace and converted to CO<sub>2</sub> before measurement via infrared detector. The analysis time is approximately 1 minute.

#### Calorific Value Determination

- Weigh ~200 to 600 mg of sample into a crucible
- For dry biomass material add ~400 mg of Paraffin Oil (LECO # 501-439) to the top of the sample as a spike
- Load crucible into vessel
- Vessel is sealed and charged with oxygen to ~450 psi



The vessel is automatically lowered into an inner water-filled chamber (bucket). The temperature in outer water-filled chamber within the instrument (jacket) is closely controlled. An electrical charge ignites the sample and the temperature increase of the bucket is precisely measured. Use of a thermodynamic model developed by LECO (TruSpeed™) enables the AC600 to determine the calorific value within 5 minutes without compromising the accuracy or precision.

## METHODOLOGY

The TruSpec CHN was calibrated using the pure Reference Material Phenylalanine (LECO #502-642). A multipoint Linear regressed calibration was utilized for Carbon and Hydrogen and a Linear calibration with a fixed zero origin for Nitrogen. Sample masses from 50 to 200 mg of the Phenylalanine Reference Material were used for calibration. When using a nominal sample mass of 150 mg the calibration covers ~22% to ~87% carbon, ~2% to 9% hydrogen and ~0.04% to ~11% nitrogen.

The TruSpec Sulfur Module was calibrated using a ~0.1% and ~0.01% sulfur in Mineral Oil Reference Material (LECO # 502-419 and #502-417 respectively). A multipoint Linear regressed calibration was utilized. When using a nominal sample mass of 100 mg the calibration covers ~0.1 to ~0.01% sulfur.

The TruSpec Micro Oxygen Module was calibrated using the pure Reference Material Dinitrobenzoic Acid (LECO #502-204). A single point (1 mg mass) calibration forced through the origin was utilized. When using a nominal sample mass of 1 mg the calibration covers ~45% to ~0.04% oxygen.

The AC600 Isoperibol Calorimeter was calibrated using the pure Reference Material Benzoic Acid (LECO #774-208) in compliance to ASTM D5865 Standard Test Method for Gross Calorific Value of Coal and Coke.

Reference Material	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen (%)	BTU/lb	Calibration/Check
Phenylalanine (R502-642)	65.4	6.7	8.5	NA	NA	NA	CHN
Benzoic Acid (R774-208)	68.85	4.95	NA	NA	26.20	11373	Calorific Value / O
Dinitrobenzoic Acid (R502-184)	39.63	1.90	13.2	NA	45.60	NA	O
~0.1% Sulfur mineral oil (R502-419)	NA	NA	NA	0.102	NA	NA	S
~0.05% Sulfur mineral oil (R502-418)	NA	NA	NA	0.0506	NA	NA	S
~0.01% Sulfur mineral oil (R502-417)	NA	NA	NA	0.0104	NA	NA	S

Table 1. Reference Materials used for Calibration and Check Samples.

## RESULTS

The fast pyrolysis process is one of the biomass-to-liquid-fuel generation processes currently being researched and implemented commercially. This process produces an oil product (BioOil) from a biomass material (typically wood). The samples chosen for this work represent the raw materials (three wood chip samples) and final product (BioOil) of a wood-based fast pyrolysis process.

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen (%)	BTU/lb
Wood chip 1	37.82	6.67	0.11	0.138	47.50	6697
	37.86	6.63	0.09	0.134	48.03	6742
	38.04	6.59	0.07	0.134	48.61	6753
	37.90	6.49	0.10	0.137	48.58	6747
Avg	37.91	6.60	0.09	0.136	48.18	6735
Std Dev	0.10	0.08	0.02	0.002	0.53	26
RSD (%)	0.25	1.17	18.46	1.52	1.09	0.38
Wood Chip 2	46.41	6.12	0.63	0.050	44.28	8084
	46.52	6.15	0.64	0.053	44.75	8110
	46.61	6.15	0.64	0.058	43.02	8050
	46.57	6.17	0.66	0.054	43.95	8107
Avg	46.53	6.15	0.64	0.056	44.00	8088
Std Dev	0.09	0.02	0.01	0.003	0.73	28
RSD (%)	0.19	0.34	1.96	5.87	1.66	0.34
Wood Chip 3	46.37	6.07	0.49	0.035	43.84	7980
	46.24	6.04	0.50	0.038	42.57	7971
	46.48	6.06	0.50	0.041	43.47	8009
	46.14	6.03	0.51	0.037	42.24	7947
Avg	46.30	6.05	0.50	0.038	43.03	7977
Std Dev	0.16	0.02	0.01	0.003	0.75	26
RSD (%)	0.35	0.30	1.63	6.62	1.74	0.32
BioOil	42.26	7.33	0.04	0.010	44.26	7445
	42.15	7.39	0.05	0.009	46.55	7403
	42.4	7.43	0.08	0.012	44.13	7369
	42.46	7.44	0.07	0.010	45.59	7442
Avg	42.32	7.40	0.06	0.010	45.13	7415
Std Dev	0.14	0.05	0.02	0.001	1.15	36
RSD (%)	0.33	0.67	30.43	12.28	2.55	0.49

Table 2. Biomass Derived Fuel Sample Data.

During this work, reference materials were run as check samples interspersed within the biomass-derived fuel samples. The results obtained on these checks verify that the instrument and its calibration remained stable.

Reference Material	Phenylalanine (R502-642)	Reference Material	Benzoic Acid (R774-208)	Reference Material	~0.05% Sulfur in Mineral Oil (R502-418)
Average (%)	65.47	Average (%)	26.44	Average (%)	0.0517
Standard Deviation	0.22	Standard Deviation	0.151	Standard Deviation	0.002
RSD (%)	0.34	RSD (%)	0.57	RSD (%)	3.87
Expected (%)	65.4	Expected (%)	26.2	Expected (%)	0.0506
Recovery (%)	100.1	Recovery (%)	100.9	Recovery (%)	102.2
# of Runs	5	# of Runs	14	# of Runs	12
Average (%)	6.65	Calorific value	11371		
Standard Deviation	0.05	Average (BTU/lb)	8		
RSD (%)	0.75	Standard Deviation	0.07		
Expected (%)	6.7	RSD (%)	11373		
Recovery (%)	99.3	Expected	100.0		
# of Runs	5	Recovery (%)	100.0		
Average (%)	8.46	# of Runs	8		
Standard Deviation	0.02				
RSD (%)	0.24				
Expected (%)	8.5				
Recovery (%)	99.5				
# of Runs	5				

Table 3. Check Sample Data.

## CONCLUSIONS

The objective of this work was to demonstrate the acceptable quantitative carbon, hydrogen, nitrogen, sulfur, oxygen, and calorific value recovery and precision in the biomass-derived fuel materials when combustion-based instruments are utilized.

The carbon, hydrogen, oxygen, and calorific values determined using the combustion instruments had excellent precision with all of the biomass-derived fuel sample's RSD values being less than ~2.5%. The nitrogen concentrations in one of the wood chip samples and the BioOil sample were approaching the lower end of the combustion instrument's analytical range (0.04% using 100 mg sample), and higher RSD results were seen in these samples (18.5% and 30.4% respectively). The sulfur results for the wood and oil samples also had some loss of precision (5.9% to 12.3% RSD) as the sulfur concentration in the samples decreased below ~0.05%. All of the data was within the expected ranges for the biomass-derived fuel material.

The combustion instruments offer laboratories many benefits.

### High Throughput and Efficiency

- Rapid Analysis Times
- ~4 minutes concurrent CHN determination
- ~2 minute S determination
- ~1 minute O determination
- ~5 minute calorific value determination

### Instrument Automation

- 120 sample position CHN
- 50 sample position S
- 30 sample position O
- Optimized semi-automated calorimeter
- Little-to-no sample pre-treatment requirements

### Low Cost/Analysis\*

- ~\$0.55 Carbon, Hydrogen, and Nitrogen
- ~\$0.45 Sulfur
- ~\$0.42 Oxygen
- ~\$0.22 Calorific Value

\*Cost represents operational costs only calculated using LECO list pricing and average US compressed gas pricing for Helium and Oxygen.