Application Note
OI Analytical, a Xylem brand • XA00298

Determination of Total Sulfur in Biocrude by Gas Chromatography (GC) with a Pulsed Flame Photometric Detector (PFPD)

PETROCHEMICAL SERIES

Introduction

Hydrothermal liquefaction (HTL) is an emerging technology for conversion of wet organic wastes, particularly sewage sludge, into transportation fuels. The intermediate product of HTL is an energy-dense biocrude. HTL of biocrude produces renewable diesel and sustainable aviation fuel. HTL is necessary to remove heteroatom content from the biocrude[1]. Sulfur is especially important to remove to meet stringent fuel specifications. Sulfur removal efficiency is influenced by the molecular makeup of the compounds that contain sulfur. It is well known that sulfur is corrosive and can cause damage to equipment and have negative impacts on production costs and quality of finished products. In this research we conducted a comprehensive analysis of total sulfur content within biocrudes derived from the HTL of sewage sludge. Varying processing parameters such as residence time and the inclusion of an oxidant were considered. Employing gas chromatography (GC) in tandem with a sulfur-specific pulsed flame photometric detector (PFPD), samples were analyzed for total sulfur levels present in the biocrudes across these different conditions.

This note presents HTL conditions, instrument conditions, QC, and sample results in order to provide a foundational understanding essential for optimizing subsequent refining processes, aiming to produce sulfur-compliant biofuels that meet stringent energy specifications and standards. Lower sulfur concentration requirements in finished products is important to minimize emission pollution.

Motivation

The global population is growing at an annual rate of 1.05%, and at this rate, it will surpass 10 billion by 2057. EPA estimates that ~4.5 Million Dry Metric Tons of treated sewage sludge were generated in 2021. Sewage Sludge (SS) is a byproduct of wastewater treatment. It is normally a mix of organic matter from human waste, food waste particles, microorganisms, trace chemicals and inorganic solids from products and medicine we use, together with water bound to these materials. SS has become a critical problem due to its environmental risk and high treatment/disposal cost. Waste-to-Energy (WTE) is to identify and advance the best available technologies for the recovery of energy or fuels from municipal solid wastes and other industrial, agricultural, and forestry residues. WTE is one of several imperatives for sustainable waste management. WTE systems can be an effective supplement to fossil fuel-based power sources while also reducing landfill requirements in urban environments, generating renewable energy, and producing revenue for municipalities and governments.

HTL is an attractive thermochemical process that converts low-quality organic matter into high-quality biocrude[2]. HTL accelerates many chemical reactions for the conversion of organic matter. HTL is a thermochemical process conducted at temperatures of 280–450 °C and pressures of 10–35 MPa, which can convert wet waste into biocrude. It offers great advantages over combustion and pyrolysis, which avoids the demand for energy-intensive drying. HTL has been one of the most promising methods for treatment of SS with high moisture. The HTL process has the ability to convert all kinds of waste to biocrude, which is comparable to fossil crude oil and can be upgraded in existing refinery set-ups.

HTL is a capital-intensive process and maximizing biocrude yield is the key to economic viability.

Figure 1. Model 5383 PFPD

Experimental

Instrumentation for this study included an OI Analytical Model 5383 PFPD (Figure 1) mounted on an Agilent 7890A GC system with a split/splitless injection port. The column used is a good general purpose column which has a built in guard column ideal for running "dirty" samples.

Instrument operation conditions are shown in Table 1. The PFPD was tuned for optimum sulfur response by optimizing the air and hydrogen flows and observing the sulfur emission on the PFPD PulseView Monitor while introducing a constant flow of Thiophene. Sulfur response from a PFPD is naturally quadratic, so sulfur was set with the square root function on in order to get linearized response over the calibration range.

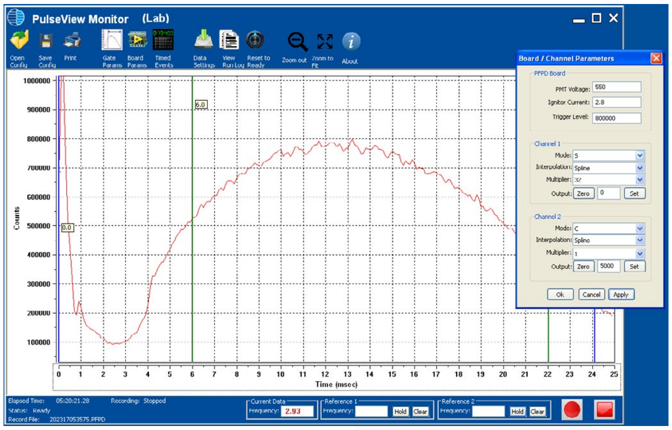
Instrument Parameters

Table 1. Instrument Parameters

Agilent 7890A GC & OIA 5383 PFPD	
Inlet	330 ˚C Split mode Split ratio 10:1 Sulfinert®-coated Restek Topaz 4 mm precision liner with Wool
GC Column	Restek Rtx-5 w/Integra-Guard 30-m x 0.32-mm ID x 1.0 µm df Helium carrier gas measured at 1.2 mL/min
Oven Program	40 ˚C for 2 minutes 10 ˚C / minute to 100 ˚C, hold 2 minutes 20 ˚C / minute to 250 ˚C 30 ˚C / minute to 330 ˚C, hold 5 minutes Total run time 25.17 minutes
Sulfur Detection	Pulsed Flame Photometric Dector (PFPD) 2-mm combustor BG-12 filter R1924 PMT Detector base temperature 250 ˚C H_2 / air ratio tuned for optimum sulfur emission: H_2 measured at ~11.5 mL/min. Air 1 measured at ~10 mL/min. Air 2 measured at ~10 mL/min 6-24 milliseconds sulfur gate (linear mode; square root on) 1-2 milliseconds hydrocarbon gate

The instrument was calibrated using the Sulfur Simulated Distillation Standard from DCG Partnership I, Ltd. This standard is comprised of thirteen mercaptans with concentration ranges from 30-60ppm. This stock was diluted in 10% toluene and 90% isooctane for a six point calibration from 1.0 to 57.2ppm. The chromatogram was integrated and areas and concentrations were used to generate the calibration curve using linear regression for total sulfur.

A Method Detection Limit (MDL) study was performed by injecting eight standards at 0.92ppm. An Initial Demonstration of Proficiency (IDOP) study was performed by injecting six standards at 11.4ppm. Both studies yielded reasonable results.



Board / Channel Parameters

PFPD Board
PMT Voltage: 550
Ignitor Current: 2.8
Trigger Level: 800000

Channel 1
Mode: S
Interpolation: Spline
Multiplier: 32
Output: 0

Channel 2
Mode: C
Interpolation: Spline
Multiplier: 1
Output: 5000

Elapsed Time: 05:20:21.28
Recording: Stopped
Status: Ready
Record File: 202317053575.PFPD
Current Data Frequency: 2.93
Reference 1 Frequency:
Reference 2 Frequency:

Figure 2. PulseView Monitor
Sulfur Emission with Board Parameters

Gate Parameters

Gate Parameters List

	--- GATE A ---				--- GATE B ---		
Mode	Start	Stop	<op>	Alpha	Start	Stop	Sqrt
S	6.0	24.0	-	0.000	0.0	0.0	ON
P	4.0	14.0	+	0.000	8.0	12.0	OFF
C	1.0	2.0	-	0.000	10.0	12.0	OFF
N	3.0	10.0	-	0.000	8.0	12.0	OFF
UD	6.0	24.0	+	0.000	8.0	12.0	OFF

Current Mode
Mode: S
A - 0.000B
☑ Enable Sqrt
A Start: 6.0 ms
A Stop: 24.0 ms
<op>: -
Alpha: 0.000
B Start: 0.0 ms
B Stop: 0.0 ms

Elapsed Time: 05:20:25.52
Recording: Stopped
Status: Ready
Record File: 202317053575.PFPD
Current Data Frequency: 2.93
Reference 1 Frequency:
Reference 2 Frequency:

Figure 3. PulseView Monitor
Sulfur Emission with Gate Parameters

Table 2. Chemical Composition of Sewage Sludge

	Sewage Sludge
C	42.9
H	7.3
N	6.9
S	1.16
O	41.7

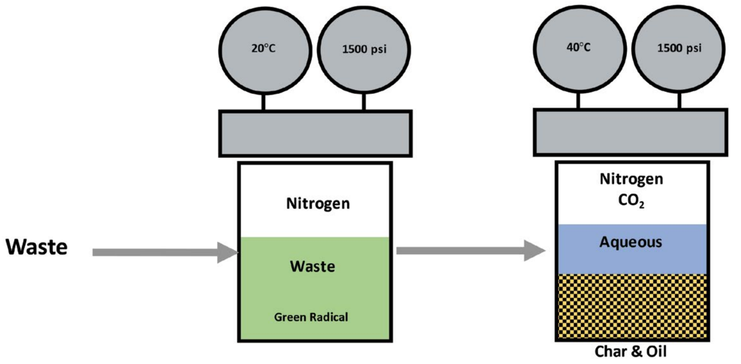


Figure 3. Worcester Polytechnic Institute (WPI) HTL

Sewage sludge was provided by Great Lakes Water Authority's (GLWA) wastewater treatment plant in southwest Detroit and underwent different types of treatments for HTL of the sludge. Reaction time was varied and some sludges had an addition of green radicals. HTL was improved by adding a green radical initiator into the reactor to maximize the biocrude yields and minimize the char yields. The HTL experiments were conducted at Worcester Polytechnic Institute (WPI) and samples were then sent to OI Analytical for analysis. Samples were diluted 100x in methanol and filtered using a PTFE 0.22 disc filter.

Results and Discussion

Calibration, MDL, and IDOC results were acceptable. The PFPD is very stable and yields consistent results over time. Since the flame is 2200 degrees C the detector is self-cleaning with no coking or soot formation even for samples with heavy hydrocarbons.

Table 3. QA/AC Results

	Avg RF	% RSD	Coef of Det R^2	MDL (ppm)	IDOC % Recovery	IDOC %RSD
Total Sulfur	6.54e-3	8.86	0.999	0.179	99.20	5.50

The introduction of a green radical initiator enhances sulfur content in biocrude. Prolonged residence time in HTL leads to higher sulfur yields in biocrude. A speciation study is needed to comprehensively understand the sulfur compounds in biocrude.
The severity of conditions required to remove sulfur depends on the molecular structure of the sulfur bearing molecule. So, sulfides and thiols are easiest to remove, then thiophenes, then benzothiophenes. Therefore speciation of the sulfurs will facilitate the hydrodesulphurization process.

Table 4. HTL Experimental Conditions and Results

Sample	Experiment	Reaction Temperature (˚C)	Reaction Time (minutes)	Radical weight percentage	Total Sulfur (ppm)
SS3	HTL	300	0	0	4790
SS4	HTL	300	10	0	2300
SS5	HTL	300	50	0	3370
SS6	HTL	300	90	0	3660
SS7	HTL+Radical	300	10	10%	1980
SS8	HTL+Radical	300	10	20%	4710
SS9	HTL+Radical	300	50	20%	4230
SS10	HTL+Radical	300	90	20%	3730
SS11	HTL+Radical	300	10	40%	3330
SS12	HTL+Radical	300	10	100%	2710

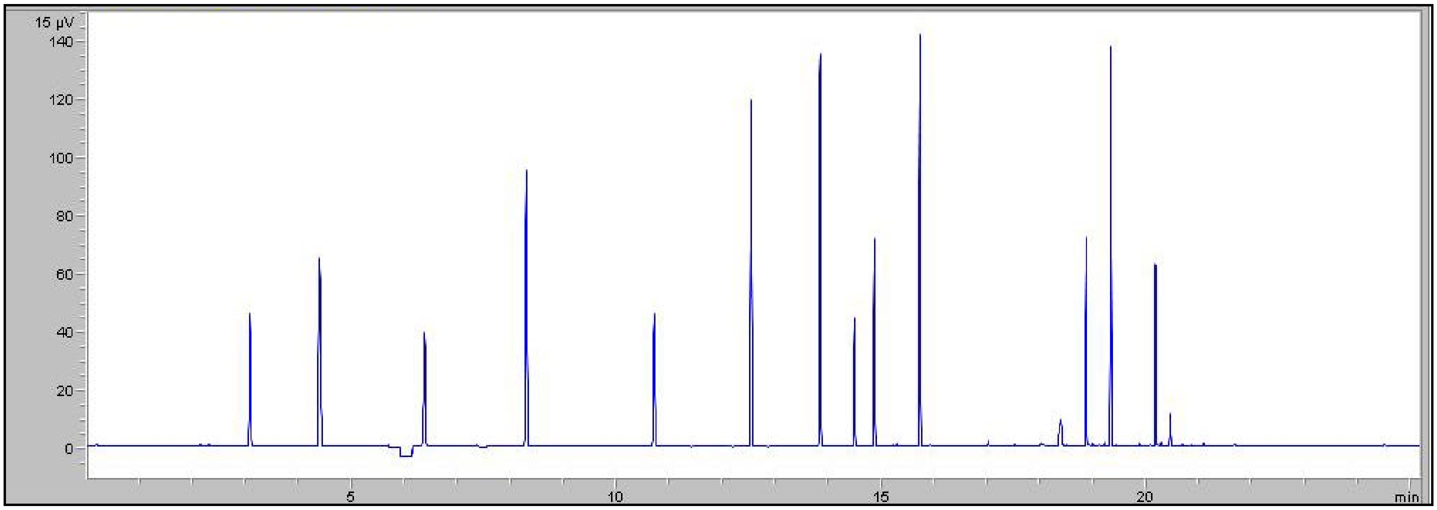


Figure 4. Total Sulfur Standard 11.4 ppm

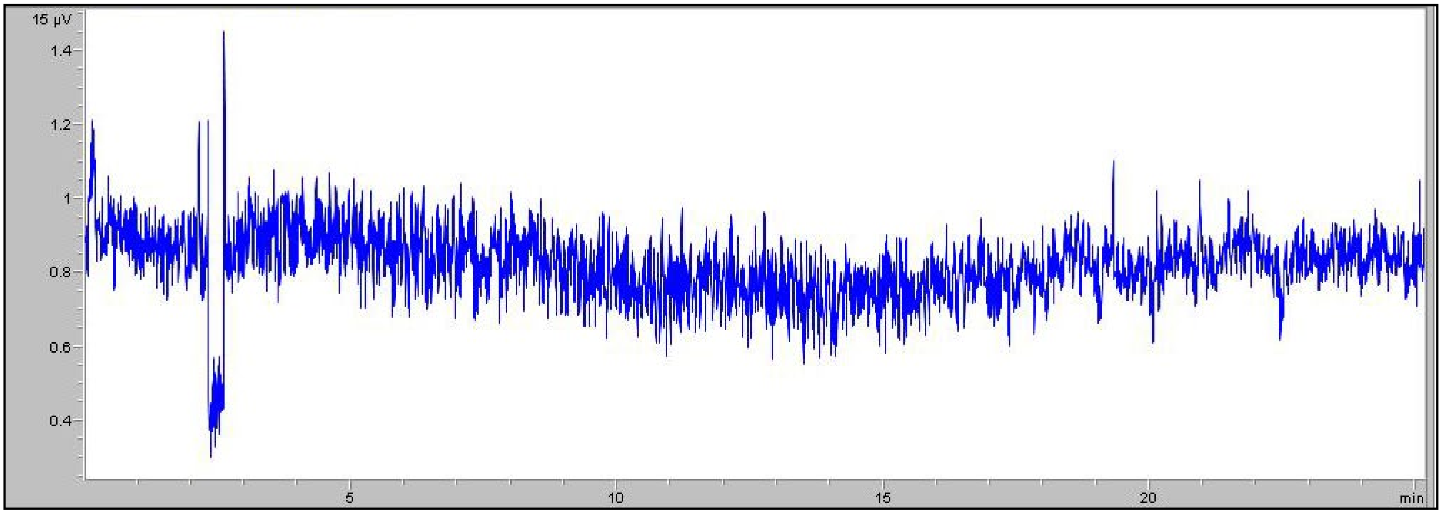


Figure 5. Method Blank

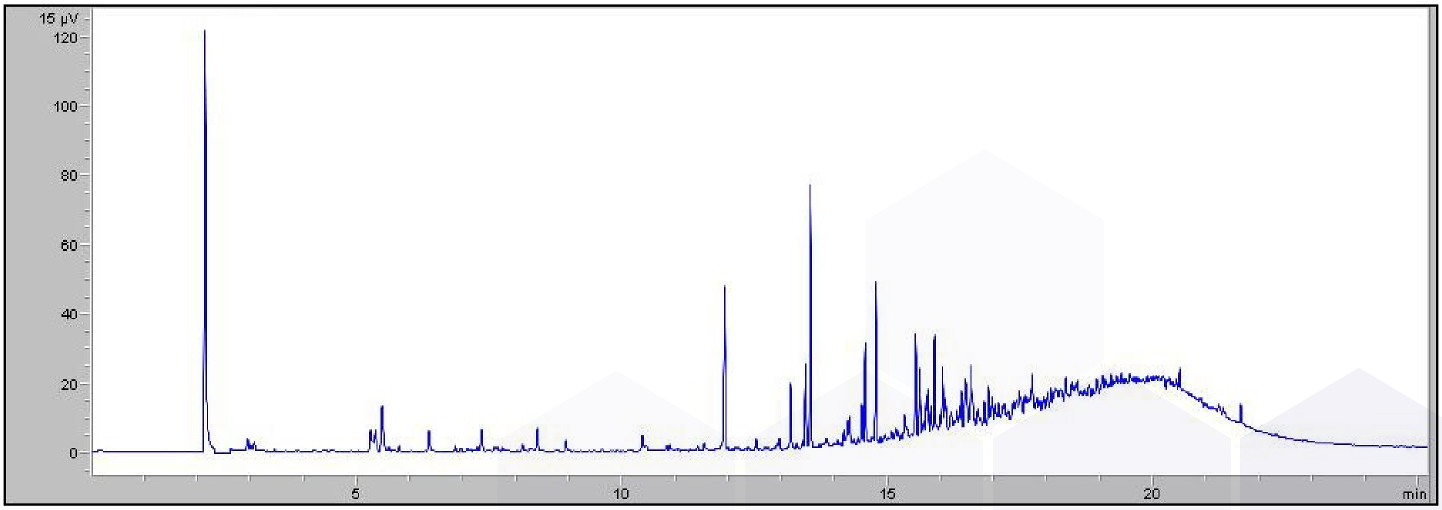
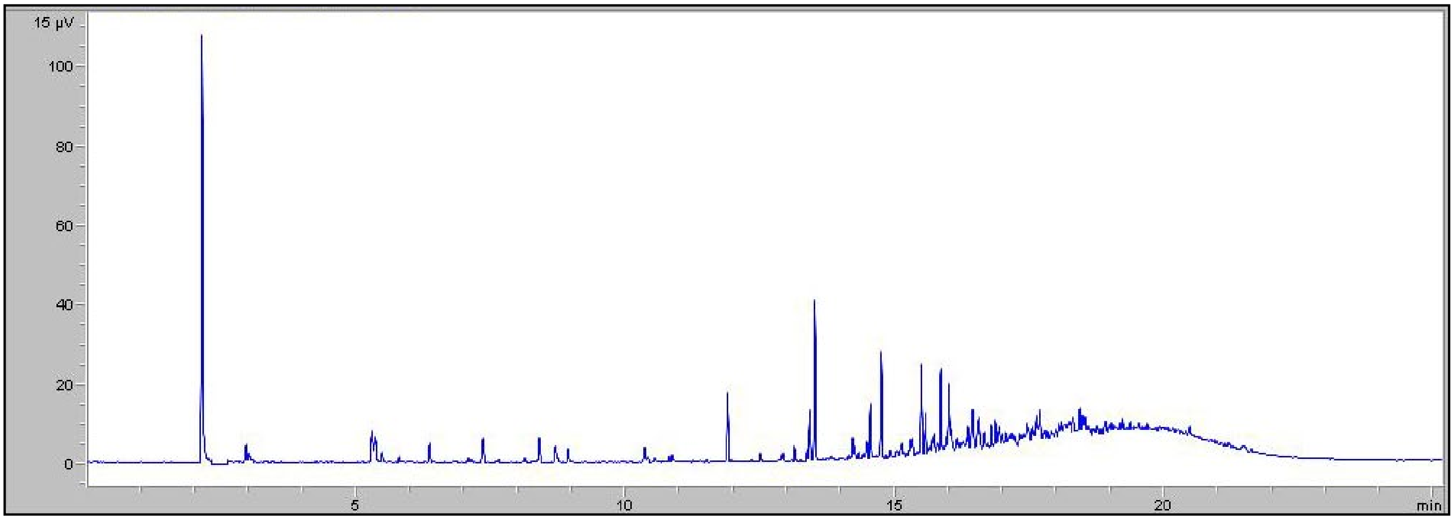


Figure 6. SS3



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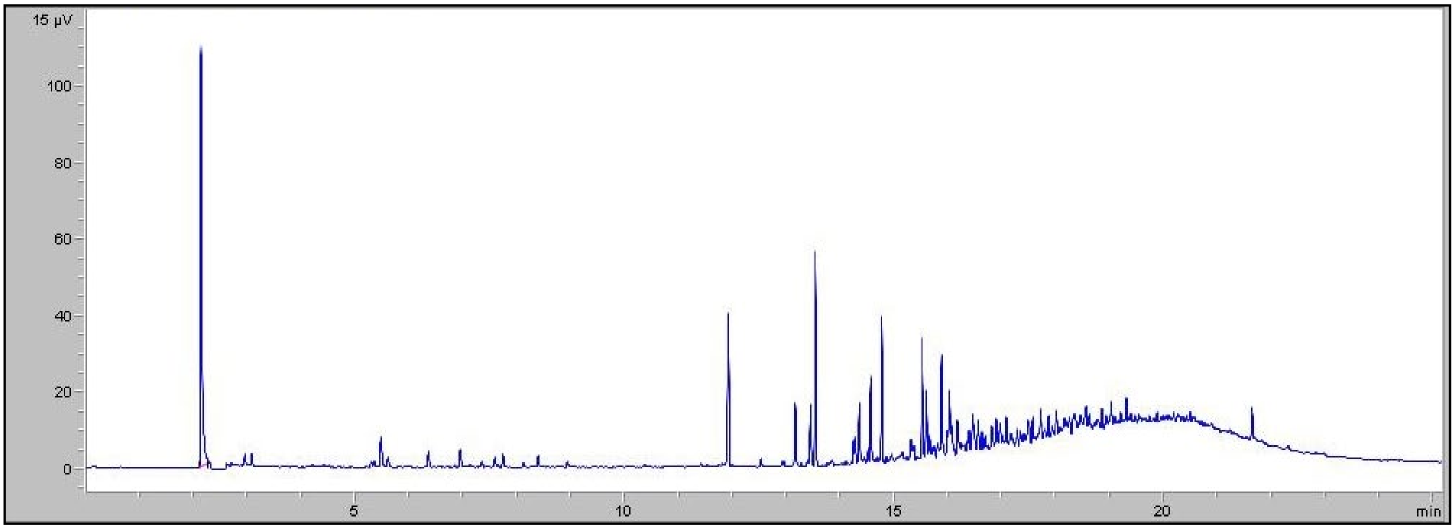

Figure 8. SS5

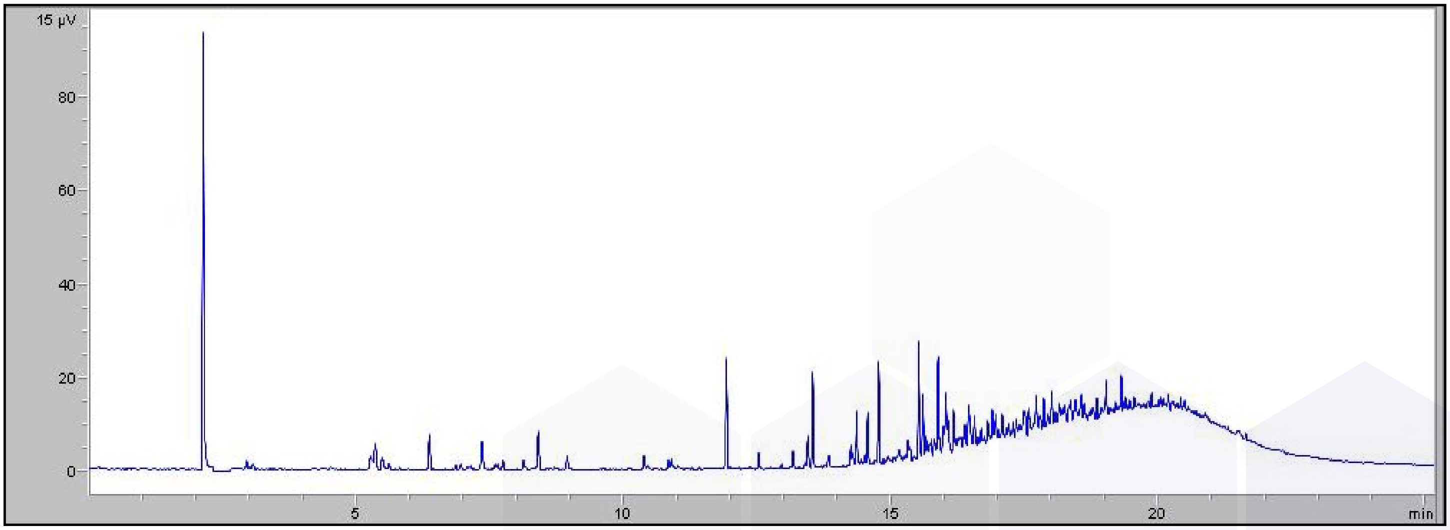

Figure 9. SS6

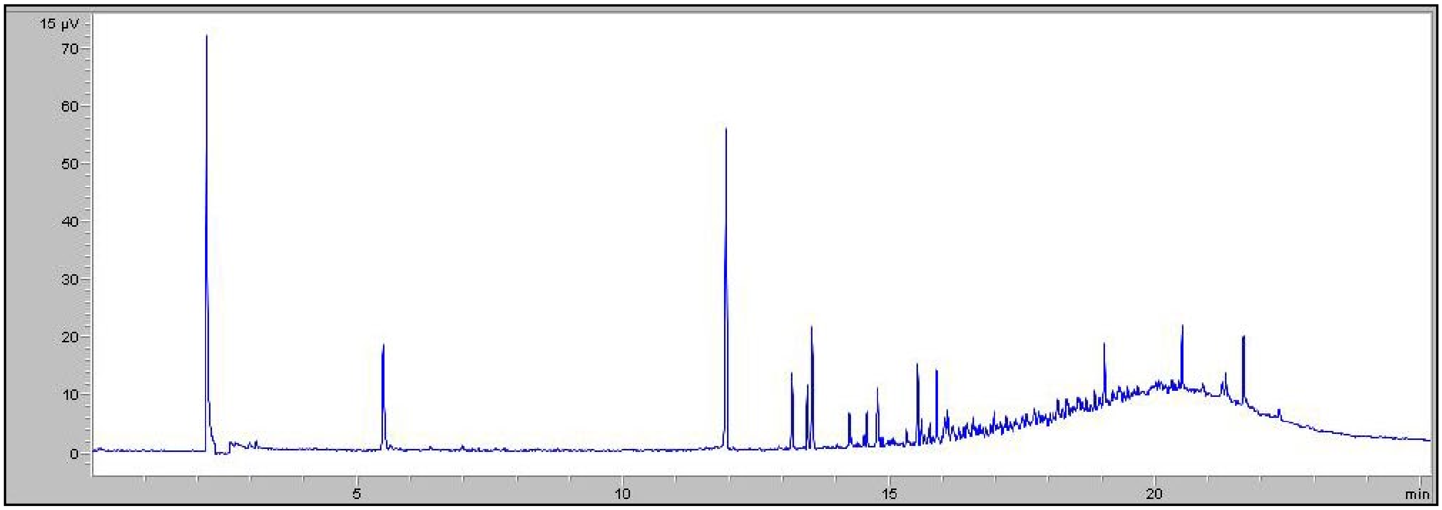

Figure 10. SS7

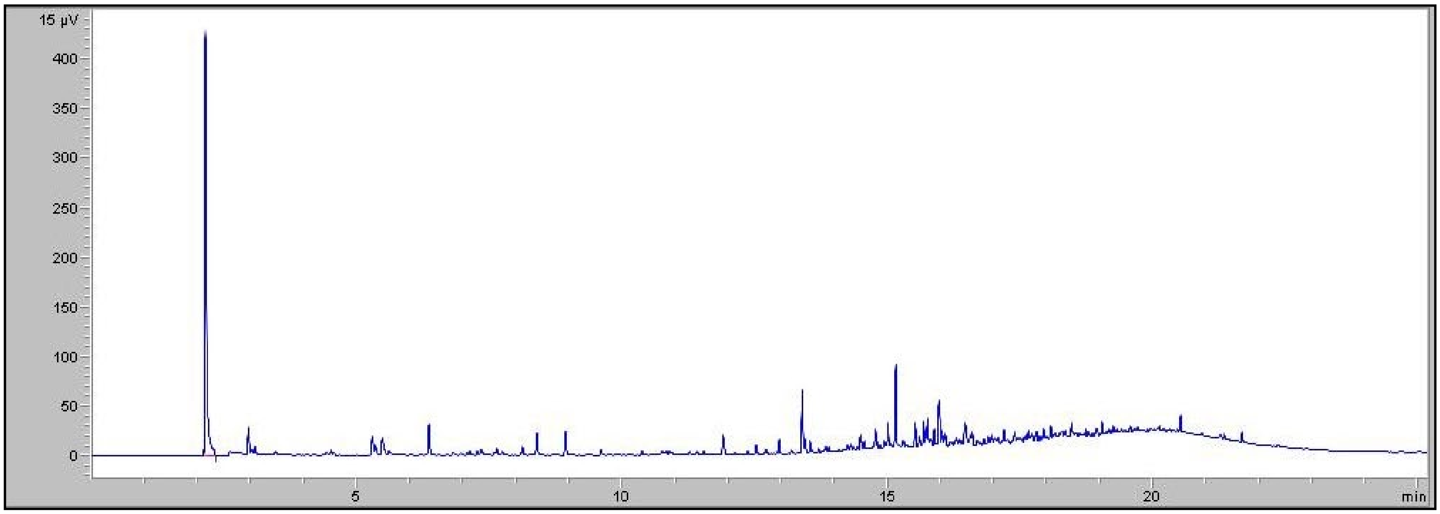

Figure 11. SS8

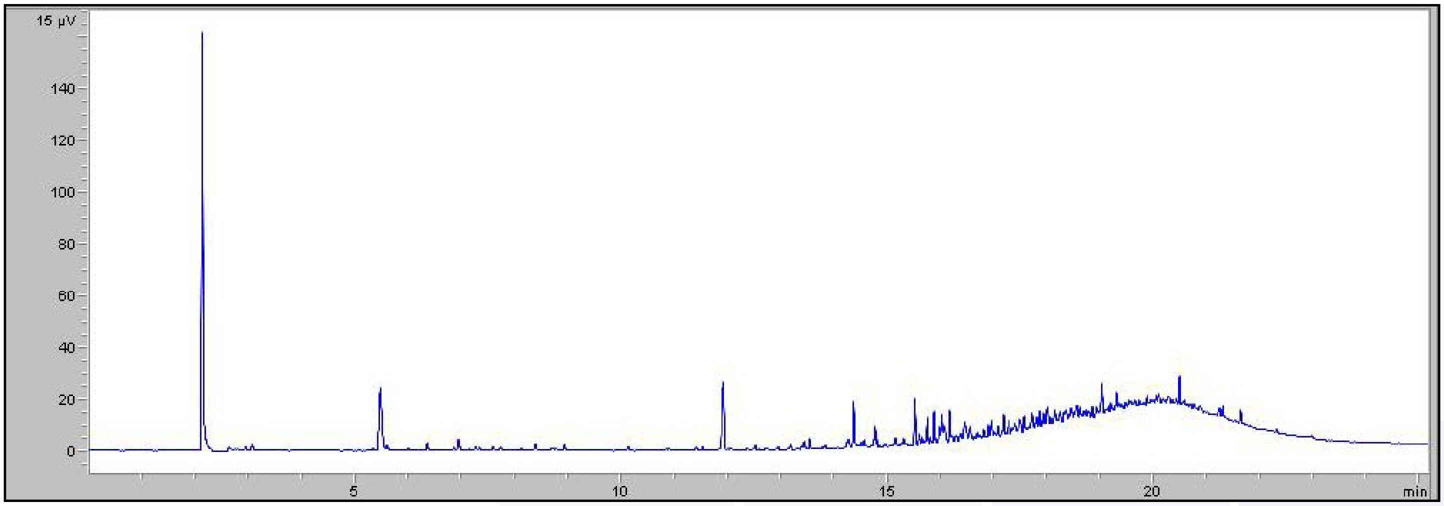

Figure 12. SS9

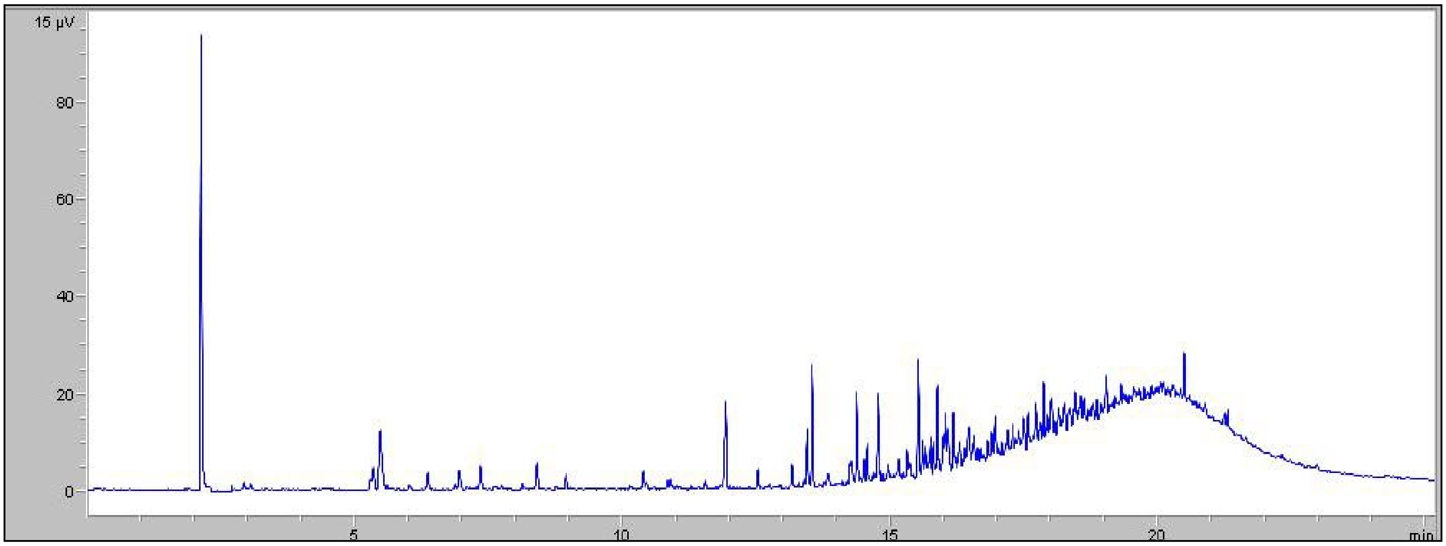

Figure 13. SS10

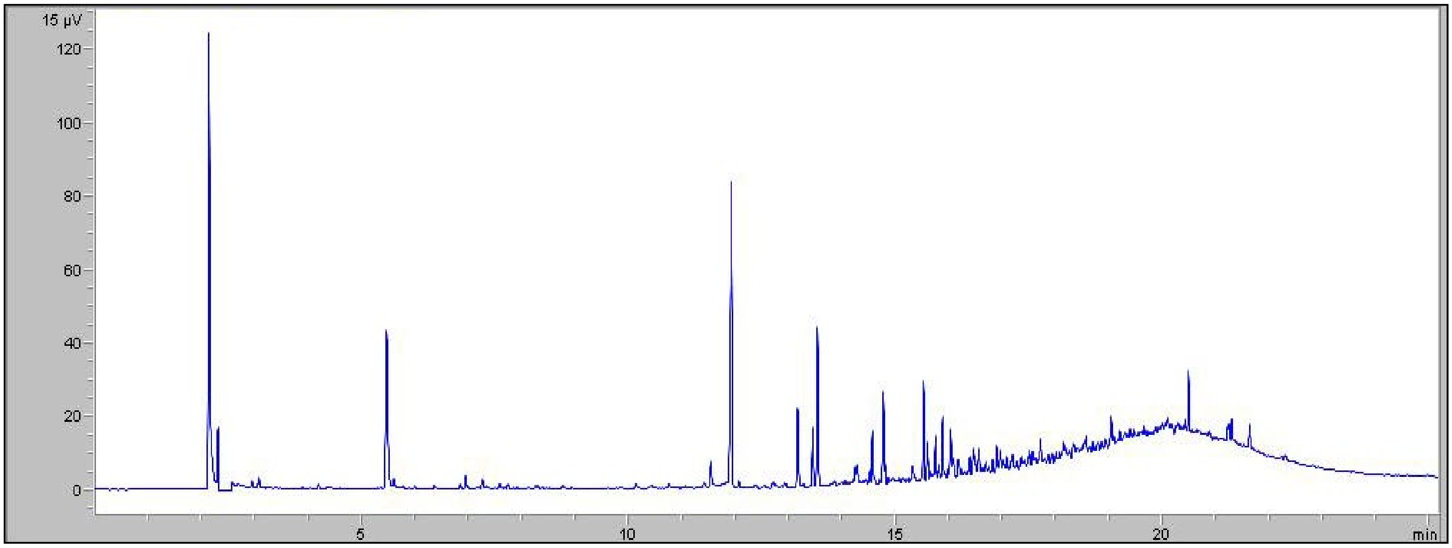

Figure 14. SS11

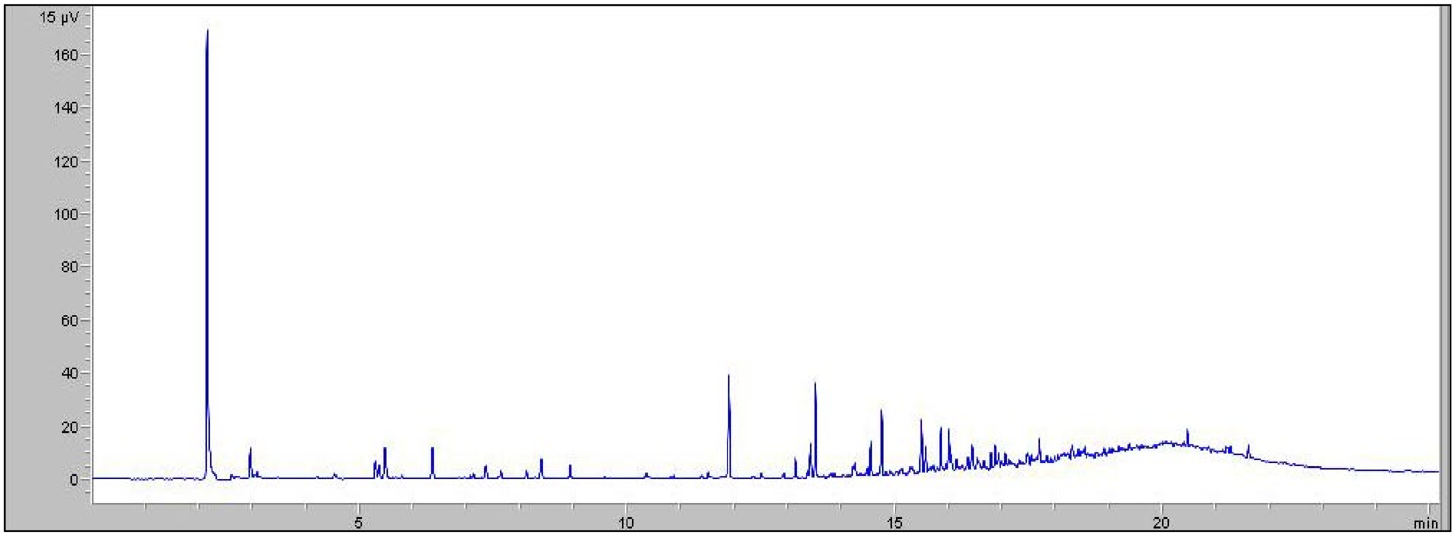

Figure 15. SS12

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Conclusions

This method is simple and robust, making it a useful tool in studying various treatments of biocrude in order to increase yields and meet sulfur requirements. The next steps will be to try to identify some of the sulfur compounds. This will be useful since different classes of sulfurs can be more difficult to remove from the product than others. One of the goals of WPI's process is to convert some percentage of the C-S bonds into C-O bonds. The PFPD is useful in monitoring the various treatments and determining what works best. More experiments will be carried out to arrive at the optimum HTL process.

Authors

Cynthia Elmore, Senior Analyst, Product Management, cynthia.elmore@xylem.com,
OI Analytical, Xylem Lab Solutions

Jakob Woodside, Associate Product Manager, jakob.woodside@xylem.com,
OI Analytical, Xylem Lab Solutions

Julian Bennett, PhD Candidate, jabennett@wpi.edu Chemical Engineering Department,
Worcester Polytechnic Institute, Worcester, MA

Aidin Panahi, PhD. Research Professor, apanahi@wpi.edu Chemical Engineering Department,
Worcester Polytechnic Institute, Worcester, MA

Michael Timko, PhD. Professor, mttimko@wpi.edu Chemical Engineering Department,
Worcester Polytechnic Institute, Worcester, MA

References

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2. LeClerc, H. O., Tompsett, G. A., Paulsen, A. D., McKenna, A. M., Niles, S. F., Reddy, C. M., ... & Timko, M. T. (2022). Hydroxyapatite catalyzed hydrothermal liquefaction transforms food waste from an environmental liability to renewable fuel. Iscience, 25(9).

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OI Analytical, a Xylem brand
1725 Brannum Lane
Yellow Springs, OH 45387

☎ +1.937.767.7241
✉ xylem-lab@xyleminc.com
🌐 oico.com

ysi.com/PFPD