31st Annual Student Symposium on Research, Scholarship, and Creative Activities

Quantitative Analysis of Olefins in Alternative Fuels Made From Conversion of Plastic Waste via GC×GC-FID

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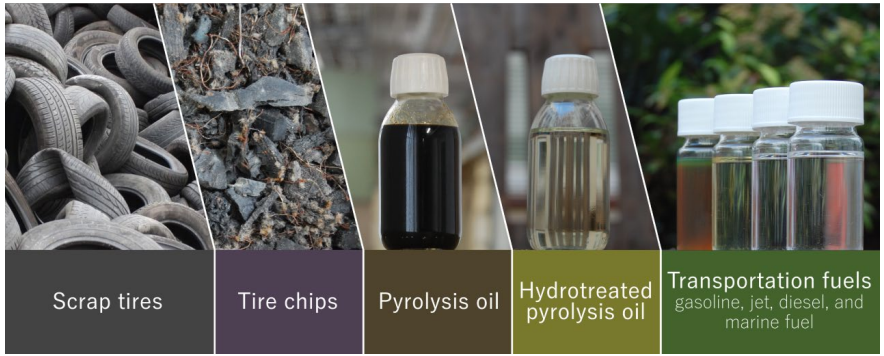
PLASTIC WASTE IN LANDFILLS

- 85% of single-use plastic waste in California is landfilled[1].
- In 2021, there were 2.3 billion units sold in the world's tire market, which amounted to 54.5 million tons of tires (2.7 billion units in 2027)[2].

CHEMICAL CONVERSION PROCESSES

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

- Pyrolysis (+ hydrotreating) of:
- plastic foils and waste tires



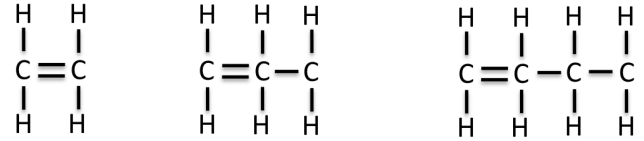
OLEFINS

ALKENES

- **Alkenes (olefins):** unsaturated hydrocarbon compounds containing at least one carbon-to-carbon double bond.
- Not commonly found in crude oils.
- Found in fuels made from conversion of plastic waste *in high concentrations.*

Alkenes C_nH_{2n}

ethene	propene	butene
C_2H_4	C_3H_6	C_4H_8

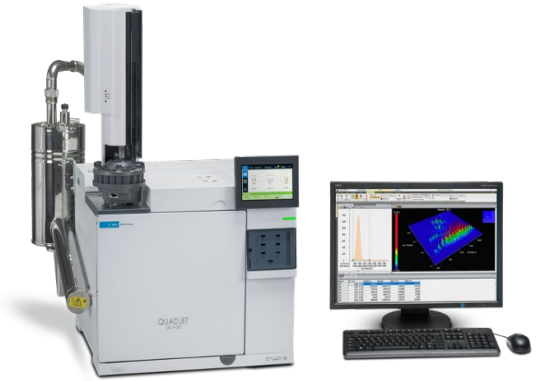


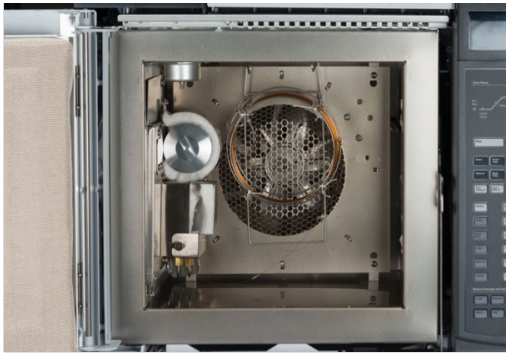
STATEMENT OF THE PROBLEM

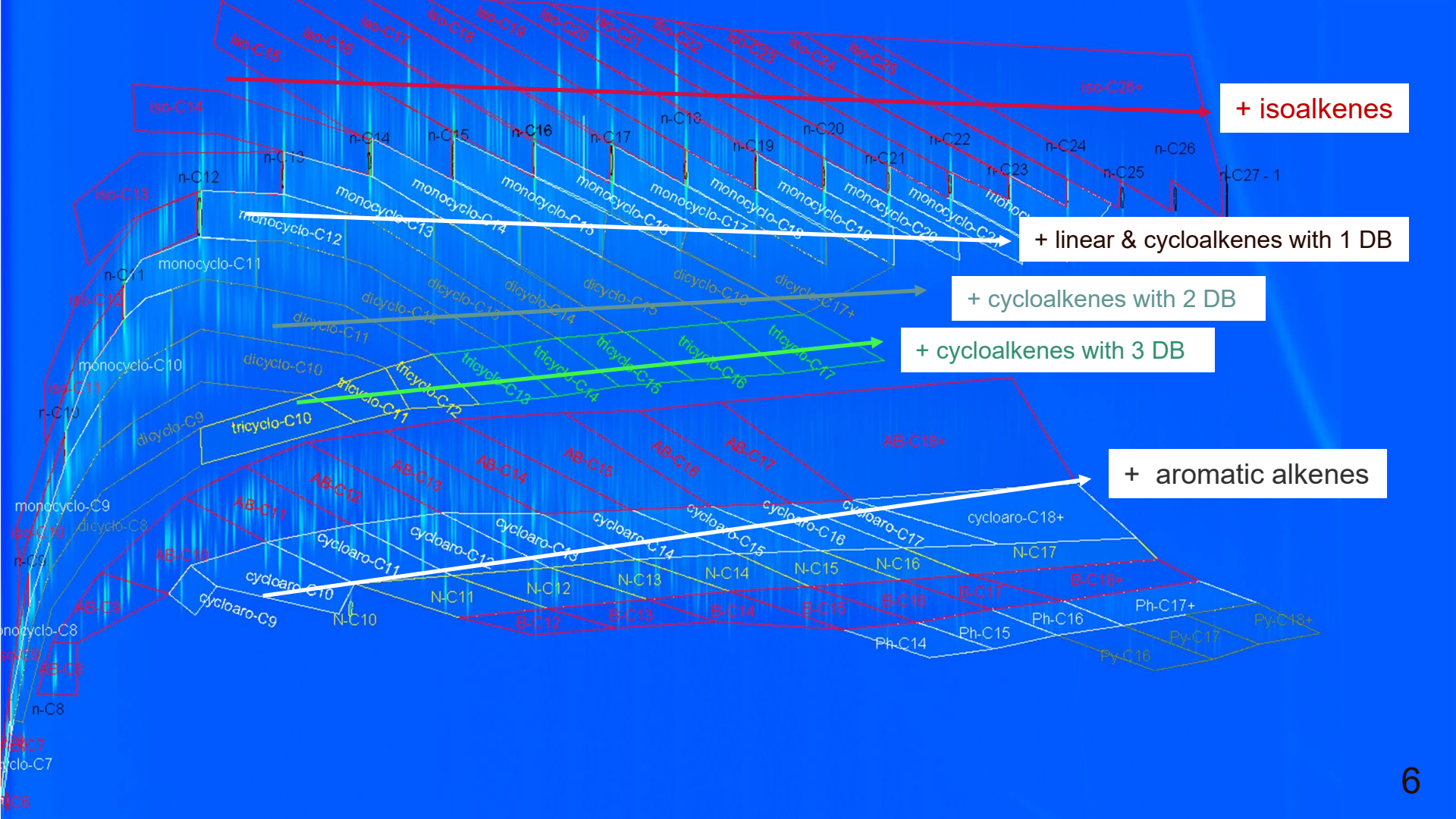
- High olefin content can be detrimental to engine cleanliness.
- Causes gum formations.
- *There are currently no methods for detailed quantitation of olefins, especially in high concentrations.*

METHODOLOGY

- Comprehensive Two-Dimensional Gas Chromatography (GC×GC)
- LECO's QuadJet GC×GC-FID with LN2 thermal modulator
- Primary (polar or mid-polar) column and the secondary (non-polar) column
- Flame ionization detector (FID)



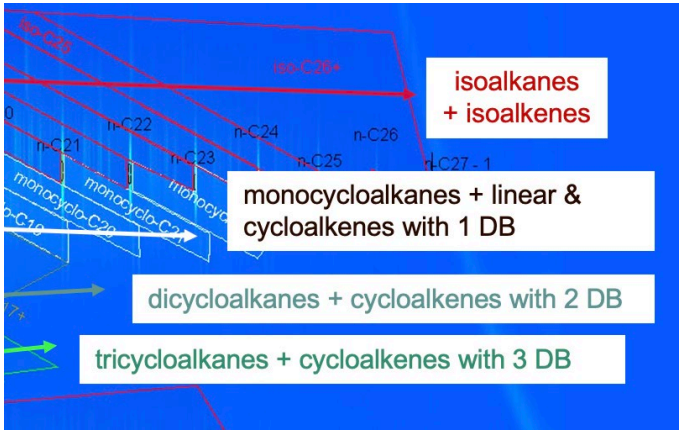



+ isoalkenes
+ linear & cycloalkenes with 1 DB
+ cycloalkenes with 2 DB
+ cycloalkenes with 3 DB
+ aromatic alkenes

CALCULATIONS

Olefins in sample

- Iso-alkenes
- Olefins with 1 double bond + Linear-alkenes
- Olefins with 2 double bonds
- Olefins with 3 double bonds



Equation

$$Wt.\%_{\,Olefin,\,C\#} = P.A._{\,Pre-Derivatization,\,C\#} - P.A._{\,Post-Derivatization\ and\ Normalization,\,C\#}$$

Example

$$Wt.\%_{\,Iso-alkene,\,C11} = P.A._{\,Pre-Derivatization,\,C11} - P.A._{\,Post-Derivatization\ and\ Normalization,\,C11}$$

SAMPLE PREPARATION

IS, DMDS, and I_2 solution

↓

70 °C oven for at least an hour

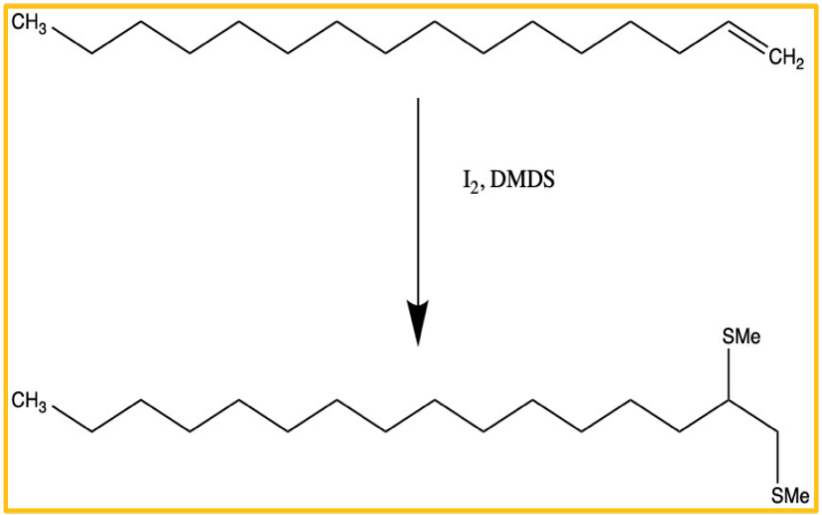
↓

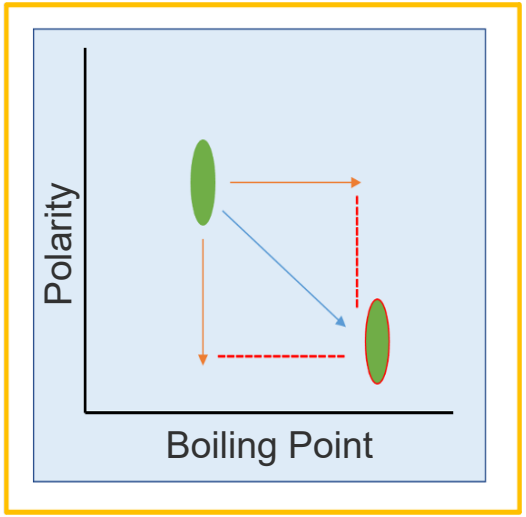
Sodium Thiosulfate

↓

Organic phase analyzed

THEORY





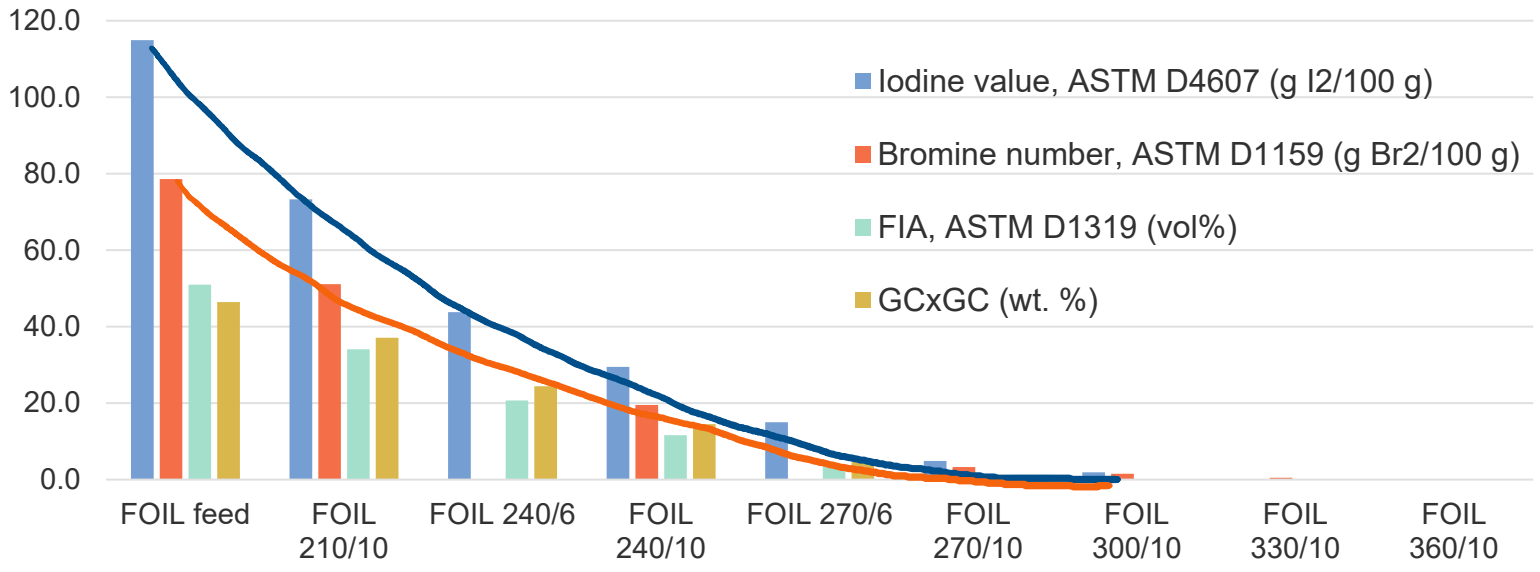
SCRAP TIRE PYROLYSIS OIL RESULTS

Before	wt. %	After	wt. %
n-alkanes	1.54	*n*-alkanes	1.54
Iso-alkanes + Iso-alkenes	0.86	Iso-alkanes	0.64
		Iso-alkenes	0.22
Monocycloalkanes + Olefins with 1 Double Bond + Linear-alkenes	4.43	Monocycloalkanes	0.96
		Linear alkenes	1.04
		Olefins with 1 Double Bond	2.43
Dicycloalkanes + Olefins with 2 Double Bonds	27.01	Dicycloalkanes	1.80
		Olefins with 2 Double Bonds	25.20
Tricycloalkanes + Olefins with 3 Double Bonds	4.60	Tricycloalkanes	1.10
		Olefins with 3 Double Bonds	3.50
Aromatics	53.66	Aromatics	53.66
Light Hydrocarbons	7.90	Light Hydrocarbons	7.90

RESULTS

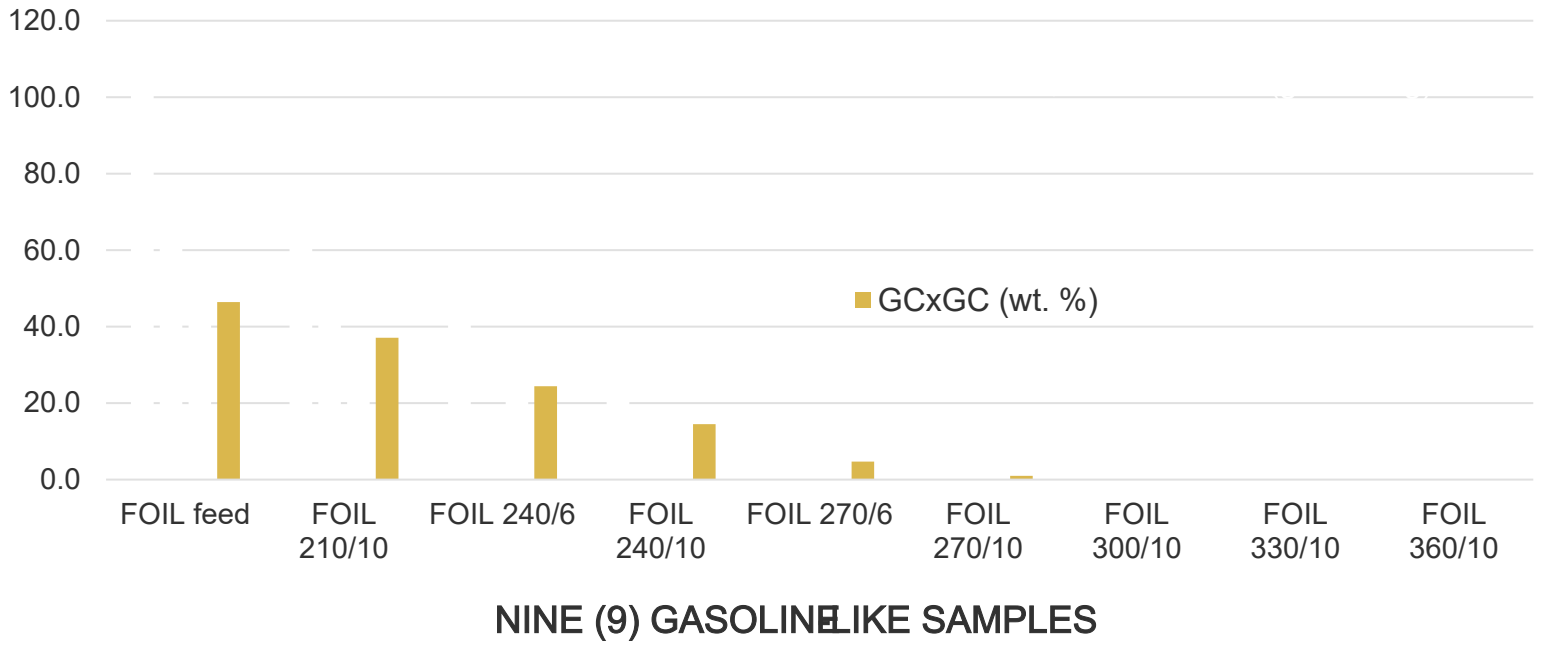
	Waste Tire Pyrolysis, Kerosene		Post Derivatization				
Monocycloalkanes	p.a.	wt. %	p.a.	After Norm. p.a.	Olefins (p.a.)	Olefin (wt. %)	Real Cyclo (wt. %)
C5	0	0.00	0	0	0	0.00	0.00
C6	0	0.00	0	0	0	0.00	0.00
C7	0	0.00	0	0	0	0.00	0.00
C8	0	0.00	0	0	0	0.00	0.00
C9	2457.75	0.46	525.59	417.13	2040.62	0.38	0.08
C10	5073.85	0.94	4278.24	3395.43	1678.42	0.31	0.63
C11	8531.58	1.59	6142.81	4875.25	3656.33	0.68	0.91
C12	3023.63	0.56	1665.03	1321.45	1702.18	0.32	0.25
C13	2498.03	0.46	1307.33	1037.56	1460.47	0.27	0.19
C14	1658.46	0.31	510.81	405.40	1253.06	0.23	0.08
C15	382.18	0.07	0	0	382.18	0.07	0.00
C16	201.36	0.04	0	0	201.36	0.04	0.00
C17	0	0.00	0	0	0	0.00	0.00
C18	0	0.00	0	0	0	0.00	0.00
C19	0	0.00	0	0	0	0.00	0.00
C20	0	0.00	0	0	0	0.00	0.00
Total	**23826.84**	**4.43**	**14429.81**	**11452.23**	**12374.61**	**2.30**	**2.13**

VALIDATION (COMPARED TO OTHER ASTM METHODS)



NINE (9) GASOLINE-LIKE SAMPLES

VALIDATION (COMPARED TO OTHER ASTM METHODS)



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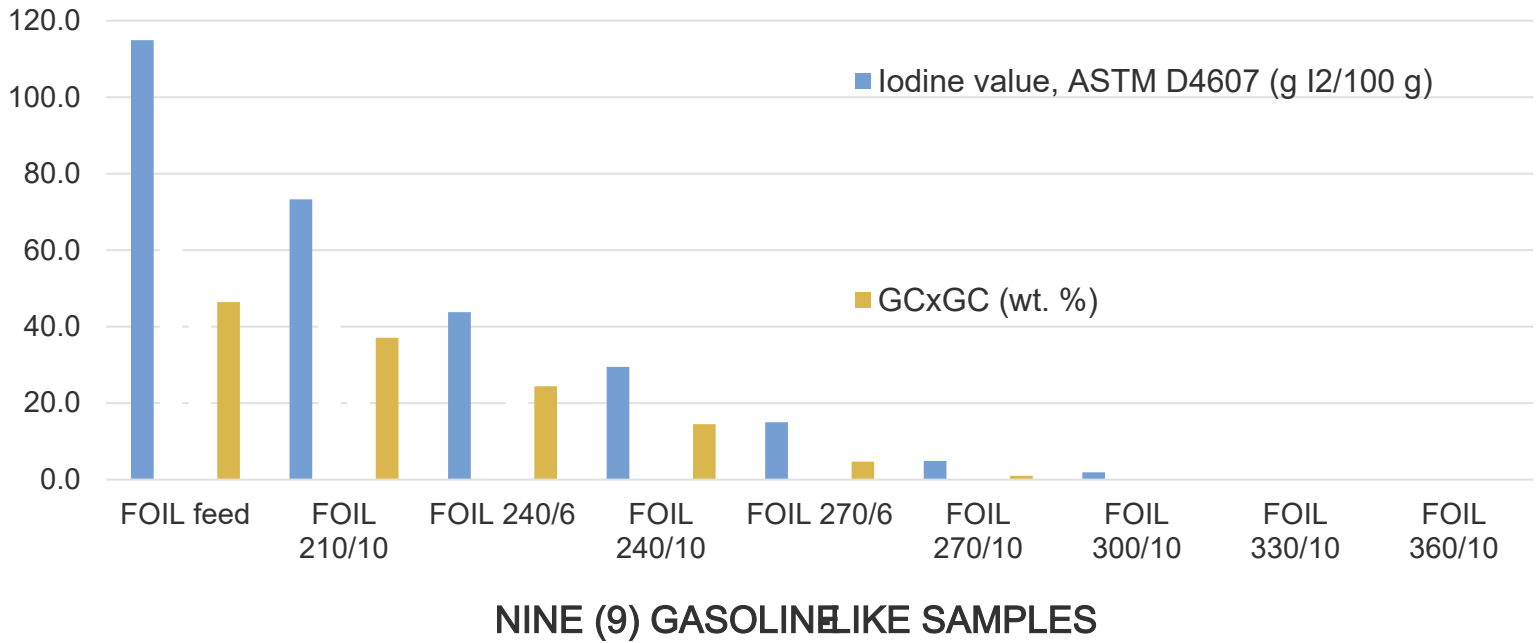

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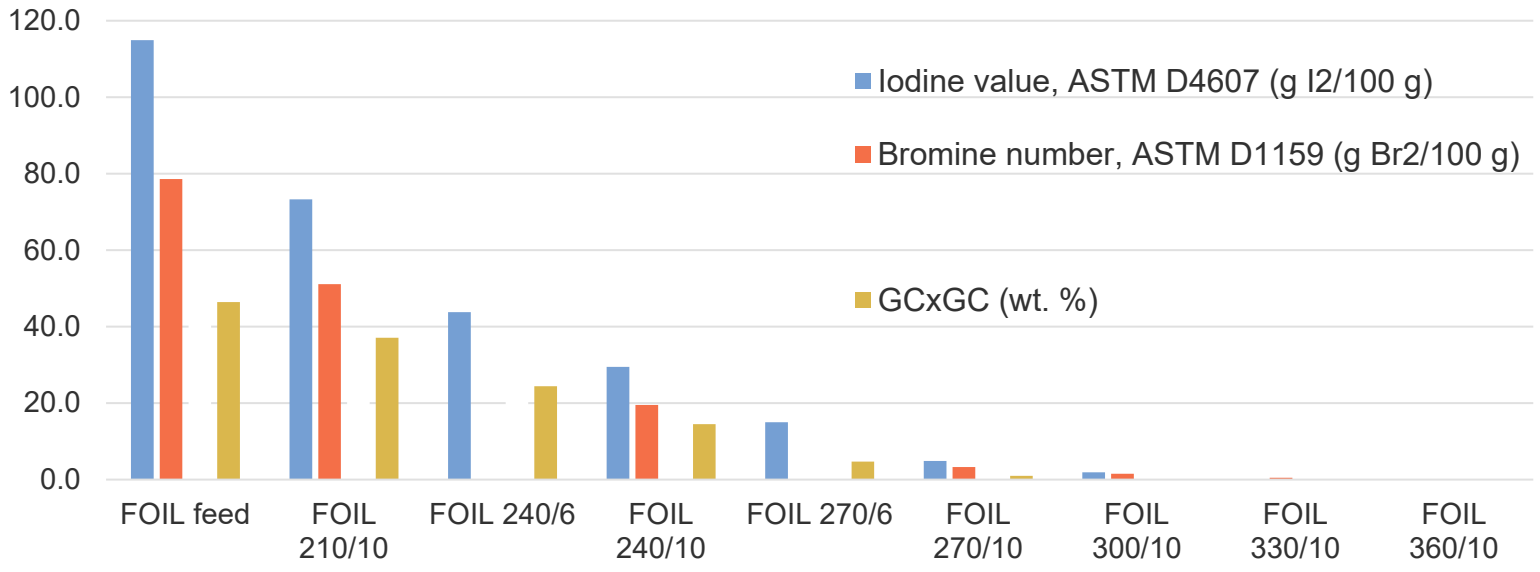

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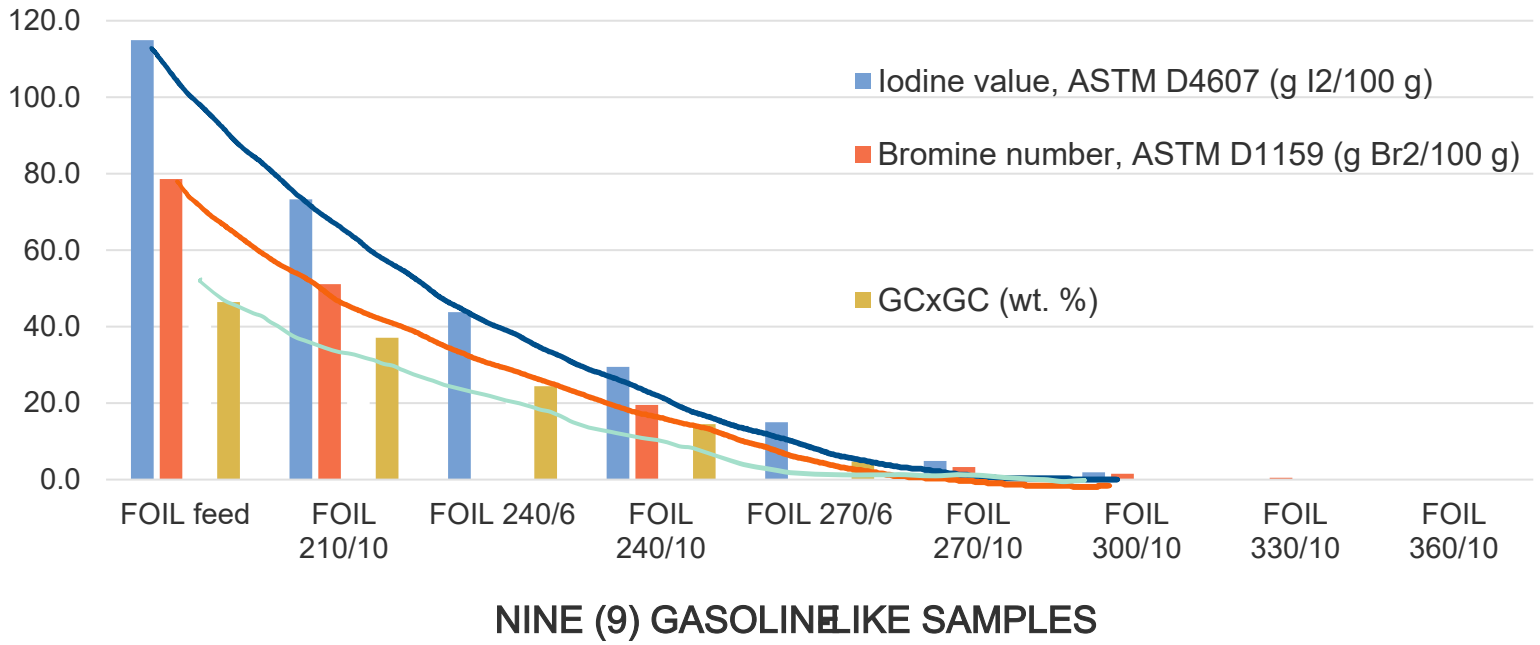

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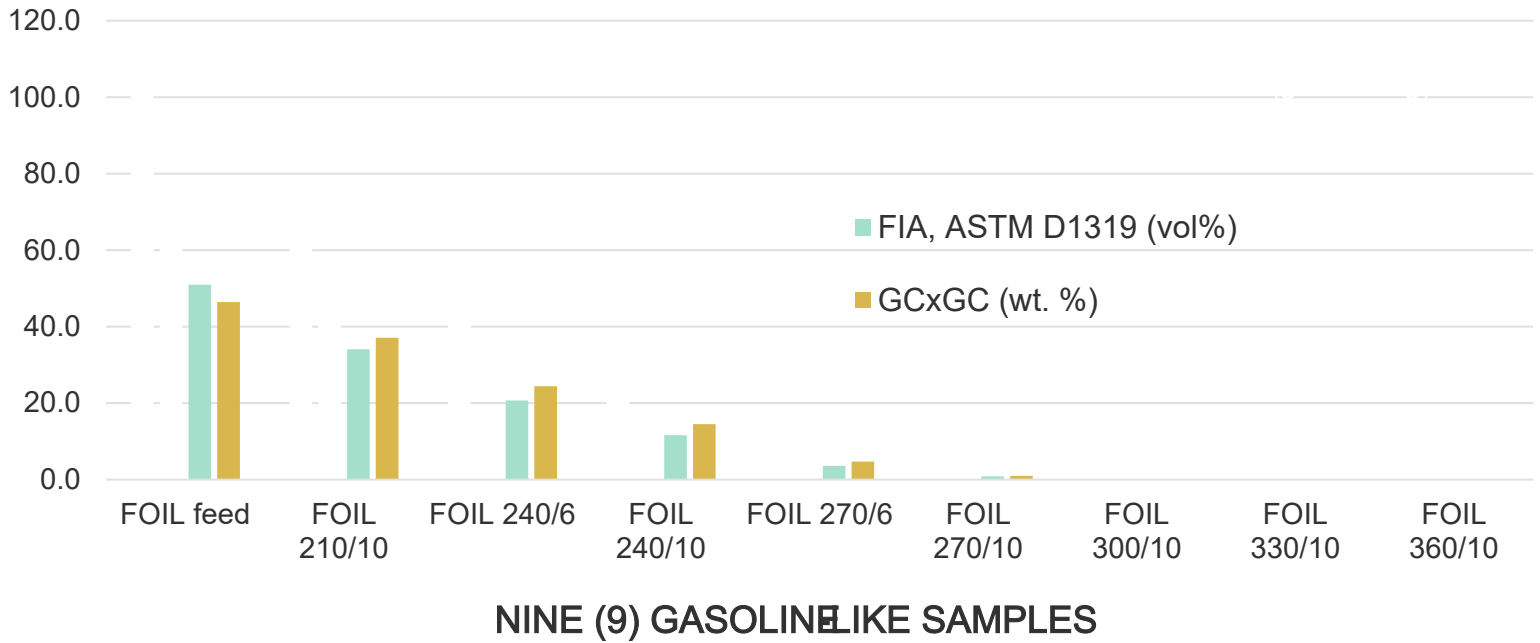

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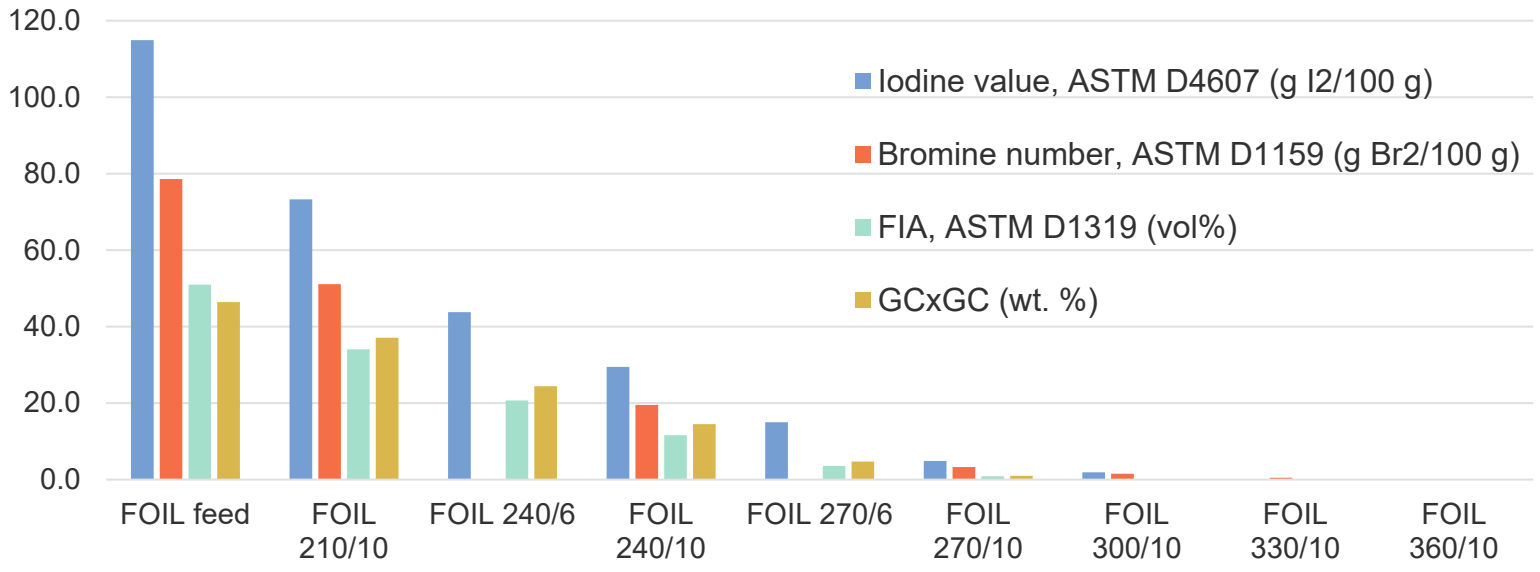

NINE (9) GASOLINE-LIKE SAMPLES

CONCLUSION AND FUTURE WORK

- We introduced a possible method for olefin quantitation in complex fuel samples in a broad distillation range especially from fuel products from plastic waste conversion.
- Validate the results using GC×GC with time-of-flight mass spectrometry (TOFMS)

Pegasus BT 4D GC×GCTOFMS

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