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Comprehensive Two-Dimensional Gas Chromatography Method Development for the Pyrolysis of Polypropylene

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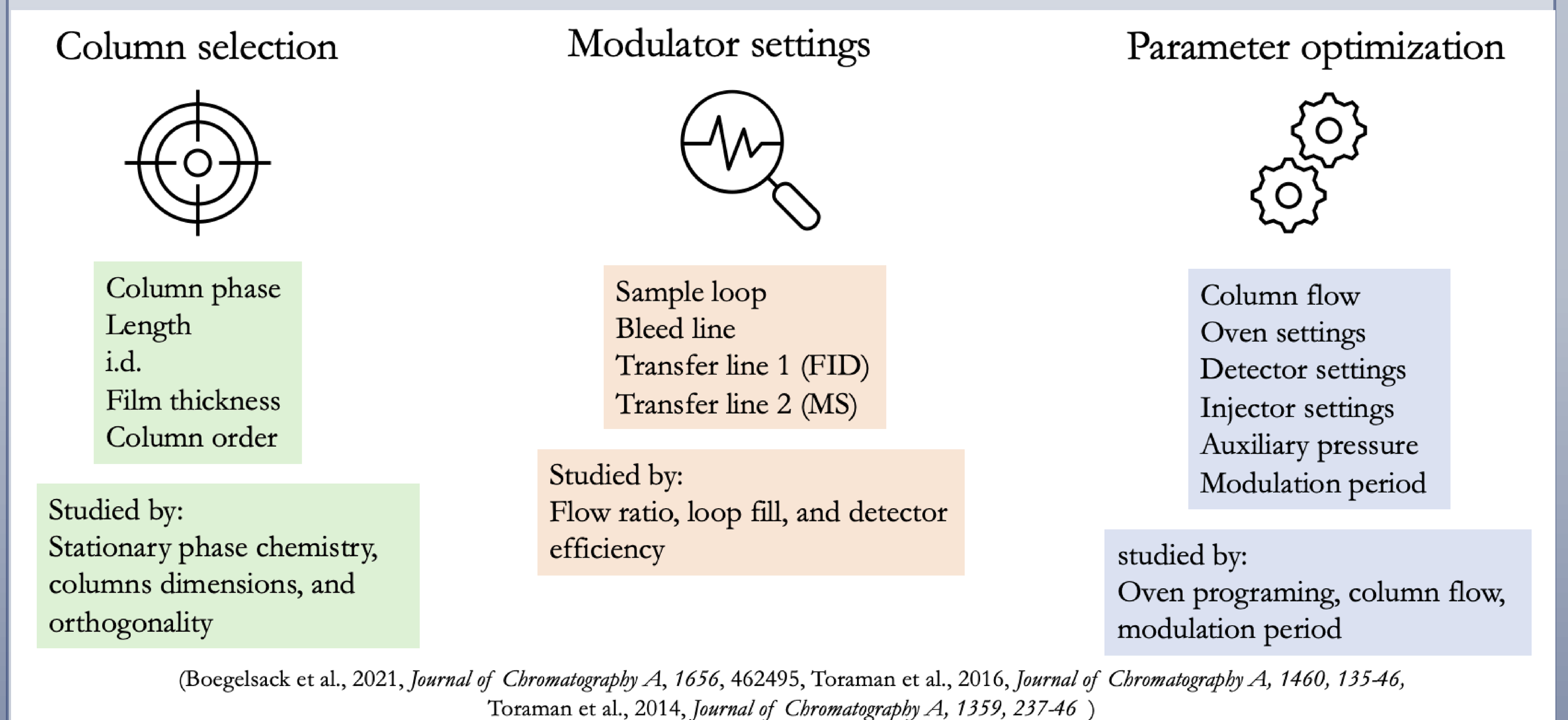
INTRODUCTION

PP is a polyolefin prepared by the addition polymerization reaction of propylene. It has been widely used due to its excellent chemical resistance, temperature resistance, and low cost. In fact, PP was the most produced polymer in 2015 [1]. Regarding PP waste, the U.S. produced 8,150 thousand tons of PP waste in 2018. However, 0.6% of PP waste was recycled [2].

Due to the low recycling rates, recycling methods need to be studied to complement mechanical recycling. Pyrolysis is considered as a promising method for the recycling of polymers. Pyrolysis is defined as the thermal or catalytic degradation of plastic waste in an inert atmosphere at moderate temperatures (300°C – 700°C) for the production of gas, oil, waxes, and char. Pyrolysis reactors have been coupled to different instruments to further characterize the pyrolysis products. Currently, pyrolysis systems have been coupled to gas chromatography with a mass spectrometer (MS) or flame ionization detector (FID) and FTIR [3]. However, these instruments cannot allow the separation of the pyrolysates due to the similarities in the polarity and boiling point, leading to a poor resolution. For this reason, comprehensive two-dimensional gas chromatography (GCxGC) has been proposed to determine the product distribution for the pyrolysis of PP. GCxGC is a technique that improves the resolution of the analytes by using two column combinations [4].



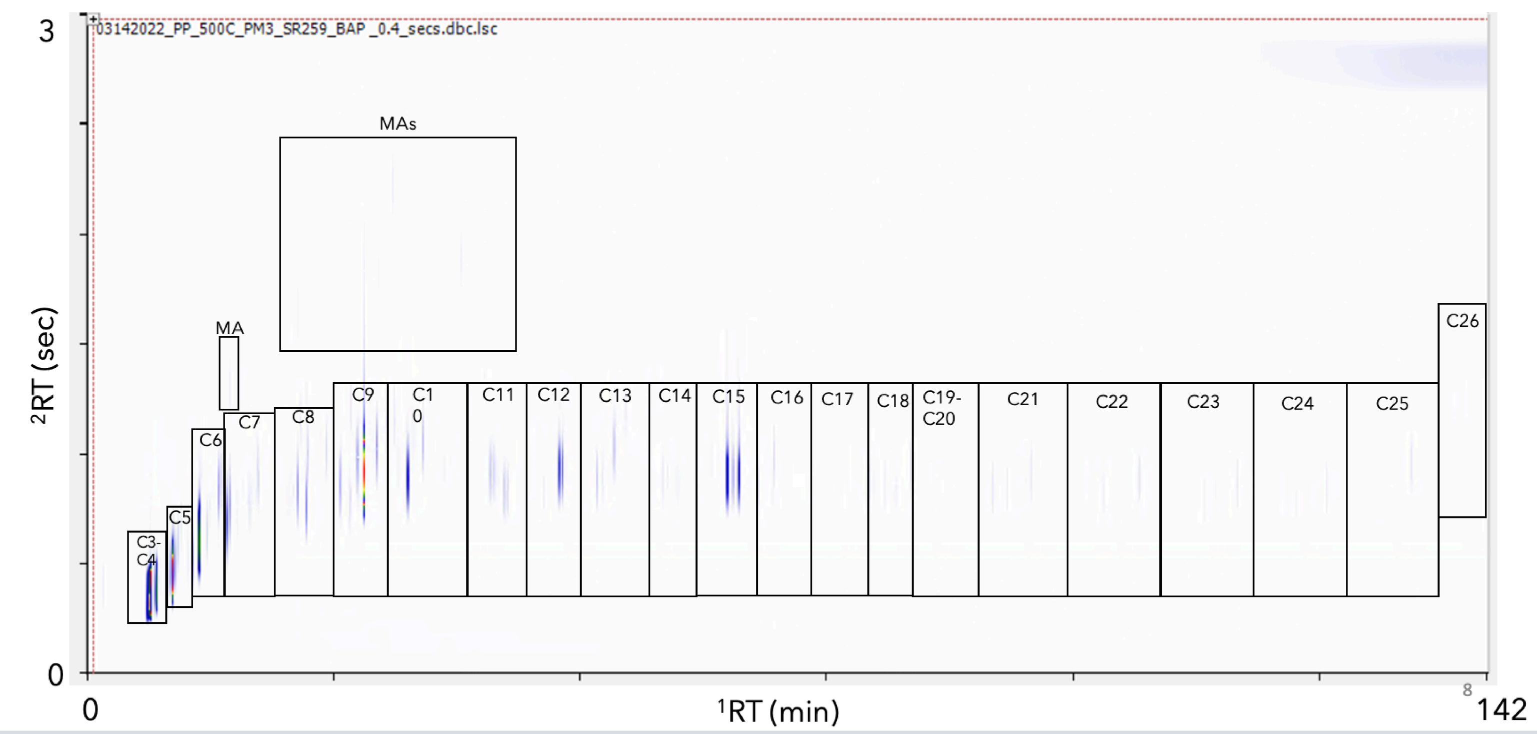
Method development for GCxGC [5]-[7]

OBJECTIVES

- Study the method development for the pyrolysis of PP using GCxGC.
- Evaluate the performance descriptors.
- Determine the product distribution for the pyrolysis of PP at 500°C.

RESULTS

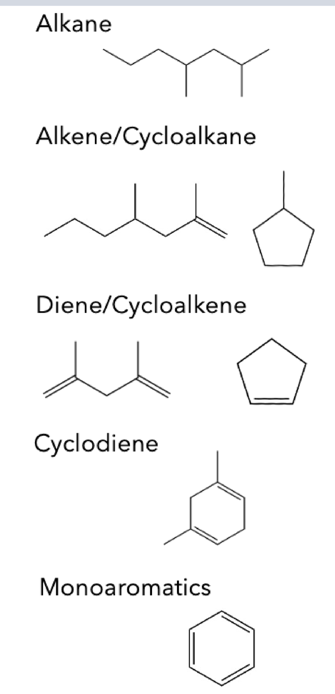
- The modulation period and oven program were evaluated for the method development. A modulation period of 3 seconds and an oven ramp of 2°C min^{-1} maximized the peaks that have a resolution higher than 1.
- The shape of the peaks was evaluated using the tailing and symmetry factors. The shape of the contour peaks was improved by using a modulation period of 3 seconds and an oven ramp of 2°C min^{-1}.



Contour plot for the pyrolysis of PP at 500°C

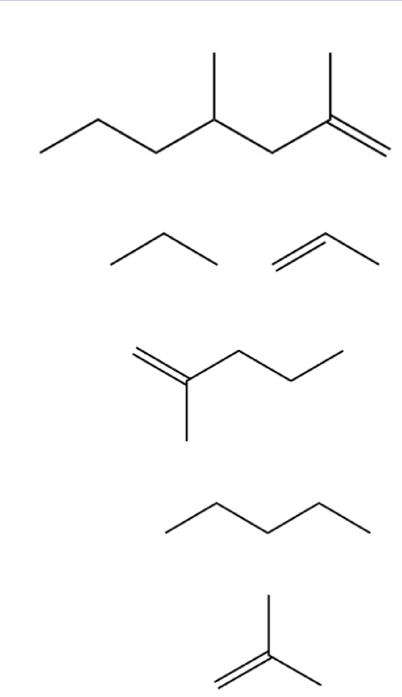
Product distribution for the pyrolysis of PP at 500°C

# carbon	Alkane/ Alkene	Alkane	Alkene / Cycloalkane	Diene / Cycloalkene	Cyclodiene	MA
C3	9.63					
C4		0.22	2.7			
C5		7.19	1.77	0.68		
C6		1.04	6.93	1.25	0.04	0.10
C7		0.07	1.63	1.60	0.02	0.09
C8		1.02	1.33	0.92	0.01	0.21
C9		0.21	**40.66**	0.82	0.03	0.09
C10		0.27	2.03	0.76	0.02	
C11		0.26	0.97			
C12		1.30	0.08			
C13			0.55	0.55		
C14		0.06	0.30			
C15		0.02	5.06			
C16-C26		0.22	0.81	0.52		
Total Area %	**9.63**	**11.87**	**64.82**	**7.09**	**0.11**	**0.50**

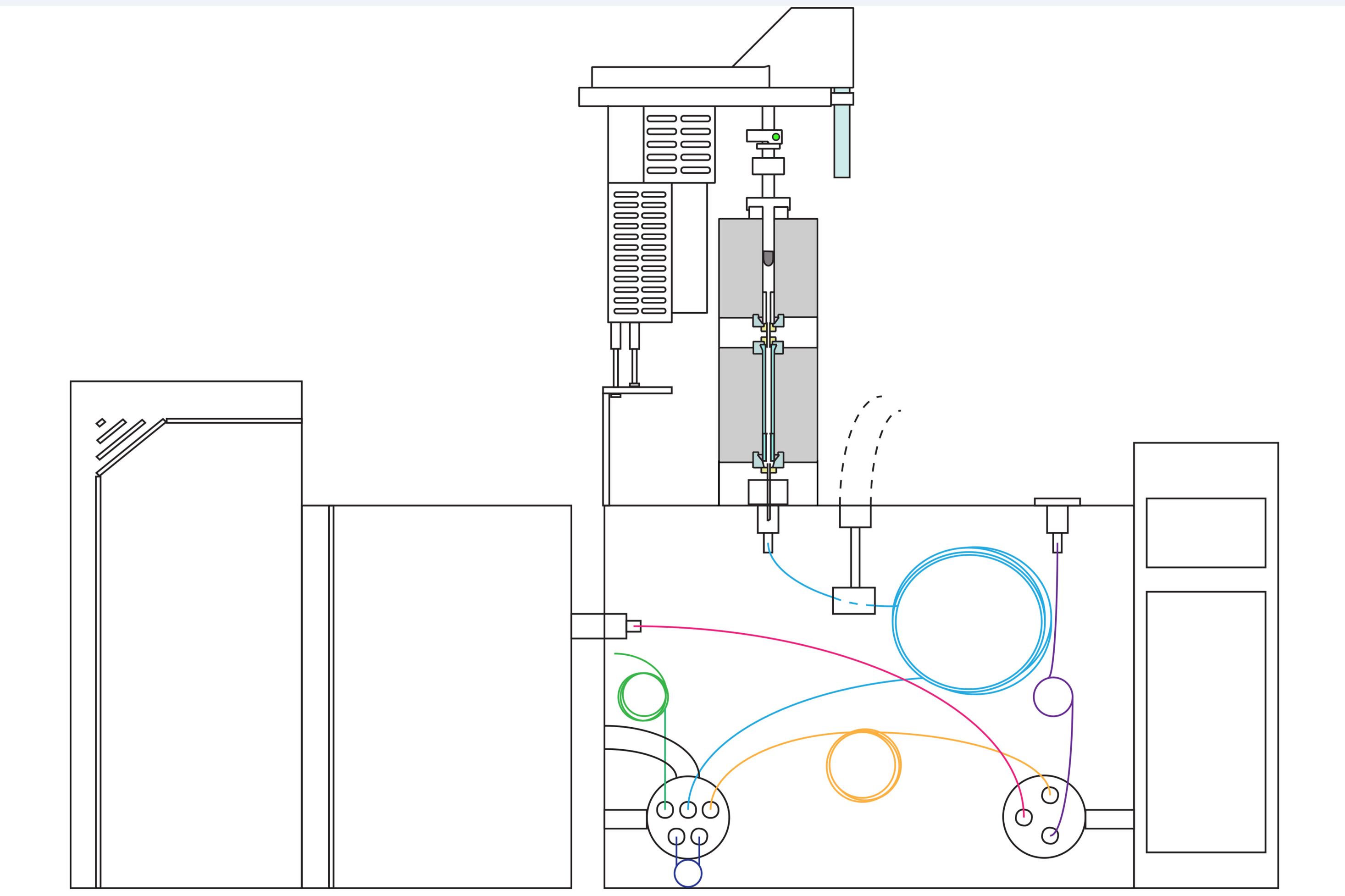


Main products identified for the pyrolysis of PP at 500°C

- 2,4-Dimethyl-1-heptane (C9H18): 38.06%
- Propane/propene (C3H8/C3H6): 9.63%
- 1-Pentene, 2-methyl- (C6H12): 6.45%
- Pentane (C5H12): 6.24%
- 1-Propene, 2-methyl- (C4H8): 2.64%



MATERIALS AND METHODS



Scheme of GCxGC coupled to FID and MS

CONCLUSIONS

- The GCxGC method development for the pyrolysis of PP was investigated by comparing modulation periods and oven ramps.
- A modulation period of 3 seconds and an oven ramp of 2°C min^{-1} optimized the method development for the pyrolysis of PP.
- The pyrolysis of PP led to the production of alkanes, alkenes, dienes, cyclic hydrocarbons, and monoaromatics.

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