

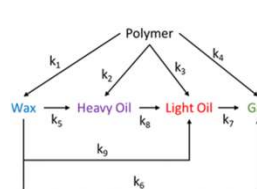
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## Fast Pyrolysis Kinetics of Post-Consumer HDPE: Investigating the Effect of Vapor Residence Time (VRT) on Reaction Products

### FAST PYROLYSIS OF POLYOLEFINS

- Goal:** Describe the yields of major products (wax, oil, non-condensable gas) of fast pyrolysis of waste polyolefin plastics as a function of heated vapor residence time (VRT)
- Background:** A low pyrolysis temperature (400-500 °C) and short VRT (<1 s) favors waxes, and a high pyrolysis temperature (>700 °C) and short vapor residence time favors gas [1]
- Hypothesis:** For fast pyrolysis of HDPE at 500 °C-600 °C, waxes will crack to oil, then gas, as VRT is extended

### APPROACH TO MODELING, EXPERIMENTS



#### Reaction Network

- The reaction network for the kinetic model was adapted from Kulas et al. [2]
- A system of ordinary differential equations (ODEs) was proposed

#### System of Equations

$$\frac{dM_P}{dt} = -k_1 M_P - k_2 M_P - k_3 M_P - k_4 M_P \quad \text{I.C. } M_P(t=0) = M_{P0}$$

$$u \frac{dC_W}{dx} = -k_5 C_W - k_6 C_W - k_9 C_W$$

$$u \frac{dC_H}{dx} = k_5 C_W - k_8 C_H$$

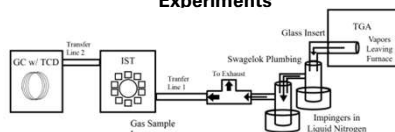
$$u \frac{dC_L}{dx} = k_9 C_W + k_8 C_H - k_7 C_L$$

$$u \frac{dC_G}{dx} = k_6 C_W + k_7 C_L - k_{10} C_G$$

- These equations can be solved analytically, and the rate constants can be determined based on independent physical relationships and iteration on experimental data

$$\text{B.C. } C_i(x=0, t) = \frac{k_i M_{P0} e^{-\frac{t}{\tau_P}}}{Q}$$

#### Experiments

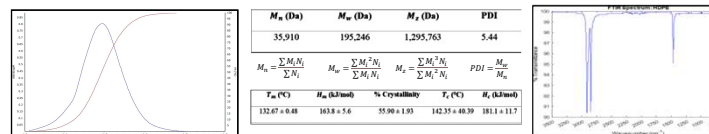


- Thermogravimetric analyzer (TGA) modified with condenser train and gas sampling system was used
- Varied heated vapor residence time by changing total gas flow rate; devolatilization time/rate remained constant
- Allowed non-condensable gases to be sampled, injected onto GC instrument with thermal conductivity detector (TCD)
- Collected condensable products, then quantified mass of light oil, heavy oil based on GC-Polyarc-FID

### RESULTS

#### Feedstock Characterization

- The HDPE that was pyrolyzed was characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

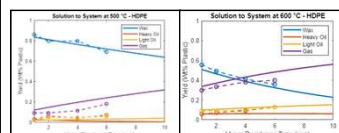


#### Apparent Activation Energies for Reaction Network

- The Arrhenius law was used with the apparent rate constants at different temperatures

Ea1 (kJ/mol)	Ea2 (kJ/mol)	Ea3 (kJ/mol)	Ea4 (kJ/mol)	Ea5 (kJ/mol)	Ea6 (kJ/mol)	Ea7 (kJ/mol)	Ea8 (kJ/mol)	Ea9 (kJ/mol)
$1.54 \times 10^2$	$2.25 \times 10^2$	$3.69 \times 10^2$	$1.77 \times 10^2$	$1.42 \times 10^1$	$1.42 \times 10^1$	$3.77 \times 10^2$	$1.51 \times 10^2$	$1.42 \times 10^1$
A1 (s <sup>-1</sup> )	A2 (s <sup>-1</sup> )	A3 (s <sup>-1</sup> )	A4 (s <sup>-1</sup> )	A5 (s <sup>-1</sup> )	A6 (s <sup>-1</sup> )	A7 (s <sup>-1</sup> )	A8 (s <sup>-1</sup> )	A9 (s <sup>-1</sup> )
$1.88 \times 10^5$	$1.63 \times 10^7$	$3.27 \times 10^{12}$	$6.37 \times 10^5$	$3.61 \times 10^4$	$7.23 \times 10^1$	$1.95 \times 10^{12}$	$9.14 \times 10^4$	$7.23 \times 10^5$

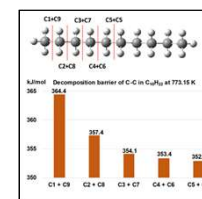
#### Projections Using Kinetic Model



Gas yield consistently increases with VRT, oil yield does not exceed 25%

Do not observe maxima in oil yields for fast pyrolysis; model would predict them if they were present!

However, this is not unexpected based on density functional theory (DFT) calculations of how cracking of a model compound, n-decane, would proceed [3]



### DISCUSSION

Kulas et al. had reported a lower wax yield, and a relatively constant NCG yield for HDPE pyrolysis at 600 °C with increasing VRT. They also reported oil yields greater than 25%. In contrast, we observe that as the heated vapor residence time is extended, we produce smaller waxes and more non-condensable gases as products. We hypothesized that this was due to cracking proceeding via an end-chain scission mechanism, which was supported by DFT calculations by our colleagues.

### CONCLUSIONS

We developed a global kinetic model for the fast pyrolysis of polyolefin plastics; and we also developed a procedure for implementing the model using experimental data. In the future, we would like to model the products of the direct oxidation of polyolefins as a function of oxygen concentration and vapor residence time.

### REFERENCES

- [1] Lopez, G.; et al. Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review. Renewable and Sustainable Energy Reviews. 2017, 73, 346-368. DOI: 10.1016/j.rser.2017.01.142
- [2] D.G. Kulas; et al. Micropyrolysis of Polyethylene and Polypropylene Prior to Bioconversion. ACS Sustainable Chem. Eng. 2021, 9, 43, 14443-14450. DOI: 10.1021/acscuschemeng.1c04705
- [3] Li, H.; et al. Hydroformylation of pyrolysis oils to aldehydes and alcohols from polyolefin waste. Science. 2023, 381, 6658, 660-666. DOI: 10.1126/science.adh1853