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CUWP
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Non-Isothermal Devolatilization Kinetics of Post-Consumer Plastics Under Oxidative Conditions

Saad Aftab and Robert C. Brown

Goals

- To obtain information regarding devolatilization kinetics which can then be used to inform hypothesis-based tests
- To highlight an advantage of "thermal oxo-degradation"
- To create a database to facilitate straightforward comparisons

Background

- Research efforts in the "thermal oxo-degradation" of plastics are inspired by the success story of the "autothermal pyrolysis" of biomass [1]

Methodology

- The plastic feedstocks which used for the study were cryogenically milled to minimize particle size, thereby both allowing for the precise weighing of samples, providing a higher specific surface area, and increasing sample homogeneity
- Non-isothermal TGA tests were performed at many different heating rates to evaluate the oxidative devolatilization of the "thin films" formed by the melted powders
- MATLAB scripts were written to automate calculations based on the data sets
  - Calculations were performed based on the Kissinger-Akahira-Sunose (KAS) method (involving linear regressions) and the Vyazovkin method (involving nonlinear optimization) – both yield similar values

See Ref. 3

$$g(\alpha) = \int_0^{\alpha} \frac{1}{f(\alpha)} d\alpha \qquad \textbf{Note: } f(\alpha) \textit{ is the reaction model}$$

$$g(\alpha) = \frac{1}{\beta} \int_0^{T} A e^{-Ea/RT}\, dT$$

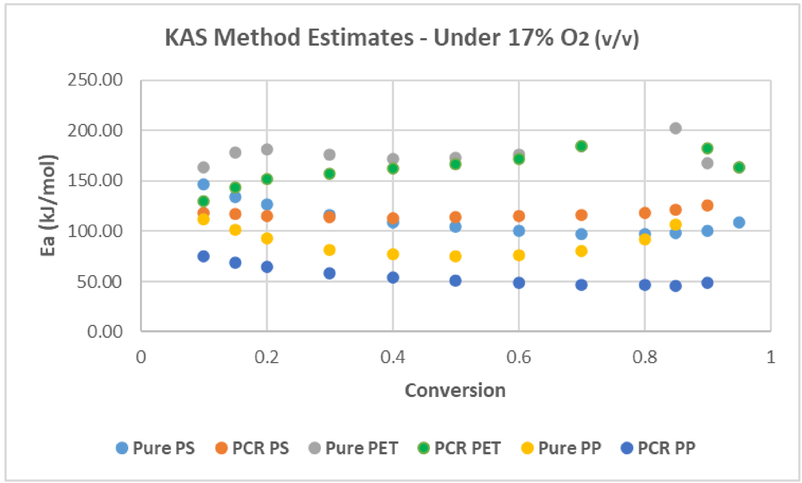
$$g(\alpha) = \frac{A}{\beta}\frac{Ea}{R} \int_x^{-\infty} \frac{1}{x^2} e^{-x}\, dx$$

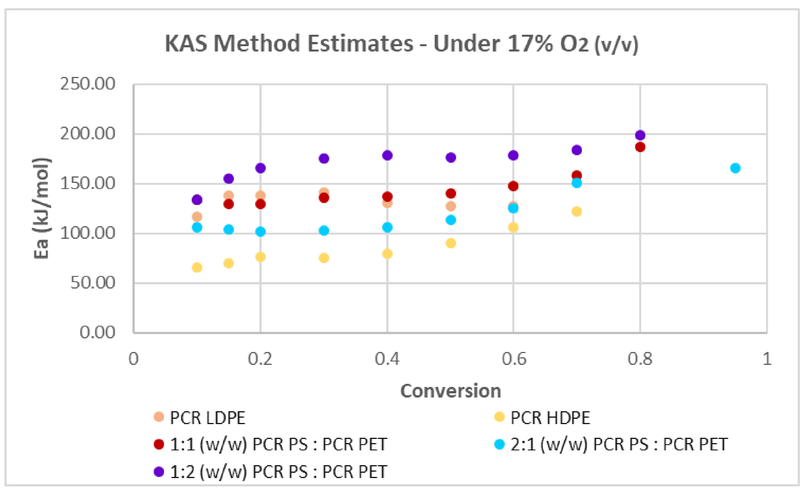
$$g(\alpha) = \frac{A}{\beta}\frac{Ea}{R} Ei(x)$$

$$g(\alpha) = \frac{A}{\beta}\frac{Ea}{R} * \frac{-e^{-x}}{x}\left(1 - \frac{2}{x}\right)$$

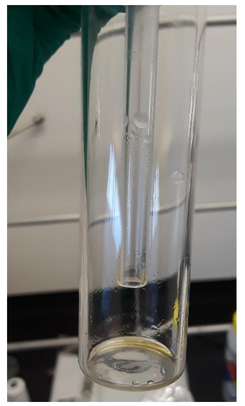
$$ln\left(\frac{\beta}{T^2}\right) = ln\left[\frac{AR}{g(\alpha)Ea}\right] - \frac{Ea}{RT} \qquad \textit{KAS Equation}$$

Preliminary Results





- The activation energies were slightly lower for the post-consumer versions of the plastics; suggesting that they did not contain additives which would inhibit the oxidation process
- The activation energies for the binary mixtures appear to be weighted averages of the activation energies of the single components
- The activation energy for post-consumer polystyrene was relatively constant with conversion compared to the other feedstocks



Oil produced from the oxidation of post-consumer polystyrene in a TGA

- Complete combustion was not observed in the TGA when these feedstocks were then degraded using this oxygen concentration at 500 °C

Summary of Results

- Activation energies were relatively constant with conversion with the exception of PET
- Pure polymers and post-consumer plastics from the corresponding polymers had similar activation energies with the exception of polypropylene

Conclusions

- The energies are lower than those reported for conventional pyrolysis
- The effect of varying the oxygen concentration needs to be investigated

Acknowledgements

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References

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