

Supercritical Water – Actions and Reactions During the Thermal Decomposition of Plastics

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Significance and Relevance

As the demand for sustainable solutions increases, particularly in the context of climate change, there is a growing need to optimize resource utilization and develop effective pathways for upcycling existing biomass and end-of-life mixed plastic waste to fuels and chemicals. This discussion focuses on the potential of near- and supercritical water for these conversions, which are currently being introduced at scale around the globe.

New work based on model compounds will be used to better describe the multiple modes of action of water and explain why the formation of coke is highly suppressed when using this approach as compared to pyrolysis.

Preferred and 2nd choice for the topic:

(1) Circular Economy; (2) Green Chem. and Biomass Transformation, Renew. Resources Transformation Preferred presentation: Oral only

Introduction and Motivations

Near- and supercritical water as a solvent dramatically improves the process of pyrolysis for the decomposition of plastics.¹ One of the major advantages is how supercritical water is able to suppress the formation of unwanted chars when compared to pyrolysis.¹ A major factor behind this is the action of water as a solvent or plasticizer; preventing the bimolecular reactions that give rise to larger molecules that form char.¹ But water is not an inert species – it is suspected of acting as a reactant (particularly described as a hydrogen donor) in this process, the pathways of which have yet to be investigated fully.² This research will expand upon the roles of water in this process as a reactant, to further our understanding of the pathways present in the HTL environment.

Results and Discussion

Does water react itself as a radical during the hydrothermal decomposition of polymers? There is conflicting evidence present in the literature as to the source of oxygenated compounds formed in this reaction. Oxygenates could be formed from water acting as a reactant or it could be formed from oxygen or air present in the reactor at the time of conducting the reaction. Using 1-dodecene as a model compound, we have investigated this further. When 1-dodecene is reacted under either pyrolysis or supercritical water conditions with an atmosphere of air inside the reactor, the organic phase consists predominantly of hydrocarbon species. However, several oxygenated species (e.g. methanol and other alcohols) can be detected in the aqueous phase post reaction via NMR. When the air atmosphere is replaced with argon, these oxygenates disappear from the product slate. Therefore, we conclude that the oxygen from air is responsible for the oxidation of the starting material to form all oxygenated products. Thus, when air or oxygen is present in the reactor to any extent, a small degree of supercritical water oxidation reactions are occurring in addition to pyrolysis, resulting in the formation of oxygenated species.





Additionally, we have sought to investigate the reactions that are responsible for the formation of aromatic molecules in the decomposition of waste tyres. The formation of aromatics has often been attributed to a Diels-Alder reaction that forms the cyclic structure, followed by a subsequent dehydrogenation reaction. Our results from the decomposition of tyres indicate that there is a different aromatization pathway possible for these substrates.

Limonene, a major product formed during pyrolysis of tyres, appears to aromatise to form p-cymene in the hydrothermal reactor.

The aromatics formed have a specificity for this isomer that is likely as a result of a chain backbiting pathway that forms the cyclic structure. Hydrothermal reactivity of isoprene alone forms a different ratio of isomers. This reaction involves isomerization of the double bond into the ring followed by dehydrogenation and appears to be catalysed by the reactor wall as when performed in a glass ampoule, no reaction is observed for limonene.

Figure 1 H-NMR of the aqueous phase obtained after 1-Dodecene reactions at 450°C and 15 min under reaction conditions; (a) Supercritical water under Ar, (b) Pyrolysis under Air, (c) Supercritical water condition under Air.

In conclusion, our model compound work has elucidated important fundamental reaction paths in SCW that will allow better process design.

References

- 1. G. Popelier, G. Dossche, S. Kulkarni, F. Vermeire, M. Sabbe, K. van Geem, *J. Anal. App. Pyrol.* **2024**, *183*, 106805.
- 2. N. Akiya, P. E. Savage, Chem. Rev. 2002, 102(8), 2725-2750.