

MOLTEN POLYMERS AS PATHWAY INHIBITORS FOR SELECTIVE BIOMASS FAST PYROLYSIS

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Abstract

Molten polymers (MPs) are thermoplastics that melt at high temperatures and have degradation timescales longer than that of biomass. This allows them to be used in biomass fast pyrolysis without decomposition. This work illustrates how MPs promote the yields of value-added chemicals via the inhibition of physical (i.e., mass transfer) or chemical (i.e., reaction) pathways in cellulose fast pyrolysis. High-density polyethylene (HDPE), polystyrene (PS), and polyethylene glycol (PEG) were used as MP inhibitors. It was found that HDPE layers inhibit evaporation of anhydrosugar oligomers, while aromatic and ether groups of PS and PEG inhibit glycosidic bond cleavage and dehydration reactions via hydrogen bond stabilization. The understanding from this work allows manipulation of cellulose pyrolysis pathways to alter the yields of key value-added products, such as levoglucosan and furfural.

Keywords

Biomass fast pyrolysis, Molten polymers, Co-pyrolysis, Pathway inhibition.

Introduction

Biomass fast pyrolysis, which operates at a temperature of 400–600 °C, a contact time of 1–5 seconds, and a heating rate greater than 1,000 °C/s, has attracted significant attention due to high yields (> 75 wt%) of liquid products. This liquid fraction, known as bio-oil, has the best potential to be upgraded into drop-in fuels or value-added chemicals. Fast pyrolysis also has the advantage of simplicity in terms of scaling up and commercialization, since the associated unit operations can be easily derived from the petrochemical counterparts. A major drawback to biomass fast pyrolysis is the diverse product distributions, making subsequent upgrading and separation operations expensive. Using catalysts to accelerate pathways to desired products have been actively researched to resolve this problem. A complementary strategy is to suppress undesired pathways via inhibition, which is commonly utilized in enzymatic, combustion, and polymerization reactions but rarely explored in biomass fast pyrolysis.

The objective of this work is to investigate the use of molten polymers (MPs) for selective promotion of product yields in biomass fast pyrolysis via the inhibition of

undesired pathways. MPs are thermoplastics that melt at high temperatures and have degradation timescales longer than that of biomass. This allows them to be used in biomass fast pyrolysis without decomposition. Using MPs in biomass fast pyrolysis promotes the yields of value-added chemicals via inhibition of physical (i.e., mass transfer) or chemical (i.e., reaction) pathways. It has the potential to reduce the need for subsequent product separation and purification and lead to intensified and inexpensive biomass conversion processes.

Experimental Methods

A custom-made, drop-in, vacuumed batch pyrolysis reactor used in our previous work (Wong et al., 2015, 2016) was employed for the pyrolysis experiments. High-density polyethylene (HDPE), polystyrene (PS), and polyethylene glycol (PEG) were used to represent MPs with no functional groups, aromatic groups, and ether groups, respectively. Co-pyrolysis of cellulose and one of these MPs were conducted. For experiments of HDPE/cellulose pyrolysis, different thickness of HDPE layers was coated on top of the cellulose. For PS/cellulose and PEG/cellulose pyrolysis, the

polymer and cellulose fractions were homogeneously mixed before the experiments. All products were analyzed by gas chromatography (GC) techniques.

Results and Discussions

Figure 1 shows the effects of physical inhibition caused by MPs on product yields from cellulose pyrolysis. Specifically, thicker HDPE layers above cellulose led to higher levoglucosan (LVG) and lower molecular weight product (LMWP) yields. Particularly, an over 27% increase in LVG yield was observed, with a total LVG yield reached over 70%, one of the highest achieved thus far compared to literature values. The results can be explained by the hypothesis that larger anhydrosugar oligomers and aerosols are trapped in the MP phase, where these compounds decompose into LVG and glucose-derived LMWPs. These experimental results support the hypothesis that MPs physically inhibit product escape.

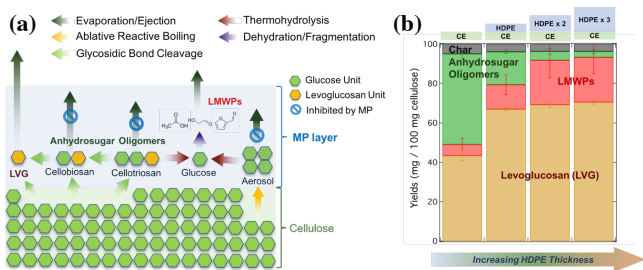


Figure 1. (a) The physical inhibition by MPs is hypothesized via the trapping of escaping molecules in the MP layer, suppressing the mass transfer (evaporation/ejection) processes and promoting the formation of levoglucosan (LVG) and LMWPs; (b) the experimental results support the hypothesis, showing that thicker high-density polyethylene (HDPE) layers on top of cellulose (CE) thin-films led to higher yields of LVG and LMWPs after fast pyrolysis.

Figure 2 shows that LVG and LMWP yields both increased in CE/HDPE pyrolysis compared to neat CE pyrolysis, likely due to the aforementioned physical inhibition effects. The yields of LVG and total LMWPs are similar in CE/HDPE and CE/PEG pyrolysis. However, individual LMWP yields are different, where the yields of small (C_1 – C_3) products (glycoaldehyde and acetic acid) are higher in CE/PEG pyrolysis. This suggests that ether moieties in PEG inhibit glucose dehydration, promoting retro-aldol fragmentation. The CE/PS mixtures gives the highest LMWP yields and the lowest LVG yields, suggesting that aromatic moieties in PS inhibit glycosidic bond cleavage. The yield of furfural, an important value-added chemical, increased over an order of magnitude.

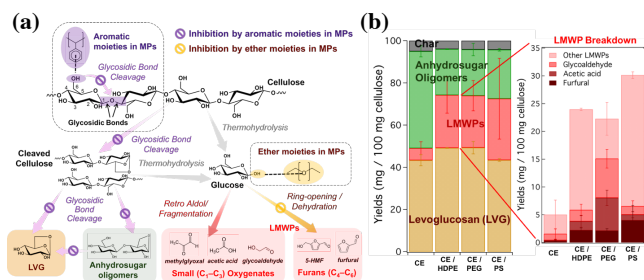


Figure 2. (a) The hypothesized chemical inhibition by MPs is via hydroxyl group stabilization. The aromatic MP moiety is hypothesized to inhibit glycosidic bond cleavage of cellulose, promoting the formation of glucose and glucose-derived LMWPs. The ether MP moiety is hypothesized to inhibit glucose dehydration, promoting the formation of small (C_1 – C_3) oxygenates via retro-aldol fragmentation; (b) the experimental results support the hypothesis that the addition of PEG (containing ether groups) in cellulose pyrolysis promotes the yields of acetic acid and glycoaldehyde, products of the retro-aldol fragmentation reaction, whereas the addition of PS (containing aromatic groups) promotes the yields glucose-derived LMWPs, particularly furfural.

Conclusions

Fast pyrolysis of cellulose in the presence of various MPs, including HDPE, PS, and PEG, was conducted in a batch reactor. It was found that HDPE layers inhibit evaporation of anhydrosugar oligomers, while aromatic and ether groups of PS and PEG inhibit glycosidic bond cleavage and dehydration reactions via hydrogen bond stabilization. Our work suggests that MPs that melt at high temperatures and have degradation timescales longer than that of biomass can potentially be used as inhibitors to promote the yields of key value-added chemicals

Acknowledgments

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References

- Wong, H.-W., Peck, J., Bonomi, R. E., Assif, J., Panerai, F., Reinisch, G., Lachaud, J., Mansour, N. N. (2015). Quantitative determination of species production from phenol-formaldehyde resin pyrolysis. *Polymer Degradation and Stability*, 112, 122-131.
- Wong, H.-W., Peck, J., Assif, J., Panerai, F., Lachaud, J., Mansour, N. N. (2016). Detailed analysis of species production from the pyrolysis of the Phenolic Impregnated Carbon Ablator. *Journal of analytical and applied pyrolysis*, 122, 258-267.