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VALORIZATION OF THE POLYMERIC CONSTITUENTS IN PLASTIC WASTES THROUGH THERMO-CHEMICAL PROCESSES BY USING VIABLE METAL OXIDES ADDITIVES

By

Labeeb ALI

Faculty Advisor

Prof. Mohammednoor Altarawneh, Department of Chemical and Petroleum Engineering

College of Engineering

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Abstract

The rapid accumulation of different types of plastic waste necessitates the development of effective and economically viable waste management operations. Such a process should ideally not only mitigate associated environmental burdens but also recycle and recover value-added products. Through incineration or pyrolysis, thermal processing has emerged as a mainstream approach to waste management of the ever-increasing loads of different categorized plastic wastes. Throughout the work of the thesis, we have utilized a multitude of complementary techniques spanning material characterizations, catalysis, kinetic modelling, and density functional theory (DFT) to comprehend the complex chemistry that underpins catalytic chemical recycling of plastic wastes. Effective chemical recycling of halogen-contaminated plastic wastes entails the removal of HCl and HBr by fixation of the halogen content and the subsequent production of pure hydrocarbon streams. Such scenarios apply to chemical recycling of the polymeric fraction in e-waste, medical waste and other plastic wastes that typically contain high loads of organic bromine and chlorine in the form of BFRs and PVC; respectively. Driven by the unprecedented accumulation of facemasks during the Covid-19 era, we commenced the project by exploring catalytic upgrading of the various polymeric fractions in the facemasks. Thus, we investigated the upgrading of fragments from the facemasks over niobium-doped CeO₂ catalysts under oxidative and pyrolytic conditions. We found that the process to convert alkyl chain polymers into methylated benzenes compounds; could be utilized as transportation fuels. In the second project, we found that the co-pyrolysis of PVC with metal oxides (MO's) at temperatures between 300 and 500°C resulted in the production of metallic chlorides. PVC with ZnO mixture captured 91.13% of the emitted HCl, whereas ZnFe₂O₄ and NiZnFe₄O₄ seized the HCl emission to 65.78% and 83.56%, respectively. During the pyrolysis reaction, Lewis acids such as ZnCl₂, FeCl₂, and NiCl₂ were formed which triggered the isomerization of cis to trans olefins that made it less favorable to undergo cyclization reactions. As such significant depreciation in the formation of benzene derivatives and poly aromatic hydrocarbons was revealed by GCMS with the inclusion of MO's, whereas it enhanced the formation of alkanes. The chemical component in the non-metallic fraction in e-waste, most of the bromine content is emitted as inorganic bromine in the form of HBr. HBr is emitted in appreciable quantities during the thermal decomposition of printed circuit board; PCB. The latter contains ~ 4% BFRs by weight. The highly corrosive, yet relatively reactive HBr, renders recovery of bromine-free hydrocarbon streams from brominated polymers in PCBs which is very challenging. Via an integrated experimental-simulation formalism, the co-pyrolysis of PCB with Al₂O₃ explores the potential of deploying alumina oxide as a debromination agent of Br-containing hydrocarbon fractions in PCBs. An experimental setup was designed on a lab scale using a flow reactor to carry out the pyrolysis and oxidation reaction of PCBs and different BFRs. TBP (Tri bromophenol) is utilized as a model compound of BFRs as their most common formulations include brominated phenolic rings. Co-pyrolysis of hematite with TBP entails a rather low cracking capacity under pyrolytic conditions. Analysis of condensate products indicates that oxidative degradation of a gaseous stream of TBP results mainly in the formation of brominated alkanes such as bromoethane and bromo-pentane. Likewise, Ion chromatography (IC) measurements disclosed a noticeable reduction in the concentrations of escaped HBr. Transformation of iron oxides into iron bromides (FeBr₂) during pyrolysis and combustion operations is evident through XRD measurements. The co-pyrolysis of tetrabromobisphenol A (TBBA; as another model compound for the bromine content in Waste PCBs) with calcium hydroxide (Ca(OH)₂) made conclusive evidence in a complete fixation of the bromine content and produces bromine-free pyrolysis oil. For instance, measurements by IC and FTIR (gas sampling cell) confirm the disappearance of HBr from the gaseous stream during co-pyrolysis of a TBBA:Ca(OH)₂ mixture between 200-500 °C. Likewise, no brominated compounds could be detected from the analysis of the condensate and gas fractions. As the collected oil is dominated by *n*-alkanes, it is concluded that Ca(OH)₂ displays both cracking and debromination capacity. DFT calculations map out important reaction pathways that operate in the initial degradation of the TBP molecule, whereas for Ca(OH)₂ and TBBA mixture, the reaction pathways for the transformation of Ca(OH)₂ into CaBr₂ via dissociative addition of HBr molecules were also investigated. Here we also report the potentiality of producing value-added products from the polymeric wastes using the GCMS by virtue of catalytic pyrolysis, co-pyrolysis, and oxidation of the considered waste materials. The thermo kinetic parameters are derived for the TBP and TBBA incorporated with hematite and Ca(OH)₂ by using the model-free (Coats-Redfern) and model fitting (KAS, FWO, and Starink models) approaches from the thermogravimetric analysis data (TGA). Obtained profiles infer that the addition of hematite to TBP systematically reduces the governing activation energy (*E_a*) in both thermochemical processes compared to neat TBP. The computed *E_a* values for the pyrolytic decomposition of pure TBBA and its mixture with Ca(OH)₂ reside in the narrow ranges of 111.7-112.1 kJ/mol and 62.8-63.4 kJ/mol, respectively. The results obtained from the kinetic parameters find direct application in reactor modeling (rotary kiln) and heat transfer design in domains related to the recycling of e-waste. Outcomes from the project are expected to pave the way toward the commercialization of a continuous chemical recycling process of polymeric waste that is based on the use of affordable additives. The project taps into optimizing a zero-emission route that could accommodate the treatment of polymeric wastes (masks, PVC, and e-waste) within the context of a waste-to-energy approach that has been recently implemented in the UAE targeting UN SDG 12. Fundamental and applied knowledge to be attained in this research are instrumental in the pursuit of closing the gap in the circular economy strategy of polymeric waste in general.

Keywords: Polymeric wastes, PVC, facemasks, e-waste, brominated flame retardants, thermo-chemical conversions, pyrolysis, kinetic modelling, debromination, dechlorination, DFT