

Waste Plastic Conversion into High-value Products using Zeolite based Catalysts

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Abstract

Plastic transformation into liquid hydrocarbons is the most promising route among all waste plastic treatment methods. Considering both environmental and commercial aspects, plastic to liquid process is beneficial as it is a sustainable route producing liquid fuel (energy) from low-cost waste plastics. High temperature pyrolysis is well adopted for the plastic to liquid conversion using fixed and fluidized bed reactor units. In view of improving quality of liquid products, heterogeneous catalyst has been incorporated along with thermal treatment. Despite, available vast studies, plastic to liquid process is still facing limitations towards successful industrial implementations. Major obstacles are associated to high temperature requirement, poor liquid yield, higher selectivity of undesired heavier hydrocarbons and short catalyst cycle length. In this context, present research work has been constructed exploring two-stage thermo-catalytic cracking of plastics at relatively lower temperature to produce fuel (diesel/gasoline) range of hydrocarbons using metal modified zeolite catalysts. Initially, polymer (PP, LDPE, and HDPE) degradation profiles were evaluated with respect to temperature and heating rates in presence/absence of catalyst using TGA. Subsequently, polymer degradation kinetics was studied adopting non-isothermal models (Kissinger-Akahira-Sunose (KAS), Starink, and Ozawa-Flynn-Wall (OFW)) to predict the kinetic parameters. Overall, the obtained kinetic results directed that presence of catalyst strongly facilitates polymer cracking and the temperature requirement is comparatively lower (300 to 400 °C) than the conventional pyrolysis route for the selected model polymer components. Using this information, experimental studies were conducted to convert mixture of polymers (PP, LDPE, and HDPE) into liquid fuels using a bottom-up two-stage cracking approach at

350 °C. A detailed comparative study, thermal cracking vs thermo-catalytic cracking was performed. It was found that presence of catalysts (ZSM-5 and Fe modified ZSM-5) significantly affects the liquid composition and provides a diesel range of hydrocarbon fraction as confirmed from different characterization techniques (GC-MS, ^1H , ^{13}C NMR, and FT-IR). Further, in view of varying liquid product composition, different framework catalysts (ZSM-5 and MCM-22) were tested. Obtained results showed that MCM-22 type catalyst having MWW framework code selectively provided $\text{C}_7\text{-C}_{12}$ range (which is specifically a gasoline range) of hydrocarbons (99.12 %) as compared to that with ZSM-5 ($\text{C}_{13}\text{-C}_{20}$ range of hydrocarbons, 73.19 %) upon polymer degradation at 350 °C using two-stage cracking approach. This was attributed to unique framework (MWW) structure of MCM-22 C having two independent pore channels. In other studies, attempts were made to produce value-added carbon nanotubes (CNTs) from plastics along with liquid and gas fuel via changing catalyst composition (5 to 15 wt.% Fe/ZSM-5) at slightly higher temperature (400 °C). CNTs were observed with the addition of Fe and at 5 wt.% Fe loading, a higher fraction of CNTs was seen in HR-TEM and FE-SEM images. This was due to possessing uniform distribution of Fe species at lower concentration (5 wt.%). Formation of CNTs was further supported by I_D/I_G ratio as obtained via Raman spectroscopy. A gradual increase in I_D/I_G ratio (0.2 to 0.7) was obtained with the increase in Fe content (5 to 15 wt%) which indicated that at higher loading (>5 wt. %), more deformed carbonaceous species (disordered sp^2 carbon) deposits due to agglomeration of Fe species. In addition, hydrogen (H_2) selectivity was found to be higher (51.34%) with 5 wt.% Fe based catalyst comparatively. Overall, 5 wt.% Fe loading was found to be optimum in terms of producing fine CNTs and hydrogen along with liquid fuel. In summary, present research work is a suitable and economical approach towards plastic waste management producing liquid and gas fuel along with value added CNTs.