Catalytic co-pyrolysis of LDPE and PET with HZSM-5, H-Beta and HY

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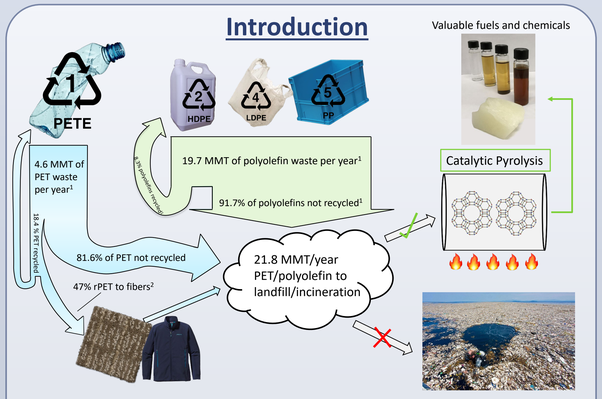
Introduction



Pyrolysis is a thermochemical process which heats feedstocks in the absence of air for the production of various chemicals and fuels. The pyrolysis of mixed plastic waste such as polyethylene terephthalate (PET) and polyolefins such as low-density polyethylene (LDPE) has the potential to divert plastic waste from our environment, forming valuable fuels and chemicals in the process. The addition of catalyst can help to decrease pyrolysis temperature and modify the product distribution in order to optimize the pyrolysis process.

Objectives

To investigate the catalytic co-pyrolysis of PET with polyolefins, we conducted catalytic pyrolysis experiments with LDPE, PET and a 1:1 LDPE:PET mixture with three different zeolite catalysts. The aims for our experiments were as follows:

- Analyze the effect of zeolite catalysts on the products formed during LDPE and PET catalytic pyrolysis
- Determination of interaction effects observed during catalytic co-pyrolysis, with a comparison of those observed in the literature[2]
- Kinetic modeling of catalytic co-pyrolysis utilizing the reaction scheme adapted from Marcilla et al. (2007) [3,4]

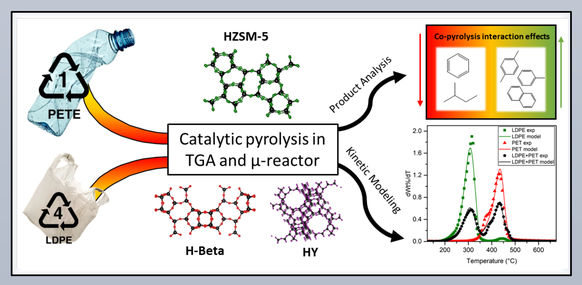
$$LDPE \xrightarrow{k_{NC,L}} G1 \ (R1)$$

$$LDPE + aC \xrightarrow{k_{C,L_1}} (1+a)LDPEC \xrightarrow{k_{C,L_2}} \alpha G2 + (1-\alpha)(Coke + aC_{coked}) + \alpha\alpha C \qquad (R2)$$

$$PET \xrightarrow{k_{NC,P}} \gamma G3 + (1-\gamma)Char \ (R3)$$

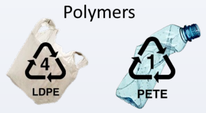
$$PET + bC \xrightarrow{k_{C,P_1}} (1+b)PETC \xrightarrow{k_{C,P_2}} \beta G4 + (1-\beta)(Coke + bC_{coked}) + b\beta C \qquad (R4)$$

Reaction scheme used for the modeling of catalytic co-pyrolysis, adapted from Marcilla et al. (2007)[3,4]



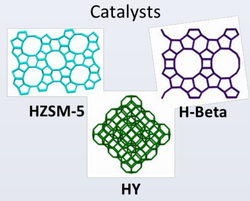
Materials and Methods

Polymers



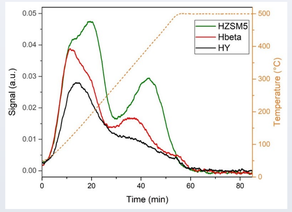
Polymer particle size <300μm

Catalysts



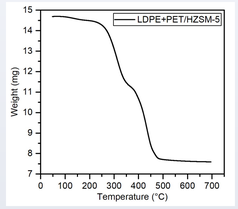
Catalyst particle size: 210μm<250μm
Calcined in air at 550°C for 5 hours
Kept in glovebox prior to pyrolysis/characterization

Catalyst Characterization
Enhanced insight on observed effects during catalytic pyrolysis



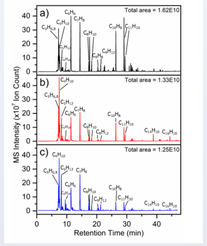
NH_3-TPD, Pyridine-TPD, Pyridine-FTIR, N_2 Physisorption, ^{27}Al NMR

Thermogravimetric Analysis (TGA)
Polymer degradation



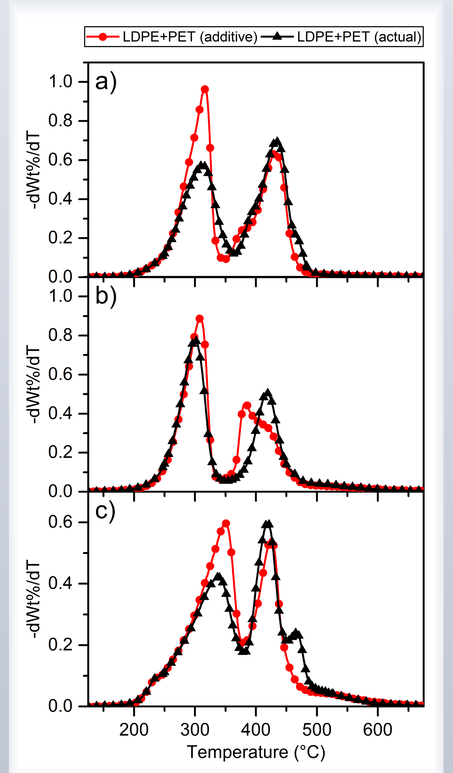
Polymer sample size: 7.5mg
Catalyst:feedstock ratio: 1:1
100 mL/min helium flow
10K/min heating rate
≥2 runs for each condition

Pyroprobe-GC/MS
Pyrolysis product identification/quantification

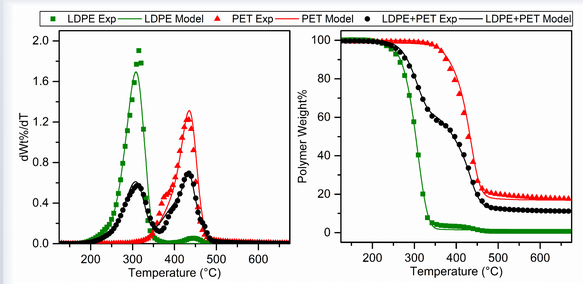


Polymer sample size = 0.2mg
Catalyst:feedstock ratio = 10:1
Pyrolysis Temperature = 500°C
Heating rate = 20,000°C/min
Flow rate = 126.5 mL/min
3 pyrolysis runs for each condition

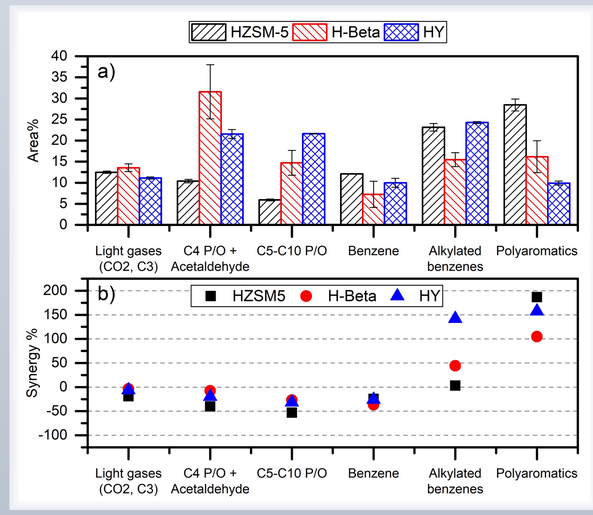
Results



Additive and actual derivative thermogravimetric curves for the catalytic co-pyrolysis of LDPE-PET over HZSM-5 (a), H-Beta (b), and HY (c) catalyst. The difference between the additive and actual curves represent the interaction effects with occur during catalytic co-pyrolysis



Kinetic modeling results for the catalytic single-stream and co-pyrolysis of LDPE and PET over HZSM-5 catalyst



GC/MS area% of main products formed during the catalytic co-pyrolysis of LDPE and PET (a), and the corresponding synergy% (b) which measures the increase or decrease in area% than would be expected from single-stream experiments

$$Synergy\% = \frac{Experimental\ area\% - Addtive\ area\%}{Addtive\ area\%} \times 100$$

Conclusions

- Interaction effects observed for all catalysts during catalytic co-pyrolysis in TGA
  - Presence of PET appears to delay degradation of LDPE
- Reaction scheme adapted from Marcilla et al. was able to capture interaction effects which occurs during co-pyrolysis, while also modeling well the single-stream experiments
- Interaction effects observed for all catalysts which showed a negative synergy% for benzene and C_4-C_{10} paraffins and olefins and a positive synergy for alkylated benzenes and polyaromatics
- HY appeared to have the largest amount of alkylated benzene synergy, demonstrating its ability to produce chemicals from plastic waste which are desirable for fuels

References

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