In-situ decreasing of contaminants in products of agricultural plastic waste pyrolysis

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Abstract

This paper discloses the possibility of in-situ contaminant decreasing during pyrolysis of contaminated polyethylene waste from agricultural sector using different metal containing catalysts. Pyrolysis was carried out at 450 and 600°C. For modification of product yield, composition and contaminant quantity Co-Mo catalyst, Ni-Mo catalyst, MoO_3, CaO, Fe_2O_3, TiO_2 have been applied. Both gas and pyrolysis oil yield could be increased by catalysts; Ni-Mo catalyst was the most efficient in gas yield increasing, while Co-Mo in pyrolysis oil yields increasing. Mainly C_2, C_3 and C_4 hydrocarbons were involved in gaseous products and they were contaminated by nitrogen, sulphur, chorine, and phosphorous. Pyrolysis oils could be characterized as hydrocarbon mixtures from C_5 to C_{26} and they consisted of S, N, P, Cl, K and Ca as contaminants. Catalysts could increase the branched and aromatic hydrocarbon content of pyrolysis oils, while decrease their contaminant level. Especially Ni-Mo catalyst showed advanced behaviour in contaminant decreasing.

Keywords: *pyrolysis, contaminants, EDXRFS, pyrolysis oil*

1. Introduction

Pyrolysis is one of the possible ways for waste plastic/polymer recycling. Many papers give excellent summary about the effect of pyrolysis parameters (temperature, raw materials, reactor construction, catalysts, etc.) to the product yield and composition, but the decreasing of contaminants in pyrolysis product is a big challenge yet. Especially S, N and Cl are the most problematic contaminants, because they are reversible and irreversible catalyst poisonings in further utilization process of pyrolysis products [1-5].

The aim of our work was to investigate the possibility of in-situ contaminant decreasing in pyrolysis using different metal containing catalysts.

2. Materials and Methods

Waste polyethylene from agricultural sector was used as raw material. Based on ICP-OES analysis it consisted of S, N, P, Cl, K and Ca as contaminants. FTIR analysis has resulted that raw material consisted of 73.1% LDPE, 19.3% HDPE, 5.1% PP, and 2.5% PS. For modification of product yield, hydrocarbon composition and contaminant quantity Co-Mo catalyst, Ni-Mo catalyst, MoO_3, CaO, Fe_2O_3 and TiO_2 have been applied.

Pyrolysis was carried out at 450ºC and 600°C. Temperature has been controlled by PID controller and measured with thermocouple. Gaseous pyrolysis products were driven in a water cooler, and the condensable fraction transformed into liquid at 20ºC. Heavy fractions had been removed from separation unit and the heavy oil separated from char by high temperature pressure filtration. Gases and pyrolysis oils were analyzed by GC, FTIR, EDXRFS methods, while heavy oils by SEC, too.

3. Results and Discussion

The yields of both gaseous products and pyrolysis oils were higher at higher temperature, or using catalysts. Ni-Mo catalyst was the most efficient in gas yield increasing, while Co-Mo in pyrolysis oil yields increasing. Higher yields of volatile products were found using catalysts with higher Si/Al ratio and pore surface areas.

Gaseous products contained dominantly C_2, C_3 and C_4 hydrocarbons. The branched content in gases could be increased by catalysts, especially by Ni-Mo catalyst. Regarding contaminants, S, Cl and P were measured in gases. Their level could be significantly decreased by CaO catalyst, while increasing in S, Cl and P levels were found using TiO_2, Ni-Mo, Co-Mo and MoO_3 catalysts.

Pyrolysis oils could be characterized as hydrocarbon mixtures from C_5 to C_{26}; n-olefin, n-paraffin, branched hydrocarbons, aromatics and naphthenic were involved in pyrolysis oils. Based on GC analysis catalyst application could increase the aromatic and branched hydrocarbon content, which was the consequence of the more intensive isomerization and aromatization reactions. Ni-Mo and Co-Mo catalysts have shown high efficiency in isomerization reactions. Pyrolysis oils consisted of S, N, P, Cl, K and Ca as contaminants. Especially Ni-Mo catalyst showed advanced behaviour in contaminant decreasing. The positive effects of catalysts to the product properties were more significant at higher temperature using MoO_3, CaO, Fe_2O_3 and TiO_2.

C_{25}+ hydrocarbons were in heavy oils, with average molecular weight of 940-1310g/mol. The average molecular weight of heavy oils and their S, N, P, Cl, K and Ca content could be decreased in thermo-catalytic pyrolysis.

The morphology of solid char was investigated by SEM method. SEM micrograph well demonstrated that contaminants were accumulated on the surface especially in case of MoO_3, CaO, Fe_2O_3 and TiO_2 catalysts.

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