

## PYROLYSIS OF CONTAMINATED, POLYOLEFIN REACH PLASTIC WASTES

N. Miskolczi<sup>1</sup>, N. Borsodi<sup>1</sup>, A. Angyal<sup>1</sup>, L. Bartha<sup>1</sup> and J. Kohán<sup>1</sup>

<sup>1</sup>University of Pannonia, Chemical Engineering and Process Engineering Institute, MOL Department of Hydrocarbon and Coal Processing, Veszprém, Hungary

<sup>2</sup> MOL Plc, Százhalombatta, Hungary  
e-mail: mnorb@almos.uni-pannon.hu

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### Abstract

*Due to the increasing amount of plastics and other wastes, their utilization is in the focus of waste management. The thermal degradation of wastes plastics is one of the suitable techniques for their recycling. Furthermore by this way wastes could be converted into valuable hydrocarbons, which are able to use as feed stock materials. The mild pyrolysis of contaminated, polyolefin reach waste plastics was investigated in a tube reactor both absence and presence of catalyst. The effects of the parameters to the properties of products (e.g. gases, naphtha, middle distillates, heavy oil) were discussed. Gases and liquids formed in degradation reactions were analysed mainly by a gas-chromatography, Fourier-transformed infrared spectroscopy, size exclusion chromatography and other standardized methods. Both the yields and structure of products have been significantly changed with pyrolysis conditions. Plastic wastes could be converted into valuable volatile fractions with yields of 35-80% depending on the applied parameters. Products had significant content of unsaturated hydrocarbons, mainly  $\alpha$ -olefins. Naphtha and middle distillates had favourable hydrocarbon distribution for fuel-like applications, but their contaminant levels were high occasionally. The levels of contaminants in different products have been affected by the applied catalysts.*

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**Keywords:** pyrolysis, waste plastics, middle distillates, contaminants, utilization

### 1. Introduction

Each year more than 300 M tons of plastic wastes are generated worldwide, therefore the recycling of plastic wastes and the utilization of products from recycling technologies are in the focus of waste managements. Plastic wastes have high so called hidden energy content, which reusing enormous energy could be saved with. The R&D activity in the area of waste recycling has been notable increasing since the 1990's. By pyrolysis or chemical recycling of both from plastic and solid wastes considerable energy could be obtain in the form of hydrocarbons. Many researchers investigate the possible of waste to fuel processes and numerous having prospective chance for industrial leading. Pyrolysis of waste plastics or polymer reach wastes both from households and industrial companies (e.g. HDPE, LDPE, PP, PS, etc.) is one of the most attractive methods for their recycling and converting to valuable hydrocarbon products.

In this work we have focused to determine the correlation between properties of raw materials and products quantity and quality in case of waste plastic pyrolysis. The mild pyrolysis of contaminated, polyolefin reach waste plastics was investigated in a tube reactor both absence and presence of catalyst. Gases and liquids formed in degradation reactions were analysed mainly by a gas-chromatography, Fourier-transformed infrared spectroscopy, size exclusion chromatography and other standardized methods. Mainly the product quantity, the

composition, impurities level and the other fuel properties such as density, heating value, pour point have been compared.

### 2. Materials and Methods

In our experimental work different waste polymers have been used: automotive wastes (LDPE, HDPE, PP, PS, ABS, PC and PA), packaging wastes (HDPE, LDPE, PP) and agricultural wastes (HDPE, LDPE, PP).

To ensure the higher yields of volatile products different catalysts were applied: Y-zeolite,  $\beta$ -zeolite and MCM-41 catalyst.

Pyrolysis of waste polymers was carried out in continuous reactor with feed rate of 10kg/h at 550°C. Raw material was mixed with the catalyst then that mixture was fed in the reactor by an extruder, where the polymer was preheated. The extruder was directly connected to the reactor beginning section. Inside the gas heated reactor the waste polymer had melted and their carbon chain cracked into fragments with lower molecular weights. For adjusting the temperature constantan thermocouples and electronic PID controllers were used both in the extruder and pyrolysis reactor. In the distillation column hydrocarbons were separated into different products.

Gases were analyzed using a Carlo-Erba Vega Series GC 6000 gas chromatograph provided with a 50 m  $\times$  0.32 mm fused silica column with Al<sub>2</sub>O<sub>3</sub>/KCl coating, at 40°C.

The composition of liquids products were analyzed by gas chromatograph (TRACE GC) with a flame ionization detector. It was provided with a 30m x 0.32mm Rtx®-1 (Crossbond® 100% Dimethyl-polysiloxane) column.

The main chemical bonds of liquids were determined with infrared technique by a TENSOR 27 type Fourier transformed infrared spectrometer in the 400-4000cm<sup>-1</sup> wave number range.

The average molecular weight of heavy oils and its distribution were measured by size exclusion chromatography (Waters system).

Hydrocarbon fraction from pyrolysis, experimental additives and reinforced plastic composites were also analyzed using standardized methods: determination of distillation curve (ASTM-D 1078), flash point (ISO 2719:2002 and MSZ 15967:1979), CFPP (MSZ EN 116:1999), viscosity (MSZ ISO 3105:1998), corrosion test (MSZ EN ISO2160:2000), liquid density measurement (MSZ EN ISO 12185) determination of sulphur content (ASTMD 6428 99), determination of nitrogen content (ASTMD 6366 99).

The concentration of other impurities in products was followed with energy dispersive X-ray fluorescence method (Phillips PW 4025/02 MiniPal), while octane and cetane numbers were determined from their infrared spectra with a ZX-101c type instrument.

### 3. Results and Discussion

The yields of products obtained from different raw materials have shown quite significant differences. The highest yields of middle distillates was found in case of raw materials from packaging sector, while the lowest from automotive area. The yields of valuable lighter fractions could be increased by the presence of any catalysts. The most efficient catalyst was the Y-zeolite for oil production, while the HZSM-5 catalyst in gas production. Results could be blamed by the differences in catalyst micro- and macropores surface areas.

Compositions of non-condensed products at 20°C are shown compounds from C<sub>1</sub> to C<sub>5</sub> hydrocarbons both catalytic and non-catalytic cases. The formation of alkenes were a bit higher than alkanes of same carbon number. Detectable amount of i-butane appeared only in the presence of catalyst, which refers to their isomerisation of effect. The calculated heating values of gases was 45.9-46.6kJ/mol, which is enough high for energy generation to heat consumption of pyrolysis.

The hydrocarbon compositions the other properties of the produced liquid fractions could be affected by the raw materials and the presence of catalysts. The highest impurities were found in case of products obtained from automotive and agricultural raw materials, but all unfavorable properties could be improved by catalysts. Catalysts can occur the isomerization of double bond and the main carbon frame, moreover occasionally led to decrease the impurity level.

The other properties of liquid hydrocarbons e.g. hydrocarbon distribution, structure, density, average molar mass, boiling point ranges, etc. have also shown

favourable properties for further energetic utilization depending on the raw materials. The boiling points were in the range of 30-270°C in case of middle distillates, while heavy oils could be characterized as hydrocarbons with boiling points over 150°C. In products Na, Ca, Na, P, K, Mg and N, S, Fe, Mo, Co were identified as contaminants.

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