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## A Comparative Study on Waste Plastics Pyrolysis Liquid Products Quantity and Energy Recovery Potential

Merve Sogancioglu<sup>a</sup>, Gulnare Ahmetli<sup>b</sup> and Esra Yel<sup>a,\*</sup>

<sup>a</sup>Selcuk University, Engineering Faculty, Environmental Engineering Department, 42075, Konya, Turkey

<sup>b</sup>Selcuk University, Engineering Faculty, Chemical Engineering Department, 42075, Konya, Turkey

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### Abstract

Plastics thermal processing is an important application for both energy recovery and feedstock recycling. In this study effects of type of plastic (HDPE, LDPE, PET, PP, PS), pyrolysis process temperature and plastic waste prewashing on pyrolysis liquid product (oil) fraction, its hydrocarbon (HC) contents and heat values were investigated. Caustic washing and batch-pyrolysis were applied by keeping pyrolysis heating rate and other conditions constant. Oil yields, C10-C40 HCs, heat values were measured and compared. HDPE type plastic wastes produced the highest oil yield while PET and PP produced the lowest yields. C10-C40 HC contents of pyrolysis oils were strongly affected from the pyrolysis temperatures and pre-washing process under identical pyrolysis conditions. The highest C10-C40 HCs were produced by HDPE pyrolysis. Statistical analysis indicated that the effect of pre-washing process on the pyrolysis oil heat value is significant for HDPE and PP type plastics. Pyrolysis temperature had almost no effects on oil heat values for washed PET and unwashed PS wastes, whereas for other plastic samples, as pyrolysis temperature increased oil heat values increased. HDPE, LDPE, PP and PS pyrolysis oils have higher calorific values than wood and some coal types. These refer to energy recovery from those types of plastics.

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*Keywords:* Plastics, pre-washing, pyrolysis oil, heat value

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\* Corresponding author. Tel.: +90-332-223 2091; fax: +90-332-241 0635.

*E-mail address:* [etarlan@selcuk.edu.tr](mailto:etarlan@selcuk.edu.tr)

## 1. Introduction

Thermoset plastics are polymeric materials including number of straight or branched cross-links between chains. Consecutive melting and reshaping availabilities make them economical products. Polyethylene (PE), polyethylene terephthalat (PET), polypropylene (PP), polystyrene (PS) are among the most common thermoplastics. PE (HDPE:  $[-\text{CH}_2-\text{CH}_2-]_n$ , LDPE:  $[-\text{CH}_2-\text{CH}_2-]_n$ ) is produced by polymerization of ethylene under high or low pressure in the presence of organo-metallic catalysts. HDPE is a straight-chain PE having 0.948-0.968 g/cm<sup>3</sup> density [1] whereas LDPE is branched-chain PE (0.910-0.925 g/cm<sup>3</sup>). PET ( $[-\text{CO}-\text{C}_6\text{H}_4-\text{COO}(\text{CH}_2)_2\text{O}-]_n$ ) is a transparent or opaque polyester produced by condensation from ethylene glycol and terephthalic acid monomers [2]. PP ( $[-\text{CH}_2-\text{CH}(\text{CH}_3)-]_n$ ) is produced by polymerization of propylene. It is similar to HDPE but more resistant [3]. PS ( $[-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-]_n$ ) is obtained by radical chain polymerization of styrene, which is produced from benzene and ethylene [3]. It is resistant to bases, weak acids, salts and solvents but not ethers, ketones, aromatic and chlorinated hydrocarbons and UV [4].

Plastic recovery can be divided into material recycling and energy recovery. The choice between these will depend on the types of plastics, the relative difficulty in total or partial segregation from other waste materials, ecological and cost aspects of process [5]. Thermal degradation of plastics is of increasing concern for feedstock recycling as their conversion to gas, liquid (oil) and solid products each of which can be used as energy source and/or chemical feedstock. Pyrolysis product compositions and yields relate directly to the reaction conditions (temperature, heating rate, pressure, presence of catalyst etc), as well as pyrolysed material structure [5-9]. Interactions between the materials in a waste feed have significant effect on the selectivity of specific liquid product components [10-12]. For example, Williams and Slaney [11] indicated that pyrolysis oil quantities and qualities of HDPE, LDPE, PP are changing with changing operational conditions of the pyrolysis reactor. Liquid product yields of PE and PP pyrolysis is higher than 80%; at high temperatures and PE and PP decomposes into a range of paraffin and olefins [12]. LDPE and PET pyrolysis oils are mainly in paraffin structure and PET pyrolysis may produce oligomers which are soft solid rather than oils containing C1-C7 hydrocarbons (HCs) while PP pyrolysis oils are mainly composed of C3 HCs [12,13]. LDPE pyrolysis oil product yield decreased from 500°C to 700°C while gas product yield was increasing [14]. Adrados et al [15] have pyrolysed the mixture of PE, PET, PP and PS at 500°C and recorded 40.9% oil yield, whereas different combinations of these plastic wastes had resulted in different oil product yields and characteristics [16]. PS pyrolysis exhibits high yields of aromatics in liquid product due to the polycyclic nature of PS and the thermodynamic challenge posed in converting cyclic compounds to aliphatic chains or alkene compounds [14,17].

These indicated that degradation products of pyrolysis process are varying with the type of pyrolysed material. Therefore, it is important to obtain a database indicating the pyrolysis product yields and qualities for each type of plastics. Moreover, it is inferred from the examples that among the operational conditions, pyrolysis temperature is one of the most important operating parameters affecting the product yield and composition. Higher operating temperature enhance bond breaking and favour the production of smaller molecules [12]. Gaseous products (C2–C4) increases and liquid products (C5–C9) decreases with increase in temperature [18]. Effect of the catalysts on the yields and structure of products becomes less significant with increasing temperature [5,19]. The purpose of this study is to compare the liquid product yields of PE, PET, PP and PS under the same pyrolysis conditions and to investigate the effect of pyrolysis temperature on this liquid product yields and heat values. Moreover, the effects of plastic waste pre-washing process is also investigated since prewashing removes impurities from the waste samples and so changing the composition of the waste to be pyrolysed.

## 2. Experimental

Waste plastics were collected from a local waste transfer station. PE, PET, PP and PS types were separated. Each sample was crushed to <8 mm size in plastic crusher. A portion of the crushed samples was washed in laboratory scale three steps washing system (washing in 42% NaOH at 90°C and then rinsing twice). Washed and unwashed plastic samples were pyrolysed at lab-scale fixed bed batch reactor pyrolysis system in which inert atmosphere was supplied with nitrogen gas. 300, 400 500, 600 and 700°C temperatures were studied at heating rate of 5°C/min in a 12 mm internal diameter vertical chromium reactor. The fluid product has passed through condenser, liquids were collected in condensation pots and non-condensed portion that is gaseous product was collected in a gasometer.

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