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# Plastic waste to liquid oil through catalytic pyrolysis using natural and synthetic zeolite catalysts



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#### ABSTRACT

This study aims to examine the catalytic pyrolysis of various plastic wastes in the presence of natural and synthetic zeolite catalysts. A small pilot scale reactor was commissioned to carry out the catalytic pyrolysis of polystyrene (PS), polypropylene (PP), polyethylene (PE) and their mixtures in different ratios at 450 °C and 75 min. PS plastic waste resulted in the highest liquid oil yield of 54% using natural zeolite and 50% using synthetic zeolite catalysts. Mixing of PS with other plastic wastes lowered the liquid oil yield whereas all mixtures of PP and PE resulted in higher liquid oil yield than the individual plastic feed-stocks using both catalysts. The GC–MS analysis revealed that the pyrolysis liquid oils from all samples mainly consisted of aromatic hydrocarbons with a few aliphatic hydrocarbon compounds. The types and amounts of different compounds present in liquid oils vary with some common compounds such as styrene, ethylbenzene, benzene, azulene, naphthalene, and toluene. The FT-IR data also confirmed that liquid oil contained mostly aromatic compounds with some alkanes, alkenes and small amounts of phenol group. The produced liquid oils have high heating values (HHV) of 40.2–45 MJ/kg, which are similar to conventional diesel. The liquid oil has potential to be used as an alternative source of energy or fuel production.

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#### 1. Introduction

In the Kingdom of Saudi Arabia (KSA) and Gulf countries, the rapid growth in population and industrial sector have increased the demand for energy, food, and water (Khan et al., 2017). The fulfilling of energy requirements with the depletion of natural resources has resulted in significant greenhouse gas (GHG) emissions and anthropogenic climate change (Sadef et al., 2016a,b). The gap between the economic growth and environmental sustainability was increasing, until recently with the new governmental policy of Vision 2030 (Vision 2030, 2016). The policy has outlined the need for sustainable technologies, policies and initiatives to mitigate the GHG emissions and produce renewable energy from indigenous sources such as wind, solar, geothermal and waste (Vision 2030, 2016).

Plastic waste is the second largest waste stream (up to 20%) after organic waste in the KSA and other Gulf countries. The KSA is the world's 6th largest plastic producer country (Khan and Kaneesamkandi, 2013). Plastic products have a very short life-

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span and mostly end up in the landfills or disposal sites (Anjum et al., 2016). Plastic waste has detrimental environmental and operational problems at landfills due to slow degradation rates and the presence of toxic dyes and additives (Demirbas et al., 2015). Plastic waste causes fire outbreak and releases air and water borne pollutants or act as a habitat for disease-causing vectors, rodents, and flies (Rehan et al., 2017). There are well-established routes to manage plastic waste, including mechanical and chemical recycling, and energy recovery technologies (Breyer et al., 2017). In these routes, pyrolysis has gained significant attention as an emerging waste to energy technology due to its economic and environmental benefits (Miandad et al., 2016a).

The absence of oxygen in pyrolysis process resists the formation of dioxins (Singh and Ruj, 2016). In economic terms, pyrolysis has an advantage over other technologies like incineration and plasma arc gasification with a lower annual capital cost (US \$17–25/t) and net operational cost (US \$2–3/t) along with production of liquid fuel and value-added products (Ouda et al., 2016). The process is completed at a temperature ranging from 400 °C to 900 °C (Nizami et al., 2015a) and liquid oil is the primary product with char and gases as by-products (Miandad et al., 2016b). The quality and yield of the liquid oil vary with the composition of feedstock,

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reactor types and the process parameters such as temperature and retention time (Rehan et al., 2016a). The pyrolysis of plastic waste can be carried out either in the presence of a catalyst (catalytic pyrolysis) or absence of a catalyst (thermal or non-catalytic pyrolysis). The pyrolysis process consists of four main steps, initiation, transfer, decomposition and termination (Nizami et al., 2015b).

In catalytic pyrolysis, the catalyst enhances the targeted reactions, reduces the reaction times and temperature, improves the liquid oil quality and increases the overall process efficiency (Serrano et al., 2012). The surface area, acidity, and pore size and volume are the key features of any catalyst that affect the pyrolysis process (Nizami et al., 2016a). Various catalysts have been used in pyrolysis of plastic waste, including FCC, silica-alumina, MCM-41 and zeolite such as Y-zeolite, HZSM, and ZSM-5 (Miandad et al., 2016a). Miskolczi et al. (2006) reported that FCC microporous catalvst increases the liquid oil vield, whereas ZSM-5 increases the gases vield due to its mesoporous structure. Ratnasari et al. (2016) indicated that microporous catalysts limit the entrance of higher hydrocarbons into the catalyst and improve the quality of liquid oil. A catalyst having high acidity decreases the liquid oil yield but increases the yield of gases (Miandad et al., 2016c). A detailed comparison of catalytic pyrolysis, using natural zeolite without any modification and synthetic zeolite catalysts, in examining the quality of liquid oil is rarely reported (Miandad et al., 2017a,b), which was the focus of this study.

In KSA, neither waste to energy facilities exist to convert any waste into energy (Nizami et al., 2017a), nor have the plastic waste and natural zeolite been characterized for their potential role in catalytic pyrolysis (Miandad et al., 2016c). The authors have previously examined and discussed the catalytic features of natural zeolite in detail using XRD, SEM, FT-IR and BET surface area analysis (Nizami et al., 2016b) and also carried out non-catalytic pyrolysis of different types of plastic waste to examine the effect of feedstock composition on the yield of pyrolysis products and liquid oil composition (Miandad et al., 2017a). These studies concluded that natural zeolite has good potential as a catalyst in the pyrolysis process to convert the plastic waste into liquid oil. This study aims to examine the catalytic pyrolysis of various types of plastic wastes such as polystyrene (PS), polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET) in the presence of indigenous Saudi Arabian natural zeolite catalyst in comparison to synthetic commercial zeolite catalyst.

#### 2. Materials and methods

#### 2.1. Feedstock preparation and reactor start-up

The feedstock consisted of disposable plates, grocery bags, disposable juices cups and drinking water bottles, which are mainly composed of PS, PE, PP and PET plastics respectively. All these types of plastic waste are the primary sources of plastic waste produced in KSA. The collected feedstock was crushed into smaller pieces (2 cm²) to get a homogenous mixture for the reactor. After

crushing the collected samples, catalytic pyrolysis was carried out for individual feedstock and their combination with the ratios of 50/50%, 50/25/25% and 40/20/20/20% (Table 1). In each experiment, 1 kg of feedstock was used. Two types of catalysts were used i.e. natural zeolite and synthetic zeolite. Synthetic zeolite was purchased from Zeolyst International, USA and used as received without any further modification (Zeolyst, 2015). Natural zeolite was collected from the Harrat-Shama, an area located in the northwest of Jeddah city, KSA (Nizami et al., 2016b). The sample was collected purely for research purposes, so it was collected without any explicit permission from the governmental or any other official agency. It is confirmed that the area did not contain any endangered or protected species. The collected sample was initially crushed, in a locally manufactured stone crusher present in Saudi geological laboratory at King Abdulaziz University Jeddah KSA, into 3–5 mm size. An automatic mortar grinder (Fritsch Pulverisette-2, Denmark) was further used to reduce the particle size down to 15-35 um after continuous 2 h crushing. The milled sample was used in the pyrolysis reactor as it is without any further surface modification or

The prepared sample of feedstock was put into the heating reactor/chamber for pyrolysis (Fig. 1). In each experiment, the feedstock was heated to 450 °C with the heating rate of 10 °C per min and retention time of 75 min (Miandad et al., 2016b). At the end of each experiment, the obtained yield was calculated by measuring the fractions of liquid, gases and char on a weight basis. The obtained liquid oil was further characterized to determine the effect of feedstock composition in the presence of natural and synthetic zeolite catalysts. In order to determine the optimum condition (450 °C and 75 min) for pyrolysis, TGA of all feedstocks was carried out under controlled conditions. In TGA,  $10 \mu g$  of each

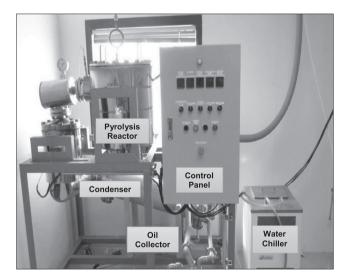


Fig. 1. Small pilot-scale pyrolysis reactor.

**Table 1**Experimental scheme of catalytic pyrolysis, each experiment with natural and synthetic zeolite catalysts separately.

Feedstock types	Feedstock quantity (kg)	Feedstock ratio (%)	Catalyst quantity (kg)	Retention time (min)	Reaction temperature (°C)	Heating rate (°C/min)
PS	1	100	0.1	75	450	10
PE	1	100	0.1	75	450	10
PP	1	100	0.1	75	450	10
PS/PE	1	50/50	0.1	75	450	10
PS/PP	1	50/50	0.1	75	450	10
PP/PE	1	50/50	0.1	75	450	10
PS/PP/PE	1	50/25/25	0.1	75	450	10
PS/PP/PE/PET	1	40/20/20/20	0.1	75	450	10

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