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Gasoline-range hydrocarbons produced from microwave-induced pyrolysis of low-density polyethylene over ZSM-5

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HIGHLIGHTS

- It is the first time that plastic was used for microwave assisted pyrolysis over ZSM-5.
- Large amount of gasoline-range hydrocarbons (74.73–88.49%) were produced.
- Less than 1 wt.% coke deposition on ZSM-5 is negligible under most conditions.
- Gaseous fractions with abundant ethylene, ethane, and hydrogen were obtained.
- The reaction mechanism of thermal degradation and catalytic reforming were proposed.

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ABSTRACT

The microwave-induced pyrolysis of low-density polyethylene (a model of waste plastics) toward its conversion into biofuels was investigated using ZSM-5 as a catalyst, generating significant amounts of gasoline-range hydrocarbons. A central composite experimental design (CCD) was done to investigate the effects of catalytic temperature and reactant to catalyst ratio on the pyrolysis-oils composition and to achieve the maximum liquid yield. The optimized condition for maximizing the yield of upgraded oil (32.58 wt.%) was at 450 °C and reactant to catalyst ratio of 2. GC–MS analysis showed that mono-ring aromatic hydrocarbons were enriched and became the most abundant compounds which varied from 74.73% to 88.49% in upgraded pyrolysis-oils, depending on the catalytic pyrolysis conditions. Both low temperature and high reactant to catalyst ratio gave rise to the formation of less desirable polycyclic aromatic hydrocarbons whereas high temperature and high ratio contributed to mono-ring aromatic hydrocarbons. The primary reaction competing with aromatic hydrocarbon production was the formation of coke which was negligible even at low catalytic temperatures. A plausible reaction mechanism was also proposed in order to shed light on the overall catalytic microwave pyrolysis of LDPE for aromatic hydrocarbons.

1. Introduction

Plastics are used extensively in daily life as well as in industries acting as an indispensable ingredient due to the versatility and low cost; thus consumption of virgin plastics has increased exponentially over the past decades [1,2]. Current per capita consumption of exploited polyolefins for any technical and packing usage was quantified at 100 kg in 2010 and predicted to rise to 140 kg in the forthcoming years [3]. The primarily used plastics were polyethylene (PE) and polypropylene with the amount of 13.6×10^9 kg and 8.9×10^9 kg respectively, accounting for 29% and 19% of total demand of plastics in 2011 [4]. Consequently the plastic wastes (approximately 26×10^9 kg) resulting from this expanding use of plastics was enormous, yet a large amount of plastic wastes (around 10×10^9 kg) was not recycled [4,5]. The widespread application of plastics caused huge economic and environmental concerns about their resourceful disposal, in spite of significant measures that have been taken to improve the valorization of plastics and recover plastic wastes (only 8% recovery of total plastics in U.S.) [1,6].

Landfills and incineration for disposal of waste plastics are commonly utilized among the conventional existing methods [2,7]. Most waste plastics generated were generally disposed in landfills, which caused a serious danger toward the environment owing to plastics degradation and subsequent contaminant generation [8,9]. An even worse perspective for waste plastics is low density and low biodegradability leading to a tremendous and long-term

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filling of landfill sites [4,10]. Energy recovery by means of energetic valorization (incineration) is prevalently applied among thermal treatment on the base of the high calorific value of waste plastics [8]. On the other hand, incineration stimulates the release of harmful compounds such as acid gases, dioxins, and furans into the atmosphere together with heavy metals causing damage toward the environment and human health [2,11]. Accordingly there is an urgent demand for addressing waste plastics in a different way to the conventional treatment systems: incineration and landfill.

The state of the art on tertiary recycling technologies and implementation is not only more feasible at different scales but also more economically viable and environmentally friendly than that of typical technologies [10]. Pyrolysis, as an effectual and versatile route for valorizing polyolefins (2/3 of waste plastics), has been highly developed with respect to environmental management among the tertiary recycling of waste plastics [10,12]. Thermal degradation of waste plastics occurs through a complex free-radical mechanism involving the scission of long polymeric molecules by exposure to elevated temperatures in an inert gas environment [1,13]. Broadly speaking, products evolved from thermal decomposition of waste plastics give rise to a heterogeneous hydrocarbon mixture of paraffins and olefins over a wide range of molecular weights [9]. Volatile and condensable hydrocarbons with their relevant concentrations varying with the dynamic conditions employed are predominant products obtained, intensifying the recovery of valuable hydrocarbons and providing the gasoline precursor for petrochemical industries [12,14]. In contrast, due to the poor heat conductibility and thermal decomposition of plastics, the process requires appreciable amounts of energy and elevated temperature [8]; another detriment exhibits that a reactively broad spectrum of products are generated from the thermal degradation of macromolecules to small molecules complicating their utilization on an industrial scale at present [8]. Therefore, pyrolysis oil has to undergo downstream catalytic upgrading to overcome the aforementioned problem prior to being used as a conventional transportation fuel.

Toward this end, catalytic pyrolysis represents an essential step forward in the enhancement of transforming waste plastics into gasoline-range hydrocarbons, eliminating the necessity for further processing [15]. The suitable catalysts introduced confers the thermal degradation an additional value to a gradual extent since an adequate catalyst can narrow the spectrum of evolved products toward an excellent selectivity contributing to more valuable products even at low temperatures [7]. The catalytic cracking furthermore demands less energy as the catalysts used either in situ or online reforming of pyrolysis volatiles can reduce the activation energy, lowering the required temperature and optimizing the quality of the product stream [16]. Zeolites have been verified to be noticeable in generating evolved hydrocarbons lumped in gasoline-range derived from the pyrolysis of waste plastics containing silica–alumina, β-zeolite, Y-zeolite, mordenite, HZSM-5, MCM-41, clinoptilolite [8,14,17,18]. Among zeolite-based catalysts, ZSM performs as a feasible catalyst displaying a sharp selectivity in the formation of branched hydrocarbons fostered by the isomerization and aromatization reactions as a function of the structure of zeolitic framework, including acid strength, external surface area and microporous texture [18]. Moreover carbonaceous coke deposited on ZSM-5 deactivates the catalyst to a lesser extent, which is mainly attributed to the tridimensional porous structure of ZSM-5 giving way to the circulation of aromatic coke precursors toward the outside of the zeolite micropores [19].

As a matter of fact, catalytic pyrolysis of polyolefins has been studied by a multitude of researchers in the presence of HZSM-5 striving to obtain hydrocarbons remarkably composed of noncondensable olefins along with low concentration of aromatic hydrocarbons in the liquid fraction [3,8,10,12,14,15,19–21]. Light olefins or aromatic hydrocarbons with low content derived from catalytic cracking of polyolefins in the presence of HZSM-5 have been investigated in fluidized bed reactors [8,15,20] and conical spouted bed reactors [3,10,12,19], respectively. Given in situ pyrolysis combining thermal cracking and catalytic cracking in a single reactor, catalysts placed in the reactors are in intimate contact with waste plastics; hence char formed as well as the liberated impurities readily deactivate the catalysts in the integrated reactions [9]. In addition, variables associated with catalysts are reactively difficult to simulate for investigating the influences of catalysts parameters alterations on products distribution. Nevertheless sequential pyrolysis and catalytic reforming are prone to noticeably mitigate the problems [3,9,22]. A downstream fixed-bed reactor introduced in the study [5] was conducive to an upward tendency in contents of aromatic hydrocarbons and light olefins mostly dependent upon the fixed bed conditions.

The larger scale implementation of the process was restricted by the sticky nature and low thermal conductivity of fused polyolefins, thereafter hindering heat and mass transfer between phases [19]. Hence an adequate reactor is crucial to overcome characteristic limitations of plastics in order to reinforce heat and mass transfer between phases reducing plastics decomposition to carbonaceous materials [3]. Microwave-assisted pyrolysis technology is one of the most ideal methods of enhancing and accelerating chemical reactions due to effective heat transfer profiles through microwave irradiation [23]. The Microwave assisted reactor herein is transparent for effectively decomposing waste plastics in accordance with satisfactory performances. In comparison with traditional pyrolysis, the microwave-induced pyrolysis which encloses the potentials of fast and selective heating, easy control of reaction conditions, low reaction temperatures and energy requirements could somewhat overcome these limitations [24,25]. In detail, the microwave-induced pyrolysis approach has been successfully investigated from plant residues [26,27]; yet little research is demonstrated for microwave-assisted pyrolysis of polymeric materials [4,28–30]. Among previous studies, thermal degradation of polyethylene was investigated [28]; Other researchers were devoted to improving the quality of products on the base of an activated carbon bed coupled with microwave pyrolysis of polyethylene [29]. In addition to pure polyolefins, waste polyolefins were disposed to efficiently convert into valuable chemicals by means of microwave-induced pyrolysis [4].

Aforementioned studies were chiefly engaged in the topics of gaseous hydrocarbons evolved from in situ or ex situ catalytic pyrolysis of polymeric materials; nonetheless there is no literature on characterizing, in depth, the evolution of individual aromatic hydrocarbons in liquid phase derived from microwave assisted pyrolysis of polyolefins over ZSM-5. As low density polyethylene (LDPE) with branched carbon chains indicates an intermediate behavior between high density polyethylene (HDPE) and polypropylene [4]; the objective of this study thereby aims to fill this knowledge gap in catalytic microwave pyrolysis of polyolefins over ZSM-5 and take advantage of low density polyethylene (LDPE) as a model compound to predict gasoline-range hydrocarbons. In this study, we will also elucidate the overall reaction mechanism for the conversion of LDPE to aromatics by microwave-assisted pyrolysis in the presence of ZSM-5. The effects of catalytic temperature and catalyst to feedstock ratio on product yields were investigated and determined the thermochemical maximum of hydrocarbon yields evolved from LDPE catalytic pyrolysis was determined. The compositions of resulting bio-oil from ZSM-5 assisted cracking in packed-bed catalysis were characterized by GC–MS; the noncondensable gas contents were analyzed by Micro-GC.