Journal of Analytical and Applied Pyrolysis 127 (2017) 31–37

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Experimental study of catalytic pyrolysis of polyethylene and polypropylene over USY zeolite and separation to gasoline and diesel-like fuels

Chantal Kassargy[a,b], Sary Awad[a,*], Gaetan Burnens[a], Khalil Kahine[b], Mohand Tazerout[a]

[a] GEPEA, UMR 6144, DSEE, IMT-Atlantique, Nantes 44307, France
[b] Modeling Centre, Lebanese University, Beirut, Lebanon

ARTICLE INFO

Keywords:
Pyrolysis
Polyethylene
Polypropylene
Catalytic cracking
USY-Zeolite
Alternative fuels

ABSTRACT

Thermal catalytic and non catalytic degradation of polyethylene (PE) and polypropylene (PP) were carried out in a batch reactor at 450 °C. The major product obtained from the non-catalytic pyrolysis of PE was 80 wt% of wax, while the degradation of PP without any catalyst produced 85.5% of liquid. In catalytic degradation, ultra-stable Y (USY) zeolite was used in a ratio of 1:10, with respect to PE and PP. In both cases, polymers were converted to liquid products with high yields (71 and 82 wt% respectively) and a low amount of coke deposit has appeared. The liquid fraction derived from the catalytic pyrolysis of PE was a mixture of C_5-C_{39} compounds and that of PP was a mixture of C_5-$C_{30.}$ This wide range of components suggests the separation of liquids into two phases in order to use them as diesel-like and gasoline-like fuels. Three temperatures of separation (130, 150, 170 °C) were tested and the physical properties were compared. Among the tested temperatures, 170 °C was the optimal temperature of separation where the distillation curves and physical properties of the light and heavy phases fitted completely those of gasoline and diesel fuels, respectively. After separation, the gasoline-like fuel which represents 60.6% of the total oil of PP and 57% of that of PE had high octane numbers (RON = 96 and RON = 97, respectively), while the diesel-like fuel which accounts for 36.5% of the total oil of PP and 35.3% of that of PE have high calculated cetane numbers (52 and 53, respectively).

1. Introduction

Due to rapid urbanization and economic development, the world's annual production of plastic materials has increased from around 1.7 million tons in the 1950s to nearly 311 million tons, of which 59 million tons are accounted for by Europe alone [1]. Due to the increase in generation, waste plastics are becoming a major stream in solid wastes, generating heavy environmental problems.

There are six main plastic components in European municipal solid waste which are high-density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC) and polyethyleneterephthalate (PET). Polyolefin materials (PE and PP) constitute the majority of plastic wastes and represent around 68% of the municipal solid wastes [2].

A major part of post consumer plastic wastes are currently landfilled or incinerated. Since these wastes are non biodegradable and the areas for landfill sites are limited, landfilling is not a suitable option for disposing plastic wastes. In addition, the use of incinerator have high cost consumption, and generates some pollutants to the air like nitrous and sulfur oxides, dusts, dioxins and furan [3]. Therefore, in order to reduce environmental charge, recycling and recovering methods should be employed. Pyrolysis is a recovery method that consists on upgrading plastic wastes into fuel oil and valuable chemicals by heating at temperature range of 400–600 °C in the absence of oxygen [4].

Thermal and catalytic degradation of waste plastics are two kinds of chemical valorization processes. The presence of catalysts in pyrolysis reduces reaction temperature and residence time, decreases energy consumption, promotes decomposition reaction and improves selectivity and the quality of the products [5].

Pyrolysis of waste polyethylene has been investigated by many researchers who found that waxes are the main products in thermal cracking. Waxes derived from thermal cracking of PE are long chain made up of linear hydrocarbons having a carbon number heavier than C_{20} and which solidify at room temperature [6]. Kiran et al. [7] studied the pyrolysis of waste polyethylene in a fixed bed reactor, at a low heating rate and reaching 600 °C. Gas and wax were the two main products obtained during the pyrolysis experiments. The wax formed caused an operating problem by plugging the product lines and condenser tubes.

In order to improve the quality of the liquid fuel produced from the

---

[*] Corresponding author.
E-mail address: sary.awad@gmail.com (S. Awad).

http://dx.doi.org/10.1016/j.jaap.2017.09.005
Received 31 January 2017; Received in revised form 3 August 2017; Accepted 6 September 2017

degradation of plastics, a range of catalysts have been utilized in the catalytic degradation of polymers. The most commonly used catalysts are solid acid ones such as zeolites and silica–alumina [8]. Lerici et al. [9] studied thermocatalytic degradation of polyethylene, polypropylene (PP) and polystyrene (PS) using the H-Y zeolite in a batch reactor at 500 °C. They reported that thermal cracking of polyolefins produced waxes and the use of catalyst yielded higher percentages of gaseous products which ranged between 42 wt% and 45 wt%, while PS yielded a greater amount of liquids (~72 wt%).

A number of authors have reported promising results on the cracking of polyolefins over several catalysts. Onu et al. [10] compared the degradation of polyethylene and polypropylene over HZSM-5 zeolite catalyst and a catalyst modified with orthophosphoric acid (PZSM-5) in a fixed bed reactor at 460–480 °C. According to their study, the quantities of liquid products with PZSM-5 are smaller than those obtained over HZSM-5 for both PP (43.3%) and PE (34.6%), and all of the liquids had high proportions of aromatic hydrocarbons.

The cracking ability of a catalyst is related to the acidity strength and the pore size which represent its main characteristics [11]. Strong acid catalysts enhance the cracking of heavier hydrocarbons into more lighter or gaseous hydrocarbons comparing to the weak acid catalysts. This was reported by Sakata et al. [12] who studied the catalytic degradation of HDPE into fuel oil over mesoporous silica (KFS-16) catalyst at 430 °C. The Product yields and composition were compared with those obtained over solid acid catalyst (silica–alumina and ZSM-5). According to their study, ZSM-5 possessing strong acid sites produced less liquid products and more gaseous products than the silica-alumina catalysts. On the other hand, KFS-16, having no acid sites, produced liquid hydrocarbons with a high yield as 71 wt%.

Sakata et al. [13] also investigated the effects of various types of solid acid catalysts such as silica–alumina, zeolite and non-acidic mesoporous silica catalysts on the degradation of polyethylene and polypropylene at 430 and 380 °C respectively in batch operation. The degradation of PP and PE into gases was accelerated when using catalysts with strong acid sites such as zeolite ZSM-5.

A number of authors have investigated the use of USY zeolite in the catalytic degradation of polyethylene and polypropylene [2,14,15]. They reported that large-pore USY zeolite produced the highest amount of liquid fraction compared to other tested catalysts like ZSM-5 zeolite which favored gas production. Moreover, the hydrocarbons formed over USY zeolite were heavier than those formed with medium-pore zeolites and the main products were alkanes with less alkenes and aromatics.

The main disadvantage of using zeolite catalyst is coke formation which is due to the deposit of heavy by-products on the catalyst surface. Coke formation occurs during catalytic reactions and causes the gradual deactivation of the catalyst which also affects the product distribution and selectivity [16]. Several authors investigated the deactivation of zeolites in polymer cracking.

Marcilla et al. [17] studied the deactivation of HZSM5 and HUSY zeolites during the catalytic pyrolysis of polyethylene and reported that HUSY showed a higher initial relative activity as it presents large pore size but it lead to a fast deactivation, while small pore size in HZSM5 prevented coke deposition.

Previous studies have compared the thermal and catalytic degradation of polyethylene and polypropylene, but most of these works were performed using catalysts that favored gas production [18] and did not focused on the quality of the liquid fraction produced. In the present work, the main objectives were to produce useful fuels from PE and PP over USY zeolite which enhance liquid formation and to investigate the quality of the liquid fraction produced. Furthermore, the influence of USY zeolite on the yield and composition of the derived oils from catalytic cracking of PP and PE was studied. Moreover, the separation of the pyrolytic oils of PP and PE into light, gasoline-like and heavy, diesel-like fractions was studied in order to find a single temperature where the boiling range distributions and physical properties of each fraction meet the gasoline and diesel fuels standards.

Table 1
Textural and acid properties of the USY zeolite.

SiO_2/Al_2O_3 (mol/mol)	15
BET surface area ($m^2\ g^{-1}$)	550
Na_2O (wt%)	0.05
Micropore volume (MPV) ($cm^3\ g^{-1}$)	0.1
Crystal size (μm)	0.7–1.0
Total acidity (mmol $NH_3\ g^{-1}$)	0.1

2. Experimental

2.1. Materials and methods

The feedstock samples for the present study were virgin plastic mainly made of PE and PP plastic types respectively thus the material variability can be eliminated. All of these plastics were granular with a particle size of, approximately, 1.8 mm–4.5 mm.

The catalyst used for the pyrolysis experiments was a commercial USY zeolite provided by TOSOH Corporation. Their main characteristics are presented in table 1. This zeolite has been selected for its medium Si/Al ratio (7.5). Indeed, for low Si/Al ratios, the number of acid sites will increase, but their strength remains relatively less pronounced. However, a higher Si/Al ratio induces a drastic decrease of the number of acid sites. In this case, “isolated” acide sites will be more reactive. Hence, the selected Si/Al ratio seems to be a good compromise in order to enhance liquid production at the expense of gases [19].

The catalyst was dried in an oven to remove moisture, and then was sieved in order to have a particle size between 200 and 800 μm. In the catalytic pyrolysis experiments the plastic/catalyst mass ratio was 10/1.

2.2. Laboratory scale pyrolysis plant

Pyrolysis reactions were led in a laboratory scale batch reactor, developed by Pyrum Innovations (Fig. 1). The reactor is 200 mm height with 90 mm diameter made of steel and heated by an electric coil with a power of 1100 W, which is connected to a programmable temperature controller. The reactor is thermally insulated with ceramic wool jacket. A thermocouple in direct contact with the sample was used to monitor the actual temperature of the process.

Prior to the experiment, the system was purged for 15 min with nitrogen (N_2) at room temperature to ensure an inert atmosphere, and then 2 series of experiments were carried out. In the first series, 100 g of PP and PE were loaded individually without any catalyst into the reactor, while in the second series; 100 g of PP and PE were mixed individually with 10 g of catalyst and loaded into the reactor. The temperature of the reactor was then raised from ambient temperature to 450 °C. The pyrolysis products pass through a stainless steel condenser cooled with tap water at 15 °C and then, the condensate is collected in a container. The uncondensed gases are discharged through an exhaust system. The products of degradation were classified into three groups: liquid products, gaseous products and residues. The liquid fraction was then characterized in order to be used as an alternative fuel oil. For this purpose liquid product was fractioned at different temperatures to find the optimal temperature for separating the liquid into gasoline-like and diesel-like oil fractions.

2.3. Liquid products characterization

The samples were analyzed to determine the main parameters. The calorific value of the samples was measured using a Parr 6200 calorimeter. The density of the pyrolytic oil was measured at room