Fuel 224 (2018) 764–773

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Gasoline and diesel-like fuel production by continuous catalytic pyrolysis of waste polyethylene and polypropylene mixtures over USY zeolite

Chantal Kassargy[a,b], Sary Awad[a,*], Gaëtan 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:
Catalytic pyrolysis
Polyethylene-polypropylene mixtures
USY-zeolite
Alternative fuels

ABSTRACT

Catalytic degradation of polypropylene (PP), polyethylene (PE) and their mixtures with different proportions (20:80, 50:50, and 80:20) using USY zeolite, was studied in a continuous pilot plant at 500 °C, with a plastic/catalyst ratio of 10:1. The liquid fraction derived from the catalytic pyrolysis of PP and that of PE was dominated by a (C_5–C_7) hydrocarbons fraction, while the gaseous products for both materials were dominated by C_3 and C_4. Based on the Gas chromatography analysis and the distillation curves, no synergetic effect was observed for different mixture compositions. As pyrolysis products of PP and PE cover a wide range of hydrocarbons, a separation into different fractions was suggested before using them as fuels.

The separation temperatures were optimized and it was found that 160 °C is the temperature at which the boiling point distribution and physical properties of light fraction of both PP and PE products can be compatible with gasoline fuel norms, and 220 °C is the temperature at which heavy fractions are compatible with diesel fuel norms. Since there is no interaction between plastics during reaction, the oil derivate from a 50%-50% mixture of PP-PE has been separated at the same temperatures and its characteristics lie between that of PP and PE. Despite that the obtained gasoline-like fraction, which represents 49% of the total oil of the 50%-50% mixture of PP-PE has a very low content in aromatics, it presents a relatively high octane number (RON = 89.8). While the diesel-like fraction which represents 20% of the total oil has a cetane number of 45.1. Finally, from 1 kg of PP for example, having an energy content of 46.4 MJ, 34.3 MJ of liquid and 8.8 MJ of gas were produced. The gasoline-like phase has an energy content of 18 MJ, the intermediate phase possesses an energetic content of 10.7 MJ while the diesel-like phase having an energy content of 6.7 MJ, could generate an electrical energy of 0.53 kWh.

1. Introduction

Waste plastics are more generated as the rate of consumption of plastic materials in the world is increasing. Recently in Europe, plastics waste accounted for 25.8 million tons in municipal solid wastes. In fact, during 2014, only 29% of collected plastic wastes were recycled in Europe while 40% were incinerated and 31% were disposed in landfills. Around half of the overall plastic production consists of polyolefins, namely, high density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP) [1].

Since plastics are not biodegradable, incineration and landfilling can contribute to health and environmental problems by causing toxic emissions harmful for human and wild life [2]. In addition, plastics' recycling is limited because of additives included during manufacturing in order to improve the quality and properties of the product. Since those substances cannot be separated or removed at the end of the product life, the quality of recycled products are reduced or even recycling has become completely impossible [3]. Pyrolysis has become a promising technology to produce hydrocarbon fuels by thermal degradation of plastics under an inert environment and at moderate temperature (430–550 °C) [4].

In order to improve the quality of the liquid fuel produced from the degradation of plastics, catalysts have been used in pyrolysis. Catalyst presents number of advantages such as (1) decreasing the reaction temperature and thus reducing the activation energy for breaking C–C bonds, (2) decreasing the residence time of plastics in the reactor, (3) improving the selectivity of the liquid by producing lower molecular weight species in the range of gasoline [5]. Solid acid catalysts such as zeolite ZSM-5 [6], Y-zeolite [7] and MCM-41[8] are the most commonly used materials. The reactions that occur in the presence of these catalysts include carbocationic cracking of pyrolysis volatiles, isomerisation, oligomerisation, cyclisation and aromatization reactions [9]. The acid content and porosity are the main characteristics of the catalysts which determine their cracking ability. The pore size and

---

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

https://doi.org/10.1016/j.fuel.2018.03.113
Received 10 November 2017; Received in revised form 14 March 2018; Accepted 15 March 2018

shape of the catalyst play a major role in the diffusion and cracking of the large molecules obtained from the degradation of the polymer to the acid sites of the catalyst. Therefore, the product distribution is influenced by the porosity of the catalyst: a low degree of cracking leads to a high yield of liquid products due to a fast diffusion of cracked products. As the degraded molecules remain longer in the pores of the catalyst, a higher gas yield is obtained due to the over-cracking [10]. Marcilla et al. [11] studied the degradation of PE in a batch process over HZSM-5 and HY zeolites at 550 °C. The main product obtained with HZSM-5 zeolite was gas while liquid and coke were more abundant with HUSY. They concluded that structure and acidity of the catalysts affect the molecular weight distribution of the product. The degradation of PE over several solid acid catalysts (SA, ZSM-5, Y zeolite, and NZ) in a fixed-bed semi-batch reactor at 450 °C was reported by Park et al. [12]. Between all the tested catalysts, HZSM-5 catalysts produced a much greater yield of gas and this was attributed to its structure which promotes the diffusion and cracking of the fragments in the pore.

The cracking activity of the catalyst is related to its acidity. Akpanudoh et al. [13] observed the influence of the acidity content of USY zeolite on the cracking of polyethylene. They concluded that liquid yield increased with acidity content to reach the maximum acidity values around 7%. Above this value, gas yield increased due to excessive cracking while below this value, polymer was not completely converted because of lack in acid sites.

Catalytic degradation of polyolefins over different catalysts (MCM-41, silica-alumina and HZSM-5 zeolite) in continuous pyrolysis was studied by a number of researchers who used furnaces or electric source to heat the reactor.

Elordi et al. [14] studied the catalytic cracking of polyolefins (HDPE, LDPE, and PP) in a conical spouted bed reactor, in a temperature range of 450–570 °C, in a continuous mode with polyolefin flow rates between 1 and 2 $g.min^{-1}$ and feeding up to 1 kg of polyolefin into a 30 g HZSM-5 zeolite catalyst bed. They reported that 500 °C is the minimal temperature to avoid the operational problems related to the wax formation. Thermal and catalytic cracking of low-density polyethylene (LDPE) over Al-MCM-41 using a screw kiln reactor was reported by Aguado et al. [15]. Hydrocarbons within the gasoline range (C_5–C_{12}) were obtained in the presence of Al-MCM-41 catalyst and the product output increased to 41 $g.h^{-1}$ when the screw speed varied to 15 rpm. Artetxe et al. [16] proposed a two-step (thermal and catalytic) system involving a conical spouted bed reactor followed by a catalytic fixed bed reactor to study the catalytic pyrolysis of HDPE. They found that increasing the residence time and temperature has a significant effect on product distribution with increasing the yield of light olefins and decreasing the yield of waxes.

The aim of the present study was to develop a continuous process for fuel production from plastic wastes, via pyrolysis, using the exhaust gas residual heat of a diesel engine as a source of heat. For this purpose, a reactor that was designed and built in IMT-Atlantique laboratories was used in this study. The influence of using Ultra-stable Y (USY) zeolite on the yield and composition of the gases and oils produced in catalytic pyrolysis of PE, PP and their mixtures in different proportions (50:50, 80:20 and 20:80) has been investigated. In addition, catalytic pyrolysis products obtained from mixtures of PP and PE were analyzed using gas chromatography analysis and distillation curves. Moreover, finding a single temperature T_1 at which the light fraction of both PP and PE products can be compatible with gasoline fuel norms and a temperature T_2 at which they are compatible with diesel fuel norms was established as well as the physical properties of each phase were measured at the optimal temperature of separation. Finally, mass and energy balances of the process were reported.

Table 1
Elemental composition of raw material.

Raw material	Elemental compositions				
	%C	%H	%N	%S	%O
PE	86,23	14,43	–	–	–
PP	86,44	14,46	–	–	–

2. Experimental

2.1. Materials

PP and PE samples were gathered from municipal waste collection facility. Feedstock was washed, dried and crushed into small pieces (< 6 mm) in order to get a homogeneous mixture.

The elemental compositions (C, H, N and O) of these plastics, presented in Table 1, were analyzed by a Thermo Electron Flash EA1112 elemental analyzer.

The elemental analysis showed that both the PP and PE fractions consisted mainly of carbon and hydrogen and by heating them in a muffle furnace at a temperature of 800 °C, no deposit of ash was recovered.

The catalyst used for the pyrolysis experiments was a commercial USY zeolite purchased from TOSOH Corporation. Its main characteristics are presented in table 2. 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

A schematic representation of the continuous pilot plant used in this study, which has been designed and built in IMT-Atlantique laboratories, is shown in Fig. 1. The plastic degradation takes place in a vertical reactor, with 800 mm of length and 104 mm of diameter, heated up to 500 °C, using the exhaust heat of a diesel engine. Prior to the reaction, plastic waste mixed with catalyst was fed by gravity into a screw conveyor which is slightly inclined and heated in order to reach the melting temperature of plastic.

After plastic pyrolysis, the produced vapors pass through a condenser cooled with tap water at 15 °C and the condensate is collected in a receptacle. Samples of non-condensable products were collected before being vented through an exhaust system.

2.3. Liquid products characterization

The samples were analyzed to determine the main parameters. The separation of pyrolytic oils was conducted using a NORMALAB NDI440 automatic distiller. Densities of light and heavy fractions were measured at 15 °C using a pycnometer M50T. An AND vibro-viscometer was used to measure the viscosity of the heavy fraction produced in each experiment at 40 °C, while its flash point was measured using a PENSKY MARTENS NPM440 device with a precision of 2 °C. A vapor pressure analyzer ERAVAP using ASTM D6378 testing method was used to measure the vapor pressure of the light fraction. The analyses were

Table 2
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