



Study on mild cracking of polyolefins to liquid hydrocarbons in a closed batch reactor for subsequent olefin recovery



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ABSTRACT

The polyolefins mild cracking experiments have been carried out in a closed batch reactor under inert nitrogen atmosphere over a temperature range from 370 °C to 420 °C and the characterization of the mild cracking products has been investigated. The objective of this work is to study the cracking mechanism and reaction path for the mild cracking of polyolefins with lower heating rate (the isothermal and non-isothermal process), and to find the appropriate operating conditions (temperature and residence time) for optimal yield of liquid hydrocarbons (oils/waxes) as the suitable feedstock of olefin recovery. The advantages of this work can be summarized as high yield of light fraction, low aromatics content and mild cracking conditions. More viscosity-reducing and less volatiles-loss can be simultaneously achieved in mild cracking of polyolefins by selecting the reasonable residence time-temperature combination. The results confirm that chain scission reactions are significantly predominant in these experimental conditions. Intramolecular hydrogen transfer and intermolecular hydrogen transfer, which are responsible for the reduction in molecular weight of liquid products, can be improved in lower temperature and longer residence time, and intermolecular hydrogen transfer can also be enhanced in the PE/PP mixture cracking. For polyolefins mixture cracking, the cracking temperature can be reduced about 20 °C, or the cracking time can be shortened significantly, and so utilizing the whole polyolefins mixture without a need of further separation is very desirable in the chemical recycling.

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1. Introduction

Plastics in modern society make a fundamental contribution to all major daily life. In Europe, the plastic industry has grown continuously for over 50 years, with the average annual growth of around 9%, and the consumption of plastics has doubled every decade since 1970s [1]. And the consumption of plastics in China has increased from 3.4 Mt in 1990 to 42.5 Mt in 2008 and the plastic wastes including those from producing process are appropriately 18 ~ 21 Mt a⁻¹ [2]. High and low density polyethylene (HDPE and LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) are main plastics in municipal solid waste. The former three plastics (HDPE, LDPE and PP) belong to polyolefin (PO) and generally make up a majority of

the plastic waste [3,4]. Pyrolysis or cracking of polyolefin in absence of air or oxygen has been widely studied in recent years [5–8] which takes place through a complex free-radical mechanism [9] and yields hydrocarbon waxes and oils, aromatics and gaseous olefins (ethylene and propylene etc.) at different conditions [10,11]. Converting waste polyolefin to light olefins, which is called as monomer recovery, is significantly important from two points of view: it is a supplement of the conventional feedstock in steam cracking, and will close the life-cycle of material.

In terms of monomer recovery process, waste polyolefin can either be pyrolyzed directly into light olefins at conditions of high temperature and short residence time in the one-step process, or be thermally decomposed into liquid hydrocarbons as the first step of two-step process and further be, as the second step, pyrolyzed into light olefins at high temperature.

Most of the one-step processes were completed using fluidized bed or similar reactor with small size of feed particle. Kaminsky et al. [12] and Simon et al. [13] received high yields of olefins at 700 °C in Hamburg pyrolysis process. Mastral et al. [14,15]

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discussed the influence of temperature and residence time on the pyrolysis of HDPE and obtained high ethylene yield at 780 °C. Scott et al. [16] obtained high ethylene yield by fast pyrolysis of linear low density polyethylene (LLDPE) at 790 °C. Other one-step processes were studied by Lovett et al. [17], Milne et al. [18] and Williams et al. [19]. Unfortunately, for the one-step process, the low thermal conductivity and high viscosity of molten polyolefin is always a huge challenge for converting solid feedstock into gaseous olefins at high temperature in a short time.

Two-step process which splits the degradation process into two separate steps has been investigated quite extensively. A two-step process consisting of a thermal pretreatment step at 350 ~ 550 °C and a thermal treatment step at 700 ~ 1100 °C was proposed by Hover et al. [20]. In the tubular reactor setup designed by Westerhout et al. [21], polyolefin was converted to a wax-like intermediate in the first tubular reactor and further converted to light olefins in the second tubular reactor. Zassa et al. [22] investigated the effect of devolatilization heating policy of the first step on the final pyrolysis yields in a two-step process. Artetxe et al. [23,24] achieved a selective high yield of waxes (C21+) in the first step of their consecutive two-step process by using the conical spouted-bed reactor (CSBR) at 500 °C.

The two-step process can also be developed as two separated sequential sub-processes. Angyal et al. [25] developed the two-step process as a cracking sub-process of PE or PP/PE and a subsequent steam cracking sub-process of light and middle distillates. Similar process was conducted by Stabel et al. [26]. In addition, co-cracking or co-pyrolysis made the two-step process be a favorable combination with the conventional steam cracking. Kirkwood et al. [27] realized the polymer cracking by connected fluidized bed reactor and steam cracker. Hajekova et al. [28] and Mlynkova et al. [29] concentrated their studies on the co-pyrolysis in the second step, where polyolefin decomposed oils/waxes were mixed with heavy naphtha and pyrolyzed in a steam cracker.

The influence of reaction conditions on the composition of oils/waxes produced in the first step is often the key points of increasing the yield of light olefins in whole two-step process, due to the relation between the yield of light olefins and the composition of feedstock [30]. Williams et al. [19] came to the conclusion that the wax produced from thermal decomposition of LDPE was a pure aliphatic material without aromatics and could be used as substitute for petroleum derived feedstock. Onwudili et al. [31] indicated that LDPE dominantly converted to liquid aliphatic hydrocarbons in a closed batch reactor at 425 °C, and the amount of aromatic would highly increase to be the main components at 500 °C. Predel et al. [32] indicated that it could obtain more usable aliphatic waxes by cracking of PP than by cracking of PE. The thermal pyrolysis study by Arabiourrutia et al. [33] indicated that waxes with a boiling point lower than 500 °C were valuable feedstock for steam cracking. Lopez et al. [34] considered that the generation of aromatics and unsaturated hydrocarbons in their cracking study by semi-batch reactor was possibly resulted from uneven heating in the unstirred batch. It is also reported that the pyrolysis can be accelerated and led to decomposition products with a shorter chain length by adding some PS to polyolefins [35]. The experimental studies by McCaffrey et al. [36] indicated that copyrolysis of PS/PE would be no more difficult than reacting the individual polymers. Ballice [37] found that the conversion of volatile hydrocarbons will be higher with increasing PP in the co-pyrolysis of LDPE/PP. However, no obvious product-changing interaction between PE and PP was observed by Predel et al. [32] and Westerhout et al. [38].

There are many studies about thermal or catalytic cracking of polyolefins for the fuel production [39], but it is seldom found there is discussion on the mild cracking of polyolefins under moderate condition (370 ~ 420 °C) in closed batch reactor, in order to obtain

higher yield of low-viscosity liquid hydrocarbons as suitable feedstock of olefin recovery by high temperature pyrolysis. The main objective of this work is to convert the polyolefins to liquid hydrocarbons for use as feedstock of subsequent olefin recovery by high temperature pyrolysis. The effects of temperature and residence time have been studied to find the appropriate operating conditions necessary for optimal yield of liquid hydrocarbons (oils/waxes) as the suitable feedstock of olefin (ethylene and propylene) recovery. The kinetic scheme for the mild cracking of polyolefins in a closed batch reactor under the isothermal and non-isothermal process, though the processes occurring in a reactor are much more complex, has also been investigated to help in understanding the mechanisms for polyolefin mild cracking, and to ascertain the predominant steps in the reaction scheme as the reaction conditions change.

2. Experimental section

2.1. Materials

High density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP) in the form of 2 ~ 4 mm grains, manufactured by Sinopec Beijing YanShan Company (Beijing, China), were used in this work as experimental materials. Their main properties are presented in Table 1.

2.2. Mild cracking reactor system

In this study, the mild cracking of polyolefins was performed in a closed batch reactor under nitrogen atmosphere. The mild cracking apparatus is shown in Fig. 1.

The reactor consists of a 1000 ml stainless steel vessel externally heated by an electric ring furnace and it is stirred using the magnetic drive to strengthen the heat-transfer. The reactor vessel is fitted with a purging gas inlet valve, a purging gas discharge valve and a gas sampling valve. The reactor is equipped with a pressure gauge to measure the internal pressure while the experiments are performed. The cooling water coil is arranged in the container to cool the reactor quickly at the end of reaction. The controller is used to control the reaction temperature and stirring apparatus. And a software developed by Xinranda company is used to complete the data acquisition.

2.3. Experimental procedure and conditions

About 200 g of PE or PE/PP sample were used in each cracking experiment. The fraction of PE in PE/PP mixture was established according to the distribution of plastics in municipal solid waste in Japan [40]. The reactor was purged by nitrogen to prevent the presence of air in the reactor before the cracking experiment started. In the cracking experiments, the reactor system was heated at rate of 3 ~ 5 °C min⁻¹.

Two series of experimental conditions, as shown in Table 2, were designed in order to study the mild cracking of polyolefins mixture at isothermal (set cracking temperature) and non-isothermal (from 200 °C to set cracking temperature) conditions in a closed batch reactor.

Table 1
Typical properties of polyolefins used in this work.

Polyolefin	Type	Density (20 °C), kg m ⁻³	Melt flow index, g (10 min) ⁻¹
HDPE	5000S	0.950	1
LDPE	LD100AC	0.923	2
PP	K7726	0.905	27

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