Journal of Analytical and Applied Pyrolysis 95 (2012) 198–204

Contents lists available at SciVerse ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

The effect of temperature, catalyst, different carrier gases and stirrer on the produced transportation hydrocarbons of LLDPE degradation in a stirred reactor

Mehrdad Seifali Abbas-Abadi*, Mehdi Nekoomanesh Haghighi, Hamid Yeganeh

Polymerization Engineering Department, Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965/115, Tehran, Iran

ARTICLE INFO

Article history:
Received 29 December 2011
Accepted 11 February 2012
Available online 19 February 2012

Keywords:
LLDPE
Pyrolysis
FCC
Stirred reactor
Carrier gas
Stirring rate

ABSTRACT

The pyrolysis of linear low density polyethylene (LLDPE) by used fluid catalytic cracking (FCC) catalyst was studied in a stirred reactor to reach the appropriate transportation hydrocarbons. In this work, the effect of process parameters such as degradation temperature, catalyst/polymer ratio (%), carrier gas type and stirring rate on the condensed yield, product composition and residence time were considered. Product evaluation was performed by GC analyzer and paraffin, naphthene, olefin and aromatic plus carbon number and average molecular weight of the products were measured under different process parameters.

Temperature and catalyst as the basic parameters show remarkable effect on the LLDPE cracking. The maximum transportation condensate yield reaches at 450 °C and 20% catalyst respectively although increase of temperature and catalyst content, decrease the residence time patently. Based on the results, molecular weight and reactivity of the carrier gas as mass transfer factor also play a key role in the process. A decrease in molecular weight of the carrier gas led to increase the condensate yield and decrease the residence time. Meanwhile increasing of the carrier gas reactivity could increase the condensate hydrocarbons. Hydrogen as reactive and lower molecular weight carrier gas increases the condensed yield patently. The study showed that stirring rate as a function of heat transfer and temperature homogenizer also affects on the condensate hydrocarbons positively. The maximum condensate yield was found to occur at 50 rpm although the residence time decreases with stirring rate increasing.

1. Introduction

Linear low density polyethylene (LLDPE) was first commercialized in the late 1970s by Union Carbide and Dow Chemical. Since that first introduction, LLDPE has seen the fastest growth rate in usage of the three major polyethylene families – low density polyethylene (LDPE), LLDPE, and high density polyethylene (HDPE) – and now comprises approximately 25% of the annual production of polyethylene around the world [1].

Today, plastics provide a fundamental contribution to our society. This kind of material is very frequent in daily life as it is found in food packaging, electricity industry, toy industry, containers, etc. The huge amount of plastic waste that resulted from the dramatic increase in polymer production gives rise to serious environmental concerns, as plastic does not degrade and remains in the municipal refuse tips for decades. Meanwhile plastic waste being more voluminous than organic waste in which they take up a lot of landfill space and are becoming a scare to environment [2]. On the other hand incineration of waste polymers results in environmental danger because of emissions of very different combustion products. Therefore, the chemical degradation of waste polymers towards clean liquid fuel or valuable chemicals has been undertaken in many papers [3–11].

Pyrolysis is an established process that can potentially be used to convert plastics to more valuable chemicals and fuels [12–15]. It is a thermal degradation of the thermoplastic polymers to produce a char, oil, and gas, all of which have potential as useful end products. There have been many studies on the pyrolysis of pure plastic materials [16,17] and mixtures of pure plastic [13,18–21].

Catalysts can promote the pyrolysis reaction to occur at lower temperatures, which implies lower energy consumptions [22]. It is certainly possible to develop commercial processes based on used fluid catalytic cracking (FCC). Therefore, a more interesting approach is that of adding polymer waste into the FCC process, under suitable process conditions with the use of zero value of used FCC catalysts, a large number of waste plastics can be economically converted into valuable hydrocarbons [23,24].

The yield and composition of pyrolysis products (non condensable, condensed and char) are highly dependent on the process temperature. It seems that it can be actively used at elevated temperatures in some reactions, such as in the Diels–Alder reaction. The formation of aromatics in the pyrolysis of polyolefin was

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* Corresponding author. Tel.: +98 02144580000x2168; fax: +98 02144580021 23.
E-mail address: M.Seyfali@IPPI.ac.ir (M.S. Abbas-Abadi).

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doi:10.1016/j.jaap.2012.02.007

accomplished using the Diels–Alder reaction, followed by dehydrogenation [25–28].

In summary, the review of the results from the literature shows the strong dependence of the carbonization products in relation to the main process parameters such as final temperature, catalyst type, polymer/catalyst ratio, pressure, heating rate and residence time. But the reports on the other process parameters like carrier gas and stirring rate as function of mass and heat transfer are very few.

Liquefaction of waste plastics has been undertaken by several investigators, involving reactions in autoclave high temperature and pressure reactors in the presence of hydrogen, or a hydrogen donor such as tetralin or oil and/or the presence of catalysts [29].

Stirring of the melt in a pyrolysis vessel greatly accelerates the heat transfer process and it can help the process for better energy saving and temperature homogeneity. Discontinuous (batch process) and continuous (alternating batch or cascade) stirred reactors are generally used in commercial-scale melt-phase pyrolysis plants. These units are relatively simple, basically consisting of a large stainless steel vessel with indirect heating (either flame or hot air), a large stirrer and possibly internals such as baffles to enhance mixing and heat exchanger surfaces [30].

The first goal of this study is to investigate the degradation temperature effect on the residence time, condensed yield and composition of LLDPE catalytic degradation using GC analyzer.

Next, this paper reports on the used FCC catalytic decomposition of LLDPE and consideration of catalyst/polymer ratio effect on the residence time, condensed yield and composition using GC analyzer. However the study on the effect of temperature and FCC catalyst on the polyolefin degradation is very much but for better comparison with carrier gas and stirrer effect, the results in this area are reported.

Furthermore relates to explore the results of a further study of polymer degradation over different carrier gas. More specifically it reports on the effect of the carrier gas molecular weight and reactivity on the residence time, yield of condensed hydrocarbons and their quality, as measured by the carbon number and average molecular weight of the condensed hydrocarbons.

An additional goal is to the effect of stirrer presence and rate on the reactor degradation of LLDPE under different stirrer rates beside the other process parameters on the residence time, condensed hydrocarbons composition of LLDPE pyrolysis.

Table 1
The specification of used FCC catalyst used in the catalytic degradation of LLDPE.

Surface area (BET)	235 m^2/g
SiO_2	80.10%
Al_2O_3	13.40%
Na	0.30%
Ca	1.54%
Si/Al	6

2. Experimental

2.1. Material

Linear low density polyethylene – "50035" grade – is supplied by Sabic petrochemical company (Saudi Arabia). Ethylene and propylene (purity 99.9%) are supplied by Tehran Petrochemical Company (Tehran, Iran). Nitrogen, argon, hydrogen and helium gas (purity 99.99%) are supplied by Roham Co.

2.2. Instruments

2.2.1. Pyrolysis process

The degradation experiments with virgin LLDPE was carried out in a 1 L stirred semi-batch reactor under atmospheric pressure and the schematic diagram is shown in Fig. 1. The fixed experimental conditions are as follows: LLDPE reactant amount of 100 g, FCC catalyst (as shown in Table 1) and carrier gas stream of 300 ml min^{-1}, heating rate of about 25 °C min^{-1} up to the final temperature. The non condensable products are vented after cooling by three condensers. The condensed hydrocarbons of each sample were stored in two small sampling bottles. The components of total condensed hydrocarbons–residue in the condenser tankers contain C3 to C15 were quantified and qualified by gas chromatography; however the non condensable products are not analyzed. The results show that the condensed hydrocarbons contain a little C3 compounds. The solid yield was determined after the reaction was finished and defined as the ratio of the solid amount produced to the initial reactant amount. The non condensable yield was calculated by subtracting the weight of the condensed hydrocarbons and solid products from the sample weight.

Paraffin, olefin, naphthene and aromatic hydrocarbons are analyzed in the condensed hydrocarbons samples by modified isotopedilution GC mass spectrometry method.

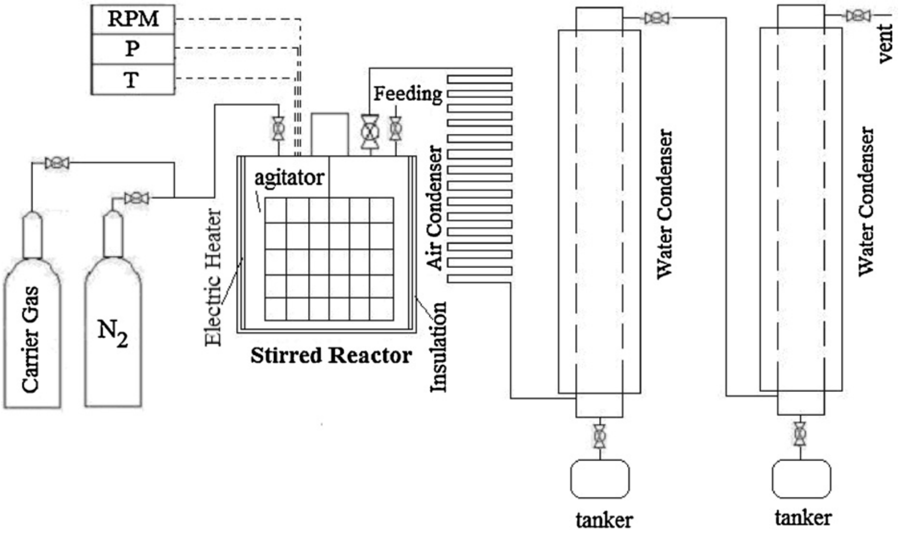

Fig. 1. Flow scheme of the laboratory stirred reactor.