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PETROCHEMICA



(Journal of Petroleum, Chemical and Control Engineering)

Conversion of Waste Solid plastic to Biofuel by Catalytic Degradation

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ARTICLE INFO: Volume: 01, Issue: 02, Pages from 006 to 013, No. of Pages: 008
Received: 02.06.2020, Revised: 20.08.2020, Accepted: 18.12.2020COR. AUTHOR: (Amritha B) amrithabaskar29@gmail.com© ASSVET International Publishing Co., All Rights Reserved

Abstract:

Without saving of fossil energy like crude oil, natural gas, or coal the present rate of economic growth is unsustainable. Biomass, hydropower, and wind energy are the alternatives to fossil fuel energy. Suitable waste management approach is another important aspect of developing biofuel. Waste is generated indirectly due to the development and modernization in all kind of products use in daily life. Plastics have been one of the materials because of their wide range of applications due to their adaptability and relatively low cost. This paper represents the present scenario of the plastic usage and methods of plastic solid waste (PSW) recycling. Recycling is divided into mainly four processes they are: primary, secondary, tertiary, and quaternary. Generally plastics have similar calorific value equivalent to that of fuel, so production of fuel from plastic by catalytic degradation would be a better solution. So the methods of converting plastic into fuel, specially pyrolysis and catalytic degradation, are the primary idea .Here we use a suitable catalyst is used to carry out the cracking reaction. The reaction due to the presence of catalyst generally lowers temperature and time. The process results in much lower product distribution of carbon atom number and higher at lighter hydrocarbons which occurs at lower temperature. The cost should be minimized to make the process more efficient from an economic perspective. The catalyst can be reused and the use of effective catalysts in lower amount can optimize this option. Here we are performing catalytic degradation with the help of certain catalyst so that minimal environment hazard is observed and higher calorific value of the crude is being obtained during the catalytic reaction. Here in this paper we are describing the mechanism and steps of catalytic pyrolysis of polyethylene and the stages are being elaborated and the list of catalysts used generally. Plastic has higher degradation and calorific value than any other waste material.

Keywords: Oil shale, recovery rate, Hydrocarbon, permeability

1. Introduction

In the environment the increased use of plastic products have higher remarkable impact on the environment due to the growing population rate. Due to increasing in their diverse and attractive applications in household and industries plastics have become indispensable material. Thermoplastics polymers make up a high proportion of waste due to this the amount is continuously increasing around the globe. Hence, waste plastics plays a very serious environmental challenge because of their huge quantity and disposal problem. Thermoplastics do not biodegrade for a very long time. The consumption of plastic materials is high and it is growing constantly in view of the advantages derived from their versatility, relatively low cost, and life. The derivative of polyolefin such as polyethylene and polypropylene, have greater consumption and production in many applications such as building, packaging, agriculture, and health care [1]. Disposal of waste plastics I a very serious environmental

problem due to the property of high durability, that is why land filling is mostly used as a disposal route. According to their origins, Plastic wastes can be classified as industrial and municipal plastic wastes; these groups have different qualities and properties and have different management methods. Plastic production growth worldwide is estimated at a rate of about 5% per year [4]. A potentially cheap source of chemicals and energy can be derived from Polymer waste. Due to release of harmful gases like dioxins, hydrogen chloride, airborne particles, and carbon dioxide, incineration of polymer causes severe air pollution problems. Because of high cost and poor biodegradability, it is not suitable to perform landfill at certain stages. Environmental challenges facing the plastic industry can be purely solved by Recycling. Recycling is performed mainly under 4 stages they are primary, secondary, tertiary, and quaternary recycling. The net cost of disposal can be performed by Chemical recycling, that is, conversion of waste plastics into feedstock or fuel that can alter the properties of plastic to that of fuel. The liquid hydrocarbons production from plastic degradation would be beneficial in that liquids are easily stored, handled, and transported. However, these aims are not easy to achieve [4]. An alternative idea to chemical recycling, which has attracted much favor recently, with the aim of converting waste plastics into basic petrochemicals is to be used as hydrocarbon feedstock or fuel for a various of downstream processes [3]. There are various methods of obtaining fuel from waste plastic are thermal degradation, catalytic cracking. [5].

2. Different Recycling Stages

1. Primary Recycling

It is also known as mechanical reprocessing. Here, the plastic waste is fed into the original production process of basic material. So that we can obtain the product with same specification as that of the original one. This process is obtained only with semi clean waste, so it is an unknown method with the recyclers. Degraded plastic waste partly substitutes the virgin material. So, the quality of the product decreases, on increasing the recycled plastic fraction in feed mixture. This type of recycling requires clean and uncontaminated waste which is of the same type as pure resin for these purpose. Steps in the primary recycling process are:

- Separation of this waste by specific type of resin and by different colors and then washing it properly,
- > The waste has better melting properties so it should be re extruded into pellets which can be added to the original resin.
- This type of recycling is very expensive because due to the requirements of particular plastic properties. If the waste can be easily resorted by resin but cannot be refrained due to mixed coloring contamination, then waste can be fed into the feed for molding application, and regarding reactants properties, it has less demanding in the market.

2. Secondary Recycling.

Secondary recycling uses PSW in the manufacturing of plastic products by mechanical means, which uses recyclates, fillers or virgin polymers. The objective of the process retaining energy which is used for plastic production to attain financial advantages. The secondary recycling process mainly uses contaminated or less separated waste. However, this waste has to be cleaned. The recycling process involves different products and it is completely different compared to the original production process.

3. Tertiary Recycling

This process is also known as cracking process. This process includes breaking down of plastics at high temperatures (thermal degradation) or at lower temperatures in the presence of catalyst (catalytic degradation), which contains smaller carbon chains. For any chemical production, the feedstock can be used as basic material of lower quality. The primary value of the raw material is losted. Due to high levels of waste contamination the tertiary recycling process is more important. Here we are able to recover the monomers of condensation polymers. Mechanisms like hydrolysis, methanolysis, or glycolysis can be used.

4. Quaternary Recycling.

The recovery of main energy content is being recovered here. As most plastic waste is incinerated because it has high heat content. Generation of the heat energy is the main advantage of this process. The incineration has residual of 20wt%, and 10 vol% of the original waste and are placed in landfills.



3. Pyrolysis process of converting plastic to fuel

3.1 Catalytic Degradation

The cracking reaction carry out by a suitable catalyst. The reaction temperature and time lowered due to the presence of catalyst. The process results in much narrower product distribution of carbon atom number and greater value at lighter hydrocarbons which occurs at lower temperatures. Further, the cost should be reduced to make the process more attractive from an economic perspective. Reuse of catalysts and the use of effective catalysts in lesser quantities can be optimized. This process can be developed into a cost-effective commercial polymer recycling process for solving the disposal of plastic waste. It also provides the higher cracking ability of plastics, and the lower concentration of solid residue in the product.

3.2 Mechanism of Catalytic Degradation

Catalytic degradation of polyolefin using TGA (Thermo gravimetric analysis) as a potential method for screening catalysts and have found that the presence of catalyst led to the decrease in the activation of apparent energy. Different mechanisms (ionic and free radical) for plastic pyrolysis proposed by different scientists are as given below. There are different steps in carbonium ion reaction mechanism such as H-transfer, chain/beta-scission, isomerization, alkylation, and aromatization which is influenced by acid site strength, density, and distribution [3]. Solid acid catalysts, such as zeolites, favor hydrogen transfer reactions due to the presence of many acid sites [5]. The majority of the acid sites in crystalline solid acids are located within the pores of the material, such as with zeolites [3]. Thus, main feature in assessing the level of polyolefin cracking over such catalysts is the micro porosity of porous solid acids. The carbonium ion mechanism of catalytic pyrolysis of polyethylene can be described as follows (Table 1).

Sr. no.	Catalyst	Pore size (nm)	Commercial name
1	USY	0.74	H-Ultrastabilised, Y-zeolite
2	ZSM-5	0.55×0.51	H-ZSM-5 zeolite
3	MOR	0.65×0.70	H-Mordenite
4	ASA	3.15	Synclyst 25 (silica-alumina)
5	MCM-41	4.2-5.2	_
6	SAHA	3.28	Amorphous silica-alumina
7	FCC-R1	_	Equilibrium catalyst
8	Silicalite	0.55×0.51	Synthesized in house

Table 1: Catalyst and commercial name used for pyrolysis

1. Initiation.

Initiation may occur on some defected sites of the polymer chains. An olefinic linkage could be converted into an on-chain carbonium ion by proton addition like

$$-CH_2CH_2CH = CHCH_2CH_2^- + HX$$

$$\longrightarrow$$
 CH₂CH₂⁺CHCH₂-CH₂CH₂ + X

The polymer chain may be broken up through β -emission:

$$-CH_2CH_2^+CHCH_2-CH_2CH_2^-$$

 \longrightarrow CH₂CH₂CH = CH₂ + ⁺CH₂CH₂⁺

Initiation can also take place through random hydride-ion abstraction by low-molecular-weight as carbonium ions (R+):

$$CH_2CH_2CH_2CH_2CH_2 - + R^+$$
$$\longrightarrow -CHCH_2^+CHCH_2CH_2^- + RH$$

The formed on-chain carbonium ion then undergoes β -scission reaction.

2. Depropagation.

The main polymer chains molecular weight may be reduced through successive attacks by acidic sites or other carbonium ions and chain cleavage, yielding inorganic oligomer fraction (C30–C80). Further, cleavage of the oligomer fraction by direct β - emission of chain-end carbonium ions leads to the formation of gas and a liquid fraction (C10–C25).

3. Isomerization.

Isomerization reactions are generally methyl-group shift. The carbonium ion intermediates can undergo rearrangement by hydrogen- or carbon-atom shifts, leading to a double-bond isomerization of an olefin as shown:

$$CH_{2} = CH-CH_{2}-CH_{2}-CH_{3}$$

$$\xrightarrow{H^{+}} CH_{3}^{+}CH-CH_{2}-CH_{2}-CH_{3}$$

$$\xrightarrow{H^{+}} CH_{3}-CH = CH-CH_{2}-CH_{3}$$

4. Aromatization.

Some carbonium ion intermediates can undergo cyclization reactions. when an hydride ion abstraction first takes place on an olefin several carbons are removed from the double bond, the resulting the formation of an olefinic carbonium ion:

$$R_1^+ + R_2CH = CH-CH_2CH_2CH_2CH_2CH_3$$

 $\leftrightarrow R_1H + R_2CH = CH-CH_2CH_2CH_2^+CHCH_3$

The carbonium ion could undergo intermolecular attack on the double bond.

3.3 Process in catalytic degradation

The various steps included in catalytic degradation are:

(1) Initiation: The doubtless breakage of the C–C bond of the main chain occurs with the heat to produce hydrocarbon radicals:

$$R_1 - R_2 \longrightarrow R_1^* + R_2^*$$

(2) Propagation. Here the hydrocarbon radicals self decomposes to produce lower hydrocarbons such as propylene. By the β -scission and abstraction of H-radicals from other hydrocarbons to produce a new hydrocarbon radical:

$$R_1^{\bullet} \longrightarrow R_3^{\bullet} + C_2 \text{ or } C_3$$
$$R_2^{\bullet} + R_4 \longrightarrow R_2 \text{ or } R_4^{\bullet}$$

(3) Termination. It is the process of recombination of two radicals elements in a compound during heating :

$$R_5^{\bullet} + R_6^{\bullet} \longrightarrow R_5 + R_6^{\bullet}$$
$$R_7^{\bullet} + R_8^{\bullet} \longrightarrow R_7 - R_8$$

4. Result

During catalytic degradation with Fe activated charcoal in Hydrogen atmosphere, hydrogenation of hydrocarbon radical (olefin) and the abstraction of the H-radical from hydrocarbon generate radicals enhancing degradation rate. The reactor contains many macromolecular hydrocarbon radicals which exist at reaction temperature lower than 400° C or a reaction time shorter than 1.0 h, and recombination occurs fastly because these radicals cannot move fast. However, these combinations can be suppressed and radicals can be hydrogenated when Fe is activated with carbon in a H2 atmosphere. Decomposition of the solid product is promoted by including low polymers whose molecular diameter is larger than the pore size of the catalysts.

5. Conclusion

Plastics are "one of the greatest innovations of the millennium" and have proved their reputation to be true. Plastic is lightweight, does not rust or rot, is of low cost, reusable, and conserves natural resources and for these reasons, plastic has gained this much popularity. The paper reveals that research efforts on the pyrolysis of plastics in different conditions using different catalysts and the process have been initiated. The present issues are minimization of waste handling costs and production cost, and optimization of gasoline range products for a wide range of plastic mixtures or waste. Large amount of plastic wastes produced can be treated with suitably designed method to produce fossil fuel alternates. The method is superior in all aspects if proper infrastructure and financial support is provided. So, a challenging process which can convert waste plastic to hydrocarbon fuel is designed and implemented then that would be a cheaper substitute for petroleum without emitting any pollutants. It would reduce the importing of crude oil and can also take care of hazardous plastic waste. The pyrolysis reactor should be designed to fit the mixed plastic waste a small-scaled and middle scaled production. Also, analysis would help reducing the capital investment and also the operating cost and thus would enhance the economic viability of the process.

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