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Study on thermal cracking of waste PE plastics

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Abstract: *The traditional oil chemical process of waste plastics has the problems of low oil quality, low efficiency and low yield. After investigation, the following technical pain points exist in the industry: intermittent process lacks pretreatment process, impurities account for more than 25%, low oil quality; coking, wax and toxic gas pollution during cracking process.The co-solution synergy experiment of low-grade coal and plastic was carried out by using the integrated annular reactor device and adding acid titanium catalyst, which overcame the problems of high oiled coke wax rate, low oil yield and poor low temperature effect of waste plastics.*

Keywords: *Integrated ring reaction kettle, Co-pyrolysis, Acid titanium catalyst, Traditional waste plastic oil chemical process*

1. Introduction

Waste plastic treatment is an urgent problem to be solved. At present, waste plastics account for about 4~20% of urban solid waste in developed countries, and the proportion of urban solid waste in China has reached 10%. The global annual production of waste plastics can reach nearly 300 million tons, accounting for about 70~85% of the annual production of plastics. Waste plastic components PE accounts for about 48%, PP about 18%, PS about 16%, other plastics such as PVC, PET accounted for about 18%. The large amount of waste plastics and the unreasonable disposal of waste plastics have caused a serious impact on the environment and cause a waste of energy and resources. Therefore, the market for efficient, environmentally friendly waste plastic treatment technology demand is very urgent. The National Development and Reform Commission of the People's Republic of China and the Ministry of Ecology and Environment issued the governance plan to increase the recycling of plastic waste. The "14th Five-year" guidelines on the high-quality development of the petrochemical industry also make relevant requirements.

1.1 Waste plastic, the low recovery rate brings harm to the environment

The plastic industry is one of the typical industries with high emission and high pollution, and it is also a potential field for China to achieve synergistic efficiency of pollution reduction and carbon reduction. As an important material in people's production and life, plastic is used efficiently and widely used. At present, no other material can be completely replaced. In this context, the use of waste plastic oil technology is crucial to the coordinated promotion of pollution reduction and carbon reduction. First, it can reduce plastic pollution. In 2023, China will produce more than 80 million tons of waste plastic, about 70 percent of which will be buried or burned, which will not only cause groundwater and soil pollution, but also release toxic gases to harm health. The oil technology of waste plastic will effectively improve the recovery rate of waste plastic and reduce pollution from the source. Second, it can reduce carbon emissions. From March 2020 to August 2023, the total monthly output of primary plastics in China reached 334 million tons. According to the calculation of 2.3 kilograms of carbon dioxide (excluding carbon emissions from upstream raw materials), the plastic industry released at least 769 million tons of carbon dioxide, accounting for about 5% of China's total carbon emissions.

1.2 The traditional treatment method of waste plastics causes serious pollution of water resources and land resources

The traditional disposal method of waste plastic is incineration, land landfill, and dumping into the ocean. Incineration and landfill all pose serious threats to soil quality, water quality and air quality. The construction and operation cost of landfill is low, but the large occupation of land resources, the obstruction and pollution of groundwater, the secondary pollution and the waste of recyclable waste plastic resources are the disadvantages of landfill. Incineration of plastic will release a large number of dioxins, furan and other harmful substances, causing serious pollution to the environment. By 2050, the total weight of plastic waste in the ocean is expected to exceed the total weight of Marine life. About 1 million seabirds and 100,000 Marine mammals are killed each year.

1.3 Oil is a strategic resource, and the waste plastic oil serves the national energy security strategy

The two sessions have proposed to ensure energy security. China's cumulative proven recoverable reserves of oil are 6.395 billion tons, of which the remaining recoverable reserves are 2.428 billion tons, ranking 12th in the world. The remaining recoverable oil reserves per capita are 1.87 tons, equivalent to 7.8% of the world's per capita level. From 2015 to 2022, China's crude oil dependence increased year by year, from 60% to 74%. Natural gas has increased to 40%. [1-3]The production of waste plastic in China will reach 77 million tons in 2022, accounting for 31% of the crude oil production in the same year; it is urgent to improve the economic value of plastic lysates and alleviate China's oil dependence.[4-5]

At present, in the resource utilization mode of waste plastics, the waste pyrolysis technology with syngas and chemical raw materials as the target products is considered as one of the most promising waste plastic utilization technologies due to the wide applicability of raw materials, low pollution and low emission. As shown in Figure 2-6, plastic waste can be converted into gas, solid, liquid and a series of chemical fuels and raw materials through pyrolysis technology and subsequent catalytic reforming.

At present, the liquid crude products obtained by simple thermal cracking (without the addition of catalyst, and by no modification method) cannot be directly used as chemicals due to their poor selectivity and low content of alkanes.[7-9]Pyrolysis-catalysis of waste plastic has been a lot of research, the use of (catalytic) pyrolysis method to convert waste plastic into commercial pyrolysis oil, such as aromatic hydrocarbon rich oil technology is a promising means of waste plastic resource utilization. In the study of waste plastics (catalytic) pyrolysis, there are single type of main flow aromatization catalyst, insufficient technical economy and adaptability, the poor selectivity and other conditions, and the development of efficient, economical and stable catalyst to improve the quality of waste plastics.[10-11]

2. Integrated circular reaction kettle

The integrated ring reactor device is, on the basis of the original reactor, equipped with double deep groove ball mixing bearing and feeding box, and the mixing support has good sealing performance and no shedding. The problem of chip removal is a common problem for the domestic mixing support of the reactor. The use of the internal feeding box structure can effectively avoid the wear of the debris drop pollutant materials. Prevent debris pollution, make the operation more stable and silent.

The annular diversion plate technology allows the heat conductivity to flow on a specific "path" to ensure uniform heating while maximizing the heat transfer area. Due to the high efficiency and speed of heat absorption or heat release, the reactor can maximize the use of temperature control for uniform heating and refrigeration, and improve the energy efficiency ratio. Precise and uniform temperature control improves yield and reduces process time, while increasing yield and reducing process costs.[13-15]

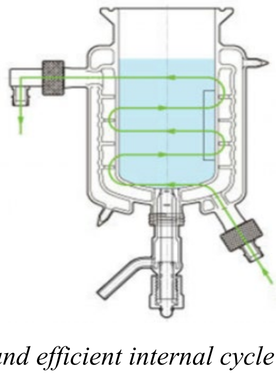

Figure 1 Intelligent and efficient internal cycle growth rate device[6]

Intelligent efficient internal cycle growth device, fluid reactants in the kettle under the vortex flow cycle mode, make solid, liquid, gas reactants increase the initial speed of liquid flow, makes the contact with heterogeneous material form high kinetic energy fluid, speed up liquid, solid, gas in the kettle shear

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force and rapid reaction, promote the internal circulation, improve the heat transfer rate and reaction conversion rate.(see Figure 1)

3. Development of characteristic titanium-containing composite catalyst

The impurity process removes C1 by using titanium-based catalyst-like solid acid substances to induce the active site for adsorption of C1 or conversion into HCI. Moreover, N is removed by neutralizing the solid acid site, thus having the advantage of introducing the same titanium-based catalyst into a simple reactor to reduce impurities while causing oligomerization. In addition, titanium series catalyst solid acid substances can not only induce olefin oligomerization, but also can induce the branching reaction and olefin displacement reaction, so can change the operating conditions in the oligomerization, for the same raw material can prepare adjustable low temperature characteristics of various physical properties of the products.

Titanium-series catalysts have a very wide range of applications. In the petrochemical field, it can be used for catalytic cracking, hydrogenation, dehydrogenation, isomerization and other reactions, which can improve the reaction rate and product selectivity, reduce the reaction temperature and pressure, and reduce the use of catalyst and the generation of waste. In the field of environmental protection, it can be used for waste gas treatment, waste water treatment, garbage treatment, etc., which can transform harmful substances into harmless substances, reduce the discharge of pollutants and the harm to the environment.

In this project, a new titanium-containing composite catalyst was prepared from tetrabutyl titanate + tetraethyl silicate + phenylphosphonic acid. The optimal ratio of Si:Si=9:1 and Si:P=1:2 was used to obtain the compound catalyst (Ti concentration was 0.457 mol/L).

4. Co-pyrolysis effect of low-rank coal and PE plastics

Compared with the distribution of different plastic pyrolysis products, PE plastic pyrolysis has a higher oil yield of 93.42wt.%。By comparing the influence of different heating rates on the distribution of PE pyrolysis products, it was found that the oil yield was the highest under the condition of 20° C / s. Comparing the distribution of co-pyrolysis products and the synergistic effect under different mixing ratios of low-order coal and PE shows that the co-pyrolysis of low-order coal and PE showed the maximum synergistic effect at the mixing ratio of 7:3.

The oligomer oil of lubricating oil base oil. The recovered oil all has a kinematic viscosity of 4.15 cSt, which can be regarded as a product group with a kinematic viscosity of 4 cSt.[16-17] In addition, the viscosity index of the lubricant base oil is more than 120. The low temperature viscosity (CCS) is 1450 cP, which is excellent and confirms that it can be used as an additive for increasing the low temperature viscosity (CCS) of lubricating oil base oil. With the oil recovered at the hydrogenation isomerization temperature, the dip point was confirmed as-29℃, which meets the dip point standard of the lubricating oil base oil. (see Figure 2)

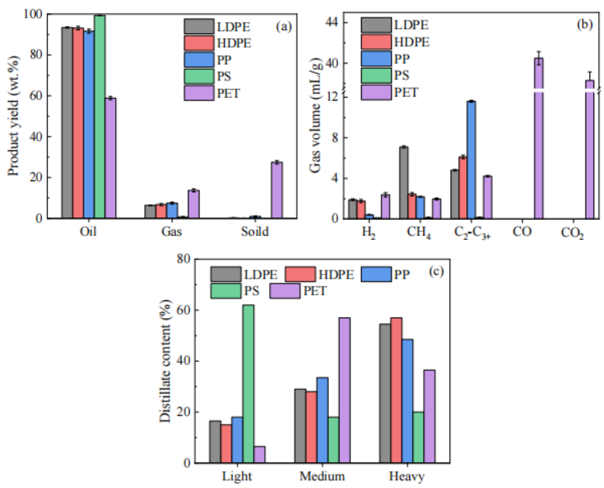

Figure 2 Comprehensive Analysis of the low-temperature performance of the products[12]

5. Digdigital segmentation device

The digital segmentation device adopts reactor, condensing system A-B intelligent connection device, and digital alarm start device to realize intelligent decoking and wax removal to ensure the continuity, automation and intelligence of production.The focusing device adopts the first A-B reactor intelligent connection device, which is connected with the coke removal alarm in the kettle. It uses A alarm-B open-A close-feed-A coke removal cycle technology. Compared with CCSS closed focusing technology, it has the advantages of simple process, convenient operation, low energy consumption, high production capacity and low price. The wax removal device adopts the first intelligent connection device of A-B condensation device, which is connected with the wax removal alarm in the condensate pipe. It uses A alarm-B open-A close-feed-A wax removal cycle technology, which has the advantages of simple process, convenient operation, low energy consumption and high production capacity.

6. Catalytic mass improvement technology

In the case of no hydrotreating, the hydroisomerization process can be used to reduce the oil content by a very small amount at the same time, and improve the low temperature characteristics of the waste plastic pyrolysis oil by supporting the hydrocarbon molecular end, so as to achieve the physical properties of high-quality lubricating oil base oil. The conventional hydrogenation reaction is not performed to remove the unsaturated double bonds, but also the molecular supports when the unsaturated double bond is removed by the hydrogenation isomerization reaction.

In order to recover the intermediate distillate (the object oil converted into lubricating oil base oil by hydrogenation structure isomerization), the waste plastic pyrolysis oil is separated at different boiling points by using a distillation device. The introduction standard of the hydrogenation process is selected based on the impurity C1, the most serious problem causing corrosion and reactor blockage in the hydrogenation process. The representative impurity that may cause corrosion of the device by conversion to HC1 is C1, and by forming NH with HC1 under operating conditions, C1 salt N that causes the blockage of the reactor is also an important impurity to be reduced. In the process of reducing impurities, in addition to removing C1, N, S, O, metals and other impurities are also removed.

In this study, (catalytic) pyrolysis and coporolysis were organically combined. By investigating the influence of process parameters on the composition and distribution of plastic pyrolysis products, the optimal matching conditions and mixing ratio of coal and polyethylene were obtained under the condition of maximum synergistic effect. By adding solid acidic titanium substances, inducing the oligomerization reaction, branching reaction and displacement reaction of olefin, and then changing the operating conditions in the oligomerization reaction, the advantages of products with various physical properties with adjusted low temperature characteristics can also be prepared for the same raw materials.

7. Conclusions

In this study, (catalytic) pyrolysis and coppyolysis were organically combined to investigate the influence of process parameters on the composition and distribution of plastic pyrolysis products, and the best matching condition of coppyrolysis and the mixing ratio of coal and PE when the maximum synergistic effect were obtained. By adding solid acidic titanium substances, inducing the oligomerization reaction, branching reaction and displacement reaction of olefin, and then changing the operating conditions in the oligomerization reaction, the advantages of products with various physical properties with adjusted low temperature characteristics can also be prepared for the same raw materials.

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