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Original Research Paper

Studies on Molecular Distillation Disposal of Petrochemical Hazardous Wastes

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ABSTRACT

In this paper, heavy residual oil and distillation residues of hazardous wastes are researched with molecular distillation separation reduction technology. The separation experiments were conducted at the condition of pressure of 15 Pa and the temperature of 260°C. Under the conditions, more than 20% heavy fractions can be recycled which can be the catalytic cracking raw material sources. The properties of residual oil, such as viscosity, density, carbon residue, sulphur content and other technical indicators are also analysed. There are very practical significance of molecular distillation technology in the recovery of high boiling point organic waste.

INTRODUCTION

In recent years, there is more developing interest on the global solid hazardous waste disposal and resource utilization (Bernadette 2012). The solid waste from petrochemical distillation residues and heavy organic matter have been mainly handled with the landfill method in the past. Due to the land resource constraints, the long-standing potential problem of hazardous waste, and toxic chemical pollution caused by industrial waste (Duan & Huang 2008), China is meeting the severe problem of hazardous waste pollution and resource utilization. Because of the complexity of petrochemical solid wastes and the influence of economic development, natural conditions, technical level factors, the chemical solid waste disposal methods are quite different. Different regions use different methods due to the imbalance of economic development (Li & Li 2011). Solid hazardous wastes which require special disposal processing are wastes with different chemical, physical and biological characteristics (The National Hazardous Waste List 1995). In this paper, the molecular distillation technology has been used to separate the conventional vacuum distillation of petrochemical residues at high vacuum, and their composition and the feasibility to be used are analysed. A new method to the traditional chemical solid waste resource utilization is provided.

It has been reported that the application of molecular distillation technology in recycling high-value raw materials in waste heavy organic matter (Zhang et al. 2012), result in the reduction of emissions of chemical distillation residue, and resource utilization. With the improvement of resource utilization and environment friendly requirements, organic heavy waste and residual oil waste will become the focus of resource utilization. In order to make heavy residual oil resource utilization, Lamia et al. (2010) adopted molecular distillation technology to study petroleum residue composition and separation technology conditions. Zhang et al. (2012) used molecular distillation modelling to waste heavy organic matter processing, and it not only can recover heavy oil, but also can be used for the separation of all organic waste residue with atmospheric pressure boiling point at 400-600°C. This technology can be cut out relatively light distillate in heavy organics to achieve separation and recycling, and the chemical structure of heavy material from residual will not be damaged by high temperature.

MATERIALS AND METHODS

Materials: Heavy residue materials provided by petrochemical plants, which have been classified as hazardous waste by Shan Dong Government. It was from low pressure distillation of restructuring and it is black, sticky solid at room temperature and atmospheric pressure. The physical and chemical properties of residue are given in Table 1.

Experimental apparatus: Molecular distillation device (evaporation area is 0.1m^2), asphaltene measuring instrument, extractor, kinematic viscosity tester (SYD-265C), open-cup flash tester (YXS type), Kang carbon residue oil product tester, inspection densimeter, stopwatch, muffle furnace: 0-1500°C.

The standard and method of determination: Viscosity of the viscosity index test: The national standard test methods (GB/2004-188).

The determination of ash content and carbon residue: The weight percentage of the ash was measured by weighing: GB/T268-83, carbon residue test was performed on carbon detector (Kang method).

The determination of flash point and mechanical impurities: Flash point was tested by open-cup flash tester (YXS type). Mechanical impurities were determined according to the national standard (GB/T511).

RESULTS AND DISCUSSION

The composition of the four components of the residue distilled with molecular distillation device at different distillation temperature: The wax was distilled from heavy residual oil by molecular distillation. The weight of wax was about 22% of the weight of heavy residual oil, which can be used as catalytic cracking oil raw materials. The other part of heavy residual oil is tested by the separation of colloidal asphaltene adsorption in extractor and silica gel column. The saturates and aromatics were analysed by chromatography-mass spectrometry. The data take the average of two experiments. The measurements of saturates, aromatics, colloids and asphaltene is given in Table 2.

Molecular distillation temperature and the viscosity and density of residue: Under the laboratory temperature of 20°C, the density of molecular distillation residue is measured by densimeter with different distillation temperature. The influence and variation in trend of different residual residue distillation temperatures on density of residual residue are shown in Fig. 1.

Under the laboratory temperature of 100°C, the kinematic viscosity of heavy ends of molecular distillation residue was measured by kinematic viscosity tester with different distillation temperatures. Kinematic viscosity change as the distillation temperature changes; the experimental data are shown in Fig. 2.

The density and viscosity of the molecular distillation

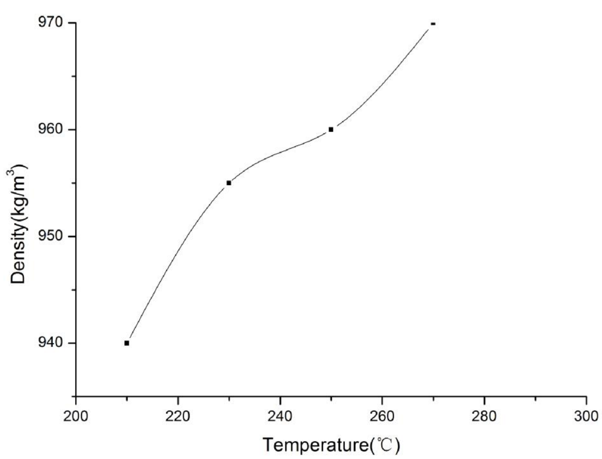

Fig. 1: The different distillation temperature molecular distillation residue density.

Table 1: The physical and chemical properties of residue.

Project	Numerical value
Relative molecular mass	480
Density (kg/m^3)	960
Boiling point (atmospheric pressure)	>500
Latent heat of vaporization (kj.kg^{-1}.°C^{-1})	220
Specific heat capacity (kJ.kg^{-1}.°C^{-1})	2.40
Mechanical impurities (%)	≤ 1.5%
Colloidal asphaltene (%)	≤ 30%
Kinematic viscosity (mm^2/s, 100 °C)	140

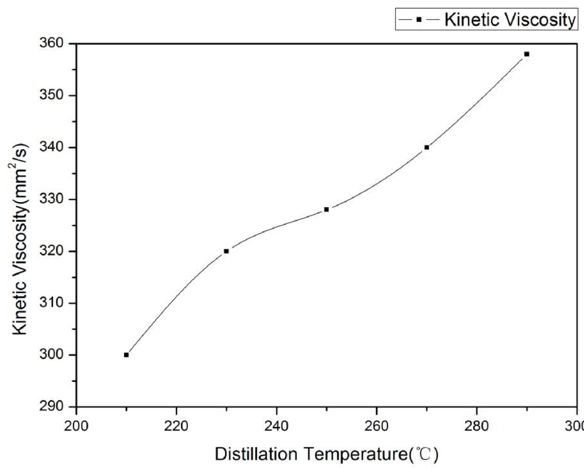

Fig. 2: Distillation temperature molecular distillation residue kinematic viscosity.

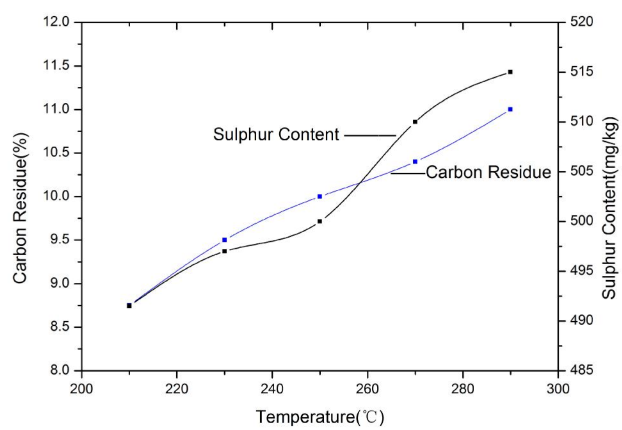

Fig. 3: The different distillation temperature molecular distillation residue, carbon residue and sulfur content.

Table 2. Molecular distillation residue in percentage content of the four components of the different distillation temperatures.

The temperature of molecular distillation °C	Saturate %	Aromatics %	Colloid %	Asphaltene %
20	19	39	21	19
200	17	38	29	15
220	15	36	29	17
240	14	30	30	2
260	14	28	31	24
280	13	27	33	26

Table 3: The heavies main technical indicators.

Distilled fractions and residues	kinematc viscosity (100°C, mm^2/s)	Density (20°C, kg/m^3)	Carbon residue (%)	Mechanical impurities (%)	Sulphur content (%)
Distillation wax fractions	322	934	0.15	0.2	≤ 3
Distillation residue	470	975	11	4	15

residue have significantly change as molecular distillation heating temperature increases even slightly. That means the density and viscosity of the molecular distillation residual oil will increase with increasing molecular distillation temperature. With the increasing distillation temperature, the evaporated heavy constituent will increase. On the other hand, the relatively light constituent in the molecular distillation residual oil will continue to decline wherein the proportion of asphaltene and resin content will increase. The density and viscosity of the residual oil becomes further large while the more complex components are distilled off in the molecular distillation process.

The determination of sulphur content and carbon residue value: The product application performance influence of sulfide from crude oil distillation residue is very strong. The sulfide not only lead to corrosion, but also pollute the environment if burnt as fuel oil with high sulphur content. It is necessary to analyse and evaluate the sulphur content in crude oil distillation residue.

As shown in Fig. 3, as the change of molecular distillation evaporation temperature, the content curve of sulphur and carbon showed a trend of increase. It means that the sulphur content of relatively light distillate composition, steamed out from molecular distillation process, is less and most of the sulfide concentrate in heavy distillate. Therefore, light distillate composition was steamed out constantly and the proportion of heavy sulphur residual oil is risen with the increase of distillation temperature.

The performance analysis of molecular distillation distillate and residue: The main performance of wax oil and residue from molecular distillation is compared and the performance test data are given in Table 3.

From Table 3, each quality index of the light fraction by molecular distillation was analysed, the light component can be used as catalytic cracking raw material recycling. Through technology application of chemical distillation on chemical distillation residue and other hazardous waste, light component in the organic matter could be cut out from residue under high vacuum. Therefore, chemical distillation can be extended to all chemical distillation residue processing and separation. The heavy ends which cut out the light component still recovered and used as fuel oil. Residue processed by molecular distillation can increase about 20% organic matter resources.

For example, fine cutting separation of the residue can recycle valuable heavy chemical industry resources. It has important practical significance for chemical hazardous waste reduction and recycling.

CONCLUSION

1. In this paper, a new molecular distillation reduction processing technology was proposed.
2. Solid hazardous waste reduction and recycling use need a variety of combined disposal techniques and approaches; government departments should introduce, digest and absorb advanced foreign technology, disposal equipment for hazardous waste, increasing investment and scientific research strength.
3. Research on heavy distillation residue oil separation method by molecular distillation can recycle more than 20% organic matter for available resources. This technology can be extended to all chemical distillation residues and hazardous organic waste recycling. Molecular distillation high vacuum can greatly reduce

atmospheric boiling point, it minimizes distillation residue, recycle use of resources, reduce the waste emissions, and has utilization significance for wastes.

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