Fuel Oil from Acrylonitrile–Butadiene–Styrene Copolymers Using a Tandem PEG-Enhanced Denitrogenation–Pyrolysis Method

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Introduction

Recycling of waste electric and electronic equipments (WEEE) polymers has drawn much attention recently. Various recycling methods have been adopted, and among them, thermal degradation of WEEE polymers into fuel has been regarded as one of the most promising methods.[1] However, in the process of recycling of acrylonitrile–butadiene–styrene (ABS) copolymers, which is a widely used polymer in electric and electronic industry, thermal degradation will produce HCN, NO_X, as well as complicated nitrogen-containing organic compounds that will not only cause environmental pollution but also cause the produced liquid to fail as fuel.[2] Therefore, the denitrogenation of WEEE plastics is a must for this process. Catalysts such as α-FeOOH, Fe-C, Ca-C, $CaCO_3$, and Y zeolite were used during pyrolysis, but the denitrogenation effects are limited.[3,4] Moreover, the catalysts may encounter the problems, such as poisoning, short catalyst life, and poor regeneration ability, which increases the difficulties of this process. On the other hand, hydrothermal methods were adopted for denitrogenation both before and after pyrolysis,[5–7] but the denitrogenation effects are still unsatisfying. Moreover, relative high temperatures and pressures are needed, which requires the use of expensive facilities. Therefore, the development of highly efficient denitrogenation of ABS under mild conditions is an area of considerable importance.

By analysis of the molecule structure of ABS, it can be seen that the complicated nitrogen-containing compounds during pyrolysis just come from the nitrile group of ABS. Therefore, it is reasonable to assume that to replace the nitrile group with other groups without nitrogen element before pyrolysis can effectively reduce the nitrogen content in oil. In this article, ABS is treated using a tandem poly(ethylene glycol) (PEG)-enhanced alkaline denitrogenation–pyrolysis method according to the structure and thermal degradation properties of ABS, that is, first ABS is denitrogenated using PEG as a phase-transfer catalyst to enhance the denitrogenation efficiency, then the denitrogenated ABS (DABS) is pyrolyzed to get clean fuels (Scheme 1). This method has the advantage of high denitrogenation efficiency under mild reaction conditions and of decreasing the probability of forming complicated nitrogen-containing compounds during pyrolysis, which are difficult to eliminate. In addition, it is beneficial to obtain clean fuel without using expensive denitrogenation catalysts during pyrolysis.

Experimental

Materials

Acrylonitrile–butadiene–styrene (ABS) 0215A, Sinopec Group, China, N%:7.4 wt % was used. All other chemicals were of analytical grade.

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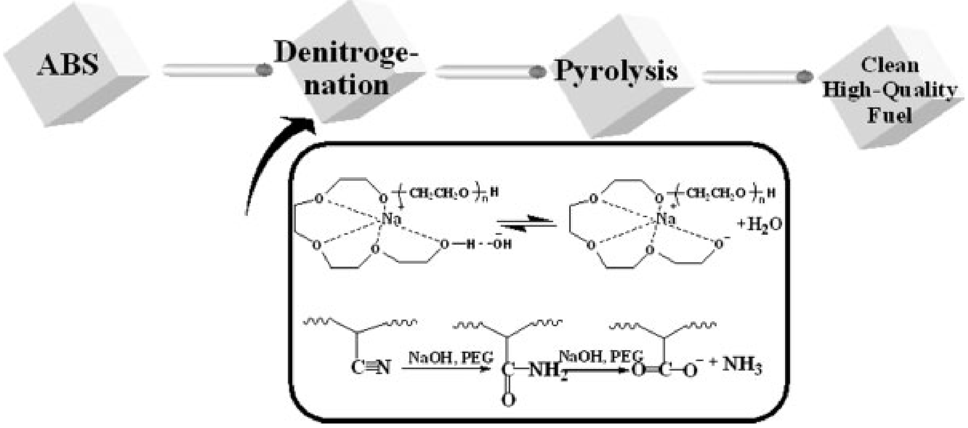

Scheme 1. A two-step process for thermochemical recycling of ABS.

PEG-enhanced alkaline denitrogenation

Alkaline denitrogenation of ABS was carried out at 160°C for 2 h in a 60-mL stainless reactor equipped with a thermometer. In a typical experiment, 1 g NaOH was dissolved in 5 mL PEG600, and then added to the ABS solution of dioxane (ABS/DOA = 1 g/5 mL). After reaction, the product was precipitated in acetic acid solution and separated, then washed with distilled water until pH = 7, then dried under vacuum at 60°C for 24 h before characterization.

Thermal degradation procedures

The thermal degradation reaction was carried out in a glass reactor by batch operation as reported earlier.[8] In a typical experiment, about 10 g of materials was added to the reactor. The air of the reactor was purged out with a nitrogen flow of 30 mL $\min^{-1}$. The reactor was heated from room temperature to 120°C during 20 min and the temperature was held for 30 min. Then, the temperature was increased from 120 to 500°C at a heating rate of 10°C $\min^{-1}$ and held until no liquid was produced. The products of degradation were classified into three groups: liquid products, which are condensable at 0°C, gaseous products, and residue.

Product characterization

The Fourier transform infrared spectra of ABS and DABS were measured with a NICOLET6700 apparatus (Thermo Electron Corporation, USA). Elemental analysis (C, H, and N) of the ABS, DABS, and pyrolysis oils was determined with an elemental analyzer (Thermo electron Flash EA1112, USA).

The pyrolysis oils were analyzed using an Agilent HP 6890N gas chromatography equipped with a 30 m × 0.25 mm × 0.25 μm DB-5 capillary column. Helium was the carrier gas at a flow rate of 0.8 mL $\min^{-1}$. The column temperature was programmed from 35 (kept for 5 min) to 210°C at 5°C $\min^{-1}$ and then to 290°C at 10°C $\min^{-1}$. The final temperature was held at 290°C for 20 min. Based on the GC analysis, the carbon number distribution of the liquids was determined using NP-gram method.[9]

The thermogravimetric analysis (TGA) experiments were performed with a TA SDTQ600 thermogravimetric analyzer (TA, USA). For each run, about 10 mg of samples was heated from 30 to 600°C at a heating rate of 10°C $\min^{-1}$ under nitrogen with a flowing rate of 30 mL $\min^{-1}$. The thermogravimetric weight loss curve (TG, %) and the derivative curve of the weight loss (DTG, %/°C) were recorded as a function of time and temperature.

Results and Discussion

Before pyrolysis, alkaline denitrogenation of ABS was conducted. The enhancing effects of PEG on denitrogenation of ABS are clearly shown in Figure 1. For ABS/DOA/NaOH system, the infrared spectrum of the product is similar to that of ABS, suggesting that the conversion of nitrile group is very low with only NaOH at mild conditions. However, with the addition of PEG600, the strength of the $-$CN stretching band (2245 cm^{-1}) obviously decreases, at the same time new peaks assigned to $-CO-NH_2$ (1670 cm^{-1}) and $-$COOH (1705 cm^{-1}) appear, indicating a readily transformation of nitrile groups. Accordingly, element analysis proves that the nitrogen content is decreased from 7.4 wt % for ABS to 3.5 wt % for DABS using PEG, resulting a 52.7% denitrogenation efficiency. The weight increase of

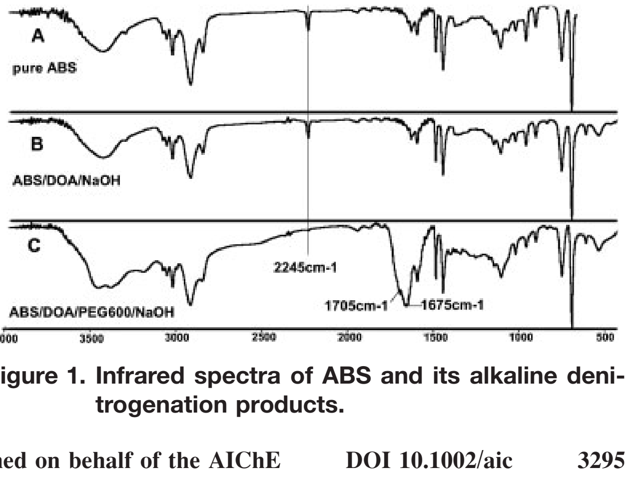

Figure 1. Infrared spectra of ABS and its alkaline denitrogenation products.

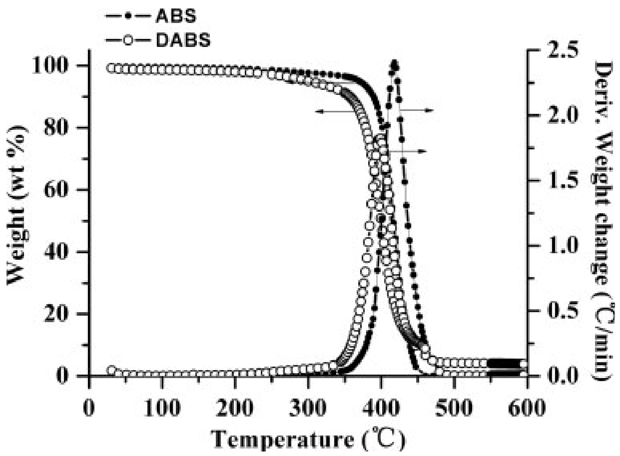

Figure 2. The TGA and DTG curves of ABS and DABS.

ABS after hydrolysis (6.9 wt %) is lower than the theoretical value (9.6 wt %) because of use of small amounts of samples and the losses during sample handling. It is reported that for cyano-containing polymers in which the nitrile groups are mostly isolated, alkaline hydrolysis is analogous to the hydrolysis of low-molecular-weight mononitriles. The nitrile groups are first transformed to amide groups, then to carboxylate groups.[10] Akimoto et al.[7] obtained 40.1% denitrogenation efficiency through hydrothermal treatment with alkaline aqueous solution at the temperature as high as 300°C. In our process, PEG probably forms chelates like "18-crown-6-like" structure occurring at the terminus of the polymer chain,[11] therefore resulting in the more effective solvation of the sodium cation that increases the reactivity of the base for nitrile group hydrolysis in dioxane, thus enhance the denitrogenation efficiency of ABS. Consequently, highly efficient denitrogenation can be realized at low temperatures when compared with normal denitrogenation processes, which reduces the energy consumption of the process and due to the mild conditions the corrosion effects, thus lowering the overall process costs significantly.

The DABS is used for pyrolysis experiment, and the results are compared with those of pyrolysis of ABS. Interestingly, as high as 94.1% decrease of nitrogen content in oil was obtained (from 1.7 wt % for ABS to 0.1 wt % for DABS). Thermal degradation of polyacrylamide and its copolymers produce a multitude of compounds including NH_3, H_2O, glutarimides, and CO_2.[12] Therefore, for DABS, a copolymer of polyacrylamide, most part of nitrogen originally in DABS is transferred to the gas phase as ammonia, which was proved by the smell of ammonia released during experiment. Ammonia can be easily absorbed in water and used for industrial applications or environmentally sound disposal. It was reported that even though the iron-based and calcium-based catalysts possess good dechlorination abilities, they only exhibited 10–30 wt % of denitrogenation ability for pyrolysis oil.[4] Our results confirm that effective denitrogenation of ABS before pyrolysis is beneficial to produce clean oil even without using denitrogenation catalysts during pyrolysis.

Table 1. Product Yields from Thermal Degradation of ABS and DABS

	Product Yield (wt %)			
Samples	Liquid (L)	Residue (R)	Gas (G)	Nitrogen Content in Liquid (wt %)
ABS	84.9	7.2	7.9	1.7
DABS	64.3	14.0	21.7	0.1

Moreover, the DABS shows different thermal degradation behaviors compared with ABS. From TGA tests (Figure 2), it can be seen that the initial degradation temperature of ABS (T_i: 5% weight loss) is shifted from 370.2 to 302.7°C, and the peak temperature (T_{max}) from 416.8 to 400.9°C. These results strongly prove an easier degradation of DABS compared with that of ABS.

In addition, the product yield is obviously changed (Table 1), that is, the liquid yield is decreased from 84.9 to 64.3 wt %, whereas the gas yield is sharply increased from 7.9 to 21.7 wt %. For the liquid product distribution (Figure 3), it can be seen that the heavy components obviously decrease, particularly the $>C_{25}$ components are prominently decreased from 24.6 wt % (ABS) to 2.9% (DABS), and the light components increase, suggesting a more effective pyrolysis process and better oil quality for DABS. More research is underway confirming these facts.

Conclusions

In conclusion, the tandem PEG-enhanced alkaline denitrogenation–pyrolysis method possesses high denitrogenation efficiency under mild reaction conditions, which is beneficial to produce clean oil via pyrolysis. Moreover, the DABS shows different thermal degradation behavior compared with ABS, that is, thermal degradation at lower temperatures and better oil quality with almost 10 times lower quantities of heavy components. Optimization of the hydrolysis conditions will decrease the nitrogen content in DABS, stressing more the potential of this method for denitrogenation of N-containing polymers.

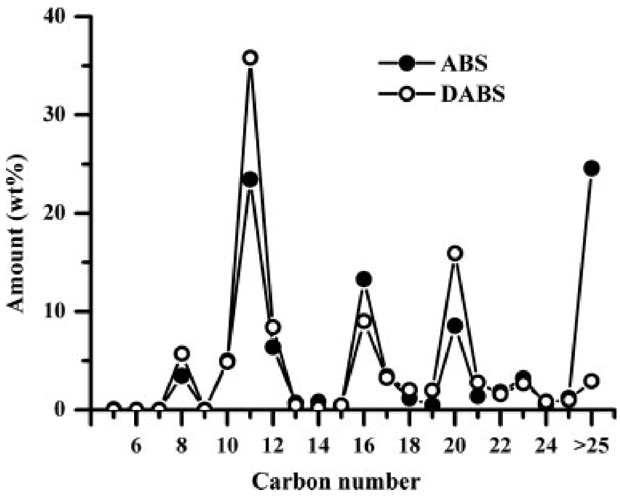

Figure 3. Carbon number distribution of thermal degradation of ABS and DABS.

Acknowledgments

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