PYROLYSIS OF OIL SHALE MIXED WITH LOW-DENSITY POLYETHYLENE

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The pyrolysis experiments on oil shale mixed with low-density polyethylene (LDPE) were carried out with the aid of thermogravimetric analyzer, differential scanning calorimetry system and distillation furnace. The results obtained indicate that a synergistic effect exists to some extent during pyrolysis of oil shale mixed with LDPE. The temperature of maximum degradation of the mixture is approximately 5 °C lower than that of oil shale. The difference in weight loss between the pure oil shale and that mixed with LDPE is 1.17% at 550 °C. Co-pyrolysis experiments of oil shale mixed with LDPE show an increased shale oil yield, and the obtained oil contains novel alkynes or allenes.

Introduction

Oil shale is the second largest solid fossil fuel resource after coal in the world [1]. China is one of the many countries with large oil shale deposits, which are estimated at 6×10^{11} tonnes [2] and are mainly located in Fushun, Northeast China [3]. So far, the only known major source of fossil energy fuel in China is oil shale, whose utilization as a substitute for petroleum is of crucial importance for state's development. It is well known that pyrolysis is the major process for obtaining shale oil from oil shale. Lots of work have been done on the characterization of oil shale pyrolysis to get oil from oil shale [4–6]. However, the main problems related to pyrolysis of oil shale include low carbon conversion efficiency and low oil yield because the ratio of hydrogen to carbon in oil shale is low [7]. Nowadays, the disposal of waste plastic materials is giving rise to increasing environmental and economic problems. Among these plastic wastes, low-density polyethylene (LDPE) that is rich in hydrogen in comparison with coal and oil shale represents the largest volume segment of the plastic wastes [8–11].

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The pyrolysis of oil shale and plastic wastes can been considered an alternative means of partial substitution of petroleum to generate the necessary energy and reduce the environmental pollution from plastic wastes. The present work was carried out in order to explore the interaction between oil shale and LDPE during pyrolysis and study pyrolysis characteristics of oil shale from Fushun Northeast China mixed with LDPE.

Experimental

Oil shale samples used in this work were taken from Fushun, China, and analysis data of oil shale are listed in Table [12]. The oil shale samples were ground, dried and sieved to particle size of less than 200 meshes. The LDPE samples with particle size ranging approximately from 0.1 mm to 0.2 mm were provided by Liaoyang Petrochemical Company, China. Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC) of oil shale, LDPE and their mixture samples (wt. ratio, 3:1) were investigated using a TA SDT2960 thermal analysis system and TA Q200 differential scanning calorimetry system. In this work about 10 mg samples were heated to 850 °C at 2 °C/min heating rate using nitrogen at 20 ml/min flow rate. The co-pyrolysis of oil shale mixed with LDPE was performed by GB/T 1341-2001 method using GDL-B low-temperature distillation furnace. The analysis of the water in the co-pyrolysis products was made according to GB/T 211-1996. The shale oil yield was calculated as follows:

$$Y = [(W_0 - W_1 - W_2)/W] \times 100 , \tag{1}$$

where W_0 is the mass of the co-pyrolysis product of the oil shale mixed with LDPE; W_1 is the mass of the pyrolysis product of the pure LDPE; W_2 is the mass of the water in the co-pyrolysis products; W is the mass of the oil shale and Y is shale oil yield.

FTIR spectra of the pure shale oil, pure LDPE oil and the co-pyrolysis mixture oil were taken by apparatus Nicolet 380.

Table. **Chemical composition of oil shale**

Composition	Content, wt.%
Kerogen	22.16
Silicon dioxide	48.14
Aluminum oxide	15.02
Ferric oxide	6.09
Potassium oxide	0.936
Magnesium oxide	0.809
Titanium oxide	0.714
Sodium oxide	0.694
Calcium oxide	0.577

Results and discussion

TG, DTG and DSC curves of oil shale, LDPE and their mixture at a heating rate of 2 °C/min are shown in Figures 1–3, respectively. The curves show that the thermal decomposition of oil shale proceeds in two steps. The first step from 50 to 100 °C is attributed to the dehydration, characterized by an endothermic peak at 86 °C (Fig. 3). The second step (at about 340–550 °C) has a weight loss of 15.2% due to the decomposition of kerogen. The maximum rate of weight loss is at 476 °C (Figures 1 and 2). The heat requirement for decomposition reaction of the kerogen is strong, as shown by the high peak in DSC curve in Fig. 3. The values of final residual weight were calculated to be about 80.1 wt.% according to the TG curve in Fig. 1.

It can be seen from TG curve in Fig. 1 that degradation of LDPE occurs almost totally in one step, which can be concluded from the presence of only one peak in DTG (Fig. 2). The TG curve shows that the thermal degradation of LDPE starts at 292 °C, and the degradation is almost complete at approximately 591 °C. The degradation rate reaches maximum at 470 °C. Two peaks corresponding to endothermic reactions are observed in DSC curve of LDPE in Fig. 3. The first peak corresponds to melting of LDPE and the second peak corresponds to the decomposition reaction of LDPE.

Figure 1 also shows that decomposition of kerogen in the oil shale overlaps with decomposition of LDPE. The degradation of kerogen and LDPE occurs between 251 to 602 °C and exhibits a total weight loss of 40%, which means that the residue yield of the mixture is lower than that of oil shale alone. In addition, the maximum temperature of the mixture degradation is 471 °C, approximately 5 °C lower than that of oil shale (476 °C), and is close to that of LDPE. In order to further investigate interactions between oil shale and LDPE, we defined a difference of weight loss, represented as $\Delta w = w_{mix} - (x_1 w_1 + x_2 w_2)$, where w_{mix} is the weight loss of mixture, x_i is the weight fraction of each material in the mixture, and w_i is the weight loss of each material in the same operational conditions. The difference of weight
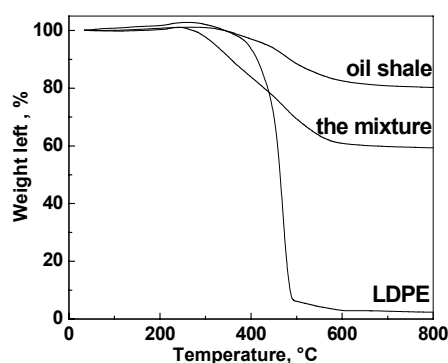

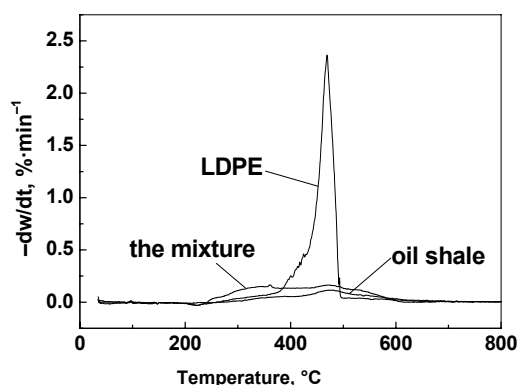*Fig. 1.* TG curves of oil shale, LDPE and their mixture.

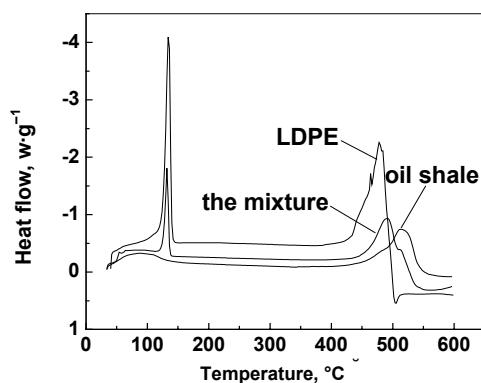*Fig. 2.* DTG curves of oil shale, LDPE and their mixture.

Fig. 3. DSC curves of oil shale, LDPE and their mixture.

loss (Δw) calculated is 1.17% at 550 °C. These experimental results indicate that there is some synergistic effect during pyrolysis of oil shale mixed with LDPE. The mechanism of the synergistic effect between oil shale and LDPE during pyrolysis can be explained as follows: in the first stage of the pyrolysis process, LDPE components can yield radicals, the transfer of hydrogen from a polyolefinic chain to oil shale will increase H/C ratio in the kerogen structure and stabilize the primary products from kerogen thermal degradation. This would result in lower degradation temperature of oil shale and lower yield of the residue.

Figure 4 shows the shale oil yield dependences on the LDPE content during the co-pyrolysis process. The pure oil shale is characterized by a very low oil yield of 5.71%, while adding of LDPE will improve the potential oil producibility of oil shale. Shale oil yield can reach 6.40% when the LDPE content in the mixture is 50%. The results further indicate that a synergistic effect exists to some extent during co-pyrolysis of oil shale mixed with LDPE.
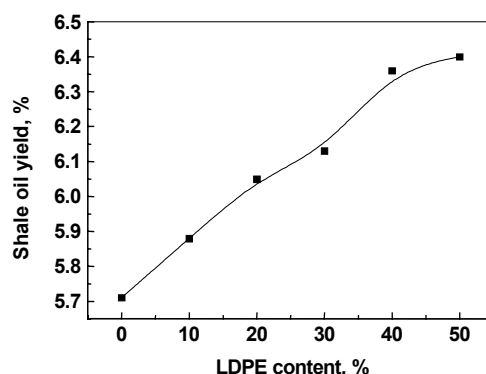
Fig. 4. Effect of the percent content of LDPE on shale oil yield.

The oil yields at pyrolysis of oil shale, LDPE and their mixture (wt. ratio 3:1) measured by GB/T 1341-2001 method at 550 °C but not at 600 °C were 5.62; 94.30 and 28.26%, respectively. The shale oil yield increases by 0.47% when oil shale is pyrolyzed with LDPE. These results are in agreement with thermogravimetric analyzer studies. The experimental data indicate the synergetic effect on the shale oil yield.

LDPE oil, shale oil and the co-pyrolysis mixture oil are characterized by FTIR spectra in order to gain some insight into structural changes in shale oil after adding LDPE (Fig. 5). The FTIR spectrum of shale oil is similar to that of LDPE oil. The broad band at 3700 cm^{-1}~3100 cm^{-1} has been attributed to water. Aliphatic hydrocarbon stretching bands are observed at 3000 cm^{-1}~2800 cm^{-1}. The peak near 1650 cm^{-1} is associated with the contribution of aromatic and olefinic carbon double bonds. Significant differences are found between the co-pyrolysis oil and that of the others. The intense absorption near 2360 cm^{-1} can be assigned to alkynes
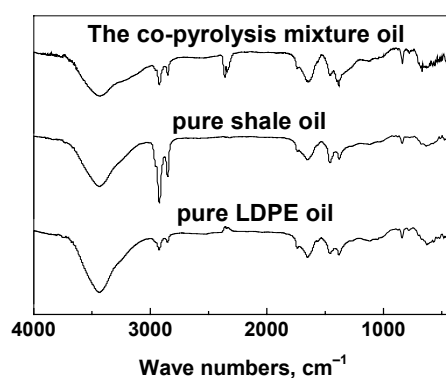

Fig. 5. FTIR spectra of LDPE oil, shale oil and the co-pyrolysis mixture oil (the content of LDPE 30 wt.%).

carbon triple bond stretching vibration, with possible contribution from C=C=C bond stretching vibration of allenes [13]. The reasons of this difference can be as follows: fixed carbon that cannot be converted to shale oil by conventional pyrolysis method is induced to alkynes or allenes by LDPE acting as a catalyst.

Conclusions

Thermogravimetric analysis reveals that two stages of weight loss are involved during the pyrolysis of oil shale mixed with LDPE. The difference in weight loss between the pure oil shale and that mixed with LDPE calculated as algebraic sums of the mixture is 1.17% at 550 °C. The temperature of the mixture maximum degradation is approximately 5 °C lower than that of oil shale. The co-pyrolysis experiment shows that adding of LDPE will improve the potential oil producibility of oil shale, and a synergistic effect exists to some extent during pyrolysis of oil shale mixed with LDPE. Analysis of the FTIR spectra shows that the co-pyrolysis oil contains novel alkynes or allenes, not occurring in shale oil or LDPE oil. Co-pyrolysis improves the quality of shale oil.

Acknowledgements

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