

Characteristics of Products by Supercritical Water Cracking in Comparison to Thermal Cracking

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Closed system polyethylene cracking was studied in a comparative supercritical water cracking and water-free thermal cracking experiment. The conditions were a reaction temperature of 425°C, reaction time of 120 minutes and, for supercritical water cracking, a water fill rate of 30%. The rate of cracking was slower in the supercritical case. The oil conversion rate was 90.2 wt% for supercritical water cracking and 71.8 wt% for thermal cracking. Generated gas was 12.0 wt% in the thermal case and 6.5 wt% in the supercritical case. In thermal cracking, the whole inside of the reactor was black after the reaction, showing large quantities of coke particulate. When the reaction time of supercritical water cracking was extended to 180 minutes, the nature and viscosity of the products were equal to those obtained from thermal cracking over 120 minutes but the oil conversion rate was higher at 77.7 wt %.

1. Introduction

High-pressure, high temperature (over 100°C) aqueous solutions can support hydrothermal reactions. Supercritical water in particular, with a temperature higher than 374°C and pressure higher than 22.1 MPa, behaves quite differently than water at ordinary temperature and pressure.

Hydrothermal cracking and upgrading high molecular weight compounds such as coal¹ and oil sand² in a supercritical state have been reported elsewhere. A recent report describes the recovery of terephthalic acid by hydrolyzing PET³, a dehydrated condensation polymer, in supercritical water. Although polyethylene is a plastic waste which is ranked first in quantity, hydrothermal cracking of polyethylene in supercritical water has not been reported elsewhere.

In this study, experiments were conducted in a water-free thermal condition (thermal cracking) and in a supercritical water condition (supercritical water cracking). The products and yields were compared to clarify the characteristics of hydrothermal cracking of polyethylene in supercritical water.

Based on the results, the effectiveness of supercritical water cracking, from an engineering perspective of practical applications of polyethylene resin conversion into oil under supercritical water conditions, was examined.

2. Experimental

2.1 Material and Method

Because it is easy to acquire and has uniform quality, high density polyethylene (Aldrich Ltd.) with a particle diameter of 4-5 mm and a density of 0.950 (referred to as PE) was used as the material for the experiment.

The reactor used is a batch, bomb-type autoclave. This high pressure reactor has an inner wall of Hastelloy C-276, a volume of 42 cm³, a maximum working temperature of 500°C and a maximum working pressure of 50 MPa.

In the supercritical water cracking experiment, the washed and dried reactor was filled with certain amounts of water and the material. A stirring ball was put into the vessel, and cone-shaped packing was placed on top of the vessel. The packing was tightened and the vessel closed with the reactor screw cap. The reactor was placed into the induction oven. A thermocouple was then set on the reactor body and shaking and heating started. After a certain reaction time, heating and shaking were stopped and the reactor was removed from the oven and cooled. When the reactor temperature fell to room temperature, gases were collected by displacing them in water. After the gases were collected, the cap of the reactor was taken off to recover the liquid products. In the case of supercritical water cracking, the products were in the aqueous and oil phases. The oil phase was extracted with benzene and the aqueous phase was separated using a separation funnel. Finally, the benzene was distilled under a reduced pressure of 100 mm Hg at 40°C using a rotary evaporator. When the weight became constant, benzene removal was considered complete and the residual oily substances were considered to be the oil recovered. The weight of the oil recovered was measured to calculate the oil conversion rate, which was determined as:

$$\text{Oil conversion rate (\%)} = [\text{oil product weight (g)}/\text{PE filled (g)}] \times 100$$

The thermal cracking experiment, conducted for comparison, followed the same procedure except that water and the stirring ball were not put into the reactor. In this experiment, the viscosity of the oil product was low enough to directly recover, without using benzene, from the reactor with a pipette.

In the case of supercritical water cracking, the water fill rate (amount of water to reactor volume) was 30%. The amount of PE was determined to give a 5:1 water/polyethylene ratio in supercritical water cracking.

2.2 Analysis of the products

The components of the gases were qualitatively and quantitatively analyzed by gas chromatography (GC). Viscosity of the oil product was measured at a constant temperature of 40°C. Components of the oil products were qualitatively analyzed using a mass spectrometer. The distillation curve of the oil product was obtained by the Simulation Distillation method (hereafter referred to as SIM/DIS) with high temperature GC.

3. Results and discussion

3.1 The products

The nature, viscosity and mass balance of the oil products from thermal and supercritical water crackings were compared. Table 1 shows the results.

"Other" is an index which represents the amount of the coke by-product sticking to the inner surface of the reactor that influenced the total mass recovered as an error. Reaction pressure was the pressure just before removing the reactor from the oven.

There were noticeable differences in the color and nature of the products from thermal and supercritical water crackings. The oil product from thermal cracking was a blackish-brown liquid oil compared to supercritical water cracking where the oil product was a clean, yellow-brown liquid and greasy at room temperature (completely molten at about 30°C).

The viscosity of the oil products from thermal cracking was 1.6 cP, while that from supercritical water cracking was 9.3 cP, showing the production of higher viscosity oils in the supercritical case.

A comparison of the nature and viscosity of the oils indicates that the rate of supercritical water cracking is slower than that of thermal cracking.

Table 1 Comparison of products

	Appearance (room temp.)	Color	Oil viscosity (40°C)	Oil conversion rate	Gas generated	Other
Thermal cracking (120 minutes)	Liquid	Blackish-brown	$1.6 \times 10^{-3} \text{Pa s}$	71.8wt%	12.0wt% (245cm ³)	16.2wt%
Supercritical water cracking (120 minutes)	Grease	Yellow-brown	$9.3 \times 10^{-3} \text{Pa s}$	90.2wt%	6.5wt% (130 cm ³)	3.3wt%
Supercritical water cracking (180 minutes)	Liquid	Blackish-brown	$1.8 \times 10^{-3} \text{Pa s}$	77.7wt%	13.2wt% (260 cm ³)	9.1wt%

Reaction temperature : 425°C

In this table; "Other"(wt%) = $\{ \text{PE filled (g)} - (\text{oil recovered (g)} + \text{gas generated (g)}) \} / \text{PE filled (g)}$

Supercritical water cracking resulted in a higher oil conversion rate of 90.2 wt%. The amount of generated gases for thermal cracking was 12.0 wt%, while that for supercritical water cracking was 6.5 wt%. This indicates that the generation of gases from supercritical water cracking was half that of thermal cracking. The "other" category in supercritical water cracking was 3.3 wt%, which was one fifth that of thermal cracking at 16.2 wt%. Thus, there are considerable differences between thermal and supercritical water crackings.

3.2 Coke by-product

In thermal cracking, the whole inner surface of the reactor had turned black after the reaction, indicating large quantities of coke particulate. This suggests that coke was also produced in the gaseous reaction. In supercritical water cracking, the color of the inner surface of the reactor was unchanged and no coke by-product was recognized in the oil.

The "other" category in supercritical water cracking includes light oil components that are co-removed with the benzene when recovering oils from the reactor after the reaction. The "other" in thermal cracking includes the so-called recovery error. To measure the amount of the light oil components that were removed together with benzene, oil products were taken for analysis, without using benzene, from the reactor. Using the SIM/DIS analysis, the weight percent of the oils below 80.099°C (the boiling point of benzene) was calculated, resulting in about 2.6 wt% in supercritical water cracking (against 7.8 wt% in thermal cracking). This may suggest that, in supercritical water cracking, the light oil components, amounting to about 2.6 wt%, were distilled and removed with benzene. The "other" category for supercritical water is 3.3 wt%. The difference of 0.7 wt% can be represented as the "other corrected". The "other corrected" is considered to include coke by-product, errors and liquid phase products. The difference of 8.4 wt% in thermal cracking is significantly large compared to supercritical water cracking, and the generation of the coke by-product has been recognized.

3.3 Oil conversion rate

In the comparison of the nature and viscosity of the oil products in Table 1, it is presumed that at the 120 minute reaction time, cracking proceeded faster in the case of thermal cracking. Generally,

as the cracking proceeds, gas generation also proceeds. Thus it is plausible that the supercritical water cracking may be accompanied by a reaction to produce coke and generate gases if the reaction time is long enough to convert the polyethylene into the oil that has a nature and viscosity equivalent to the oil produced by thermal cracking. This could result in a lower oil conversion rate.

To examine this supposition, the reaction time of supercritical water cracking was extended to as long as 180 minutes and this produced oil products with a nature and viscosity equivalent to oil products in thermal cracking. The results are shown in Table 1.

When comparing results in the 180 minute reaction of supercritical water cracking to those in the 120 minute reaction of thermal cracking shown in Table 1, the nature and viscosity of the oil products are almost equal but the supercritical water cracking gives a smaller percent of "other" and a larger percent of gas generation. The oil conversion rate in supercritical water cracking is still higher than that in thermal cracking in the 120 minute period.

It was also found that in the supercritical water cracking, the whole inner surface of the reactor had turned slightly black after the reaction. This suggests coke production but in a very small quantity. On the contrary, a large quantity of coke was produced in thermal cracking.

When comparing the 120 minute and 180 minute reaction times for supercritical water cracking, the percent of "other" is higher in the 180 minute case. This may be caused by the extended recovery loss that occurred in the removal of the benzene used to recover the oils. Then oils were recovered again, without using benzene, directly from the reactor, and these oils were analyzed by SIM/DIS. The obtained value was 8.1 wt% and this may suggest that the light oil components corresponding to 8.1 wt% were distilled and removed with the benzene used for oil recovery. In this case, the "other corrected" is 1.0 wt%. This value is small compared to that for thermal cracking, also indicating that coke generation does not easily occur in supercritical water cracking.

As described above, the results may be summarized as follows: Although there are no major differences in the nature and viscosity of the oil products of thermal and supercritical water crackings, the supercritical case shows an inhibition of coke production and a higher oil conversion rate. This suggests that these two crackings have potentially different reaction mechanisms, caused by hydrogen donation in a certain manner and radical stabilization/inhibition of per-cracking due to the existence of supercritical water. It is commonly known that the existence of hydrogen gas inhibits coke production during the thermal cracking of high molecular hydrocarbons⁴.

4. Conclusion

- (1) In supercritical water cracking, the generation of coke, which is unavoidable in thermal cracking, is inhibited.
- (2) In supercritical water cracking, the oil yield from polyethylene is high compared to the thermal cracking.

References

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