

THERMAL DECOMPOSITION CHARACTERISTIC OF VACUUM RESIDUE IN ATHABASCA TAR SAND BITUMEN

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INTRODUCTION

To develop and establish the effective use of tar sand bitumen in the future, it is necessary to clarify the reaction characteristics related with the information of chemical structure. There were many studies on the chemical structure of tar sand bitumen¹⁻³⁾, and many kinetic reaction models were also proposed. However the study on the reaction characteristics concerned with the chemical structure is few^{4,5)}. The initial upgrading step in the conversion of bitumen to synthetic crude is the thermal decomposition of heavy macromolecule in bitumen, which would be the simplest reaction. This study aims at elucidating the thermal decomposition characteristic of vacuum residue in bitumen on the basis of conversion and chemical structure changes.

EXPERIMENTAL

Sample preparation

The used raw-bitumen is Athabasca tar sand bitumen (C: 82.6, H: 10.5, N: 0.5, O: 2.3, S (diff): 4.1 wt%). Two kinds of sample series were prepared by a vacuum distillation based on ASTM D1160. One is the light fraction (boiling point range, 723K under) and vacuum residue. The other is the blended sample of vacuum residue with light fraction by various weight fractions.

Thermal decomposition reaction

Thermal decomposition reaction was conducted in a 60 cm³ autoclave with an electromagnetic stirrer. The autoclave was heated at 90 K/min by an infrared image furnace and cooled at 100 K/min by blowing air. Connecting the reactor with a 500 cm³ buffer vessel kept the pressure almost constant through each reaction. Five grams of sample were loaded in the reactor. The reaction temperature and pressure were 693 K and 10 MPa in N₂, respectively.

Product characterization

After each reaction, a product was recovered with dichloromethane. Produced gas yield was obtained from the data of TCD gas chromatograms.

Boiling point distribution of the product was measured by a thermogravimetric analysis (SD-TGA), which was in good agreement with the standard distillation method (ASTM D2892^{6,7)}. The distribution was plotted as a function of boiling point index that is not true one but fairly corresponds to it.

Samples for the ¹H-, ¹³C-NMR measurements were dissolved in deuteriochloroform. Both spectra were obtained with a α -500 type Fourier transform spectrometer (JEOL Ltd.). ¹³C-NMR spectra were obtained by using a pulse width of 11.5 μ s, total of 1000 transients and gated decoupling to ensure quantitative results. Tris(acetylacetonate)chromium(III)(Cr(acac)₃) was used as the relaxation reagent⁸⁾. From conventional ¹H-NMR spectra, aromatic-H_{ar}, H α , H β and H γ illustrated hydrogen distribution.

Elemental analyses were carried out with a CHNO analyzer. Molecular weight measurements were made with a KNAUER vapor pressure osmometer.

RESULTS AND DISCUSSION

Thermal decomposition characteristics of vacuum residue

Figure 1 shows the variation of product yields with reaction time for the vacuum residue. Yields of heavy and light components in a sample were calculated from SD-TGA data and a cut point between both components was 723 K. Loss was a volatile matter that was lost in product recovery from a autoclave, and might be low molecular hydrocarbons such as hexane and heptane. With the progress of the reaction, gas, loss and light component gradually increased.

To discuss the degree of decomposition of macromolecule in vacuum residue, a conversion was defined as the weight ratio of decrease of heavy component to initial one. Figure 2 shows the change in conversion and average molecular weight with the reaction time. At 0 min of nominal reaction time, no remarkable change of molecular weight was observed, but it was reduced to almost half up to 10 min. This suggests the decomposition of macromolecule in the vacuum residue. The molecular weight was finally almost constant, namely, about 400. While the conversion gradually increased with the progress of the reaction.

Chemical structural change during thermal decomposition reaction

Figure 3 shows the weight change of various carbon types by unit gram of vacuum residue with the reaction time. Carbon weight by unit gram was calculated based on the carbon distribution obtained from ^{13}C -NMR, elemental analysis data and product yield. Carbons are assigned six types from the chemical shifts in ^{13}C -NMR spectra^{9,12}, named as methyl carbons, methylene carbons, α -methylene carbons, unsubstituted aromatic carbons, bridgehead aromatic carbons and substituted aromatic carbons.

In Fig. 3, a remarkable weight decrease of α -methylene carbons was recognized in the initial stage of reaction. Methylene carbons and unsubstituted aromatic carbons had gradually weight decreasing and increasing tendency with the progress of the reaction, respectively. While, the values of weight of the other carbons were almost constant.

Carbons assigned α -methylene carbons included α -methylene carbons on an aliphatic methylene bridge and a side chain except for ethyl group, and methine carbons in a naphthenic ring¹². Methylene carbons included methylene carbons in a naphthenic ring and β or further position on a side chain from an aromatic ring, α -methylene carbons on an ethyl group, and methine carbons on a side chain.

In the initial stage of reaction, the decomposition of an aliphatic bridge including in a macromolecule, resulting in the reduction of molecular weight to half in Fig. 2, could explain the remarkable weight decrease of α -methylene carbons. At the same time, the dehydrogenation of naphthenic ring and the cleavage of an aliphatic chain would bring about mainly the weight increase of unsubstituted aromatic carbons and decrease of methylene carbons. With the progress of the reaction, these reactions would be prior.

To confirm the above consideration, numbers of aromatic and naphthenic rings in an average molecule were estimated¹³ as shown in Fig. 4. The naphthenic ring number changed in unique manner with the reaction time. Considerable decrease of naphthenic ring number up to 10 min was corresponding with the reduction of molecular weight to half resulting from the decomposition of a macromolecule. Furthermore, the naphthenic ring number increased at 30 min by a ring formation on a still remaining aliphatic chain. On the contrary, the aromatic ring number decreased in the initial stage of reaction, but was not the reduction to half. This also suggests the dehydrogenation of naphthenic ring. Subsequently aromatic ring number gradually increased after 30 min.

The conversion at 0 min of reaction time was not so high in spite of the reduction of molecular weight to half. The values of molecular weight and estimated total carbon number in an average molecule were about 540 and 38, respectively. According to our boiling point calculation¹⁴, the boiling point of this average molecule should be at least 790 K. At 60 min of reaction time, the boiling point of product would be 720 K as the total carbon number fell to about 30. Consequently, the conversion was still low in the initial stage of the reaction, and gradually increased with the progress of reaction.

Influence of light component on conversion of heavy one in a bitumen

To clarify the decomposition characteristics of heavy component in the presence of light one in bitumen, vacuum residues blended with light fraction in different ratios were prepared. If the thermal decomposition of heavy and light components occur independently each other, the conversion should not change regardless of light fraction content. In Fig. 5, the change in conversion at 60 min of reaction time with weight content of light fraction is shown. The conversion decreased with the increase of the weight content of light fraction. This suggests that the light component affects the conversion of heavy component to light one. In this section, interactions between the heavy and light components in a thermal decomposition would be clarified on the basis of chemical structure changes in a product.

Figures 6 and 7 show differences in the weight of aromatic and aliphatic carbon types by unit gram before and after reaction versus the weight ratio of light component to heavy one in a blended sample, respectively. The plots are scattered to some extent in both figures. A dashed line and open symbols were calculated on the assumption that the thermal decomposition of heavy and light components occurs independently each other, and a solid line is smoothing experimental values indicated by solid symbols. As a vacuum residue contains about 30 wt% of light component by SD-TGA, the minimum weight ratios in both figures are not zero but about 0.5. The differences in weight of aromatic and aliphatic carbons before and after reaction of 60 min became plus and minus values, respectively. If examined in detail, weight increase of unsubstituted aromatic carbons was remarkably kept down with the increase of light component content, and weight decrease of α -methylene carbons was also controlled by light component. The weight differences of other carbons were almost equal between calculated and observed ones in the presence of light component. These controls of weight change would be explained by some interpretations on the interaction between heavy and light components in the thermal decomposition. The condensed naphthenic ring formation and the polymerization of light component with heavy one would contribute the weight increase of α -methylene carbons. The control of dehydrogenation on a naphthenic ring would bring about the weight decrease of unsubstituted aromatic carbons.

Summarizing above discussion, the thermal decomposition characteristic of a blended sample was related with the chemical structure changes, though a detailed reaction scheme could not be illustrated at the present time.

CONCLUSIONS

A thermal decomposition characteristic of vacuum residue in bitumen is discussed from conversion and chemical structure changes.

In the initial stage of reaction, cleavage of aliphatic bridge occurs, resulting in the decrease in average molecular weight. With the progress of the reaction, the dehydrogenation at naphthenic rings and release of low molecular weight hydrocarbon from side chain take place, therefore a remarkable change of average molecular weight was not observed, but the conversion is gradually increasing.

In the thermal decomposition of residue with the light fraction, the conversion decreased with the increase in weight ratio of light fraction in blended samples. Polymerization of the light component with the heavy one would be suggested.

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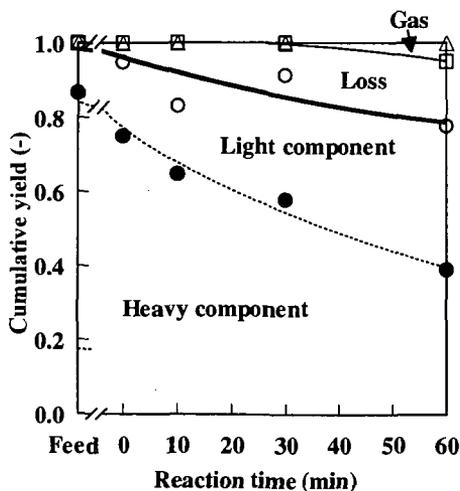


Fig. 1 Change in cumulative yield of product with reaction time

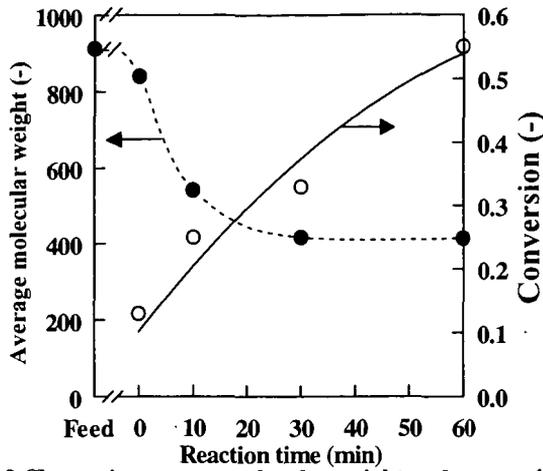


Fig. 2 Change in average molecular weight and conversion with reaction time

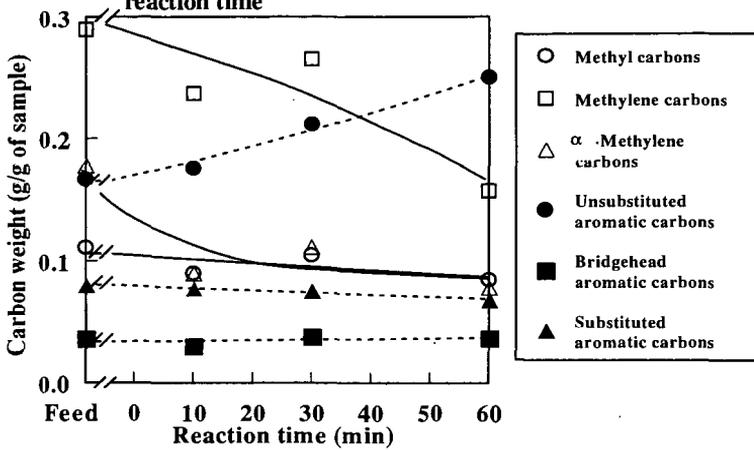


Fig. 3 Change in carbon weight by unit weight of sample with reaction time

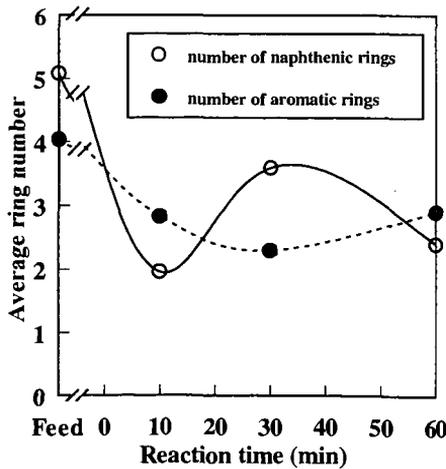


Fig. 4 Change in aromatic and naphthenic ring with reaction time

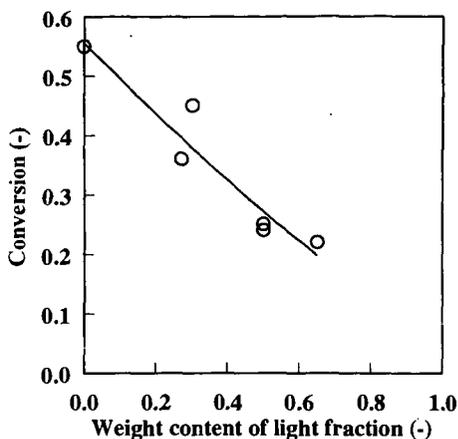


Fig. 5 Change in conversion for blended sample with weight content of light fraction

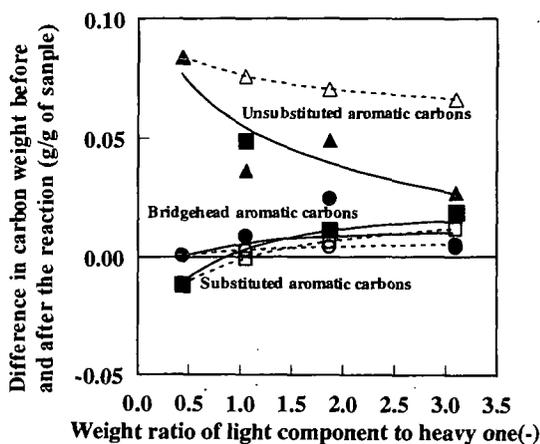


Fig. 6 Change in weight difference of aromatic carbons with weight ratio of light component to heavy one

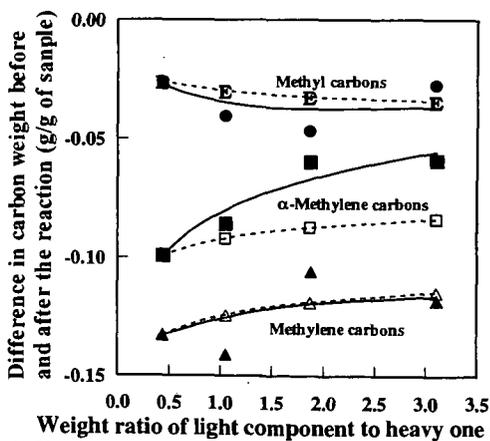


Fig. 7 Change in weight difference of aliphatic carbons with weight ratio of light component to heavy one