

STUDY ON INTERACTION BETWEEN COAL AND MODEL PLASTICS DURING LIQUID-PHASE CATALYTIC COLIQUEFACTION

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ABSTRACT

Coliquefaction of Tanitoharum coal with PP, PS, high-density PE was carried out using red mud plus sulfur as the catalyst, at 430 °C for 60 min under 7 MPa initial pressure of hydrogen. There existed almost linear relationship of coal concentration in coal/plastics mixture with conversion to THF-soluble (THFS) or oil yield for the mixture of coal/PP, coal/PS or coal/PE in case of tetralin. Observed oil yield at 75 % of coal concentration for any coal/plastics mixture was slightly larger than that calculated. The use of decalin gave lower values of conversion, yields of THFS in VR and oil, particularly at coal concentration of 75% for the coal/PE mixture, compared to those calculated, while a similar tendency as to interaction in respect of conversion, yields of THFS in VR, oil, and gas was observed for the mixture of coal/PP and coal/PS. However, when the coal was reacted with mixed plastics of PP, PS and PE at coal concentration of 50 %, the interaction observed for the coal/PE mixture disappeared, and higher oil yield than that calculated was obtained. The results suggested interaction between PE and the other plastics (PP, PS) is larger than that between coal and PE. It is also suggested from the results for the coal/PP mixture that radicals from PP cracking was used for stabilization of radicals from the coal and PP, instead of hydrogen donated from gas and solvent. Higher values of conversion and oil yield for the use of decalin were obtained, compared to tetralin. The results indicated that a good hydrogen donor solvent would not be necessary in case of the use of catalyst for coliquefaction of coal with waste plastics.

Keywords: coal liquefaction, model compounds, waste plastics

1. INTRODUCTION

Under conventional direct coal liquefaction process, large amount of hydrogen gas is consumed to stabilize radical fragments from thermal cracking of coal. At present the price of produced coal liquid does not compete with that of crude oil, due to not only the severe operating conditions, but also the expensive production cost of hydrogen gas. Coprocessing of coal with heavy oil containing high concentrations of sulfur and heavy metals, has been investigated to improve the economical feasibility¹⁾. On the other hand, large amounts of waste plastics is being generated in Japan, mostly not recycled. The shortage of landfilling site has become more serious in recent years. Thus, coliquefaction of coal with heavy oil and waste plastics would be an attractive process of overcoming environmental problems and further enhancing economical feasibility. However, few studies have reported on this reaction, due to the complicated reaction system²⁾. We have conducted a model experiment of coliquefaction of coal with waste plastics using dibenzyl as a coal model compound to clarify the reaction mechanism, and investigated interactions between coal and plastics, and between the plastics, in respect of conversion, product distribution and composition of distillate oil³⁾.

In this study, catalytic coliquefaction of coal with model plastics was conducted under the same reaction conditions as those for the model experiment. Interaction between the coal and plastics was investigated in respect of conversion, product distribution, and H₂ transferred from gas or solvent, and the reaction mechanism involved was discussed.

2. EXPERIMENTAL

Catalytic coliquefaction of Tanitoharum coal (-100 mesh, C 75.91, H 5.66, N 1.62, S 0.37, O 16.44 (wt% daf (dry ash free) base)) with model plastics (PP, PS, high-density PE) and their mixture (1/1/1 by weight) was carried out at 430 °C for 60 min in a 500-ml magnetically stirred autoclave. Tetralin or decalin was used as the solvent. Red mud (total Fe 28.37 wt%) plus sulfur (1/1 by weight) was used as the catalyst. Weight ratio of (daf coal + plastics)/solvent/red mud was 100/150/3/3. Gas atmosphere was 7 MPa initial pressure of hydrogen gas. After the reaction, the measurement of gas volume and GC analysis were conducted for the product gas. Main part of the product liquid (plus any unconverted solid reactant and catalyst) was separated into distillate oil (-538 °C) and vacuum residue (+538 °C, VR) by vacuum distillation. The product liquid in part was subjected to Soxhlet extraction with hexane, tetrahydrofuran (THF) sequentially. Conversion to hexane & THF-soluble (THFS), yields of oil, hexane & THF-soluble in vacuum residue (THFS in VR), gas, and hydrogen gas consumption were measured, based on the weight of daf coal plus plastics by conventional methods. The composition of the distillate oil was analyzed using FID/GC. H₂ transferred from solvent was calculated from mass balance of naphthalene, decalin for the use of tetralin as the solvent

or tetralin, naphthalene for the use of decalin, before and after the coliquefaction⁴).

3. RESULTS AND DISCUSSION

Coliquefaction of coal with PP, PS or PE using tetralin

In Fig. 1, conversion to THFS, yields of oil, THFS in VR, and gas for coliquefaction of Tanitoharum coal with each of PP, PS or PE using tetralin were plotted against coal concentration in coal/plastics mixture.

Without any coexisting reactant, for each of the coal, PP, PS and PE, conversion of 99.7, 100, 100, 31.9 wt%, oil yield of 37.4, 76.4, 94.0, -1.2 wt%, yield of THFS in VR of 41.1, 13.9, 2.9, 28.8 wt%, and gas yield of 11.9, 10.1, 4.0, 3.9 wt%, respectively were obtained. PE was most difficult to be converted to THFS and oil among the reactants, while PS was almost converted to oil. For PP, conversion was very high, and larger yield of THFS in VR was produced, compared to PS. Gas produced from PP was largest among the plastics. For the coal, oil yield was much lower than those for PP and PS, in spite of very high conversion, and production of THFS in VR was largest among the reactants.

In case of coliquefaction, there existed almost linear relationship of coal concentration with conversion to THFS or oil yield. Oil yield at 75 % of coal concentration for the mixture of coal/PP, coal/PS or coal/PE was higher by 4.9, 4.8, 3.3 wt% respectively than that calculated (arithmetic mean value of results for each reactant). As to THFS in VR, almost linear relationship against coal concentration was obtained for the mixture of coal/PS or coal/PE, but observed values for the coal/PP mixture were higher than those calculated. As to gas yield, observed values for any coal/plastics mixture were lower than those calculated. The difference between the calculated value and the observed value was very large for the coal/PP mixture, compared to the other coal/plastics mixture.

Fig. 2 shows H₂ transferred from gas and solvent in this reaction as a function of coal concentration in coal/plastics mixture.

H₂ transferred from gas or tetralin (mmol/g-daf reactant) was 15.5, 4.6 for the coal, 4.4, 1.9 for PP, 6.6, 3.1 for PS, and 0.94, 0.62 for PE, respectively. H₂ transferred from gas or tetralin for coal was largest among the reactants. It was observed that larger amounts of H₂ from gas or tetralin was transferred for PS than for PP. The amounts of H₂ transferred was small for PE. However, it is thought by considering the difference in conversion between PP and PE that the values for PE would become similar to those for PP when 100 wt% of conversion is obtained for PE.

For the coal/PE mixture, almost linear relationship of H₂ transferred with coal concentration was recognized. For the coal/PS mixture, H₂ transferred from gas were a little larger than those calculated, while H₂ transferred from tetralin were a little lower than those calculated. No difference in total of H₂ transferred between the observed value and the calculated value was observed. For the coal/PP mixture, H₂ transferred from gas or tetralin was lower than that calculated. The results from Figs. 1 and 2 for the coal/PP mixture suggest that radicals from PP cracking would be used for stabilization of radicals from the coal and PP, instead of hydrogen donated from gas and solvent.

Decomposition of PE proceeds as radical chain reaction. In the model experiment of coliquefaction of dibenzyl (DB) as a coal model compound with model plastics using tetralin and the same catalyst, conversion and yield of THFS in VR were higher than those calculated, suggesting that radicals from DB decomposition would secondarily attack PE³. However, the tendency for the coal/PE mixture as seen in Figs. 1 and 2 is different from that in the model experiment. On the other hand, the mixtures of coal/PP and coal/PS showed almost the same tendencies as those from the model experiment.

Coliquefaction of coal with PP, PS or PE using decalin

In Fig. 3, conversion to THFS, yields of oil, THFS in VR, gas, and H₂ transferred for coliquefaction of the coal with each of PP, PS or PE using decalin were plotted against coal concentration in coal/plastics mixture.

Without any coexisting reactant, for each of the coal, PP, PS and PE, conversion of 96.6, 100, 100, 77.3 wt%, oil yield of 42.6, 83.3, 92.5, 15.6 wt%, yield of THFS in VR of 36.4, 3.7, 3.5, 57.8 wt%, gas yield of 12.9, 14.5, 5.0, 3.9 wt%, and total of H₂ transferred from gas and decalin of 18.8, 9.8, 7.7, 2.1 mmol/g-daf reactant, respectively were obtained. Here, (H₂ transferred from gas)/(total H₂ transferred) were 3-7 %. Thus, H₂ transferred from decalin were small, compared to tetralin. The use of decalin instead of tetralin remarkably accelerated PE decomposition. This result indicates that the increase in hydrogen donorability of solvent inhibits PE decomposition, probably due to more rapid stabilization of radicals from PE cracking by hydrogen donation from solvent. For PP, yield of THFS in VR decreased, while yields of oil and gas increased a little. For PS, there was no large difference observed between decalin and tetralin, in respect of conversion, yields of THFS in VR, oil and gas. For the coal, the use of decalin instead of tetralin gave a little lower conversion, while oil yield became a little larger.

In case of decalin, considerably different coliquefaction behavior was obtained for the

coal/PE mixture, compared to tetralin. Conversion, yields of oil and THFS in VR were lower than those calculated, although there existed linear relationship of coal concentration with gas yield and total of H₂ transferred. The differences in conversion, yields of oil and THFS in VR between the observed value and the calculated value were very large at coal concentration of 25 %. The differences were not observed in case of tetralin. Hydrogen donation from hydrogen donor solvent to radicals is much faster than that from hydrogen gas even for catalytic coal liquefaction. For the use of decalin, radicals from cracking of the coal and PE would exist for longer time, compared to tetralin, resulting in larger interaction between radicals to polymerize to give THF-insoluble fraction. On the other hand, in the model experiment of coliquefaction of DB with model plastics using decalin and the same catalyst, PE decomposition proceeded more effectively with coexistence of the coal model compound, giving higher values of conversion and oil yield⁹. Thus, the results in Figs. 1-3 indicate that the coal would interacted with PE in a different way, compared to the coal model compound of DB. In case of coliquefaction of the coal with PP, almost linear relationship of coal concentration with conversion or oil yield was obtained. Yield of THFS in VR were higher than those calculated, while gas yield and total of H₂ transferred were lower than those calculated. The tendency for the coal/PP mixture was same, compared to that for the use of tetralin. The differences in total of H₂ transferred between the observed value and the calculated value became larger than those for the use of tetralin. From the results, more effective use of radicals from PP cracking for stabilization of radicals from the coal and PP instead of hydrogen could be expected. For the coal/PS mixture, there existed almost linear relationship of coal concentration with conversion, yield of THFS in VR. Oil yield and total of H₂ transferred were a little higher than those calculated, while gas yield was lower than that calculated. The tendency in respect of conversion, yields of oil, THFS in VR and gas was similar to that for the use of tetralin.

Coliquefaction of coal with mixed plastics of PP, PS and PE

Table 1 shows results of coliquefaction of the coal with mixed plastics of PP, PS and PE using tetralin or decalin and the same catalyst. Coal/mixed plastics was 1/1 and PP/PS/PE was 1/1/1. Two kinds of calculated value (cal¹: arithmetic mean value of results from the coal/PP, the coal/PS and the coal/PE (1/1 mixture), cal²: arithmetic mean value of results for each reactant) are also shown in this table.

Coliquefaction using tetralin gave a little higher gas yield, lower values of conversion and yield of THFS in VR, compared to cal¹. On the other hand, conversion and THFS in VR also became lower, compared to cal² but gas yield was larger. There existed almost no difference in oil yield between the observed value and the calculated value, not depending on the way of calculation. Coliquefaction using decalin gave the same gas yield, higher values of conversion and oil yield, and a little lower yield of THFS in VR, compared to cal¹. On the other hand, almost the same conversion, lower yields of THFS in VR and gas, and higher oil yield were observed, compared to cal². The results indicate that PE decomposition proceeded more effectively with the coexistence of PP and/or PS during coliquefaction of the coal with the mixed plastics, although PE decomposition inhibited by coexistence of the coal in case of coliquefaction of the coal with PE alone. It is also suggested that the results reflected larger interaction between PE and the other plastics (PP, PS) than that between coal and PE. Lower gas yield in case of tetralin or decalin, compared to cal², as seen in Table 1 was probably due to inhibition of gas production by the coexistence of PP, also shown in Figs.1 and 3. Total of H₂ transferred for the use of tetralin or decalin was only a little lower, compared to cal², due to the low concentration of PP in coal/plastics mixture.

As also seen in Table 1, higher values of conversion and oil yield for the use of decalin were obtained, compared to tetralin. The results indicate that a good hydrogen donor solvent would not be necessary in case of the use of catalyst for coliquefaction of coal with waste plastics.

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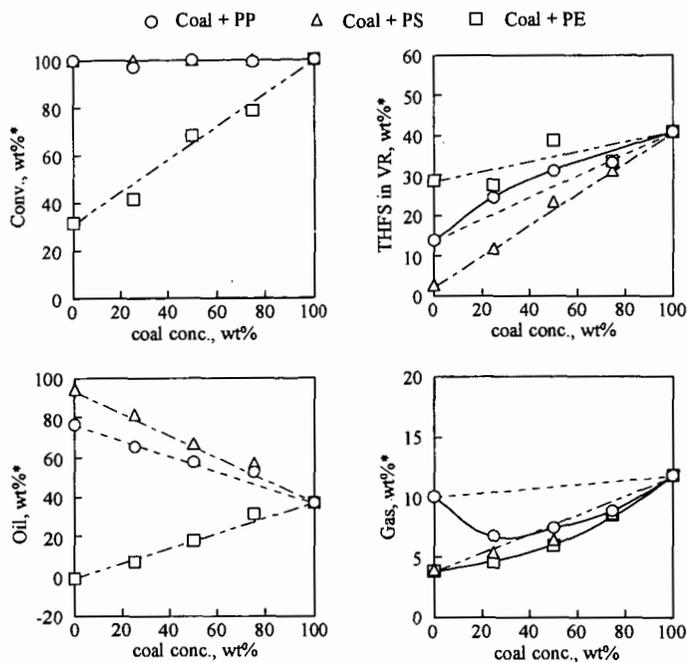


Fig. 1 Coliquefaction of Tanitoharum coal with plastics using tetralin as the solvent at 430 °C for 60 min under 7 MPa initial pressure of hydrogen gas
* based on daf reactant

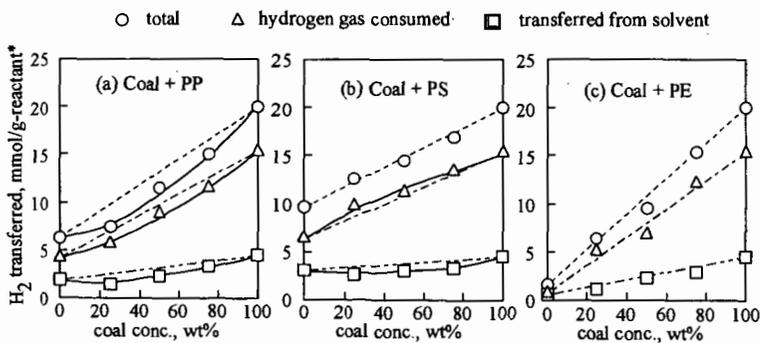


Fig. 2 Hydrogen transfer under coliquefaction of Tanitoharum coal with plastics using tetralin as the solvent at 430 °C for 60 min under 7 MPa initial pressure of hydrogen gas

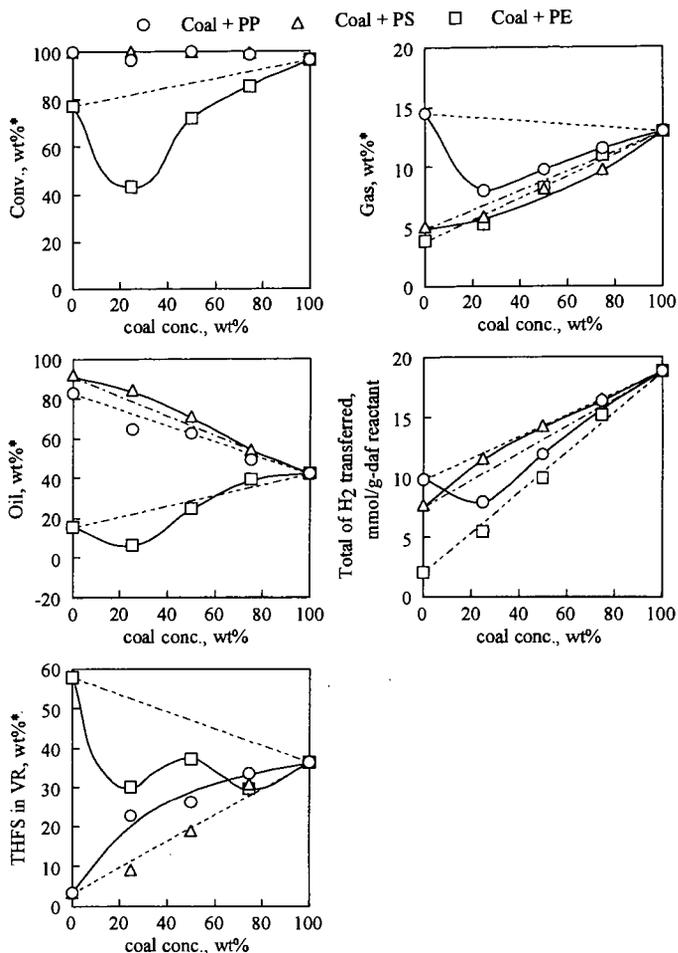


Fig.3 Coliquefaction of Tanitoharum coal with plastics using decalin as the solvent at 430 °C for 60 min under 7 MPa initial pressure of hydrogen gas

* based on daf reactant

Table 1 Coliquefaction of Tanitoharum coal with mixed plastics of PP, PS and PE at 430 °C for 60 min
(coal/mixed plastics = 1/1, PP/PS/PE = 1/1/1 (by weight))

| Solvent | Conv. (wt%) | THFS in VR (wt%) | Oil (wt%) | Gas (wt%) | Total of H ₂ transferred (mmol/g-daf reactant) | |
|----------|-------------|------------------|-----------|-----------|---|------------------|
| Tetralin | 85.31 | 26.65 | 47.75 | 7.50 | 12.41 | observed |
| | 89.31 | 31.38 | 47.38 | 6.64 | 11.80 | cal ¹ |
| | 88.52 | 28.17 | 46.90 | 8.92 | 12.95 | cal ² |
| Decalin | 93.31 | 25.39 | 57.57 | 8.84 | 12.04 | observed |
| | 90.64 | 27.43 | 53.12 | 8.77 | 12.08 | cal ¹ |
| | 94.53 | 29.02 | 53.22 | 10.37 | 12.70 | cal ² |

¹ arithmetic mean value of results for the coal/PP, the coal/PS or the coal/PE (1/1 mixture)

² arithmetic mean value of results for each reactant