

HYDROGEN TRANSFER DURING COAL LIQUEFACTION DETERMINED BY $^2\text{H}/^1\text{H}$ MEASUREMENT

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ABSTRACT

Liquefaction of Highvale coal was carried out with tetralin under 6.9 MPa H_2 gas pressure at 400°C and 450°C. The natural ^2H contents of the gas, tetralin, and coal differed substantially and were utilized as tracers of hydrogen transfer. The effect of Fe_2O_3 catalyst, reaction time, and temperature on hydrogen transfer were studied. Products from autoclave tests were separated into light oil, oil, pentane soluble, pentane insoluble - benzene soluble, benzene insoluble - THF soluble, and THF insoluble fractions. At the initial stage of coal liquefaction, hydrogen transfer or exchange between feed gas and coal derived products predominated. But, hydrogen transferred from tetralin was dominant in the more advanced stages of coal liquefaction. Fe_2O_3 catalyst accelerated the interaction between hydrogen gas feed and the coal derived products.

INTRODUCTION

The role of hydrogen is important during coal liquefaction and the control of hydrogen transfer is central to optimizing product distribution. Thus, many attempts have been made to elucidate the mechanisms of hydrogen transfer by deuterium tracer [1] [2], NMR [3] [4] and radioisotope tracer method [5] [6]. Recently, stable isotope methods were used to study coprocessing reactions [7]. In this study, the stable isotope technique was used to identify two separate hydrogen transfer mechanisms during coal liquefaction.

The natural isotopic ratio ($^2\text{H}/^1\text{H}$) in hydrogen gas, coal and tetralin differ substantially. Products derived from coal have $^2\text{H}/^1\text{H}$ ratios that may approach either that of tetralin or feed gas identifying the source of the hydrogen. The size of the shifts reflect the relative proportions of hydrogen transfer into coal from gas or tetralin.

EXPERIMENTAL METHODS

Materials. Highvale coal (analysis: C, 71.6; H, 4.4; O, 23.0; N, 0.7; S, 0.3; ash 13.7 wt%, dry basis) was ground to <100 mesh and dried at 110°C for 3 days under vacuum condition. Tetralin, H_2 , catalyst (Fe_2O_3) and sulfur were obtained from commercial sources.

Liquefaction procedure. All reactions were done in a 150 ml stirred autoclave. The coal (12g), tetralin (36g), iron oxide (Fe_2O_3 , 1.2g), sulfur (0.18g), and H_2 were charged into the autoclave at an initial pressure of 6.9 MPa. The autoclave was heated at 15°C/min and maintained at 400°C and 450°C for 0 min, 60 min and 120 min. For

comparison, tetralin alone, was treated with H₂ and catalyst. After reaction, the autoclave was cooled by blowing air. The volume of gas products was measured and collected in Teflon bags for analysis.

Light oil and oil were obtained by vacuum distillation after filtration of the reaction products. The vacuum residue was extracted to four parts PS (pentane soluble), PI-BS (pentane insoluble - benzene soluble), BI-THFS (benzene insoluble - THFS soluble), and THFI (THF insoluble). A 30 m OV-101 capillary column was used to characterize the liquid products.

Analytical procedure. The feeds and products were analyzed for ²H/¹H by conventional methods of stable isotope geochemistry described previously [7]. The isotopic ratios are determined by isotope ratio mass spectrometry, and the data are reported in the conventional delta notation, relative to the international standard, SMOW.

$$\delta D = \frac{([^{2}\text{H}/^{1}\text{H}] - [^{2}\text{H}/^{1}\text{H}]_{\text{SMOW}}) / [^{2}\text{H}/^{1}\text{H}]_{\text{SMOW}} \times 1000}{[^{1}\text{H}/^{2}\text{H}]_{\text{SMOW}} = 1.558 \times 10^{-6}}$$

The δD of the coal was -174 ppt, that of tetralin, -105ppt, H₂, -480ppt. The error on replicate analyses was ± 3 ppt.

RESULTS AND DISCUSSION

Liquefaction of Highvale coal was carried out in tetralin and H₂. Fig. 1(a) and Fig. 1(b) show the effect of reaction time and the action of Fe₂O₃ catalyst on product distribution at 400°C. THFI decreased with reaction time. Conversion of THFI was a little higher with catalyst than without catalyst. BI-THFS, PI-BS, light oil and gas increased gradually with time. The yield of PS and oil increased slightly with reaction time. These observations indicate that cracking of coal to products lighter than PS was difficult at 400°C. Less light oil and gas were produced when Fe₂O₃ catalyst was added.

The distribution of products from the 450°C runs are shown in Fig. 2(a) and Fig. 2(b). The initial rate of cracking coal was very rapid, nearly 65 % of coal was already converted at 0 min, or when the reactor reached operating temperature. BI-THFS decreased slightly with reaction time without catalyst. With catalyst, BI-THFS gave a low yield already at 0 min. The yield of PI-BS increased at first, but then decreased after 60 min of reaction time. PS, light oil and crack gas increased gradually. The early yield of PI-BS at 450°C was higher than that at 400°C. These trends show that the conversion of coal to PI-BS was rapid and PI-BS was decomposed gradually to PS.

When tetralin was treated without coal but with catalyst at 450°C, naphthalene, 1-methylindan and butylbenzene were produced in small amounts (2.0 wt%, 2.8 wt%, and 1.4 wt%). Therefore, under the experimental conditions, dehydrogenation and decomposition of tetralin was less than 6 wt% in presence of catalyst, and 5 wt% in

absence of catalyst at 450°C. Mainly naphthalene was produced from tetralin during coal liquefaction. 1-Methylindan and butylbenzene were identified in the product. The yield of these compounds in the oil was 1.5 wt% and 4.3 wt% at 400°C and 450°C from the 60 min runs. The δD of tetralin before and after reaction with catalyst at 450°C and 400°C in absence of coal was -105 ppt, -114 ppt and -115 ppt. These small shifts in deuterium content implied no more than 1.5% of hydrogen of the tetralin exchanged with feed gas.

Fig. 3 shows the amount of naphthalene produced in oil at 400°C during coal liquefaction. Naphthalene increased linearly with THFI conversion without catalyst. But, with catalyst, naphthalene increased only gradually. Under this reaction condition, where hydrogenation of naphthalene is very slow [8], the Fe_2O_3 catalyst accelerates hydrogenation of naphthalene back to tetralin. In the tests without catalyst, the amount of naphthalene corresponds to hydrogen transferred from tetralin to coal. Fig. 4 shows hydrogen transfer from tetralin at 450°C. Hydrogen was donated from tetralin to coal when high conversion of coal was achieved.

Fig. 5 shows the δD of the products obtained without catalyst. The δD of products decreased at 400°C with THFI conversion. These products approached the isotopic composition of the feed gas (-480ppt). In contrast, at 450°C, δD of the coal derived products, excluding oil and light oil, increased with THFI conversion. The increase in δD of the higher temperature products reflects hydrogen donation from the tetralin solvent ($\delta D = -105$). Fig. 6 shows the isotope ratio of all the product fractions at 0 min of reaction time. The δD of PS, PI-BS, BI-THFS, and THFI were from -190 ppt to -230 ppt. These negative shifts from original δD of Highvale coal ($\delta D = -174$ ppt) show that H_2 was more reactive towards coal than was tetralin. More extensive hydrogen exchange was observed in the presence of catalyst.

The δD of products at 60 min are shown in Fig. 7. The δD of fractions from 450°C were higher than that of products at 400 °C. This suggests that at 450°C, hydrogen transfer from tetralin is dominant. The larger shifts of δD with catalyst show that the Fe_2O_3 catalyst accelerated the interaction of H_2 gas and coal. Inspection of the δD values shows that hydrogen from tetralin preferentially reacts with heavier molecular weight fractions THFI and BI-THFS. In contrast, hydrogen in PS and PI-BS reflects more exchange with feed.

These observations show that hydrogen transfer during coal liquefaction proceeds by at least two different pathways. Initially, hydrogen transfer to coal is dominated by absorption of feed hydrogen gas. But, as reactions proceed, hydrogen transfer and exchange between tetralin and coal derived products become increasingly more important. The decrease of δD of the light oils reflect the incorporation of low- 2H feed gas showing

that the light oil was produced by cracking of coal directly followed by hydrogenation with feed gas.

CONCLUSION

1. Two separate mechanism of hydrogen transfer to coal products were identified. Hydrogen transfer from feed gas occurs at the earliest stages of liquefaction whereas hydrogen transfer from tetralin dominates the more extensive, later stages.

2. Fe_2O_3 catalyst accelerated the interaction between hydrogen feed gas and the coal derived products.

3. Hydrogen from tetralin preferentially goes into heavier fraction such as THFI and BI-THFS. Hydrogen in PS and PI-BS is more exchangeable with feed gas.

4. The efficiency of producing products lighter than PS from coal at 400°C was low. When Fe_2O_3 catalyst was added, light oil and gas production was even less. The cracking rate of coal to PI-BS was fast but this fraction gradually decomposed to PS at 450°C .

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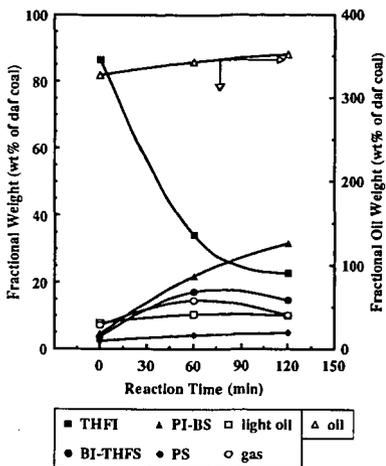


Fig.1(a) Product distribution with catalyst at 400°C.

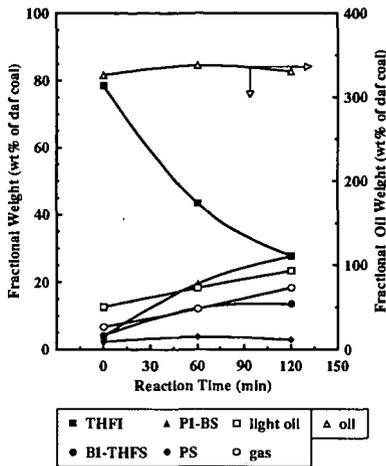


Fig.1(b) Product distribution without catalyst at 400°C.

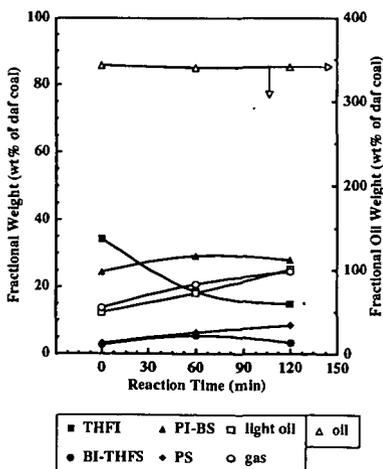


Fig.2(a) Product distribution with catalyst at 450°C.

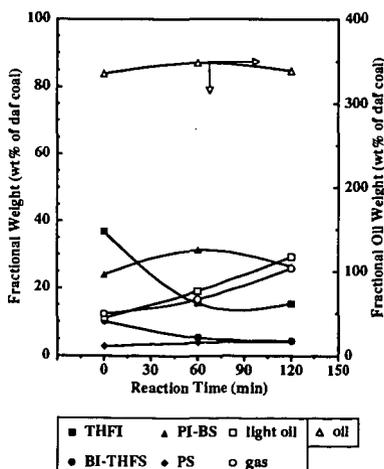


Fig.2(b) Product distribution without catalyst at 450°C.

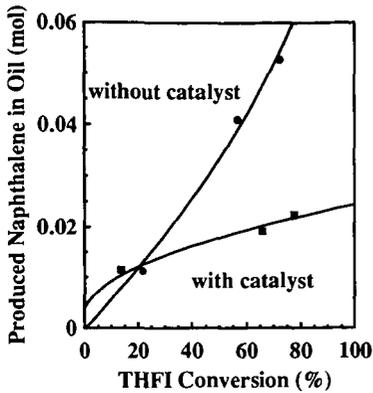


Fig.3 Amount of naphthalene produced in oil at 400°C.

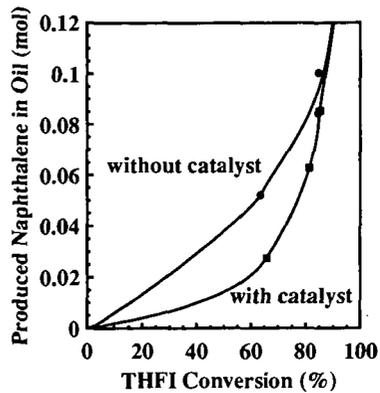


Fig.4 Amount of naphthalene produced in oil at 450°C.

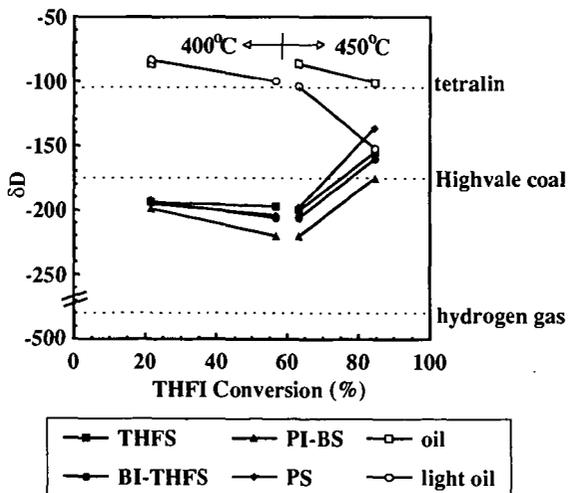


Fig.5 Shifts in $^2\text{H}/^1\text{H}$ of products as a function of THFI conversion without catalyst.

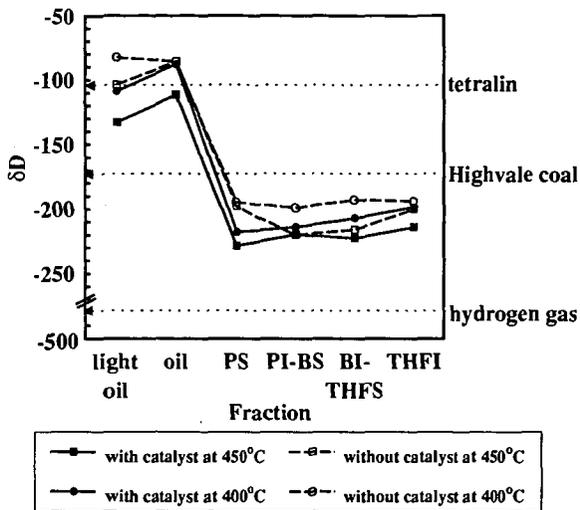


Fig.6 Isotope distribution in products at 0 min

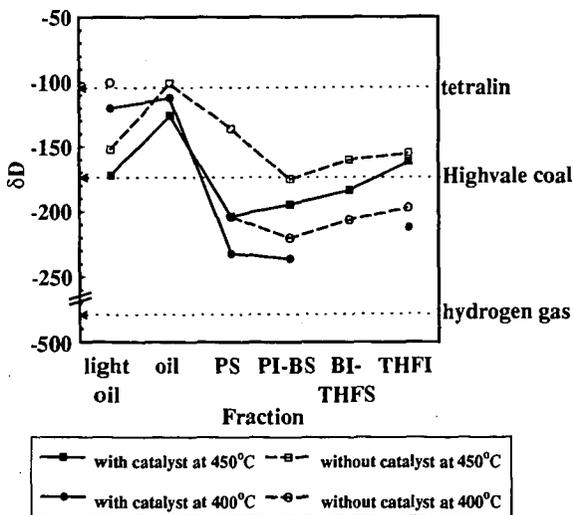


Fig.7 Isotope distribution in products at 60 min