

AUTOClave STUDIES INTO THE HYDROLIQUEFACTION OF COAL LIQUIDS:
THE EFFECT OF RECONTACTING THE CATALYSTS

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ABSTRACT

Fresh and used catalysts (CoMo, NiMo, ZnMo and ZnW) were used in hydro-liquefaction experiments with a Point of Ayr coal liquid over five contacts (2h, 400°C, 19MPa hydrogen) in spinning/falling basket autoclaves. For all catalysts conversions to low boiling point material, H:C ratios of distillation fractions, sulphur contents of the hydroliquefied liquids and carbon contents and specific surface areas of the catalysts were unaffected by repeat contact. However, the sulphur contents of the Mo-containing catalysts did increase with contact reflecting gradual sulphidation of the catalysts by the H₂S produced by desulphurisation of the coal feed; the sulphur content of the ZnW catalyst did not increase after the first contact.

INTRODUCTION

Aspects of coal liquefaction have been much researched, particularly with the re-emergence of interest caused by the oil crises in the 1970's. The types of reactors used in the studies have been various, ranging from small 'bomb' type microautoclaves through larger autoclaves and bench-scale continuous reactors to larger scale pilot or demonstration plants. The use of differently sized and designed high pressure equipment for liquefaction studies further complicates an already complex system and allows only limited comparison of results.

In a continuous reactor, particularly of the trickle bed type, intimate contact between the coal liquid and the catalyst will be maintained throughout the pass of the liquid feed. In an autoclave, particularly of the stirred design, the contact between the liquid and the catalyst will not be as intimate. The action of the stirrer will induce a centrifugal force which will tend to throw the liquid away from the catalyst surface. Consequently, it can be visualised that less strongly adsorbed molecules will spend a shorter time at the catalyst surface so that reaction rates and mechanisms could be very different from those observed in continuous reactor studies. In addition, steady state conditions can be readily investigated in a continuous reactor whereas, for a single contact in an autoclave, steady state conditions may not have been established and changes in catalyst activity will become more relevant.

EXPERIMENTAL

The coal liquid was one of two batches supplied by British Coal Research Establishment (CRE) and was produced by dissolving Point of Ayr coal in a process recycle solvent. The catalysts were prepared by the technique of incipient wetness using an alumina support supplied by Akzo Chemie, the Netherlands following a procedure described previously (1).

The hydroliquefaction experiments were carried out in spinning/falling basket autoclaves manufactured by Baskerville Scientific Instruments; a full

description of the autoclaves is given elsewhere⁽²⁾. The experiments used 100g of the coal liquid and 4.0g of catalyst at a hydrogen pressure of 19MPa at a reaction temperature of 400°C for 2h. After the experiment the liquid product was transferred to a glass jar and stored under nitrogen; the catalyst was removed from the autoclave basket, rinsed with tetrachloroethane in an ultrasonic bath, air dried and stored in glass vials. In order to ensure that sufficient catalyst was available to take samples for analysis the following number of experiments were carried out for the five contacts: 1st contact, 5; 2nd contact, 5; 3rd contact, 4; 4th contact, 3; and 5th contact, 2 experiments making a total of 19 experiments per catalyst.

The hydrocracked product was separated into various boiling point fractions by vacuum distillation before analysis by gas chromatography using a Perkin Elmer Model Sigma 3B Chromatograph attached to a JJ Model CR 600 Pen Recorder and a LDC Model 300 Computing Integrator; 0.5 µl of a 1 wt% solution of the fraction in cyclohexane was injected onto a 25m x 0.32 mm OV 101 capillary column using a temperature program of initial temperature 80°C, ramp rate 5°C min⁻¹. Some carbon, hydrogen and sulphur analysis was carried out on the liquid products and used catalysts. A Leco Model CHN Determinator was used for carbon and hydrogen analysis and a Leco Model SC 132 Sulphur Determinator was used for sulphur analysis. The specific surface area analysis of the used catalysts was by nitrogen adsorption using a Micromeritics instrument.

RESULTS AND DISCUSSION

Repeat contact experiments were carried out with the bimetallic catalysts CoMo, NiMo, ZnMo and ZnW; the catalysts were prepared to contain 15 wt% of Mo or W (as its common oxide) to the mass of the alumina support and 3 wt% of the oxides Co, Ni or Zn. The amounts of material bpt <260, <275, 275-450 and >450°C (calculated from a combination of the masses of the distillation fractions and their g c analysis) are expressed as wt% of the hydrocracked liquid (HL) for CoMo-catalysed experiments in the bar chart figure 1; the bar chart in figure 2 shows similar values for the average of the four catalysts. Both figures show that the amounts of the various bpt fractions were not significantly dependent upon repeat contact. Overall there was a tendency for conversion to low bpt material (<260 or <275°C) to be slightly higher after the first contact, i.e. with fresh catalyst and to fall after the 5th contact; the high first contact value would result from the initial higher surface area of the fresh catalyst and the low 5th contact value could have resulted from gradual catalyst sintering causing some of the catalyst to pass through the holes in the basket mesh.

The bar chart in figure 3 shows the wt% of hydrophenanthrenes (excluding perhydrophenanthrene), phenanthrene and material boiling below naphthalene in HL for ZnMo-catalysed experiments; the zero contact refers to the coal liquid feed (CL). It can be seen that the amounts were not influenced by repeat contact. The amounts of hydrophenanthrenes and material bpt below naphthalene were more than those in CL and the amounts of phenanthrene tended to be lower.

The values of the H:C ratios for the boiling point fractions obtained after vacuum distillation of the HL's from CoMo-catalysed experiments, shown in figure 4, again indicate no dependence on repeat contact. The H:C ratios decreased with increasing bpt of the fraction. The sulphur contents of the HL's for all the four catalysts are shown in figure 5 with no dependence on repeat contact. The lower values for the two Zn catalysts only reflected the use of a different batch

of CL whose sulphur content was less. In terms of the sulphur contents of the distillation fractions for NiMo and CoMo the average values, for the five contacts were 0.01, 0.02, 0.03 and 0.27% for the cold trap, the <250°C, the 250-275°C and 275-450°C fractions respectively, i.e. most of the sulphur in the recoverable material residing in the 275-450°C fraction which would represent the recycle solvent. There was very little change in the values with repeat contact showing that the solvent fraction will be recycled with a relatively high level of sulphur but that the sulphur concentration would not increase with recycle and the catalyst desulphurisation capacity would not be impaired. The level of sulphur in the recycle solvent is quite surprising bearing in mind the relative ease of desulphurisation compared with the denitrogenation or deoxygenation. Most, if not all, of the sulphur remaining will be in a ring in clusters and the likelihood is that some preferential adsorption on the catalyst surface has prevented some of the sulphur-containing molecules from reaching the catalyst surface.

The values for carbon contents and specific surface areas for the used ZnMo catalysts are shown in figure 6 and the sulphur contents of all the used catalysts are shown in figure 7. Only the sulphur contents of the catalysts showed any dependence on repeat contacts and the increase in sulphur content for Mo-containing catalysts indicated gradual sulphidation of the metal content of the catalysts. For the W-containing catalyst, ZnW, the sulphur contents remained relatively constant after the first contact, probably indicating that only the Zn content was sulphided and that the level of H₂S produced by desulphurisation was inadequate to cause sulphidation of the W content. Since it is accepted that presulphidation of Mo and W-containing catalysts enhances their activity, it might have been expected that catalyst activity would increase with contact because of sulphidation. However, it has been reported that 'in situ' sulphidation of catalysts does not lead to enhanced activity for autoclave studies⁽¹⁾, probably because of rapid carbon deposition, and hence increasing sulphidation with contact would be unlikely to enhance activity. In addition, it has been shown in further experiments with a presulphided CoMo catalyst that repeat contact did not affect conversion to low bpt material.

CONCLUSIONS

The investigation has shown that constant catalyst activity was attained after a single contact in the autoclaves. (Other work has shown that this situation also exists at longer reaction times and at different temperatures.) The conversions to low bpt material (hydrocracking), the H:C ratios (hydrogenation) and the carbon deposited on and the specific area of the catalysts (deactivation) as well as the contents of specific materials, e.g. phenanthrene and hydrophenanthrenes, were all unaffected by repeat contact in the autoclaves. Consequently, single contacts for hydroliquefaction investigations should be representative of steady state conditions. However, the results obtained from autoclave studies would not necessarily be reproduced in other types of reactors.

ACKNOWLEDGEMENTS

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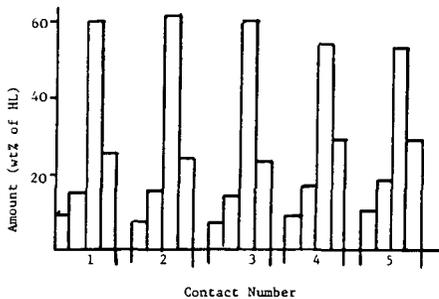


Figure 1. Variation of amounts of fractions with repeat contact with CoMo
 For each contact: 1st bar - $<260^{\circ}\text{C}$;
 2nd bar - $<275^{\circ}\text{C}$; 3rd bar - $275\text{-}450^{\circ}\text{C}$;
 4th bar - $>450^{\circ}\text{C}$. HL = hydrocracked liquid.

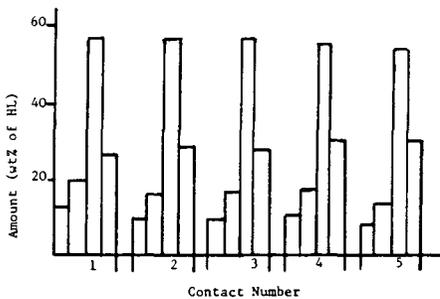


Figure 2. Variation of amounts of fractions with repeat contact - average values for all catalysts.
 For each contact: 1st bar - $<260^{\circ}\text{C}$;
 2nd bar - $<275^{\circ}\text{C}$; 3rd bar - $275\text{-}450^{\circ}\text{C}$;
 4th bar $>450^{\circ}\text{C}$. HL = hydrocracked liquid.

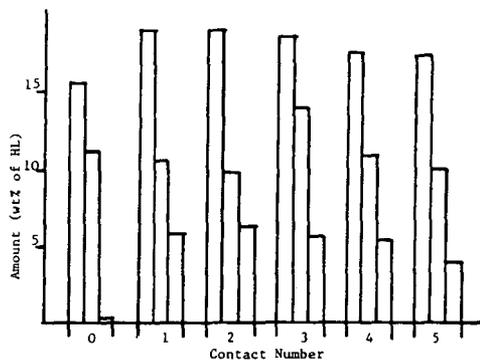


Figure 3. Variation in amounts of hydrophenanthrenes (1st bar), phenanthrene (2nd bar) and material bpt < naphthalene (3rd bar) with repeat contact. HL = hydrocracked liquid; 0 contact indicate coal liquid feed.

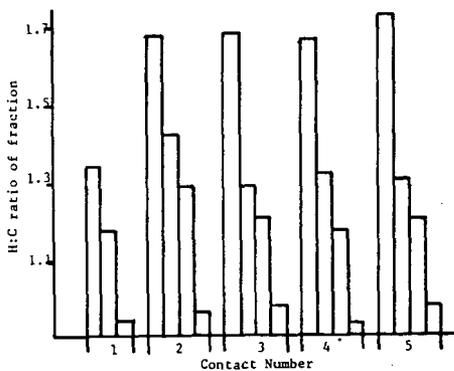


Figure 4. Variation of H:C ratio of distillation fractions with repeat contact. For each contact: 1st bar - cold trap; 2nd bar - 250°C; 3rd bar - $250\text{--}275^{\circ}\text{C}$; 4th bar - $275\text{--}450^{\circ}\text{C}$

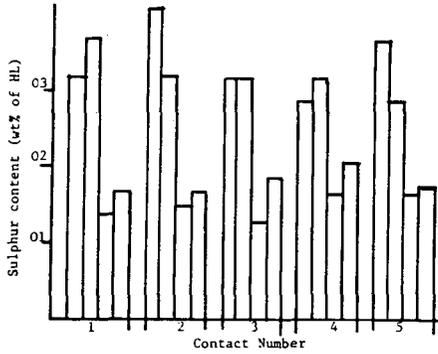


Figure 5. Variation of sulphur content of hydrocracked liquid (HL) with repeat contact. For each contact: 1st bar - CoMo; 2nd bar - NiMo; 3rd bar - ZnMo; 4th bar - ZnW.

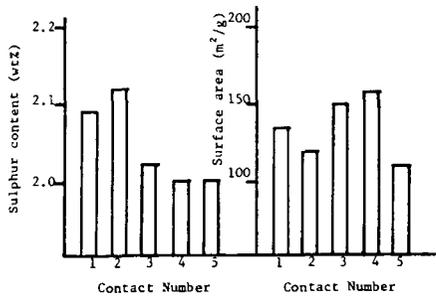


Figure 6. Variation of sulphur content and specific area of catalysts with repeat contact.

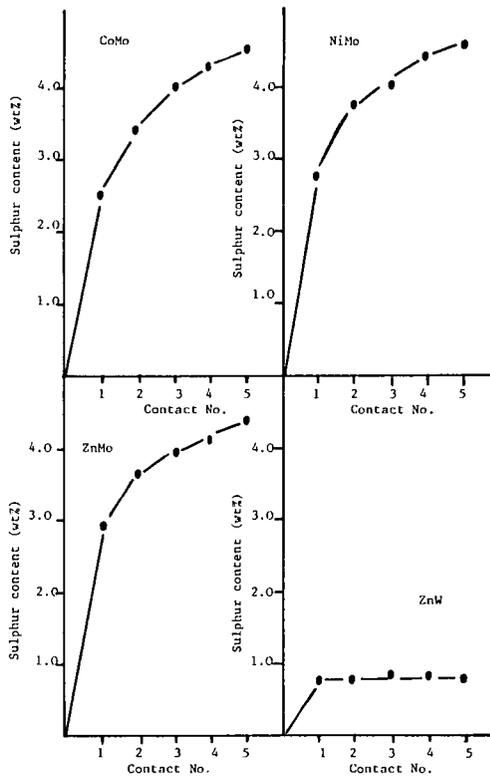


Figure 7. Variation of sulphur content of catalysts with repeat contact.