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CATALYSTS FOR HYDROPROCESSING MIXTURES OF HEAVY OIL AND COAL

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ABSTRACT

Mixtures of one part coal and two parts residual oil from vacuum distillation of an Alberta heavy oil were hydroprocessed in a semi-continuous autoclave system with nickel, cobalt, molybdenum, tungsten and calcium catalysts. Low severity experimental conditions were such that the hydroprocessing reactions proceeded at the threshold of coking. A constant flow of hydrogen at a pressure of 3.4 MPa (500 psig) was supplied to the reactor during these tests. The light hydrocarbons were collected from the exiting gases in a cold trap for elemental analysis and simulated distillation. The heavier products were characterized by solvent extraction as oil, asphaltenes, preasphaltenes and THF insolubles. Catalysts were compared on the basis of conversion of THF insolubles, yields of oil, asphaltenes and preasphaltenes, and sulphur content of the distillates. As expected, cobalt-molybdenum type catalysts performed well, enhancing oil production and conversion of THF insolubles. Petrographic analysis of the THF insolubles indicate that these catalysts also inhibited coke formation to a certain extent. The solubility data also indicate that a gain in pentane-soluble oil is accompanied by a comparable loss in the THF insoluble portion of the product whereas other fractions change to a lesser extent.

INTRODUCTION

The hydroprocessing of mixtures of heavy oil (or bitumen) and coal, which is also called coprocessing, is an interesting alternative to conventional coal liquefaction processes in Canada where large deposits of both coal and heavy oil are found in geographical proximity. The concept of coprocessing is not new (Boomer and Saddington, 1935) but has recently become more attractive in view of the possible increase in distillate yield based on the amount of oil used and the potential decrease in capital cost due to the elimination of recycle streams of coal-derived liquids in the coprocessing plant.

Small bench-scale and process development units have been built in recent years in Canada, the United States and elsewhere (Aldridge and Bearden, 1981; Gatsis, 1982; Rosenthal and Dahlberg, 1982; Moschopedis et al., 1983; Yan and Espenscheid, 1983; Monnier, 1984). Recent publications indicate that reasonable yields of oil can be obtained and that partial demetallization of the oil is possible (Kelly, 1985). As in the upgrading of heavy oils, the presence of catalysts can reduce the coking tendency of the feedstock and improve the liquid product quality.

The effects of various catalysts on the hydroprocessing of mixtures of coal and residual bitumen were investigated in a series of preliminary tests in a semi-continuous reactor system at low severity. The objective was to assess this method for the purpose of comparative testing of different catalysts. The conversion of coal, the yield of oil, the formation of coke and the removal of heteroatoms were the principal aspects investigated.

EXPERIMENTAL

The catalytic hydroprocessing of coal and heavy fractions of bitumen was studied in a stirred autoclave of 300 mL capacity, equipped to operate under continuous hydrogen flow. The pressure inside the autoclave was maintained at 3.4 MPa (500 psig) with a back-pressure regulator. A cold trap was placed before the back-pressure regulator to remove distillates from the outlet gases. Series of 3-h and 5-h tests were carried out at 370, 400 and 430°C. Long reaction times were chosen to accentuate the hydroprocessing selectivity of the catalysts and to enhance distillate yield. The H₂ flowrate was set at about 275 mL (STP)/min which was sufficient to replace the internal gas volume in about 15 min. The system temperature and pressure were chosen so that reactions occurred at the threshold of coking.

The hydrocarbon feedstock was a mixture of 33 wt % Forestburg subbituminous C coal as received and 67 wt % Cold Lake vacuum bottoms (CLVB) from an Alberta heavy oil reservoir. As shown in Table 1, CLVB is about 80 wt % oil (pentane soluble) and contains about 5.5 wt % sulphur. Table 1 also gives the proximate and ultimate analysis of the coal used as fine particles of less than 0.150 mm diameter (minus 100 mesh). Sixty grams of coal and heavy oil were placed in a reactor liner to simplify handling.

Two coal-supported catalysts were prepared by impregnating particles of Forestburg coal (200-100 mesh) with aqueous solutions of cobalt nitrate and ammonium paramolybdate. The metal loadings of these two catalysts were 5.4 wt % Co and 5.5 wt % Mo-2.0 wt % Co. The surface area as measured by gas adsorption and mercury porosimetry was about 25 m²/g in each case. Cobalt-molybdenum supported on alumina (Harshaw HT-400E) and nickel-tungsten on silica-alumina (Harshaw Ni-4301) were

also used as catalysts in a powder form (minus 100 mesh). Their surface area exceeded $180 \text{ m}^2/\text{g}$. Molybdenum was also impregnated on TiO_2 particles using a solution of ammonium paramolybdate and then calcined at 355°C for 5 hours, which gave a catalyst with a surface area of about $30 \text{ m}^2/\text{g}$. Calcium hydroxide was used as is and also after molybdenum impregnation to explore its coke-suppressing capacity. Table 2 gives the composition of each catalyst and the weight of metals charged in the autoclave by addition of 1.6 or 3.2 g of catalyst.

On completing a test run, the oil remaining in the autoclave (between the wall and the metal liner) was drained. The distillates with aqueous portions were collected from the trap and separated. Tetrahydrofuran (THF) was used for removing residues from the metal liner and afterwards evaporated from them in a vacuum oven.

The residues were analyzed by solvent extraction for the oil content (defined as pentane soluble), asphaltenes (pentane insolubles-toluene solubles), preasphaltenes (toluene insolubles-THF solubles) and THF insolubles. The total oil yield was calculated by adding the weight of distillates and the oil drained from the autoclave to the weight of pentane solubles. The distillates were characterized by elemental analysis and by simulated distillation. The outlet gases were analyzed by gas chromatography. The formation of coke was established by performing a petrographic analysis of samples of THF insolubles.

RESULTS AND DISCUSSION

Five catalysts were evaluated in 5-h tests at 400°C. Yields of oil, asphaltenes and preasphaltenes versus conversion of THF insoluble material are shown in Fig. 1. These yields are expressed as weight per cent of the feed mixture of coal and bitumen on a moisture- and ash-free basis (maf). Since the unreacted coal and the coke formed during testing are all insoluble in THF, the conversion of coal cannot be directly determined from solvent extraction data. The yields of oil, asphaltenes and preasphaltenes are also depicted in the bar graph of Fig. 2. In all cases, only the runs with the largest oil production are shown. Figure 2 also presents the fractions of oil, asphaltenes and THF insolubles contained in the feed mixture on a maf basis.

Figure 1 indicates that the conversion of THF insolubles and the production of oil are enhanced with catalysts. Without catalyst, less than 8 wt % of the THF insolubles initially present in the autoclave was converted. The addition of cobalt-molybdenum catalysts led to a 50 to 60% reduction in THF insolubles and to oil yields as high as 60 wt % of the maf feed.

Moderate conversions and oil yields were obtained when cobalt on coal or nickel-tungsten on silica-alumina were used. The poorer performance of the Ni-W catalyst observed in this study, and previously reported by (Weller, 1956), is in contrast with its usually effective performance in the hydrotreating of petroleum distillates. The same amount of nickel or cobalt charged in the autoclave helped produce similar amounts of oil. The coal conversion was determined to be slightly higher with the Ni-W catalyst, which could have been affected by the acidic catalyst support. For calcium hydroxide, only marginal improvements in conversions and oil yields were observed, not significantly different from test runs without catalysts.

Figure 1 indicates that the fraction of asphaltenic products remains about constant whereas the portion of preasphaltenes somewhat decreases with increasing conversion. In addition, Fig. 2 indicates that an increase in oil is paralleled by a reduction in THF insolubles.

A comparison of catalyst performance in Fig. 2 reveals that only the two cobalt-molybdenum catalysts provide significant gain in oil, the alumina-supported catalyst being the more effective. However, it should be noted that for all catalysts, the product oil is lighter than CLVB, with at least 35 wt % of oil boiling at less than 420°C, the initial boiling point (IBP) for CLVB. A certain degree of oil hydrocracking is indicated by the formation of gaseous products, particularly when no catalysts or less effective ones were used. The formation of an aqueous phase was accompanied by extraction of phenols. The water condensed in the trap contained up to 6 wt % phenols. Gas chromatographic analysis of the outlet gases indicated the presence of light alkanes (CH_4 , C_2H_6 , C_3H_8 , C_4H_{10}), olefins (C_2H_4 , C_3H_6), H_2S , CO_2 , H_2O and traces of CO . However, hydrogen accounted for at least 90 mol % of the outlet gases at any given time. As expected, the hydrogen concentration increased at the outlet throughout the experiment.

Figure 3 presents the yields of oil, asphaltenes and preasphaltenes obtained from coprocessing tests performed at three temperatures with the $\text{Co-Mo/Al}_2\text{O}_3$ catalyst. The conversion of THF insolubles in these tests at 370, 400 and 430°C is 39, 53 and -17 %, respectively. As shown in the figure, the asphaltene yield decreases with increasing temperature while the preasphaltene fraction peaks and THF-insoluble fraction bottoms at 400°C. At 370 and 400°C, the yields of oil and asphaltenes plus preasphaltenes remain constant.

The optical micrographs, presented in Fig. 4, illustrate how the coal particles are affected by addition of $\text{Co-Mo/Al}_2\text{O}_3$ in tests performed at 370°C. Without catalyst, the coal particles, mainly vitrinite, have a smooth surface broken only by a few fractures (Fig. 4A). In the presence of Co-Mo catalyst, the vitrinite particles are extensively attacked and fractionated, in places producing "mosaic" type structures (Fig. 4B). This shows further evidence of coal conversion. In either case, no coke formation was detected by petrographic analysis.

The second set of optical micrographs, obtained from tests performed at 400°C, provides evidence that the presence of a catalyst inhibits the coke formation during coprocessing (Fig. 5). In the absence of catalysts (5A), small spheres of coke, which are emphasized by polarization of the incident light plane, are adhering to the edge of coal particles. With Co-Mo catalyst, anisotropic coke (petroleum coke) is not present (5B).

At 430°C, the fraction of THF insolubles sharply increases to 35 wt %, indicating substantial coke formation (Fig. 3). This was accompanied by a decrease in oil yield from 58 to 34 wt % maf feed and also a decrease in asphaltenic and preasphaltenic yields. The formation of coke is confirmed by the optical micrograph shown in Fig. 6, where coal particles are bonded with anisotropic petroleum coke. The extent of coke formation indicates insufficient hydrogen transfer within the reaction mixture at these conditions (Belinko et al., 1979). Coke formation, in terms of the increase in THF insolubles, was found to be greater with the other catalysts.

The effect of support acidity on product distribution was investigated in a series of 3-h tests performed at 400°C. The product yields presented in Fig. 7 indicate that catalysts with acidic support, such as Co-Mo/Al₂O₃ and Mo/TiO₂, performed better while Ca(OH)₂ impeded the performance of Mo in terms of oil production.

Figure 8 shows the sulphur content in the distillates collected in the trap in relation to the reduction in THF insolubles for experiments performed at 400°C. Up to 50% additional sulphur removal was achieved when the Co-Mo catalysts were used. The presence of alumina supports further improved the sulphur removal achieved by coal-impregnated catalysts. It should be noted, however, that non-acidic supports, such as active carbon have been found to provide excellent performance in hydrodesulphurization (De Beer et al., 1984). In the present study it is quite likely that cleavage at the carbon-sulphur bonds, facilitated by Co-Mo catalysts, provided the extra oil yield obtained when using these catalysts.

CONCLUSIONS

Hydroprocessing of coal and heavy oil was investigated using a variety of catalysts. It was shown that the addition of an appropriate catalyst can affect oil yield, product quality and coke formation. Cobalt-molybdenum catalysts were effective in all of these aspects. It is concluded that the experimental procedures described in this study can be used for further catalyst evaluations under a variety of processing conditions.

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Table 1 - Characteristics of feedstocks

Forestburg subbituminous C coal

Ultimate analysis (wt %)

Carbon	64.04
Hydrogen	3.87
Sulphur	0.53
Nitrogen	1.65
Oxygen	20.41

Proximate analysis (wt %)

Moisture	9.2
Ash	7.8
Volatiles	46.5
Fixed carbon	36.5
(by difference)	

Cold Lake vacuum bottoms

Ultimate analysis (wt %)

Carbon	84.04
Hydrogen	9.94
Sulphur	5.46
Nitrogen	0.63
Oxygen	0.50

Other characteristics

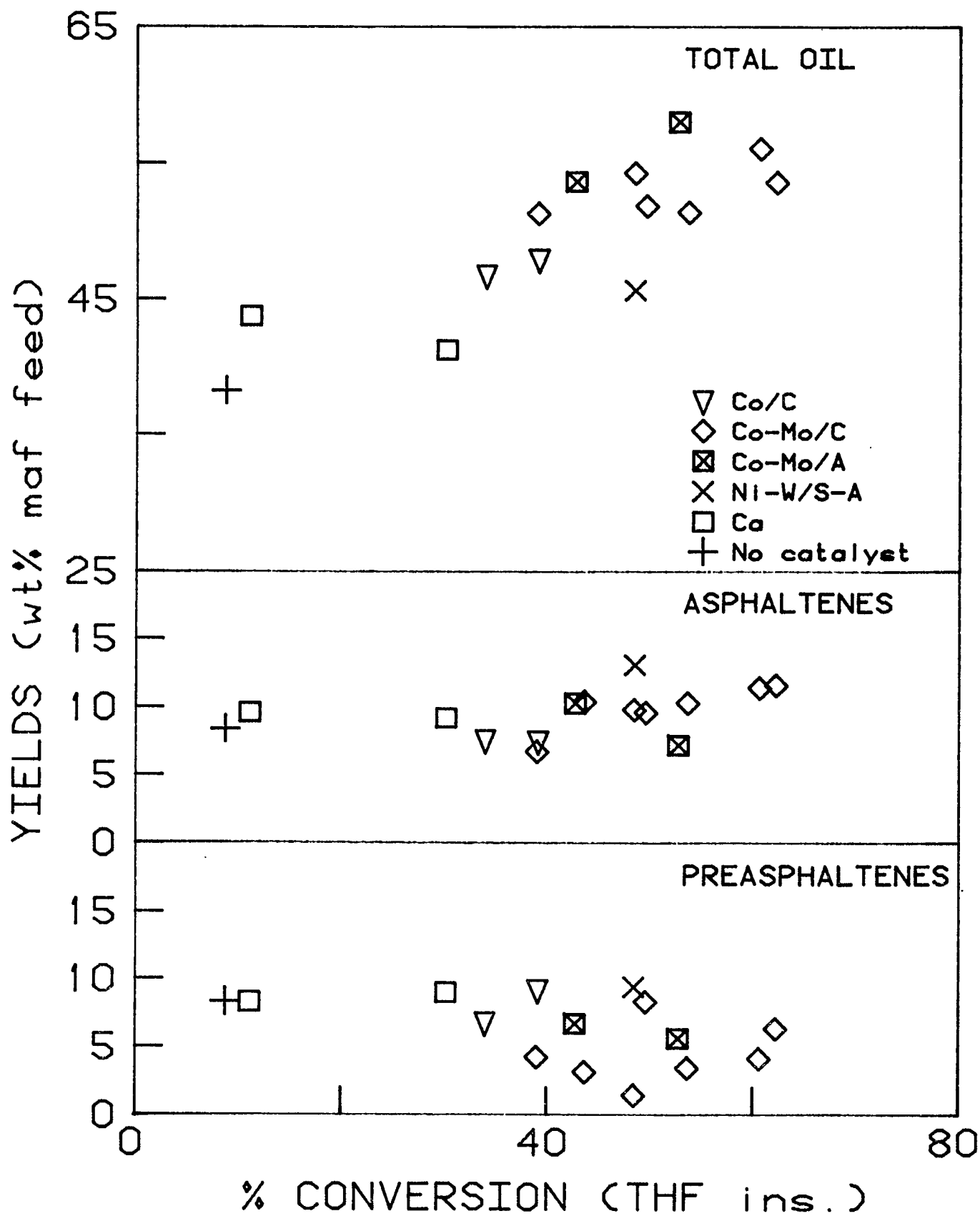
IBP	420°C
Oil	72.3%
Asphaltenes	27.7%
-525°C	20%
+525°C	80%

Table 2 - Catalysts for hydroprocessing mixtures of coal and heavy oil

<u>Catalyst</u>	<u>Composition (wt %)</u>		<u>Weight of metal (g) per run</u>	
Co-Mo/coal	Mo	5.5	Mo	0.178
	Co	2.0	Co	0.065
Co-Mo/Al ₂ O ₃	Mo	8.9	Mo	0.287
	Co	2.6	Co	0.084
	Al ₂ O ₃	83.4	Al ₂ O ₃	2.67
Ni-W/SiO ₂ -Al ₂ O ₃	W	19	W	0.608
	Ni	5	Ni	0.16
	SiO ₂	54	SiO ₂	1.728
	Al ₂ O ₃	8.7	Al ₂ O ₃	0.278
Mo/TiO ₂	Mo	18.6	Mo	0.298
	TiO ₂	70.8	TiO ₂	1.133
Co/coal	Co	5.4	Co	0.173
Ca(OH) ₂			Ca	1.742
Mo-Ca(OH) ₂	Mo	10.4	Mo	0.166
	Ca	48.6	Ca	0.555

LIST OF FIGURES

1. Yields of oil, asphaltenes and preasphaltenes as functions of conversion of THF insolubles in catalytic hydroprocessing at 400°C.
2. Yields of oil, asphaltenes, preasphaltenes and THF insolubles for catalysts tested in hydroprocessing of coal and heavy oil at 400°C (O = oil, W = aqueous phase, A = asphaltenes, P = preasphaltenes T = THF insolubles, R = gas and loss).
3. Yields of oil, asphaltenes, preasphaltenes and THF insolubles for Co-Mo/Al₂O₃ tested in hydroprocessing at 370, 400 (R.T. = 5 h) and 430°C (R.T. = 3 h).
4. Optical micrographs of coal particles (400x magnification) after hydroprocessing in heavy oil at 370°C without catalyst (4A) and with Co-Mo/Al₂O₃ (4B).
5. Optical micrographs of coal particles (400x magnification) after hydroprocessing in heavy oil at 400°C without catalyst (5A) and with Co-Mo/Al₂O₃ (5B).
6. Optical micrographs of anisotropic coke bonding coal particles (400x magnification) after hydroprocessing at 430°C with Co-Mo/Al₂O₃.
7. Yields of oil, asphaltenes, preasphaltenes and THF insolubles for Mo and Co-Mo on various supports tested at 400°C (Letters defined in Fig. 2).
8. Sulphur content of distillates as a function of conversion of THF insolubles in catalytic hydroprocessing at 400°C.



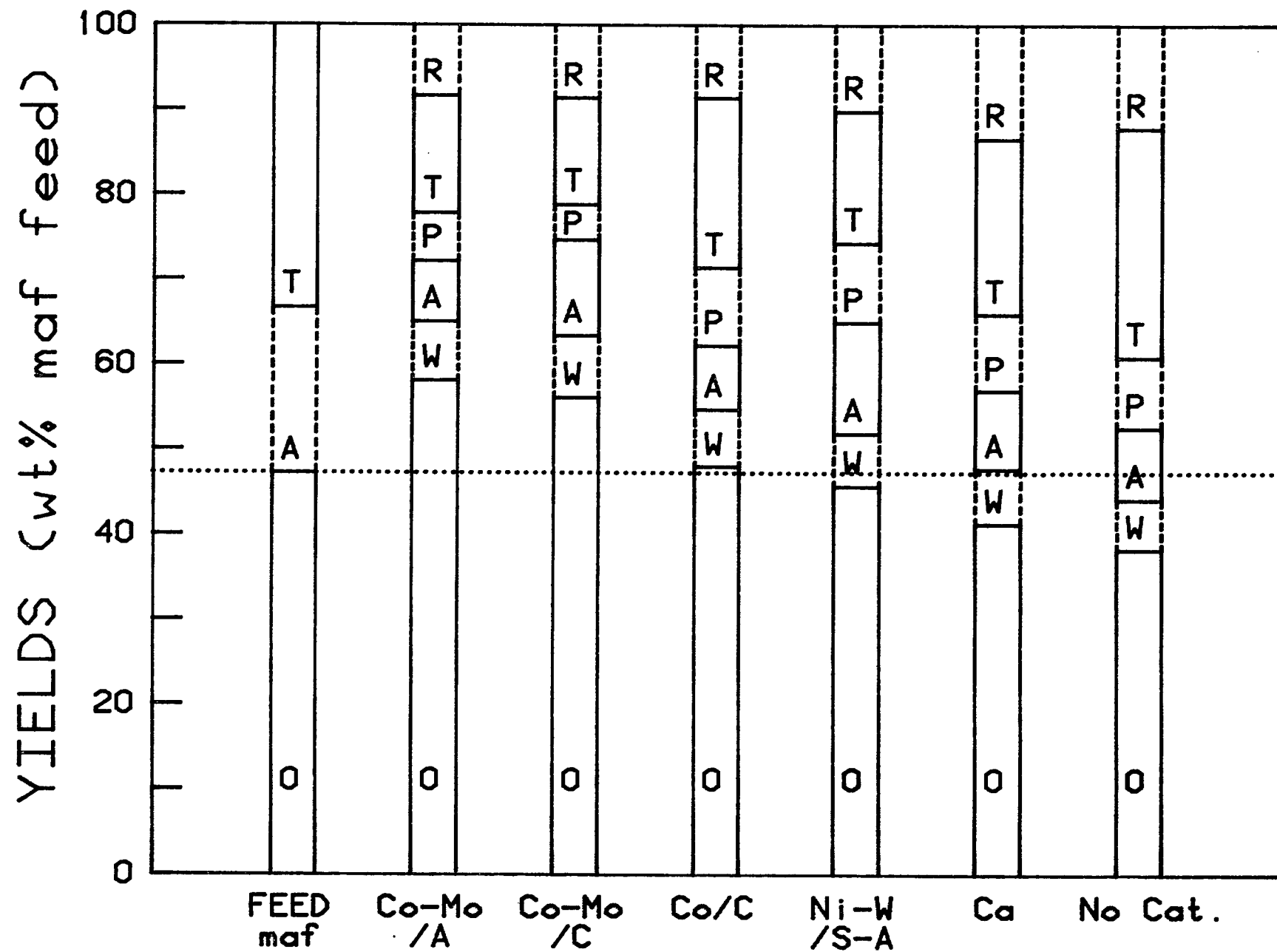


Fig 2

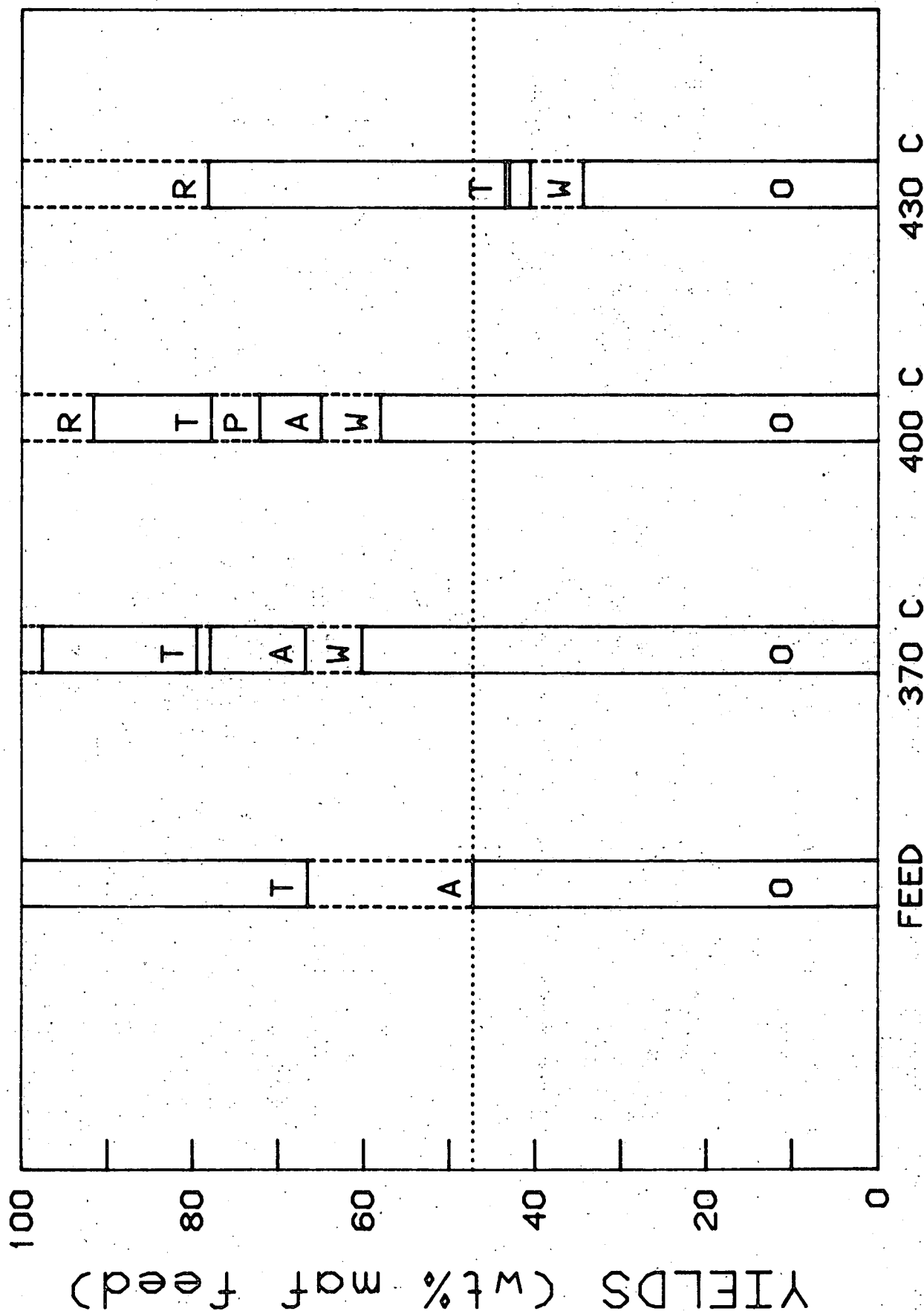
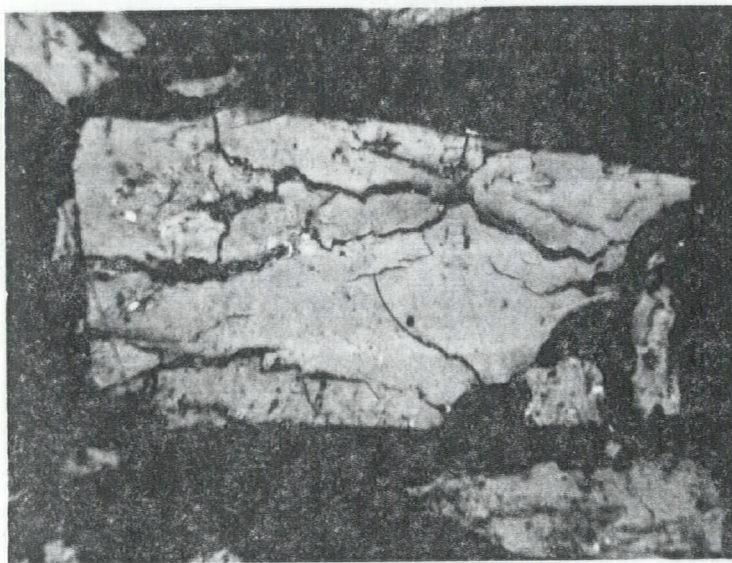


Figure 4



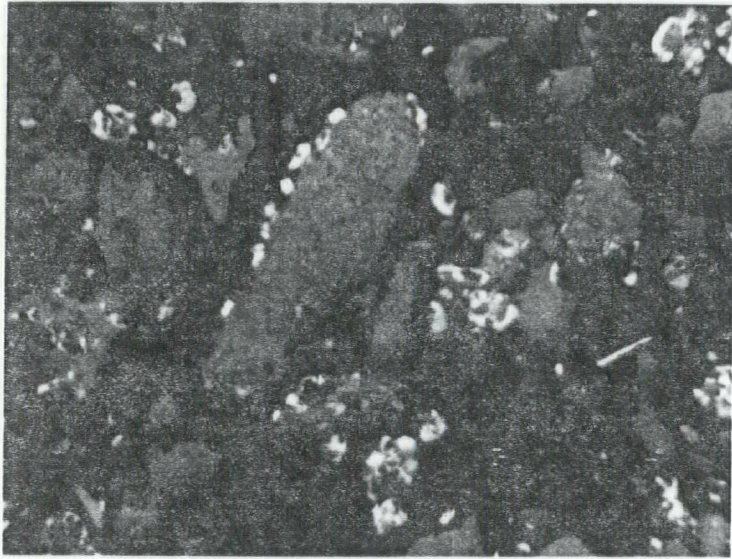
4A



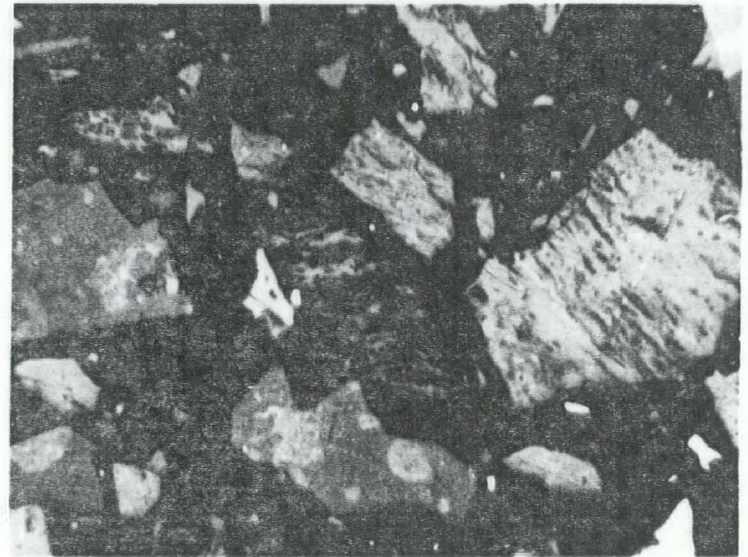
4B

50 μ

Fig 4



5A



5B

50 μ

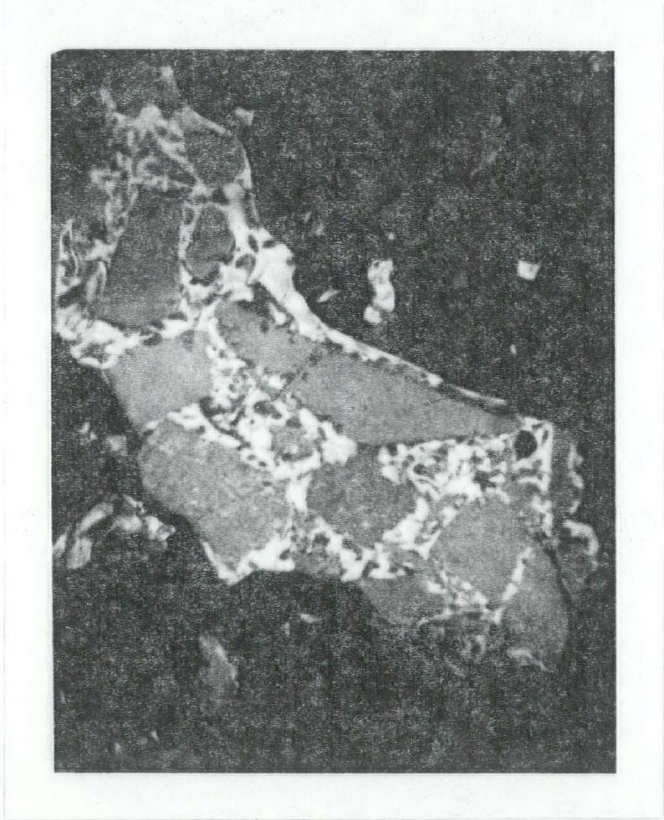
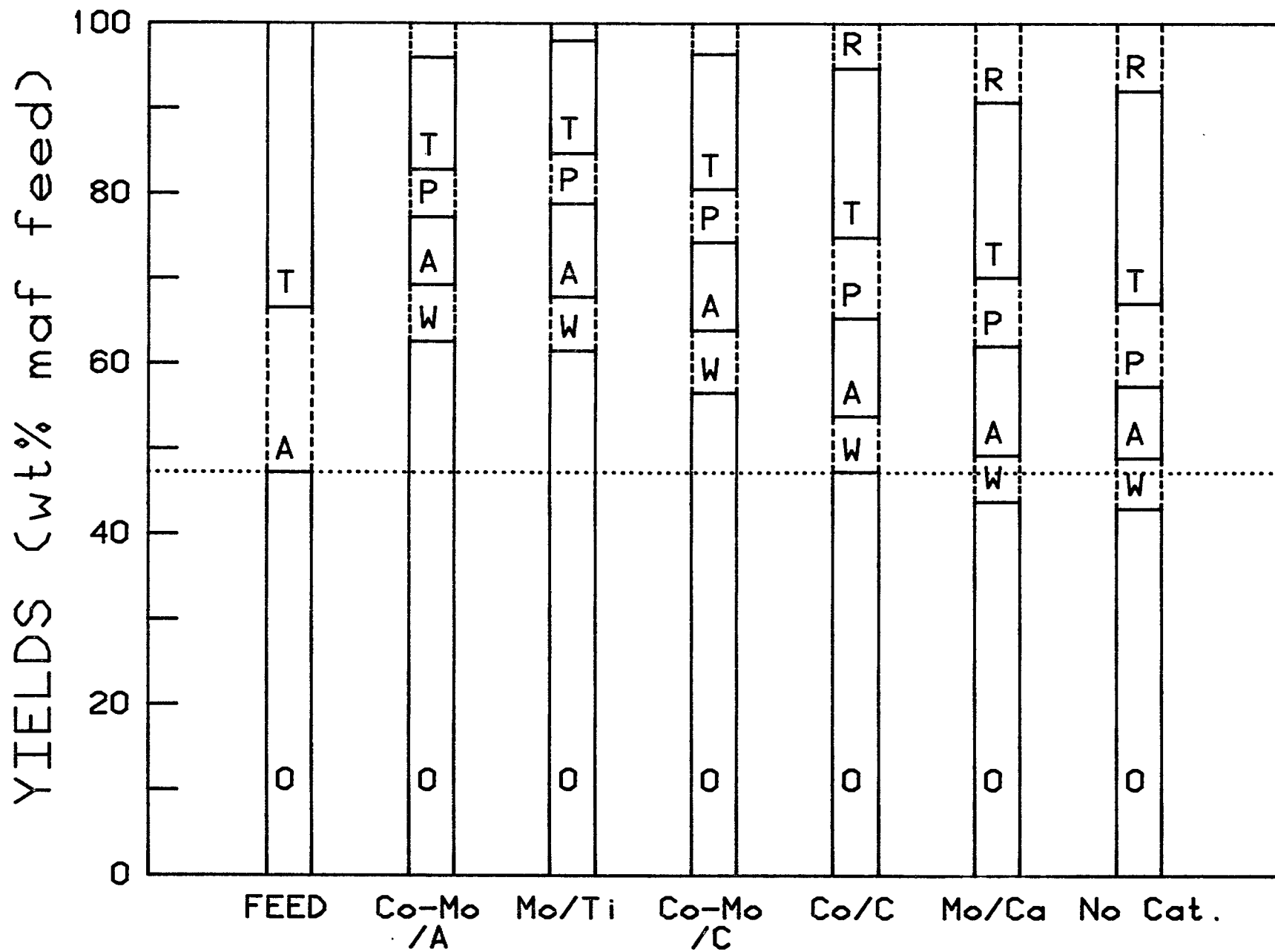


Figure 6



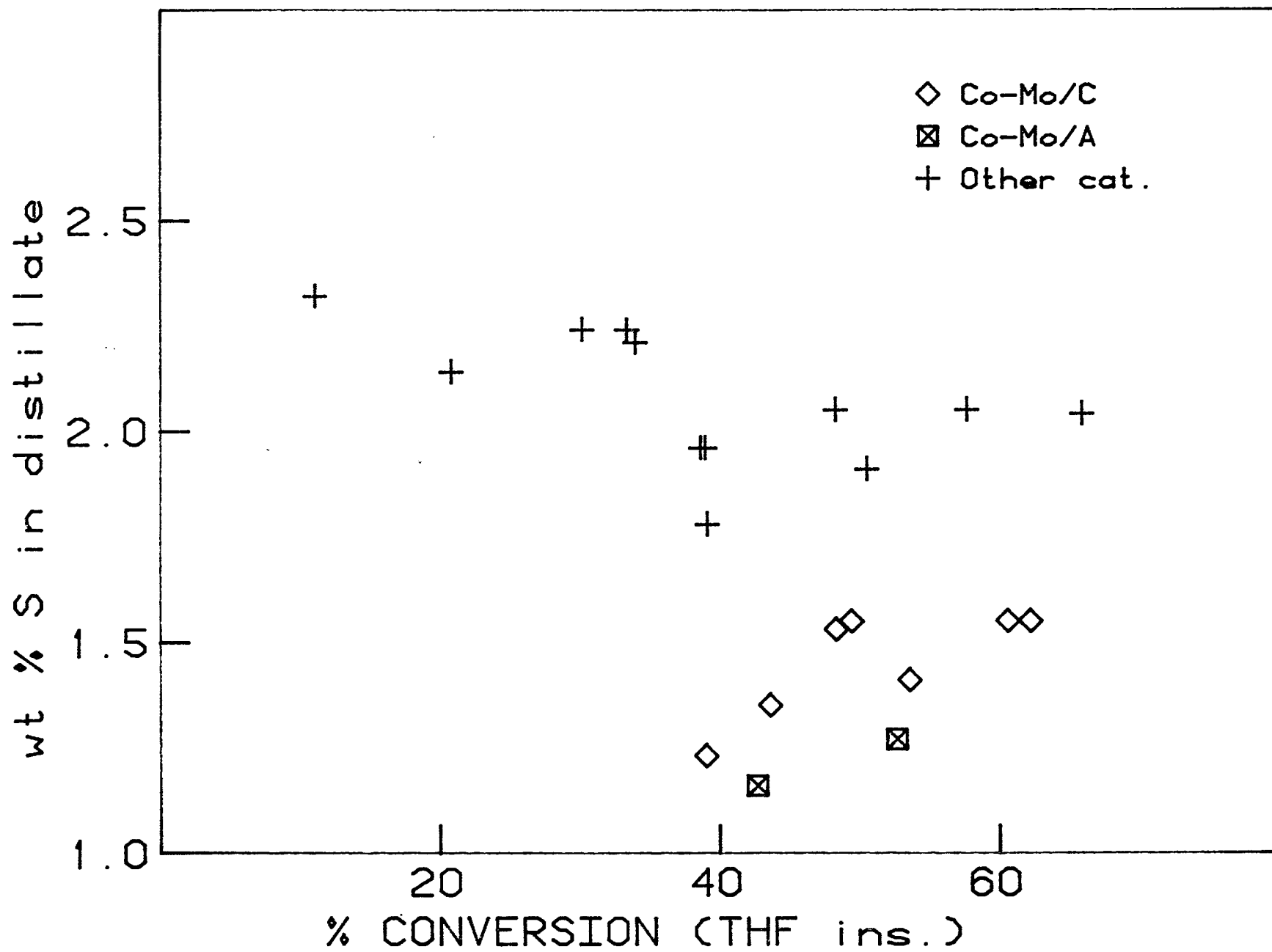


Fig. 8