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THE NATURE OF PRODUCTS FROM THE LIQUEFACTION OF SUB-BITUMINOUS COALS IN THE PRESENCE OF PETROLEUM RELATED RESIDUES

S.M. Ahmed, S.A. Fouda, P.M. Rahimi and H. Sawatzky

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ABSTRACT

Characterization of distillable hydrocarbons obtained during co-processing of Cold Lake vacuum bottoms and sub-bituminous coal, have been undertaken. These products were separated by solid-liquid chromatography technique into compound-types namely, saturates, mono-, di, and polynuclear aromatics, and polar materials. The effect of co-processing variables and severity on the composition of these hydrocarbons, have been discussed. The salient feature appears to be the increased production of saturates and mononuclear aromatic compounds with increased severity.

INTRODUCTION

The coprocessing of sub-bituminous coals with petroleum related residues has particular attraction in Canada, because of large resources of this coal and of bitumen/heavy oils that are within reasonable proximity of each other. Considerable liquid contributions can be obtained from coal if added during the upgrading of the bitumen/heavy oils. The bitumen/heavy oils can act as hydrogen donors for the coal liquefaction and the coal could have beneficial effects on the upgrading of the bitumen/heavy oils.

In this work the products from coprocessing of a typical Alberta sub-bituminous coal with the vacuum distillation bottoms from a bitumen have been studied. The processing reactions are complex in particular, as the two feeds influence each other. A major objective was the determinations of the products derived from coal and those derived from bitumen. Another objective was to shed light on the synergism between the conversion of the bitumen residue to distillable products and the liquefaction of the coal.

A major concern, which is a major reason for this study, is the effect of coal derived liquids on the quality of the products as refining feedstocks. The addition of coal derived liquids might add considerably to the cost of upgrading to desired end products.

EXPERIMENTAL

The processing products were obtained from bench scale continuous operations in which slurries of coal in the bitumen were processed under hydrogen pressure. The samples studied had been taken under steady state conditions.

The total products were transferred to a distillation unit. A naphtha fraction and a fraction with a bp. of 205 - 524°C was obtained. A residual oil was obtained from the distillation residue by pentane extraction of the +524°C product as shown in figure 1.

The naphtha was separated by FIA into saturates, olefins and aromatics. The olefins in these studies are considered to be a part of the saturated or non-aromatic fraction. The aromatics were assumed to consist of only alkyl benzenes and the average molecular weight determined was 106.

The fraction distilling at 205-524°C was separated into saturated hydrocarbons, mono, di and polynuclear aromatic and polar compound fractions on a dual silica gel-alumina column according to a modified API-60 method that had been developed in our laboratory. The molecular weight of the aromatic fractions were determined by vapour phase osmometry.

All aromatic fractions were determined on mole basis and the aromatics in the naphtha were summed with the mononuclear aromatics. The saturates from the naphtha as well as the C₁, C₄ gases were summed with the saturates in the heavier distillates.

Comparison of aromatics on mole basis would directly indicate the changes on number cluster and would be unaffected by reductions in molecular weight and more meaningful than on weight basis. All values have been calculated on the basis of ash-free slurry feed.

RESULTS AND DISCUSSION

Coal Concentration

According to the elemental analyses of the two feed components which is shown in table 1, it would appear that since they are so different, that the nature of products would become substantially different when coal derived products were added to those from the bitumen. Therefore, the nature of the products should be affected by the proportion of coal in the feed.

The effect of adding various amounts of coal to the feed on the elemental analyses of the 205-524°C distillates is shown in table 2.

There are small decreases in hydrogen content and small increases in nitrogen content. In the case of the hydrogen, the addition of molecular hydrogen could account for the smaller than expected decreases and the hydrogen consumption in general did increase in proportion to the amount of coal in the feeds.

While the sulphur levels were lowered and those of oxygen increased, they are difficult to explain at this time. Of course the accuracy of the oxygen content is doubtful as it was obtained by difference.

The effect of different coal concentrations in the feed on the composition of the products is illustrated in table 3. The yields of the distillates were very similar regardless of the amounts of coal.

The amounts of saturates decreases slightly with the amount of coal. The mononuclear aromatics decrease at 10% then increase at 20% and decrease again at 25%, of coal; with exception of the run with 20% coal, the di's appear constant and the poly's increase with the coal. The run with 20% did involve greater hydrogen consumption and this might explain the higher amount of mono and lower of di and poly aromatics.

At this stage in our studies, we don't know the amounts of heterocycles in the aromatic fractions. In other studies, on the upgrading of bitumen/heavy oils, considerable amounts of benzothiophenes and dibenzothiophenes were found in the di and polynuclear aromatic fractions respectively. Probably benzo and dibenzofurans will be found in these studies as well.

It would be expected that the polar materials would increase substantially with increasing amounts of coal, however, this has not been the case at these levels of coal.

Conversion to Distillable Products

In table 4, are shown the results obtained at different levels of conversion to distillable products or severity of processing conditions at 20-25% coal in feeds. The amount of C₁-C₄ gases, naphtha and the 205-524°C fractions all increases as does the polar material. The amounts of di and polynuclear aromatic compounds are virtually identical.

When these results are plotted as shown in figure 2, there appears to be a linear relationship with levels of severity. However, the mono's increase to a larger extent compared with the other aromatic compounds, which might indicate that some of them are formed at their expense.

The elemental analyses of the distillates are shown in table 5. With increasing processing severity, the level of oxygen in the distillates decreases drastically.

Hydrogen Consumption

Increases in coal concentration, temperature, pressure, residence times, all affect hydrogen consumption to some degree. However, in general this is not well understood and difficult to interpret. At lower levels of conversion to distillable products, the hydrogen consumption is low, but it does not necessarily increase directly with conversion. At more severe processing severities there is evidence that dehydrogenation occurs as well as hydrogenation. The amount of water that was produced was related to hydrogen consumption.

The effects of hydrogen consumption on the composition of the products are shown in table 6.

There are marked increases in the moles of mononuclear aromatic compound with increases in hydrogen consumption. There is even a suggestion from the limited data that it increases slightly exponentially as will be seen in the next figure. The saturated compounds increase at first and then are steady. The di + polynuclear aromatics increase at first and then decrease. This is shown in figure 3. It might be interpreted that at the higher levels of hydrogen consumption, the mono compounds are formed from the di and polynuclear aromatics.

CONCLUSION

The results obtained so far do not shed much light on processing reactions, but they confirm that the systems being studied are quite complex. However, it appears at this time at the levels up to 25% of coal in feed, that the contribution of coal derived liquids to the bitumen/heavy oil products would not significantly degrade the distillate qualities as refinery feedstocks.

TABLE 1

ELEMENTAL ANALYSIS (WT %)

	<u>BITUMEN RESIDUE</u>	<u>COAL (MAF)</u>
CARBON	83.07	70.8
HYDROGEN	9.85	4.3
SULPHUR	5.80	0.6
NITROGEN	0.53	1.9
OXYGEN (DIFF)	0.73	22.4

TABLE 2

ELEMENTAL ANALYSES OF THE 205-524°C DISTILLATES
DURING INCREASE OF COAL IN FEED (WT %)

% COAL IN FEED	C	H	N	S	O(DIFF)
0	85.41	11.16	0.28	2.70	0.45
10	85.12	10.91	0.34	1.98	2.37
20	85.18	10.76	0.38	2.05	1.63
25	85.45	10.78	0.40	2.30	1.07

TABLE 3

EFFECT OF COAL CONCENTRATION (WT %)

COAL IN FEED(MAF)	DISTILLATE (205-524°C)	NAPHTHA	SAT	MONO -----	DI MOLES-----	POLY	POLAR	GAS (C ₁ -C ₄)	RESIDUAL OIL	TOTAL OIL
0	53.4	9.1	37.14	0.047	0.028	0.026	7.50	6.2	9.92	72.68
10	51.9	9.4	36.56	0.035	0.026	0.027	8.36	6.5	13.06	74.36
20	48.8	10.7	35.70	0.047	0.020	0.020	7.33	6.1	10.71	70.21
25	52.6	9.9	35.55	0.041	0.028	0.031	8.17	6.3	10.10	72.59

TABLE 4

EFFECT OF SEVERITY OF PROCESSING

YIELD OF DISTILLABLE PRODUCTS	DISTILLATE 205-524°C	NAPHTHA	SAT.	MONO	DI	POLY	POLAR	GASES	RESID. OIL
				-----	MOLES	-----			
43.7	34.6	7.3	21.97	0.029	0.013	0.013	5.86	1.8	29.6
65.6	48.8	10.7	35.70	0.047	0.021	0.021	6.54	6.1	10.7
78.7	58.6	11.8	42.08	0.056	0.029	0.025	9.44	8.3	4.5

TABLE 5

ELEMENTAL ANALYSES OF THE 205-524°C DISTILLATES
AT DIFFERENT LEVELS OF SEVERITY (WT %)

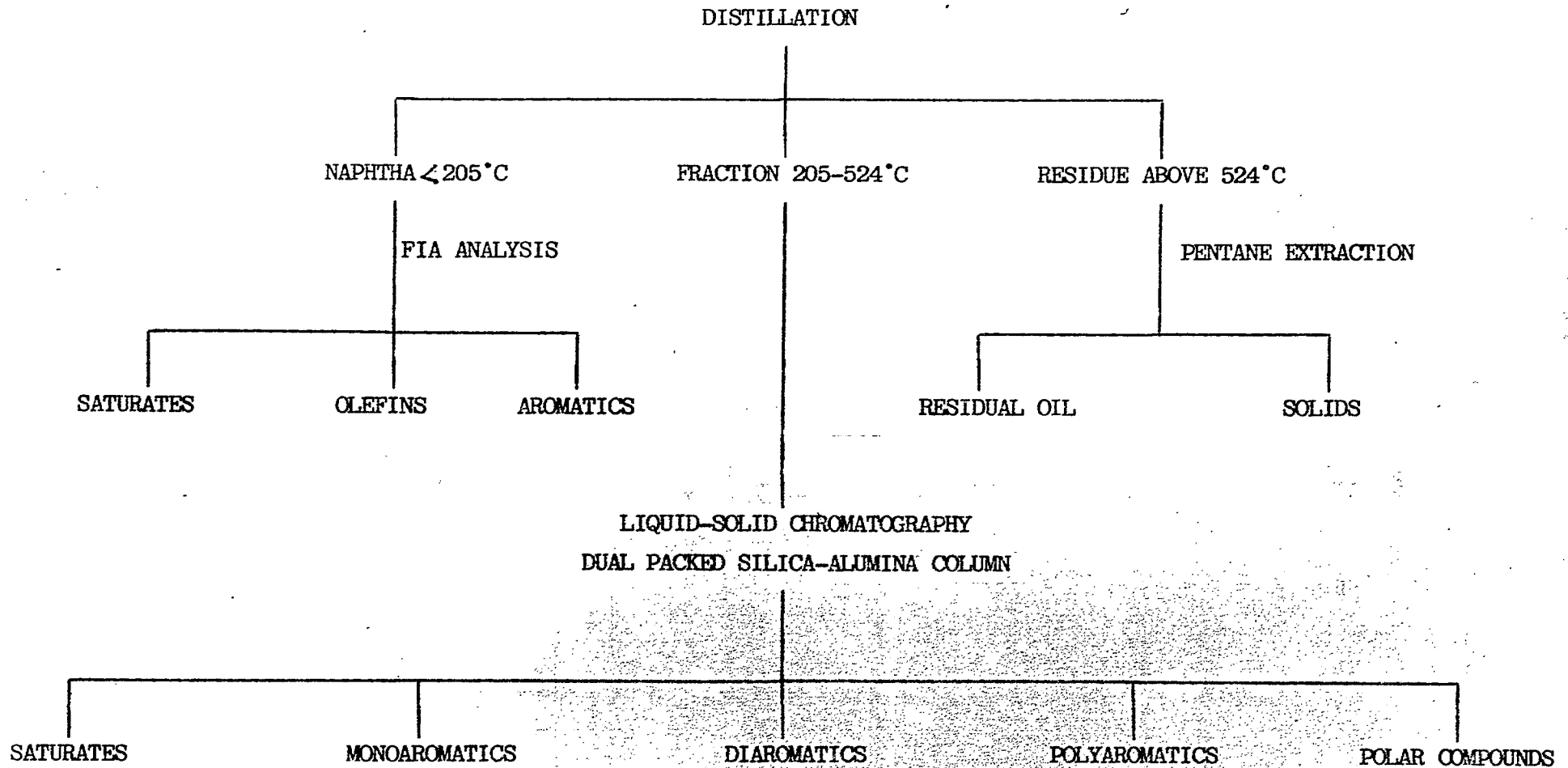
YIELD OF DISTILLATE PRODUCTS	C	H	N	S	O(DIFF)
43.7	84.33	11.10	0.27	3.37	0.90
65.6	85.18	10.76	0.38	2.05	1.63
78.7	85.41	11.76	0.28	2.7	0.45

TABLE 6

EFFECT OF HYDROGEN CONSUMPTION (WT %)

CONSUMPTION	DIST.	NAPHTHA	CONV.	SAT	MONO	DI	POLY	POLAR	GAS	RES OIL	TOTAL OIL
					-----MOLES-----				C ₁ -C ₄		
1.50	34.5	7.3	41.8	22.0	0.029	0.013	0.013	5.86	1.8	29.6	71.4
2.24	51.9	9.4	61.3	36.6	0.033	0.026	0.027	7.2	6.5	13.1	74.4
3.25	48.8	10.7	59.5	35.7	0.047	0.021	0.021	6.54	6.1	10.7	70.2

DISTILLATION & SEPARATION OF SLURRY PRODUCTS OF
COLD LAKE VACUUM BOTTOMS WITH SUB-BITUMINOUS COALS



DISTILLATION AND SEPARATION (SCHEMATIC DIAGRAM)

FIGURE 1

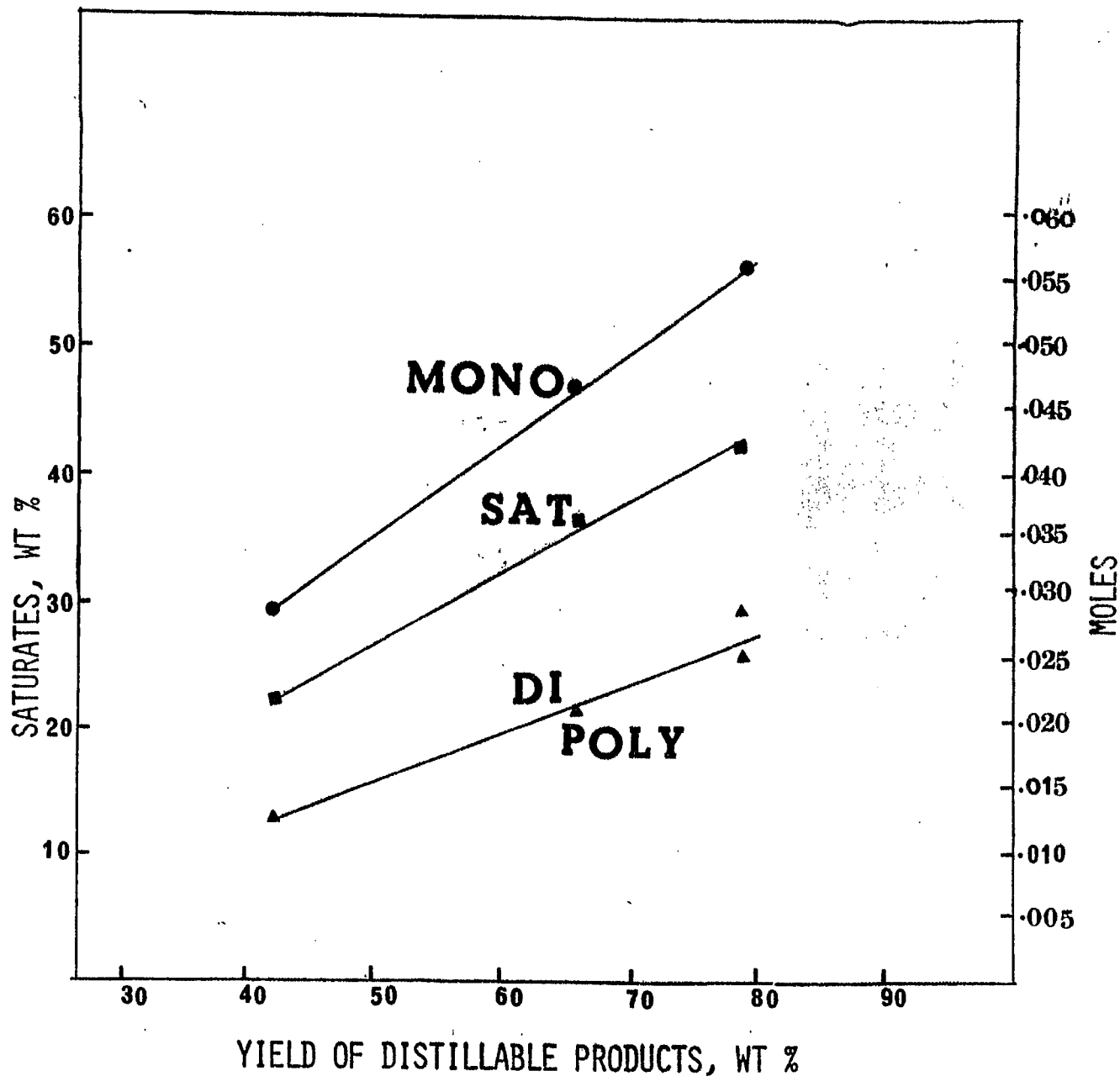


FIG - 2. EFFECT OF SEVERITY ON HYDROCARBON COMPOSITION