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**EFFECT OF COAL CONCENTRATION ON PRODUCT  
DISTRIBUTION IN CANMET COPROCESSING**

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## Effect of Coal Concentration on Product Distribution in CANMET Coprocessing

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### ABSTRACT

The effect of feed coal concentration on the characteristics of distillate products was investigated using High Performance Liquid Chromatography (HPLC) and Field Ionization Mass Spectrometry (FIMS). The distillates were obtained by coprocessing Forestburg subbituminous coal and Cold Lake vacuum bottoms from Alberta in a nominal 1 kg/h bench scale unit. Distillates from three different coal concentration experiments at 3.7, 23.9 and 39.5 wt % on a maf slurry feed basis were chosen for this study. Gross distillate (205-525°C) characteristics were determined using elemental analysis and  $^1\text{H}$  NMR. Results are consistent with the fact that as coal concentration is increased, more coal-derived liquids contribute to the distillate.

The distillates were separated into five different fractions using a Polar Amino Cyano (PAC) column. Analysis of the fractions indicated that increasing coal concentration from 3.7 wt% to 23.9 wt% results in an increase in the amount of polar materials and a subsequent decrease in the amount of saturated compounds. The weight percent of monoaromatics and polyaromatics were not effected by the amount of coal present in the slurry feed. The number and weight average molecular weights of the distillates boiling between 205-525°C and their hydrocarbon-type fractions decreased as the coal concentration increased. Each hydrocarbon-type fraction was analyzed by  $^1\text{H}$  NMR and FIMS to determine the effect of coal concentration on compound-type distribution. The results show that increasing coal concentration has a significant effect on compound-type distribution and, in part, coal may enhance the upgrading of bitumen. Based on preliminary isotopic mass balance measurements which take advantage of the difference between the  $^{13}\text{C}/^{12}\text{C}$  ratio of coal and bitumen, the amount of coal-derived carbon in the coprocessing distillate was estimated.

## INTRODUCTION

In the coprocessing of coals and bitumens or petroleum resids both components of the feedstock are upgraded and contribute to the overall distillate product. In order to understand basic coal and oil interactions in coprocessing and to better evaluate different processing concepts, it is necessary to know what effect replacing part of the oil feed with coal has on the properties of the distillate product. This is especially relevant if coprocessing is to be critically compared with hydrocracking of the heavy oil only, since any advantage gained by coprocessing could be offset by negative changes in overall product quality.

The effect of feed coal concentration on process performance in coprocessing has been investigated by HRI, CANMET and PETC. A synergistic effect has been reported by HRI for pitch(+975°F) conversion at 50 wt % coal in the feed(1-2). For CANMET coprocessing, a synergistic effect in terms of distillate yield has been shown to exist for coal concentrations of less than 5 wt % in the feed(3). Miller(4) has also observed a rapid increase in distillate yield in the coprocessing of Wyodak subbituminous coal and heavy oil fractions with increasing coal concentrations to about 5 wt % coal. At PETC an increase in heptane solubles has been observed with specific coal and oil combinations containing up to 30 wt % coal in the charge to a microautoclave(5). A number of other investigators also refer to synergism during coprocessing(6-7). In the coprocessing of oil shales and coals a similar synergistic effect has also been reported i.e., the reactivity of the oil shale was enhanced in the presence of coal(8).

Coal conversion has also been shown to be effected by feed coal concentration in coprocessing. For instance, McLean et. al.(1) reported an increase in coal conversion as a function of coal concentration at lower process severities. It can also be expected that different levels of coal concentration in coprocessing feeds will affect distillate product quality. Detailed characterization of distillates is not only required for understanding of secondary upgrading but also for any economic evaluation or comparison of different processes.

This paper presents the results of work which was carried out to study the effect of feed coal concentration on the quality of distillates obtained in coprocessing Forestburg subbituminous coal and Cold Lake vacuum bottoms in the CANMET process.

## EXPERIMENTAL

Coprocessing experiments were performed in a 1-L continuous-flow stirred tank reactor (CSTR) unit with a nominal capacity of 1 Kg/h of slurry feed. Product samples were collected over 1-h periods once steady state was reached. For all the experimental runs reported in this paper, material balance closures were within  $\pm 5$  wt %. Other details of the experimental unit are available elsewhere(3).

The analyses of the coal and solvent used in these experiments is given in Table 1. All experiments were carried out in the presence of  $\text{FeSO}_4$  impregnated on part of the coal feed. Its concentration was kept constant for the three different coal concentrations of 3.7, 23.9 and 39.5 wt % on a maf slurry feed basis used in this study. Coprocessing experiments were performed at  $450^\circ\text{C}$  ( $723^\circ\text{K}$ ) with the total pressure maintained at 13.8 MPa, a nominal space velocity of 1 kg/h/l and a nominal hydrogen feed rate of 4 l/minute at  $25^\circ\text{C}$  and 101 KPa.

Slurry products were fractionated using a spinning band still. Water and naphtha (IBP- $205^\circ\text{C}$ ) fractions were collected at atmospheric pressure. Distillation was continued under vacuum and a light gas oil (LGO) fraction was collected at an atmospheric equivalent  $205\text{-}335^\circ\text{C}$ . Two heavy gas oil fractions were also collected, heavy gas oil 1 (HGO 1:  $335\text{-}415^\circ\text{C}$ ) and heavy gas oil 2 (HGO 2:  $415\text{-}525^\circ\text{C}$ ).

To determine gross distillate properties the light and heavy gas oil fractions were mixed proportionally and then analyzed. Analyses were performed to determine elemental composition (carbon, hydrogen, nitrogen and oxygen by CHN 240 Perkin Elmer analyzer and sulphur by LECO analyzer) and aromaticity:  $f_a$  (by  $^1\text{H}$  NMR applying the Brown Ladner treatment). The distillates ( $205\text{-}525^\circ\text{C}$ ) were deasphalted (less than 1 wt % asphaltene) using 20 volumes excess pentane before being subjected to chromatographic analysis.

#### *HPLC Separation of Distillates*

The liquid chromatograph used was a Perkin Elmer LC series 4 equipped with an ASV-1 automatic switching valve, a LC-25 RI detector, LC-75 spectrophotometric detector and LC-100 computerized recorder. The distillate fractions ( $205\text{-}525^\circ\text{C}$ ) of coprocessing runs containing 3.7 wt% and 23.9 wt % coal were separated by HPLC into saturates, monoaromatics, polyaromatics and polars using a semi prep., 25 cm x 1.3 cm, Polar Amino Cyano column (PAC). Saturates, monoaromatics and polyaromatics were eluted using pentane at a flow rate of 5.5 cc/min. The polars were eluted in two parts in a back-flash mode using methyl-tert-butyl ether (MTB) designated as Polars 1, and tetrahydrofuran (THF) designated as polars 2. This procedure was repeated until a sufficient amount of material of each fraction was collected for analyses. The quantity of each fraction was measured gravimetrically after removing the solvent. Recovery of better than 95 % was obtained in each case.

#### *Field Ionization Mass Spectrometry*

FIMS was used to analyze distillate ( $205\text{-}525^\circ\text{C}$ ) fractions obtained in the coprocessing of 3.7 wt % , 23.9 wt % and 39.5 wt % coal with bitumen. Saturates, monoaromatics, polyaromatics and polars 1 fractions of coprocessing runs with 3.7 wt % and 23.9 wt % coal were also analyzed by FIMS. All FIMS analyses were performed at the facilities of SRI International, Menlo Park, CA. The detailed procedure of this technique has been published previously (9-10).

## RESULTS AND DISCUSSION

CANMET coprocessing involves the simultaneous upgrading of coal and bitumen/heavy oils in a once through operation using  $\text{FeSO}_4$  as a disposable catalyst. If coal-derived liquids contribute to the distillate products, the chemical composition of coprocessing distillates is expected to be different from that of hydrocracking distillates and may change with varying coal concentration. It is also possible that coal-derived liquids enhance the upgrading of bitumen, converting larger molecules to smaller molecules by providing hydrogen to bitumen-derived radicals. It was concluded that a detailed analysis of coprocessing distillates obtained at different levels of coal concentration would help in providing a better understanding of these solvent-coal interactions.

### *Effect of Coal Concentration on Product Characteristics*

From material balance considerations it can be concluded that in CANMET coprocessing experiments up to 40-50 wt % of the converted coal ends-up in the distillate. This assumes that there is no positive interaction between coal and bitumen or that the excess distillate over what would be expected from the bitumen portion of the feed reacted separately, is assumed to be derived from coal. Since it is expected that coal-derived liquids would contribute more to the heavier fractions of coprocessing distillates, it was decided to perform detailed characterization of the 205-525°C fractions. The general characteristics of the distillates generated using the three different coal concentrations are shown in Table 2. Nitrogen and oxygen increased as coal concentration increased while the sulphur content decreased. There is a slight increase in aromaticity and a corresponding decrease in H/C atomic ratio as coal concentration increases. These results can be rationalized in terms of an increasing contribution of coal-derived liquids to coprocessing distillates as coal concentration is increased.

Chromatographic separation of the distillates obtained from two coprocessing experiments containing 3.7 and 23.9 wt % maf coal are shown in Figure 1. Saturated hydrocarbons account for about 44 wt % of the distillate at 3.7 wt % coal and about 35 wt % of the distillate at 23.9 wt % coal. The amount of monoaromatics and polyaromatics did not change significantly as coal concentration increased. However, relatively more polar compounds (polars 1) eluted in back-flush mode with Methy-tert-butyl ether decreased slightly and THF-eluted hydrocarbons (polars 2) increased significantly. It appears that by adding more coal the quality of the products changes significantly. As will be discussed later, the characteristics of each fraction are also affected by increasing coal concentration.

These changes in product quality can be rationalized in terms of the contribution of more coal-derived liquids to the distillate as coal concentration is increased and/or enhancement in upgrading of the bitumen in the presence of coal. From the limited analysis shown in Table 3 it can be seen that there are no significant changes in the gross properties of the saturates and monoaromatics fractions at two levels of coal concentration. However, polyaromatics showed a decrease in aromaticity and consequently an increase in H/C atomic ratio. Aromaticity and nitrogen content of the polars 1 fraction increased significantly with increasing coal concentration. The lim-

ited amount of polars 2 fractions did not permit more detailed analyses. Table 4 lists the number and weight average molecular weights of the distillates and their hydrocarbon-type fractions. It is interesting to note that the molecular weights, both in distillates and the fractions decreased as coal concentration increased. The results indicate that the presence of coal enhances bond breakage in saturate and monoaromatic fractions. For polyaromatics, since molecular weight and aromaticity decreased, the presence of higher coal concentration appears to enhance both bond breakage and hydrogenation. The decrease in molecular weight and a large increase in aromaticity of the polars 1 fraction suggests that the contribution of coal-derived liquids to this fraction has increased with increasing coal concentration.

$^1\text{H}$  NMR analysis of the hydrocarbon-type fractions is shown in Table 5. Proton type distribution as defined by their chemical shifts(11) is illustrated in this table as a function of coal concentration. These analyses suggested slightly higher amounts of cyclic structures in the saturated fraction with 23.9 wt % coal. Little change in the proton distribution of monoaromatics was observed as coal concentration increased. The intensities of condensed aromatic protons in polyaromatics fractions decreased whereas alkyl beta and gamma protons increased as a result of increasing coal concentration. The results may be rationalized in terms of increasing the amounts of alkyl substituted polyaromatic compounds. For the polars 1 fractions the increase in coal concentration resulted in an increase in the condensed and uncondensed aromatic protons and a decrease in the alkyl beta and gamma protons. These results show that the amount of components with the higher number of aromatic rings and lower degree of alkyl substitution is increased with increasing coal concentration.

#### *FIMS Analysis of Distillates and their Hydrocarbon-type Fractions*

Field ionization mass spectrometry has been used extensively in the characterization of coal-derived liquids(12-16). Boduszynski et.al.(17-18) applied a combination HPLC (using a micro Bondapak  $\text{NH}_2$  column) and FIMS to characterize distillates and residues isolated from the liquefaction of Wyodak coal. The micro Bondapak  $\text{NH}_2$  column separated polycyclic aromatic hydrocarbons according to the number of aromatic rings (double bond) regardless of the type of alkyl substitution. FIMS separated these compounds according to nominal mass and Z values. The combination of HPLC/FIMS revealed detailed information on the composition of the hydrocarbons in heavy coal liquids. Recently FIMS has also been used in characterization of saturated hydrocarbons isolated from tar sand bitumens (19). In order to obtain fully quantitative data from FI mass spectra it is necessary to assume unit compound sensitivities. The intensities of the parent ion peaks are proportional to concentration and after correction for the natural abundance of  $^{13}\text{C}$  isotope, these can be converted to wt %.

In the present study, coprocessing distillates and their hydrocarbon-type fractions mentioned earlier were analyzed by FIMS to determine changes in compound-types due to the presence of different levels of coal in the coprocessing feed. The amino-cyano column used in this work has a similar separating power compared to the micro Bondapak  $\text{NH}_2$  column. However, due to the low concentration of each double bond series, polyaromatics were not separated according to their number of double bonds and were collected as one fraction.  $^1\text{H}$  NMR analysis of the saturated fractions showed that these fractions

were contaminated with small amounts of monoaromatics and olefins (area ratios of 96:2:2 respectively).

In the following analysis of the FIMS data, the methodology described by Boduszynski et.al.(18) was used as a basis for this study. The raw data from FIMS analysis was arranged into 14 columns each one unit apart. The peaks within each column were fourteen mass units ( $-\text{CH}_2$ ) apart. The seven even-numbered and seven odd-numbered mass series (homologous series or Z series) were each two units apart. The concentration of each peak (compound-type) can be obtained directly from the FI spectrum in mole % if unit compound sensitivities are assumed. Since it is very unlikely that all the different components present in coprocessing distillates have the same sensitivity toward ionization, for quantitative comparison of individual compounds or homologous series the term "% intensity" or "apparent concentration" is used throughout this text. Because of the possibility of the overlap of different homologous series in FI spectra, prior chromatography separation is essential. Only limited information can be obtained from the FI spectra of unfractionated distillates. The % intensities of the apparent homologous series from  $Z=+2$  to  $Z=-10$  did not change significantly by varying coal concentration from 3.7 to 39.5 wt %. However, in all the apparent homologous series increasing coal concentration resulted in an increase in the intensities of relatively lower molecular weight compounds and a decrease in the intensities of relatively higher molecular weight compounds. These results are reflected in the lower molecular weights of the distillates shown in Table 4.

The Z-series type analyses for saturates and monoaromatics obtained from coprocessing distillates using 3.7 and 23.9 wt % coal are shown in Table 6. Since these two fractions were separated from the polyaromatics prior to FIMS analysis, it is not expected that there would be any interference between  $\text{C}_n\text{H}_{2n-12}$  homologous series represented by tricycloalkylbenzenes (3 double bonds) and naphthalenes (5 double bonds) and the acyclic  $\text{C}_n\text{H}_{2n+2}$  alkane series. As shown in Table 6, while the apparent concentration of homologous series  $Z=+2$  to  $Z=-4$  increased slightly, series  $Z=-6$  did not change and series  $Z=-8$  and  $Z=-10$  decreased with increasing coal concentration. It should be mentioned that because of partial fragmentation of the saturate fractions the evaluation of part of the FI mass spectra below about 200 was difficult. Also, because of this fragmentation the total recovery (after correction for  $^{13}\text{C}$ ) of homologous series  $Z=+2$  through  $Z=-10$  was between 82-85 %. The saturate fractions consist of various homologous series ranging from acyclic alkanes ( $Z=+2$ ) through hexacyclics ( $Z=-10$ ). Acyclic alkanes in the saturate fraction obtained using 3.7 wt % coal range from about  $\text{C}_{13}$  to  $\text{C}_{39}$  with  $\text{C}_{22}$  ( $M/Z=310$ ) being the most abundant. In the saturate fraction obtained using 23.9 wt % coal, acyclic alkanes range from about  $\text{C}_{13}$  to  $\text{C}_{35}$  with  $\text{C}_{19}$  ( $m/z=268$ ) being the most abundant. This trend or the reduction in the range of the carbon skeleton and the change of maximum intensity to lower carbon number (molecular weight) as a function of increasing coal concentration was observed for all homologous Z series in the saturated fractions. This may imply that the addition of coal, in part, enhances the upgrading of bitumen. The formation of saturated hydrocarbons, even the acyclic homologous series  $Z=+2$ , from coal cannot be ruled out. Monocyclic alkanes ( $\text{C}_n\text{H}_{2n}$ ,  $Z=0$ ) consist of various alkyl cyclohexanes covering a broad mass range from  $\text{C}_{13}$  to  $\text{C}_{41}$  in the case of 3.7 wt % coal and  $\text{C}_{13}$  to  $\text{C}_{38}$  for the case of 23.9 wt % coal. The highest intensity in the

later case can be assigned to alkyl substituted cyclohexanes having molecular weight of  $m/z=266$ . The intensity of this peak is increased more than twice upon increasing coal concentration from 3.7 wt % to 23.9 wt %. The next homologous series belong to dicyclic alkanes ( $C_nH_{2n-2}$ ,  $Z=-2$ ) which cover similar mass ranges as monocyclic alkanes. Possible structures which can be assigned to this series are alkyl-substituted saturated indanes, decalins and bicyclohexanes. The most abundant species in the dicyclic homologous series of saturated fractions obtained using 23.9 wt % coal belongs to  $m/z=278$ . A possible structure that can be assigned to this molecular weight is  $C_5$  substituted decalin. The concentration of overall tricycloalkane homologous series did not change significantly as coal concentration was increased. The prominent peaks in this homologous series with 3.7 wt % coal are those at  $m/z=374$ , 346 and 318 whereas with 23.9 wt % coal the prominent peaks are at  $m/z=262$ , 276, 248 and 234. The peak at  $m/z=262$  in the liquefaction of Wyodak coal has been assigned to  $C_{19}H_{34}$  tricyclic terpene. The intensity of this peak increased by a factor of two with increasing coal concentration from 3.7 to 23.9 wt %. The apparent concentration of the tetracyclic homologous series ( $C_nH_{2n-6}$ ) in both saturated fractions is very similar. The increase in the intensities of individual peaks due to the presence of higher coal concentration is not as pronounced as in the previous series. The prominent peak at  $m/z=288$  in the saturated fraction with 23.9 wt % coal can be assigned to a  $C_3$  alkyl substituted tetracyclic compound. The peaks at  $m/z=372$  and 400 in both saturated fractions exhibited similar concentrations. These two peaks were also detected in liquids derived from Wyodak coal and were assigned to cholestane ( $C_{27}H_{48}$ ) and stigmastane ( $C_{29}H_{52}$ ) respectively. There may be some interference between pentacyclic alkanes ( $C_nH_{2n-8}$ ) and monoaromatic hydrocarbons due to incomplete chromatographic separation. This source of interference has been reported earlier by Boduszynski et.al. (18). This overlap makes assignment of each peak to a particular compound more difficult. The overall intensity of pentacyclic alkanes was reduced in the saturated fraction as coal concentration increased. This may indicate that the major source of pentacyclic in coprocessing distillates is bitumen. In both saturated fractions, prominent peaks with the initial mass at  $m/z=370$  can be assigned to pentacyclic triterpanes of hopanes and gammacerane which were also identified in liquids from Wyodak coal (18). The contribution of  $C_nH_{2n-10}$  homologous series to the saturated fractions is relatively small and decreases with increasing coal concentration.

The homologous series for monoaromatics are represented from  $C_nH_{2n-6}$  through  $C_nH_{2n-18}$ .  $C_nH_{2n-6}$  is represented by alkyl substituted benzenes and there may be an overlap between this series and tetracyclic alkanes. Although the apparent overall concentration of alkyl benzenes did not change significantly with increasing coal concentration, the intensities of the peaks from about  $m/z=190$  ( $C_{14}H_{22}$ ) to  $m/z=302$  ( $C_{22}H_{38}$ ) increased significantly. The largest increase in the concentration of homologous series of monoaromatics due to an increase in coal content appears to take place in the  $C_nH_{2n-8}$  and  $C_nH_{2n-10}$  series (Table 6). These series also dominated the monoaromatic fraction of coal-derived liquids obtained in the liquefaction of Wyodak coal (18). The most likely components of the  $C_nH_{2n-8}$  series are alkyl-substituted indanes, tetralins and cyclohexylbenzenes. There is a possibility that this series may overlap with pentacyclic alkanes. Possible structures that can be assigned to prominent peaks in the  $C_nH_{2n-10}$  series are alkyl-substituted tetrahy-



droacenaphthalenes, hexahydrofluorenes and octahydrophenanthrenes and/or-anthracenes. The intensities of the two peaks at  $m/z=186$  and  $m/z=200$  which may be assigned to the above compounds were increased almost five times as the coal concentration increased from 3.7 to 23.9 wt %. The prominent peaks in the  $C_nH_{2n-12}$  series are in the range of  $m/z=240$  ( $C_{14}$ ) to  $m/z=296$  ( $C_{22}$ ) and the monoaromatic fraction obtained in coprocessing with 23.9 wt % coal exhibited a higher concentration of these compounds. In the monoaromatic fraction obtained in the liquefaction of Wyodak coal the peaks in this mass range were assigned to alkyl-substituted octahydrocyclopentanophenanthrene, decahydropyrene and octahydrobenzofluorene.

The apparent concentration of polyaromatic fractions is shown in Table 7. Since no chromatographic separation according to the number of double bonds was carried out on this fraction, there is a possibility that each homologous series overlaps with the next (i.e.  $C_nH_{2n-12}$  with  $C_nH_{2n-26}$ ). For this reason the Z-series for this fraction is referred to as an "apparent Z-series". However, it is clear from the apparent Z-series of the FI mass spectra that two and three rings components predominate. The  $C_nH_{2n-12}$  series is represented by alkyl-substituted naphthalenes and its apparent concentration increased with increasing coal content. The peak at  $m/z=170$  is assigned to  $C_3$  naphthalene and its intensity almost doubled as coal concentration increased from 3.7 to 23.9 wt %. Dibenzothiophene with an initial peak at  $m/z=184$  should also appear in this column. However, because of chromatographic separation this compound most likely will be concentrated in the polar fractions. The homologous series  $C_nH_{2n-14}$  contributes significantly to the polyaromatic fractions in both distillates (22.4-26.7 %). The initial peak at  $m/z=154$  can be assigned to either biphenyl (6 double bonds) or acenaphthalene (5 double bonds). The prominent peaks in both polyaromatic fractions are concentrated between  $m/z=154$  and  $m/z=252$ . Other possible structures which can be assigned to this homologous series are alkyl-substituted binaphthyl and acenaphthalenes, cyclopentanonaphthalenes, tetrahydrophenanthrenes and/or anthracenes. Dibenzofurans with an initial peak at  $m/z=168$  also appear in this column. The % intensity of this peak almost doubled with increasing coal concentration. The apparent concentration of the homologous series  $C_nH_{2n-16}$  did not change significantly when coal concentration was increased. The intensity of the peak at  $m/z=194$  which can be assigned to phenylindane doubled with increasing coal concentration from 3.7 to 23.9 wt %. The intensities of the peaks between  $m/z=166$  and  $m/z=264$  remained relatively constant with increasing coal content. Possible components in this series are unsubstituted and alkyl-substituted fluorene, dihydropheanthrene and/or anthracene. The overall concentration of the  $C_nH_{2n-18}$  homologous series did not change with increasing coal concentration, however, the distribution of components shifted toward lower molecular weights. In both polyaromatic fractions it is clear from the intensities of the individual components that more than one series is involved. Possible components in this series are unsubstituted and alkyl-substituted anthracenes and/or phenanthrenes. The concentration of these components in the polyaromatic fraction increased with increasing coal concentration. The homologous series of  $C_nH_{2n-20}$  accounts for approximately 19 % of the polyaromatic fraction and its overall intensity was not affected by changing the coal concentration. Possible components in this series include unsubstituted and alkyl-substituted dihydropyrenes and tetrahydrochrysenes. The presence of other compounds such as tetrahydronaphthol and phenoxycyclohexane in this homologous series cannot be ruled

out. The contribution of the homologous series  $C_nH_{2n-22}$  and  $C_nH_{2n-24}$  to the polyaromatic fraction is relatively small and is decreased by increasing coal concentration. One of the prominent peaks in the  $C_nH_{2n-22}$  series is pyrene ( $m/z=202$ ) the intensity of which increased slightly with increasing coal concentration.

The FI mass spectra of the polars 1 fractions are complicated and require further chromatography separation in order to obtain structural information. The total % intensities of even-numbered columns in the FI mass spectra after correction for  $^{13}C$  in both polar fractions (3.7 and 23.9 wt % coal) was about 61 %. A substantial amount of nitrogen containing compounds belong to this fraction and their concentration in each homologous series increased with increasing coal concentration. For example, quinoline, tetrahydroquinoline, carbazole and their alkyl-substituted series are among a few nitrogenous compounds which can be named.

#### *Isotopic Mass Balance Calculations*

Isotopic mass balance measurements previously have been applied to determine the contribution of coal-derived liquids to coprocessing distillates(19). This method takes advantage of the difference in  $^{13}C/^{12}C$  ratio between coals and bitumens/heavy oils which is in order of 3-5 parts per thousand. It has been demonstrated by using Athabasca bitumen and Vesta subbituminous coal from Alberta that increasing the coal concentration in coprocessing results in an increase in the coal-derived carbon in the coprocessing distillate. Preliminary results from applying this technique to the distillates used in this study indicated that they contain from 20 to 40 wt % coal-derived carbon and the amount of this carbon increased with increasing coal concentration.

#### **CONCLUSIONS**

The results of this work show that varying coal concentration in the coprocessing feed effects the characteristics of the distillate products. While the oxygen and nitrogen contents increased with increasing coal concentration, the sulphur content decreased. The molecular weight of the distillate(205-525°C) and its hydrocarbon-type fractions decreased with increasing coal content of the feed. This was rationalized both in terms of the contribution of more aromatic coal-derived liquids to the distillate and the enhancement in upgrading of the bitumen in the presence of coal.

The amount of coal in the feed has a direct effect on the hydrocarbon-type and compound-type distribution in the distillate. FIMS analysis of the hydrocarbon-type fractions indicated that the concentration of acyclic, monocyclic and dicyclic compounds increased with increasing coal concentration. The fraction of monoaromatics obtained with higher coal concentration contains higher concentrations of substituted indanes, tetralins and poly hydrogenated acenaphthalenes, fluorenes, phenanthrenes and anthracenes. The polyaromatic fractions mainly consist of two and three rings aromatic components the concentration of which are significantly increased with increasing coal concentration.

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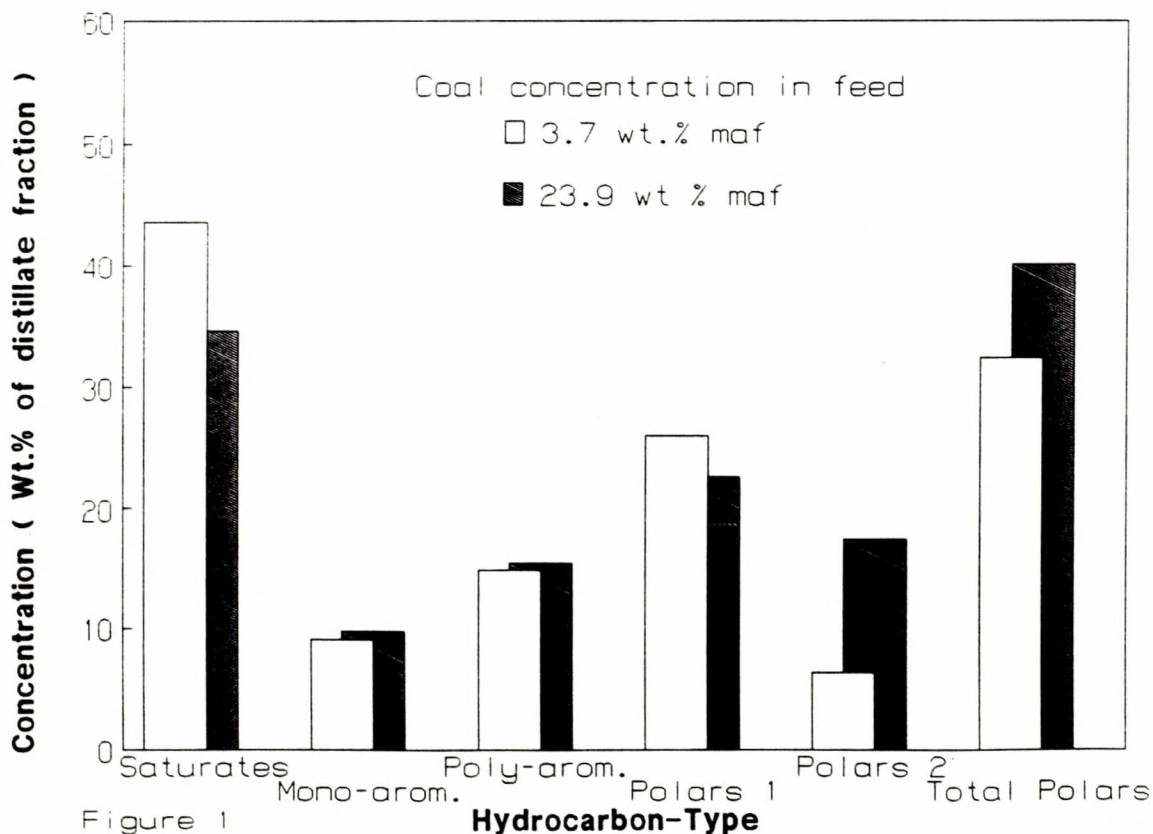
## REFERENCES

1. McLean, J.B. and Duddy, J.E. *J. Am. Chem. Soc. Div. Fuel Chem. Preprints* 31(4), 169, 1986.
2. Duddy, J.E., MacArthur, J.B. and McLean, J.B. Proceedings of the Direct Liquefaction Contractors' Review Meeting, U.S. DOE, Pittsburgh Energy Technology Center, October 20-22, Monroeville, Pa., 1986.
3. Kelly, J.F., Fouda, S.A., Rahimi, P.M. and Ikura, M. Proceedings of the Coal Conversion Contractors' Review Meeting, November 14-16, 1984, Calgary, Alberta, report SP85-4(ed. James F. Kelly), CANMET, Energy, Mines and Resources Canada, 1985.
4. Miller, R.L. presented at the 13th Biennial Lignite Symposium on Technology and Use of Low Rank Coals, May 21-23, Bismark, N.D., 1985.
5. Lett, R.G. and Cugini, A.V. Proceedings of the Direct Liquefaction Contractors' Review Meeting, U.S. DOE, Pittsburgh Energy Technology Center, October 20-22, Monroeville, Pa., 1986.
6. Shinn, J.H., Dahlberg, A.J., Kuehler C.W. and Rosenthal, J.W. Proceedings: Ninth EPRI Contractors' Conference on Coal Liquefaction, report EPRI AP-3825-SR, EPRI, Palo Alto, California, 1985.
7. De Vaux, G.R., Johanson, E.S. and Chervenak M.C., *Alternative Energy Sources*, ed. T. Nejat Veziroglu, Volume 7, p. 3267, 1978.
8. Miller, R.L. and Baldwin, R.M. *J. Am. Chem. Soc. Div. Fuel Chem Preprints* 31(4), 152, 1986.
9. Malhotra, M., Coggiola, M.J., Young, S.E., Tse, D. and Buttrill Jr. *J. Am. Chem. Soc. Fuel Chem Preprints* 30(1), 192, 1985.
10. Boduszynski, M.M., Hurtubise, R.J., Allen, T.W. and Silver, H.F. *Fuel* 65:223, 1986.
11. Winschel, R.A. Robbins, G.A. and Burke, F.P., Proceedings: Tenth Annual EPRI Contractors' Conference on Clean Liquid and Solid Fuels, report EPRI AP-4253-SR, EPRI, Palo Alto, California, 1985.
12. Yoshida, T., Maekawa, Y., Higuchi, T., Kubota, E., Itagaki, Y., Yokoyama, S. *Bull. Chem. Soc. Jpn.* 54:1171, 1981.
13. Yoshida, T., Maekawa, Y., Shimada, T. *Anal. Chem.* 54:976, 1982.

14. St.John, G.A., Butrill, S.E., Anbar, M. In "Organic Chemistry of Coal", Larsen, J.W., Ed., American Chemical Society: Washington DC, 1978, ACS Symp. Ser. No. 71.
15. Butrill, S.E., Jr. *Org. Coat. Plast. Chem.* 43:330, 1980.
16. Whitehurst, D.D., Butrill, Jr., S.E., Derbyshire, F.J., Farcasiu, M., Odoerfer, G.A. and Rudnick, L.R. *Fuel* 61:994, 1982.
17. Boduszynski, M.M., Hurtubise, R.J., Allen, T.W. and Silver, H.F., *Anal. Chem.* 55:225, 1983.
18. Boduszynski, M.M., Hurtubise, R.J., Allen, T.W. and Silver, H.F., *Anal. Chem.* 55:232, 1983.
19. Holmes, S.A. and Raska, K.A. *Fuel* 65:1539, 1986.
20. Ohuchi, T., Steer, J., Muehlenbach, K. and Carson, D. *Fuel Processing Technology* in press.

#### FIGURES

### H.P.L.C. SEPARATION OF DISTILLATE FRACTION ( 205-525 °C )



**Table 1- Analysis of feedstocks**

<b>Forestburg Coal</b>		<b>Cold Lake vacuum bottoms</b>	
<u>Proximate Analysis</u> (as received, wt %)		Specific gravity, 15/15°C	1.038
Moisture	19.2	Pentane insolubles, wt %	23.8
Volatile	34.0	Distillate (-525°C), wt %	16.7
Fixed C	39.1	Residue (+525°C), wt %	83.3
Ash	7.7	CCR, wt %	17.1
<u>Ultimate Analysis</u> (dry basis, wt %)		<u>Elemental composition</u> (wt %)	
Carbon	64.04	Carbon	83.34
Hydrogen	3.87	Hydrogen	9.69
Sulphur	0.53	Sulphur	5.84
Nitrogen	1.65	Nitrogen	0.45
Oxygen <sup>a</sup>	20.41	Oxygen <sup>a</sup>	0.68
Ash	9.5		
		<u>Metal content</u>	ppm
		V	235
		Ni	93
		Fe	18

<sup>a</sup>by difference

**Table 2- Elemental analysis(wt %) and aromaticities of distillate(205-525°C) fractions**

Coal <sup>a</sup> Concentration	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	f <sub>a</sub>	H/C
3.7	86.0	10.8	0.43	2.58	0.38	29.0	1.50
23.9	85.2	11.0	0.52	1.96	1.12	30.0	1.55
39.5	85.2	10.5	0.60	1.88	1.30	33.0	1.48

<sup>a</sup> wt %, based on maf slurry feed.

**Table 3- Elemental analysis(wt %) and aromaticities of hydrocarbon-type fractions**

Coal <sup>a</sup> Concentration	Saturates	Mono- aromatics	Poly- aromatics	Polars 1	Polars 2	
3.7						
	C	85.7	86.0	83.7	83.9	80.6
	H	13.9	11.3	9.5	8.4	10.8
	N	< 0.1	< 0.1	< 0.1	0.69	< 0.1
	f <sub>a</sub>	--	29.0	47.0	55.0	--
	H/C	1.95	1.57	1.36	1.20	1.60
23.9						
	C	85.5	86.5	86.3	82.9	82.0
	H	14.1	11.4	10.4	7.7	10.8
	N	< 0.1	< 0.1	< 0.1	2.0	< 0.1
	f <sub>a</sub>	--	28.0	42.0	64.0	--
	H/C	1.98	1.58	1.44	1.11	1.58

<sup>a</sup> wt %, based on maf slurry feed.

**Table 4- Molecular weight distribution of distillates(205-525°C) and their hydrocarbon-type fractions**

Coal <sup>a</sup> Concentration	205-525°C fraction	Saturates	Mono- aromatics	Poly- aromatics	Polars 1
	Number(and weight) average molecular weight <sup>b</sup>				
3.7	308(340)	352(395)	346(388)	256(281)	344(381)
23.9	270(300)	321(352)	296(320)	225(242)	321(364)
39.1	244(270)	---	---	---	---

<sup>a</sup> wt %, based on maf slurry feed

<sup>b</sup> Determined using FIMS

**Table 5- Proton distributions of hydrocarbon-type fractions**

proton type	chemical shift	saturates		mono- aromatics		poly- aromatics		polars 1	
Coal Concentration (wt % , maf slurry feed)		3.7	23.9	3.7	23.9	3.7	23.9	3.7	23.9
Proton Distribution, Area %									
condensed aromatics	10.5-7.15	---	---	---	---	17.0	12.2	16.3	25.8
uncond. aromatics	7.15-4.7	---	---	8.3	8.1	7.5	5.9	6.5	9.4
cyclic alpha	4.7-2.5	---	---	11.2	11.7	12.3	9.0	15.2	16.5
alkyl alpha	2.5-2.0	1.4	1.0	12.8	14.0	14.1	10.8	9.8	15.4
cyclic beta	2.0-1.4	6.5	9.7	13.5	14.7	11.8	12.6	12.0	10.4
alkyl beta	1.4-1.0	62.9	59.6	34.6	33.8	21.7	27.0	28.3	13.7
gamma	1.0-0.5	29.2	29.6	19.6	17.7	15.6	22.5	11.9	8.8

**Table 6- Apparent concentration of saturates and monoaromatics homologous series**

Hydrocarbon-type	Saturates		Mono-aromatics	
Coal Concentration (wt %, maf slurry feed)	3.7	23.9	3.7	23.9
Z series	Apparent Concentration (% Intensity)			
+2	9.5	11.3		
0	15.6	18.1		
-2	12.9	14.9		
-4	10.2	11.8		
-6	14.3	14.0	16.6	15.9
-8	11.8	9.6	17.4	21.7
-10	7.8	5.3	16.9	22.5
-12			14.8	14.6
-14			12.3	9.7
-16			8.3	6.4
-18			5.7	3.9

**Table 7- % Intensities of polyaromatic homologous series**

Coal Concentration (wt %, maf slurry feed)	3.7	23.9
Apparent Z series	% Intensity	
-12	17.3	20.3
-14	22.4	26.7
-16	15.0	13.2
-18	11.3	11.4
-20	19.1	18.6
-22	8.7	6.5
-24	4.1	2.5