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CANMET
Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

BIBLIOGRAPHY OF CANMET PUBLICATIONS ON COPROCESSING

COAL PROCESSING SECTION
SYNTHETIC FUELS RESEARCH LABORATORY
ENERGY RESEARCH LABORATORIES

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ENERGY RESEARCH PROGRAM
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INTRODUCTION

Coprocessing refers to the processing of mixtures of coal and oil with the objective of liquefying the coal and upgrading the oil simultaneously. World-wide interest in the concept has recently increased. Active R&D programs are now underway in the U.S., West Germany, Japan and the U.K. In Canada, pioneering research work has been carried out at the Energy Research Laboratories of CANMET. This has resulted in an extension of CANMET's hydrocracking technology for bitumen and heavy oils to coprocessing. Negotiations are underway to transfer the technology to industry and to accelerate its eventual commercialization.

This bibliography has been prepared to provide a one-source reference to the reports and publications generated to date at CANMET on coprocessing technology. All entries are listed chronologically under each major subheading. Each entry includes a brief abstract highlighting significant aspects.

INTRODUCTION

Le cotraitement consiste dans le traitement de mélanges de charbon et d'huile dans le but de liquifier le charbon et d'améliorer l'huile simultanément. Récemment, il y a eu un renouveau de l'intérêt pour ce concept, à l'échelle mondiale. Des programmes de R-D sont présentement réalisés aux É.-U., en Allemagne de l'Ouest, au Japon et au Royavme-Uni. Au Canada, les travaux de recherche initiaux ont été effectués aux Laboratoires de recherche sur l'énergie du CANMET. Ces activités ont contribué à faire progresser la technique d'hydrocraquage du bitume et des huiles lourdes mise au point par le CANMET, de façon à inclure le cotraitement. Des négociations sont en cours en vue de transférer la technique à l'industrie et d'accélérer les démarches visant sa commercialisation future.

La présente bibliographie a été préparée en tant que source de référence relative aux rapports et publications portant sur la technique du cotraitement, produits à ce jour au CANMET. Toutes les entrées sont présentées par ordre chronologique sous chaque sous-entête principale. Un court résumé soulignant les aspects importants de la technique accompagne chaque entrée.

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PUBLICATIONS IN REFEREED JOURNALS

1. Kelly, J.F.

1981: "Coal Liquefaction in Canada - The CANMET Program"; CIM Bulletin (Technical Papers) Vol. 74; No. 826; pp. 72-80.

Research and development on the production of liquid fuels from coal is rapidly expanding worldwide. Almost every industrialized country is engaged in coal liquefaction research and process development. In Canada, the federal government through CANMET is actively supporting coal liquefaction research and development in a number of areas.

A review of the basic principles and some of the processes in the production of liquid fuels from coal is presented with reference to the characteristics of the Canadian coal resource base. An overview of the CANMET coal liquefaction contract program is presented and specific results from the batch autoclave studies carried out with Saskatchewan lignite and Nova Scotia high-volatile bituminous coals are discussed. The development of a laboratory-scale continuous-flow coal liquefaction unit at the Energy Research Laboratories of CANMET to investigate the coprocessing of coal and bitumen/heavy oil is also described.

2. Poirier, M.A., Rahimi, P.M. and Ahmed, S.M.

1984: "Quantitative Analysis of Coal Derived Liquid Residues by TLC with Flame Ionization Detection"; Journal of Chromatographic Science 22(3); pp. 116-119.

A reliable method for the determination of maltenes, asphaltenes, preasphaltenes (MAP), and tetrahydrofuran (THF) insolubles in coal liquefaction distillation residues is needed to establish the degree of coal conversion during the development of coal liquefaction processes. A method for the determination of MAP involving thin layer chromatography (TLC) and quantitative flame ionization detection (FID) is described. The THF insolubles content is calculated by difference. This method is applicable to bitumen, heavy oils, and coal-derived liquid distillation residues. The maltenes are separated from the asphaltenes and preasphaltenes on a TLC silica gel "chromarod" using n-pentane:isopropanol (95:5) developing solvent. The asphaltenes are then separated from the preasphaltenes with benzene: isopropanol (80:20) developing solvent. Results are compared with the sequential solvent extraction procedure.

3. Monnier, J. and Kriz, J.F.
   1986: "Catalysts for Hydroprocessing Mixtures of Heavy Oil and Coal"; Industrial and Engineering Chemistry - Product Research and Development <u>25</u>; pp. 537-541.

Mixtures of one part coal and two parts residual oil from vacuum distillation of an Alberta heavy oil were hydroprocessed in a semicontinuous autoclave system with nickel, cobalt, molybdenum, tungsten, and calcium catalysts. A constant flow of hydrogen was supplied to the reactor during these tests performed at the threshold of coking. Catalysts were compared on the basis of conversion of THF insolubles; yields of oil, asphaltenes, and preasphaltenes; and sulfur content of the oil collected from the exiting gases. As expected, cobalt-molybdenum type catalysts performed well, enhancing oil production and conversion of THF insolubles. Petrographic analysis of the THF insolubles indicates that these catalysts also inhibited coke formation to a certain extent. A gain in pentane-soluble oil was found to be accompanied by a comparable loss in the THF-insoluble portion of the product, whereas other fractions changed to a lesser extent.

4. Potter, J., Kaybett, B., McDougall, W.J., Vasu Nambudiri, E.M., Rahimi, P.M. and Price, J.T.
   1986: "Petrographic Characterization of the Solid Products of Coal-Pitch Coprocessing"; Canadian Mineralogist; Vol. 24, pp. 219-228.

Petrographic studies were conducted on four solid residues resulting from the hydrogenation process of 1) Forestburg sub-bituminous coal alone, 2) the coal with a non-coking solvent (anthracene oil), 3) pitch (Cold Lake vacuum-bottom deposits), and 4) a mixture of coal and pitch. The purpose was to determine the amounts of coal- and pitch-derived solids in the residues. All the residues were produced under identical severe conditions of liquefaction to promote the formation of solids. The coal processed with anthracene oil gives, a residue consisting mainly of isotropic huminitic solids. If the coal is hydrogenated under similar conditions but without a solvent, the predominant residual solids are anisotropic semicokes displaying coarse mosaic textures, which form from vitroplast. The residual products from the hydrogenated Cold Lake vacuum-bottom deposits are also dominantly anisotropic semicokes; these display coarse mosaics and flow textures, and form by the growth and coalescence of mesophase spherules. Both coal- and pitch-derived solids are identified in a residue produced by coprocessing the Forestburg coal with the pitch from the Cold Lake vacuum-bottom deposits. It is concluded that the huminite macerals in the coal generate the fine-grained, mosaic-textured semicokes, whereas the pitch produces the coarse mosaics and flow-textured semicokes.

5. Monnier, J., Dénès, G., Potter, J. and Kriz, J.F.
1987: "Catalysts Supported on Hydrous "Titanates" for Hydroprocessing Mixtures of Heavy Oil and Coal"; Journal of Energy and Fuels 1; pp. 332-338.

Hydroprocessing catalysts were prepared by ion exchange of a sodium hydrous "titanate" support with aqueous solutions of transition metals (Ni, Co, Mo, Zn) or main-group elements (Sn, Al). These catalysts were tested in an autoclave system with a constant flow of hydrogen for the hydrocracking of mixtures of 1 part of subbituminous coal and 2 parts of residual oil from vacuum distillation of an Alberta heavy oil. The operating pressure and temperature were chosen so that the hydrocracking reactions occurred at the threshold of coking. Catalysts were compared on the basis of yields of oil, asphaltenes, and preasphaltenes, conversion of THF insolubles, and sulphur content in the hydrocarbon distillates collected from exiting gases. The presence of semicoke was determined by petrographic analysis of samples of THF insolubles. Mössbauer spectroscopy provided information on the chemical changes occurring to the tin active sites during reaction, and X-ray powder diffraction provided data on the nature of the crystalline phases present in these catalysts and on their average particle dimension. Experimental results indicate that some metal-exchanged hydrous "titanates" can help produce more pentane-soluble oil and less gas than commercial hydrotreating catalysts.

6. Rahimi, P.M., Fouda, S.A. and Kelly, J.F.
1987: "Coprocessing Using H_2S as a Promoter"; Fuel, 66,
pp. 1215-1218

Coprocessing of Forestburg subbituminous coal with Cold Lake vacuum bottoms in the presence of H_2S as a promoter using a continuous-flow bench scale pilot plant resulted in high coal and pitch conversions and distillate yields. On the basis of the results, it is proposed that H_2S acts as a hydrogen donor under coprocessing conditions. The hydrogen transfer from H_2S to radicals that are formed from coal or bitumen can take place directly or via coal-derived liquids. The activity of H_2S under coprocessing conditions is also compared with the activity of pulverized coal impregnated with iron sulphate.

EQUIVALENT TO PUBLICATIONS IN REFEREED JOURNALS - RESEARCH REPORTS AND CONFERENCE PROCEEDINGS

1. Kelly, J.F.
   1980: "Coal Liquefaction - A Technical Perspective"; Division Report ERP/ERL 80-67(R), CANMET, Energy, Mines and Resources Canada. (19 pages)

A technical position paper is presented on the nature and status of coal liquefaction technology in the Canadian research and development environment. Basic engineering ideas involved in coal liquefaction process development taking into account the different properties of Canadian coals are presented. The status of coal liquefaction technology in Canada is reviewed. The approaches, priorities and problems in the future development of Canadian expertise and the implementation of the technology in Canada are discussed. The ideas and concepts described in this report influenced other departmental documents on coal utilization and conversion.

2. Taylor, G.W., Kelly, J.F. and Reeve, D.A.
   1981: "Potential Coal Liquefaction Developments in Canada to the Year 2020"; Volume of reports compiled by the National Committees, Coal Liquefaction Task Force, World Energy Conference; Conservation Commission, London; 1982. (18 pages)

This report, which was prepared from the perspective of CANMET, presents estimates of the impact of coal liquids production on future Canadian liquid fuel supplies. The Canadian coal resource base is reviewed in terms of the potential for liquefaction. The status of coal liquefaction activities is reported including current contract programs. Potential future developments are discussed on a province-by-province basis taking into account the local resource base and infrastructure.

3. Kelly, J.F.
   1981: "The CANMET Coal Liquefaction Contract Program"; Proceedings of the 2nd World Congress of Chemical Engineering, Vol. II, pp.86-90. October 4-9; Montreal, Quebec.

This report presents a comprehensive technical review of the CANMET coal liquefaction contract program with special emphasis on coprocessing and "skimming" options. Experimental results from the coprocessing of an Alberta subbituminous coal with topped (+480°C) Athabasca bitumen are presented. These results demonstrate (in contradiction to the normal assumption at that time) that bitumen does not behave in the same manner in terms of benzene insoluble organic residue and liquid yield when processed in the presence of coal as when processed alone. Also, the results of a statistical optimization study of the supercritical gas extraction of an Alberta coal are presented as part of an investigation of the "skimming" of valuable liquid hydrocarbons from low-rank coals. Liquid yields in the range of 20 to 30 wt % maf coal are reported.

4. Poirier, M.A., Rahimi, P.M. and Ahmed, S.A.
   1983: "Quantitative Analysis of Coal-derived Liquid Residues by TLC with Flame Ionization Detection"; Division Report ERP/ERL 83-13(OPJ), presented at Chemical Characterization of Coal-derived Liquids Meeting, Pittsburg, PA; May 19-20.

A reliable method for the determination of maltenes, asphaltenes, preasphaltenes (MAP) and tetrahydrofuran (THF) insolubles in coal liquefaction distillation residues is needed to establish the degree of coal conversion during the development of coal liquefaction processes.

A new method is described for the determination of MAP, which involves thin layer chromatography (TLC) and quantitative flame ionization detection (FID). The THF insolubles content is calculated by difference. This method is applicable to bitumen, heavy oils and coal-derived liquid distillation residues.

The maltenes are separated from the asphaltenes and preasphaltenes on a TLC silica gel "chromarod" using n-pentane/isopropanol (95:5) developing solvent. Results are compared with the sequential solvent extraction procedure.

5. Skubnik, M.
1983: "Additive Preparation Unit, A Proposal"; Division Report ERP/ERL 82-58(CF).

The additive product is a mixture of ferrous sulphate and low rank coal. The proposed additive preparation unit is comprised of equipment allowing for further development and production of 125 kg batches of wet impregnated or dry mixed products. Wet impregnation uses a Vacuum Pan Dryer for water removal from coal-water pastes. The dry mixing process blends commercially pulverized dry coal. Alternatively, the additive can be prepared in the pan dryer and subsequently ground in a fluid energy mill. Replacement of the fluid energy mill with a Szego mill would be advantageous.

6. Skubnik, M.
1983: "Additive Slurry Evaporation Tests"; Division Report ERP/ERL 83-14(CF).

Equipment suitability tests with the originally proposed Vacuum Pan Dryer for the additive preparation from coal-iron sulphate-water slurry were not successful. Instead the equipment manufacturer proposed and carried out a series of successful tests on a Double Drum Dryer. Drying time was shortened and the temperature gradually increased from ambient to the final value.

7. Farnand, B.A., Rahimi, P.M. and Fouda, S.A.
   1984: "Membrane Filtration for Solid-Liquid Separation of Coal/Heavy Oil/Bitumen Coprocessing Product"; Division Report ERP/ERL 84-03(INT).

Coprocessing slurry products consist of a mixture of solids and liquids. Solid-liquid separation is one of the most important steps in any liquefaction process. To separate slurry products into liquids and solids by distillation is relatively time consuming. A new method using membranes was developed for solid-liquid separation. Preliminary results indicate that membrane filtration technique is much less time consuming than distillation. However, the qualities of liquid products obtained from filtration were not identical to those obtained by distillation.

8. Monnier, J.
   1984: "Review of the Coprocessing of Coals and Heavy Oils of Petroleum Origin"; CANMET Report 84-5E; Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada (8 pages)

This report reviews the various simultaneous cohydrogenation processes that are currently being recommended for coal and heavy oils of petroleum origin. The different coprocessing schemes are described, and the utilization of various catalysts and additives is discussed. A comprehensive bibliography of recent papers, patents and research reports is presented.

9. Monnier, J.
   1984: "Etat actuel des recherches sur l'hydrogénation simultanée du charbon et des huiles lourdes dérivées du pétrole"; CANMET Report 84-5F; Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada (8 pages).

Ca rapport traite de l'hydrogénation simultanée du charbon et des huiles lourdes dérivées du pétrole. On y décrit différents procédés d'hydrogénation simultanée ainsi que l'utilisation de catalyseurs et d'additifs. La bibliographie contient de nombreuses références d'articles scientifiques, de brevets et de rapports techniques.

10. Kelly, J.F., Fouda, S.A., Rahimi, P.M. and Ikura, M.
    1984 "CANMET Coprocessing: A Status Report", Division Report ERP/ERL 84-52(OPJ); Proceedings of the CANMET Coal Conversion Contractors' Review Meeting, November 14-16, Calgary, Alberta. (22 pages)

CANMET is developing a process to simultaneously liquefy coal and upgrade bitumen, heavy oil or petroleum residues. This coprocessing concept is similar to a direct hydroliquefaction process in which the normal coal-derived recycle oil is replaced with an externally supplied bitumen or other solvent. Alternatively, it can be viewed as an extension of the CANMET hydrocracking process where much greater coal concentrations are employed in the feed. The net result is a single-stage process which combines aspects of both coal liquefaction and heavy oil hydrocracking technologies.

At the Synthetic Fuels Research Laboratory of CANMET a continuous bench-scale unit has been used to demonstrate the feasibility of the concept using Forestburg subbituminous C coal from Alberta and Cold Lake vacuum bottoms as solvent. The same coal has also been processed with an anthracene oil solvent to allow direct experimental comparison of product qualities and yields between coprocessing and liquefaction.

The characteristics of coprocessing were investigated by changing the major process variables over wide operating ranges including the base case of simple hydrocracking of the solvent. A number of significant trends were observed especially with respect to the effect of coal concentration in the slurry feed. These results are discussed including the nature of potential coal-solvent synergism during coprocessing.

11. Fouda, S.A., Ikura, M. and Kelly J.F.
1985: "Coprocessing of Canadian Lignites and Bitumen"; Division Report 84-44(OPJ); Preprints of the Spring National Meeting of the A.I.Ch.E., March 24-28; Houston, Texas. (16 pages)

Simultaneous upgrading of Canadian lignites and bitumen under various operating conditions was investigated in a continuous hydrogenation unit. Results indicate that:

- coprocessing of lignites and vacuum bottoms is feasible and the results are comparable to those obtained from subbituminous coal using the same coprocessing medium;
- coal and pitch conversions appear to increase linearly with temperature over the range investigated;
- distillate and gas yields appear to increase linearly with increasing pitch conversion;
- hydrogen (equivalent) consumption ranges from 2 to 3 wt % of slurry feed (maf); and
- qualities of distillates are comparable to those of No. 6 fuel oil.

12. Potter, J., Kybett, B., McDougall, W., Nambudiri, E., Rahimi, P.M.
1985 "The Petrographic Characterization of Solid Products from Coal Bitumen Coprocessing"; Division Report ERP/ERL 85-18(OPJ); Proceedings of the Geological Association of Canada - Mineralogical Association of Canada, Fredericton, N.B.; May 15-17.

When vitrinite-rich Forestburg subbituminous coal is processed at high temperature with hydrogenated anthracene oil (HAO) the solid products comprise isotropic char with minor fine grained mosaic texture semicokes derived from vitrinite.

When bitumen is hydrogenated at the same temperature the solid products are mostly anisotropic semicokes with textures ranging from fine grained to dominantly coarse mosaics and flow domain formed by growth and coalescence of anisotropic mesophase spherules.

Coal-derived and bitumen-derived solids are identified in the solid products from Forestburg coal-bitumen coprocessing. The bitumen-derived solids are anisotropic semicokes displaying coarse mosaic textures and flow domains.

13. Rahimi, P.M., and Kelly, J.F.
    1985: "The Use of H_2S as Promoter in Coprocessing Low-Rank Canadian Coals and Bitumen"; Division Report ERP/ERL 85-17(OPJ); Proceedings of the 1985 International Conference on Coal Science; October 28-November 1; Sydney, Australia.

The use of H_2S as a promoter in coprocessing low-rank Canadian coals (subbituminous and lignite) and bitumen was examined under a wide range of severities. It was shown that, in general, the use of H_2S (5-15 wt %, based on maf coal) results in higher coal conversion and distillate yield for subbituminous coal but has little or no beneficial effect for lignite. Hydrogen sulphide was also effective in preventing or reducing coke formation during coprocessing. The effect of H_2S as a promoter for the water-gas shift reaction under coprocessing conditions and the existence of a possible synergism between coal and bitumen are discussed.

14. Monnier, J. and Kriz, J.F.
    1985: "Catalytic Hydroprocessing of Mixtures of Heavy Oil and Coal"; Division Report ERP/ERL 85-13(OPJ); Preprints of the Division of Petroleum Chemistry, Chicago Meeting of the American Chemical Society, September 8-13, 30(3), pp. 513-520.

Mixtures of coal and heavy oil of petroleum origin were processed in a semicontinuous autoclave system. Low severity experimental conditions were such that the hydroprocessing reactions proceeded at the threshold of coking. Nickel, cobalt, molybdenum, tungsten and calcium catalysts were tested in a slurry of one part subbituminous coal and two parts bituminous oil. A constant flow of 500 psig hydrogen 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 light hydrocarbons.

It was shown that the addition of an appropriate catalyst can affect the oil yield, the product quality as well as the coke formation. Cobalt-molybdenum catalysts were effective in all of these aspects. Up to 50 % of additional sulphur removal in the product oil was achieved when the Co-Mo catalysts were used.

15. Coulombe, S., Rahimi, P.M., Fouda, S.A., Ikura, M. and Sawatzky, H.
    1985: "Influence of Reducing Gas in the Coprocessing of Coal and Bitumen"; Division Report ERP/ERL 85-09(OPJ); National Meeting of the American Chemical Society, Chicago, Illinois; September 8-13.

Characterization of products obtained during coprocessing of Cold Lake vacuum bottoms and subbituminous coal under two reducing gases and at two levels of severity has been undertaken. The composition of the products is shown and hydrocarbon-type separation has been done on the distillates over 205°C combined with the residual oil. The influence of reducing gases (hydrogen or synthesis gas) is discussed. Results show how the use of synthesis gas would be preferable to pure hydrogen at low severity.

16. Fouda, S.A. and Kelly, J.F.
    1985: "CANMET Coprocessing of Low Rank Canadian Coals"; Division Report ERP/ERL 85-63(OPJ); Proceedings of the 1985 DOE/FE Direct Liquefaction Contractors' Review Meeting, Pittsburgh, Pennsylvania, November 19-21.

An extensive research program is underway at CANMET on the simultaneous liquefaction of coal and upgrading of heavy oil or petroleum residues. CANMET coprocessing is a single stage, once through process, that utilizes an inexpensive throw-away catalyst. It can be viewed as an extension of the CANMET hydrocracking process with high coal concentrations in the slurry feed.

In this paper, process performance using different feedstocks is discussed. Using Cold Lake vacuum bottoms as a coprocessing medium, eight coal feedstocks were tested. The process was shown to be technically feasible for all the coals. There were marginal variations among the low rank coals in the distillate yields and qualities and in coal conversions. Similarly, using an Alberta subbituminous coal, four residues were tested. The process was shown to be feasible for all the residues tested. It was found that the residues originating from bitumens/heavy oils result in higher pitch conversion and higher distillate yields than those originating from conventional crudes. The distillates produced from conventional crude residues, however, are of better quality than those produced from bitumen/heavy oil residues.

17. Monnier, J. and Kriz, J.F.
    1986: "Metal Hydrous Titanates for Hydroprocessing Mixtures of Heavy Oil and Coal"; Division Report ERP/ERL 85-60(OPJ); Preprints of the 10th Canadian Symposium on Catalysis, Kingston, Ontario, June 15-18, pp. 1-8.

Hydroprocessing catalysts were prepared by ion exchange of a sodium hydrous titanate support with aqueous solutions of transition metals. These catalysts were tested in a semi-continuous autoclave system with a constant flow of hydrogen, for the hydrocracking of mixtures of one part subbituminous coal and two parts residual oil from vacuum distillation of an Alberta heavy oil. The operating pressure and temperature were chosen so that the hydrocracking reactions occurred at the threshold of coking. Catalysts were compared on the basis of yields of oil, asphaltenes and preasphaltenes, conversion of THF insolubles and sulphur content in the hydrocarbon distillates collected from exiting gases. The presence of coke was determined by petrographic analysis of samples of THF insolubles. Experimental results indicate that some metal exchanged hydrous titanates helped produce more pentane-soluble oil and less gas than commercial hydrotreating catalysts.

18. Rahimi, P.M., Fouda, S.A. and Kelly, J.F.
1986: "Coprocessing Using H_2S as a Promoter"; Division Report ERP/ERL 86-04(OPJ); To be presented at the 192nd National Meeting of the Fuel Division of the American Chemical Society, Anaheim, California, September 7-12.

CANMET coprocessing involves the simultaneous upgrading of coal and heavy oil using a disposable catalyst in a once-through mode of operation. Batch autoclave studies were performed to demonstrate that H_2S is an effective promotor in coprocessing of low-rank coals and bitumens. The present study extended the initial work to experiments in a bench-scale CSTR system to verify the batch results and to compare the use of H_2S with an iron based disposable additive.

Preliminary results using Forestburg coal and Cold Lake vacuum bottoms indicate that H_2S is an effective catalyst and can enhance distillate yields and coal conversions. Higher product yields are possible when using H_2S compared to the use of an iron based additive, at least at lower processing severities. Experimental results on product qualities are also discussed.

19. Farnand, B., Rahimi, P.M. and Fouda, S.A.
1986: "Characterization of Naphtha Produced from Coprocessing Coal-Heavy Oil"; Division Report ERP/ERL 86-93(J).

Capillary gas chromatography proved useful for characterizing naphtha produced from coprocessing coal and heavy oil at various conditions. Increasing the coal concentration in the feedstock resulted in higher contents of phenols, indane and cyclohexanes in the naphtha product. Increasing the reaction temperature resulted in higher contents of phenols and indane, indicating a greater contribution of coal to the naphtha product at higher severities. The combined use of hydrogen sulphide and iron sulphate as promoter resulted in higher contents of indane, alkanes and cycloparaffines in the naphtha than the use of either alone.

20. Rahimi, P.M. and J.F. Kelly
1986: "Size Exclusion Chromatography for Characterization of Heavy Oil/Bitumen Vacuum Bottoms as feedstocks for Coprocessing"; Division Report ERP/ERL 86-78(TR).

Cold Lake vacuum bottoms, a potential feedstock for coprocessing, has been separated according to molecular weight on Styragel 100 $_f$ using preparative gel permeation chromatography (GPC). The average molecular weight (determined by vapour pressure osomometer) of 10 arbitrary fractions obtained by this fractionation technique ranged from 228 to 2074. Using an analytical GPC equipped with Shodex columns (divinyl benzene polymer) a linear relationship was found between the log Mn of fractions and retention volumes. Elemental analysis of the fractions showed an increase in nitrogen and sulphur contents as a function of molecular weight. H/C atomic ratios increased with decreased molecular weight and peaked at 648 g/mol. Conversely, aromaticity decreased sharply to a minimum at 548 g/mol and then increased gradually as molecular weight increased.

21. Fouda, S.A. and Kelly, J.F.
1987: "Coprocessing of High-Volatile Bituminous Coals"; Preceedings of the 1987 International Conference on Coal Science, Coal Science and Technology II, (J.A. Moulijn et. al ed.) Elsevier, Amsterdam, pp. 387-390. Division Report ERP/ERL 87-38(OPJ).

A continuous-flow bench-scale unit was used to test three coals: Illinois #6, a U.S. hvC bituminous coal, Prince Mine, hvB and Lingan mine, hvA coals from eastern Canada. The three coals were tested using Cold Lake vacuum bottoms as the coprocessing medium. An iron based additive was used as a catalyst. Slurries of each coal in Cold Lake vacuum bottoms were processed under a range of operating conditions. The reaction temperature was varied in the range of 425-455°C, the total pressure was varied in the range of 10.4-17.3 MPa, the space velocity was in the range of 0.66-2.00 kg/h/L; and the coal concentration tested was in the range of 20-30 wt % daf slurry. Under these conditions the performance parameters examined were the yield structure, the coal conversion to tetrahydrofuran solubles, the pitch conversion; and the extent and origin of coke formation. The effect of operating conditions on these performance parameters is discussed for each of the three coals. A comparison is made of the behaviour of the coals under similar operating conditions and typical results on the coprocessing of Forestburgh subbituminous coal are also included for comparison.

Examination of the toluene insolubles of the product distillation residues for the three bituminous coals as well as those for Forestburgh subbituminous coal showed that coke formation occurs to varying extents, increasing as the coal rank increases. There is petrographic evidence that the coke formed originated essentially from the coal portion of the feedstock.

The performance of the coals as coprocessing feedstocks was also found to be related to their surface area. The specific surface area decreased in the order of increasing rank: Forestburgh Illinois #6 Prince Lingan. The extent of coke formation observed can be explained in terms of the available coal surface area.

22. Fouda, S.A. and Kelly, J.F.
1987: "The Behaviour of Bituminous Coals Under Coprocessing Conditions"; Proceedings of the 1987 U.S. DOE Direct Liquefaction Contractors Review Meeting, Pittsburgh, Pennsylvania, October 6-8, Division Report ERP/ERL 87-56(OPJ)

Three high-volatile bituminous coals - Illinois No. 6, a hvbC from the U.S., Prince Mine, a hvbB and Lingan mine, a HvbA from eastern Canada - were tested for CANMET coprocessing with Cold Lake vacuum bottoms, using a bench-scale continuous-flow stirred tank reactor unit. The tests were carried out at 425-455°C, pressures in the range of 10.4-17.3 MPa, 0.6-2 kg/h/l space velocities and coal concentrations of 18-30 wt % maf in slurry feed. It was shown that the response of performance parameters to operating conditions depends strongly on coal rank.

The formation of anisotropic solids, as determined by petrographic analysis, was more noticeable for bituminous coals than for the subbituminous coal and increased with coal rank. For bituminous coals, the extent of coke formation was related to their swelling and thermoplastic characteristics.

Increasing the operating pressure resulted in a significant increase in the measured coal conversion for high-rank coals whereas the effect was marginal for the subbituminous coal. Conversely, increasing the operating temperature resulted in higher coal conversion for the subbituminous coal, whereas the regressive reactions offset the effect for bituminous coals.

Under identical conditions, although the low-rank coal resulted in higher overall distillate yield, the bituminous coals produced higher yields of the naphtha fraction. Comparison of the yields of residue components shows that bituminous coals produce lower yields of residual oils and much higher yields of asphaltenes and preashphaltenes than low-rank coals.

23. Potter, J., W.H. Dawson, P. Rahimi, and W.J. McDougall
1987: "Petrographic Characterization of Coprocessing Residues"; Division Report ERP/ERL 86-64(OPJ), Proceedings at the 1987 International Conference on Coal Science, Coal Science and Technology II, (J.A. Moulijn et. al. ed). Elswier, Amsterdam, pp. 391 -

Results from petrographic analysis of the THF insolubles in CANMET coprocessing products were used to calculate coal conversion and the extent of retrogressive coking reactions. Petrographic techniques can also be used to assign the origin of the coke i.e. coal, oil or both. The analyses were carried out on samples prepared by hydrogenation of coal alone, hydrogenation of coal in anthracene oil, the coprocessing of coal with Cold Lake vacuum bottoms (CLVB) and finally, from hydrogenation of solvent refined coal (SRC). The results were substantiated by scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDS).

All standard samples except coal-derived liquid coke (SRC coke) were prepared by hydrogenation or coprocessing (under severe conditions to promote coke formation), at 450°C, 5.5 MPa, (800 psi) H_2 (cold) and 1 hr. residence time in a 300 mL autoclave. Coal-derived liquid coke was generated by hydrogenation of SRC (obtained by liquefaction of Forestburg coal, in tetralin, at 420°C) in a bomb reactor.

The components were characterized on the basis of the morphological properties such as shape, form, and particle size and optical properties such as reflectance, fluorescence and anisotropy. The components were altered coal, intermediate bituminous solids, coal-derived liquid, CLVB-derived solids and a composite of coal + CLVB-derived solids.

Quantitative characterization of the THF insolubles obtained by coprocessing Foresburgh subbituminous coal and CLVB, is possible using petrographic analysis. The origins of the residue components can also be determined reasonably well if a number of control samples are provided as reference. These results can be substantiated by elemental analysis (SEM-EDS). It is concluded that the coal-CLVB residue is predominately derived from coal.

24. Chase, J.D. and McNabb, C.A
    1987 "Instrumentation for 2 bbl/day Coprocessing Pilot Plant (PP3): Instrument Loop Drawings and Panel Layout, Connection Diagrams: Contract 03SQ-23440-S-9182", Division Report ERP/ERL, 87-03(INT).

Engineering to provide connection drawings for 520 instrument loops from piping and instrumentation diagrams (P&ID's) was provided in Sept. 1986 by Monenco Consultants Ltd. in Phase I under contract to Supply and Services Canada for Energy, Mines and Resources (DSS 03SQ-23440-S-9182). Phase I has also involved the design of association instrument panels including panel layout and panel wiring diagrams in sufficient detail to allow mechanical and electrical construction of each panel. Cable groupings and junction box design are included in the engineering. Six copies of the report were provided in two volumes by Monenco: Volume 1, "Instrument Loop Diagrams", and Volume 2, "Instrument Panel Drawings".

Phase II of this contract involves construction of instrument panels (cabinets) and installation, connection and field wiring of all instrumentation.

25. Chase, J.D.
    1987: "Engineering Documentation for Coprocessing Pilot Plant: Piping and Instrument Diagrams (P&ID's) for 2 bbl/day (PP3) Pilot Plant at EMR", Division Report ERP/ERL 87-07(INT).

This report brings together the main task of a contract (04MK.23375-4-7072) to Partec Lavalin Inc. for the Energy Research Laboratory to provide engineering documentation for a 2 bbl/day coprocessing pilot plant. This main task involves the production of 13 piping and instrument diagrams P&ID's for the hydrocracking pilot plant which handles a feedstock comprised of up to 45% slurry of ground coal in heavy oil or bitumen. These P&ID's will be the basis from which the piping and instrumentation is fabricated. Instrument panel drawings and instrument loop drawings are prepared directly from the P&ID's.

Some additional background material (including the sequence of events which preceded this contract, and also various milestones during this contract) are provided, which is fitting for this, the first report, on EMR's coprocessing pilot plant facility.

26. Monnier, J., Fairbridge, C.W., Brown, J.R. and Kriz, J.F.
    1988: "Molybdenum Catalysts Supported on Hydrous "Titanates" for Low Severity Coprocessing of Heavy Oil and Coal"; Division Report ERL 87-28(OPJ); Proceedings of the 9th International Congress on Catalysis, Calgary, Alberta, June 26-July 1.

Molybdenum catalysts promoted with nickel, cobalt and aluminum were prepared by ion exchange of a sodium hydrous "titanate" support. These catalysts were tested in an autoclave system with a constant flow of hydrogen for the low severity coprocessing of one part of subbituminous coal and two parts of residual oil from vacuum distillation of an Alberta heavy oil. X-ray photoelectron spectroscopy provided information on the difference between cobalt-molybdenum active sites on hydrous titanates and alumina. Experimental results indicated that the coal conversion and the product distribution were affected by the relative acid site density of the catalysts which was evaluated by dynamic adsorption of ammonia. The molybdenum catalysts on titanates have shown advantages which can be attributed to the following characteristics: increased electronegativity of Mo an Co, making the reactants more strongly adsorbed; wider range of pore diameters enhancing diffusion within the pores of hydrocarbon molecules; suitable acid site density for proper solvent enrichment in terms of hydrogen transfer capability; larger number of active sites per unit surface area as shown by O_2 chemisorption; and fewer acid sites where coke could form.

CONFIDENTIAL LABORATORY REPORTS

1. Fouda, S., Kelly, J.F. and Rahimi, P.M.
   1982: "The Coprocessing Behaviour of Cold Lake Vacuum Bottoms and an Alberta Subbituminous Coal"; Division Report ERP/ERL 82-53(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (67 pages)

A continuous flow hydroliquefaction bench-scale unit was used to study the coprocessing behaviour of Cold Lake vacuum bottoms and Forestburg subbituminous C coal from Alberta. The feasibility of coprocessing this feedstock was demonstrated. The effect of process variables on the behaviour of the system was investigated.

Increasing the reactor temperature over a wide range had a significant effect on distillate yield, hydrogen consumption and pitch conversion. The slurry space velocity was varied over an operating range of commercial interest. Considerable decrease in distillate yield, hydrogen consumption and pitch conversion was observed with increasing space velocity. Increasing the operating pressure did not greatly affect the distillate yield. An increase in the distillate yield was observed on increasing the hydrogen flow rate.

For the range of coal concentrations studied, the distillate yield and the pitch conversion remained constant while a slight increase in the hydrogen consumption was noted. Under the operating conditions examined the estimated coal conversion had an average value of 87 wt %. Experimental evidence was provided to support the hypothesis that distillate obtained in the process originates from both the heavy oil and the coal.

2. Rahimi, P.M., Fouda, S. and Kelly, J.F.
   1982: "Characteristics of Distillates, Gases and Residues Obtained in the Coprocessing of Cold Lake Vacuum Bottoms and an Alberta Subbituminous Coal"; Division Report ERP/ERL 82-54(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (93 pages)

The effects of process variables on the characteristics of gross products (distillate, residue and gases) obtained in the coprocessing of Cold Lake vacuum bottoms and Forestburg subbituminous C coal from Alberta were investigated. A continuous bench-scale flow hydroliquefaction unit was used for all experiments. The process variables considered in this study were temperature, space velocity, coal concentration and total pressure. The hydrogen feed rate was kept constant.

Temperature and space velocity had a significant effect on the H/C atomic ratios of both the distillate and the residue. For the distillate, a lower H/C atomic ratio at very high temperatures was accompanied by a sharp increase in the aromaticity. Increasing temperature and residence time had consider able effect on the heteroatom removal. The molecular weight distribution ($\bar{M}n$) of the distillate decreased significantly with increasing temperature and residence time. The formation of gaseous hydrocarbons (C_1-C_4) were more pro nounced at higher temperatures and residence times. Increasing the operating pressure over a wide range did not significantly affect H/C atomic ratio, molecular weight and aromaticity of the distillate.

For the range of coal concentrations studied, a slight increase in the molecular weight of liquid products was noted. The aromaticity (f_a) of the liquid products appeared to have some dependence on coal concentration. The validity of this dependency requires further investigation.

3. Kelly, J.F.
   1983: "The CANMET Coprocessing R&D Program - Division Report ERP/ERL 83-36(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (9 pages)

This report attempts to provide a semi-technical overview of the current status of the CANMET research program on the coprocessing of coal and oil mixtures. Most of the accomplishments to date have been with respect to coprocessing viewed as an extension of CANMET hydrocracking but using much greater coal concentrations in the slurry feed. Under this mode of operation it has been demonstrated experimentally that the overall product slate does not change with the addition of coal to the feed in a wide range of concentrations. For high concentrations, a coal/oil synergism which leads to the production of more total liquid during coprocessing than that obtainable from hydrocracking an equivalent amount of coal-free oil has recently been observed. The reasons for this synergism are not fully understood and much more experimental work is needed including further confirmation. However, its technical and economic significance gives great impetus to the research and development program.

Compared with conventional coal liquefaction processes coprocessing has been shown to produce three times the total liquid yield. This is based on reactors of equivalent size, processing the same coal and the same amount of total slurry feed and is primarily a result of the elimination of the downstream process derived recycle solvent. The weight of distillate produced per unit weight of hydrogen consumed (hydrogen consumption efficiency) has also been shown to be much greater for coprocessing compared with coal liquefaction. In fact, coprocessing hydrogen consumption efficiencies are better than those of the more advanced two-stage coal liquefaction processes now under development.

4. Fouda, S.A. and Kelly, J.F.
   1983: "The Coprocessing of an Alberta Subbituminous Coal and a Distillate Fraction of Cold Lake Heavy Oil"; Division Report ERP/ERL 83-45(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (58 pages)

A continuous flow hydroliquefaction unit was used to study the coprocessing behaviour of a Cold Lake heavy gas oil fraction and Forestburg subbituminous C coal from Alberta. Experiments were conducted under a number of process conditions and the performance of the gas oil fraction as a coprocessing feedstock was compared with that of Cold Lake vacuum bottoms.

As a coprocessing feedstock, heavy gas oil required more severe operating conditions than vacuum bottoms for the same net distillate production. However, coal conversions were in the same range as those in vacuum bottoms under comparable conditions. Pitch conversions were significantly lower than those in vacuum bottoms. Negative pitch conversion values were obtained at low temperatures and low coal concentrations. This was attributed to possible polymerization caused by interactions between the primary coal products and the gas oil fraction.

The overall process performance of vacuum bottoms was more favourable compared with the gas oil fraction. Use of vacuum bottoms resulted in better distillate yields and qualities and easier operability.

5. Poirier, M.A., Rahimi, P.M. and Ahmed, S.M.
   1983: "Analysis of Coprocessing Distillation Residues Boiling Above 525°C by Pyrolysis TLC and Solid State Carbon-13 NMR"; Division Report ERP/ERL 83-03(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (14 pages)

The estimation of coal conversion in coprocessing runs is very important in order to evaluate a process. A complete analysis of the coprocessing distillation residue boiling above 524°C arising from coprocessing bitumen and coal is described. The residue is dissolved in tetrahydrofuran (THF) and the maltene, asphaltene, preasphaltene and THF insolubles contents are determined by pyrolysis thin layer chromatography. The dry THF insolubles portion consisting of residual coal and/or coke was analyzed by solid state carbon-13 NMR. Quantification of the coal residue is accomplished by correlation of the H/C ratio of a sample with other H/C ratios obtained with standard mixtures of different amounts of coal in coke. Seven samples were analyzed by this method and results are presented.

6. Ahmed, S.M., Fouda, S.A., Rahimi, P.M. and Sawatzky, H.
   1983: "Compound Type Studies of Coprocessing Products of Cold Lake Vacuum Bottoms and an Alberta Subbituminous Coal"; Division Report ERP/ERL 83-22(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (27 pages)

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

7. Ikura, M., Fouda, S.A. and Kelly, J.F.
 1984: "Coprocessing of an Alberta Subbituminous Coal and Cold Lake Vacuum Bottoms Using Synthesis Gas: I - Gross Performance "; Division Report ERP/ERL 84-26(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (37 pages)

The effects of synthesis gas in the continuous coprocessing of Forestburg (Alberta subbituminous) coal and Cold Lake vacuum bottoms were investigated using a continuous stirred tank reactor. The results were compared with those from hydrogen only runs carried out under similar process conditions. It was observed that:

- gross performances such as coal and pitch conversions, gas, distillate, and residue yields, and heteroatom removal for synthesis gas runs were very similar to those for the hydrogen only runs;
- when synthesis gas was used, significantly less reducing gas (hydrogen equivalent) was required when compared with the hydrogen only case.

8. Ikura, M., Fouda, S.A. and Kelly, J.F.
 1984: "Coprocessing of an Alberta Subbituminous Coal and Cold Lake Vacuum Bottoms Using Synthesis Gas: II - Characteristics of Distillates"; Division Report ERP/ERL 84-29(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (32 pages)

A continuous stirred tank reactor was used to investigate the coprocessing of Cold Lake vacuum bottoms with Forestburg subbituminous C coal using synthesis gas or hydrogen as the reducing gas. Distillate characteristics such as yield distribution, PONA analyses, aromaticity, hydrogen addition, simulated distillation, and heteroatom removal were compared. It was found that:

- The overall yields for the two cases are virtually identical at a given pitch conversion but the use of synthesis gas requires considerably less hydrogen (equiv.) to produce a given quantity of distillates.
- Synthesis gas tends to produce more light gas oil and less naphtha than hydrogen only.
- Synthesis gas easily reduces the process water formation by at least 50 wt %.
- Synthesis gas increases the aromatics in the distillates compared with hydrogen only.
- The H/C ratio of the distillates from the synthesis gas runs remains nearly constant as pitch conversion increases whereas that from the hydrogen runs slightly increases. The crossover between the two cases occurs near 40 wt % pitch conversion. The shift of the boiling point distribution curves and the change in the specific gravity of distillates reflect the above crossover.
- The sulphur content decreases drastically with increasing pitch conversion but the nitrogen content increases slightly. The use of synthesis gas or hydrogen gas results in similar heteroatom removal.

9. Ikura, M., Fouda, S.A. and Kelly, J.F.
   1984: "Coprocessing of an Alberta Subbituminous Coal and Cold Lake Vacuum Bottoms Using Synthesis Gas: III - A Proposal on Two Stage Coprocessing"; Division Report ERP/ERL 84-47(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (37 pages)

Hydrogen utilization was examined using experimental data obtained by a single-stage continuous stirred tank reactor. It was found that:

- Hydrogen addition to coal/vacuum bottoms is effective at low pitch conversion when rapid coal solubilization takes place and at high pitch conversion when severe hydrocracking dominates.
- As expected two-stage operation improves the H/C ratio of the distillate product, slightly increases distillate yield and slightly reduces C_1-C_4 generation. However, hydrogen utilization efficiency may be slightly inferior (hydrogen only) or superior (synthesis gas) to single-stage operation depending on the type of reducing gas employed.

10. Rahimi, P.M., Price, J.T. and Kelly, J.F.
1984: "Are Bitumens/Heavy Oils Hydrogen Donors? - Quantitative Determination of Hydrogen Donor Abilities of Bitumens and Pitch Materials using 1,1'-Binaphthyl and Anthracene"; Division Report ERP/ERL 84-18(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (41 pages)

Hydrogen donor abilities of bitumens/heavy oils as potential solvents for coprocessing with coals and pitch materials, specifically CANMET hydrocracked pitches as additives for co-carbonization, were investigated. Using 1,1'-binaphthyl, it was demonstrated that bitumens are generally better hydrogen donors than tetralin in the absence of hydrogen gas. When coal and bitumens are coprocessed in the hydrogen atmosphere, in terms of coal dissolution, bitumens appear to be less superior than tetralin. These results are rationalized in terms of the different mechanisms involved in coal liquefaction (in tetralin) versus coprocessing (in bitumens).

CANMET hydrocracked pitch materials were shown to be good hydrogen donors. In agreement with these results adding small amounts of CANMET pitches improved the coking properties of non-coking coals almost as effectively as commercially available pitches. It was shown that using two different hydrogen acceptors, the trend in hydrogen donor abilities of various pitches changed. These results indicate that in both the coal liquefaction and co-carbonization processes the selection of coal is as important as the selection of solvent and pitch, i.e., a solvent which may be excellent in terms of coal solubilization for a particular coal may be the worst solvent for another. No correlation was obtained between hydrogen donor ability of pitch materials and aromaticity (fa) when 1,1'-binaphthyl was used as hydrogen acceptor. However, using anthracene as hydrogen acceptor, a relatively good correlation was obtained between fa and hydrogen donor ability. At fa = 53-68, hydrogen donor ability was shown to be at its maximum. It was also demonstrated that pitches having higher hydrogen donor abilities do not necessarily perform the best as modifiers in co-carbonization experiments.

11. Rahimi, P.M. and Kelly, J.F.
    1984: "The Behaviour of Forestburg Subbituminous C Coal and Cold Lake Vacuum Bottoms During Coprocessing with Syngas and H_2S"; Division Report ERP/ERL 84-35(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (40 pages)

The effect of H_2S as promoter for water-gas shift reaction was demonstrated in earlier studies. The effect of H_2S both as a promoter for water-gas shift reaction and coal liquefaction under coprocessing conditions using Forestburg subbituminous C coal from Alberta and Cold Lake vacuum bottoms was investigated. In general, it was found that H_2S promotes coal conversion and higher distillate and pitch conversion are obtained only at moderate temperatures. At low temperatures, increasing CO concentration resulted in a decrease in coal conversion whereas distillate and pitch conversion did not change significantly. Addition of external water was essential for high coal conversion, however, distillate and pitch conversion decreased slightly. Increased temperature resulted in an increase in distillate and pitch conversion whereas coal conversion remained relatively constant. Using less amounts of H_2S, increased temperature caused the distillate and pitch conversion to increase but coal conversion decreased slightly. Under coprocessing conditions, external water addition, and temperature promoted shift reaction in the presence of H_2S. Sulphur contribution to distillate fraction and hexane insolubles upon addition of H_2S was found to be small and in some cases negligible. The fact that coprocessing resulted in almost the same distillate as obtained from bitumen alone indicates that there is a synergism between coal and bitumen under coprocessing conditions.

12. Rahimi, P.M. and Kelly, J.F.
    1984: "The Use of H_2S as a Promoter for the Water-Gas Shift Reaction Under Coprocessing Conditions"; Division Report ERP/ERL 84-34(CF); CANMET, Energy Research Laboratories, Energy, Mines and Resources Canada. (47 pages)

The effect of H_2S as a promoter for water-gas shift reaction was examined under coprocessing conditions using Estevan lignite and Cold Lake vacuum bottoms (CLVB). It was shown that at moderate temperatures H_2S had a significant positive effect on the shift reaction and coal conversion/distillate yield. Since H_2S did not show any positive effect on coal conversion and distillate yield when it was used with H_2 only and the above feedstocks, it is concluded that the increase in coal conversion, distillate and pitch conversion is the result of water-gas shift promotion by H_2S to drive the shift reaction equilibrium to generate more nascent hydrogen.

The effects of temperature and residence time on product distribution were also studied. In the presence of H_2S increasing the temperature had little effect on coal conversion but had a significant effect on distillate yield and pitch conversion. An optimum residence time was determined.

Finally, in the absence of H_2S the distillate yield obtained from coprocessing using CO/H_2 was very close to that expected from CLVB alone. However, in the presence of H_2S there appears to be a synergism between coal and CLVB since the distillate yield obtained from the coprocessing mixture was higher than that expected from bitumen only.

13. Fouda, S.A. and Kelly, J.F.
    1984: "Cold Lake Heavy Oil Fractions as Coprocessing Media"; Division Report ERP/ERL 84-25(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (27 pages)

A continuous flow stirred tank hydroliquefaction unit was used to test four different media for coprocessing with Forestburg subbituminous C coal. The four media were fractions or blends of fractions from Cold Lake heavy oil. The process performance was compared under identical operating conditions. The four media were ranked according to their performance in terms of distillate yields and quality as well as hydrogen utilization.

14. Rahimi, P.M. and Kelly, J.F.
    1984: "Coprocessing Behaviour of Cold Lake Vacuum Bottoms and Forestburg Subbituminous C Coal using H_2S as a Catalyst"; Division Report ERP/ERL 84-21(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (69 pages)

The use of H_2S as promoter in coal liquefaction has been reported in numerous publications. H_2S in the presence of metal oxide catalysts is shown to be effective in increasing coal conversion. Under coprocessing conditions using Fe_2O_3 as a catalyst, it was demonstrated that the total liquid yield increased by adding H_2S to reduce coke formation in coal liquefaction. H_2S has also been used as a catalyst for water-gas shift reaction in liquefaction of North Dakota lignite. Since bitumens/heavy oils are susceptible to coke formation under coprocessing conditions the use of H_2S would not only prevent coke formation but would also increase coal conversion and distillate yield.

Coprocessing behaviour of Cold Lake vacuum bottoms and Forestburg subbituminous C coal was examined under a variety of conditions using H_2S as catalyst. Generally, it was found that H_2S promotes coal dissolution and higher distillate and pitch conversion are obtained using H_2S. H_2S appears to be more effective at lower temperatures for the production of distillate and coal conversion. As the reaction temperature increases H_2S has a less pronounced effect, especially on distillate yield. It was shown that in the absence of any catalyst, H_2S is able to reduce or prevent coke formation. A plausible mechanism for the catalytic activities of H_2S under coprocessing conditions is discussed.

A comparison of H_2S as a homogeneous catalyst with CANMET additive indicated that H_2S is a better catalyst (especially at lower temperatures) than CANMET additive for the production of distillate materials. In terms of coal conversion, H_2S performed better than a Co-Mo catalyst. However, when used with Co-Mo similar results were obtained.

15. Rahimi, P.M., Ikura, M., Fouda, S.A. and Kelly, J.F.
 1984: "Hydrocarbon-Type Analysis of Distillate Products Obtained Under Coprocessing Conditions Using a Thin Layer Chromatography Pyrolysis Technique"; Division Report ERP/ERL 84-03(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (23 pages)

The use of a thin layer chromatography/flame ionization detector (TLC/FID) pyrolysis technique for the quantitative analysis of coprocessing heavy distillate products was investigated. It was demonstrated that the quantitative hydrocarbon-type analysis (saturates, aromatics and polars) of the coprocessing of Cold Lake vacuum bottoms and Forestburg subbituminous C coal can be carried out in a relatively short time and with high precision by pyrolysis TLC. The success of this method of analysis depends mainly on the type of standards used for calibrating the FID detector. The standards used in this work were obtained under conditions similar to those of the products being analyzed. Ten coprocessing distillates (205-525°C) were analyzed for saturates, aromatics and polars. This quantitative hydrocarbon-type analysis allowed a comparison of the nature of the products obtained when hydrogen was used in the process with those produced when syngas was used. The effect of temperature and space velocity on product distribution is also discussed.

16. Huibers, J., Kelly, J.F. and Fouda, S.A.
 1984: "Bitumen Refining of Coal Using a Rapid Injection Autoclave"; Division Report ERP/ERL 84-37(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (40 pages)

Short residence time (SRT) coal liquefaction was studied using a newly constructed rapid injection autoclave. This report outlines the commissioning of the autoclave, determination of operating procedures and short residence time (SRT) experiments conducted to determine the optimum conditions for producing the highest coal conversion. A review on catalysts, a description of the autoclave, and a comparison with other SRT reactors are given.

The rapid injection autoclave was successful in achieving fast heatup and cooldown rates for SRT studies. The coal was kept below 75°C in the charge cylinder, however, it was discovered that coal was collecting in the gas lines. Under low pressures of nitrogen pressure, the optimum conditions for coal conversion were determined. At higher temperatures, coke formation predominates and liquid yields drop while gas yields increase steadily with temperature.

It is recommended that a blank run be done to study the changes in the solvent and gas composition during heatup. An experiment to determine the mixing rate of the initial feed slurry under reaction conditions would be beneficial. Additional runs should be made to determine the effect of residence time on coal conversion.

17. Dawson, W.H. and Rahimi, P.M.
1985: "Estimation of Metal Concentrations in CANMET Additives by Thermogravimetric Analysis"; Division Report ERP/ERL 85-28(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (15 pages)

The use of thermogravimetric analysis (TGA) for the analysis of CANMET additives was investigated. It was demonstrated that the proximate analysis and the metal content of an additive can be determined in less than 20 min. The results obtained in this work are shown to be comparable to those obtained using a well-established Inductively Coupled Plasma method. The TGA profiles are sensitive to the metal:coal ratio. This suggests that it may be possible in future studies to deduce some information regarding metal-coal interactions.

8. Chase, J.D.

1985: "Design Correlations for Slurry Feed Section of PP3: Pipe and Pump Sizing for Slurry Feed System", Section Report PDS-85-01 (CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada. (15 pages)

The design basis for the co-processing pilot plant invovles slurries with coal up to 30 to 50% concentration. Although there has been much work in the area of synthetic fuels involving coal in coal liquids, water and alcohol, little has been done with high solids concentration in liquids with high viscosity such as vacuum bottoms or bitumen.

As a result of above we requested input from Partec Lavalin as an additional amendment on their engineering documentation of PP3 project. The basis of the Partec Lavalin and other input was that liquid velocity in the slurry recycle line between the slurry preparation room and the preheater in the main process area in Bay 3 must be 2 to 2.5 ft/sec. In order to maintain this velocity and keep pressure drops reasonable (say below 300 psi) then large slurry line pipe diameter at least 3" and perhaps 6" would be required. Since the length of this line would be about 200 ft the cost and volume of such a line and associated values would be high.

Since the writer was not convinced that the 2.5 ft/sec "rule of thumb" for slurries was independent of slurry properties especially viscosity, several days of engineering-type R&D (mainly a literature search) was carried out. The correlations found are considered adequate.

The aim of this brief report is to bring together some calculations, slurry viscosity results and correspondence and to draw conclusions and make a recommendation on slurry recirculation pipe and pump size.

19. Rahimi, P.M., Kelly, J.F. and Jean, G.
    1986: "Estimation of Coke in the Presence of Altered Coal Using Fourier Transform Infrared"; Division Report ERP/ERL 86-6 (CF); Energy Research Laboratories, CANMET, Energy Mines and Resources Canada. (15 pages)

Fourier transform infrared spectroscopy was used to monitor the changes in the intensities of functional groups occurring during coprocessing coal and bitumen/heavy oil. It was found that aliphatic C-H stretching near 2900 cm^{-1}, oxygen functionalities near 1700 cm^{-1}, aromatic rings with -OH groups near 1650 cm^{-1}, methylene groups at 1450 cm^{-1} and O-C bonds at 1280 cm^{-1} all decreased significantly. Quantitative analysis of coke and altered coal was also accomplished using a synthesis technique. Aliphatic and aromatic C-H stretching of a synthesized spectrum using 65 wt % bitumen coke and 35 wt % altered coal could be subtracted to the base line from aliphatic and aromatic C-H stretching of a coprocessing residue. In the present work the origin of coke (bitumen-coke or coal-derived coke) could not be identified. However, work is in progress to generate coal-derived coke which will be used for a synthesis spectrum. It has been shown that this technique for quantitative analysis of coke and altered coal is strongly dependent on the nature of standards.

20. Ikura, M., Kelly, J.F.
    1986: "Coal Solubilization into Bitumen in a Continuous Short Contact Time Reactor"; Division Report ERP/ERL 86-09 (CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada (26 pages)

The solubilization of Forestburg subbituminous coal into Cold Lake vacuum bottoms was investigated using a continuous short contact time reactor. The operating temperature, pressure, and residence time were varied from 375°C to 450°C, 10.4 MPa to 17.3 MPa, and 12 min to 32 min respectively. It was found that:

- coal solubilization is negligible at 375°C but 95% complete at 450°C within 15 min;

- the rate of coal solubilization is rapid in the first 15 min, but decreases at longer residence times,

- increasing operating pressure from 10 MPa to 17 MPa accelerates coal solubilization,

- up to 50% of oxygen in the feed is removed during coal solubilization,

- the use of petrographic analyses alone for quantitative study of coal solubilization is very difficult. However when the data from petrography and solvent extraction are combined, meaningful information is obtained.

21. Ikura, M., Kelly, J.F.
    1986: "Two-Stage Coprocessing of an Alberta Subbituminous Coal and Cold Lake Vacuum Bottoms"; Division Report 86-26(CF), Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada (30 pages)

Two-stage coprocessing of a Forestburg subbituminous coal and Cold Lake vaccum bottoms was performed. The effects of process variables such as recirculation gas velocity, temperatures in the first and second stages, operating pressures, and slurry space velocity were examined. The first stage temperature was varied from 375°C to 425°C, and for the second stage from 450°C to 455°C. The operating pressure was varied from 10.44 to 17.34 MPa, the superficial gas velocity in the second stage from 0.3 to 2 cm/s, and the slurry space velocity in the second stage from 0.8 to 1.2 kg/h/L.

It was found that the recirculation gas velocity has important effects on the coal and pitch conversion. There is an optimum recirculation gas rate which results in the maximum pitch conversion at given operating temperature, pressure and slurry space velocity. There is a minimum recirculation gas rate to obtain the ultimate coal conversion at given operating temperature, pressure and space velocity.

The pitch conversion increases almost linearly with decreasing slurry space velocity in the hydrocracking second stage.

22. Fouda, S.A., Kelly, J.F. and Ng, S.
    1986: "Operability and Initial Results of the Coprocessing of High-Volatile Bituminous Coals". Division Report ERP/ERL 86-27(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada (31 pages)

Three high-volatile bituminous coals were tested for coprocessing with Cold Lake vacuum bottoms. Illinois #6 from the United States was processed using the same procedure adopted for low-rank coals. Prince Mine and Lingan Mine coals from Eastern Canada exhibited flow problems during coprocessing. Tests showed that the flow problems are due to the swelling and plastic behaviour of the two coals and to some extent due to coke formation. The problematic tendencies of the coals were related to their ranks. Bituminous coals resulted in higher asphaltenes and preasphaltenes yields, lower residual oil yields and lower distillate yields compared with low-rank coals.

The reactivity of bituminous coals in terms of liquefaction is equal to or more than that of low-rank coals. This reactivity is offset by their higher tendency to form insoluble anistropic solids.

23. Skubnik, M.
    1987: "The Additive preparation Unit - Manual of Operation and Commissioning"; Division Report ERL 86-07(CF); Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada (20 pages)

Construction of the additive preparation unit (APU) was completed and the unit is ready for commissioning. The first part of this report describes the unit operation, shows a process flow sheet rate, givens instructions for the startup, steady state and shut-down procedures as well as measures on the fire and explosion prevention. The second part of the report deals with commissioning which should be done in two steps: first step - equipment performance tests in which data on dryer and classifier performance are generated and all other equipment as well as safety devices tested; second step - a commissioning run in which, while verifying design parameters of this highly automated unit, a representative sample of the additive shall be prepared. The unit is rated at approximately 115 kg of additive production per shift. The unit starting material is a 60 wt % water slurry. The production rate is limited by the dryer rated at 32.5 kg/hr of a low moisture content additive.

ORAL PRESENTATIONS

1. Kelly, J.F. "Coal Liquefaction in Canada - The CANMET Program"; Division Report ERP/ERL 80-61(OPJ); presented at 63rd Canadian Chemical Conference, Ottawa, Ontario; June 8-11, 1980.

2. Kelly, J.F. "The CANMET Coal Liquefaction Contract Program"; Division Report ERP/ERL 81-34(OP); presented at 2nd World Congress of Chemical Engineering, Montreal, Quebec; October 4-9, 1981.

3. Kelly, J.F., Fouda, S. and Rahimi, P. "The Coprocessing of Canadian Low-Rank Coals and Bitumens"; Science and Technology of Synfuels: I, Broadmoor Hotel, Colorado Springs, Colorado; March 1-3, 1982.

4. Kelly, J.F. "The CANMET Program"; presented at Coal Liquefaction Seminar, University of Calgary, Calgary, Alberta; May 5, 1982.

5. Poirier, M.A., Rahimi, P.M. and Ahmed, S.A. "Quantitative Analysis of Coal-Derived Liquid Residues by TLC with Flame Ionization Detection"; Division Report ERP/ERL 83-13(OPJ); presented at Chemical Characterization of Coal-derived Liquids Meeting, Pittsburg, PA.; May 19-20, 1983.

6. Ahmed, S.M., Fouda, S.A., Rahimi, P.M. and Sawatzky, H. "The Nature of Products from the Liquefaction of Subbituminous Coals in the Presence of Petroleum Related Residues"; Division Report ERP/ERL 83-51(OP); presented at the Confab 83 on Fossil Fuel Chemistry, Saratoga, Wyoming; August 2-5, 1983.

7. Dawson, W.H., Hayden, A.C.S., Braaten, R.W. and Rahimi, P.M. "Analysis of Wood Combustion and Coal Liquefaction by Carbon-13 CPMS NMR"; Division Report ERP/ERL 84-03(OP); presented at Experimental NMR Conference, Delaware; April 8-9, 1984.

8. Dawson, W.H., Rahimi, P.M., McKinnon, M.S. and Fyfe, C.A. "Characterization of Coal Liquefaction Residues by Solid State NMR"; Division Report ERP/ERL 84-34(OP); presented at 31st Canadian Spectroscopy Symposium, Ste-Jovite; October 1-3, 1984.

9. Kelly, J.F. and Fouda, S.A. "CANMET Coprocessing: An Extension of Coal Liquefaction and Heavy Oil Hydrocracking Technology"; presented at DOE Direct Liquefaction Contractors' Review Conference, Albuquerque, New Mexico, October 17-18, 1984.

10. Kelly, J.F., Fouda, S.A., Rahimi, P.M. and Ikura, M. "CANMET Coprocessing: A Status Report"; Division Report ERP/ERL 84-52(OPJ); presented at CANMET Coal Conversion Contractors' Review Meeting, Calgary, Alberta; November 14-16, 1984.

11. Fouda, S.A., Ikura, M. and Kelly J.F. "Coprocessing Canadian Lignites with Bitumen"; presented at American Institute of Chemical Engineers, Spring National Meeting, Houston, Texas, March 24-28, 1985.

12. Potter, J., Kybett, B., McDougall, W., Nambudiri, E., Rahimi, P.M. and Price, J. "The Petrographic Characterization of Solid Products from Coal-Bitumen Coprocessing"; Division Report ERP/ERL 85-18(OPJ); presented at Geological Association of Canada - Mineralogical Association of Canada, Fredericton, N.B.; May 15-17, 1985.

13. Coulombe, S., Rahimi, P.M., Fouda, S.A., Ikura, M. and Sawatzky, H. "Influence of Reducing Gas in the Coprocessing of Coal and Bitumen"; Division Report 85-09(OPJ); presented at 190th National Meeting of the American Chemical Society, Chicago, Illinois; September 8-13, 1985.

14. Monnier, J. and Kriz, J.F. "Catalytic Hydroprocessing of Mixtures of Heavy Oil and Coal"; Division Report ERP/ERL 85-13(OPJ); presented at 190th National Meeting of the American Chemical Society, Chicago, Illinois, September 8-13, 1985.

15. Kelly, J.F. "Coprocessing Technology - A Canadian Synthetic Fuels Opportunity"; Division Report ERP/ERL 85-45(OPJ); presented as the 1985 ERCO Award Lecture at the 35th Canadian Chemical Engineering Conference, Calgary, Alberta, October 6-9, 1985.

16. Rahimi, P.M. and Kelly, J.F. "The Use of H_2S as a Promoter in Coprocessing Low-Rank Canadian Coal and Bitumen"; Division Report ERP/ERL 85-17(OPJ); presented at International Conference on Coal Science, Sydney, Australia; October 28-November 1, 1985.

17. Fouda, S.A. and Kelly, J.F. "CANMET Coprocessing of Low Rank Canadian Coals"; Division Report ERP/ERL 85-63(OPJ); presented at DOE/FE Direct Liquefaction Contractors' Review Meeting, Pittsburgh, Pennsylvania; November 19-21, 1985.

18. Monnier, J. and Kriz, J.F. "Metal Hydrous Titanates for Hydroprocessing Mixtures of Heavy Oil and Coal"; Division Report ERP/ERL 85-60(OPJ); presented at the 10th Canadian Symposium on Catalysis, Kingston, Ontario, June 15-18, 1986.

19. Ikura, M. "CANMET Coal-Oil Coprocessing (in Japanese)", presented at the Coal Utilization Committee, Japanese Society of Promotion of Science (Ministry of Education, Japan), Tokyo, Japan, Sept. 25, 1986.

20. Ikura, M. "Coal-Oil Coprocessing", presented at the Joint Technical meeting for Canada-Japan Coal Liquefaction Cooperation, Tokyo, Japan, Sept. 29-Oct. 3, 1986.

21. Ikura, M. "Basics of Coal-Oil Coprocessing (in Japanese)", presented at Himeji Institute of Technology, Himeji, Japan, October 6, 1986.

22. Rahimi, P.M., Fouda, S.A. and Kelly, J.F. "Effect of Coal Concentration on Product Distribution in CANMET Coprocessing"; Division Report ERP/ERL 87-29(OPJ); Presented at the EPRI 12th Annual Fuel Science and Conversion Meeting, Palo Alto, Calf., May 12-14, 1987.

23. Baltus, R.E. and Rahimi, P.M. "Characterization of Oil Residual Fractions using Hydrodynamic Measurements"; presented at the spring meeting of the A.I.Ch.E; Huston, Texas, May 1987.

24. MacPhee, J.A., Nandi, B.N. and Rahimi, P.M. "Le Comportment Thermogravimétrique de Charbons Canadians"; Presented at the 55th ACFAS Congress, Ottawa, Ontario, May 19-22, 1987.

25. Potter, J., Dawson, W.H., Rahimi, P.M. and McDougall, W.J. "Petrographic Characterization of Coprocessing Residues"; Presented at the 1987 International Conference on Coal Science, Maastricht, The Netherlands, October 26-30, 1987.

26. Baltus, R.E., and Rahimi, P.M. "Determination of the Size and Conformation of Bitumen Fractions"; Presented at the Annual Meeting of A.I.Ch.E.; New York, N.Y., April, 1987.

27. Fouda, S.A. and Kelly, J.F. "The Behaviour of Bituminous Coals Under Coprocessing Conditions"; Division Report ERP/ERL 87-56(OPJ). Presented at the 1987 US DOE Direct Liquefaction Contractors' Review Meeting, Pittsburgh, Pennsylvania, October 6-8, 1987.

28. Fouda, S.A. and Kelly, J.F. "The Coprocessing of High-Volatile Bituminous Coals"; Division Report ERP/ERL 87-38(OPJ). Presented at the International Conference on Coal Science, Maastricht, The Netherlands, October 25-30, 1987.

29. Mikhlin, A.J. and Ikura, M. "Benefication of Low-Rank Canadian Coals for Coprocessing using Oil Agglomeration", presented at the 37th Canadian Chemical Engineering Conference, Montreal, Québec, May 19-22, 1987.

30. Kelly, J.F. "Research and Development Directions in Coporcessing"; invited presentation at the U.S. DOE New Direction R&D for Direct Coal Liquefaction Workshop, Pittsburgh, Penna., October 5-6, 1987.

31. Monnier, J., Fairbridge, C.W., Brown, J.R. and Kriz, J.F. "Molybdenum Catalysts Supported on Hydrous "Titanates" for Low Severity Coprocessing of Heavy Oil and Coal"; Division Report ERL 87-28(OPJ); presented at the 9th International Congress on Catalysis, Calgary, Alberta, June 26-July 1, 1988.

CONTRACT FINAL REPORTS

1. "Investigation to Determine the Feasibility of Using Bitumen as Solvent for Coal Liquefaction - Phase I and II", Sandwell Beak Research Group, January 1980. (Confidential)

2. "Characterization of Solid Residues from Coal Liquefaction Processes - Phase I", University of Regina, March 1981.

3. "Thermal Hydrogenation of Bitumen/Coal Slurries Using Simulated Syngas", Saskatchewan Power Corporation, July 1981. (Confidential)

4. "Characterization of Solid Residues from Coal Liquefaction Processes - Phase II", University of Regina, March 1982. (Confidential)

5. "Demonstration and Testing of the Use of H_2S as a Promoter in Coal Liquefaction", Sandwell Technologies, May 1983. (Raw Data, Confidential)

6. "Characterization of Solid Residues from Coal Liquefaction Processes - Phase III", University of Regina, June 1983.

7. "Characterization of Solid Residues from Coal Liquefaction Processes - Phase IV", University of Regina, May 1984. (Confidential)

8. "Characterization of Solid Residues from Coal Liquefaction Processes", University of Regina, Energy Research Unit, June 1985. (Confidential)

9. "Application of the Centrax A Separation Process to Liquid Products from Ten Different Coprocessing Slurry Samples", Sandwell Technologies, July 1985. (Confidential)

10. "Characterization of Solid Residues from Caol Liquefaction Processes", University of Regina, Energy Research Unit, June 1986 (Confidential).

11. "Characterization of Solid Residues from Coal Liquefaction Processes", University of Regina, Energy Research Unit, June 1987 (Confidential).

12. "Investigation of the Use of Spherial Oil Agglomeration in the Benefication of Low Rank Canadian Coals as an Integral Part of CANMET Coprocessing Process", SNC Inc. Feb. 1987 (Confidential).

13. "CANMET Coprocessing Technology Technical and Economic Evaluation: Synthetic Crude Oil Production", Partec Lavalin, February 1987. (Confidential).

14. "Characterization of Tin Catalysts by Mössbauer Spectroscopy", Concordia University, March 1987.

15. "Mathematical Modelling of Coprocessing Kinetics", Lobbe Technologies Ltd., November 1987.

16. "Evaluation of Atmospheric Flash Pyrolysis for Coprocessing Residues", Waterloo Research Institute, December 1987.