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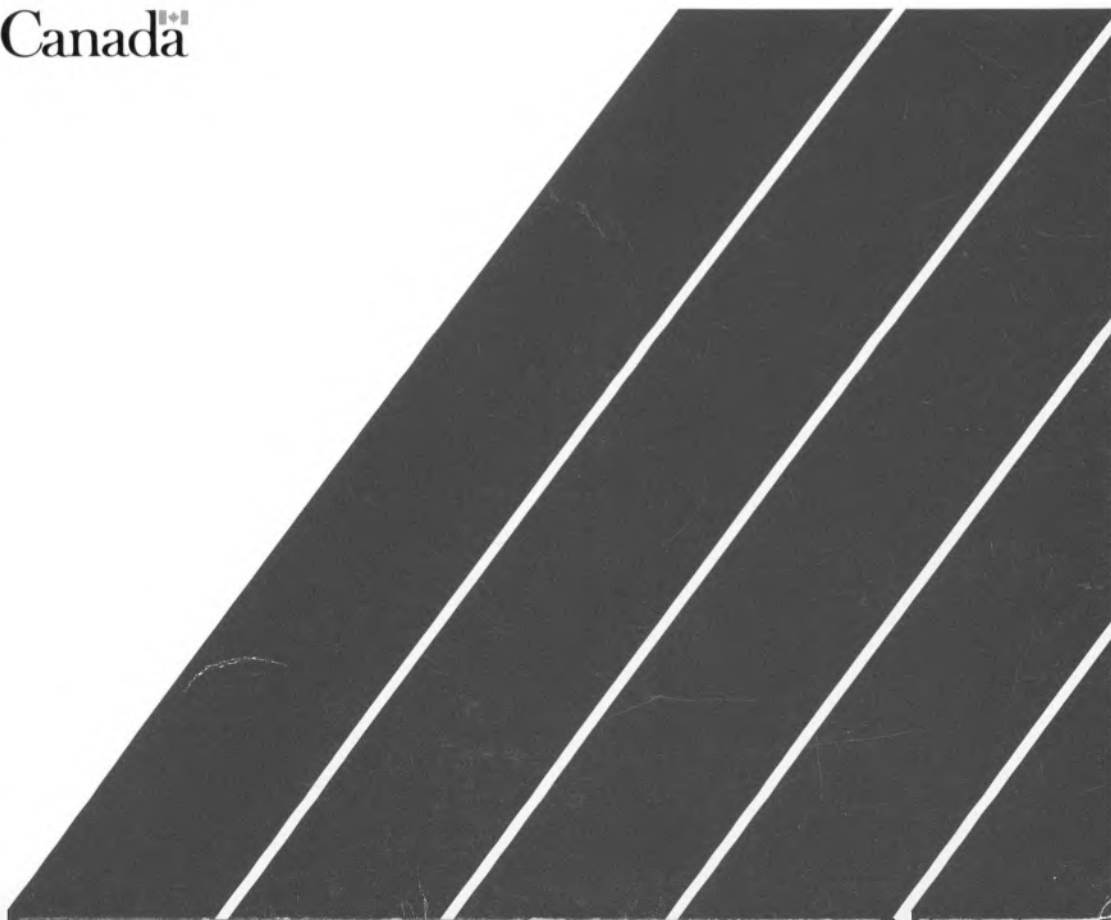
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BIBLIOGRAPHY OF CANMET PUBLICATIONS ON COPROCESSING

COAL PROCESSING SECTION
SYNTHETIC FUELS RESEARCH LABORATORY

ENERGY RESEARCH PROGRAM
DIVISION REPORT ERL 89-78(TR)

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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 Royaume-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 25; 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: "Coproprocessing Using H_2S as a Promoter"; Fuel, 66,
pp. 1215-1218

Coproprocessing 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 coproprocessing 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 coproprocessing conditions is also compared with the activity of pulverized coal impregnated with iron sulphate.

7. Farnand, B.A., Rahimi, P.M. and Fouda, S.A.
1988: "Characterization of Naphtha Produced from Coprocessing Coal-Heavy Oil"; Fuel Processing Technology, 19, pp. 153-164

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 high contents of phenols, indan and cyclohexanes in the naphtha product. Increasing the reaction temperature resulted in higher contents of phenols and indan, 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 indan, alkanes and cycloparaffins in the naphtha than the use of either alone.

8. Ikura, M. and Last, J.A.
1988: "Flash Hydropyrolysis of Bituminous Caking Coal"; Fuel Processing Technology, 20, pp. 257-268

It is known that the continuous operation of pyrolysis and flash hydropyrolysis of bituminous coals is difficult because of their caking properties. The agglomeration of caking coals was overcome by blending high-volatile bituminous coal with non-caking diluents. Continuous flash hydropyrolysis of Prince Mine (high-volatile bituminous A) coal/diluents mixtures was carried out under various operating conditions. Temperature was varied from 665 to 790°C, residence time 3.7 to 7.3 s, and pressure was kept at 12.5 MPa. Results are discussed in terms of product yields and analysis. BTX in the organic liquids, and the quality and combustibility of char are discussed.

9. Ikura, M., Kelly, J.F. and Capes, C.E.
1989: "Selective Oil Agglomeration of Lignite using Vacuum Bottoms only as an Integral Part of Coprocessing", *Energy & Fuels*, 3, pp. 132-136

The low cost of Canadian low-rank coals makes them prime feedstocks for coprocessing with bitumens and heavy oils. Depending on the coal concentration in the feed slurry, the high mineral matter in some of these coals can cause operational problems as well as reduce the overall process efficiency and the net liquid product yield. To reduce the mineral-matter content in the feed slurry, oil agglomeration can be used for coal beneficiation as an integral part of coprocessing. However, an optimum integrated approach requires the use of undiluted bitumen or heavy-oil feedstocks as a bridging liquid. Also, low-rank coals as well as oxidized higher rank coals often possess a relatively hydrophilic surface. This makes the application of oil agglomeration extremely difficult. A novel method of beneficiating low-rank coals for coprocessing by oil agglomeration using a part of the feed bitumen has been conceived and developed. This method overcomes the hydrophilic surface problem of low-rank coals and allows the use of undiluted coprocessing feed oils as viscous as vacuum bottoms. Experimental results on the beneficiation of a Canadian lignite with vacuum bottoms are presented. The efficiency of the process was evaluated in terms of combustibles recovery and mineral-matter rejection. The on a mf basis) with Interprovincial Pipe Line (IPPL), Coal Lake, and Lloydminster vacuum bottoms indicated that oils with widely different viscosities could be employed as a bridging liquid without dilution. A parametric study on the agglomeration of the same lignite with IPPL vacuum bottoms resulted in 51-97 wt % combustibles recovery and a corresponding 77-42 wt % mineral-matter rejection. The effects of vacuum bottoms concentration, operating temperature, and processing time on the beneficiation performance are discussed.

10. Szladow A.J., Chan, R.K., Fouda, S.A. and Kelly, J.F.
1989: "Kinetics of Heavy Oil/Coal and Coprocessing"; *Energy & Fuels*, 3, pp. 136-143

Reaction engineering models were developed for coprocessing of heavy oil and coal. The properties of the coprocessing products, lumped by their solubility and distillation points, were found to be independent of the severity of the process. The effects of temperature and space velocity on coprocessing showed the product yield structure to be determined primarily by the determined primarily by temperature. Two types of reaction networks, a sequential network and a parallel network, were tested for correlating coprocessing data. The criteria used for evaluation of the developed model were the percent of variance explained by the model and the accuracy of the model. The final, selected model explained 90% of the target, 92.5% variance. Testing of the developed models to the assumptions made showed that the choice of model is determined primarily by the yield structure of the products and not by the assumptions made about the gas holdup or the amount of product flashed at the reactor temperature and pressure.

11. Rahimi, P.M., Fouda, S.A., Kelly, J.F., Malhotra, R and McMillen, D.F.
1989: "Characterization of CANMET Coprocessing Distillate at Different Coal Concentrations"; Fuel, 68, pp. 422-429

The effect of feed coal concentration on the characteristics of gross and fractionated coprocessing distillates was investigated. Elemental analysis, ^1H n.m.r., high performance liquid chromatography (h.p.l.c.) and field ionization mass spectrometry (f.i.m.s.) were used in this study. The distillates (205-525 $^{\circ}\text{C}$) were obtained by coprocessing Forestburg subbituminous coal at three concentration levels, 3.7, 23.9 and 39.5 wt % (based on a maf slurry feed) and Cold Lake vacuum bottoms from Alberta in a nominal 1kg/h bench-scale unit. Gross distillate characteristics as determined by elemental and ^1H n.m.r. analyses indicate that as coal concentration is increased, more coal-derived liquids contribute to the distillate. For detailed analysis, distillates from 3.7 and 23.9 wt % coal concentration 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 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 wt % of monoaromatics and polyaromatics was not affected by the amount of coal present in the slurry feed. The number and weight of the distillates boiling between 205⁰C-525⁰C and their hydrocarbon-type fractions decreased as the coal concentration increased. Each hydrocarbon-type fraction was analysed by ¹H n.m.r. and f.i.m.s. 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 that take advantage of the difference between the ¹³C/¹²C ratio of coal and bitumen, the amount of coal-derived carbon in the coprocessing distillate was estimated.

12. Fouda, S.A., Kelly, J.F. and Rahimi P.M.

1989: "Effect of Coal Concentration on Coprocessing Performance"; Energy and Fuels, 3, pp. 154-160

In an effort to assess coprocessing as a primary upgrading technology, a study was carried out on the effects of coal concentration on the overall process performance. Slurries containing 0-39.5 wt % maf subbituminous coal in Cold Lake vacuum bottoms were processed in a continuous-flow bench-scale unit under the same operating conditions. The tests were carried out in a single-stage CSTR unit with once-through operation using a dispersed slurry-phase disposable additive. Marked improvement in the process operability was observed with the addition of coal. Increased distillate yields were obtained at low coal concentration. In the range of 10-30 wt % maf coal concentration, the distillate yield was constant and was equal to that for the no coal case. The gross distillate quality changed only marginally with coal concentration. The sulfur removal did not change, but the oxygen removal increased with coal concentration. The extent of anisotropic solids formation was markedly decreased by adding coal, and the extent of vanadium and nickel removal increased with increasing coal concentration. The results show that no significant penalties were observed in terms of process yields or product

qualities by including coal in the feed to operate in the coprocessing mode. Moreover, beneficial effects such as the inhibition of coke formation and the enhancement of metals removal were observed.

13. Sekhar, M.V.C. and Rahimi, P.M.

1989: "Upgrading of Coprocessing Naphtha by Hydrotreating"; Advanced in Hydrotreating Catalysts, Studies in Surface Science and Catalysis, 50, pp. 251-261

A naphtha fraction representing about 15 wt % of the total liquid yield derived from coprocessing of Cold Lake vacuum bottoms and 30 wt % Forestburg subbituminous coal from Alberta was hydrotreated in a bench-scale continuous trickle bed reactor. The hydrotreating tests were performed using a commercially available nickel molybdenum catalyst and under conditions similar to those utilized in commercial units. Presulphiding was carried out in the liquid phase using a diesel fuel spiked with carbon disulphide. Hydrotreating produced a clear liqued product from a feedstock that was dark brown, suggesting extensive hydrodenitrogenation and hydrodesulphurization. Sulphur and nitrogen conversions of the order of 99.5 and 99.95% respectively were achieved under relatively mild conditions.

EQUIVALENT TO PUBLICATIONS IN REFEREED¹⁰ 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 Com-
mission, 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).

Ce 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: "Coproprocessing 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 (sub-bituminous 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: "Coproprocessing 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 promoter 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 μ using preparative gel permeation chromatography (GPC). The average molecular weight (determined by vapour pressure osmometer) 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 M_n 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 preasphaltenes 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). Elsevier, 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) H₂ (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 and 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.

27. 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"; Proceedings of the 9th International Congress on Catalysis, 1, Editors, M.J. Phillips and M. Ternan, Publisher, Chemical Institute of Canada, pp. 182-189

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 subbituminous coal and two parts 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.

28. Ikura, M., Kelly, J.F. and Capes, C.E.
1988: "Beneficiation of Lignite by Oil Agglomeration as an Integral Part of Coprocessing"; Division Report ERP/ERL 88-04(OPJ), Preprints of papers presented at the 195th ACS National Meeting and the third Chemical Congress of North America, Toronto, Ontario, June 5-11, 1988; ACS Division of Fuel Chemistry Preprints 33, No. 1, 1988

The low cost of Canadian low-rank coals makes them prime feedstocks for coprocessing with bitumens and heavy oils. Depending on the coal concentration in the feed slurry, the high ash level in some of these coals can cause

operational problems as well as reduce the overall process efficiency and the net liquid product yield. To reduce the ash content in the feed slurry, oil agglomeration can be used for coal beneficiation (deashing) as an integrated approach requires the use of undiluted bitumen or heavy oil feedstocks as a bridging liquid. Also, low-rank coals as well as oxidized higher rank coals often possess a relatively hydrophilic surface. This makes the application of oil agglomeration extremely difficult.

A novel method of beneficiating low-rank coals for coprocessing by oil agglomeration using a part of the feed bitumen for coprocessing has been conceived and developed. This method overcomes the hydrophilic surface problem of low-rank coals and allows the use of undiluted coprocessing feed oils as viscous as vacuum bottoms.

Experimental results on the beneficiation of a Canadian lignite with vacuum bottoms are presented. The efficiency of the process was evaluated in terms of combustibles recovery and ash rejection. The agglomeration of Willowbunch lignite (ash content from 20 to 22 wt % on a mf basis) with Interprovincial Pipe Line (IPPL conventional crude) vacuum bottoms resulted in 51 to 97 wt % combustibles recovery and corresponding 77 to 42 wt % ash rejection. The effects of vacuum bottoms concentration, operating temperature, and processing time on the beneficiation performance are discussed.

29. Rahimi, P.M., Fouda, S.A. and Kelly, J.F.
1988: "Effect of Coal Concentration on Product Distribution in CANMET Coprocessing"; Proceedings of the Twelfth Annual EPRI Constructors' Conference on Fuel Science and Conversion, Palo Alto, May 13-14, 1987, pp. 17-1: 17-15

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 (205-525⁰C) characteristics were determined using elemental analysis and ¹H n.m.r. 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 205-525⁰C and their hydrocarbon-type fraction was analyzed by ¹H n.m.r. and f.i.m.s. 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 ¹³C/¹²C ratio of coal and bitumen, the amount of coal-derived carbon in the coprocessing distillate was estimated.

30. Chase, J.D. and Liu, D.D.S.

1988: "The New Coprocessing Pilot Plant at CANMET's Energy Research Laboratories"; Preprints of the 195th ACS National Meeting and 3rd Chemical Congress of North America, Toronto, June 5-10, 1988, Vol. 33 No. 1, pp. 42-49

Whereas the bench-scale facilities are being used to investigate the effect of the progress variables on the product yields and quality in short experimental runs, the large pilot plant will be used to solve problems that normally result

from long experimental runs lasting up to 60 days. Further, the pilot plant will be able to generate more accurately yield data that is not normally possible with smaller bench scale units, and will enable the production of the much larger quantities of products needed for the detailed assessments required for commercialization. This paper describes the coprocessing pilot plant which is now being commissioned at CANMET's Energy Research Laboratories.

31. Szladow, A.J., Chan, R.K., Fouda, S.A. and Kelly, J.F.
1988: "Kinetics of Heavy Oil/Coal Coprocessing"; Preprints of the 195th ACS National Meeting and 3rd Chemical Congress of North America, Toronto, June 5-10, 1988, Vol. 33 No. 1, pp. 141-153

CANMET has been conducting research and process development work on coprocessing of Canadian heavy oil/bitumen and coal since 1979 including studies of the kinetics and mechanisms of coprocessing. As a continuation of the program, CANMET and Lobbe Technologies undertook a project on a mathematical modelling of coprocessing kinetics with emphasis on the development of reaction engineering models for improved process performance and operation. This paper describes the reaction networks proposed and the reaction model selected for the coprocessing reaction.

32. Fouda, S.A. and Kelly, J.F.
1988: "Effect of Coal Concentration on Coprocessing Performance"; Preprints of the 195th ACS National Meeting and 3rd Chemical Congress of North American, Toronto, June 5-10, 1988, Vol. 33 No. 1, pp. 179-184

This paper describes the effects of increasing coal concentration on the coprocessing of Forestburg coal with Cold Lake vacuum bottoms using a continuous-flow bench-scale unit. The coal concentration was varied in the range of 0-39.5 wt % maf.

33. Ikura, M.
1989: "Rheology of Coal and Vacuum Bottoms Slurries"; Division Report ERL 89/76 (J)

The rheological behaviour of coal-oil slurries was investigated using a high volatile bituminous coal and a lignite in combination with a medium crude oil and the vacuum bottoms of various origins; conventional oil derived and synthetic crude derived vacuum bottoms. All experiments were conducted under atmospheric pressure and moderate temperatures using a Haake viscometer equipped with a Searle type sensing head. The viscosity of oils ranged from less than 50 to more than 2 million mPas. The shear rate was varied from 1 to 200 (1/s), coal concentration in slurry from 0 to 56.7 wt %, and temperature from 50 to 128°C. Three ranges of coal particles size 63-74 μm , 125-149 μm , and 20-293 μm were used. The effect of shear rate, coal concentration, particle size and temperature of flow behaviour of coal-oil slurries are discussed, and a master curve that can describe the relative viscosity of all slurries is presented.

34. Dukhdin-Lalla, L., Yushun, S., Shaw, J.M. and Rahimi, P.M.

1989: "Phase Splitting of Complex Hydrocarbon Mixtures" Proceedings of the 5th International Conference on Fluid Properties and Phase Equilibria for Chemical Process Design, Banf, Alberta, April 30-May 5, 1989, pp. 93-1: 93-8

Significant fluctuations in the light oil yield obtained from laboratory and pilot scale models of heavy oil upgrading, coal/oil coprocessing and direct coal liquefaction processes, arising from apparently minor perturbations in operating conditions, are frequently attributed to synergism. Some aspects of observed synergistic behaviour are explained in terms of relevant liquid-liquid and fluid-fluid equilibria. Partial phase diagrams for simple and complex hydrocarbon mixtures including model solvent mixtures:

pyrene/naphthalene/tetralin, and bitumen/heavy oil/anthracene oil mixtures are presented. As the projected or actual operating conditions for hydrogenation processes and the temperature and pressure regions over which the mixtures can experience phase splitting overlap, previously reported synergism is related to phase splitting and compounding factors such as catalyst wetting and localized reagent depletion.

35. Rahimi, P.M., Dawson, W.H. and Kelly, J.F.

1989: "Determination of hydrogen donor ability of heavy oils/bitumens and its effects on coal dissolution"; Division Report, ERL 89-33 (OPJ)

The hydrogen donor ability of several heavy oil/bitumens used in CANMET coprocessing was determined using chemical methods (1,1'-binaphthyl and sulphur as hydrogen acceptors) and ^{13}C NMR technique. The degree of hydrogen donor ability (HDA) of these materials was compared with model compounds such as tetralin, 9,10-dihydroanthracene and liquefaction solvents such as hydrogenated anthracene oil and raw anthracene oil. Results showed that the coprocessing solvents have similar hydrogen donor abilities regardless of their origin as determined by the above methods. In support of these findings, solubilization of Forestburg subbituminous coal in both nitrogen and hydrogen atmospheres was similar. Further, the coal conversion to THF solubles was not affected by either the saturates or the asphaltene contents in these oils/bitumens. However, depending on the method used, the measured HDA of heavy oils/bitumens was higher or lower than tetralin. Factors such as the physical interaction between solvent and coal are discussed.

36. Dukhdin-Lalla, L., Yushun, S., Shaw, J.M. and Rahimi, P.M.

1989: "Phase splitting of complex hydrocarbon mixtures"; Division Report ERL 89-34 (OPJ)

Significant fluctuations in distillate yield obtained from laboratory and pilot scale coal/oil coprocessing and direct coal liquefaction processes, arising from apparently minor perturbations in operating conditions can be explained, in part, by phase splitting at elevated temperatures. The transition from vapour-liquid to vapour-liquid can occur at temperatures as low as 650 K. As the projected or actual operating conditions for hydrogenation processes and the temperature and the pressure region over which the mixtures can experience phase splitting overlap, previously reported synergistic behaviour is related to consequential phenomena including: hydrogen depletion in the dispersed liquid phase, polymerization reactions and the distribution of catalyst among the phases.

37. Dukhdin-Lalla, L., Yushun, S., Shaw, J.M., and Rahimi, P.M.
1989: "Phase splitting of complex hydrocarbon mixtures and in coprocessing"; Division Report ERL 89-47 (J)

Research funded under DSS contract #23440-8-9084/01-SS concerned the possible role of liquid-liquid equilibria in direct hydrogenation processes for heavy oil, bitumen and coal. More specifically, we addressed the question does phase splitting arise in coprocessing among feed materials or reactor effluent and if so under what circumstances. The original proposal and working statement are appended. These documents, comprising appendices I & II, provide background information and describe the scope of the research in detail. Even though severe coking problems were encountered (these problems and their resolution are described in the interim report, appendix III), and only limited quantities of materials were available, the objectives set out in the working statement were largely realized. We showed, for example, that coal liquid/heavy oil and coal liquid/bitumen mixtures exhibit phase splitting under processing conditions but that the composition ranges are outside of the ranges normally encountered in coprocessing.

38. Rahimi, P.M., Dawson, W.H. and Kelly, J.F.
1989: "Determination of H-donor ability of heavy oils/bitumens and its importance in coprocessing"; Division Report, ERL 89-63 (OP)

Although limited amounts of transferable hydrogens are present in heavy oils/bitumens, high coal conversions are usually obtained. Good correlation using sulphur as hydrogen acceptor, was obtained between coal dissolution in heavy oils/bitumens and H-donor ability. It was shown that in coprocessing, coal dissolution is not affected by the concentration of saturates and asphaltenes fractions. In terms of coal dissolution and under the process conditions employed in this work, there is little difference between bituminous and conventional resids.

39. Rahimi, P.M., Fouda, S.A. and Kelly, J.F.

1989: "CANMET coprocessing operability using a bench scale unit"; Division Report, ERL 89-64 (OP)

The objectives of the present work were to assess the operability of CANMET coprocessing using a bench-scale unit and to study the upgradability of CANMET coprocessing distillate. Distillate yield and pitch conversion remained relatively constant at 63 wt % and 74 wt % respectively during 182 hrs. operation. Coal conversion of about 82 wt % was reported during this run. From these results operability of the process was demonstrated. A total of 42 K of slurry product collected within run was distilled and were used to study upgradability of these materials.

40. Fouda, S.A., and Kelly, J.F.

1989: "The Coprocessing of an Eastern Canadian Bituminous Coal and Petroleum Residue"; Division Report, ERL 89-44 (OPJ). Was also published in the Proceedings of the 1989 International Conference on Coal Science, Tokyo, Japan, October 23-27, 1989, paper No. E63P pp. 899-902

Donkin Morien high volatile bituminous coal from Nova Scotia was coprocessed with a Venezuelan petroleum residue using the CANMET technology. Slurries containing 20-30 wt % maf coal in the petroleum residue were processed in a single-stage, once-through operation, in the presence of the CANMET disposable iron-based additive. A 1 kg/h stirred tank reactor unit was used to carry out the experimental runs. The slurries were processed at temperatures in the range of 450-460°C, space velocities in the range of 0.5-1.0 Kg/h/L and 17.3 MPa total pressure.

A special procedure was adopted to overcome the operational problems associated with the thermoplastic properties of the coal. The new procedure allowed problem-free operation without the expenses associated with the previously adopted upstream coal pretreatment. It was possible to achieve coal conversions and pitch conversions as high as 93 wt % and 80 wt % respectively.

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 hydrolquefaction 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 considerable effect on the heteroatom removal. The molecular weight distribution (M_n) of the distillate decreased significantly with increasing temperature and residence time. The formation of gaseous hydrocarbons (C_1-C_4) were more pronounced 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: "Coproprocessing of an Alberta Subbituminous Coal and Cold Lake Vacuum Bottoms Using Synthesis Gas: III - A Proposal on Two Stage Coproprocessing"; 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 C₁-C₄ 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: "Coproprocessing 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.

Coproprocessing 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 involves 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 vacuum 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 anisotropic 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, gives 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.

24. Potter, J., Fouda, S.A. Dawson, W.H., McDougall, W.J. and Vasu, E.M.
1989: "Characterization and Genesis of Insoluble Residues from Coprocessing of High-Volatile Bituminous Coals and Cold Lake Vacuum Bottoms"; Division Report ERL 89-39 (CF).

Toluene insoluble residues obtained from the coprocessing of high-volatile bituminous coals (Lingan, Prince, Donkin Morien and Illinois NO. 6) with Cold Lake vacuum bottoms (CLVB) were characterized using petrographic methods supplemented by SEM-EDS. The genesis of the various components was confirmed by SEM-EDS: coal-derived solids are enriched in Al, Si and Fe whereas CLVB-derived are depleted in Al, Si and Fe and enriched in S. Residues from the CLVB and high-volatile bituminous A and B coals contained solids from the oil (CLVB) as well as the coal. Those from high-volatile bituminous C coal and resembled the residues from subbituminous coals in that the solids were mainly derived from the coal.

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 H₂S 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.
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