SUMMARY

Current efforts towards development of a coal-oil coprocessing configuration are reviewed. Coprocessing, combined processing of coal and heavy oils, has been found to provide several distinct advantages over direct coal liquefaction processes. Among these advantages are:

1) A significantly reduced and, in some cases eliminated, recycle stream.

2) Lower coke yields than would have been expected with oil alone.

3) High yields of high quality, demetallized liquid oil products.

4) Flexibility in process severity.

5) Coal feed flexibility.

6) Ability to process residual, high metals content oils.

The conditions that most investigators use for coprocessing are severe enough to cause massive coking if oil and hydrogen were each processed alone. The ability to operate under these conditions with low (manageable) coke yields presents a significant advantage over conventional oil upgrading processes in that it is possible for a refiner to obtain high yields of a demetallized refinery feedstock using coprocessing technology.

INTRODUCTION

Coprocessing is a novel concept that has emerged from the direct coal liquefaction experience. Coprocessing consists of the treatment of coal in a heavy oil stream; certain unexpected but very desirable synergistic effects are found when these two forms of fossil fuels, coal and heavy oils, are processed together. Indeed, it appears that coprocessing may provide a bridge to processing coal and coal-derived materials in existing refinery infrastructures (Shinn, 1984). It is felt that a process which utilizes the

coprocessing concept could easily be converted to or could lead to conversion to an improved direct coal liquefaction process.

Coprocessing consists of heating coal, plus heavy oil, to 670-725 K with hydrogen (or an equivalent, such as hydrogen/hydrogen sulfide) gas. The products are separated into solids and liquids and it is expected that the inorganic elements in the added coal, plus those (chiefly Ni and V) in the heavy oil, will be concentrated in the separated solids or residue pitch. Because the "unconverted" coal is chemically quite different from the liquids produced by coprocessing, the separation of solids (heavy pitch) and the liquids produced should not be difficult; addition of various anti-solvents (paraffins) should enhance this separation.

The heavy oil (the slurrying medium) and the coal may not be chemically compatible but the heavy oil must be capable of acting as a means of slurrying coal to the reactor while the coal itself should be converted to liquids during the process.

The area of coprocessing is understood to have the following constraints:
1)   It will either be a once-through process or one that utilizes a small recycle stream.
2)   One constituent of the feed will be a heavy oil that acts as host for the coal.
3)   The other constituent will be coal or a coal derived material.
4)   An added catalyst may be used.

The heavy oils used in coprocessing form slurries with the coal and also may act as hydrogen donors to the coal. It has been claimed that the bitumen does not act as a hydrogen donor when an hvA bituminous coal is used (Moschopedis, 1980). However, Moschopedis found that Great Canadian Oil Sands, Ltd. (GCOS) coker gas oil gave 70% and the lighter oil fractions of the

Athabasca bitumen gave 100% of the coal conversion observed as when using tetralin, considered by many to be among the better hydrogen donor solvents in direct coal liquefaction.

Coal/oil coprocessing has the potential to offer significant benefits for the production of petroleum feedstocks or transportation fuels in that it:

1) Can eliminate all or most of the recycle oil.

2) Can use a low cost coal along with a poor quality heavy oil to produce high-quality distillate fuels.

3) Can use existing refinery capacity and infrastructure.

4) Has the potential to be commercialized in a short time.

5) Can provide fuel products which meet latest environmental regulations.

6) Provides operators with feedstock flexibility.

A review of the current state-of-the-art coprocessing technology is presented. This review attempts to highlight some of the major findings to date.

REVIEW OF COPROCESSING STUDIES

Heavy oils are considered as a source of hydrogen donor solvent for coal liquefaction because of the comparatively high hydrogen/carbon ratio. The known reserves of heavy oils in the United States have been estimated at some 110 billion barrels, about one-third of which is recoverable by conventional technology. When using heavy oils in a liquid fuels production process, the many problems that have been encountered in upgrading this oil via conventional techniques must be kept in mind.

There are several ways of thermally upgrading heavy oils and pitches (pitch defined here as material boiling above 800 K (975F). One way is by

carbon rejection: i.e. thermal cracking to convert pitch to distillate oils and a heavy, carbonaceous residue, usually termed coke. There are several commercial processes which are in use, including delayed coking and Flexicoking. These processes are not complex, operating at low pressures in the absence of a catalyst. However, they produce relatively low liquid levels of unstable distillates containing large amounts of sulfur. Substantial downstream processing of the products is necessary and disposal of residue is a problem.

Newer technologies for upgrading heavy oils are represented by H-Oil and L-C Fining. Catalytic hydrocracking at high pressures gives improved yields of stable, largely desulfurized distillates plus a sizable pitch fraction. The potential disadvantages of this route include high pressure, high hydrogen consumption, high residue disposal, and high catalyst costs. These costs are strongly dependent on the feed metals in the heavy oil being processed.

Coprocessing has been advanced as an option to upgrade the heavy oils and coals simultaneously. Many of the oils that have been used in coprocessing research represent the lower quality heavy oils. These oils include Cold Lake and Athabasca GCOS bitumen from Canada, West Texas, Boscan (a particularly difficult crude to upgrade) from Venezuela, Maya from Mexico, Heavy Arabian, etc. These low quality heavy oils have historically been difficult to upgrade. Processing these heavy oils in hydrogen without an added catalyst would result in massive coking, up to 12-15 wt% coke yield (Moschopedis, 1980). The coprocessing research to date has not only resulted in upgrading these oils, but has done so, in most cases, with coke yields lower than 10 wt%.

The most remarkable finding is that the addition of coal to the heavy oil seems to either inhibit coking or, in some way, to allow circumvention of the

coking problem expected to occur. A second discovery is the removal of nickel and vanadium from the distillable oil.

A description of the various coal and oil feedstocks referred to in this review is listed in Tables II-2 and 3.

Some Coprocessing Studies Carried Out At Mobil

Yan and Espenscheid (1983) studied the liquefaction of coal in fluid catalytic cracking (FCC) bottoms products at temperatures of 590-700 K (600-800F) and pressures of 0-7 MPa. The coal feedstocks used were an hvA bituminous coal and a lignite; the hosts used were coal tar and FCC bottoms. They conducted batch experiments with combinations of these feedstocks. The pressure in their experiments was supplied by the equilibrium vapor pressure of the products (such as CO_2, CO, H_2O, etc.) at reaction temperatures. Their results are summarized in Table II-4.

Coal conversions of 60-70% of the lignite and 85-90% of the bituminous coal were reported. These conversions are reported to be comparable to conversions obtained in coal liquefaction studies. Apparently the FCC bottoms were as good a slurrying medium for the coal as the coal derived liquids used in conventional coal liquefaction studies.

The effects of processing parameters were also investigated. The dependence of coal conversion on temperature appears to be linear. Very little conversion of the coal occurs below 615 K (650F) which is consistent with conventional direct coal liquefaction results (Guin, 1975).

Coal conversion to liquid oils decreased with decreasing pressure. The effect of pressure on coprocessing yields is summarized in Table II-5. At low pressures, very little CO and CO_2 are formed compared to the amount formed at 4.3 MPa. On the other hand, higher methane yields are obtained at the lower

pressures. It appears that the cracking reactions are dominant (over hydrogenation reactions) at the lower pressures.

Yan and Espenscheid also studied the effect of heavy oil and coal type on coprocessing yields. The coal conversion was higher when the FCC bottoms were used as the host or solvent than when coal tar was used as the host. The FCC bottoms have a higher level of aromatic benzylic hydrogen than does the coal tar. The investigators concluded that high boiling aromatic solvents contribute significantly to coal conversion and that hydrogen transfer between the heavy oil and the coal might enhance coal dissolution, yielding a better quality product. Coal conversion increases with higher α hydrogen content and decreases with higher β hydrogen content.

Coal conversion was higher for the hvA bituminous coal than for the lignite. Moschopedis, (1980) has suggested that the presence of significant amounts of inertinites in the lignite decreases the reactivity of the lignite. The benzene soluble material and the total liquid product were lower for the lignite than for the bituminous coal. On the other hand, distillate yields for the two coals were similar, which may indicate that coal type, while affecting conversions, may not significantly affect distillate product yields. This can probably be attributed to the large concentration of heavy oil in the system.

CANMET Processing

Hydrocracking

An interesting development in coal/oil combined processing technology is the CANMET hydrocracking process developed by the Canada Centre for Mineral and Energy Technology (Menzies, 1981). This hydrocracking process has been developed to thermally upgrade heavy and residual oils. The key to the

process is the use of a coal-based additive, used to upgrade the heavy oil while suppressing the formation of coke. This may be considered coprocessing because of the small amount of coal-based additive used, but since it is primarily used to upgrade oil it will be classified as a hydrocracking process.

The coal-based additive used in the CANMET hydrocracking process is a lignite or subbituminous coal impregnated with an inorganic salt, usually iron sulfate. To prepare the additive, approximately 70 wt% coal is impregnated with 30 wt% of the inorganic salt. Approximately 0.5% to 5.0% of additive is combined with the oil in the reactor. The additive, a coal-based material, dissolves in the host material (the bitumen). The process operates at fairly high severities: temperatures greater than 1075 K (800F), pressures greater than 10.3MPa H_2, and 3.0 LHSV. At these conditions, with heavy and residual oils, massive coking (greater than 10-15%) would occur in the absence of any additive or catalyst. Suprisingly, the coal-based additive appears to suppress this coke formation.

In addition to suppressing the formation of coke, the residue from the coal additive has been found to contain most of the metals that existed in the oil feed. The liquid products from the CANMET reactor tend to be very low in metals. This is a tremendous advantage, since metals would cause problems in downstream upgrading operations.

In the CANMET hydrocracking process, the mixture of feed and additive is heated and, along with hydrogen, flows upward through an ebullated bed-type reactor. The solids in the ebullated bed are composed of additive residues and removed feed metals. The additive decomposes in the reaction process and its residues leave with the pitch product.

Many crudes have been successfully processed, including Athabasca bitumen 533 K+ (500 F+), Lloydminster 615 K+ (650F+), Cold Lake 670 K+ (750F+), Laguna 727 K+ (850F+), and Boscan Crudes 615 K+ (650F+). The reported yields from CANMET hydrocracking of these heavy oils are summarized in Table II-6.

The CANMET hydrocracking process has been so promising that a 5,000 BPSD pilot plant is being constructed by Petro-Canada (who have been granted sole licensing rights for commercialization of the process). Construction of the pilot plant is scheduled to be completed within one year.

Coprocessing

The developers of the CANMET hydrocracking process, Energy Research Laboratories, are now investigating expansion of their hydrocracking technology to a coprocessing application. Kelly et al. (1984) have used up to 30 wt% coal with Cold Lake bitumen and CANMET's coal based additive in studies designed to expand CANMET's hydrocracking technology to a coprocessing application. The processing sequence is similar to the CANMET hydrocracking process with the exception that 30 wt% of the feed oil is replaced with coal. The conditions used in the coprocessing studies are similar to those used in their hydrocracking studies.

Kelly et al. performed a study designed to study the feasibility and process interactions associated with coprocessing. They compared the product yields from the coprocessing experiments with those obtained from CANMET's hydrocracking and coal liquefaction processes. The yields from these runs (which were made at similar operating conditions) are summarized in Table II-7. The distillate yield from the coprocessing runs lies between the liquefaction and hydrocracking runs. In fact, the distillate yield can be predicted from the distillate yields in the two cases. Apparently, they

observe no synergism between the coal and the oil toward higher distillate yield. This may not be entirely valid since in the hydrocracking case (which they designate as the "no-coal" case) there is up to 5% coal present in the reactor as the coal based additive. Some investigators have observed that a synergism resulting in higher distillate yields occurs in the presence of only 2-5 wt% of coal (Miller, 1985).

The conversion of coal is similar for the coprocessing (where Cold Lake bitumen is used as the slurrying medium) and coal liquefaction cases (where hydrogenated anthracene oil is used). Apparently the Cold Lake bitumen is as good a slurrying medium for the coal as hydrogenated anthracene oil.

Kelly et al. also studied the effects of operating conditions on coprocessing Forrestburg subbituminous C coal and Cold Lake bitumen. Specifically, they evaluated the effect of temperature, space velocity, and coal concentration.

It appears that temperature has a greater effect on coal conversion to liquid oil products than does space velocity, though coal conversion appears to be a linear function of both temperature and space velocity.

Coal concentration has a large effect on both distillate yield and coal conversion. There is an optimal coal concentration at which there is maximum distillate yield and coal conversion at a low coal concentration (approximately 5-10% coal). In fact at these low coal concentrations a definite synergism is observed towards higher distillate yield. Exceeding this coal concentration causes the distillate yield to fall off sharply. Coal conversion, unlike the distillate yield, continues to remain constant (and even to rise slightly) as the optimal coal concentration is exceeded. Over all ranges of coal concentration, the quality of the distillate product in

coprocessing remains constant, and is of higher quality than the distillate from coal liquefaction.

CANMET coprocessing has sparked considerable interest in Canada and elsewhere. Currently, studies are underway to adapt CANMET's 5000 BPSD hydrocracking unit to incorporate coprocessing technology.

Co-Refining Work At Chevron

The Chevron Research Company has developed what is referred to as the Co-Refining Process (Shinn, 1984). This coprocessing operation is actually a direct outgrowth of Chevron's two-stage Coal Liquefaction Process (CCLP). During development of their CCLP Chevron found that coal and oil could be synergistically upgraded in a two-stage reactor system similar to their direct coal liquefaction unit.

The Co-Refining process employs a two-stage reactor system. A slurry of coal and heavy or residual oil is fed to the first reactor stage, which is predominately for the dissolution of the coal and thermal treatment of the oil. The effluent from the first stage is separated to remove the solids residue, and the liquids are fed directly to the second stage where the products are catalytically upgraded through hydrogenation and hydrocracking reactions. The two-stages are close coupled so that reactive species from the first stage can be promptly upgraded.

Shinn ran a series of tests to evaluate the Co-Refining concept using various ranks of coals and bitumens as feedstocks. The effect of coal rank and bitumen type were evaluated and the results are summarized in Table II-8. McElroy hv bituminous coal consumed slightly less hydrogen in the Co-Refining process than Cx Ranch Wyoming subbituminous coal but had a slightly higher coal conversion. Conversion of the 800 K+ (975F+) fraction of the oil

as well as the distillate yield were similar for both the bituminous and subbituminous coals. This may indicate that coal quality, while affecting coal conversion, may not affect the conversion of the oil or final distillate yield.

The effect of bitumen type on Co-refining yields was more significant. Boscan crude required more hydrogen than the Kern crude while achieving similar levels of coal conversion. Much of this hydrogen appears to be used in upgrading the oil because, historically; Boscan crude has been an extremely difficult crude to process. Its main applications to date have been as fuel oil or asphalt.

The Co-refining process promises to provide a smooth transfer for a refinery to go from processing predominately a petroleum crude to the processing of coal-derived fuels. Additionally, coprocessing provides advantages to a refiner in that it has the following desirable characteristics: (a) high yields of quality products, (b) flexibility in process severity in each of the two stages, (c) coal feed flexibility, (d) ability to process residual, high-metals content oils, and (e) a high hydrogen efficiency utilization.

Work Done By HRI

Hydrocarbon Research (HRI), along with the Canadian Coal Liquefaction Corporation and the Ontario-Ohio Synthetic Fuels Corp., Ltd. is developing a coal/oil coprocessing configuration to liquefy coal while upgrading heavy or residual oil (MacArthur, 1985). Their two-stage process incorporates some recent advances made in both HRI's H-Oil and H-Coal technologies.

The proposed coprocessing configuration is similar in concept to Chevron's Co-Refining process with some exceptions. The first stage appears

to be an ebullated bed catalytic reactor for contacting a slurry of coal and oil with hydrogen. Additional hydrogen is mixed with the reactor effluent as it is fed to the second reactor, which operates at a slightly higher temperature than the first. The products from the second reactor are separated to recover product fuels and residue.

A bench-scale program has been conducted to demonstrate the feasibility of HRI's catalytic two stage coprocessing configuration. The feedstocks used in this program were an Alberta subbituminous coal and Cold Lake atmospheric residuum. Yields obtained from processing these feedstocks in the two stage coprocessing configuration and for H-Oil and H-Coal processing of the individual feedstocks are presented in Tables II-9 and 10.

The coprocessing yields lie between H-Oil and H-Coal but coprocessing appears to give some distinct advantages over either process. Among these advantages are: higher hydrogen efficiencies for a process using coal as a feedstock, high levels of demetalation (which facilitates downstream processing), and, importantly, the elimination of a large recycle stream to slurry the coal.

Economic studies were made to determine the feasilibility of two-stage coprocessing for syncrude production at a remote site upgrader and for integrating coprocessing to an existing refinery. In both cases HRI concluded that coprocessing could be economically feasible. Future work is being planned to further evaluate catalytic two-stage coprocessing at HRI.

Work Done By Alberta Research Council

Moschopedis et al. (1982) of the Coal Research Department, Alberta Research Council, have investigated the liquefaction of coal using heavy oils

and bitumens for Exxon. In their experiments they have processed pulverized Alberta hvC bituminous coal with various slurrying media. They also ran control experiments in which the heavy oils were processed at reaction conditions with no coal present.

Figure II-2 summarizes the effect of oil-type on coal conversions. The best conversions of coal were obtained when tetralin was used as the slurrying medium. The effect of using a catalyst with tetralin, though, was minimal; the catalyst increased coal conversion from 48 to 52%. The use of a catalyst more significantly affected the yields obtained from processing coal in an oil medium. In one case the presence of the catalyst resulted in enhanced coal conversion, from 22 to 41% for Lloydminster bitumen. Moschopedis et al. concluded that heavy oils compare favorably to tetralin as slurrying media for coal, especially in the presence of a catalyst.

The type of slurrying medium used also influences the dependence of coal conversion on temperature. The dependence of coal conversion on temperature was determined for two feedstocks (coker gas oil and GCOS bitumen) for two cases, with and without a catalyst present. The coker gas oil experienced an upper limit of coal conversion with respect to temperature (approximately 673K) with no catalyst present. If the temperature exceeded this upper limit, the conversion of coal to liquid oils fell off drastically. The GCOS bitumen, on the other hand, did not show this same upper limit with respect to temperature in the absence of a catalyst. When a catalyst is present the behavior of the two solvents appears to act in opposite ways. The GCOS bitumen experienced an upper limite with temperature (around 673K) after which conversion leveled off. However, coal conversion with coker gas oil as a slurrying medium continued to rise even above this temperature. It appears that these results can be traced to the action of the feed oils with no coal

present. The coker gas oil gives virtually no coke yield at 723 K with a catalyst and a coke yield of 11.6% without a catalyst. The GCOS bitumen, on the other hand, has a higher coke yield at 723K with a catalyst (43%) than without a catalyst present (26.2%). This may help explain the behavior of coal conversions with the two oils as a function of temperature.

A conclusion based on this data is that no appreciable conversion of the coal occurs below 615 K (640F). This is compatible with earlier coal liquefaction studies which show that essentially no thermal dissolution of the coal occurs below this temperature (Guin, 1975).

Work Done At The University Of Wyoming

Miller (1985), of the University of Wyoming, has investigated liquefaction of Wyodak subbituminous coal with six bitumen slurrying media. His work is not entirely coprocessing, though, because he also uses an additional coal derived solvent in all his work. But his results merit discussion in a coprocessing evaluation. The heavy oils ranged from a heavy 727 K+ (850F+) mid-Continental residual oil to a middle distillate boiling range shale oil that had been mildly hydrotreated. Two coal derived solvents, obtained from Wyodak coal, were tested for comparative purposes. The conditions used in his experiments were similar to those used in most of the research on coprocessing technology, namely a temperature 700 K (800F), a slightly higher pressure of 13.8MPa, and a higher liquid hourly space velocity of 4.0.

Miller observed an apparent synergism between the coal and the oil leading to higher distillate yields. This synergism appears to occur over all ranges of coal concentrations that he tested (0 to 50% coal in total feed). He attributed this to increased reactivity of the heavy oil in the presence of

coal. Miller observed a maximum coal conversion with respect to coal concentration of 40%. This is not in agreement with the work of Kelly (1984) who found that optimum coal conversions occurred at coal concentrations less than 30% by weight. This discrepancy can be attributed to many factors. Among them are: a) different oils and coals were used, b) Kelly used an additional coal-based additive in his studies, or c) Miller used an additional coal-derived solvent in all his work.

Miller found that coal conversion depended on the boiling range of the slurrying medium used. The highest coal conversions were obtained with the heaviest slurrying medium, the lowest with the lightest slurrying medium (the middle distillate boiling range shale oil).

The distillate yields obtained with the heavy oils and bitumens were markedly higher than the distillate yields with direct coal liquefaction (35.4% and 12.6% respectively). He also observed that, with no coal present, the distillate yields for the heavy oil or bitumen were significantly lower (35.4% with coal present and 1.2% with no coal).

Finally Miller found that, with no catalyst present, a distillate yield of 35.4% was obtained; with an iron oxide catalyst present a distillate yield of 46.5% was obtained. The iron oxide catalyst did not have the same effect in the runs in which no bitumen was used with the coal and coal-derived solvent.

Work Done At Auburn University

Curtis, Guin et al. (1984) used five bitumen slurrying media and tetralin in upgrading a Clovis Point subbituminous coal, an hv bituminous Illinois #6 coal, and a Blacksville mine coal. Their studies compared results using an inert atmosphere with use of a hydrogen atmosphere. Highest coal conversions

in an inert atmosphere were obtained using tetralin (57%). The highest coal conversion with a heavy oil host was 36%. The coal conversion results are summarized in Figure II-3. They concluded that the heavy oils were not as good hydrogen donor solvents as tetralin. They also noted that the heavy oils used were low in α hydrogen content and high in β hydrogen. Yan et al. (1983) already showed that coal conversion increases with increasing α hydrogen content and decreases with increasing β hydrogen content. The coal conversions and the content of α and β hydrogens for each oil are shown in Table II-11. These data seem to agree with Yan's conclusions.

The Auburn workers observed that the use of a hydrogen atmosphere and a catalyst enhanced coal conversions and also lessened the difference between coal conversions obtained with tetralin and with a heavy oil. Tetralin still had the highest conversion of any of the slurrying media used. When petroleum solvents were used, however, coal conversions of over 70% were achieved.

They concluded that, in the absence of any added catalysts, coal conversion was a function of both slurrying medium viscosity and Conradson Carbon content. The heavy oil with the lowest viscosity and Conradson Carbon content would yield the highest level of coal conversion. No correlations were evident between coal conversions and heavy oil properties in the presence of a catalyst.

They also ran a variable (parameter) study to determine the optimal operating conditions for coprocessing. The optimal conditions found with coal and heavy oil were:

Temperature	=	698K
Pressure	>	3.5MPa (500 psig)
LHSV	=	0.67 hr-1
Catalyst	=	Co/Mo supported

The conditions seem reasonable with the exception of the LHSV. Other investigators (notably Kelly (1984) for CANMET) used much higher LHSV's in their coprocessing schemes.

Work Done By The Kerr-McGee Corporation

The Kerr-McGee Corporation is currently investigating a coal-heavy oil coprocessing configuration. In their coprocessing scheme the bitumen feed will be obtained from the bottoms of the product of a bitumen upgrader. This heavy oil stream is combined with a bottoms recycle stream. The total stream is mixed with 30% coal and the resultant slurry is fed along with hydrogen to a coal liquefaction unit. The products from the unit are separated, recovered, and/or recycled.

Kerr-McGee has investigated the feasibility of this coprocessing scheme using an Illinois #6 coal and an Ohio #5 coal together with the host oil, Cold Lake bitumen. They also conducted traditional direct coal liquefaction experiments for comparison purposes. Coal conversions of over 90% were obtained in both the coprocessing and direct coal liquefaction cases. The product yields are summarized in Table II-12. Approximately 60% of the nickel and 75% of the vanadium were rejected with the ash in this scheme.

Kerr-McGee claims that their coprocessing configuration is very favorable for processing coal and bitumens simultaneously, mainly because of its flexibility. Further testing of this configuration is planned.

Lummus Corporation

Lummus plans to further investigate their Lummus Crest Inc. (LCI) coprocessing scheme (Schindler, 1985). A reduced crude or residual oil is initially hydrocracked. Lummus claims that the hydrocracking step will make

the gas oil and unconverted residual fractions more hydroaromatic, assuming that the more hydroaromatic the slurrying medium the better it will be as a slurrying medium for coal liquefaction. The remainder of the process is similar in concept to other coprocessing schemes.

Lummus has not disclosed actual results but has projected the conversions anticipated for their configuration. They feel that they will be able to convert 90% of the 800 K+ (975F+) material and 82% of the coal. On a weight basis, they feel they will obtain 45.5 Kg (100.5 lb) distillate to 975F product (they base their yields on a total feed of 51.5 Kg (113.3 lbs). They project a coke yield for their process of 2.5 Kg (5.6 lbs).

CHARACTERIZATION OF COAL-OIL COPROCESSING

The major results from the studies of coprocessing to date can be summarized as follows:

1) Lower coke yields are obtained in coprocessing than would have been anticipated based on processing the oil alone at coprocessing conditions.

2) The concentration of coal used affects coprocessing conversions and yields.

3) Coal rank and heavy oil type affect coprocessing conversions and yields.

4) Processing conditions (temperature, pressure, and liquid hourly space velocity) significantly affect coprocessing results.

5) Hydrogen utilization efficiency appears to be higher for coprocessing than for coal liquefaction.

6) There seems to be a synergism between the coal and the oil to give higher distillate yields.

7) The addition of iron catalysts (or a similar inorganic catalyst) enhances distillate yields and coal conversions.

8) The conversions are apparently thermal in nature, due to the high heteroatom contents of the lighter products. Therefore a cracking catalyst, such as Co/Mo supported on a silica-alumina base, may further enhance coprocessing conversions and yields.

9) The contact time (reaction time) affects yields and conversions.

Coke Inhibition Characteristics Of The Coal

The conditions that most investigators use for coprocessing studies are severe enough to cause massive coking if oil and hydrogen were processed alone, as in hydrovisbreaking. Apparently the coal either catalytically or non-catalytically inhibits the formation of coke.

The ability to inhibit the formation of coke can be due to a catalytic coke inhibiting function present in the coal, such as pyrite or other mineral contained in the coal, or to the ability of the coal to capture the bulk of the coke and coke precursors that are formed in the reaction and remove them from the reaction.

Two findings tend to support the position that coal catalytically inhibits the formation of coke. The first result is that asphaltene conversions as high as 70-80% are reported. At these high levels of asphaltene conversions it would appear that the mechanism of coke inhibition is for the coal to selectively destroy coke precursors. This could be done by catalytically facilitating the hydrogenation of coke precursors, preventing "polymerization" to coke. The second finding is that the addition of iron

enhances the distillate yields even further. The iron may raise the distillate yields possibly by enhancing the catalytic activity of the coal (or mineral matter contained in the coal).

If coal provides a catalytic inhibiting function then dispersion of the coal in the oil will play a significant role. Coal is dissolved in the oil so that any catalytic behavior of the coal would be finely dispersed in the coal/oil mixture. Fine dispersion of catalyst in the reactive mixture is important because coke formation is not location specific. Asphaltenes, which may be primarily responsible for coke formation, are colloidally dispersed throughout the oil. Any coke-inhibiting activity would need to be at least as dispersed as the asphaltenes (or any other element responsible for the coke yields).

Coal may also provide a good surface for attracting and carrying coke precursors and coke, thereby providing a convenient mechanism for removing coke from the reactor. Some investigators have suggested that coke can nucleate on the coal's surface. Nandi et al. (1978) observed that coke tended to nucleate within the coal structure. They found that fusinite and semifusinite macerals were unreacted after passing through the reactor and served as sites for coke and mineral matter deposition.

Coal Concentration

The concentration of coal used significantly affects coprocessing yields and coal conversions. Enhanced (synergistic) distillate yields are obtained at low coal concentrations. At higher concentrations Kelly (1984) and Miller (1985) seem to disagree on the effect of coal concentration. Miller suggests that synergistic effects are seen up to a coal concentration of 50%, with the optimum lying at 40%. Kelly stated that above the low concentrations of coal

the distillate yields correspond to the case in which no coal is used. The difficulty in accepting this conclusion from Kelly is that his "no coal" case contained up to 5% coal based additive. At this level of coal concentration it is possible that he observed the synergism in the hydrocracking or the "no coal" case. Kelly observed that coal conversions fall off sharply at high coal concentrations.

Distillate quality does not appear to be a function of coal concentration. Kelly found that the quality of the distillate was constant over all ranges of coal concentrations that he observed (approximately 5-50%). He also found that the distillate is of higher quality in coprocessing than in direct coal liquefaction. The oil aids in more efficient conversion of the coal to a better quality distillate than the coal derived solvent in coal liquefaction.

Coal Rank

Coal quality and type significantly affect yields and conversions obtained in the direct liquefaction of coal. Possibly, since the slurrying medium in coprocessing is not derived from the feed coal, the yields and conversions for coprocessing will not be as dependent on the feed coal type as in direct coal liquefaction. Also, since the heavy oil represents 2/3 of the feed to a coprocessing reactor, the effect of changes in coal feed quality may be buffered.

It is the type and quality of the coal used that seems to have a large affect on coal conversions. The conversion of the heavy oil (or the slurrying medium) as well as the distillate yield (and the distillate's quality) seem to be unaffected by the coal type (Shinn, 1984). This may represent a

significant benefit for coprocessing in that the strict controls required for direct coal liquefaction may not be needed for coprocessing.

Shinn observed that McElroy West Virginia hv bituminous coal consumed slightly less hydrogen than Cx Ranch Wyoming subbituminous coal at a slightly higher level of coal conversion. This result can probably be traced to the original properties of the coal. Cx Ranch Wyoming has a higher oxygen content than the McElroy West Virginia hv bituminous coal (18.3% and 5.8% oxygen respectively). The oxygen removal requires two hydrogen atoms per molecule of oxygen which, at the oxygen content of the CX Ranch Wyoming, would significantly affect hydrogen consumption of the CX Ranch Wyoming coal.

It is well known that coal mineral matter behaves as a catalyst during liquefaction of coal to oil. Morooka et al. (1978) found that the mineral matter exhibited up to 12% of the activity of a cobalt-molybdenum supported catalyst. This activity was observed even though the mineral matter appeared not to be fully sulfided (when H_2S was added to the reaction mixture it was totally consumed by the coal's mineral matter). It appears that if the mineral matter catalytically inhibits formation of coke, then the content of the mineral matter would affect the liquid yields as well as the quality of the liquid products.

The state of the mineral matter in coal could also affect coprocessing yields. To fully understand the effect of coal type on coprocessing, the nature and content of the mineral matter should be studied. Also, these studies should address the proper relationship between the iron sulfides and H_2S.

Heavy Oil Type

The nature of the slurrying medium plays an important role in coprocessing. Shinn (1984) observed that Boscan crude consumed more hydrogen in coprocessing applications than either Kern crude or Heavy Arabian atmospheric tower bottoms for similar levels of coal conversions. Historically Boscan crude has been a difficult crude to upgrade; its primary use to date has been as a road asphalt or fuel oil. This would probably account for the increased hydrogen consumption.

Moschopedis et al. (1982) also observed the effect of heavy oil type on coprocessing yields. He observed that the dependence of coal conversion on temperature was affected by the solvent used. He traced this effect back to the coking tendency of the slurrying oil. He concluded that the heavy oils that produced higher coke yields with no coal at elevated temperatures would be poorer slurrying media at elevated temperatures.

The boiling fraction used can also affect the coprocessing yields. Miller (1985) found that higher boiling range material was a better slurrying medium for coals than lighter (middle distillate range) material.

Operating Parameters

Temperature strongly affects coal conversion. Moschopedis et al. (1982) found that coal conversion varies linearly with temperature. He also observed that the nature of the slurrying medium influences coal conversion's dependence on temperature.

There also exists a lower limit of coal conversion with respect to temperature. No appreciable conversion of the coal occurs below 615 K (650F). This result agrees with earlier coal liquefaction work which

concluded that no appreciable thermal dissolution of the coal occurs below
this temperature.

Kelly (1984) found that coal (and oil pitch) conversion varies linearly
with temperature and contact time (or liquid hourly space velocity). Upon
varying the temperature range by 60F he observed coal conversion differences
of 40% and pitch conversion differences of 60%. He observed coal conversion
differences of 15% and pitch conversion differences of 30% upon varying the
contact time or liquid hourly space velocity range by 1 LHSV (approximately a
difference of one hour in contact time).

Pressure also affects coprocessing yields. Yan (1982) observed that coal
conversions decreased as much as 10% with a pressure difference of 4.1 MPa
(600 psig). He also observed that pressure affects the composition of the
off-gas from the reactor. At the lower pressures there is a lower yield of
CO_x compounds and a significantly higher yield of methane. This would
indicate that there is more vapor phase hydrogenation than liquid phase, and
that heteroatom removal is lower for the lower pressures.

Efficiency Of Hydrogen Utilization

Kelly (1984) claimed that coprocessing uses hydrogen more efficiently
than direct coal liquefaction; the hydrogen utilization efficiencies are 15.5
and 6.0, respectively. The difference in hydrogen efficiency in the two
processes could be due to the fact that the hydrogen content of the heavy oil
is higher than the hydrogen content of a coal derived solvent. Much of the
hydrogen goes to upgrading the solvent in coal liquefaction and would reduce
the hydrogen utilization efficiency. The hydrogen content of the heavy oil is
approximately 10% and for the coal derived solvent it is around 7%. Hydrogen
utilization efficiency is defined here as:

$$H(eff) = \frac{wt\%(C4-975F) \text{ liquid product yield}}{wt\% \text{ hydrogen consumption}}$$

If the slurrying medium, which is a C4-975F liquid, requires large amounts of hydrogen, then this hydrogen would tend to decrease the hydrogen utilization efficiency.

The low hydrogen content, among other properties, of the coal derived solvent may also explain why the distillate quality of the coprocessing products is higher than the distillate quality of coal liquefaction products. Since the slurrying medium accounts for about 2/3 of the feed to the coprocessing or liquefaction reactors, then the quality of the slurrying medium will have a large impact on the quality of the distillate products. Another explanation for the higher quality of coprocessing's distillate products is that the metals end up in the pitch product. These metals, if contained in the liquid products, would tend to reduce the quality of the liquid products.

Thermal Nature Of Conversion In Coprocessing

The conversions obtained in coprocessing appear to be thermal in nature and only slightly catalytic. This can be demonstrated by the conversions and product yields for upgrading of heavy oils via the CANMET process, as shown in Table II-6. Several important points are derived from these results. First, the conditions and yields for coprocessing are indicative of thermal upgrading processes. Secondly, the hydrogen consumption per unit volume of converted 800 K+ (975F+) bottoms for these processes is 1000-1600 SCFB. For a catalytic

hydrogenation process the hydrogen consumption would be on the order of 3000 SCFB. Hydrovisbreaking processes (which use a thermal mechanism) consume approximately 1500 SCFB, which is in the same region as coprocessing.

The high sulfur contents reported for each boiling fraction should be pointed out. Sulfur contents of 2.13% in the gas oil, 1.74% in the furnace oil (450-615 K or 350-650F), and 0.61% in the naphtha fractions are high compared to a catalytic hydrogenation process, which would have much lower sulfur contents in each boiling fraction, more in the range of 0.2%, 0.1%, and even less in each fraction, respectively. These results seem to indicate that the mechanism of conversion of the oil in coprocessing is mostly thermal in nature. The sulfur contents of the total oil products from the various coprocessing schemes are similar to each other. This indicates that coprocessing occurs predominately via a thermal mechanism.

REFERENCES:

Curtis, C. Guin, J., Pass, M., and Tsai, K., "Combined Upgrading of Coal and Petroluem Residua," Presented at Chemical Engineering, Auburn University, Alabama (1984).

Guin, J.A., Tarrer, A.R., Taylor, E.L., and Green, S.C., "A Photographic Study of Coal Dissolution," ACS, Div. Fuel Chem. Prepr. 20 (1): 66 (1975).

Kelly, J., Fouda, S., Rahimi, P., and Ikura, M., "CANMET Co-Processing: A Status Report," Synthetic Fuels Research Laboratory (September 1984).

Lunin, G., and Silva, A.E., "The CANMET Hydrocracking Process," Presented at the 30th Canadian Chemical Engineering Conference, Edmonton (1980).

McArthur, J., Boehm, F., Liron, A., and Shannon, R., "Coal/Oil Co-Processing of Canadian Feedstocks," presented at the Tenth Annual EPRI Contractors Conference on Coal Liquefaction, Palo Alto, California (April 23-25, 1985).

Menzies, M.A., Hepton, J., Silva, A.E., and Logie, R.B., "High Conversion Residuum Hydrocracking with the CANMET Process," Presented at the National Petroleum Refiners Association Annual Meeting, San Antonio (1981).

Miller, R., "Use of Non-Coal Derived Heavy Solvents in Direct Coal Liquefaction," presented at the Tenth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, California (April 23-25, 1985).

Morooka, S. and Hamrin, C.E., "Hydrodesulfurization of Thiophene by Coal Mineral Matter and a Cobalt-Molybdate Catalyst in a Pulse Reactor," FUEL, 57, pp. 776-780 (1978).

Moschopedis, S.E., "Use of Oil Sands Bitumen and Its Derivatives as Hydrogen Donors to Coal," FUEL, 59, p. 67 (1980).

Moschopedis, S.E., Hawkins, R.W., Fryer, J.F., and Speight, J.G., "Use of Heavy Oils (and Derivatives) to Process Coal," FUEL, 59, pp. 647-653 (1980).

Moschopedis, S., Hawkins, R., and Speight, J., "Effects of Process Parameters on the Liquefaction of Coal Using Heavy Oils and Bitumens," Fuel Processing Technology, 5, pp. 213-228 (1982).

Nandi, B.N., Pruden, B.B., Parsons, B.I., and Montgomery, D.S., "Microscopic Changes in the Coal-Based Catalysts Used in the Hydrocracking of Athabasca Bitumens," FUEL, 57, pp. 723-726 (1978).

Rhodes, D., "Comparison of Coal and Bitumen-Coal Process Configuration," Presented at the Tenth Annual EPRI Contractors' Conference, Palo Alto, California (April 23-25, 1985).

Schindler, H., Chen, J., Peluso, M., and Schiffer, A., "Coal Liquefaction by Coal/Oil Coprocessing," presented at the Tenth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, California (April 23-25, 1985).

Shinn, J., Dahlberg, A., Kuehler, C., and Rosenthal, J., "The Chevron Co-Refining Process," Proceedings of the Ninth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, California (1984).

Yan, T.Y., and Espenscheid, W.F., "Coal Liquefaction Process," U.S. Patent 4,151,066 (1979).

Yan, T.Y., "Coal Liquefaction Process," U.S. Patent 4,317,711 (1982)

Yan, T.Y., "Coal Liquefaction Process," U.S. Patent 4,344,976 (1982).

Yan, T.Y., and Espenscheid, W., "Liquefaction of Coal in a Petroleum Fraction Under Mild Conditions," Fuel Processing Technology, 7, pp. 121-133 (1983).