

REACTIVITY SCREENING OF FEEDSTOCKS FOR CATALYTIC COAL/OIL CO-PROCESSING

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ABSTRACT

HRI is currently conducting a four-party funded program to develop and demonstrate catalytic coal/oil co-processing using HRI's proven ebullated-bed reactor technology. The initial task in the research program was to determine reactivities of four coals (Illinois No. 6 and Ohio No. 5/6 bituminous, Alberta sub-bituminous and Texas lignite) and four petroleum residuums (Cold Lake, Maya, West Texas Sour, and Canadian IPL), both separately and in combination, using a 20cc microautoclave reactor. Experimental conditions and analytical procedures were developed to properly approximate ebullated bed conditions at the small, batch scale and to allow estimation of both coal and petroleum residuum conversions. Over 200 single-stage microautoclave tests were conducted studying severity, feedstock ratio, and catalyst effects. An interesting synergistic response was noted which indicates optimum performance at 50/50 coal/oil ratio for one particular feedstock pair. Initial results from a single-stage run in a continuous bench unit verified the trends noted in the microautoclave study.

INTRODUCTION

Hydrocarbon Research, Inc. (HRI) has developed and commercialized ebullated-bed reactor technology for the catalytic hydroconversion of both coal and heavy oil. The H-Oil® Process has been commercially demonstrated in both single- and two-stage process configurations, and the H-Coal® Process has been successfully scaled up through the 200 ton/day Catlettsburg pilot plant. While economic conditions have prevented the commercial application of direct liquefaction technology, coal/oil co-processing has gained increasing attention as a more commercially viable, nearer term way to introduce coal-derived liquid fuels into the market place. HRI's COILSSM Process for co-processing was demonstrated on a bench unit scale as early as 1974⁽¹⁾, and more recently a two-stage process configuration was demonstrated on a Canadian feedstock combination of potential commercial interest⁽²⁾. In 1985, a four-party funded program was started to further develop and demonstrate catalytic coal/oil co-processing using HRI's ebullated-bed reactor technology. The program sponsors, objectives and elements are listed in Table 1. This paper focuses on the results of the microautoclave reactivity screening program.

MICROAUTOCLAVE DESCRIPTION AND PROCEDURES

With the recent increase in interest in co-processing, numerous investigators have reported results of batch reactor reactivity studies at various scales⁽³⁻⁶⁾. Many of these approaches tend to take a conventional coal liquefaction approach, by characterizing the effectiveness of petroleum oils as coal liquefaction "solvents". In coal/residuum co-processing, the oil is not a process solvent as such, but rather a reactant, and its reactions/conversions are of equal - or even greater, depending on specific conditions - importance than those of the coal. The opposite approach to this is to view co-processing as an extension of refining technology, treating the coal as an additive, usually in limited quantities^(7,8). HRI's program was set up to consider a broad range of potential applications using catalytic ebullated-bed co-processing. The microautoclave experimental and analytical procedures were specifically developed to reflect this, and are in many respects considerably different than those used by other workers. Some discussion is therefore necessary to explain the basis for these differences.

The 20cc microautoclave reactor used in these studies is shown in Figure 1. Solvent, coal, residuum, and catalyst are charged batchwise in the appropriate amounts prior to mounting the reactor. Following pressure-testing, the desired H₂ (or N₂) pressure is established. Due to the volume of gas lines above the reactor itself, it is essentially an "infinite source" hydrogen system, and no adjustment of operating pressure due to temperature is usually required. The entire assembly is shaken vertically with approximately one-inch strokes at 460 rpm, with temperature control by immersion in a fluidized sand bath heater. Dual sand baths are available for simulation of two-stage, close-coupled processing. Two identical microautoclave reactors are always operated side-by-side. A cold trap is provided to collect any light liquids lost during operation or depressuring.

Following each run the reaction is quenched by immersion in a water bath, and slowly depressured. The reactors and cold traps are then removed, and the products are combined and subjected to the workup procedures described in Figure 2. The use of the catalyst basket allows separation of product solids from catalyst extrudates. Ash-balancing then allows calculation of coal conversion. If necessary, product ashes can be checked for catalyst metals to distinguish coal ash from attrited catalyst. TGA simulated distillation is used to estimate product residuum contents and calculate residuum conversions. For selected runs, solvent precipitation was used to calculate asphaltene and preasphaltene components in the product residuum, although this is of lesser utility in co-processing than in coal liquefaction since petroleum residua contains very low levels of insolubles.

As noted above, HRI's microautoclave operating procedures and conditions are specifically designed to most properly approximate the conditions of an ebullated-bed reactor, and are in many cases quite different than those "typically" used in the industry. Some specifics include:

- Catalyst Type and Loading - The ebullated-bed reactor operates with conventional extrudate catalysts at very high loadings (up to 50% of the reactor volume is occupied by catalyst). Our microautoclave experiments typically charged a catalyst/feedstock ratio of 1/1 to reflect this. Techniques such as grinding of catalyst are not representative. The catalyst used typically is process-presulfided in a pilot unit, and the use of the catalyst basket allows separation from reaction products. Some assumptions are necessary in calculation procedures to account for items such as IOM deposition on catalyst, catalyst attrition, etc. during an experiment.
- Feedstock Dilution with Distillate Products - The ebullated bed is a well-mixed reactor, due to the typically high ratio of internal recycle to fresh feed. As a result, reaction occurs in a concentration represented by the products. No batch reactor can properly model a CSTR from the standpoint of fundamental kinetics, so a compromise has to be made. Since the initial conversion reactions in coal liquefaction are critical, an attempt is made to simulate the reactor environment in which they occur. Thus, microautoclave reactor charges are made up with a high level of distillate diluent. An attempt is made to approximate, to the extent possible, the properties of the distillate materials which would be expected to be produced from the feedstocks and conditions of interest. The distillate solvents used are generally materials produced in substantial quantities from larger pilot plant operations on the feedstocks of interest.
- Product Analyses - Coal conversion to THF-solubles is calculated in a fairly typical manner. As noted above, conversions based on solubilities in other solvents are not considered to be especially meaningful for co-processing. A simulated distillation procedure was developed using a Perkin-Elmer TGS-2 Thermogravimetric Analyzer (TGA), which allows estimation of 975°F+ conversions. No attempt is made to generate data such as gas yields or distillate product distribution or quality. Such data are difficult to generate reliably on such a small scale. Even if this could be done, the results would not be meaningful for scaleup due to the large impacts of the distillate diluents and the major differences between batch and continuous units, on any scale.

SCREENING STUDY CONDITIONS

A five-point, low-to-mild severity condition matrix was used to screen each feedstock and combination of interest, as shown in Table 2. As noted, a 4/1/1 charge ratio of distillate solvent/reactant (coal and oil)/catalyst was used. Severities ranged from 2-20 STTU, based on HRI's conversion model developed for coal conversions. It is recognized that the time/temperature relationships for co-processing may not be truly represented by the STTU model, but it was used as a convenient way to express both severity parameters. The matrix used provides a comparison of three residence times at one temperature (800°F), and three temperatures at one residence time (30 minutes). All severities are lower than those typically encountered in larger scale operations. This serves to keep conversions low enough so that kinetic reactivity differences can be properly observed.

FEEDSTOCK PROPERTIES

Some properties of the four coals and four oils studied are listed in Table 3. The Cold Lake feedstock was available as a deep-cut ASB from previous HRI H-Oil® studies, while the other three oils were provided as crude oils and were batch vacuum-distilled to approximately the same residuum content prior to the reactivity studies. All four coals were subjected to standard HRI bench unit preparation procedures (crushing, pulverizing to -70 mesh, drying to 2-10% moisture, and screening) and were further vacuum dried immediately prior to microautoclave testing. Three diluent solvents were also used, as shown. The Illinois-derived solvent was used for Ohio and Illinois bituminous coals, the Wyodak solvent for Alberta sub-bituminous coal and Texas lignite, and the Cold Lake solvent for all petroleum oils. Except for a few solvent-specific runs, solvents were blended in the same ratios as the feedstocks for each run.

PROGRAM OUTLINE

Over two hundred tests were conducted under the program, as noted in Table 4. The co-processing feedstock pairs chosen for evaluation were based on program sponsors' concerns and represent meaningful commercial candidates. No work was done on the Illinois No. 6 coal, since it was being extensively studied in HRI's parallel DOE funded coal liquefaction program. Most of the discussion to follow centers on the Ohio coal/Cold Lake ASB pair, which was the most extensively studied in 1985 (including both single- and two-stage process variable studies in the continuous bench unit). This combination has been selected by OOSFC as the basis for a prototype commercial facility to be located in Ohio.

INDIVIDUAL FEEDSTOCK REACTIVITIES

Figures 3 and 4 show STTU response curves for the Ohio coal and the Cold Lake ASB. Similar curves were generated for each of the other feedstocks. In order to provide a quantitative reactivity ranking, kinetic rate constants were back-calculated from the data assuming various batch reactor models. For the oils alone, a second order fit was found to be the most satisfactory, as shown in Figure 5. While it is unlikely that the conversion reactions are truly second order, in the sense of being bimolecular, such a model fit is not unusual in systems of this type, where the "reactant" is not a single component but rather a range of components with different reactivities. For the coals, a more complex model would be required to separate the effects of coal conversion to THF-solubles, the fraction of converted coal which forms 975°F+ residuum, and the kinetics of conversion of the residuum. Realizing these deficiencies, the coal data were force-fit to the same simplified second order 975°F+ conversion model so that a direct comparison of oils, coals, and co-processing pairs could be made. These results are shown in Table 5. As expected, the oils are considerably more reactive to total 975°F+ conversion at low severities than the coals. It is notable that the co-processing pairs do not necessarily fall in either the order or magnitude which would be expected from the individual feedstocks, indicating that synergistic interactions do occur. It is also notable that the feedstock pair (Ohio/Cold Lake) studied most extensively in the

program does not represent the "best" choice based on reactivities, but was chosen based on commercial considerations.

OHIO COAL/COLD LAKE ASB CO-PROCESSING

Figure 6 shows the reactivity curves for a 50/50 blend of Ohio coal and Cold Lake ASB. The drop off in 975°F⁺ conversion at 20 STTU may be indicative of some regressive reaction due to poor solvent quality, as this is the highest temperature point (825°F) in the grid. The STTU axis has been extended to include a point at a typical bench unit operating severity. It is notable that there was no problem in achieving high (90% plus) coal conversion to THF solubles. This was true of all the pairs studied, indicating that the inherently poor hydrogen donor properties of the petroleum oils can be overcome by catalytic, ebullated-bed co-processing.

Figure 7 shows the effect of coal to oil ratio on conversions in a low severity test (10 STTU). As expected, the THF conversion increases as the coal concentration increases, since a higher percentage of the solvent is then coal-derived as well. The 975°F⁺ conversion response is far less explainable. The individual feedstock points at 0 and 100% are connected, to represent expected conversions based on strict linear averaging. At coal concentrations up to 50%, conversions near or above this line occur, indicating a positive synergy. Surprisingly, at coal concentrations of 67-75%, a large negative interaction occurs, and 975°F⁺ conversions are actually lower than those for coal alone. Each of these points was found to be reproducible. The most likely explanation for this phenomenon is that the presence of the petroleum oils sufficiently reduces the solvent quality in this range to cause a large drop in the conversion of the coal residua. At the lower coal concentrations, this effect is offset by the improved conversions of the petroleum residua. Interestingly, this effect shows itself only in the 975°F⁺ conversions and not in the THF conversions. It should be noted here that coal/oil ratio studies with other feedstock pairs do not show this same negative behavior (at least not to this extent), but in all cases the response is non-linear.

Since this trend was interesting and unexpected, it was decided to repeat the coal/oil ratio studies at a higher severity, typical of bench unit process conditions. This was done to coincide with the single-stage bench run, which provided comparative results in the single-stage, integrated bench unit at 33, 50 and 67% coal. These results are shown in Figure 8. Note that the complex ratio response curve for 975°F⁺ conversion has been reproduced, although the extent of the negative deviations at 67-75% coal are reduced. The bench unit data, at 33 and 50% coal, provide excellent agreement with the microautoclave data. The bench data at 67% coal do show some negative effect, although not as pronounced as in the microautoclave. One key difference is that each bench data point represents several days of continuous, integrated operation with solvent quality equilibration, while microautoclave solvents are artificially composited. It should also be noted that the tie points at 0 and 100% coal were not determined on the bench unit, so that the extent of positive/negative synergy may not be directly comparable. The 50% coal case has been shown to be economically preferred at several severities at least in part due to synergistic reactivity effects.⁽⁹⁾

CONCLUSIONS

HRI's microautoclave has been shown to be an effective tool for comparing reactivities of coals, oils, and combinations for catalytic coal/oil co-processing. Specific improvements in experimental and analytical procedures were implemented to expand the utility of the microautoclave from coal liquefaction into oil and co-processing. Data generated on the Ohio coal/Cold Lake ASB combination led to some unexpected results, which were later confirmed by continuous bench unit studies.

ACKNOWLEDGEMENTS

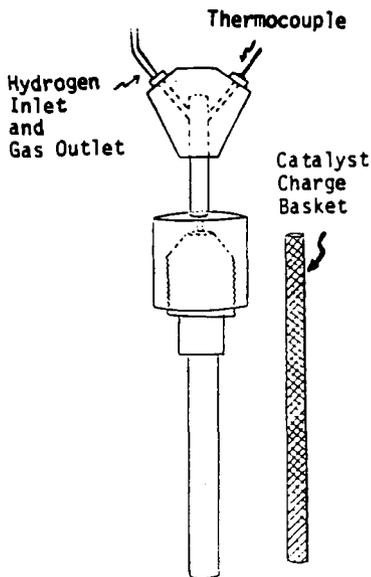
HRI wishes to acknowledge the program sponsors and their representatives who have contributed to the technical content of this work. Some of the feedstock analytical data presented were generated by the Alberta Research Council.

REFERENCES

1. U. S. Patent 4,054,504.
2. "Coal/Oil Co-Processing of Canadian Feedstocks" J. B. MacArthur, F. Boehm, A. Liron, R. H. Shannon. Proceedings: Tenth Annual EPRI Contractors' Conference on Clean Liquid and Solid Fuels, October, 1985.
3. "Evaluation of Process Parameters for Combined Processing of Coal with Heavy Crudes and Residua", C. W. Curtis, et al. Ind. Eng. Chem. Process Des. Dev., 1985, 24, 1259-1266.
4. "Use of Non-Coal Derived Heavy Solvents in Direct Coal Liquefaction" R. L. Miller. Proceedings: Tenth Annual EPRI Contractors' Conference on Clean Liquid and Solid Fuels, October, 1985.
5. "Lumnus Co-Processing", M. Green. DOE's (PETC) Direct Liquefaction Contractors' Conference, Pittsburgh, November 19, 1985
6. "Coal Liquefaction Co-Processing", J. Gatsis, et al. DOE's (PETC) Direct Liquefaction Contractors' Conference, Pittsburgh, November 19, 1985
7. "The Chevron Co-Refining Process", J. Shinn, et al. Proceedings of 9th Annual EPRI Contractors' Conference on Clean and Solid Fuels, March 1984.
8. "Co-Processing of Canadian Lignites and Bitumen", S. Fouda, et al. AIChE National Meeting, March 1985.
9. "HRI's Coal/Oil Co-Processing Program - Phase I", J. E. Duddy. Presented at EPRI's 11th Annual Conference on Clean Liquid and Solid Fuels, May 1986.

MICROAUTOCLAVE REACTOR

FIGURE 1



MECHANICAL DESIGN

- 20cc Internal Volume
- Maximum Inlet Hydrogen Pressure 3000 psi
- Operations to Liquefaction Temperature
- Thermal and Gas Inlet Coupling
- 347ss Material of Construction
- External Cap Threads
- Reactor Cap Redesign
- Cold Traps
- Catalyst Basket
- Utilizes Whole Extrudate Catalyst

TESTING CAPABILITIES

- Thermal Tests Varying Charge, Feed Ratios, Temperature, Time
- Catalytic Tests Varying Charge, Feed Ratios, Temperature, Time

FIGURE 2

PRODUCT WORKUP PROCEDURES

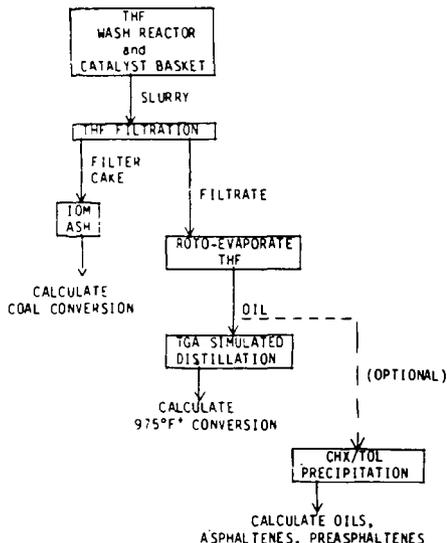


FIGURE 3

CATALYTIC REACTIVITY OF OHIO No. 5/6 COAL

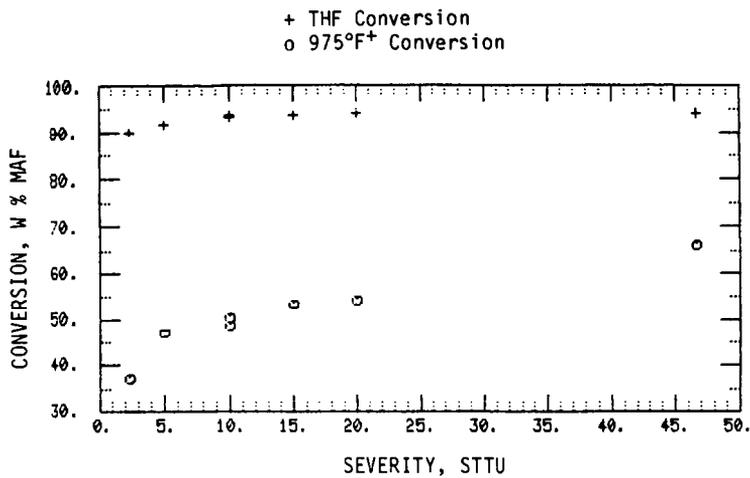


FIGURE 4

CATALYTIC REACTIVITY OF COLD LAKE ASB

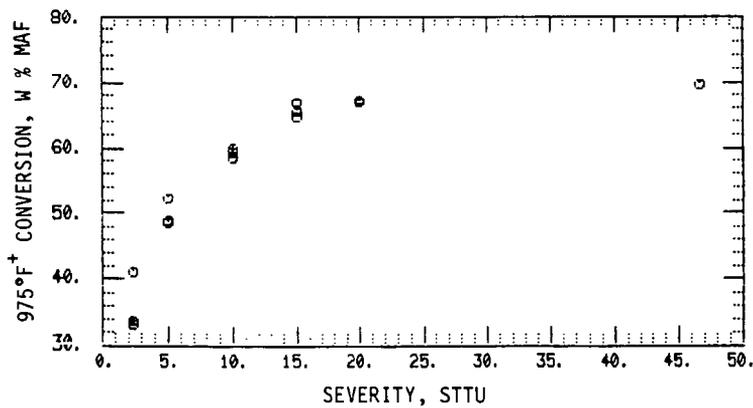


FIGURE 5

CALCULATED SECOND ORDER RATE CONSTANTS FOR
975°F+ CONVERSION OF OIL FEEDSTOCKS

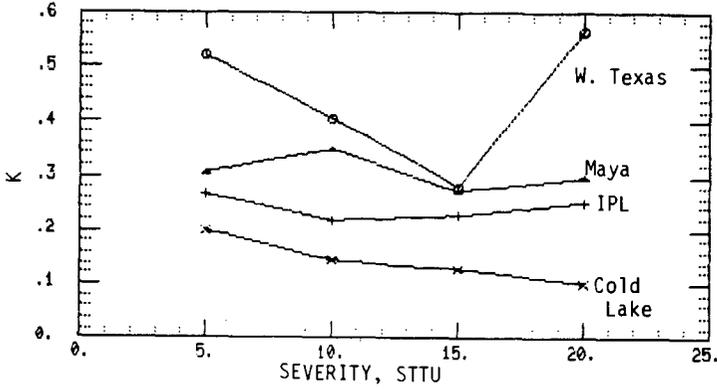


FIGURE 6

CATALYTIC CO-PROCESSING OF 50/50 BLEND OF
OHIO NO. 5/6 COAL AND COLD LAKE ASB

+ THF Conversion
o Total Feed 975°F+ Conversion

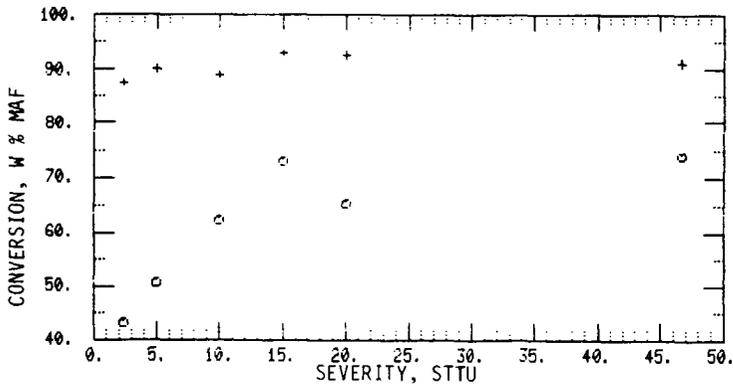


FIGURE 7

CATALYTIC CO-PROCESSING OF OHIO NO. 5/6 COAL AND COLD LAKE ASB
EFFECT OF COAL CONCENTRATION

(SEVERITY: 10 STTU)

+ THF Conversion
 o Total Feed 975°F+ Conversion

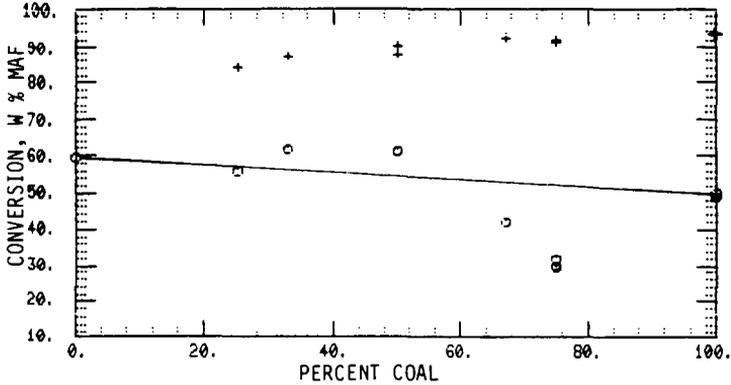


FIGURE 8

CATALYTIC CO-PROCESSING OF OHIO NO. 5/6 COAL AND COLD LAKE ASB
EFFECT OF COAL CONCENTRATION

(BENCH RUN SEVERITY)

+ THF Conversion
 o 975°F+ Conversion
 x Bench Unit 975°F+ Conversion Data

