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CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL

NINTH QUARTERLY REPORT FOR THE PERIOD

1 OCTOBER 1994 - 31 DECEMBER 1994

A.G. Comolli
E.S. Johanson
L.K. Lee
V.R. Pradhan
R.H. Stalzer

FINAL

WORK PERFORMED UNDER CONTRACT

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HYDROCARBON TECHNOLOGIES, INC.
PO BOX 6047, NEW YORK & PURITAN AVENUES
LAWRENCEVILLE, NJ 08648

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JUNE 1995

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ABSTRACT

This quarterly report covers the activities of Catalytic Multi-Stage Liquefaction of Coal during the Period October 1 - December 31, 1994, at Hydrocarbon Research, Inc. in Lawrenceville and Princeton, New Jersey. This DOE Contract Period was from December 8, 1992 to December 7, 1994 and has been extended to September 30, 1995.

The overall objective of this program is to produce liquid fuels from coal by direct liquefaction at a cost that is competitive with conventional fuels. Specifically, this continuous bench-scale program contains provisions to examine new ideas in areas such as: low temperature pretreatments, more effective catalysts, on-line hydrotreating, new coal feedstocks, other hydrogen sources, more concentrated coal feeds and other highly responsive process improvements while assessing the design and economics of the bench-scale results.

This quarterly report covers work on Laboratory Scale Studies, Continuous Bench-Scale Operations, Technical Assessment and Project Management.

SUMMARY

This report describes the following: i) laboratory support for the bench run CMSL-08, ii) the continuous bench scale run CMSL-07 and iii) the continuous bench-scale run CMSL-08.

Laboratory support for CMSL-08 consisted of studying the mixing/dissolution behavior of co-mingled plastics with coal and recycle solvent slurry. Using these pre-mixed feeds containing coal, plastics, and recycle oil, microautoclave tests were also carried out, both with supported and dispersed catalysts to evaluate the reactivity mixed feed under coal conversion conditions.

The main objective of bench-run CMSL-07 was to evaluate the effect of using a mixture of syngas and H_2O as a reducing gas in two stage liquefaction of Black Thunder coal with reduced operating pressure. Using supported catalyst in both stages as well as a feed dispersed catalyst in the presence of $CO/H_2O/H_2$ as the reducing gas results in an improvement in the overall quality of the product oil at normal operating conditions. Decreasing the operating pressure while using $CO/H_2O/H_2$ as the reducing gas resulted in a decrease in overall performance as measured by distillate yield, coal conversion and resid conversion. It also resulted in a decrease in the quality of the product oil. The negative effects of lowering the operating pressure on overall performance and product oil quality can largely be mitigated by slightly increasing the severity and by increasing the feed dispersed catalyst addition rate. This demonstrates the possibility of performing high quality coal liquefaction at substantially reduced operating pressure with a potential for significant cost savings by reducing the capital investment needed for a higher pressure operating system.

The bench-run CMSL-08 was successfully carried out for 23 continuous days spread over five conditions to investigate the effects of co-liquefying the primary plastic constituents of the municipal solid waste on the process performance. This bench run was a follow up of the earlier exploratory work Hydrocarbon Research, Inc. had carried out in the PDU-scale continuous operations during the DOE-sponsored POC-02 run. During this bench run, the conditions were chosen to seek for the optimum set of operating severity/catalysts for converting plastics together with Illinois No. 6 coal. A conscious effort was made to maintain the process under a net positive solvent-balance during the continuous operations, thereby minimizing any intrusive effects of an external make-up oil. The first stage reactor was provided with both the supported Ni-Mo/Alumina and the dispersed sulfated iron-molybdenum catalyst to ensure sufficient activity for the depolymerization of plastics in this stage, while the second stage reactor was a back-mixed thermal reactor with no supported catalyst but with the converted dispersed catalyst only.

TASK 2 - LABORATORY SCALE STUDIES

LABORATORY STUDIES IN SUPPORT OF CMSL-08

The laboratory support for CMSL-08 consisted of experiments, conducted in relation to the pre-reactor handling (mixing/dissolution and pumping) of the coal/solvent/plastic mixtures. In essence, two dissolution tests were conducted at 33 and 50 W% co-mingled plastics with Illinois No. 6 Crown II mine coal (ca. 5 % moisture). Tank-4 material (L-814), a petroleum-derived oil, was used as solvent with solvent-to-total feed being 1.5. Thus, all compositions and ratios to be used during CMSL-08 were simulated in these tests. The approach used was to make, at room temperature, a slurry of coal and solvent, heat it to about 220°C and then add co-mingled plastics to the slurry. After allowing the slurry to sit for about 45 minutes at temperature, the hot mixture was visually examined for homogeneity and overall appearance. All the samples tested appeared homogeneous, fluid-like, and free of lumps. Therefore, it appeared that such coal/plastics/solvent mixtures would not pose any pumping problems. Upon cooling to room temperature, the mixture took on the appearance of a plasticized and grainy filter cake material. This approach is certainly different from that employed successfully during the POC-02 run, although the new approach is less complicated as it will need only one pre-mix tank at high temperatures (200-220°C) instead of three (as during POC-02) and would also make the foaming problem due to moisture in coal more manageable. As a result, this was the approach that was followed for the pre-reactor handling of the coal/plastics with recycle solvent during the CMSL-08 bench run.

The microautoclave tests, carried out under conditions similar to those planned for the bench scale run, indicated as high as 90-92 W% maf conversion (based upon THF solubility of products) for coal+plastics combined feed (with 33 and 50 W% mixed plastics with coal). The conversion numbers presented here are higher than those obtained in the microautoclave tests that used separately added coal and mixed plastics feed. This shows a distinct advantage of predissolving and premixing mixed plastics with coal/solvent slurries.

TASK 3 - BENCH-SCALE STUDIES

RUN CMSL-07 (227-84)

IMPACT OF LOW PRESSURE SYNGAS ON LIQUEFACTION IN A CATALYTIC / CATALYTIC MODE OF OPERATION

SUMMARY

The main objective of this run, to evaluate the effect of using a mixture of CO/H₂ as a reducing gas in two stage liquefaction of Black Thunder coal with reduced operating pressure, was met with 19 days of continuous operation. Both reactors were charged with Shell S-317 catalyst and operated in a fully ebullated mode with ammonium heptamolybdate as an additional feed catalyst.

Condition 1 extended from Periods 1 to 7 using pure CO/H₂ as the reducing gas for the first stage and H₂ for the second stage. Also, for this condition and all subsequent conditions, water was injected upstream of the preheater in order to obtain an overall water content of 40 wt% of the dry coal in the feed slurry. This condition served as a base case for comparison. Condition 2 was identical to Condition 1 except the back pressure was reduced from 17.2 MPa to 13.8 MPa. Condition 3 was identical to Condition 2 except the back pressure was further reduced from 13.8 MPa to 10.3 MPa. Due to the poor performance experienced during Condition 3, Condition 4 was increased in overall reactor severity and the addition rate of the feed catalyst was increased from 200 ppm to 500 ppm of molybdenum on a dry coal basis.

Coal conversion at 17.3 and 13.8 MPa was normal for subbituminous coal at 92.1-92.4 wt% maf coal. Coal conversion at the low pressure condition of 10.3 MPa dropped to 89.7 wt%, but an increase in feed catalyst addition rate and reactor severity raised conversion to 91.7 wt%. The resid conversion shows the same trend in dropping from 92.4 wt% maf coal to 80.6 wt% from the high pressure condition to the low pressure condition and then reversing this trend with the increased feed catalyst addition rate and reactor severity at the low pressure condition to 89.6 wt%. The gas make shows very little dependency on reactor pressure, the C₁-C₃ yield varying only from 7.1 to 7.8 wt% maf coal.

The distillate yield decreases in quantity and quality as the catalyst ages and the operating pressure was decreased. During the final condition with the highest catalyst age and lowest operating pressure the increase in reactor severity and feed catalyst addition rate actually increases the distillate yield quantity and quality to values comparable to those achieved during the first two conditions.

The hydrotreater feed consisted of three different process streams, the first stage separator overheads (SOH), the second stage atmospheric still overhead (ASOH), and the overheads from the second stage hot separator. The hydrotreater product was the bottoms from the second stage cold separator (SOH). The second stage hot separator process stream was not sampled and

analyzed. The first stage SOH sulfur content ranged from 455 to 1574 ppm, the nitrogen content ranged from 141 to 2329 ppm, and the H/C ratio ranged from 1.52 to 1.60. The second stage ASOH sulfur content ranged from 30 to 109 ppm, the nitrogen content ranged from 120 to 2843 ppm and the H/C ratio ranged from 1.38 to 14.8. The hydrotreated product, the second stage SOH, had a negligible sulfur content, generally less than 1 ppm, a nitrogen content always less than 1 ppm, and a H/C ratio of 1.74 to 1.83.

Using supported catalyst in both stages as well as a feed catalyst, in the presence of CO/H₂ as the reducing gas resulted in an improvement in the overall quality of the product oil at typical operating conditions using H₂ as the reducing gas. Decreasing the operating pressure while using CO/H₂ as the reducing gas results in a decrease in overall performance as measured by distillate yield, coal conversion, and resid conversion. It also results in a decrease in the quality of the product oil. The negative effects of lowering the operating pressure on overall performance and product oil quality can largely be mitigated by slightly increasing the severity and by increasing the feed catalyst addition rate. This demonstrates the possibility of performing high quality coal liquefaction at substantially reduced operating pressure with a potential for significant cost savings by reducing the capital investment needed for a higher pressure operating system.

OBJECTIVES, BACKGROUND AND SCOPE OF WORK

The main objective of this run was to evaluate the effect of using a mixture of CO/H_2 as a reducing gas in two stage liquefaction of Black Thunder coal. Specifically, one technical objective was to determine the relative performance of CO/H_2 vs. H_2 in a fully ebullated two stage system with ammonium heptamolybdate as a feed catalyst. The other technical objective was to determine the impact of lowering system pressure on distillate yield, residuum conversion and coal conversion while using a mixture of CO/H_2 as the reducing gas.

The production of hydrogen constitutes one of the major operating costs of coal liquefaction. Alternative sources of hydrogen such as synthesis gas, a mixture of carbon monoxide and hydrogen coming directly out of a gasifier or reformer, can potentially reduce operating cost by 10-15%. It is known that in the presence of an alkali salt, a mixture of CO/H_2 and steam is very effective in solubilizing high oxygen containing low rank coals at relatively low severity conditions, usually below 400°C .

A successful operation with promising results such as improved liquefaction yields, kinetics, and hydrogen efficiency of the CTSL process was demonstrated during CMSL-3 (227-79) and CMSL-4 (227-81). The interstage separation used during CMSL-3 and CMSL-4 was instrumental in removing CO_x off-gases, thereby reducing hydrogenation of these gases to methane/water at the expense of the valuable hydrogen.

Operation using syngas while feeding Black Thunder subbituminous coal was demonstrated in Run CMSL-3 with promising results, i.e. improved yields, kinetic and hydrogen efficiency. This exceptional performance was obtained using ammonium heptamolybdate (AHM) in the feed to a non-supported catalyst first stage followed by a supported Ni/Mo catalyst second stage. The AHM used in CMSL-3 was equivalent to 1500 ppm Mo on a dry coal feed basis. CMSL-4 was similar to CMSL-3 except that instead of using AHM as a feed catalyst the first reactor was also charged with supported catalyst and operated as an ebullated bed. During these runs problems were experienced with the CO feed rate. This caused the H_2 partial pressure to be lower than originally planned. However, even at a reduced H_2 partial pressure, process performance did not drop off sharply, but was fairly comparable to higher partial pressure operation. This fortuitous observation that a CO/H_2 reducing gas might not require the same pressure as pure hydrogen provided the impetus for this low pressure liquefaction test.

The liquefaction of Black Thunder mine coal was evaluated using CO/H_2 as the reducing gas in the first stage and H_2 as the reducing gas in the second stage. The main process variable evaluated for this test program was the reactor pressure. This varied in the second stage from 17.2 to 10.3 MPa (2500 to 1500 psi). The effect of increasing the feed rate of the feed catalyst (AHM) at the low pressure condition was also investigated.

RUN PLAN

CMSL-07 involved two equal volume ebullated bed reactors as well as adding AHM as a feed catalyst. A simplified process flow diagram is presented in *Figure 1*. Coal was dissolved in the first-stage in the presence of syngas and steam, while the primary coal liquids were further upgraded in the second stage under a hydrogen atmosphere. An interstage separator was installed to remove gases and light distillates (as separator overhead, SOH) generated from the first stage and to recover any excess CO/H₂. Fresh hydrogen was injected into the second stage. Products from the second stage were recovered using a hot separator (as a separator overhead, SOH) and a continuous atmospheric still (CAS) which has atmospheric still overheads (ASOH) and CAS bottoms as the outlets. The CAS bottoms were pressure filtered in a batch mode into pressure filter liquid (PFL) and pressure filter cake (PFC). The PFL was used as recycle solvent and as buffer liquids for the ebullating pump operations. The first stage SOH, second stage SOH and second stage ASOH were combined as the feed to the hydrotreater.

The run plan is given in *Table 1*. Four process conditions were chosen for this run. The actual operating conditions are presented in *Table 2*.

Condition 1 extended from Periods 1 to 7 and used a mixture of CO and H₂ as the reducing gas for the first stage and pure H₂ for the second stage. Also, for this condition and all subsequent conditions, water was injected upstream of the preheater in order to obtain an overall water content of 40 wt% of the dry coal in the feed slurry. This condition served as a base case for comparison. Condition 2 was identical to Condition 1 except the back pressure was reduced from 17.2 to 13.8 MPa (2500 to 2000 psi). Condition 3 was identical to Condition 2 except the back pressure was further reduced from 13.8 MPa to 10.3 MPa (2000 to 1500 psi). Due to the poor performance experienced during Condition 3, overall reactor severity in Condition 4 was increased, in overall reactor and the addition rate of the feed catalyst was increased from 200 ppm to 500 of molybdenum ppm on a dry coal basis.

Tri-nonyl polysulfide (TNPS) and hydrogen sulfide were added to the first and second stage, respectively. The target sulfur addition rate to the first stage was 1 wt% of dry coal and 3 wt% to the second stage.

Coal

Wyoming subbituminous coal, Black Thunder Mine, was used as the feedstock. The coal analyses of the feed (HRI-6213) are presented in *Table 3*. This batch of coal was previously evaluated in POC-02. This coal has approximately 11.5 wt% moisture and an ash content of 6.0 wt% (dry basis).

Start-up/Makeup Oil

The start-up/make-up oil used during this run was a coal-derived recycle solvent generated during POC-01 (PDU RUN 260-04). The elemental analysis and boiling point distribution are shown in *Table 4*. This oil contained 15.1 wt% of 524°C+ resid and had a H/C molar ratio of 1.26.

Catalyst

Fresh Shell S-317 1/32" extrudates (HRI-5394) were charged to both the first and second stage ebullated beds. The hydrotreater was charged with Criterion C-411 trilobed catalyst (HRI-6135). The catalyst was presulfided during normal start-up operations. In addition a feed catalyst was used throughout the run consisting of an aqueous solution of ammonium heptamolybdate. This was added at a concentration level of 200-500 ppm of molybdenum based on the dry coal feed.

PERFORMANCE AND RESULTS

The overall operation performance is presented in *Figures 2-6* and *Table 5*. The daily material balance average was 97.5 wt% (*Figure 2*). The reactor temperatures are presented in *Figure 3* and show a very small variation from target values except for a slight drop in K-2 temperature during Period 15. The space velocity is presented in *Figure 4* and shows smooth operation for the entire run, except for Period 15, with a value of 600 kg dry coal/hr/m³ catalyst. The overall process severity is presented in *Figure 5* showing an initial relative severity of 1.0 for Conditions 1, 2 and 3 and a severity of 1.3 for Condition 4. The first 3 periods show a lower severity due to normal startup conditions. The unit back pressure is presented in *Figure 6*.

Coal Conversion

Coal conversion during Condition 1 was 92.4 wt% maf coal, *Figure 7*. It initially began low during the startup condition, probably due to the quality of the recycle oil. The Condition 1 value of 92.4 wt% maf coal is what would be expected for Black Thunder coal at these process conditions with a pure H₂ reducing gas system. In Condition 2 the coal conversion initially dropped approximately 1% with the drop in pressure but it then increased to 92.1 wt% maf coal. During Condition 3 the coal conversion dropped continuously to a value of 89.7 wt% maf coal. The recycle oil also decreased in quality with the resid reaching a level of 17.6 wt% and off-line filtration times increased from a normal value of 1/2 hour to 6 hours and longer. Due to this difficult operation and poorer performance, the first stage reactor temperature was increased from 388 C to 399 C, and the addition rate of the feed catalyst was increased from 200 ppm to 500 ppm dry coal. During Condition 4, coal conversion increased to a value of 91.7 wt% maf coal. This is only 0.7% less than during the base condition, Condition 1, and 2.0 wt% higher than during Condition 3.

524°C+ Residuum Conversion and Yield

Residuum conversion, calculated by dividing the 524 °C+ residuum yield by the weight of maf coal, is normally a strong function of catalyst age, *Figure 8*. Due to aging of the catalyst in a Bench Unit, resid conversion is expected to decrease over the course of the run as the residuum yield increases. Within a condition this dependency on catalyst age can be seen, but comparing between conditions is more difficult. From condition 1 through Condition 3 the resid conversion dropped from 92.4 to 80.6 wt% maf coal. How much of this is due to the decrease in operating pressure and how much is due to catalyst aging is difficult to evaluate. During Condition 4 the resid conversion rose to a value close to that of condition 1, at 89.6 wt% maf coal. This condition was at the same pressure as Condition 3 and at a 10°C higher temperature in Reactor 1 and with the higher addition rate (2.5 times higher) for the feed catalyst. These changes resulted in an increase in resid conversion of at least 9% from Condition 2.

C₁-C₃ Gas Make

The gas make for this test was typical for Black Thunder coal, a light gas (C₁-C₃) make of 7.1 to 7.8 wt% maf coal and a heavy gas (C₄-C₇) make of 2.9 to 3.4 wt% maf coal, *Figure 9*. The light gas make shows a slight dependency on operating pressure, increasing as the pressure decreases. However, this dependency is so slight that it might not be significant. The heavy gas yield shows no dependency on the operating pressure. A correction was made to the methane production due to the reforming of H₂ and CO. The slight drop on light gas make in Condition 4 is probably due to the increase in the slurry feed catalyst by 2.5 times.

C₄-524°C Distillate Yield

The distillate yield and distribution is more difficult than normal to explain (*see Figure 10 and Table 5*). Because of the large amount of "makeup oil" that was used during this run. This "makeup oil" is not the typical makeup oil used during a bench operation which would consist of a single outside oil (usually the start-up oil) that would be used on an as-needed basis when there wasn't sufficient process derived oil available from the pressure filtrations. This "make-up oil" consisted of both the normal start-up oil, PFL generated from previous periods (and even conditions) and oil which was toluene extracted from the pressure filter solids. The toluene extracted oil would lag behind the process from 2-5 days. These various oil streams were used on an as-need basis whenever they became available. All these streams are not normally analyzed, and when they were used they were all weighed together as a single "makeup oil" charge so that the individual recycle rates are not known. This causes some difficulties in calculating the normalized yields, especially as these streams are extremely rich in resid. The composition of the make-up oil was, therefore, estimated based upon available information. This leads to a larger level of uncertainty than normal in interpreting these results.

Condition 1 shows an extremely good overall yield of 67.0 wt% maf coal, *Figure 10*. Additionally this yield is of above average quality being all of lighter oil fractions. Condition 2 shows the results of a lower residuum conversion as the overall distillate yield decreases to 61.4 wt% maf coal. This is still a good yield, because the yield is virtually all lighter oils, though there is the start of a shift in quality toward heavier oils. Condition 3, at the lowest pressure, severity and feed catalyst addition rate, showed the poorest performance. The total distillate yield dropped to only 53.0 wt% maf coal, and there is a strong shift toward heavier oils. This is also the condition with the largest problem in calculating the quality of the "make-up oil" which is further complicated as this was the condition that also used the greatest quantity of "makeup oil". Condition 4 results are a strong improvement over Condition 3, being comparable to conditions 1 and 2. The total distillate yield was 63.6 wt% maf coal, between the total yields for Conditions 1 and 2. The quality is directly comparable to Condition 2 in terms of the distribution among the various boiling fractions.

Hydrogen Consumption

The hydrogen consumption is presented in *Figure 11*. Hydrogen consumption during Conditions 1 and 2 is very typical of the liquefaction of subbituminous coal under these operating conditions. During Condition 3, hydrogen consumption dropped by over 1 wt%, paralleling the overall drop in performance during this condition. However, during Condition 4, concurrent with the increase in performance is an increase in hydrogen consumption back to a typical level. This shows that even with the reduced hydrogen partial pressure during this condition, the slight increase in reactor severity and the increase in the feed catalyst addition rate compensated for the lower pressure.

INSPECTION OF PRODUCTS

Analyses of the liquid products are presented in *Tables 6-10*.

The first stage SOH and second stage ASOH were actually two of the three feed streams to the hydrotreater, the other being the second stage Hot Separator Overheads, which was not sampled. The second stage SOH is the product from the hydrotreater (see *Figure 1* for the simplified flow scheme). The nitrogen, sulfur and H/C atomic ratios for the first stage SOH, second stage SOH and ASOH are presented in *Tables 6-8*.

The sulfur content of the first stage SOH rises sharply from Condition 1 to Condition 2, from 455 to 937 ppm, and from Condition 2 to Condition 3, from 937 to 1574 ppm. This demonstrates the pressure dependence for sulfur removal in the first stage reactor. From Conditions 3 to 4 the sulfur content dropped back down over 1000 ppm to near its initial level at 506 ppm. This clearly shows the benefit of the slight increase in K-1 temperature and feed catalyst addition rate. The ASOH sulfur shows a similar trend, rising from an initial value of 30 ppm in Condition 1 to 95 ppm in Condition 2 to 109 ppm in Condition 3 and then dropping down to 76 ppm in condition 4. The second stage SOH, the hydrotreater product, has a negligible sulfur content throughout the run generally less than 1 ppm, showing that the hydrotreater is doing an excellent job of removing sulfur.

The nitrogen content of the first stage SOH started at an initial value of only 141 ppm in Condition 1 but rose to a value of 2329 ppm in Condition 2, 2250 ppm in Condition 3 and 2878 ppm in Condition 4. The ASOH shows the same pattern, starting at an initial low level of 120 ppm and then rising to 2843 in Condition 2, 2357 in Condition 3, and 2587 in Condition 4. These results are due to the fresh catalyst in the reactor being initially extremely active in the removal of heteroatoms and then sharply dropping off. The second stage SOH, the hydrotreater product, had a negligible nitrogen content throughout the run (less than 1 ppm), showing that the hydrotreater is doing an excellent job of removing the nitrogen.

The H/C atomic ratio was consistently higher for the second stage SOH, (ranging from 1.74 to 1.83), as compared to either the first stage SOH (ranging from 1.52 to 1.60) or the ASOH, (ranging from 1.38 to 1.48). This demonstrates that the hydrotreater is increasing the hydrogen content of the product.

The pressure filter liquid (PFL) properties for each condition are summed up in *Table 9*. As the catalyst aged the resid content of the PFL increased, from 19.8 wt% to 37.6 wt%, and the H/C atomic ratio decreased from 1.07 to 0.91. The cyclohexane and toluene insolubles also increased, from 29.03 to 86.85 and 2.64 to 27.04 respectively, as the run progressed, and the PFL became richer in asphaltenes and pre-asphaltenes. At the end of Period 14 and the beginning of Period 15, a large amount of "make-up" oil (63 wt% of the PFL used) was needed by the unit,

and this resulted in a sudden sharp change in the values of the properties used to evaluate the quality of the PFL. After this point the same trends for these properties exists as did before. The pressure filter cake (PFC) analysis is presented in *Table 10*.

CO SHIFT CONVERSION

CO interacts with coal either directly or indirectly via nascent hydrogen formed from the water-gas shift reaction. The WGS reaction :

is slightly exothermic, hence low temperature tends to shift the reaction towards the right.

In calculating the amount of CO and CO₂ in the off gas, a small correction was made based on the amount of CO and CO₂ produced from the coal. This correction was based on actual values from previous bench tests operating at similar conditions. The CO conversion is based on the disappearance of CO from the system:

$$\text{CO Conversion} = \frac{\text{CO}_{\text{in}} - \text{CO}_{\text{out}}}{\text{CO}_{\text{in}}} \times 100\%$$

Figure 12 provides a visual summary of the CO conversion over the course of the run. These values are much higher than the equilibrium of 45% calculated for typical coal liquefaction conditions. These results follow the trend demonstrated previously during CMSL-3 and CMSL-4 where the CO conversion also reached as high as 93.2%.

CONCLUSIONS

CMSL- 7 was a very successful bench program which significantly advanced the operating conditions under which coal liquefaction can occur in the presence of $\text{CO}/\text{H}_2\text{O}/\text{H}_2$ as the reducing gas. The main objectives of this run were achieved within the 19 days of continuous operation; three different operating pressure were evaluated as well as the effect of increased reactor severity and increased feed catalyst addition on low pressure operation. Samples of the various process streams were obtained for characterization of properties. The following conclusions can be drawn based upon these results :

- Using supported catalyst in both stages as well as a feed catalyst in the presence of CO/H_2 as the reducing gas results in an improvement in the overall quality of the product oil at normal operating conditions.
- Decreasing the operating pressure while using CO/H_2 as the reducing gas results in a decrease in overall performance as measured by distillate yield, coal conversion and resid conversion. It also results in a decrease in the quality of the product oil.
- The negative effects of lowering the operating pressure on overall performance and product oil quality can largely be mitigated by slightly increasing the severity and by increasing the feed catalyst addition rate. This demonstrates the possibility of performing high quality coal liquefaction at substantially reduced operating pressure with a potential for significant cost savings by reducing the capital investment needed for a higher pressure operating system.

RUN CMSL-08 (227-85)

EVALUATION OF COAL-PLASTICS CO-LIQUEFACTION IN CTSL MODE

SUMMARY

CMSL-08 (Run 227-85) was successfully carried out for 23 continuous days spread over five conditions to investigate the effects of co-liquefying the primary plastic constituents of municipal solid waste on the performance of a two-stage hydroconversion process in a 25 kg/day bench unit. This bench run was a follow up of the earlier exploratory work which was carried out in a 3 ton per day process development unit under a separate DOE "Proof-of-Concept" Contract. Although this work at the larger scale demonstrated the operational and technical feasibility of this type coprocessing, the interpretation of the results was clouded by the fact that the continuous operation was never under solvent-balance, i.e., employed significant proportions of the external make-up oil as a part of the recycle stream for the process. During this bench run, conditions were chosen to seek the optimum set of operating severity/catalysis for converting plastics together with Illinois No. 6 coal. A conscious effort was made to maintain the process under a net positive solvent-balance during the continuous operations, thereby minimizing any intrusive effects of an external make-up oil. The first stage reactor was provided with both supported Ni-Mo/Alumina and dispersed sulfated iron-molybdenum catalyst to ensure sufficient activity for hydrogenation of recycled solvent and for depolymerization of plastics, while the second stage reactor was a backmixed thermal reactor with no supported catalyst but with the converted dispersed catalyst, aiming at further depolymerization of the plastics and coal derived resid to lower molecular weight products.

The first two run conditions, Conditions 1 and 2 at a feed space velocity of 480 kg/hr/m³ reactor, compared process performance, product yields and quality between "coal-only" feed and "coal and mixed-plastic (25 W%)" combined feed (the mixed-plastic part of the feed was 50 W% HDPE, 35 W% polystyrene, and 15 W% PET). These two conditions established that performance with coal-plastics co-liquefaction was very similar, in terms of conversions and product yields, to direct coal liquefaction. Condition 1, with coal-only feed, resulted in about 96% total conversion, 91% resid conversion, and 72% distillate yield (all maf basis); the light gas yield and hydrogen consumption were high (11.4 and 7.5% maf respectively). Condition 2, with 25 W% co-mingled plastics in the feed with coal, resulted in about 96% total conversion, over 85% resid conversion, and 71% distillate yield; thus overall performance was maintained despite deactivation of the first stage supported catalyst. The light gas yield and hydrogen consumption were also lower during Condition 2 (9% and 6.9% maf respectively). Condition 3, with a higher feed space velocity of 640 kg/hr/m³, higher second stage K-2 temperature, and 25 W% mixed plastics in the feed, resulted in a drop in distillate yields and 524°C⁺ resid yield. The solvent-to-feed ratio had to be increased to about 2 in transition to Condition 4 with 33 W% mixed plastics in the feed and a space velocity of 480 kg/hr/m³. Due to the compensating effects of increased catalyst age (deactivation) in the first stage and a reduced space velocity during this condition as compared to the previous one, process performance was maintained. Light gas formation and

hydrogen consumption were lower during Condition 4, probably as a result of the increased plastics concentration in the feed. The last run condition, Condition 5, was similar to Condition 4 in terms of feed space velocity and reactor temperatures although instead of using mixed plastics, pure HDPE was used at 33 W% of the feed. Overall process performance deteriorated steeply during Condition 5, with distillate yield just over 50 W% maf and resid conversion of 62 W% maf.

Overall operations during this run were smooth, except for a few feed pump interruptions. The material balance was excellent (the average for the entire run was 100 W%) and the net recycle solvent-balance was positive throughout the run. The results from this bench run serve as a guide for further work in combined processing of coal and waste plastics.

BACKGROUND, OBJECTIVE, AND SCOPE OF WORK

CMSL-08 had the following technical objectives:

1. To investigate the effect of co-liquefying plastics (HDPE, PS, and PET) with coal on the yields and quality of the distillates from two-stage catalytic liquefaction of a bituminous coal in a solvent-balance operating mode.
2. To determine the effect of low-severity catalytic first stage close-coupled with a high-severity thermal (with dispersed slurry catalyst only) second stage reactor on the overall performance of the coal plus plastics co-liquefaction process.
3. To obtain samples of different process streams to assess their characteristics and shed light on the chemistry of converting polymeric plastics with bituminous coal.

An in-line hydrotreater was used during this run. Both the separator overhead oil and the ASOH streams were processed through the hydrotreater along with the unit knockouts. In order to characterize the quality of the unhydrotreated separator overhead stream, the hydrotreater was bypassed in Period 9. It was brought back on-line at the beginning of Period 10 and used until the end of the run.

RUN PLAN

The Run Plan, shown in *Table 11*, included five run conditions that were selected to meet the technical objectives specified above. Only the first condition was chosen to run on the coal-only feed for comparisons under similar process severity conditions. A solvent/feed ratio between 1.5-2.0, planned throughout the run, was based upon the earlier experience at the PDU level. Conditions 2 through 4 were chosen to study the effects of mixed plastics concentration in the

feed (@ 25 and 33 w%) and feed space velocity, while the last condition, Condition 5, investigated the effects of using HDPE at 33 W% of feed with coal on the process performance.

Feed

Illinois No. 6 Crown II Mine (L-811), the same coal that was used in PDU 260-04 operations, was used for CMSL-08 bench run. Two millimeter-size beads of high density polyethylene (HDPE), polystyrene (PS), and polyethylene terephthalate (PET) were used in preparing the combined feed. None of the feed plastics had any significant solubility in quinoline, the solvent used for solubilization and extraction of pressure filter solids from bench operations to determine conversions (to liquid and gaseous products). The analyses of the coal and plastics are shown in *Table 12*.

Start-up and Make-up Oil

Tank 4 Oil, L-814, a mixture of petroleum-derived and hydrotreated make-up oil used during POC-02 operations, was used for the start-up. The analysis of this oil is shown in *Table 13*.

Catalysts

Shell-317 1/32" extrudate catalyst (Ni-Mo/Al₂O₃) was used for the first stage reactor during CMSL-08. The catalyst was presulfided during startup using TNPS (tertiary di-nonyl polysulfide). Sulfated iron-molybdenum dispersed catalyst was added to reactor K-1 at 100 ppm Mo (and 700 ppm Fe) relative to feed and was carried over to the thermal reactor K-2 to provide some catalytic activity. The hydrotreater unit (HTU) was charged with triblobe Ni-Mo supported catalyst (Criterion C-411) that is believed to be Ni-Mo on alumina.

SYSTEM CONFIGURATION

Two reactors of the same volume were employed in this run. The first stage reactor (K-1) was charged with a supported catalyst and was operated as an ebullated bed. The second stage reactor (K-2) was operated as a back-mixed reactor with no supported catalyst. The second stage effluent was separated into a heavy bottoms stream, consisting of high boiling liquid/solid resid and a light overhead stream consisting of low boiling distillate liquids and gases. The bottoms stream was subsequently distilled under atmospheric pressure to remove light ends, as atmospheric still overheads (ASOH). Both the ASOH and the overhead stream from the hot separator (O-1 overheads) were fed to the top of the in-line hydrotreater. The hydrotreated product was the primary liquid product. The bottoms from the atmospheric still were filtered at elevated temperature and pressure to produce a solid-free liquid (PFL) and an oil-containing filter cake (PFC). Toluene extraction operation was used to recover the majority of the oil from the filter cake. The PFL and part of the solvent-extracted oil constituted the recycle solvent for slurring the feed. A simplified schematic diagram, along with the location of the sampling points, is shown in *Figure 13*.

FEED SLURRY PREPARATION

Laboratory tests indicated that a temperature of 220°C was needed to produce a homogeneous mixture of coal, mixed plastics, and recycle solvent. Pulverized coal (4-6 w% moisture), was mixed with recycle solvent at a temperature below 100°C in an agitated tank. The temperature was then raised slowly to 220°C, and a preweighed quantity of mixed-plastics was added to the hot coal/solvent slurry in small increments to avoid plugging of the recirculating pump. The resultant coal/plastics/oil mixture was continuously agitated at 220°C for about two hours to ensure homogeneity and complete melting of the plastics. Six to eight hour batches of feed slurry were prepared.

PERFORMANCE AND RESULTS

The average material balance (*Figure 14*) for the entire run (CMSL-08) was 100.1 w%. The Operating Summary of individual Periods during CMSL-08 is shown in *Table 14*. *Figures 15 and 16* show the operating conditions during CMSL-08 (feed space velocities, reactor temperatures, feed compositions, feed tank temperatures, and recycle ratios oil-to-solids). Except for the Condition 3, the total feed space velocity was maintained at about 480 kg feed/hr/m³ of reactor. The higher space velocity of 640 kg/hr/m³ during Condition 3 adversely affected operations and overall process performance. Reactor K-1 temperature was maintained in the 432-435°C range, while reactor K-2 temperature was varied between 440°C at the beginning to about 454°C during Conditions 3 through 5 to provide a high enough severity for hydrocracking the plastics. The oil-to-solids ratio was varied from 1.5 to about 2.0 to maintain pumpability of the feed slurry at higher plastics concentration in the feed. It can also be seen in *Figure 16* that due to the increased viscosity of the feed, the slurry mix tank temperature had to be progressively increased to maintain pumpability.

One of the primary objectives of CMSL-08 was to investigate coal/waste co-liquefaction under steady-state or equilibrated process conditions. An important factor in such processing is the net recycle solvent/balance. This has to be positive to ensure that no external make-up oil is needed for the slurry preparation, as the use of make-up oil would cloud the interpretation of the reaction data. It was feared that plastics, under typical coal liquefaction conditions, would result in substantial formation of light oils with resultant shortage of heavy recycle oil (400°C⁺ material). As shown in *Figure 17*, this was not the case. Even at recycle ratios between 1.5-2.0, overall net recycle solvent balance, calculated as net pressure filter liquid (PFL) production, was positive and increased progressively with the catalyst age during Conditions 2 through 5.

The calculation of daily material balances, coal conversions, normalized product yields, and other process performance-related indicators were carried out using available computer programs. Overall process performance during CMSL-08 is summarized in *Table 14* and is discussed in details in the following sections.

Total Feed (Coal+Plastics) Conversion

Typical feed conversions (based on the solubility of pressure filter solids in quinoline), obtained during equilibrated periods of different conditions of CMSL-08, are shown in *Figure 18*. Feed conversions were steady between 95 to 96 W% throughout the course of the run. The presence of plastics in the feed or the nature of the plastics did not seem to affect conversions.

524°C+ Residuum Conversion

Residuum conversion values varied between 62 and 91 W% (maf feed), as shown in *Figure 19*. The decrease in resid conversion from Condition 1 to 5 which was steeper than the normal trend (about 10 w% drop in both resid conversion and distillate yields), is explained on the basis of reactor K-1 supported catalyst deactivation. Therefore, it is believed that compounds boiling above 524°C were formed from the plastic component of the feed, especially the least reactive HDPE, as exemplified by the overall process performance during the last condition when HDPE alone was used with coal.

C₄-524°C Distillate Yield

Distillate yields, shown in *Figure 20*, followed a trend similar to that for resid conversions in going from Condition 1 to 5. Interestingly, distillate yields for Condition 1 (coal-only feed) and Condition 2 (coal+plastics) were similar (70 % maf feed); but decreased for the high space velocity Condition 3 and was maintained for Condition 4. Yields plummeted sharply in going from Condition 4 to 5 as a result of using 33 W% HDPE in the feed and the long catalyst age.

Hydrogen Consumption and Efficiency

Hydrogen consumption (*Figure 21*), varied between 1.8 to 7.5 W% (not feed). As expected, chemical hydrogen consumption decreased in going from coal-only operation. The coal/mixed plastics coprocessing. This was due to the lower light gas make during co-liquefaction operations and the higher chemical hydrogen content of the combined feed. Since C₄-524°C distillate yield was maintained in going from Condition 1 to 2, hydrogen efficiency with coal/plastics operation was always higher (*Table 14*) than with coal-only operation.

PRODUCT DISTRIBUTION

C₁-C₃ Gas Yields

As shown in *Figure 22* and *Table 14*, the normalized C₁-C₃ gas yields for CMSL-08 varied between 5.2 and 11.4 W% maf feed. The light gas yield was highest (11.4 W%) during the coal-only operation of Condition 1, but the yield decreased significantly during coal/plastics co-liquefaction operations (Conditions 2 through 5). The lowest gas yield was obtained during the last run condition which was with 33 W% HDPE and coal. These findings indicate that plastics, especially HDPE, are more refractory towards hydroconversion than Illinois No. 6 coal under the process severity/catalyst combinations used.

C₄-177°C Naphtha Yields

C₄-177°C Naphtha Yields are listed in *Table 14*. The yields of naphtha fraction varied between 12-24 W% maf feed. Run Condition 2, where the feed consisted of 25 W% co-mingled plastics and coal, resulted in over 23 W% light naphtha yield. Yields were also over 20 W% for Conditions 1, 3 and 4, but went down during Condition 5 as 38 w% HDPE was used in the feed with coal.

177-343°C Middle Distillate Yields

As shown in *Table 14*, the middle distillate yields were the highest selectivity yields among the distillate products. Varying between 18-40 W% maf feed. The highest middle distillate yield was obtained for Period 6 (Condition 1); and yields decreased steadily as the run progressed in the same fashion as the overall distillate yields.

343-524°C Heavy Distillate (Gas Oil) Yields

The heavy distillate yields for CMSL-08 varied between 12-22 W% maf feed, as shown in *Table 14*. Again, the highest gas oil yield was obtained for Condition 5, primarily the result of the catalyst aging effect coupled with the presence of 33 W% HDPE in the feed, which tends to give high boiling fractions.

524°C* Residual Oil Yields

The resid yields followed a normal increasing trend (*Figure 20*), commensurate with catalyst deactivation, in going from Condition 1 to 4. The nature of the feedstock, either coal-only or coal plus plastics, did not appear to influence the normal variation in resid yields. Condition 5, with hard-to-convert HDPE alone, resulted in a sharp increase in the resid yield from about 20 W% during Condition 4 to about 34 W% (both maf feed) for Period 22.

C₊524°C Distillate Yield/Selectivity

The selectivity of different distillate boiling fractions is shown in *Figure 23*. As shown in this Figure, Periods 7 and 8 in Condition 2 resulted in better selectivity distribution (higher selectivity to naphtha and middle distillate fractions) than most of the other periods.

INSPECTION OF PRODUCTS

Different product fractions (First-Stage/Second-Stage Vent Gases, CAS Bottoms, SOH, PFL, and PFS) from Work-up Periods 6, 11, 16, 20, and 22/23A were analyzed in detail. These analyses are listed in *Tables 15 through 20*.

SOH oil stream represents the net light distillate (IBP-343°C) from CMSL-08. While the hydrotreater unit was on-line the (entire run except for Period 9), the only distillate stream out was the SOH, as the O-1 hot separator overheads, ASOH, and unit knockouts were fed directly to the hydrotreater. The properties of the SOH oil for the work-up periods are shown in *Table 15*. The SOH oils had a typical boiling range of 66-370°C. The API gravities were high (> 35), and H/C atomic ratios were also high (1.73-1.82), especially during coal-plastics co-liquefaction operations. IBP-177°C, the lightest fraction of the SOH-oil was also higher during co-liquefaction operations than for the coal-only Condition 1. The heteroatoms level (nitrogen and sulfur) were extremely low throughout the run, indicating a very successful operation of the in-line hydrotreater. Typically, sulfur levels below 15 ppm and nitrogen levels were below 5 ppm were obtained for the SOH oil. The properties of SOH-oil, (H/C ratios and heteroatom contents), are shown in *Figure 24*.

The API gravity of the PFL varied between -8.1 to 11, while the 524°C⁺ resid content increased from 29.9 to 64.2 W% as shown in *Figure 26*. Detailed inspections of PFL and PFS for the work-up periods during CMSL-08 are shown in *Tables 16 and 17*. Interestingly, the API gravities and the H/C atomic ratios were, in general, significantly higher for the PFL streams obtained from co-liquefaction conditions than for the coal-only feed Condition 1. At the same time, the resid content of the PFL increased with catalyst age; this indicates that substantial contributions to PFL were made by the reacted/converted plastics. From the solubility behavior of the PFL resid fraction, it can be seen (comparing toluene and cyclohexane insolubles for Conditions 2 and 3 with 1) that more paraffinic (or waxy) type products from the plastics were contributing to resid formation in the PFL. The preasphaltene (toluene insolubles) and asphaltene (cyclohexane insolubles) contents of the PFL are listed in *Table 16* and are plotted in *Figure 25*. The solubility behavior of the PFL resid fraction from Conditions 2 and 3, with the combined feed, was better than with the coal-only Condition 1.

INTERSTAGE SAMPLES

Interstage samples are samples of first stage reactor slurry, that are withdrawn from the ebullating line on the reactor. These samples shed light on the performance of the first stage reactor in terms of feed and resid conversions. Interstage samples were collected during Periods 7A, 12A, 17A, and 21A to represent Work-up Periods in each of the selected run conditions. An interstage sample for the last run condition could not be obtained, as the sampling bomb plugged during Period 21A sample withdrawal. The interstage samples were pressure filtered hot and both the PFL and PFS were analyzed and worked-up separately. The pressure filter liquids was subjected to ASTM D-1160 distillation while the pressure filter solids were extracted with quinoline to determine coal conversions. *Tables 18 and 19* list all the information that was derived from the interstage samples analyses. The same behavior is observed for the API gravity and H/C ratio variations in going from the coal-only feed Condition 1 to the coal plus plastics Condition 2. API gravity improved while the H/C ratio increased significantly. Similarly, the toluene and cyclohexane solubility of the PFL resid fraction improved significantly. The resid fraction from the interstage PFL samples also appears to be waxy or more paraffinic in nature. This happened in spite of the overall increase in the total resid content of the PFL material. These results seem to point to significant resid material resulting from the HDPE in the feed.

HYDROTREATER PERFORMANCE

The in-line hydrotreater performed exceptionally well during CMSL-08. As shown in *Table 20*, the net process distillates exiting the hydrotreater as SOH contained, on average, less than 15 ppm sulfur and less than 5 ppm nitrogen. The H/C atomic ratio of the net distillates was high (1.8). In order to obtain a distillate sample before hydrotreating, during Period 9 the HTU was by-passed. The nitrogen and sulfur contents, as well as H/C atomic ratios, of the unhydrotreated distillates and their individual flowrates (ASOH, KO and O-1 Overheads) are shown in *Figure 27*. Over 95 W% of the nitrogen and sulfur in the HTU feed streams was removed by the hydrotreater to yield a premium distillate of less than 10 ppm N and S with a high H/C (1.78) ratio.

EXTERNAL SAMPLES

As mentioned earlier, a number of samples of different process streams from CMSL-08 were obtained the Consol, Inc. and for members of the Consortium of Fossil Fuel Liquefaction Science. These samples, their amounts, and the operating periods when these were withdrawn are shown in *Table 21*.

CONCLUSIONS

CMSL-08 was a very successful bench run from both the technical and operational standpoint. Over 22 days of continuous operation were completed without any major issues/interruptions, and the main technical objectives of the run were achieved. Three plastics/coal ratios, the effects of HDPE alone, and space velocity were studied. Samples of different process streams were obtained for the property characterization/assessment. The following conclusions can be drawn based on the results obtained during CMSL-08:

- Under similar reaction severity, 100% coal and 75 coal/25 W% plastics resulted in similar overall process performance. With plastics in the feed, the light gas make and hydrogen consumption were lower at the same level of total conversion and distillate yields than for coal-only.
- In general, plastics, especially HDPE, were harder to convert to 524°C⁻ material than either coal or the PS and PET components of the co-mingled plastic feed. This was evident from the waxy nature and solubility behavior of the PFL resid fraction from the co-liquefaction work-up periods.
- From the trends in process performance and reaction severity, it is clear that plastics demand more severe depolymerization/cracking environment than Illinois No. 6 coal. It is believed that an acidic additive (having a small percentage of PVC in the plastics feed might help, as small amounts of chlorine would be available to acidify the dispersed/supported catalyst) and high reactor temperatures (about 454°C) would help solve the problem (should also be better if this is done under atmospheric pressure).
- In-line hydrotreating was very effective for producing premium distillates with less than 10 ppm each sulfur and nitrogen.

RECOMMENDATIONS

Based upon the experience and findings from the bench run CMSL-08, the following recommendations are made for future R & D in this area:

- Higher reaction severity in coal/plastics conversion reactor for depolymerization of plastics. The effective temperature range for plastics seems to be between 430-450°C (from 30-60 minutes residence times).
- Mild hydrocracking/depolymerization step for waste plastics prior to their coprocessing with coal.
- Using petroleum-derived low quality vacuum resid for slurring the plastics and their pre-conversion before coprocessing with coal; in such a mode, recycle system could be eliminated.

TASK 4- TECHNICAL ASSESSMENT

No technical assessment activity was conducted during this quarter.

TASK 5- PROJECT MANAGEMENT

A paper on the findings from the CMSL Run No. 8, studying the co-liquefaction of coal with plastic wastes, was submitted for a presentation at the ACS national meeting to be held in Anaheim, CA, during April 2-6, 1995.

TABLE 1

CMSL-07 RUN PLAN

Coal : Black Thunder Mine Coal (HRI-6213)
 Catalyst: Hydrotreater: Criterion C-411 Trilobed (HRI-6135)
 K-1 & K-2: Shell-317 (HRI-5394)
 Additive: 200 ppm Mo as AHM additive

Condition		1	2	3	4
Periods		1-7	8-11	12-15	16-18
Feed gas:	1st Stage	CO/H ₂	CO/H ₂	CO/H ₂	CO/H ₂
	V/V %	75/25	75/25	75/25	75/25
	2nd Stage	H ₂	H ₂	H ₂	H ₂
Back Pressure, MPA		17.2	13.8	10.3	10.3
Temp, C					
	1st Stage	388	388	388	388
	2nd Stage	441	441	441	441
	Hydrotreater	379	379	379	379
Feed Catalyst (AHM) (ppm dry coal)		200	200	200	200
Solvent/Coal Ratio		1.2	1.2	1.2	1.2
Space Velocity (2nd Stage)					
lb dry coal/hr/ft ³ reactor		44.4	44.4	44.4	66.6
kg dry coal/hr/m ³ reactor		711	711	711	1067

TABLE 2

CMSL-07 ACTUAL RUN CONDITIONS

Coal : Black Thunder Mine Coal (HRI-6213)
 Catalyst: Hydrotreater: Criterion C-411 Trilobed (HRI-6135)
 K-1 & K-2: Shell-317 (HRI-5394)
 Additive: 200-500 ppm Mo as AHM additive

Condition		1	2	3	4
Periods		1-7	8-11	12-15	16-19
Feed gas:	1st Stage	CO/H ₂	CO/H ₂	CO/H ₂	CO/H ₂
	V/V %	75.5 / 24.5	75.2 / 24.8	75.0 / 25.0	74.8 / 25.2
	2nd Stage	H ₂	H ₂	H ₂	H ₂
Back Pressure, MPA		17.2	13.7	10.3	10.4
Temp, C					
	1st Stage	388	388	388	399
	2nd Stage	443	443	444	442
	Hydrotreater	379	379	379	379
Feed Catalyst (AHM) (ppm dry coal)		200	200	200	500
Solvent/Coal Ratio		1.2	1.2	1.2	1.2
Space Velocity					
lb dry coal/hr/ft ³ reactor		43.6	43.5	44.0	44.4
kg dry coal/hr/m ³ reactor		699	697	704	711

TABLE 3**ANALYSIS OF FEED COAL FOR CMSL-07**

HRI No.	6213
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MOISTURE CONTENT	11.47
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PROXIMATE ANALYSIS, WT% Dry Basis

Volatile Matter	43.48
Fixed Carbon	50.52
Ash	6.00

ULTIMATE ANALYSIS, WT% Dry Basis

Carbon	69.95
Hydrogen	4.50
Sulfur	0.39
Nitrogen	0.89
Ash	6.00
Oxygen (by diff.)	18.27

H/C RATIO, mol/mol	0.77
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TABLE 4

ANALYSIS OF START-UP SOLVENT / MAKE-UP OIL FOR CMSL-07

HRI No.	L-809
°API Gravity	6.3
ELEMENTAL ANALYSIS, Wt%	
Carbon	88.62
Hydrogen	9.32
Sulfur	0.58
Nitrogen	0.18
H/C RATIO, mol/mol	1.26
ASTM D-1160 DISTILLATION, °C	
IBP	311
5 V%	335
10 V%	343
20 V%	360
30 V%	378
40 V%	387
50 V%	406
60 V%	425
70 V%	445
80 V%	488
88 V%	524
Weight Percents	
IBP-343°C	9.71
343-454°C	59.51
454-524°C	15.24
524°C+	15.15
Loss	0.39

TABLE 5

CONDITION AVERAGE PROCESS PERFORMANCE FOR CMSL-07

CONDITION	1	2	3	4
Catalyst Age (kg Dry Coal/kg Cat)	157	269	352	488
REACTOR TEMPERATURES, °C				
K-1 Temperature	388	388	388	399
K-2 Temperature	444	443	444	442
Space Velocity (2 ND Stage) (lb Dry Coal/hr/ft ³ Reactor) (kg Dry Coal.hr/m ³ Reactor)	43.6 699	43.5 697	44.0 704	44.4 711
Relative Severity Index (1 @ 388 / 443 C & 321 SV)	1.05	1.04	1.06	1.28
1 ST Stage Gas Feed, V%				
H ₂	24.5	24.8	25.0	25.2
CO	75.5	75.2	75.0	74.8
PROCESS PERFORMANCE, WT% (MAF COAL)				
Coal Conversion	92.40	92.10	89.70	91.65
524+ C Conversion	92.40	88.00	80.65	89.6
C4-524C Distillate Yield	67.00	61.4	53.05	63.55
Hydrogen Consumption	8.31	7.25	6.14	7.42
NORMALIZED YIELDS, WT% (MAF COAL)				
C ₁ -C ₃ Gases	7.26	7.34	7.83	7.12
C ₄ -C ₇ Gases	3.39	2.75	2.90	3.34
IBP-177 °C	20.79	18.74	14.78	17.71
177-260 °C	18.94	16.25	18.47	16.02
260-343 °C	26.33	21.14	24.58	25.03
343-454 °C	-0.70	2.61	-6.97	2.48
454-524 °C	-1.74	-0.12	-0.66	-0.98
524+ °C	0.01	4.11	9.02	2.05
Unconverted Coal	7.59	7.88	10.35	8.35
Water	19.41	19.52	19.44	19.46
CO	0.52	0.52	0.51	0.51
CO ₂	5.12	5.20	5.09	5.09
NH ₃	1.04	.95	0.73	0.95
H ₂ S	0.40	.38	0.13	0.37
H ₂ Consumption	-8.31	-7.25	-6.14	-7.42

TABLE 6
ANALYSIS OF ASOH FOR CMSL-7

CONDITION	1	2	3	4
PERIOD	7	11	14	19
GRAVITY, °API				
IBP, °C	154	144	180	175
FBP, °C	351	363	346	346
ASTM D-86 DISTILLATION, WT%				
IBP-177 °C	1.08	2.04	0.0	0.11
177-260 °C	21.25	21.22	19.32	20.91
260-343 °C	72.17	70.74	77.61	75.69
343+ °C	4.85	5.89	2.96	2.97
Loss	0.65	0.11	0.11	0.32
ELEMENTAL ANALYSIS, WT%				
Carbon	88.31	88.15	87.95	88.01
Hydrogen	10.87	10.54	10.12	10.37
Sulfur (ppm)	30	95	109	76
Nitrogen (ppm)	120	2843	2357	2587
H/C RATIO, mol/mol	1.48	1.43	1.38	1.41

TABLE 7
ANALYSIS OF 1ST STAGE SOH FOR CMSL-7

CONDITION	1	2	3	4
PERIOD	7	11	14	19
GRAVITY, °API	26.8	26.4	26.6	24.0
IBP, °C	83.8	78.3	82.2	76.1
FBP, °C	399	406	404	406

ASTM D-86 DISTILLATION, WT%

IBP-177 °C	25.17	26.78	26.70	25.27
177-260 °C	10.74	12.95	13.18	13.19
260-343 °C	24.61	23.44	25.14	22.86
650+ °C	37.58	35.94	34.53	37.91
Loss	1.90	0.89	0.45	0.77

ELEMENTAL ANALYSIS, WT%

Carbon	86.76	86.63	86.63	85.81
Hydrogen	11.55	11.31	11.20	10.89
Sulfur (ppm)	455	937	1574	506
Nitrogen (ppm)	141	2329	2250	2878
H/C RATIO, mol/mol	1.60	1.57	1.55	1.52

TABLE 8

ANALYSIS OF 2ND STAGE SOH (HYDROTREATER OUTLET) FOR CMSL-7

CONDITION	1	2	3	4
PERIOD	7	11	14	19
GRAVITY, °API	36.2	36.8	37.6	33.7
IBP, °C	53.9	58.3	65.0	68.9
FBP, °C	379	389	358	402

ASTM D-86 DISTILLATION, WT%

IBP-177 °C	29.02	32.22	31.90	28.12
177-260 °C	25.71	25.80	32.02	23.69
260-343 °C	33.89	30.92	30.94	33.14
650+ °C	9.60	10.23	4.78	13.77
Loss	1.78	0.83	0.36	1.28

ELEMENTAL ANALYSIS, WT%

Carbon	86.45	86.86	86.41	87.00
Hydrogen	13.15	13.09	12.93	12.58
Sulfur (ppm)	7.1	<1.0	<1.0	<1.0
Nitrogen (ppm)	<1.0	<1.0	<1.0	<1.0
H/C RATIO, mol/mol	1.83	1.81	1.80	1.74

TABLE 9
ANALYSIS OF PFL FOR CMSL-7

CONDITION	1	2	3	4
PERIOD	7	11	14	19
GRAVITY, °API	1.8	-4.4	-8.0	-5.1
IBP, °C	293	311	289	306
ASTM D-1160 DISTILLATION, WT%				
IBP-343 °C	7.25	4.76	4.19	2.95
343-454 °C	51.32	47.44	44.24	47.68
454-524 °C	15.44	15.81	15.88	16.61
524+ °C	25.52	31.81	34.99	32.14
Loss	0.47	0.18	0.70	0.62
ELEMENTAL ANALYSIS, WT%				
Carbon	91.13	90.46	90.29	90.18
Hydrogen	8.10	7.36	6.88	7.18
Sulfur	0.048	0.050	0.166	0.104
Nitrogen	0.36	0.44	0.61	0.02
H/C RATIO, mol/mol	1.07	0.98	0.91	0.96
CCR, WT%	53.72	60.82	70.85	62.93
CYCLOHEXANE INS, WT%	29.03	70.14	86.85	61.19
TOLUENE INS, WT%	2.64	11.33	27.04	10.19

TABLE 10
ANALYSIS OF PFC FOR CMSL-7

CONDITION	1	2	3	4
PERIOD	7	11	14	19
ELEMENTAL ANALYSIS, WT%				
Carbon	65.10	66.18	72.41	70.66
Hydrogen	4.50	4.18	4.88	4.83
Sulfur	0.87	0.71	1.48	0.68
Nitrogen	0.47	0.57	0.74	0.62
Oxygen				
Ash				
H/C RATIO, mol/mol	0.83	0.76	0.81	0.82
COMPOSITION, WT%				
ASTM Ash	25.64	24.37	15.63	19.70
S in ASTM Ash	3.02	2.73	3.26	2.99
Mo in ASTM Ash	0.485	0.352	0.432	0.940
Quinoline Insolubles	53.43	54.94	41.40	44.84
n-Pentane Insolubles	61.66	63.85	61.02	60.09
Toluene Insolubles	56.33	58.30	47.73	49.53

TABLE 11

CMSL-08 Modified Run Plan

Feeds: Illinois No. 6 Crown II mine coal, HDPE, Polystyrene, and PET
 Back Pressure: 2500 psig

Catalysts: K-1: Shell-317 Supported + Dispersed Sulfated Fe/Mo Oxide
 K-2: Sulfated Fe/Mo Oxide carried over from K-1
 Hydrotreater: HRI-6135 (Criterion C-411 Trilobed)

CLOSED-COUPLED CTSL OPERATION WITH IN-LINE HYDROTREATER

	1	2	3	4	5
Condition	1-6	7-11	12-16	19-21	21-23
Period					
Feed Composition, W%	100	75	75	50	67
Coal	0	12.5	12.5	25	33
HDPE	0	8.75	8.75	17.5	0
Polystyrene	0	3.75	3.75	7.5	0
PET					
Temperature, C					
1st Stage	432	432	432	432	432
2nd Stage	443	443	454	454	454
HTU	379	379	379	379	379
Space Velocity	480	480	640	480	480
kg feed/h/m ³ Reactor					
Solvent/Total Feed, w/w	2/1.5	1.5	1.5	1.5	2
Feed Catalyst*					

*The total space velocity was reduced from 40 to 30 during Period 18 as a result of operating difficulties at higher space velocities; the dispersed catalyst addition rate was also doubled from 100 ppm Mo during Period 19 to improve process performance.

TABLE 12

Analysis of Coal and Plastic* Feedstocks for CMSL-08

HRI NO.	L-811	6235	6236	6237
Material	Illinois #6	HDPE	Polystyrene	PET
Moisture Content	4			
Proximate Analysis, W% Dry Basis				
Volatile Matter	41.48			
Fixed Carbon	48.08			
Ash	10.44			
Ultimate Analysis, W% MAF Basis				
Carbon	67.85	85.27	90.81	61.9
Hydrogen	4.55	14.61	7.71	4.13
Sulfur	3.99	0.037	0.01	0.01
Nitrogen	1.33	0.01	0.06	0.03
Oxygen (by diff.)	11.36	0.073	1.41	33.9
H/C Atomic Ratio	0.8	2.06	1.02	0.8

* All three plastics were initially completely insoluble in either quinoline or cyclohexane. The proximate analyses, S-in-Ash, Sulfur Forms, and Mineral Matter Forms Analyses are being done

TABLE 13

ANALYSIS OF START-UP/MAKE-UP OIL FOR CMSL-08

HRI No.	L-814
API Gravity	0.4
Elemental Analysis, W%	
Carbon	88.96
Hydrogen	8.25
Sulfur	2.22
Nitrogen	0.19
Oxygen	0.38
ASTM D-1160 Distillation, deg C	
IBP	295
5 V%	337
10 V%	360
20 V%	380
30 V%	395
40 V%	411
50 V%	423
60 V%	435
70 V%	453
80 V%	492
84 V%	510
WEIGHT PERCENTS	
IBP-329 C	5
329-440 C	53.99
440-510 C	22.18
550 + C	18.36
LOSS	0.47
% Aromatic Carbon	80.03
% Cyclic Hydrogen	44.36

TABLE 14

**CMSL-08: PROCESS PERFORMANCE SUMMARY
COAL/WASTE PLASTICS CATALYTIC CO-LIQUEFACTION**

Unit	227	227	227	227	227
Run	85	85	85	85	85
Condition	1	2	3	4	5
Period Number	6	11	16	20	22
Run Hours (end of Period)	144	264	384	480	528
W% Plastics in Feed	0	25	25	33	33
Dispersed Catalyst Loading, ppm Mo	100	100	100	200	200
Stage I Cat. Age, kg Feed/kg Cat	252	457	711	884	966
Stage I Feed Space Velocity kg Feed/hr/m3 reactor vol.	515.2	473.6	624	481.6	473.6
Oils/Solids Ratio	1.5	1.6	1.8	2.1	1.9
Total Material Recovery % (Gross)	102.2	98.4	96.7	101.2	99.6

ESTIMATED NORMALIZED YIELDS:

W% MAF FEED

C1-C3 in Gases	11.35	9.14	9.02	7.41	5.17
C4-C7 in Gases	4.81	3.27	3.41	3.17	3.27
IBP-177 C	15.86	20.48	19.00	17.63	8.80
177-260 C	17.99	12.57	8.59	11.16	7.60
260-343 C	21.14	19.85	12.27	16.88	10.72
343-454 C	10.18	11.84	15.18	11.54	14.24
454-524 C	2.29	2.94	5.60	4.22	6.43
524 + C	4.74	10.53	17.15	19.67	33.83
Unconverted Feed	3.90	4.07	4.50	4.40	4.22
Water	9.04	7.34	6.90	5.92	4.85
COx	0.67	0.80	0.86	0.57	0.16
NH3	1.50	1.08	1.04	0.82	0.27
H2S	3.98	2.98	2.84	2.52	2.24

Hydrogen Consumption	7.46	6.91	6.35	5.71	1.80
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PROCESS PERFORMANCE

Feed Conversion *, W% maf Feed	96.10	95.90	95.50	95.60	95.80
524 + C Conversion, W% maf Feed	91.40	85.40	78.40	75.90	62.00
C4-524 C Distillates, W% maf Feed	72.30	71.00	64.00	64.40	51.00
Hydrogen Efficiency, Kg Dist./Kg H2	9.69	10.27	10.08	11.28	28.33

*Based upon Quinoline Solubility of Products.

TABLE 15

CMSL-08: SEPARATOR OVERHEAD (SOH) INSPECTIONS

Unit	227	227	227	227	227
Run	85	85	85	85	85
Condition	1	2	3	4	5
Period Number	6	11	16	20	23A
Gravity, API	35.4	36.4	37.7	37.6	35.4
IBP, deg C	59.4	79.4	57.2	63.9	77.2
FBP, deg C	365.6	379	378.9	377.2	399.4
ASTM D-86 Distillation, Composition					
W % IBP-177 C	28.2	37.1	47.5	37.5	31.6
W% 177-260 C	31.8	22.2	20.9	23.4	24.2
W% 260-343 C	34.3	33.1	24.6	32.4	32.7
W% 343 + C	5.1	6.6	4.8	6.2	11.2
W% Loss	0.6	1	2.2	0.5	0.3
Elemental Analysis					
Carbon, W%	86.61	86.47	86.76	86.74	86.18
Hydrogen, W%	12.91	12.83	12.46	12.88	13.07
Sulfur, ppm	6.43	15.6	5.47	115.2	9.9
Nitrogen (Antek), ppm	< 1	8.1	< 1	5.2	3.85
Oxygen, W%	0.48	0.7	0.78	0.38	0.75
H/C ATOMIC RATIO	1.79	1.78	1.72	1.78	1.82

TABLE 16

CMSL-08: PROPERTIES OF THE PRESSURE FILTER LIQUID (2nd STAGE)

Unit	227	227	227	227	227
Run	85	85	85	85	85
Condition	1	2	3	4	5
Period Number	6	11	16	20	23A
Gravity, API	-4	3.7	11	-5.6	-8.1
IBP, deg C	263.3	291.7	296.7	282.8	319.4
ASTM D-1160 Distillation, Composition					
W % IBP-343 C	10.18	5.16	5.34	5.07	1.57
W% 343-454 C	44.95	35.05	34.84	25.09	21.19
W% 454-524 C	14.41	12.89	14.6	12.19	12.2
W% 524 + C	29.91	46.23	44.81	56.87	64.17
W% Loss	0.55	0.67	0.41	0.8	0.87
Elemental Analysis					
Carbon, W%	89.74	87.8	88.03	87.03	87.72
Hydrogen, W%	7.64	9.13	10.84	9.86	7.52
Sulfur, W%	0.285	0.378	0.433	0.455	0.683
Nitrogen, W%	0.76	0.63	0.4	0.68	1.33
Oxygen, W%					
H/C ATOMIC RATIO	1.02	1.25	1.48	1.36	1.03
CCR, W% PFL	18.85	5.47	9.81	29.1	31.6
CYCLOHEXANE INSOLUBLES, W%	20.58	13.84	15.39	31.57	39.3
TOLUENE INSOLBLES, W%	4.97	6.73	9.55	9.47	18.03

TABLE 17

CMSL-08: INSPECTION OF THE PRESSURE FILTER SOLIDS (2nd STAGE)

Unit	227	227	227	227	227
Run	85	85	85	85	85
Condition	1	2	3	4	5
Period Number	6	11	16	20	23A
Elemental Analysis					
Carbon, W%	46.27	47.3	47.15	44.76	44.5
Hydrogen, W%	3.16	3.55	3.11	2.89	2.93
Sulfur, W%	3.47	3.32	3.52	3.62	3.66
Nitrogen, W%	0.48	0.53	0.61	0.53	0.65
Oxygen, W%	45.7	45.3	45.62	48.2	48.26
H/C ATOMIC RATIO	0.82	0.90	0.79	0.78	0.79
Composition, W%					
TGA Resid	69.64	77.13	80.8	83.6	71.31
TGA Ash	44.51	43.77	46.06	45.77	45.65
Ash (Quinoline Filtration)	43.45	43.63	44.86	44.64	44.96
ASTM Ash, W%	44.55	43.32	44.3	45.52	45.65
S in Ash, W%	1.39	0.95	0.88	1.29	1.2
Unconverted Coal/Feed (Adj.)	14.6	20.98	23.58	26.21	25.66

TABLE 18

CMSL-08: PROPERTIES OF THE FIRST STAGE PRESSURE FILTER LIQUID

Unit	227	227	227
Run	85	85	85
Condition	1	2	3
Period Number	6	11	16
Weight % PFL	79.36	72.16	85.2
Gravity, API	-6.6	-4.9	-6
IBP, deg C	271.1	280	323.9
ASTM D-1160 Distillation, Composition			
W % IBP-343 C	7.9	4.1	1.0
W% 343-454 C	35.7	29.1	27.0
W% 454-524 C	12.4	13.8	16.0
W% 524 + C	43.3	52.3	55.5
W% Loss	0.7	0.7	0.5
Elemental Analysis			
Carbon, W%	89.2	87.8	87.8
Hydrogen, W%	7.3	10.3	7.6
Sulfur, W%	0.4	0.6	0.9
Nitrogen, W%	0.9	0.3	1.0
Oxygen, W%	2.6	1.0	2.7
H/C ATOMIC RATIO	1.0	1.4	1.0
CCR, W% PFL	25.4	27.9	28.3
CYCLOHEXANE INSOLUBLES, W%	37.1	20.4	32.1
TOLUENE INSOLBLES, W%	10.6	6.2	11.4

TABLE 19

CSML-08: INSPECTION OF THE FIRST STAGE PRESSURE FILTER SOLIDS

Unit	227	227	227
Run	85	85	85
Condition	1	2	3
Period Number	6	11	16
Elemental Analysis			
Carbon, W%	51.8	80.7	54.1
Hydrogen, W%	3.2	6.2	3.0
Sulfur, W%	3.1	3.4	4.1
Nitrogen, W%	0.6	0.9	0.7
Oxygen, W%	41.3	8.8	37.4
H/C ATOMIC RATIO	0.7	0.9	0.7
Composition, W%			
Ash (Quinoline Filtration)	39.8	11.0	39.6
ASTM Ash, W%	40.9	11.2	39.8
S in Ash, W%	2.8	2.2	2.0
Unconverted Coal/Feed (Adj.)	18.1	9.7	30.6

TABLE 20
PERFORMANCE OF AN IN-LINE HYDROTREATER

	<u>Feed*</u>		<u>Product</u>
	<u>O-1 Ovhd</u>	<u>ASOH+KOs</u>	<u>SOH-Stg II</u>
Flowrate, g/h	330.0	134.0	465.0
Nitrogen, ppm	221.0	116.0	8.0
Sulfur, ppm	505.0	473.0	15.6
H/C Atomic Ratio	1.5	1.5	1.8

*Flowrates are based upon the HTU Offline Condition.

TABLE 21**CMSL-08 : EXTERNAL SAMPLES**

Sample Description	Amount, gm	From Periods
Feed Slurry	300	6, 11, 16, 20, 23A
CAS Bottoms	300	6, 11, 16, 20, 23A
SOH Oil	300	6, 11, 16, 20, 23A
ASOH Material	300	6, 11, 16, 20, 23A
Pressure Filter Liquid	300	6, 11, 16, 20, 23A
Pressure Filter Solid	300	6, 11, 16, 20, 23A
Interstage (K-1) Slurry	200	6, 11, and 16

Figure 1

HTI SYNGAS - H₂ TWO-STAGE COAL LIQUEFACTION SCHEME

CMSL-7 (227-84)

MATERIAL BALANCE

FIGURE 2

CMSL-7 (227-84)

REACTOR TEMPERATURES

FIGURE 3

■ STAGE 1 ▼ STAGE 2

FIGURE 4

CMSL-7 (227-84) SPACE VELOCITY

CMSL7 (227-74)

FIGURE 5

RELATIVE SEVERITY

1 @ T1=388C T2=443C SV=711 (K-2 CAT)

CMSL7-7 (227-84)

UNIT BACK PRESSURE

FIGURE 6

CMSL-7 (227-84)

COAL CONVERSION

FIGURE 7

FIGURE 8

CMSL-7 (227-84)

RESIDUUM CONVERSION & YIELD

CMSL-7 (227-84)

FIGURE 9

GAS YIELD

■ C1-C3 ▲ C4-C7

CMSL-7 (227-84)

DISTILLATE YIELDS

FIGURE 10

CMSL-7 (227-74)

HYDROGEN CONSUMPTION

FIGURE 11

CMSL-7 (227-84)

CO CONVERSION

FIGURE 12

SIMPLIFIED SCHEMATIC FOR CMSL-08

FIGURE 13

FIGURE 15

CMSL-08: COAL/PLASTICS CO-LIQUEFACTION Daily Operating Conditions

FIGURE 14

CMSL-08: COAL/PLASTICS.CO-LIQUEFACTION The Daily Material Recovery Balances

FIGURE 16

CMSL-08: COAL/PLASTICS CO-LIQUEFACTION

Feed Tank Temp/Oil-to-Solids Ratio

■ SMT Temp □ Oil/Solids

FIGURE 17

CMSL-08: COAL/PLASTICS CO-LIQUEFACTION Solvent Balance (Net PFL Production)

FIGURE 18

CMSL-08: COAL/PLASTICS CO-LIQUEFACTION

Total Feed Conversion

FIGURE 19

CMSL-08: COAL/PLASTICS CO-LIQUEFACTION

Total 524 C+ Resid Conversion

FIGURE 20

CMSL-08: COAL/PLASTICS CO-LIQUEFACTION **C4-524 C Distillate & 524 C+ Yield**

FIGURE 21

CMSL-08: COAL/PLASTICS CO-LIQUEFACTION Hydrogen Consumption

FIGURE 22

CMSL-08: COAL/PLASTICS CO-LIQUEFACTION

Light C1-C3 Gas Yield

CMSL-08: Selectivity of Distillate Fractions for Work-up Periods

FIGURE 23

FIGURE 24

CMSL-08: COAL/PLASTICS CO-LIQUEFACTION

Properties of C4-370 C Distillates

FIGURE 25

CMSL-08: COAL/PLASTICS CO-LIQUEFACTION Solubility of PFL Product