CATALYTIC MULTI-STAGE LIQUEFACTION (CMSL)

DOE/PC/92147--T2-Vol. I

WORK PERFORMED UNDER DOE CONTRACT
No. DE-AC22-93PC92147

FINAL REPORT

RECEIVED
FEB 07 1997
OSTI

VOLUME I

RECEIVED
USDOE/PETC
96 DEC 10 PM 1:24
ACQUISITION & ASSISTANCE DIV.

Hydrocarbon Technologies, Inc.
1501 New York Avenue
Lawrenceville, NJ 08648

November, 1996

CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL (CMSL)
FINAL REPORT

VOLUME I

A.G. Comolli
P. Ganguli
W.F. Karolkiewicz
Theo L.K. Lee
V.R. Pradhan
G. Popper
T. Smith
R.H. Stalzer

WORK PERFORMED UNDER DOE CONTRACT
No. DE-AC22-93PC92147
October 1992 to December 1995

HYDROCARBON TECHNOLOGIES, INC.
1501 New York Avenue
Lawrenceville, NJ 08648

November 1996

CLEARED BY
PATENT COUNSEL

CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL (CMSL)

FINAL REPORT

TABLE OF CONTENTS

VOLUME I

VOLUME II

SECTION II DETAILS OF BENCH UNIT OPERATION (continued)

CMSL-6 - Run CMSL-6 (227-83) Evaluation of a Sulfated Iron-molybdenum Dispersed Slurry Catalyst for Thermal/Catalytic Liquefaction of Sub-bituminous Coal

CMSL-7 - Run CMSL-7 (227-84) Low Pressure Syngas Liquefaction of Sub-bituminous Coal in a Catalytic/Catalytic Mode of Operation, With AHM Molybdenum Additive

CMSL-8 - Run CMSL-8 (227-85) Evaluation of Coprocessing Plastics with Illinois Coal in a Catalytic/Thermal Mode with Sulfated Fe/Mo Additive

CMSL-9 - Run CMSL-9 (227-87) Evaluation of an All Dispersed Slurry Catalyst Multi-stage Back-mixed Reactor System For Liquefaction Sub-bituminous Coal and Coal/Plastics Coprocessing, using Molyvan Molydbenum and Iron Dispersed Catalysts

CMSL-10 - Run CMSL-10 (227-88) Evaluation of a Combined Iron-molybdenum Dispersed Slurry Catalyst System For Liquefaction of Sub-bituminous Coal

CMSL-11 - Run CMSL-11 (227-89) Evaluation of a Combined Iron-molybdenum Dispersed Slurry Catalyst System For Direct Liquefaction of Sub-bituminous Coal And Its Coprocessing With Municipal Plastic Waste

VOLUME III

SECTION III - DETAILED ECONOMIC EVALUATIONS

VOLUME I

SECTION I

ABSTRACT

CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL (CMSL)
FINAL REPORT

TABLE OF CONTENTS

LIST OF TABLES

CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL (CMSL) REPORT

ABSTRACT

Reported herein are the details and the results of laboratory and bench scale unit experiments that were conducted at Hydrocarbon Technologies, Inc. (HTI), under DOE Contract No. DE-AC22-93PC92147 during the period of October 1, 1992, to December 31, 1995. The program results described herein build on the previous technology base and investigating additional methods to improve the economics of producing transportation fuels from coal. This included purely physical parameters, coal treatment and variation in solvent to coal ratio, the use of syngas to replace part of the hydrogen as the reducing gas, the use of dispersed catalyst in addition to and replacing the supported catalyst, and the co-processing of coal with plastic waste material. The overall objective of this program is to produce liquid fuels from direct coal liquefaction at a cost that is competitive with conventional fuels. This report includes the results of an economic assessment of the various process strategies that were evaluated during this program.

Hydrocarbon Technologies, Inc. (HTI) has completed a research and development program, originally schedule for 24 months but was extended to 36 months, and which incorporates new concepts and ideas from HTI and Pittsburgh Energy and Technology Center, and builds on continuing developments at DOE—sponsored university and private contractor laboratories. These studies were performed in a continuous bench scale unit that is representative of commercial operations. This bench unit is unique in that it can be operated as a single, two, three or four stage reactor system, as an ebullated-bed, back-mixed, plug-flow continuous stirred tank reactor, or as a fixed bed system with provisions for interstage sampling in-line hydrotreating, and alternative solid separation systems. The bench scale unit was further modified during the program to include a hot slurry mixing system, an interstage separator, a hydrotreater, and a pretreater.

Technical assessment has shown that for coal only operations the cost of equivalent crude oil of $29 per barrel from Black Thunder Mine sub-bituminous coal can be attained, a reduction of $3 per barrel from that for earlier CTSL. Factors resulting in this improvement are: a) interstage removal of vapors which lowered the vapor load in the reactors for a more efficient reactor design; b) lower oil/coal ratio for slurry in feed coal; d) in-line hydrotreating downstream of the second stage reactor.

Prospectively substitution of mixed plastics for a portion of the coal fed would reduce the equivalent crude oil cost by as much as $10 per barrel. An equivalent crude oil cost for an operation with 50% plastic as low as $20 per barrel was estimated for a configuration that was not necessarily optimum, which used Mo and Fe additives only with no extrudate catalyst.

The direct addition of Synthesis Gas (50-84% CO) to the liquefaction reactors in place of high purity hydrogen increased the cost of equivalent crude oil by $0.4—$1.5 per barrel.

Catalyst additives, Mo as Molyvan lubricant additive and FeOOH, have the principal effect of increasing coal conversion over that obtained with supported Ni-Mo catalyst, by as much as 5% with sub-bituminous coal.

With only dispersed catalysts higher temperatures are required with increased light gas yields which reduced the advantage of lower catalyst concentration.

The lowest slurry oil/coal ratio successfully employed was 0.9 kg/kg.

When synthesis gas, 75-84% CO, was fed to the liquefaction reactor a supported Ni-Mo catalyst was very effective in promoting the shift reaction of Co to H_2, but also converted a large proportion of the CO to CH_4. With only catalyst additive, the proportion of CO reacted to H_2 was only 1/2—2/3 as great, but no CH_4 was formed.

Interstage removal of vapors with sub-bituminous coal conserved H2 by rejecting CO2 before it could be converted to CH_4 by supported catalyst in the second stage. The conservation was greatest with only catalyst additive in the first stage.

EXECUTIVE SUMMARY

The U.S. Department of Energy (DOE) and its predecessors have sponsored the development of coal liquefaction since the 1950s. As a result the United States has assumed a leading role in the advancement of direct coal liquefaction and coal utilization technologies. The cost of liquid fuel products from single stage technologies in the early 1980s, such as H-Coal, EDS, and SRC-II processes, was in the $50-70/barrel range. With the subsequent development of two-stage technologies, the yields and quality of distillates improved, consequently significantly lowering the cost of finished liquids from coal to about $35/barrel, equivalent to crude oil at about $30/barrel. Futher development is required to reduce the product costs of liquefaction by more than $5/barrel to be competitive with current crude oil prices.

The 36 month program described herein builds on the previous technology base while investigating other methods to improve the economics of producing transportation fuels from coal. This program looked at operating conditions, coal treatment and variation in solvent to coal ration, the use of syngas to replace part of the hydrogen as the reducing gas, the use of dispersed catalyst in addition to and replacing the supported catalyst; and the co-processing of coal with plastic waste material. The overall objective of this program is to produce liquid fuels from direct coal liquefaction at a cost that is competitive with conventional fuels.

Table 1 summarizes the principal variables studied in the eleven runs of the current program. The principal variables studied were: a) Use of molybdenum and iron additives in place of extrudate catalyst in one or both liquefaction stages; b) Use of synthesis gas in place of high purity hydrogen as the first stage feed gas; c) Lower pressure levels than the 17.2 MPa pressure generally used; d) Interstage withdrawal of vapors which proved to have product distribution and engineering advantages; and e) substitution of plastics for a portion of coal feed.

Economic evaluation studies were based on a fully-integrated grass-roots commercial facility to manufacture finished gasoline and diesel fuel liquid products. The liquefaction plant is a mult-train facility and the feed processing capacity has been selected assuming the construction of maximum-sized heavy-walled pressure vessels to carry out the liquefaction reactions. Liquefaction plant bottoms are gasified to meet a part of the hydrogen requirements of the complex. All utility needs in the complex are internally produced. Natural gas is imported to meet fuel requirements and for hydrogen manufacture. The equipment sizes and costs within the liquefaction plant have been factored from detailed engineering studies. The costs and operating requirements of the other process facilities and the off-sites have been estimated from the Baseline Design Study, developed by Bechtel for DOE. The Bechtel Baseline Design Study also provided the economic criteria and financing basis used in this evaluation.

A summary of the technical/economic evaluations is given in Volume I, Section II of this report. The experimental details of the eleven runs of the program are given in Volume I, Section III and Volume II of this report. The details of the technical evaluations are given in the Volume III of the report. Following are specific conclusions from this program.

- The addition of sodium lignolsulfonate surfactant did not improve the performance of the CTSL process either in terms of product yields or product quality.

- Lowering the solvent-to-coal ratio from previous typical values of 1.5-2.0 to 0.9 has a large positive benefit on the CTSL process. Increased distillate yields (8-9%) and resid conversion (4%) and improved recycle oil quality as measured by API gravity, H/C ratios and W% nitrogen and sulfur were obtaned. Capital costs are also reduced because of lower carrier liquid requirements.

- Interstage vapor product separation is very effective in enhancing liquefaction kinetics in the second stage reactor, thereby giving very high levels of resid conversion and light distillate yields. For sub-bituminous and low rank coals, hydrogen efficiency is also improved by removal of some of the oxygen as CO_2 after the first stage, preventing its conversion to CH_4. Also by reducing vapor flow in each reactor the amount of coal fed to each reactor can be increased resulting in appreciable reduction in plant and product costs.

- In-line hydrotreating is very effective for producing premium distillate with less than 10 ppm each sulfur and nitrogen, especially when about a third of the distillate product is obtained as a first stage reactor overhead during interstage product separation.

- The use of syngas as a replacement for hydrogen is technically feasible but has no apparent benefit with the bituminous and sub-bituminous coals that were evaluated.

- Dispersed catalyst, either substituting for supported catalysts or in addition to supported catalyst in both stages results in improved process performance, principally in increasing conversions of sub-bituminious coal by up to 6%, compared to operations with supported catalyst only.

- Recycling of dispersed Mo catalyst by recycling part of the ashy atmospheric still bottoms did not have any significant impact on the overall activity of the dispersed catalyst sytem.

- Use of 200-300 ppm Mo dispersed catalyst, without supported catalyst, was effective and gave lower product cost than systems using supported catalysts. Economic performance may be virtually the same with 110 ppm Mo. 5000-1000 ppm Fe in addition to Mo did not improve process performance sufficiently to compensate for the cost of the Fe additive.

- Overall process performance was significantly improved using plastics in the feed with coal, with decreased hydrogen consumption.

- When feeding a subbituminous coal, it was found that plastics had synergistic effects on coal conversion in terms of improved the C_4-524°C premium distillate yield.

- Reactivity of HDPE is improved under coal liquefaction conditions when other polymers, such as polypropylene and polystyrene, are present.

- Co-processing coal with 33% real life municipal solid waste resulted in 3-5 w% increase in distillate yield, one half the light hydrocarbon gas yield and decreased hydrogen consumption compared to "coal only" operations at the same conditions of severity and catalyst concentrations.

- From the trends in process performance and reaction seveity, it is clear that plastics require a more severe depolymerization/cracking environment than coal.

- Based on the results of "coal-only" operations performed during this program, it is estimated that premium oil products can be produced from coal at an equivalent crude oil price of less than $28/B. Coal/waste plastic coprocessing further reduce this to $20/B.

- The lowest equivalent crude oil price for coal-only operations was $28.70 per barrel for an operation with Black Thunder Mine sub-bituminous coal at 17.2 MPa pressure, using Ni/Mo supported catalyst in the both stages, and using an interstage separator and feeding the maximum amount of coal to each reactor because of the reduced vapor flow in such a configuration. With 33% of a commercially available recycled plastic substituted for a portion of the coal this cost was lowered to $21.80 per barrel.

- Operation at pressures at 10.3 MPa were successful and had equivalent crude oil price comparable to that at higher pressure when catalyst utilization is increased to maintain process performance.

- Reduction of the residence time from 30 to 5 minutes in a preheater/pretreater coil for activation of dispersed iron catalyst did not result in loss of process performance.

Operationally, this CMSL program was very successful with good on-stream efficiency and trouble-free incorporation of direct coupled in-line hydrotreating, interstage separation and product let-down, coil and reactor catalyst additive pretreatment, 3 stage configurations, and integration of dispersed and supported catalyst operations.

The extremely interesting results of this program lead to some recommendations for further work:

- Further studies are needed to optimize dispersed catalysts systems, which may include wet cake addition of dispersed iron catalyst, which could more economical than dry powder addition.

- The processing of 'real life' MSW plastics needs to be further explored and optimized.

- The efficacy of the dispersed catalyst reactor configuration should be investigated in coprocessing operations using low quality petroleum resids, waste plastics and coal.

- An alternative mode of processing should be investigated in which plastics are separately depolymerized/cracked in a back-mixed reactor in the presence of a suitable acidic catalyst and the resulting heavy slurry products (after gas and light distillate separation) mixed with coal and coal-derived recycle solvent, and fed to two-stage coal liquefaction. This follows as plastics, being inherently different from coal, both physically and chemically, require altogether different process severity/catalysts from than coal. The depolymerization/cracking reactor could operate under atmospheric pressure and would not be very capital intensive; also since the plastics-derived products are richer in hydrogen, hydrogen requirements for the overall proces would be lower.

CATALYTIC MULTI-STAGE COAL LIQUEFACTION
(Summary of Bench Run Conditions)

Table 1

RUN					RED. GAS		CATALYST					TEMP (C)		SV	
CMSL	227-	END DATE	DAYS	COAL	1ST STG	2ND STG	DISPERSED	1ST STG	2ND STG	Hydrotreater	Pretreater	1ST STG	2ND STG	Kg/hr /m3	Variable Studied
1	77	2/28/93	14 1/3	WYOMING	H_2	H_2	Mo FeOOH	None	NiMo	Yes	Yes	440	413	477-547	Coal Treatment
2	78	5/6/93	17 1/3	ILLINOIS	H_2	H_2	None	NiMo	NiMo	No	No	400-414	427-433	296-535	Solvent/Coal Ratio (1.1 to 0.9) Surfactant Added
3	79	7/21/93	15	WYOMING	CO/H_2O H_2	H_2	AHM	None	NiMo	No	No	388-399	427	318	Syngas as Reducing Gas Interstage Vapor Separation
4	81	3/23/94	17	WYOMING	CO/H_2O H_2	H_2	None	NiMo	NiMo	Yes	No	388-399	427-438	357-377	Reaction Severity and Syngas
5	82	4/20/94	16	ILLINOIS	CO/H_2O H_2	H_2	None	NiMo	NiMo	Yes No	No	399-413	427-441	320-480	Interstage Vapor Separation, In-Line Hydrotreating and Syngas
6	83	9/12/94	17	WYOMING	H_2	H_2	Mo on FeOOH	None	Reco. NiMo	Yes	No	427-449	413-429	480-640	Sulfated Iron-Molybdenum Dispersed Slurry Catalyst Ashy Recycle
7	84	10/21/94	19	WYOMING	CO/H_2O H_2	H_2	AHM	NiMo	NiMo	Yes	No	388	441	320-480	Pressure Syngas 10.4-17.2 MPa
8	85	12/20/94	23	ILLINOIS PLASTICS	H_2	H_2	Mo on FeOOH	NiMo	None	Yes	No	432	443-454	481-641	Feed Plastic Content (0, 25, 33%) Oil/Solids Ratio (1.5, 1.6, 1.8, 2.1) HDPE in Plastic (33, 100%) R1 Tmp (432 to 443 C), R2 Tmp (432 to 454 C)
9	87	5/18/95	41	WYOMING PLASTICS	H_2	H_2	Moly-van-A FeOOH	None	None	Yes	Yes	443-449	449-460	640	Feed Plastic Content (0,33, 50%) HDPE in Plastic (40, 100%) FeOOH (0, 10000 ppm) HTI vs. Exxon
10	88	6/29/95	16	WYOMING	H_2	H_2	HTI Fe Moly-van-A	None	None	Yes	Yes	441-449	449-460	481-801	Molyvan-A (0, 100 ppm) Wet Catalyst Cake
11	89	9/1/95	17	WYOMING PLASTICS	H_2	H_2	HTI Fe HTI Fe-Mo	None	None	Yes	Yes	441-449	449-460	641-721	Feed Plastic Content (0, 25, 33%) Plastic From Monmouth Recycling Oil/Solids Ratio (1, 1.5)

VOLUME I

SECTION I

PROJECT OVERVIEW

CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL (CMSL)
FINAL REPORT

VOLUME I

SECTION I - PROJECT OVERVIEW

TABLE OF CONTENTS

CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL (CMSL)
FINAL REPORT

VOLUME I

SECTION I - PROJECT OVERVIEW

TABLE OF CONTENTS
(continued)

VOLUME I

SECTION I - PROJECT OVERVIEW

LIST OF TABLES

VOLUME I

SECTION I - PROJECT OVERVIEW

LIST OF FIGURES

CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL (CMSL) REPORT

VOLUME I

SECTION I - PROJECT OVERVIEW

1.0 BACKGROUND

The U.S. Department of Energy (DOE) and its predecessors have sponsored the development of coal liquefaction since the 1950's. As a result, the U.S. has assumed a leading role in the advancement of direct coal liquefaction and coal utilization technologies. Recent developments in two-stage catalytic coal liquefaction technology at Hydrocarbon Technologies Inc.[1] (HTI) and at the Wilsonville Project using ebullated-bed technology have increased the yield and quality of distillates has led to more favorable economics to a distillate cost reduction of about 30% and more favorable economics.

The cost of liquid fuel products from single stage technologies in the early 1980's such as the piloted H-Coal, EDS and SRC II processes, was in the $50-70 per barrel range. With previous two-stage technologies, the yields of high quality distillates had been improved by over 50%, resulting in a product cost of $35 per barrel, this is competitive with crude oil at about $30 per barrel. Further effort was required to reduce the product costs from liquefaction by more than $5 per barrel to be competitive with products from crude oil.

HTI is active in trying to scale up and commercialize direct coal liquefaction technology in the U.S. and world-wide. HTI desires to continue research development of these technologies with the objective of reducing investment and operating costs and the cost of producing coal liquids so they can add to the market for refined products in the U.S. A commercial coal liquefaction industry in the U.S. would provide liquid transportation and utility fuels, using high sulfur feedstocks, and reduce our reliance on petroleum imports, improve the U.S. balance of payments deficit, and provide energy security. In addition, development of a lower cost process would provide a Clean Coal Technology which could be exported around the world.

Hydrocarbon Technologies, Inc. (HTI) has completed a research and development program (originally scheduled for 24 months but extended to 36 months) which incorporated new concepts and ideas from HTI and PETC and builds on continuing developments at DOE-sponsored university and private contractor laboratories. These studies were performed in a continuous bench-scale unit with a flow scheme representative of commercial operations. These bench units are unique in that they can be operated as a single, two, three or four stage reactor system, as ebullated-bed back-mixed, plug flow, continuous stirred tank reactor or fixed

---

[1] Formerly known as Hydrocarbon Research Inc (HRI). While the company has been restructured, the personnel and equipment at the HTI R&D Center have not changed

bed systems with provisions for interstage sampling, on-line hydrotreating and alternative solid separation systems.

The personnel of HTI have a commitment to coal liquefaction that goes back more than 30 years to the invention of the H-Coal® Process, a direct, catalytic hydro-liquefaction process, invented in 1964. In 1979, the goal of making coal liquefaction commercially competitive with petroleum took a major step forward with the opening of the nation's largest coal liquefaction plant using the H-Coal Process. Located in Catlettsburg, Kentucky, the demonstration plant was designed to convert 600 tons of coal a day into about 1,800 barrels of desulfurized heavy oil (for electric power generation or other industrial purposes) or 200 tons per day coal into 675 barrels of synthetic crude (for high-octane gasoline and low-sulfur home heating oil). Following the success of the Catlettsburg facility, HTI participated with Bechtel in the complete design and engineering of a 20,000 tons/50,000 barrels per day grass roots H-Coal Process to be located in Breckinridge, Kentucky. This base of experience in large scale ebullated-bed processes is unique to HTI and has resulted in the development of a body of technology, design information, and personnel which enables HTI to develop improved coal liquefaction technology. In the mid 80's coal liquefaction took a step forward with the development of Catalytic Two-Stage Liquefaction (CTSL).

The Catalytic Two-Stage Liquefaction (CTSL) process has been under DOE sponsored development since its inception in 1983. A key feature of the CTSL Process, which distinguishes it from other two-stage processes, is the first-stage, low-temperature, catalytic ebullated-bed reactor. Coal is dissolved in the recycle solvent at a slow rate allowing the catalytic hydrogenation reactions to keep pace with free radical formation. The second stage, operating at a higher temperature, completes residual oil and coal conversion, removes heteroatoms and produces high quality distillates at higher yields than competing technologies.

As a result of the controlled rate of liquefaction in the catalytic environment, recycle solvent quality is maintained and improved, thus providing very favorable hydrogen transfer and product stabilization. Solvent quality of the heavy distillates exiting the first stage is better than that of the recycled oils entering. As a result, the reactions in the second stage occur in an improved solvent environment, completing coal and residuum conversion and heteroatom removal without approaching a severity that causes significant dehydrogenation of the first-stage products.

Other distinguishing features of HTI's Catalytic Two-Stage Liquefaction (CTSL) Process are:

- Increased distillate oil yields from 3 bbl/ton (Catlettsburg H-Coal data) to over 5 bbl/ton, an increase of 50%, with a lower sulfur and nitrogen contents.

- Application of commercial ebullated-bed catalysts with further improvements in economics by cascading of more active first-stage catalyst into the second-stage. A recently demonstrated rejuvenation procedure holds promise for further cost reduction.

- Extinction recycle and conversion of 399°C$^+$ oils.

- Improved hydrogen utilization by process adjustments that maximize the amount of consumed hydrogen incorporated into the distillate liquid products.
- Production of more aliphatic/petroleum-like oils than other direct liquefaction processes with less than 10 ppm nitrogen and sulfur content in the light oil fractions.
- Improved energy efficiency and reduced costs through low temperature/high temperature reaction staging and reduced recycle slurry requirements (recycle to coal ratios reduced from 2.5/1 to 1/1).

This report on Catalytic Multistage Liquefaction (CMSL) discloses further process improvements, notably the incorporation of active dispersed catalyst systems, the interstage separation of vapors, and the addition of in-line hydrotreating.

2.0 PROGRAM DESCRIPTION

The objective of this project is to evaluate novel process concepts for direct coal liquefaction by modification of the Catalytic Two-Stage Liquefaction (CTSL) process. The tasks involved process studies in a continuous bench-scale unit. A technical assessment was performed which includes a design and economic study to complement DOE's Baseline Design and Modeling efforts. This report examines more effective hydrogenation catalysts, low temperature pretreatments of catalyst additives low solvent to coal feed ratios, in-line hydrotreating, interstage separation of vapors, alternative reducing gases and coal feedstocks of national interest.

The Statement of Work is as follows :

Task 1.0 Project Management Plan

Task 2.0 Laboratory Studies

- a. Pretreatment and low temperature activation
- b. Coal feedstock evaluation
- c. Catalyst qualification
- d. Catalyst deactivation studies
- e. Solvent quality testing
- f. Product quality testing
- g. Process modeling combined with bench-scale results
- h. Product hydrotreating and refining

Task 3.0 Continuous Bench-Scale Operations

- a. Combinations of dispersed and supported catalyst
- b. Alternative feedstock testing
- c. In-line hydrotreating
- d. Promotors, hydrogen sources and pretreatments
- e. Coal slurry feeds
- f. Process improvements

Task 4.0 Technical Assessment

3.0 PROGRAM OBJECTIVES

The program results described herein build on the previous technology base while investigating other methods to improve the economics of producing transportation fuels from coal. This investigation has included purely physical parameters (coal treatment and variation in solvent to coal ratio), the use of syngas to replace part of the hydrogen as the reducing gas, the use of dispersed catalyst in addition to and replacing the supported catalyst and the co-processing of coal with plastic waste material. The overall objective of this program is to produce liquid fuels from direct coal liquefaction at a cost that is competitive with conventional fuels. Specifically to:

- Improve the effectiveness and lower the costs of catalysts.
- Investigate coal pretreatment and low temperature hydrogenation.
- Test hydrogen sources and improve hydrogen management to reduce the cost of liquid fuels to less than $30.00 per barrel.
- Improve the quality and acceptability of fuels from direct liquefaction, addressing concerns of the 1990 Clean Air Act Amendment.
- Evaluate coals of national interest and identify coals that have a good potential for liquefaction at mild conditions.
- Improve process efficiency and reduce carbon oxide emissions during processing.
- Provide data for baseline design of in-line hydrotreating and lower solvent to coal operations.
- Screen new concepts using continuous bench-scale units prior to higher cost "proof of concept" demonstration.

4.0 BENCH UNIT DESCRIPTION

4.1 Basic Unit

Bench-Scale Unit No. 227, as shown in *Figure 1.1*, has two 2000cc catalytic ebullated-bed reactors in series, with reactor temperatures controlled by electrically-heated fluidized sandbaths. The reactors are close-coupled, that is effluent from stage one flows directly into stage two without product separation. The units operate continuously with typical run lengths of fifteen to thirty days and longer runs are possible, if desired. The unit is fully integrated in terms of providing coal slurry mixing, feed preheat, reaction and product separation/recovery, as part of the continuous operation.

Unit 227 is designed to operate at temperatures up to 480°C (900°F) and pressures as high as 20.9 MPa (3000 psig). It can process coal, coal/oil or oil only feeds at rates between (25 and 100 pounds per day). Each stage is capable of operating in a catalytic ebullated-bed mode. Nuclear detectors are utilized to detect and control reactor catalyst bed levels.

Feed slurry, consisting of coal and oil, is circulated around a slurry mix tank and pumped to reaction pressure by a piston feed pump. Fresh hydrogen is mixed with the slurry and charged to the first stage reactor. Hydrogen is also fed directly to the second stage. Both reactors typically use conventional ebullated-bed hydrogenation/hydroconversion catalysts. Ebullation of each reactor is maintained by a remote positive displacement pump/hot check system.

This unit is provided with equipment necessary to safely and effectively separate process derived oils and solids. The total effluent from the second stage passes into the hot separator. The vapors from this vessel pass through a water-jacketed cold separator, where water and light distillate products are condensed. Slurry from the hot separator and liquid from the cold separator are flashed through letdown valves to low pressure. Gases produced from this flashing are combined with the hydrogen-rich vent gas to produce a single gas stream which is metered, sampled and analyzed. The condensed separator overhead contains a water phase and the light hydrocarbon liquid products.

The separator bottoms slurry enters the atmospheric still, which provides effective topping of any recycled material. Atmospheric overheads (ASOH) are blended on-line with separator overheads to make one product. Atmospheric bottoms are processed off-line in a batch mode using either a pressure filter or a vacuum still for solid separation, to provide solids-free oil which is recycled for use in preparing the feed coal slurry.

Bench Unit 227 is operated for research, process development and process demonstration purposes. It is, therefore, critical to obtain very tight material balance closures. All unit feed and product stream rates are accurately measured. All samples, as well as identifiable system leaks (such as from pumps), are identified and quantified. Any material losses are quickly identified, and corrective action is taken to eliminate or minimize reoccurrence.

The bench unit is complemented by a Turnbull Control System (TCS) Maxi-Vis IV computerized data acquisition and storage system. The system is comprised of TCS software, TCS board-mounted signal processors, a Digital Equipment Company (DEC) MicroVAX 3400 computer with four terminals for operator interface. This system automatically acquires temperature, pressure, and other process related data directly from the operating units. Spot two-minute data is averaged on an hourly basis by TCS software and stored as hourly averages on the MicroVAX. The MicroVAX communicates these hourly averages to HTI's main computer, a DEC VAX 3095 via DECNET and Ethernet either hourly or on demand.

The VAX 3095 computer has a number of satellite terminals and personal computers throughout HTI's facilities. The hourly averaged data is utilized in calculating material balances, conversions and yields for eight-hour subperiods and for twenty-four hour yield periods. Through the use of standard report writers, the information is directly transferred to the final report. Graphics and statistical assistance are available on the VAX 3090 to allow more detailed evaluation of the data and preparation of technical report documents.

4.2 Unit Modifications During This Program

Hot Slurry Mixing Tank System

During part of this program a hot slurry mixing system was used for preparing the feed batches because of the need to transport the high coal concentration slurries into the reactor at pumpable viscosities and transporting slurries containing dissolved waste plastic along with coal. This system could mix slurries and heat them to proper temperatures for maintaining pumpability. Coal and solvent were mixed and the feed batches prepared in a predetermined proportion every six to twelve hours and were then transferred over to the feed charge pot. The slurry was then pumped continuously to the liquefaction reactors.

Interstage Separator

When an interstage separator was-used, the effluent from the first stage reactor passes into the interstage separator (actually at 340°C); the separator bottoms are then sent directly to the second stage ebullated bed reactor, K-2. The interstage separator overhead products are collected as Stage I SOH product after they have been separated from the non-condensibles in the cold separator. The non-condensible streams both from the interstage separator and from the second stage cold separator from the unit are metered, sampled for GC analyses and sent to flare. The interstage separator was used during syngas operation to recover any unreacted CO/H_2O. Fresh hydrogen was injected into the second stage.

Hydrotreater

When the hydrotreater was operated, the second stage vapors were sent directly to the hydrotreater. When the interstage separator was used, the first stage SOH would be pumped into the in-line hydrotreater. Also, for some operations the ASOH from topping the separator bottoms was pumped into the in-line hydrotreater. The first stage SOH and the ASOH were both sampled and weighed. Since the second stage SOH flowed directly to the hydrotreater, sampling was not possible with this stream.

Pretreater Reactor

For activation of the dispersed catalyst a pretreater reactor was used during some of the runs. The pretreater was a one half volume (1000 cc) back-mixed vessel placed between the feed tank and the first liquefaction reactor. Also, in later runs this pretreatment was effected by a coil preheater with a lower residence time.

5.0 BENCH UNIT STUDIES

This program consisted of a series of eleven CMSL bench scale runs studying:

- Physical Process Changes, including low solvent/coal ratios, addition of Surfactant with the coal feed, and withdrawal of first stages vapors before passing the slurry phase to the second stage reactor;
- Substitution of H_2/CO synthesis gas in place of high purity hydrogen as hydrogenating gas in the first stage. These operations included some operations with the system pressure lowered to 10.3 MPa from the level of 17.2 MPa usually employed;
- Use of iron and molybdenum catalyst additives fed with the coal in place of Ni/Mo extrudate catalyst in the first stage or in both stages;
- Co-processing of coal/plastic mixtures using specific plastics including HDPE, polystyrene, HIPS, PET, and polypropylene. Also, a plastic mix obtained from a commercial recycling facility was evaluated successfully;
- Economic evaluations were carried out using most of the operating results to evaluate the impact of the various parameters that were studied upon the cost of finished products in terms of an equivalent cost crude oil to produce the same products in a conventional refinery.

The details of each of the eleven CMSL runs in this programs are given in Section II Volume I and II of this report. The details of the economic evaluations are included in Section III Volume III..

The following sections of this program summary discuss the results of the five major areas specified above.

6.0 PHYSICAL PROCESS CHANGES

The major changes in operating procedures were:

- Determination of minimum practicable solvent recycle rates (Run CMSL-2);
- Installation of an interstage separator to withdraw first stage vapors from the process (Runs CMSL-3, CMSL-4 and CMSL-5), in connection with the use of Synthesis Gas feed to the first stage in portions of those runs which is discussed in more detail below. However, some of the operations of these runs had high purity hydrogen feed to both stages, which is discussed here;
- The use of a surfactant as proposed by the Jet Propulsion Laboratory (Run CMSL-2);
- In-line hydrotreating of the vapor product leaving the second stage reactor, along with middle distillate obtained by atmospheric pressure distillation of the slurry phase leaving the reactor.

  Runs CMSL-2, CMSL-4 and CMSL-5 used Shell S-317 1/32" extrudate catalyst, pre-sulfided during the start-up, in both stages. In Run CMSL-3 there was no extrudate catalyst in the first stage, and 1500 ppm molybdenum additive was included with the coal feed.

The major conclusions from these tests were:

- The lowest recycle solvent to coal ratio that was successfully used was 0.9 Kg/Kg;
- The interstage withdrawal of vapors with high purity hydrogen fed to the first stage, caused 3.5-6.5 W% increased elimination of CO_2 from the process in operations with sub-bituminous coal. This effect leads to a reduction in the potential hydrogen utilization because it avoids the formation of CH_4 and H_2O by the reaction of CO_2 in the second stage. The higher proportion of incremental CO_2 formation was with no extrudate catalyst in the first stage while adding 1500 ppm Mo with the feed coal, and the lower amount was with extrudate catalyst in the first stage. With a bituminous coal feed such an impact upon CO_2 formation was not apparent. Other process results with interstage withdrawal were equivalent to or superior to those obtained in the conventional two-stage operation. An ancillary potential advantage of interstage separation is the halving of vapor loading in each of the stages, permitting longer reactors (which is controlled by the allowable vapor velocity) with more coal feed per liquefaction train and simplified process configuration and lower product cost, which is discussed below in the summary of the economic evaluations;

- The addition of 2 W% of sodium lignosulfonate surfactant did not appreciably change the pattern of process results in the bench unit operations that had been apparent in the prior operations without the surfactant. Microautoclave tests did show a positive role of the surfactant at lower temperatures, 399°C, but such an advantage was not apparent at the higher temperatures used in the bench unit operations, 433°C;

- In-line hydrotreating consistently produced light/middle distillate products with sulfur and nitrogen content below 50 ppm, more usually below 10 ppm, and as low as 1 ppm (Run CMSL-7 which was a syngas operation (75% CO) with extrudate catalyst in both liquefaction stages).

6.1. Run CMSL-2 - Low Solvent/Coal, Surfactant

This run consisted of four different operating conditions. The first three conditions used solvent-to-coal ratios of 1.1 and 0.9, at two levels of severity of feed rate and reactor temperatures. There was an intermediate effort using a ratio 0.8, which was unsuccessful. In the final condition 2 W% of sodium lignosulfonate was added to the coal feed. The coal feed for the run was from Burning Star Mine No. 6.

A modified slurry feed preparation system was installed for Run CMSL-2. This system used a mixing tank that uniformly mixed 12-hour batches at temperatures of 93-232°C (200-450°F) which maintained pumpable slurry viscosity before transferring it to feed charge plot of the unit. Before the run this system was tested off-line successfully at various coal loadings. After Condition 1 of the run (at 1.1 solvent-to-coal loading), when this ratio was lowered to 0.8 in the seventh day, plugging developed in the feed pump discharge line and the unit was shut down. Operations were then resumed at a ratio of 0.9, which continued smoothly until the end of the 17 2/3 day run.

This direct liquefaction of bituminous Illinois No.6 coal in the CTSL mode, indicated superior process performance at the higher coal loadings (47-53 W% of feed slurry), when compared to the results of earlier bench runs at loadings of 33-40 W% coal, namely Run 227-37(I-18) which also used the Shell S-317 catalyst and Run 227-78(CC-16) which used Akzo AO-60 1/16" extrudate catalyst. The indicated advantage of Run CMSL-2 was about 8-9% higher C_4-524°C distillate yield with 4 W% higher 524°C+ resid conversion, than obtained in those two runs. Such improvements are not necessarily the consequence only of the low solvent/coal ratio used in Run CMSL-2, but also other evolutionary improvements in the process over the course of the CTSL program. Such improvements include more effective catalyst presulfiding using TNPS in Run CMSL-2, and deeper stripping of light ends from the recycle solvent so as to increase the proportion of residual oil in the recycled solvent and reduce the rejection as net product of the amount of the oil containing residual oil. Run CMSL-2 demonstrated that superior process performance could be maintained at relatively low solvent/coal ratios, and readily pumpable feed slurries were obtained at 0.9 solvent/coal ratio with the solvent containing as much as 42 W% of 524°C+ residual oil. The fractions of the recycle oil from CMSL-2 contained appreciably more hydrogen and less nitrogen and sulfur than in similar fractions of the products from the other two runs, indicating improved hydrogenation performance of the liquefaction catalyst.

The final operation (Condition 4) of the run with the addition of 2 W% sodium lignosulfonate appeared to continue without modification of the downward trend of distillate yield, with increased residual oil yield, evident in previous operations of the run. However, this operation with the surfactant had possibly slightly higher coal conversions, 93.0-93.2% compared to 92.4-92.9%, than comparable earlier operation of the run. Microautoclave testing showed a positive role of the surfactant at lower temperature, 399°C (750 °F), declining to no advantage as the temperature was increased to 441°C (825 °F). The first and second stage temperatures for the Bench Test were 413° and 433° C.

6.2. Run CMSL-3 - Interstage Separation

The primary purpose of Run CMSL-3 was to evaluate the use of synthesis gas (CO and H_2) in the first stage of the for liquefaction of sub-bituminous Wyoming Black Thunder Mine coal, using a catalyst additive in the first stage. The bench unit was modified to provide for the withdrawal of the vapor phase at the outlet of first stage, so that pure hydrogen only could then be added to the second stage. However, as reference operation the first Condition of Run CMSL-3 fed pure hydrogen to both stages as an evaluation of the effect of the interstage withdrawal of vapors.

The system for interstage withdrawal of vapors was installed for use in Run CMSL-3 for the operations with the synthesis gas feed. The first stage vapors are cooled to ambient with the condensate separated at pressure from the light gases, which are metered, sampled and analyzed. High purity hydrogen was fed to the second stage along with the slurry phase from the first stage. The first of the four conditions of the run was a reference operation with pure hydrogen being fed to both stages.

Based on microautoclave screening studies, the catalytic agent in the first stage was dispersed molybdenum-additive (ammonium heptamolybdate), 1500 ppm Mo added to dry coal feed, There was no extrudate catalyst in the first stage while the second stage was an ebullated bed of Shell S-317 supported Ni-Mo extrudate catalyst.

In the operation with pure hydrogen feed to the first stage the off gas from that stage contained considerably more CO_2, 7.4 W% of maf coal, than had been produced in earlier CTSL operations where first stage vapors passed into the second stage, 0.8 W% of maf coal. This difference and a consequent reduction of H_2O and CH_4 yields, effected a reduction in hydrogen consumption of about 0.8 W% of maf coal. In the conventional CTSL operations this amount of CO_2 would be converted to water and CH_4 when passed into the second stage.

Other differences in the results of this CMSL-3 operation with pure hydrogen feed to the first stage from those of the equivalent conventional CTSL operations were higher coal conversion (4.2%), higher residual oil yield (1.7%, with a residual oil concentration almost twice as high as in the CTSL operation), and lower C_4-524°C distillates yield (3.0 W%). The improved coal conversion and higher residual oil yield reflect the substitution of the molybdenum additive for the first stage extrudate catalyst. The inferior distillate yield is not consistent with the lower light gas yield, higher coal conversion, and small increase in residual oils which should result in a net increased distillate yield of about 2.5W%. This discrepancy is because the experimental decrease in water yield was only 20% of the increased CO_2 yield rather than the stoichiometric proportion of 70%, a difference of 3 W% of maf coal.

6.3. Run CMSL-4 - Interstage Separation

The primary purpose of Run CMSL-4 was to evaluate the use of synthesis gas (CO and H_2) in the first stage in the liquefaction of sub-bituminous Wyoming Black Thunder Mine coal, with extrudate catalyst in both stages. However, the first of four conditions of the run was a reference operation with pure hydrogen being fed to both stages. In this operation with pure hydrogen feed to the first stage the off gas from that stage contained considerably more CO_2, 4.3 W% of maf coal, than had been produced in earlier CTSL operations where first stage vapors passed into the second stage, 0.8 W% of maf coal. This difference and a consequent reduction of H_2O and CH_4 yields, effected a reduction in hydrogen consumption of about 0.3 W% of maf coal. In the conventional CTSL operations this amount of CO_2 would be converted to water and CH_4 when passed into the second stage. Compared to the operation with the additive catalyst in the first stage in Run CMSL-3, in Run CMSL-4 there was 3.1 W% of maf coal less CO_2 and 0.6 W% more CH_4 in the off-gas from the first stage. The extrudate catalyst in the first stage apparently promotes the conversion of CO_2 (and CO) to CH_4 to a greater degree than with additive catalyst.

6.4. Run CMSL-5 - Interstage Separation, In-line Hydrotreating

This run of 16 days duration involved four sets of operating conditions. The coal feed for this run was Crown II Mine Illinois No. 6 Coal. The first three sets of conditions were with fresh hydrogen being fed to both of the stages, with the interstage vapors being withdrawn and only slurry phase passing to the second stage, at two levels of temperature-feed rate severity. For second of these conditions, 2 W% (on coal) H_2S was added to the second stage to learn of any impact on process results. The fourth condition substituted a 75/25 v%/v% CO/H_2 synthesis gas as the first stage gaseous feed, while fresh hydrogen was fed to the second stage. The solvent-to-coal ratio throughout the run was 0.9, without any operating problems.

The system for interstage withdrawal of vapors had been installed for use in Run CMSL-3. In Run CMSL-5 the first stage condensate was pumped to the inlet of the in-line hydrotreating reactor which was in the vapor line downstream of the second stage liquefaction reactor. The hydrotreater feed also included the ASOH, which was a 120-370°C distillate that was distilled at atmospheric pressure from the second stage product slurry.

The first operations of Run CMSL-5, at high coal space velocity of 108 Kg/h/M^3 (catalyst) (67 lb/hr/f^3) and reactor temperatures 413° and 441°C (775° and 825°F) resulted in high values of coal conversion (96%), 524°C+ resid conversions (94%), and C_4-524°C distillates yield (79% of maf coal). These values are about 3% higher than obtained without interstage separation in Run CMSL-2. However, they mostly reflect the higher reactivity of Crown II mine coal compared to the Burning Star Mine coal which showed a similar margin in microautoclave testing of the two coals. The vent gas from the first stage contained relatively small amounts of CO and CO_2 (averaging 0.3 W% of dry coal), indicating little advantage of interstage separation with this higher rank, relatively low oxygen content coal in avoiding possible methanation if allowed to pass through to the second stage.

The Hydrotreated product contained 17-50 ppm sulfur and 10 ppm or less of nitrogen when operated at 357°C or 379°C (675° or 715°F). The hydrodesulfurization of organic sulfur was 97-98%, and hydrodenitrogenation 91.4-96.3%.

The principal conclusions from the results of Run CMSL-5 are the following:

- C_4-524°C Distillate yield of up to 79 W% of maf coal was obtained with this Illinois No. 6 coal.
- The apparent reaction kinetics of residual oil conversion is only minimally affected by interstage withdrawal of the vapors. That is, the relation to catalyst age of residual concentration in the system was virtually the same for the two modes of operations.
- The addition of sulfiding agent to the second stage, to compensate for the withdrawal of H_2S in the first stage vapors, did not appreciably alter the pattern of catalyst deactivation apparent in progressive increased residual oil concentration in the slurry phase liquid product, lowered hydrogen contents, and increased nitrogen and sulfur contents.
- In-line hydrotreating produces premium full range distillate product with less than 10 ppm nitrogen, and as low as 17 ppm sulfur.

7.0. OPERATIONS WITH SYNTHESIS GAS FEED

Much work has been reported in the literature of work performed at the University of North Dakota and the Pittsburgh Energy Technical Center indicated the effective hydro-liquefaction of coals using Synthesis Gas in place of high purity hydrogen. The work in the current CMSL program has confirmed virtual equivalent liquefaction performance when using Synthesis gas of that type of operation, but has indicated that some problems with CH_4 Synthesis from the CO (with extrudate Ni-Mo catalyst) and relatively low utilization of the CO when dispersed catalysts were used.

- Synthesis Gas (15-25% hydrogen, 75-85% carbon monoxide) was fed to the first stage in portions of Runs CMSL-3, CMSL-4, CMSL-5, and CMSL-7. In these runs the product vapors from the first stage were separated, using an interstage vapor-liquid separator, from the slurry phase which continued on to the second stage where pure hydrogen was added.

- In Run CMSL-3 the feed coal was from the Wyoming Black Thunder Mine, along with 1500 ppm molybdenum additive, with extrudate Ni-Mo catalyst only in the second stage):

- In Run CMSL-4 the feed coal was also the Black Thunder Mine coal with extrudate Ni-Mo catalyst in both stages;

- In Run CMSL-7 the feed coal was also the Black Thunder Mine coal along with 200-500 ppm molybdenum additive with extrudate catalyst in both stages;

- In Run CMSL-5 the feed coal was Illinois No. 6 coal from the Crown II Mine and there was extrudate Ni-Mo catalyst in both stages.

- In Run CMSL-7, in addition to operations at the normal pressure 17.2 MPa (2500 psig), there were operations at pressures of 13.7 and 10.3 MPa.

The principal conclusions from these operations were the following:

- The product distribution when feeding syngas to the first stage was not appreciably different from that obtained when hydrogen was fed to the first stage.

- The conversion of CO to hydrogen was fairly efficient, 75%, when extrudate catalyst was used in the first stage approaching the amounts to be expected if the water gas shift reaction with water attained equilibrium at the temperatures used.

- However, when there was no extrudate catalyst in the first stage, the CO conversion, 45%, was far less efficient with equilibrium ratios a full order of magnitude lower than thermodynamic equilibrium values.

- The extrudate catalyst, however, did promote some synthesis of CH_4 from the CO which reactions consumed up to 50% of the CO reacted.

- When the only catalyst in the first stage was the molybdenum additive there was essentially no formation of CH_4 from CO.

- The yield of distillate liquids for the lowest pressure operations was appreciably lower than for the operations at the normal pressure. This decrease could be offset in part by an increase in catalyst usage.

7.1 Run CMSL-3 - 75% CO, 1500 ppm Mo, S-317 Second Stage Catalyst

Conditions 2, 3, and 4 of this 15 day run with the Black Thunder Mine Coal used the synthesis gas feed (75% CO) to the first stage, along with water (40 W% of the coal feed, or 1 mole/mole CO) to promote the water gas shift reaction to produce hydrogen. About 45% of the carbon monoxide was converted, which indicated a considerable degree of the shift reaction promoted by the molybdenum additive in the first stage although somewhat less than the amount to be expected if the shift reaction had reached equilibrium. The water gas equilibrium ratio (H_2*CO_2/CO*H_2O) during Run CMSL-3 was 0.4-0.8, compared to an equilibrium values of about 12-13 at the first stage temperatures, 388-399°C. With the synthesis gas feed the CH_4 formation in the first stage was no higher than had been obtained in the Condition 1 operations of the run where the first stage feed was pure hydrogen, indicating that the molybdenum additive did not promoted CH_4 synthesis from the carbon monoxide.

The principal change in overall process results in switching to Syngas feed from pure hydrogen was an increase in coal conversion from 89.5% to 92% and a corresponding increase in C_4-524°C distillate yield to a value of 64.6% of maf coal, and virtually the same hydrogen consumption for the two modes of operation. The CH_4 formation in the second stage was slightly higher when synthesis gas was fed to the first stage than when hydrogen was fed to that stage (and hydrogen to the second stage), an average of 2.1 W% compared to 1.4 W% of maf coal fed. Nominally, a CO-Coal adduct was transferred from the first to the second stage where it was converted to CH_4, This increment of second stage CH_4 formation corresponds to 1% of the CO fed to the first stage.

However, apparently first stage performance was not as effective with the Syngas feed, with a lower conversion in first stage, 86.3% against 91.5%, and a higher residual oil concentration in liquid phase, 47.6% against 36.9%, indicating less secondary reaction of the residual oil. Also, the condensate from the interstage vapors contained less hydrogen, 11.37 W% against 11.74%. Overall, there did not appear to be a substantial disadvantage in net product distribution in the Syngas operation.

7.2 Run CMSL-4 - 86% CO, S-317 Catalyst in Both Stages

Synthesis gas (86% CO) was fed to the first stage, along with water (40 W% of the coal feed, or 1 mole/mole CO) to promote the water gas shift reaction to produce hydrogen, during Conditions 2, 3, and 4 of this 17 day run with the Black Thunder Mine Coal, using extrudate catalyst in both stages. About 70-75% of the carbon monoxide was converted, which indicated a higher degree of the shift reaction promoted by extrudate catalyst in the first stage than occurred in Run CMSL-3 with the molybdenum additive, much closer to the amount to be expected if the water gas shift reaction had reached equilibrium. The water gas equilibrium ratio (H_2*CO_2/CO*H_2O) during Run CMSL-4 was 7.0-7.2 compared to equilibrium values of about 12-13 at the first stage temperatures, 388-399°C. In Run CMSL-4 with the synthesis gas feed the CH_4 formation in the first stage was 3-5 W% of maf coal higher than had been obtained in the Condition 1 operations of the run where the first stage feed was pure hydrogen, indicating that the extrudate catalyst promotes CH_4 synthesis from the carbon monoxide. This incremental first stage CH_4 formation corresponded to 5-6 M% of the CO in the synthesis gas.

Also, the CH_4 formation in the second stage was higher when synthesis gas was fed to the first stage than when hydrogen was fed to that stage (and hydrogen to the second stage), an average of 3.0 W% compared to 1.2 W% of maf coal fed, similar to the pattern of these yields of Run CMSL-3, although in Run CMSL-4 this increase in CH_4 yield was over twice as great. Nominally, dissolved CO or a CO-Coal adduct was transferred from the first to the second stage where it was converted to CH_4. This increment of second stage CH_4 formation corresponds to 2-3 M% of the CO fed to the first stage. Also, second stage C_2 and C_3 hydrocarbon yields apparently increased when feeding syngas to the first stage, by an average of 0.4 and 0.3 W% of maf coal, respectively, small differences but statistically significant.

The principal change in equilibrated overall process results in switching to Syngas feed from pure hydrogen was an increase in coal conversion from 86.8% to 87.6% and a corresponding increase in C_4-524°C distillate yield to 58.5% of maf coal, and virtually the same hydrogen consumption for the two modes of operation. However, during the initial operations with the synthesis gas feed conversions were as high as 89.9% before stabilizing at the lower level. A subsequent higher severity operation, by a factor of 1.5-1.6, increased coal conversion by 3.2%, but the C_4-524°C distillate yield increased by only about 0.4 W%. Further operations of the run encountered falling CO feed rates, which had an interval with conversions as high as 92.1% when the CO feed concentration was 66%, but declined finally to 86.8% when the CO feed fell further to about 20% of the earlier rates, with about 30% CO in the syngas. Apparently, there is an optimum value of the CO concentration with respect to obtaining the maximum coal conversion.

The overall results show that syngas feed to the first stage, along with interstage venting, can maintain or perhaps slightly improve conversion and distillate yields. For the sub-bituminous coal, the interstage venting in itself results in increased CO_2 yield resulting in lowered CH_4 and H_2O yields, and lowered hydrogen consumption. The extrudate catalyst is a relatively effective water gas shift reaction catalyst, but also promotes the formation of CH_4 and other light hydrocarbons from CO, which secondary reactions in this run consumed in effect about 52% of the CO that was reacted in the first stage (considering the hydrogen consumed in forming the light hydrocarbons and water).

7.3. Run CMSL-5 - 75% CO, Extrudate Catalyst in Both Stages

During Condition 4 of this 16 day run with the Crown II Mine Illinois No. 6 Coal, using extrudate catalyst in both stages, Synthesis gas (75% CO) was fed to the first stage, along with water (30 W% of the coal feed, or 0.5 mole/mole CO at the target rates) to promote the water gas shift reaction to produce hydrogen. Conditions 1, 2, and 3 had pure hydrogen fed to both stages.

At the target rates 41% of the carbon monoxide was converted, probably because the limited availability of H_2O for the water gas shift reaction. The water gas equilibrium ratio ($H_2*CO_2/CO*H_2O$) during this operation in Run CMSL-5 was about 5 compared to equilibrium values of about 12 at the first stage temperatures, 399°C, indicating that the extrudate catalyst was fairly effective in promoting the shift reaction. In Run CMSL-5 with the synthesis gas feed the CH_4 formation in the first stage was 3.9% of maf coal higher than had been obtained in the Condition 3 operations of the run where the first stage feed was pure hydrogen, indicating that the extrudate catalyst promotes CH_4 synthesis from the carbon monoxide. Also, there were similar increases in the yields of C_2 and C_3 hydrocarbons of 0.4 and 0.3 W% of coal fed. This incremental first stage light hydrocarbon formation corresponded to 14 M% of the CO reacted.

In addition, the light hydrocarbon formation in the second stage was higher when synthesis gas was fed to the first stage than when hydrogen was fed to that stage (and hydrogen to the second stage), with 0.8 W% higher CH_4 yield and possibly 0.1 W% higher C_2 and C_3 yields. As in Runs CMSL-3 and CMSL-4-4, apparently, dissolved or entrained CO or a CO-Coal adduct was transferred from the first to the second stage where it was converted to CH_4. This increment of second stage hydrocarbon formation corresponds to 3 M% of the CO reacted.

The principal change in equilibrated overall liquefaction results in switching to Syngas feed from pure hydrogen was very little impact on coal conversion at 94.9% and 95.1% of maf coal, but the C_4-524°C distillate yield fell from 72.8 W% of maf coal to 69.7 W%, reflecting a corresponding increase in yield of 524°C+ residual oil. Hydrogen consumption by the coal was slightly lower, by 0.2 W% of coal, with the syngas feed. In general, during the syngas operation all of the liquid product fractions that had not passed through the hydrotreater had hydrogen contents that were 0.6-1.3 W% lower than in the previous operation with hydrogen feed. While some of this decline is associated with increased catalyst age, it was approximately twice as great as had been experienced over a similar interval of the earlier operations of the run. Similarly, the increase in residual oil yield for this syngas operation was over twice as great as expected based on the trends earlier in the run.

Subsequent to this target operation with syngas the CO flow fell off (while the hydrogen flow to the first stage was maintained), finally to one-fifth of the intended value, so that the CO concentration in the syngas decreased to 37%. The increase in residual oil concentration in the product oil was partially reversed, but the distillate oils produced had a higher proportion of heavy distillates.

These Syngas results were inferior to those expected for a hydrogen only operation. However, the use of a low proportion of water to CO probably did not permit complete utilization of the CO addition.

7.4. Run CMSL-7 - 75% CO, Extrudate Catalyst in Both Stages Molybdenum Additive Fed with Coal

This 19 day run feeding Black Thunder Mine sub-bituminous coal used syngas (75% CO, with 1.0 H_2O/CO) feed to the first stage throughout the run. Both reactors were charged with Shell S-317 Ni-Mo extrudate catalyst, and in addition ammonium heptamolybdate (AHM) was fed with the coal to the first stage. Normal system pressure (17.2 MPa or 2500 psig) was used initially, lowered for Condition 2 to 13.8 MPa, and finally to 10.3 MPa for Condition 3. In Condition 4, a restart with 26% fresh extrudate catalyst added to the first stage when a plug formed when withdrawing a first stage slurry sample, the first stage temperature was increased by 11°C and the molybdenum addition was increased from 200 ppm to 500 ppm.

The operations at 17.2 MPa pressure of Run CMSL-7 gave the coal conversion level, 92.4% of maf coal, experienced in Run CMSL-3 associated with use of molybdenum additive with the feed coal, and high conversion of CO in the first stage, 88%, associated with the use of extrudate catalyst in the first stage in Run CMSL-4. This operation achieved virtual elimination of the heavy oil product boiling above 343°C (650°F) with a distillate yield of 70 W% of maf coal. Lowering the pressure to 13.8 MPa had little impact on coal conversion, but increased residual oil yield by 4.1 W% and lowered distillate yield to 65 W%. The further reduction of pressure to 10.3 MPa resulted in a lower coal conversion, 89.7%, increased residual oil yield to 9.0 W%, and lowered distillate yield to 56 W%. The resumption of operations in Condition 4, at the lowest pressure level, gave improved coal conversion, 91.6%, improved residual oil yield, 2 W%, and improved distillate yield, 67%. These improvements are the consequence of the increased amount of molybdenum additive, the addition of some fresh catalyst to the first stage, and possibly some regenerative effect of the light oil washing of the first stage catalyst that was recharged before Condition 4. These results show that the use of lower pressures can be compensation for by increased catalyst utilization.

The light gas yields from coal were not significantly different at the three pressure levels. However, there appeared to be appreciably less CH_4 formation in the first stage, presumably from CO, at the lower pressure levels. Hydrogen consumption (including that in the distillate hydrotreater downstream of the second stage reactor) was 25% lower in the operations at 10.3 MPa pressure than in those at the 17.2 MPa pressure, primarily reflecting the higher proportion of higher boiling, lower hydrogen content product fractions.

Throughout the run the hydrotreated distillates contained less than 1 ppm of nitrogen or sulfur. The distillates that were hydrotreated had contained less hydrogen, by 0.2-0.6 W%, for the low pressure operation than for the high pressure operation. The heavier distillates and residual oil products contained progressively less hydrogen, by 1.5-3.0%, as the run continued and the system pressure was lowered.

In Run CMSL-7, in the operations at 17.2 MPa the formation of CH_4 in first stage was considerably more than in a reference operation in Run CMSL-4 where the first stage feed gas was 100% hydrogen, indicating CH_4 synthesis from the CO in the syngas feed of Run CMSL-7. For Run CMSL-7, this incremental CH_4 formation corresponded to about 5% of the CO reacted in operations at 17.2 MPa pressure. However, in subsequent operations at 13.7 and 10.3 MPa pressure the first stage CH_4 formation apparently declined markedly to very little more than in the reference CMSL-4 operation. Such a pattern is consistent with thermodynamics, and possibly kinetics, of the CH_4 synthesis reaction from CO and hydrogen, which is increased by the square of the pressure, although even at 10.3 MPa pressure and 388°C at equilibrium there would be virtually complete conversion of CO to CH_4. However, in the final operation of the run at 10.3 MPa there was again a considerable amount of CH_4 formation, about 7% of the CO reacted. This change might be ascribed to the use of the increased amount of molybdenum additive and addition of some fresh catalyst before this final operation, so that the apparent impact of the lower pressures on CH_4 formation is put into question.

Run CMSL-7 demonstrated that with extrudate catalyst in both stages improved coal conversion was obtained by the addition of 200 ppm of molybdenum with the feed coal, while promoting efficient conversion of CO to H_2 in the first stage, although the extrudate catalyst has the disability of converting an appreciable proportion of the CO to CH_4. Lowering pressure from 17.3 MPa to 10.3 MPa resulted in appreciably lower distillate yield, which effect can be mitigated by increased catalyst utilization. The nitrogen and sulfur contents of the hydrotreated distillate product were very low at the various pressure levels.

8.0 DISPERSED CATALYSTS FOR COAL LIQUEFACTION

The various operations which used additives with feed coal with or in place of Shell S-317 Ni-Mo extrudate catalysts were:

- Run CMSL-1 evaluated variously a molybdenum additive (300 ppm as AHM, ammonium heptamolybdate) and coal-impregnated hydrated iron oxide (FeOOH, 5000 ppm Fe) with Ni-Mo extrudate catalyst only in the second stage.

- Run CMSL-3 was a similar operation using 1500 ppm molybdenum (as AHM) additive, which involved conventional operations with H_2 fed to both stages, and also operations with syngas feed to the first stage.

- Run CMSL-6 used an HTI prepared molybdenum containing sulfated iron oxide additive (7% Mo, 43% Fe) at additive rates of 100-700 ppm of Mo and 600-4300 ppm of Fe, with Ni-Mo extrudate catalyst recovered after Run CMSL-4 (an operation with out additives) in the second stage. Also, 25-40% of the recycled solvent was unfiltered second stage product slurry which had the effect of increasing catalyst additive concentration through the reactors.

- Run CMSL-7 used 200-500 ppm molybdenum additive (AHM), with Ni-Mo extrudate catalyst in both stages, in operations with syngas feed.

- Run CMSL-10 used no extrudate catalyst, but used an HTI prepared $FeOOH/SO_4$ additive (5000 ppm Fe) along with a molybdenum additive (0 and 100 ppm as Molyvan A lubricant additive).

- All of these operations were with Wyoming Black Thunder Mine sub-bituminous coal. Runs CMSL-8, CMSL-9 and CMSL-11 used variously dispersed catalysts in co-liquefaction of coal/plastics. In Run CMSL-8 there was a single period operation feeding only Crown II Illinois No. 6 bituminous coal.

The principal conclusions from this series of tests were:

- The operations with 5000 ppm Fe as FeOOH and 300 ppm in Run CMSL-1 and no first stage catalyst apparently improved coal conversion and distillate yield by 2-4% compared to the standard CTSL operation with extrudate catalyst in both stages.

- The operations with only 1500 ppm Mo additive in Run CMSL-3 with no first stage catalyst, using and interstage separator but with pure hydrogen feed to the first stage reactor, gave conversions 4.5% lower, and distillate yield 3 W% lower, than had been obtained in Run CMSL-1. However, the Run CMSL-3 conditions were less severe, with about 15-20°C lower temperatures, so that the results with these two catalyst configurations might be more nearly equal at common conditions.

- The operations with the sulfated Mo/Fe additive in Run CMSL-6 resulted in coal conversions that were the highest in this series of runs, up to 94.5%, and distillate yields that similarly high, as high as 66 W% of maf coal. Lowering the Fe/Mo additive amounts from 4300/700 ppm to 1230/200 ppm resulted in 0.5% lower conversion, and 2.5 W% lower distillate yield. A higher severity operation, temperatures increased by 15°C, with 615/100 Fe/Mo additive resulted in about same distillate yield with a 5 W% decrease in residual oil yield being balance by a similar increase in C_1-C_3 gas yield. The nominal recycle of the additive did not appear to have any appreciable effect.

- In Run CMSL-10, without extrudate catalyst in either stage, a 5000 ppm Fe sulfated hydrated catalyst additive appeared to be ineffective with a relatively low distillate yield of 57 W% of maf coal although coal conversion was moderately high at 92%. This operation became difficult to maintain as the recycle solvent containing 46 W% residual oil became very viscous. The addition of 100 ppm Mo (as Molyvan lubricant additive) improved operability and increased distillate yield to 64 W%, conversion to 94%, while lowering the residual oil yield by 5 W%. A subsequent operation with coal rate increased to 650 Kg/M^3 reactor lowered the distillate yield by 4 W% because of increased residual oil yield. Introduction of the iron additive as wet filter cake proved to be as effective as adding it as a dry powder. The heavy distillate products from these operations were of lower hydrogen content and appreciably higher oxygen content than those produced when extrudate catalyst was used.

- In Run CMSL-7 with the extrudate catalyst in both stages and 200 ppm Mo (AHM) additive in an operation with Syngas feed, discussed above in the section concerning the Syngas operations, the coal conversion, 92.4%, was higher than would be expected for operations where no catalyst additive was used. The yield C_4-524°C distillate was 67 W% of maf coal, which was the highest of the various coal only operations of this program, because of virtual elimination of residual oil product and low C_1-C_3 gas yield.

8.1. Run CMSL-1 - Molybdenum (AHM) and Hydrated FeOOH additives Shell S-317 Second Stage Catalyst.

The molybdenum additive (300 ppm) was added as 5 W% solution of ammonium heptamolybdate (AHM) mixed with the feed coal slurry, and the hydrated FeOOH iron catalyst (5000 ppm Fe) was impregnated on the coal matrix using an incipient wetness technique developed by the Pittsburgh Energy Technical Center [2]. There were operations using both additives together, and with the molybdenum additive alone. A pretreater reactor was installed before the first stage liquefaction to activate the iron catalyst at a moderate temperature (302°C), before going to the liquefaction reactors which were at 441°C and 413°C. There was extrudate Ni-Mo catalyst only in the second stage liquefaction reactor.

The results of Run CMSL-1 have been compared to those from the previous CTSL liquefaction program, Run CC-1 which used no additives and extrudate catalyst in both stages, and Run CC-15 which used the impregnated hydrated FeOOH additive (5000 ppm Fe) alone and extrudate catalyst in the second stage only. While these operations were not at identical operating conditions some conclusions can be drawn. Adjusted to comparable operating conditions the use of the combined molybdenum/iron additives resulted in improved process performance for liquefaction of sub-bituminous coal over that obtained from the use either of iron or molybdenum catalyst alone or the use of the extrudate Ni-Mo/Al_2O_3 catalyst in the first stage.

With the iron/molybdenum additives, CMSL-1 achieved higher or equal coal and resid conversions, by 1-2 W% of maf coal, higher yields of distillate products, also by 1-2 W% of maf coal, with a better or equal distribution of the distillate products which contained less heavy distillates, than the other two modes of operation. Such performance was obtained using 46 to 66% higher coal throughput in Run CMSL-1, reactor temperatures that were higher by about 5°C. Coal conversions were generally 93.5-94.0% of maf coal in equilibrated operations and C_4-524°C distillate yield of about 64% of maf coal. The final operations of Run CMSL-1, using the molybdenum additive only, had a lower distillate yield by about 3 W%, reflecting a corresponding increase in residual oil yield, which might be ascribed to deactivation of the second stage catalyst.

However, the impregnation procedure, which added about 1.5 W% nitrogen to the coal, introduced additional nitrogen to the coal matrix which caused an increase in the NH_3 in the products and more nitrogen in the liquid products. The in-line hydrotreater removed about 75% of the nitrogen and sulfur from the light products and increased the H/C ratio from 1.66 to 1.74, for the final operation without the FeOOH additive.

---

[2] Cugini, A. Utz, U.S. Patent 5,096,570 March 17, 1992 "Method for Dispersing Catalyst on Particulate Material"

8.2. Run CMSL-3 - Molybdenum Additive, Shell S-317 Second Stage Catalyst

Run CMSL-3 used 1500 ppm molybdenum additive (as AHM) mixed with the feed coal slurry, with no extrudate catalyst in the first stage and Shell S-317 Ni-Mo extrudate catalyst in the second stage.

The primary purpose of Run CMSL-3 was to evaluate the use of synthesis gas (CO and H_2) in the first stage of the for liquefaction of sub-bituminous Wyoming Black Thunder Mine coal, using a catalyst additive in the first stage. The bench unit was modified to provide for the withdrawal of the vapor phase at the outlet of first stage, so that pure hydrogen only could then be added to the second stage. However, as reference operation the first Condition of Run CMSL-3 fed pure hydrogen to both stages as an evaluation of the effect of the interstage withdrawal of vapors. Lower reactor temperatures were used during Run CMSL-3 than in earlier runs, 388°C and 427°C first and second stage temperatures, respectively, compared to 440°C and 413°C in Run CMSL-1.

The hydrogen only operation of Run CMSL-3 had a coal conversion, 89.5%, about 4.5% lower than had been obtained Run CMSL-1 with the FeOOH/300 ppm Mo additives, and a C_4-524°C distillate yield, 61.6 W%, that was lower by 3 W% of maf coal. This difference in coal conversion corresponds fairly closely to that expected because of the differences in reactor temperatures for the two runs. Similarly, the 3 W% lower C_1-C_3 gas yield of Run CMSL-3 corresponds to that expected because of the difference in reactor temperatures. A complicating factor in this comparison was the interstage withdrawal of vapors in Run CMSL-3 (which was not done in Run CMSL-1) which caused the withdrawal of about 7.0 W% of CO_2 in that stream, and increased the production of carbon oxides plus water to 26 W% compared to 23%. Nominally, the performance with 1500 ppm molybdenum additive in Run CMSL-3 can be considered equivalent to that with the FeOOH/Mo additives during Run CMSL-1.

8.3 Run CMSL-6 - Sulfated Fe/Mo Additive, Partially Deactivated Shell S-317 Second Stage Catalyst

Run CMSL-6 tested the performance of dispersed Fe/Mo slurry catalyst in powdered form added with the coal slurry being fed to the first stage reactor. This additive was molybdenum-containing sulfated iron oxide prepared at HTI that contained 43% Fe and 7% Mo. There was S-317 Ni-Mo extrudate catalyst was in the second stage reactor only. No interstage product separator was used in this run. An in-line hydrotreater was employed to treat the second stage vapors and recycled atmospheric still overhead that was obtained by distillation of the product slurry from the second stage. The Shell S-317 catalyst in the second stage reactor was partially deactivated as the second stage catalyst during earlier operations of Run CMSL-4, where it had processed 520 kg-coal/kg-catalyst.

The addition of the fresh Fe/Mo catalyst additive was at rates that corresponded to 100 to 700 ppm of molybdenum and 615 to 4300 ppm of iron relative to coal. In addition, a portion (25 to 40%) of the recycle to slurry the feed coal was unfiltered second stage product slurry containing coal solids and some of the additives, so that amounts of additives fed to the first stage increased to 140-1030 ppm molybdenum and 860-6345 ppm iron.

Coal conversions remained between 93.5 and 94.5% of maf coal throughout the run, combining the effects of the catalyst additive and the recycle of coal solids in the unfiltered solvent recycle. Distillate yields (C_4-524°C) varied between 62 and 66 W% of maf coal, 2 to 5% higher than during Run CMSL-1 (with hydrated iron oxide impregnated catalyst and 300 ppm molybdenum additive) or Run CC-15 (with hydrated iron oxide impregnated catalyst). The distillate yield was possibly lowered by 2 W% when the amount of Fe/Mo additive lowered from 4300/700 ppm to 1230/200 ppm. A subsequent lowering of the Fe/Mo additive to 615/100 ppm with the first/second stage temperatures increased from 427/413°C to 441/427°C resulted in distillate yield in the same range, with a decrease in residual oil yield by 6 W% being balanced by a similar increase in C_1-C_3 light gas yield. With this change the hydrogen consumption increased from 7.1-7.6 W% of maf coal to 7.9 W%. Subsequent lowering the proportion of solids containing recycle from 40% to 25% did not cause an appreciable change in product distribution.

Samples of the first stage slurry indicated coal conversions of 92.5 to 93.5 % of maf coal in the first stage. These high values were due to the activity of the sulfated dispersed catalyst added 100 ppm Mo and 615 ppm Fe relative to feed coal.

The "recycled" catalyst contained in the ashy CAS bottoms was not found to have a significant impact on the overall activity of the total dispersed catalyst system, in the range of total dispersed catalyst contents of 133 to 216% of the fresh dispersed catalyst quantity. While this indicates there was little residual activity in the recycled catalyst, the operability with up to 50% ashy recycle demonstrates its feasibility at probably appreciably lower cost than that when solids free recycle is used.

Throughout Run CMSL-6 excellent heteroatom removal from the distillate products was obtained. Organic HDS was 97-98%, and the HDN was between 88 and 94%. The in-line hydrotreater was operated at 368° and at 379°C treating the vapors from the second stage reactor and recycled atmospheric overheads obtained by distillation of the product slurry from the second stage. The 343°C endpoint products were clean, colorless or light straw color and contained less than 30 ppm nitrogen and 10 ppm sulfur.

8.4 Run CMSL-10 - Sulfated hydrated Iron Catalyst Additive, with Mo additive (Molyvan). No extrudate catalyst in either stage.

Run CMSL-10 used for liquefaction of sub-bituminous coal various dispersed iron and molybdenum catalysts in the two-stage operation with no extrudate catalyst in either stage. This run was a follow-up on Run CMSL-9 which was a similar all dispersed catalyst system in operations with coal and with coal/plastics feeds. In Run CMSL-9 the results of the coal only operations was found to supersede the process performance obtained with in operations using ebullated beds of supported catalysts. The dispersed catalysts are more economical than the supported catalysts and offer the considerable potential of lower operational costs by virtue of the elimination of the expensive ebullated bed reactors. Run CMSL-10 tested operations with the addition of 5000 ppm Fe using HTI prepared sulfated hydrated iron catalyst, alone, and with the addition of 100 ppm Mo, added as Molyvan A lubricant additive. There were tests with the Fe additive used as dry powder, and later in the run with it added as wet filter cake. A pretreater reactor, of half the size of the liquefaction reactors, at 302°C was used before the liquefaction reactors to activated the Fe additive. Relatively high liquefaction reactor temperatures were used, 441°C first stage temperature with 449°C second stage, and with 449 and 460°C temperatures in the final operations. Coal feed rates were higher than generally used during the program at 480 to 800 $Kg/h/M^3$ reactor. The internal recycle flow that is used when ebullating an extrudate catalyst bed was employed so as maintain a nominally well mixed reactor at essentially uniform temperature.

The first condition, at coal space velocity of 680 $Kg/h/M^3$ reactor with 5000 ppm Fe alone as dry powder, indicated that this catalyst additive was relatively ineffective, with a C_4-524°C distillate yield of 57 W% of maf coal, 9 W% 524°C+ residual oil, yield and 92% coal conversion. Feed slurry flow during this operation became difficult to maintain when recycle solvent became very viscous as its 524°C+ residuum content increased to 46 W%. For the second condition, 100 ppm of molybdenum was added and the coal feed rate was lowered to 480 $Kg/h/M^3$, which improved operability and improved the process results to C_4-524°C distillate yield of 64 W% of maf coal, with the residual oil yield lowered to 4 W%, and coal conversion increased to over 94%, while lowering the residual oil content of the recycled solvent to 34 W%. For the third condition the Fe additive was added to feed slurry as wet filter cake and the coal rate was increased back to 680 $Kg/h/M^3$ which lowered the C_4-524°C yield to 61 W% of maf coal, and increased 524°C+ residual oil yield to 9 W%, but maintained coal conversion above 94%, while the residual oil content of the recycled solvent was virtually unchanged. These results, superior to those of the first condition, confirm the beneficial impact of the molybdenum addition and the feasibility of the use of wet filter cake for the Fe additive.

In the final condition of the run the coal feed rate was increased to 730 $Kg/h/M^3$ reactor, and the reactor temperatures were increase by 5-6°C. A problem appeared when the filtration of the second stage slurry to obtain recycle solvent could not be completed in time available. Consequently, some of product slurry had to by-pass the filter and be used as portion of the recycle solvent, so that total recycled solvent contained about 5.4 W% ash and 3.3 W% unreacted coal. The yield of C_4-524°C distillate was possibly 1.5 W% higher than during the third condition reflecting an increase in coal conversion to 96.5%, due in part to the recycling of unreacted coal.

The vapor product hydrotreated downstream of the second stage reactor contained less than 50 ppm each of sulfur and nitrogen, somewhat more than obtained when extrudate catalyst had been used in the second stage reactor, but still reflecting a considerable amount of hydrodesulfurization and hydrodenitrogenation. The H/C of this treated product declined from 1.87 to 1.76 in the course of the run. The 260-524°C distillate product remaining in the heavier liquid product PFL had a considerably lower proportion of hydrogen with H/C ratios of 1.00-1.12, with the higher ratios in the operations using 100 ppm molybdenum additive. Also, there had been relatively little hetero-atom removal from these distillates with indicate oxygen contents (by difference) of 2-4 W%. In Run CMSL-1, with extrudate catalyst in the second stage, this distillate H/C ratio was 1.35, and its indicated oxygen content was 0-1 W%. These distillate fractions produced in Run CMSL-10 will require more intensive downstream hydrotreating with a greater hydrogen consumption and more loss of product in removing the hetero-atoms.

9.0 CO-PROCESSING OF COAL/PLASTIC FEEDS

Three runs investigated the Co-Processing of coal with plastics.

- Run CMSL-8 processed 25-33% mixed plastics (HDPE, polystyrene, and PET) with Illinois No. 6 bituminous coal using as catalyst using sulfated iron-molybdenum dispersed catalyst with extrudate catalyst in the first stage.
- Run CMSL-9 used only dispersed iron and molybdenum catalysts with no extrudate in either stage in operations with 33-50% of the mixed plastics, and with 33% HDPE with Black Thunder Mine sub-bituminous coal.
- Run CMSL-11 had the same catalyst utilization matrix as Run CMSL-9, with one-half the additives, and attempted operations with a second plastic mix and also tested a characteristic plastic mix obtained from a commercial recycling facility.

The principal conclusions from the results of these runs were:

- With mixed plastics the yield of distillate product was as high as 75% of the solids fed when feeding 33-50 W% plastic along with Black Thunder Mine sub-bituminous coal. This yield was 13 W% higher than the yield when feeding only the coal. This operation in Run CMSL-9 used no supported catalyst with 300 ppm Mo (Molyvan) and 10,000 pm Fe (sulfated hydrated Ferrous Oxide) additives.
- In Run CMSL-11, with 25-33 W% of a plastic component obtained from a commercial recycling facility, the yield of distillates was 67-68 W% of solids fed, which was 4-5 W% higher than when feeding the Black Thunder Mine coal alone, using 100 Mo ppm and 5,000 ppm Fe additives and no extrudate catalyst;
- In Run CMSL-8, which processed 25-33 W% of mixed plastics with Illinois No. 6 coal using Ni-Mo extrudate catalyst in the first stage and fed a sulfated Fe/Mo catalyst (615/100 ppm) with the coal, the distillate yield was 71 W% of the solids feed, the same yield as in coal-only operations of the run;
- HDPE (High Density Polyethylene) by itself did not appear to be converted to distillates as readily as the mixed plastics. In Run CMSL-8, in effect, no distillates were derived from the HDPE, although nominally 93% of the HDPE was converted to a filterable residual oil product. In Run CMSL-9, 58% of the HDPE appeared to be converted to distillates, while with the mixed plastics this proportion was 85 W% or greater. Since the mixed plastics tested contained 40-50% HDPE there appears to be a synergistic effect of the other plastic components upon the conversion of HDPE to lighter products;
- The hydrogen utilization in liquefying the plastic components was very low, nominally 1-4 W% of the plastic fed, so that combined so that the combined coal/plastic hydrogen consumption was 0.5-2.5 W% lower than when feeding coal only.

- A plastic mix containing 27% high impact polystyrene (HIPS) could not be completely homogenized with the recycle solvent so that its test was aborted (Run CMSL-11);

9.1 Run CMSL-8 - 25-33% Mixed Plastics, Illinois No. 6 Coal, Sulfated Fe/Mo Catalyst Additive, Extrudate Catalyst in First Stage.

Run CMSL-8 tested co-processing of Illinois coal with the primary plastic constituents of municipal solid waste. This Run was a follow up of earlier exploratory work in the larger HTI Process Development Unit which demonstrated the technical feasibility of such an operation, but was not able to operate within solvent balance. The plastic feeds for Run CMSL-8 were a mixed plastic (50% HDPE, 35% polystyrene, and 15% PET) and HDPE alone. The plastics amounted to 25-33% of the solids feed. The catalyst configuration for Run CMSL-8 was S-317 supported Ni/Mo catalyst in the first stage and no supported catalyst in the second stage. A dispersed catalyst additive, sulfated iron-molybdenum (100 ppm Mo, 615 ppm Fe)was added along with the coal feed and passed through both stages

Condition 1 of the run was a "coal only" operation which served as a reference for the results for the operations with plastic feed. In Condition 2 substituting the mixed plastic for 25% of the coal, conversion of the solids was unchanged at 96%, and the yield of C_4-524° distillate was virtually unchanged at 71% (maf feed). The non-distillable filterable product oil (" resid") yield increased by 6% and C_1-C_3 gas yield declined by 2%, and hydrogen consumption was lower by 0.5%. For Condition 3, the second stage temperature was increased by 11°C, and solids feed rate was increased by a factor of 1.33, and the principal effect was a further increase in "resid" yield by 6.5%, and a corresponding decrease in C_4-524°C distillate yield. For Condition 4, the amount of plastics was increased to 33% of the solids feed and the solids feed rate was lowered to the original value, which resulted in a further increase in "resid" yield of 2.5%, but with 1.6% lower light gas yield, and 0.6% lower hydrogen consumption, and about the same distillate yield as for Condition 3. In Condition 5, the plastic feed was changed to all HDPE, which increased the "resid" yield by a further 14 W% to 34%, so that the yield of distillate fell to 51%. Some of the progressive decline in distillate yields might be associated with deactivation of the supported catalyst in the first stage.

If the increments of yields for the later conditions compared those for Condition 1 were solely derived from the plastic, in the Condition 2 operation 65 W% of mixed plastic was converted to C_4-524°C distillate, 28 W% was contained in the filterable "resid", 2.5 W% was converted to C_1-C_3 Gases, and 5 W% was retained in the filter cake product, with an incremental hydrogen utilization of 3.6 W% of the plastics added. For Condition 3, with the higher feed rate, the proportion of plastics appearing as filterable "resid" increased to 54 W% with corresponding decreases in the other yield constituents. For Condition 4, with the mixed plastics increased to 33% of the feed, the increase in filterable "resid" yield was 50% of the plastics fed. For Condition 5, with only HDPE as the plastics feed, the incremental filterable "resid" yield was 93% of the plastics fed, and essentially no incremental distillate product was formed from the HDPE. The Condition 2 results suggests some of HDPE in the mixed plastic was converted to distillates, indicating a synergistic effect of the polystyrene and PET in promoting the conversion of the HDPE to distillates.

The 23 day was operationally smooth and indicated the feasibility of such Co-processing operations. However, because of increasing viscosity of recycled solvent through the run, relatively high solvent/solids ratios and feed slurry temperatures were used as the run continued.

9.2 Run CMSL-9 - 33-50% Mixed Plastics, Black Thunder Mine Coal, Mo (Molyvan) and Fe Additives, No Extrudate Catalyst

Run CMSL-9 tested co-processing of Black Thunder Mine sub-bituminous coal with the primary plastic constituents of municipal solid waste during the final 12 days of the 41 day run. The plastic feeds included a mixed plastic (40% HDPE, 27% polystyrene, and 33% polypropylene) and HDPE alone. The plastic amounted to 33-50% of the solids fed. No supported catalyst was charged to either of the two liquefaction stages. Dispersed catalyst additives were fed to the first stage, consisting of 300 ppm of solids feed of Mo (as Molyvan A, an inexpensive commercial lubricant additive) along with, separately, 10,000 ppm Fe (HTI prepared $FeOOH/SO_4$), and passed through both stages. A relatively high solids feed rate, 660 $Kg/h/M^3$, was used throughout the run, compared to rates of 330-500 $Kg/h/M^3$ usually used in the earlier CMSL runs.

The first operation of the run with plastic feed, Condition 7 of the run, with 33% of the mixed plastic had a C_4-524°C distillate yield of 75.4 W% of maf solids feed, which was 13 W% higher than had been obtained earlier in the run, Condition 6, at comparable conditions with only coal as the solids feed. Hydrogen consumption was 1.2 W% lower with the plastic feed. Next in Condition 8, with the plastic feed changed to HDPE alone the yield of distillate fell to 61.0 W%, approximately the yield in the coal only operation, but with hydrogen consumption lower by 1.6 W%. This indicated relatively low reactivity of HDPE is similar to that obtaining in Run CMSL-8. Next in Condition 9, feeding 50% of the mixed plastics, the distillate yield increased to 74.3 W%, while the hydrogen consumption fell further by 0.7 W% to 60% of the amount in the coal only operations of Period 6.

Assuming the increment of yields for these plastic operations compared to those of Condition 6, feeding only coal, were solely derived from the plastic, in Condition 7 nominally over 90 W% of the mixed plastic was converted to C_4-524°C distillates, with less than 10% remaining as filterable "resid" and in the filter cake, 6% converted to C_1-C_3 Gases, with 2 W% hydrogen consumption. In Condition 8, with HDPE plastic only, the incremental C_4-524°C distillate yield was 58 W%, with 34% remaining as filterable "resid", 4% converted to C_1-C_3 Gases, and 4% retained in the filter cake product. In Condition 9, feeding 50% mixed plastics, the incremental C_4-524°C yield was 85 W% of the plastic fed, with 10% remaining as filterable "resid", 5% converted to C_1-C_3 gases, and 2% retained in the filter cake product, with 1% hydrogen consumption.

With the mixed plastics in Run CMSL-9, 27-29% of the solids feed were converted to naphtha range product, compared to 12% in the coal only operations of the run. This difference corresponded 46-50 W% of the plastics fed. With the HDPE the yield of naphtha range product was only slightly higher than in the coal only operation. The vapor phase product oil, with constituents boiling up to 343°C, which had passed through the in-line hydrotreater downstream of the second stage reactor, had a high H/C atomic ratio, 1.76-1.87, for the Co-processing operations. During the coal-only operations this ratio was 1.52. For Co-processing operations this hydrotreated product contained 9-34 ppm of sulfur, and 10-47 ppm of nitrogen.

In Run CMSL-9 the plastic convertibility and conversion to distillates was considerably greater than in Run CMSL-8, particularly that of the HDPE. Several factors were different between the two runs: A) for Run CMSL-9 the catalyst was 300 ppm Mo and 10,000 ppm Fe with no supported catalyst, while in Run CMSL-8 there was supported Ni/Mo catalyst in the first stage and the additives were 100 ppm Mo and 625 ppm Fe; 2) The coal feed was Black Thunder Mine Sub-bituminous coal for Run CMSL-9, and Illinois No. 6 bituminous coal for Run CMSL-8; 3) Run CMSL-9 was at a higher thermal severity, with first and second stage temperatures of 449°C and 460°C, respectively, compared to 432°C and 454°C for Run CMSL-8, which corresponded to a factor of 1.55 in combined thermal severities.

9.3 Run CMSL-11 - 25-33% Plastic Mix From Commercial Recycler, Black Thunder Mine Coal, Mo (Molyvan) and Fe Additives, No Extrudate Catalyst

Run CMSL-11 tested Co-processing of Black Thunder Mine sub-bituminous coal with plastic constituents of municipal solids waste. Additive catalyst, 100 ppm Mo and 5,000 ppm Fe, was fed to the first stage along with the solids feeds, and there was no supported catalyst in either stage. The initial run plan included a test using mixed plastics of 40% HDPE, 33% polypropylene (PP), and 27% of high impact polystyrene (HIPS). However, it was found that one of these plastics, possibly HIPS, would not completely homogenize with the recycle solvent and pumping of the highly viscous feed slurries was not possible. The plastic feed was then changed to a waste plastic mix obtained from a commercial recycling facility (approximately 50% HDPE, 33% PP, and 27% PS) and there were fewer operating problems during this operation. The waste plastic mix was washed to remove paper and metal scrap. The test program included a reference coal only operation (Condition 2), an operation with 33% of the commercial mixed plastic (Condition 3A), and an operation with 25% of the commercial mixed plastic (Condition 3B). The temperature/residence time severity was the same as used in Run CMSL-9.

With substitution of plastics for the portion of the coal feed the yields of C_4-524°C distillate increased from 63% of the maf solid feed to 67% (Condition 3A, with 33% plastics) and 68% (Condition 3B, with 25% plastics). Remarkably, C_1-C_3 light gas yields with the plastics feeds were less than half that in the coal only operation, 7-8 W% of dry feed compared to 17 W%. Also, 177 C endpoint naphtha yields were lower with the plastics than in the coal-only operation, 13-16 W% of dry solids compared to 20.5 W%. Hydrogen consumption also was considerably lower with the plastic feeds, 3.8-4.7 W% of dry solids compared to 6.5 W%.

Assuming the increment of yields for these plastic operations compared to those of Condition 2, feeding only coal, were solely derived from the plastic, in Condition 3A, with 33 W% plastics, nominally 72 W% of the mixed plastic was converted to C_4-524°C distillates, with 26% remaining as filterable "resid" and 4% retained in the filter cake product. The difference in C_1-C_3 gas yields indicated an inhibiting effect of plastics upon C_1-C_3 gas formation from the coal, in effect an inhibition of gas formation corresponding to 5 W% of plastics added. In Condition 3B, with 25% plastics, the incremental formation of C_4-524°C distillate corresponded to 76% of the plastics added, and 31% remaining as filterable "resid" and 7% retained in the filter cake. The C_1-C_3 gas yields during Condition 3B indicate an even more pronounced inhibition of the plastic upon this yield than during Condition 3A. The incremental hydrogen consumption for the plastics operations were -1.6 and -0.6 W% of the plastics fed, nominally indicating the plastics served as hydrogen donors for the coal.

Another feature of the product distributions was that the Run CMSL-11 distillate product derived from the plastics was of relatively high boiling range. Apparently, virtually no naphtha range product was derived from the plastic, with 2/3 or more of the distillate being in the 343-524°C boiling range.

In addition to the use of the use of heterogeneous plastic for the first time in Run CMSL-11, two factors might have caused the lower conversion to distillate products in Run CMSL-11 than was obtained in Run CMSL-9 with mixed plastics: A) the commercial waste plastic used in Run CMSL-11 had a higher proportion of HDPE; and B) half as much additive catalyst was used in Run CMSL-11. However, the Run CMSL-9 performance with 100% HDPE did not indicate the inhibiting effect upon light gas yield, naphtha formation, and hydrogen consumption that was indicated in Run CMSL-11.

When the in-line hydrotreater was on line the distillate product contained about 50 ppm of sulfur and nitrogen. These analyses reflected 98-99% removal of these elements compared to the product when the hydrotreater was off line. However, they are somewhat higher than obtained in Run CMSL-9 with mixed plastics, where the hydrotreated sulfur contents were 9-34 ppm and the nitrogen contents were 10-47 ppm. The differences can be attributed to the heterogeneous nature of plastic used in Run CMSL-11, or the lower amount of dispersed catalyst in the liquefaction reactors used in this run.

10.0 ECONOMIC ASSESSMENT

Economic assessment of the results of Runs CMSL-2 through CMSL-11 were performed to establish the merits of the various operating parameters that were studied in those runs. These evaluations were done for fully-integrated grass-roots commercial complex, as a multi-train liquefaction facility on a scale that is considered commercially feasible, about 10,000 tons per day coal producing 40-45,000 barrels per stream day of finished gasoline and diesel fuel products. Natural Gas is imported to meet fuel needs of the complex and generate hydrogen requirements in excess of that met by the liquefaction gas by-products and partial oxidation of unconverted liquefaction product and residual oil. Product costs are expressed as an equivalent crude oil cost, which is the cost of crude oil that would produce equivalent products in a conventional petroleum refinery. The costs and operating requirements of other process facilities, including utilities, and off-sites have been estimated using information derived the Baseline Design Study, developed by Bechtel for DOE. Table 1.1 summarizes the economic assumptions. The details of the economic evaluations for each operating period of the ten bench unit runs that were considered are given in Volume III.

Table 1.2 Summarizes similarly the equivalent crude oil prices for the three runs with Illinois No. 6 coal that studied:

- Impact of reduction of the recycle solvent/coal ratio;
- The use of a surfactant;
- The use of an interstage separator to withdraw first stage vapor product before passing the slurry phase to the second stage;
- Elimination of supported extrudate catalyst from the second stage while feeding a molybdenum/iron additive;
- Substitution of plastics for a portion of the coal feed.

Table 1.3 Summarizes the equivalent crude oil prices for each of the seven runs with Black Thunder Mine sub-bituminous coal that variously studied:

- The impact of the use of synthesis gas in place of high purity hydrogen as first stage gaseous feed;
- The use of molybdenum and iron additives in place of the supported extrudate Ni/Mo catalyst for one or both stages;
- Reduction of the operating pressure from 17.2 MPa to 13.8 MPa and 10.3 MPa;
- Substitution for a portion of coal feed of prepared plastic mixtures and of a mixture obtained from a commercial recycling facility.

These tables indicate two equivalent crude oil prices.

- The first, a conventional design, assumes that all of the vapors pass through both stages;
- And the second assumes the use of an interstage separator with only half of the vapors passing through the individual stages. A limiting factor in ebullated bed reactor design is the vapor velocity in the reactor, which for a given solids feed space velocity limits the height of the reactor and the amount of coal that can be fed to the reactor. With the vapor rate halved, as with the interstage separator, the length of reactor can be doubled and the amount of coal feed to the reactor increased proportionally, which lowers the number of liquefaction trains and results in reduced investment because of the lower number of auxiliary vessels, piping, and instrumentation. The "maximum coal rate" equivalent crude oil cost given these tables assumes this modification of the conventional design.

The economic impact of the operating parameters that were studied were as follows:

- In this study with the conventional process design, the lowest projected equivalent crude oil price using Black Thunder Mine coal was $30.40 per barrel (For Run CMSL-9 Period 5), which is $2.2 per barrel lower than that for a reference operation (Run CMSL-4, Period 5, with Ni-Mo extrudate catalyst in both stages and with no additives). The CMSL-9 operation used 300ppm Mo additive and no extrudate catalyst.
- In this study with the modified process design, the lowest projected equivalent crude oil price using Black Thunder Mine coal was $28.70 per barrel (For Run CMSL-4, Period 5, which used extrudate catalyst in both stages), which is $3.90 per barrel lower than that for the same operation using the conventional process design. With the modified process design, the estimated equivalent crude oil prices were slightly higher for the various evaluations of operations which used catalyst additives at $29.2-$29.80 per barrel;
- The lowest projected equivalent crude oil price using Illinois No.6 coal was $27.60 per barrel, which had interstage removal of vapors, permitting modified process design, using Ni-Mo extrudate catalyst in both stages (Run CMSL-5). This cost was $4.00 per barrel lower than that of reference operation without interstage separation (Run CMSL-2);
- The lowest projected equivalent crude oil cost for co-processing of plastics and coal as $19.80 per barrel with 50% of a prepared plastic mixture with Black Thunder Mine coal using Mo and Fe additives and no extrudate catalyst. A similar operation with 33% of a commercially obtained plastic mixture cost had a cost of $21.80 per barrel. A co-processing operation with Illinois Coal had a cost of $26.00 per barrel using only catalyst additives and a prepared plastic mixture;

- Interstage Vapor Separation - With interstage separation in Period 8 of Run CMSL-5 the cost was $0.60 per barrel lower than in Period 10 of Run CMSL-2 in operations with Illinois coal (although there differences in the coal feed and some of the operating conditions). In this case, modification of the process design taking advantage of the lower vapor rates consequent to the use of the interstage separator lowered the equivalent crude oil price by an additional $2.50 per barrel. In general, for the other such evaluations summarized in these tables the modified process design lowered the equivalent crude oil cost by $0.5-4.90 per barrel.

- Use of Synthesis Gas - Using synthesis gas containing 84% CO increased the equivalent crude oil price by $1.50 per barrel compared to operations with high purity hydrogen (operations with Black Thunder Mine Coal in Run CMSL-4). When the synthesis gas contained 75% CO this increase was $2.60 per barrel (Run CMSL-3). When it was assumed that the synthesis gas contained 50% CO the equivalent crude oil price was lower by $0.40 per barrel than with high purity hydrogen (Compare Period 7 of Run CMSL-7 with Period 5 of Run CMSL-4, although the Run CMSL-7 operation included 200 ppm Mo additive, which probably contributed to the economic improvement).

- Lower Pressures - In the conventional design operations at a pressure of 10.3 MPa had a equivalent crude oil price $0.80 lower than that at a pressure of 17.2 MPa (Run CMSL-7). The lower pressure operation did use 500 ppm Mo additive compared to 200 ppm used in the higher pressure operation. With the modified process design the lower pressure cost was $0.20 per barrel higher than the higher pressure cost.

- Catalyst - The catalyst configuration for operations with Black Thunder Mine coal with the lowest equivalent crude oil cost for the conventional design, $30.40 per barrel, was in Run CMSL-9 with 300 ppm molybdenum additive and no extrudate catalyst, $2.20 per barrel per lower than for the CTSL configuration of the supported catalyst in both stages of Run CMSL-4. Other configurations using additives with extrudate catalyst only in the second stage had slightly lower costs than that of the reference CTSL operation of Run CMSL-4: in Run CMSL-3 with 1500 ppm molybdenum additive the equivalent crude oil price was lower by $0.50 per barrel; in Run CMSL-6 with 100 ppm/615 ppm of sulfated Mo/Fe additive this price was lower by $0.7 per barrel.

  With no supported catalysts in either stage and 5,000-10,000 ppm Fe (sulfated hydrated iron oxide dispersed catalyst additive) with 100-300 ppm molybdenum additive (Molyvan) the equivalent crude oil price were $2.5-3.00 higher (Runs CMSL-9, CMSL -10, and CMSL-11) than for the reference operation with extrudate catalyst in both stages. The principal reason for the increased cost was high cost of the relatively high amounts of the iron additive.

- For operations with Illinois Coal, with a catalyst configuration of a supported catalyst in the first stage only and sulfated 100 ppm Mo/625 ppm Fe additive the equivalent crude oil price was about $2.10 per barrel higher than that of a reference operation with extrudate catalyst in both stages (Compare Period 6 of Run CMSL-8 with Period 4 of Run CMSL-2).

- Plastic/Coal Co-processing - The lowest equivalent crude oil price indicated in this study was $19.80 per barrel for the Co-processing Black Thunder Mine coal with 50% of an HTI prepared mixed plastic in Run CMSL-9, with the process modification for the maximum coal rate. A comparably low cost, $21.80 per barrel, was indicated for the operation in Run CMSL-11 using 33% of a plastic mix obtained from a commercial recycling facility. These operations were with no supported catalyst in either stage and 100-300 ppm molybdenum additive (Molyvan), and 5,000-10000 ppm Fe (sulfated hydrated iron oxide) dispersed catalyst additive which had relatively high equivalent crude oil costs in the coal only operations. These costs were $9.4-11.50 per barrel lower than those of equivalent operations feeding coal only. When the Co-processing used 33% HDPE as the plastic component the equivalent crude oil price was $4.00 per barrel lower than that of the equivalent coal-only operation (Run CMSL-9). Note that the plastics were assumed to be delivered at no cost to the liquefaction plant, although there was an allowance for preparation of the plastics for slurry preparation at the plant site.

- Co-processing of Illinois Coal with 25-33% of the HTI prepared plastic mix gave an equivalent crude oil price $4.9-6.80 per barrel lower than the equivalent coal-only operation (Run CMSL-8). The catalyst configuration for this operation, sulfated 100-200 ppm Mo/625-1230 ppm Fe additive, had a relatively high equivalent crude oil cost in the corresponding coal-only operations. The lowest equivalent crude oil cost for the Co-processing operations was $26.00 per barrel. Using 33% HDPE as the plastic component increased the equivalent crude oil cost by $7.30 per barrel, which was $3.00 per barrel higher than that of the corresponding coal-only operation.

- Reduction of Recycle Solvent Flow - Lowering the recycle ratio from 1.06 kg/kg to 0.9 kg/kg lowered the equivalent crude oil price by $0.90 per barrel (Compare Periods 4 and 10 of Run CMSL-2 with Illinois No. 6 coal);

- Use of Surfactant - With 2% surfactant this cost was increased by about $0.20 per barrel (Compare Periods 13 and 16 of Run CMSL-2);

Other economic studies of the impact of the changes in the operating configuration indicated the following:

- The reduction in downstream product treating investment would be about 2.5 times the additional cost of an in-line hydrotreater in the liquefaction train resulting in saving of about $0.20 per barrel of equivalent crude oil product;

- Elimination of catalyst pretreater reactor for activation of the dispersed iron catalyst reduces the equivalent crude oil cost by $0.50 per barrel. In Run CMSL-11 a preheater coil replaced this pretreater reactor which had been used in the earlier CMSL runs with the dispersed iron catalysts, and in effect such a savings might be applied to the costs of such earlier runs.

11.0 MAJOR CONCLUSIONS

The program results described have investigated purely physical parameters, coal treatment and variation in solvent to coal ratio, the use of syngas to replace part of the hydrogen as the reducing gas, the use of dispersed catalyst in addition to and replacing the supported catalyst and the co-processing of coal with plastic waste material. The overall objective of this program, to improve the production of liquid fuels from direct coal liquefaction at a cost that is competitive with conventional fuels, was well satisfied. Following are specific conclusion from this program:

- The addition of sodium lignolsulfonate surfactant did not improve the performance of the CMSL process either in terms of product yields or product quality.

- Lowering the solvent to coal ratio from previous typical values of 1.5-2.0 to 0.9 provides a significant benefit: An increase in distillate yields (8-9%) and resid conversion (4%); Improved recycle oil qualities as measured by API gravity, H/C ratios and nitrogen and sulfur contents.

- Interstage product separation is very effective in enhancing liquefaction kinetics in the second stage reactor, resulting in high levels of resid conversion and light distillate yields. An interstage separator lowers the vapor flow per stage so that the coal feed to a reactor can be increased which results in lower plant investment and product cost.

- In-line hydrotreating is very effective for producing premium distillate with less than 10 ppm each sulfur and nitrogen, especially when about a third of the distillate product is obtained as a first reactor overhead during interstage product separation.

- The use of syngas as a replacement for hydrogen is technically feasible. Syngas with the addition of a dispersed catalyst can achieve comparable performance to pure hydrogen at 60% of the operating pressure.

- The use of a dispersed catalyst in addition to supported catalyst in both stages results in improved process performance compared to using only using a supported catalyst in both reactors or using a dispersed catalyst and a supported catalyst only in the second reactor.

- Recycling of the dispersed Mo catalyst by recycling part of the ashy atmospheric still bottoms did not improve process performance.

- The use of only a dispersed catalyst (a combination of 50-100 ppm Mo and, 5,000 ppm of HTI's iron catalyst) without any supported catalyst was very effective in the CMSL process, but of high cost because of the cost of the amounts of iron additive used;

- When plastics were added to the coal feed process performance was improved, with lowered hydrogen utilization, due to the high hydrogen content of the plastics.

- With a sub-bituminous coal, it was found that plastics had synergistic effects on coal conversion with increased C_4-524°C premium distillate yields.

- Reactivity of HDPE is improved when other polymers such as polypropylene and polystyrene are present.

- At the same process conditions as used in coal-only operations, coal/plastics coprocessing using 33% municipal solid waste recycle resulted in 3-5W% higher distillate yield and as much as 50% lower yield of light hydrocarbon gases, and hydrogen consumption that decreased from 6.5W% during the coal-only operation to 3.9-42W%

- From the trends in process performance and reaction severity it is apparent that plastics require a more severe depolymerization/cracking environment than coal.

- Economics based on the results of the "coal-only" operations performed during this program indicate that liquids can be produced from coal at an equivalent crude oil price of $27 per barrel. The introduction of coal/waste plastic coprocessing can reduce this further to $20 per barrel.

- Significant cost reduction can be obtained by:

    - Use of molybdenum additive with no supported catalyst, which was the lowest cost case for the conventional process design in these studies;

    - Use of molybdenum additive or sulfated Fe/Mo additive along with supported catalyst in one or both stages which had lower costs than using only supported catalyst;

    - Use of the lowest possible ratio of solvent to coal while maintaining a pumpable slurry feed, found to be 0.9 kg/kg in this program;

    - Interstage vapor separation which has the advantages of eliminating some of the oxygen in sub-bituminous coal as CO_2, conserving hydrogen which would otherwise be required to form water and CH_4, and of permitting modification of the liquefaction reactor design because of lowered vapor flow in each stage;.

    - The use of an in-line hydrotreater which lowers downstream treating investment and overall plant investment.

- Little or no economic benefit was demonstrated of substituting synthesis gas for pure hydrogen in liquefaction.

- The use of lower operating pressure, combined with synthesis gas, was at best an economic standoff.

12.0 RECOMMENDATIONS

- Based upon the promising results obtained during this program, more studies are warranted for: the optimization of dispersed catalysts employed for the process; convertibility of HDPE to light liquids; and impact of coprocessing on the product quality and end-use applications.

- The processing of 'real life' MSW plastics needs to be further explored and optimized. Additionally, work needs to be done with different MSW mixes to evaluate how this would affect the process operability and the final product qualities.

- The efficacy of the dispersed catalyst reactor configuration should be investigated for co-processing of low quality petroleum resids with waste plastics and coal.

- The wet cake addition for a dispersed catalyst, which is much more economical than the dry powder addition, should be investigated further.

- An alternative mode of co-processing should be investigated, in which plastics are separately depolymerized/cracked in a back-mixed reactor in the presence of a suitable acidic catalyst and the resulting heavy slurry products (after gas and light distillate separation) are mixed with coal and coal-derived recycle solvent as feed for two-stage coal liquefaction. Such processing is sensible since plastics, being inherently different from coal both physically and chemically, require altogether different process severity/catalysts from coal. The depolymerization/cracking reactor could be at atmospheric pressure and would be of low cost. Also since the plastics-derived products entering coal liquefaction will be richer in hydrogen (about 9-10 W% hydrogen compared to 5 W% of coal) hydrogen requirements for the overall process would be lower. This scheme also provides for a more efficient and better way for converting plastics to chemicals/fuels in an environmentally acceptable manner.

Table 1.1

Major Assumptions Used in Economic Analysis	
DCF rate of return, %	15
Project life, years	25
Depreciation term, years	10
Depreciation type	straight-line
Construction period, years	4
Draw-down during construction, %	
First year	4
Second year	26
Third year	45
Fourth year	25
Escalation during construction, %/year	3
On-stream factor, days/year	
First-year	237
Second year	292
Thereafter	328.5
Equity, %	25
Interest rate on debt	8
Inflation rate, %/year	3
Federal income tax rate, %	34
Debt life, years	25
Interest rate during construction, %	8
Working Capital	
Owner's cost, % of capital cost	5
Product revenue, % annual cost	50
Maintenance, % of capital cost	1
Byproduct revenue, % of annual cost	10

TABLE 1.2

ECONOMIC EVALUATION OF BENCH UNIT CMSL RUNS RESULTS

Illinois No. 6 Coal Operations

Run CMSL	2	2	2	2	5	5	5	8	8	8	6	8
Period	4	10	13	16	8	11	13	6	11	16	20	22
1st Stage Catalyst	S-317	S-317	S-317	S-317	S-317	S-317	S-317	S-317	S-317	S-317	S-317	S-317
2nd Stage Catalyst	S-317	S-317	S-317	S-317	S-317	S-317	S-317	---	---	---	---	---
Additive, ppm								Mo 100 Fe 615	Mo 100 Fe 615	Mo 100 Fe 615	Mo 200 Fe 1230	Mo 200 Fe 1230
Temperatures, °C												
1st Stage	400	400	414	413	413	413	399	432	432	432	433	433.00
2nd Stage	428	428	433	433	441	427	427	439	441	454	454	455.00
Solids Feed, Kg/h/M^3	296	296	535	458	462	317	317	481	481	641	481	481
Pressure, MPa	17.2	17.2	17.2	17.2	17.2	17.2	17.2	17.2	17.2	17.2	17.2	17.2
CO, V% (3)	0	0	0	0	0	0	75	0	0	0	0	0
Recycle Solv., Kg/Kg Solids	1.06	0.9	0.9	0.9	0.9	0.9	0.9	1.5	1.6	1.8	2.1	1.90
Plastics, W% of Solids	0	0	0	0	0	0	0	0	25 (1)	25 (1)	33 (1)	33 (2)
Surfactant, W%	0	0	0	2.0	0	0	0	0	0	0	0	0
Interstage Separator	No	No	No	No	Yes	Yes	Yes	No	No	No	No	No
Equivalent Crude Oil Oil Cost, $/Barrel												
Conventional Design	31.56	30.70	31.56	31.72	30.12	30.65	32.78	33.68	38.84	31.67	29.30	36.57
Maximum Coal (4)					27.64	27.99	29.77	32.84	26.62	29.12	25.95	

(1) Mixed HDPE, Polystyrene, Polypropylene
(2) HDPE
(3) Feed Gas to First Stage
(4) With Interstage Separator, Reducing Vapor Load in Each Stage,
Permitting Longer Reactors and Greater Coal Feed Per Reactor with Fewer Liquefaction Trains.

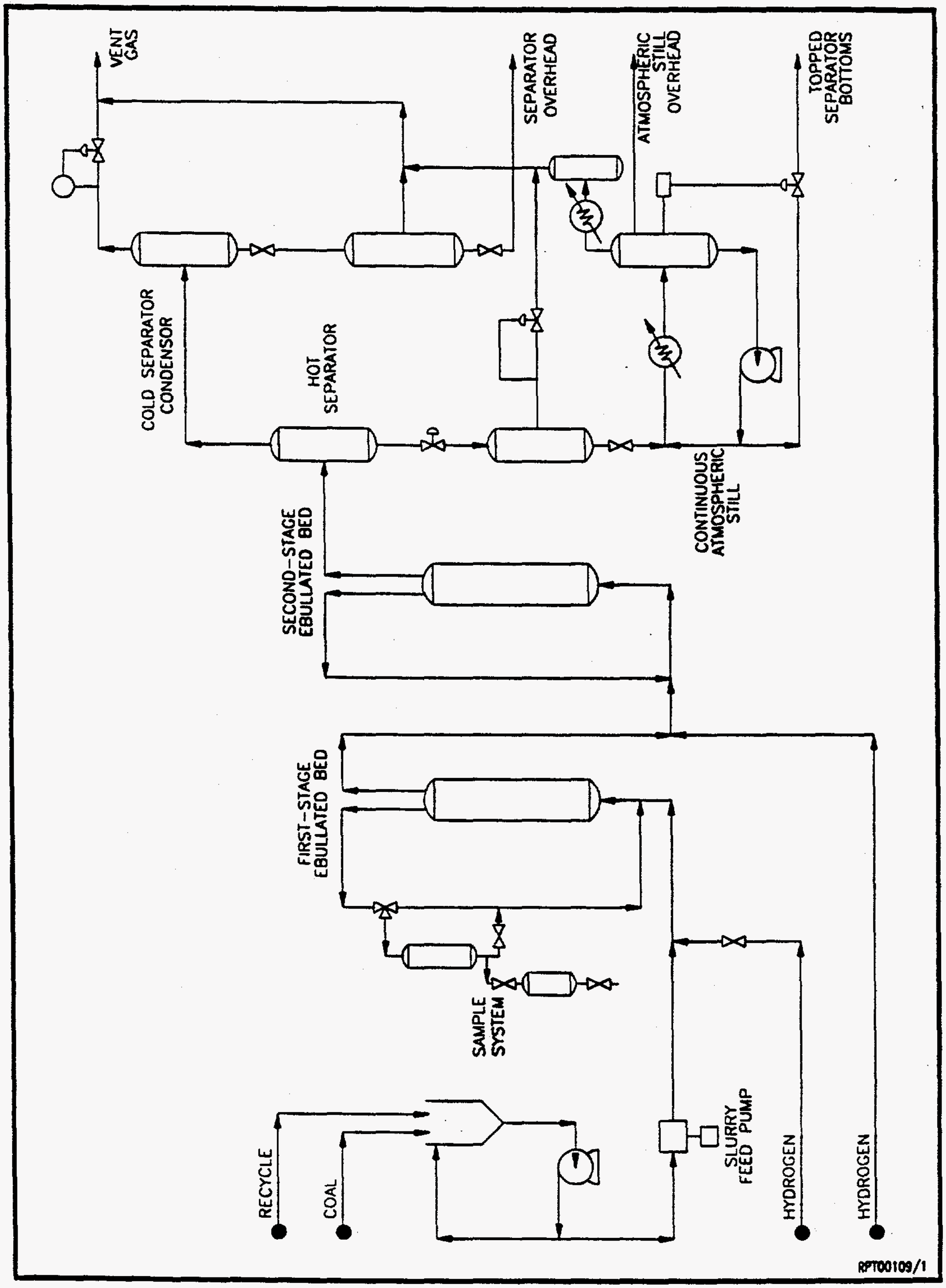
TABLE 1.3
ECONOMIC EVALUATION OF BENCH UNIT CMSL RUNS RESULTS
Black Thunder Mine Coal Operations

Run CMSL	4	4	3	3	6	7	7	7	9	9	9	9	10	10	11	11
Period	5	12	5	12	17	7	11	19	5	29	38	41	9	18	10	16
1st Stage Catalyst	S-317	S-317	---	---	---	S-317	S-317	S-317	---	---	---	---	---	---	---	---
2nd Stage Catalyst	S-317	S-317	S-317	S-317	S-317	S-317	S-317	S-317	---	---	---	---	---	---	---	---
Additive, ppm			Mo, 1500	Mo, 1500	Mo, 100 Fe, 615	Mo, 200	Mo, 200	Mo, 500	Mo, 300	Mo, 300 Fe, 10000	Mo, 300 Fe, 10000	Mo, 300 Fe, 10000	Mo, 100 5000, Fe	Mo, 100 5000, Fe	Mo, 100 5000, Fe	Mo, 100 5000, Fe
Temperatures, °C																
1st Stage	400	414	399	399	437	427	427	427	427	440	448	449	441	449	450	450
2nd Stage	427	438	427	427	432	443	443	443	449	559	461	462	448	457	459	459
Solids Fee, Kg/h/M^3	308	370	304	304	455	321	321	321	673	673	673	673	415	721	671	688
Pressure, MPA	17.2	17.2	17.3	17.2	17.2	17.2	13.8	10.3	17.2	17.2	17.2	17.2	17.2	17.2	17.2	17.2
CO, V% (4)	0	84	0	75	0	0	0	0	0	0	0	0	0	0	0	0
Plastics, W% of Solid	0	0	0	0	0	0	0	0	0	0	33 (2)	50 (1)	0	0	0	33 (3)
Interstage Separator	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	No	No	No	No	No	No	No	No
Equivalent Crude Oil Oil Cost, $/Barrel																
Conventional	32.62	34.17	32.08	34.65	31.94	32.25	32.2	31.46	30.39	35.02	30.97	23.57	35.56	31.58	35.10	25.69
Design Maximum Coal (5)	28.70	33.69	29.17	32.04		31.26	32.20	31.46	29.83	33.22	26.70	19.81	35.14	28.90	33.77	21.79

(1) Mixed, HDPE, Polystyrene, Polypropylene
(2) HDPE
(3) Monmouth Recycling Curbside Recycled Plastic
(4) Feed Gas to First Stage
(5) With Interstage Separator, Reducing Vapor Load in Each Stage,
Permitting Longer Reactors and Greater Coal Feed per Reactor with Fewer Liquefaction Trains

FIGURE 1.1

EBULLATED BED BENCH UNIT 227



CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL (CMSL)
FINAL REPORT

VOLUME I

SECTION II

DETAILS OF BENCH UNIT OPERATIONS

RUN CMSL-1

VOLUME I

SECTION II - RUN CMSL-1

TABLE OF CONTENTS

RUN CMSL-1 (227-77)
EVALUATION OF MOLYBDENUM ADDITIVE AND PRE-DISPERSED IRON CATALYSTS IN TWO STAGE LIQUEFACTION

VOLUME I

SECTION II - RUN CMSL-1

TABLE OF CONTENTS
(Continued)

VOLUME I

SECTION II - RUN CMSL-1

LIST OF TABLES

VOLUME I

SECTION II - RUN CMSL-1

LIST OF FIGURES

SECTION II - RUN CMSL-1

RUN CMSL-1 (227-77)
EVALUATION OF MOLYBDENUM ADDITIVE AND PRE-DISPERSED IRON CATALYSTS IN TWO STAGE LIQUEFACTION

1.0 SUMMARY

The objective of this run was to evaluate the effectiveness of a molybdenum additive in conjunction with iron-impregnated Wyoming sub-bituminous coal in thermal/catalytic two stage liquefaction. A secondary objective of this run was to evaluate the effect of in-line hydrotreating on the product quality. The operating run plan for the run is summarized in *Table 2.1.2*

The 300 ppm of molybdenum catalyst was added as a 5 W% ammonium heptamolybdate (AHM) solution. The iron catalyst was impregnated on the coal matrix using an incipient wetness technique developed by the Pittsburgh Energy Technology Center[1]. Black Thunder Mine Coal was impregnated with hydrated iron oxide (FeOOH) at 5000 ppm of iron using this technique. A pretreater stage at 300°C (572 °F) activated the iron catalyst prior to the thermal stage at 441°C (825°F). The catalytic stage was an ebullated bed reactor at 413°C (775 °F) with Shell S-317 extrudate Ni-Mo catalyst.

The space velocity was 480 Kg/h/M^3 reactor (30 lb/hr/ft^3) for Conditions 1 and 3 and 542 Kg/h/M^3 (34 lb/hr/ft^3) in Condition 2. The performance of the iron catalyst was evaluated based on Condition 3 using untreated coal. The results were also compared with previous operations that had the following first stage catalysts: 1) NiMo supported catalyst, 2) impregnated iron, but no dispersed molybdenum, or 3) no catalyst.

Run CMSL-1 (227-77) was completed on February 28, 1993 after 14 1/3 days of operation. A repeat condition to quantify deactivation and better judge the iron catalyst performance was eliminated because of operating difficulties, but general catalyst evaluations were still possible. By most performance standards, the difference between Condition 3 (without iron catalyst) and Condition 1 (with iron catalyst) was not significantly more than could be ascribed to second stage catalyst deactivation.

The in-line hydrotreater improved the quality of the light products. It reduced the nitrogen content by 74% and the sulfur content by 76%. The H/C ratio increased from 1.66 to 1.74.

Comparing the results of this run with those of Run CC-1, Period 16, which was a catalytic/catalytic operation at 30% lower space velocity at 5°C lower temperature, there was

---

[1] Cugini, A., Utz, B., U.S. Patent No. 5,096,570, March 17, 1992, "Method for Dispersing Catalyst onto Particulate Material"

1.5 W% higher conversion in Run CMSL-1 with the dispersed catalyst but resid conversion was unchanged, and distillate yield was 1.6 W% lower. Compared to those of Run CC-15, which was a thermal/catalytic operation with the same iron additive but no molybdenum additive at 40% lower space velocity and 13°C lower temperature, the coal conversion was 1.2 W% higher in Run CMSL-1, resid conversion similarly higher, and the distillate yield was also higher by 3.4 W%.

Because of different operating conditions and catalyst ages of the selected periods in Runs CMSL-1, CC-1, and CC-15, the effects of different first stage catalysts on process performance could not be properly compared. However, the results of this run has bolstered the conclusion reached from Run CC-15 that the dispersed iron catalyst is very effective for coal liquefaction, and the presence of molybdenum improves resid conversion and product distribution. However, the nitrogen added to the coal by the impregnation procedure may be somewhat detrimental.

A process simulation model developed by HTI for two-stage liquefaction of subbituminous Black Thunder Mine Coal was utilized for proper comparison of the results of the selected periods of these runs with those of projected standard runs. Two-stage coal liquefaction (CTSL) performance using Shell S-317 Ni-Mo 1/32" extrudate catalysts in both stages and Black Thunder Mine subbituminous coal as feed was chosen as the standard for comparison with the performance of the selected periods of selected runs. Results of this comparison can be summarized as follows:

(i) The cases with first stage Fe-Catalyst (Fe-Case), Molybdenum Catalyst (Mo-Case), and Fe as well as Molybdenum Catalysts (Fe-Mo-Case) have coal conversion 2-4 W% higher than that for the standard case.

(ii) The presence of Molybdenum catalyst in the first stage seems to improve resid conversion and C_4-199°C distillate yield.

(iii) The Fe-Case has higher resid yield and 199-524°C yield than the Mo-Case. The Mo-Case has higher C_4-199°C yield than the Fe-Case. In terms of C_4-524°C distillate yield and hydrogen consumption, the performance of these two cases are not significantly different from each other.

(iv) The performance of the Fe-Case and Fe-Mo-Case are more or less equivalent except that the presence of molybdenum in the first stage improves resid conversion and C_4-199°C distillate yield. High apparent water yield in Fe-Mo-Case is eliminating the beneficial effects of this case.

(v) The overall performance of the Fe-Case, Mo-Case, and Fe-Mo-Case are not significantly different from each other. Beside coal conversion, the overall performance of these cases are not in any respect superior to the standard case.

2.0 BACKGROUND, OBJECTIVE, AND SCOPE OF WORK

In Run CMSL-1 (227-77) the performance of the pre-dispersed iron and the dispersed molybdenum catalysts were evaluated in a two-stage mode of operation. The first liquefaction stage was a backmixed thermal reactor (without supported catalyst) and was controlled at 441°C (825°F). The second stage was an ebullated bed containing Shell S-317 (Ni-Mo 1/32″ extrudate) catalyst at 413°C(775°F). The volumes of both stages were identical. Prior to the first liquefaction stage, the pre-dispersed iron catalyst precursor was activated in a pretreater at 300°C (572°F). The supported catalyst in the second stage was sulfided during the startup period, and hydrogen sulfide was injected continuously at 3 W% of feed coal throughout the run. The hydrogen sulfide also was available to sulfide the 300 ppm (of coal) Mo in the ammonium heptamolybdate additive.

An in-line hydrotreater was used to improve the quality of the light distillate throughout the run, except for the final 8 hours during which the unhydrotreated products were collected. It operated at 349°C (660°F) with Criterion 411 NiMo catalyst.

The original run plan is presented in *Table* 2.1.1 Due to unit operation difficulties experienced during the run, the run plan had to be modified. The operating conditions actually used are given in *Table 2.1.2*. The run consisted of three conditions. Condition 1 was at reactor temperatures of 439°C (823°F) for the first stage and 413°C (775°F) for the second stage with a space velocity of 480 Kg/h/M^3 reactor (30 lb/hr/ft^3) reactor. Condition 2 was at the same temperatures but the space velocity was increased 15% to 542 Kg/h/M^3 (34 lb/hr/ft^3). The second condition also used the iron impregnated coal. Condition 3 was identical to the first except the untreated coal was used. However, dispersed molybdenum catalyst was used in all three conditions.

3.0 PROGRAM RESULTS AND ANALYSES

The operating summary for Run CMSL-1 giving the conversions, and product yields obtained from two stage liquefaction of iron-treated and untreated coals in the presence of a molybdenum additive are shown in *Table 2.1.3.* The last day of each condition (Periods 5, 7, and 14) represented the steady state operations for each of the three operating conditions. Detailed analyses of the products from these periods were used to calculate normalized yields and to assess product quality. In addition the yields were calculated for Period 4 using Period 5 product analyses.

3.1 Process Performance

CMSL-1 (Bench Run 227-77) was compared to CC-15 (Bench Run 227-75) and to CC-1 (Bench Run 227-55). All three of these programs used sub-bituminous coal from the Black Thunder mine and Shell S-317 1/32" extrudates as the supported catalyst in the second stage of a two stage reactor system. CMSL-1 and CC-15 also used a pretreater before the first stage to activate a dispersed catalyst. CC-1 used Shell S-317 1/32" extrudate catalyst in both stages and there was no pretreater. Within the limitations of the available data, the periods chosen from each bench run were selected for similar catalyst ages, temperature staging, and space velocities.

Three periods were chosen from CMSL-1 with a range of catalyst ages form 196 to 530 kg coal/kg catalyst. Two periods were chosen from CC-15 with catalyst ages of 228 to 316 kg coal/kg catalyst. One period was chosen from CC-1 with a catalyst age of 456 kg coal/kg catalyst. The temperatures for all three CMSL-1 periods used were 440°C (824°F) for the first stage and 413°C (775°F) for the second stage. For CC-15 these temperatures were 427°C (801°F) and 412°C (774°F) respectively. While this is a wider range of catalyst ages and temperatures than would be ideal, it still allows valid comparisons to be made among the various chosen periods. The most significant difference among the three bench runs chosen is their relative space velocities. Using CC-1 as the standard space velocity, CC-15 was slightly lower than the standard, by 4 to 9%, while CMSL-1 was substantially higher than the standard, by 45 to 66%.

A summary table of pertinent operating parameters and process results for the chosen periods from the three different bench runs is presented in *Table 2.1.4.*

3.1.1 Coal Conversion

Coal conversions on a moisture and ash free basis for the entire run are given in *Figure 2.1.1.* Coal conversions for Condition 1 were very consistent, ranging from 93.6 to 94.0 W%. For Condition 2 the coal conversion was also in this range at 93.4 W%. In Condition 3, which included a partial startup and shutdown, coal conversions initially were low, but by the end of the condition it was in line with the previous results at 93.9 W%.

Figure 2.1.2 compares the coal conversions during the three bench runs. The difference between the coal conversions with the molybdenum and iron catalysts and with only the molybdenum catalyst for CMSL-1 was negligible. Comparing CMSL-1 to CC-15 and CC-1 indicates that CMSL-1 had the highest coal conversion of the three runs even though it also had the highest space velocity and consequently the lowest residence time. This was partly due to the higher temperatures of the reactors in CMSL-1. The most significant difference was with the no-additive-catalyst condition (CC-15, Period 11), which had only 90.0% coal conversion, 2-4% lower than in the other operations considered.

3.1.2 524 °C+ Resid Conversion

Figure 2.1.3 gives the 524 °C+ resid conversions on a moisture and ash free basis for CMSL-1, CC-15 and CC-1. For CMSL-1 the resid conversion showed the normal decrease that was expected as the catalyst extrudate deactivates over the course of the run.

Comparing CMSL-1 Period 14 with a catalyst age of 530 kg coal/kg catalyst with CC-1 Period 16 with a catalyst age of 456 kg coal/kg catalyst shows equal resid conversion at 89.1 W%. This indicates that the catalyst system in CMSL-1 (consisting of slurried catalyst and a second stage supported catalyst) was deactivated no quicker, if not slower, than the catalyst system used in CC-1 (supported catalyst in both stages). This similar level of resid conversion for equivalent catalyst ages was achieved even though CMSL-1 was operated at a 45 to 46 W% higher throughput resulting in a lower residence time.

Comparing CMSL-1 Period 5 with a catalyst age of 196 kg coal/kg catalyst with CC-15 Period 8 with a catalyst age of 228 kg coal/kg catalyst shows that CMSL-1 with both a molybdenum and iron slurried catalyst performed better (by 3.8 W%) than iron slurry catalyst alone. And it obviously performed better than when no slurry catalyst was used as in CC-15 Period 11. This should be a valid comparison despite the 13°C higher temperature in CMSL 1, which should be offset by the lower residence time.

Figure 2.1.4 compares the resid conversion as a function of catalyst age for Runs CMSL-1 and CC-15. The CMSL-1 run, using the molybdenum/iron and molybdenum only catalyst systems, always had a higher resid conversion than did CC-15 with just the iron catalyst system. Additionally the rate of deactivation as measured by the slope of the graph was also lower for the molybdenum system by 54%.

3.1.3 H_2 Consumption

Figure 2.1.5 gives the hydrogen consumption on a dry coal basis for CMSL-1, CC-15 and CC-1. The hydrogen consumption for CMSL-1 varied from 8.06 W% to 8.5 W%, a very small range. In fact, the hydrogen consumption among all three runs only varied from 7.82 Wt% to 8.5 W%. This narrow-range distribution could not clearly show the effects of different operating parameters and first stage catalysts used in the three runs. However, hydrogen consumption in Run CC-1 case appears to be somewhat low.

3.2 Product Distribution

3.2.1 C_1-C_3 Gas Yield

Figure 2.1.6 gives the C_1-C_3 gas yield, on a dry coal basis, for CMSL-1, CC-15 and CC-1. The C_1-C_3 gas yield varied between 8.9 and 10.4 W% during Run CMSL-1. CMSL-1 Periods 5 and 7 with both the molybdenum and iron dispersed catalysts had lower gas yields than Period 14 using just the molybdenum catalyst by 1.1 W%, than CC-15 Period 8 using just the iron catalyst by 0.8 W%, and than CC-1 Period 16 using the supported catalyst by 1.0 W%.

3.2.2 C_4-199 °C Naphtha Yields

Figure 2.1.7 gives the C_4-199 °C naphtha yield on a dry coal basis for CMSL-1, CC-15 and CC-1. The naphtha yield during CMSL-1 varied between 18.5 and 20.9 W% for the three conditions and appears to be independent of the presence of the iron slurry catalyst. The molybdenum/iron and molybdenum only catalyst systems compared favorably to the iron only catalyst system and were slightly worse than the supported catalyst system by 1.5 W% (comparing the CMSL-1 Period 14 and CC-1 Period 16).

3.2.3 199-343 °C Middle Distillate Yield

Figure 2.1.8 gives the 199-343°C middle distillate yield on a dry coal basis for CMSL-1, CC-15 and CC-1. The middle distillate yield during CMSL-1 showed a typical decrease from 35.1 to 29.1 W% as the run progressed due to catalyst deactivation. Comparing similar catalyst ages for CMSL-1 (Period 14) and CC-1 (Period 16) indicates that CMSL-1 had a higher middle distillate yield of 33.5 W%. Comparing similar catalyst ages for CMSL-1 (Period 5) and CC-15 (Period 8) shows that CMSL-1 had a higher yield by 4.2 W%. The molybdenum/iron catalyst system had a better middle distillate yield than either the iron catalyst system or the supported catalyst system.

3.2.4 343-524 °C Heavy Distillate Yield

Figure 2.1.9 gives the 343-524 °C heavy distillate yield on a dry coal basis for CMSL-1, CC-15 and CC-1. The heavy distillate yield during CMSL-1 exhibited only part of the increasing trend that would normally be expected as the catalyst deactivated. Period 14 had the same yield as period 7 even though it has nearly twice the catalyst age. Comparing similar catalyst ages for CMSL-1 (Period 14) and CC-1 (Period 16) shows that CMSL-1 had a lower heavy distillate yield of 2.6 W%. Comparing similar catalyst ages for CMSL-1 (Period 5) and CC-15 (Period 8) shows that CMSL-1 had a lower yield by 5.5 W%. The molybdenum/iron catalyst system had a lower heavy distillate yield than either the iron catalyst system or the supported catalyst system.

3.2.5 524 °C+ Resid Yield

Figure 2.1.10 gives the 524°C+ resid yield on a dry coal basis for CMSL-1, CC-15 and CC-1. The resid yield during CMSL-1 showed the expected trend of increasing yield as the catalyst deactivated, from 2.18 W% in Period 5 to 4.54 W% in Period 14. Comparing similar catalyst ages for CMSL-1 (Period 14) and CC-1 (Period 16) shows that CMSL-1 had a higher resid yield by 1.54 W%. Comparing similar catalyst ages for CMSL-1 (Period 5) and CC-15 (Period 8) shows that CMSL-1 had a lower resid yield by 2.49 W%. The molybdenum/iron catalyst system had a lower resid yield than the iron catalyst system and a higher resid yield than the supported catalyst system.

3.2.6 C_4-524 °C Total Distillate Yield

Figure 2.1.11 gives the total C_4-524°C distillate yield on a moisture and ash free basis for CMSL 1, CC-15 and CC-1. The total distillate yield during CMSL-1 had the expected trend of decreasing as the catalyst deactivated, from 64.5 W% in Period 5 to 60.7 W% in Period 14. Comparing similar catalyst ages for CMSL-1 (Period 14) and CC-1 (Period 16) shows that CMSL-1 had a lower total distillate yield by 1.6 W%. Comparing similar catalyst ages for CMSL-1 (Period 5) and CC-15 (Period 8) shows that the yields were similar, only 0.4 W% higher for CMSL-1. These comparative yields, especially between CMSL-1 and CC-15, were not significantly different even though the relative yields of most of the cuts were different.

3.2.7 Distillate Selectivity

Distillate selectivity is a measure of the relative yields of the various cuts. The yields of each cut from each period are normalized to 100% of the total distillate yield and are presented in *Figure 2.1.12*. Comparing similar catalyst ages for CMSL-1 (Period 14) and CC-1 (Period 16) shows that CMSL-1 had 1.9% less naphtha, 6.2% more middle distillate, and 4.3% less heavy distillate. Comparing similar catalyst ages for CMSL-1 (Period 5) and CC-15 (Period 8) shows that CMSL-1 had 2.1% more naphtha, 7.0% more middle distillate and 9.1% less heavy distillate. CMSL-1 had a lighter distillate product than either CC-15 or CC-1.

3.3 Evaluation of Performance of Different First Stage Catalysts---Part I

3.3.1 First Stage Catalyst Performance Comparison:

To study the relative performance of different first stage catalyst additives, the product yields, conversion and hydrogen consumption data for a few selected periods of the Runs 227-75, 227-77 (CMSL-1) and 227-55 were compared. All these runs used subbituminous coal from the Black Thunder Mine. They also used Shell S-317 1/32" extrudate Ni-Mo catalyst in the second stage. However, they used different catalysts in the first stage.

Run 227-77 (CMSL-1) used molybdenum additive with or without predispersed iron catalysts in the first stage. Run 227-75 used predispersed iron catalyst or no catalyst in the first stage. Run 227-55 used Shell S-317 Ni-Mo catalyst extrudates in both stages.

Because of the variation in operating conditions and catalyst age in the selected periods of these runs, their product yield and conversion data cannot give a clear picture of the effects of different first stage catalysts on process performance. It is necessary to compare the results of these runs with those of standard case projected runs at those operating conditions in order to determine the relative performance of the first stage catalyst additives.

Coal liquefaction performance using Shell S-317 Ni-Mo 1/32" extrudate catalysts in both stages and Black Thunder Mine subbituminous coal as feed was chosen as the standard case for comparison with the performance of the selected runs.

Using earlier experimental data and correlations, a simulation computer program was developed at HTI to make projections for product yields, conversion, and hydrogen consumption in two stage coal liquefaction process using Shell S-317 1/32" extrudate Ni/Mo catalysts in both stages. This simulation program was utilized to project the process performance of the standard case at the operating conditions and catalyst age of the selected runs mentioned earlier.

These projected data are compared with the actual process performance data for a few selected periods of these runs. The difference (D* = actual - projected for CTSL with extrudate catalyst in both stages) of actual and projected yields, conversion, and hydrogen consumption data for different selected periods compares the performance of different first stage catalysts with the selected standard.

In order to verify the accuracy of the simulation program, projections for three standard cases are compared with the actual experimental results from Runs 227-55-6, 227-55-15, and 227-55-16 using Shell S-317 extrudate catalyst in both stages. Runs 227-55-15 and 227-55-16 had topped separator bottom recycle operation. The D* values for these runs are presented in the following table:

	Run 227-55-6 D*	Run 227-55-15 D*	Run 227-55-16 D*
C_4-524°C, W% MAF	-0.86	2.26	-2.1
Coal Conversion, W% MAF	-0.14	1.03	0.78
Resid, W% MF	0.43	-0.06	-0.54
C_1-C_3, W% MF	0.18	-0.54	1.06
C_4-199°C, W% MF	-1.77	-1.61	-2.03
199-524°C, W% MF	1.82	3.7	0.06
Hydrogen Consumption, W% MF	0.19	0.00	0.32

The D* values for Run 227-55 show an excellent agreement between actual and projected data considering accuracy range of experimental data. The D* for coal conversion, C_4-524°C yield, hydrogen consumption, C_1-C_3 gas yield, and resid yield are all within ±1 W% range. The D* for C_4-199°C and 199-524^{0}C liquid product yields are in the ± 2 W% range.

The D* values for Run 227-55-15 and 227-55-16 also show good agreement between actual and projected values. The D* data for coal conversion, hydrogen consumption, C_1-C_3 gas yield and resid yield are all within ±1 W% range. The D* data for C_4-524°C yield are within ±2.3 W% range.

Similar comparison was made for Run 227-75-11T using no catalyst in the first stage and Shell S-317 extrudate catalyst in the second stage. The purpose of this comparison was to determine the effect of reactor volume occupied by the extrudates on coal conversion. Because of the volume occupied by the extrudate catalysts, the projected case has less residence time in the reactor resulting in lower coal conversion. Reaction kinetic estimates shows that coal conversion can be lower by 2.0 W% due to this effect. However, the D* for coal conversion was 4.06 W%. The D* of 4.0 W% will be selected as standard for the case of the first stage not having extrudate catalyst.

Run 227-75-14T used predispersed iron catalyst in the first stage and Shell S-317 catalyst in the second stage and the Run 227-77-14T (CMSL-1) used molybdenum slurry catalyst in the first stage and Shell S-317 catalyst in the second stage. The D* values for these runs compare the relative performance of iron catalyst and molybdenum catalyst in the first stage for the two stage coal liquefaction process. For the convenience of discussion, the relevant D* values for the iron-case and for the molybdenum-case are presented below:

	D* For Fe-Case	D* For Mo-Case
C_4-524°C, W% MAF	-2.18	-1.58
Coal Conversion, W% MAF	6.96	5.86
Resid, W% MF	5.05	1.18
C_1-C_3, W% MF	1.74	2.58
C_4-199°C, W% MF	-4.18	0.15
199-524°C, W% MF	2.15	-1.63
Hydrogen Consumption, W%	0.7	1.24

The above table shows that coal conversions are significantly higher in both Fe-case and Mo-case than those in the standard case. Taking into consideration of reactor volume effect, at least 2-3 W% of coal conversion can be credited to the effect of dispersed iron and molybdenum catalysts. These results indicate that the intimate contact of catalyst active sites and coal molecules does enhance coal conversion.

The C_4-524°C distillate yields are 1-2 W% lower than the standard case due to high resid yield and C_1-C_3 gas yield in iron and molybdenum catalyst cases. Hydrogen consumptions in these two case are approximately 1 W% higher than the standard case. It appears that although more coal is converted in Fe-case and Mo-case, the converted coal appear in the resid and gas yields.

The above comparison shows that beside coal conversion, the performance of the iron catalyst or molybdenum catalyst in the first stage are not in any respect better than that of the standard case. In overall performance, the standard case appears to be somewhat superior to the Fe-case or Mo-case.

Relative comparison of the Fe-case with the Mo-case shows that relative coal conversion is slightly higher for the Fe-case, but resid yield is significantly lower in the Mo-case and relative C_4-524°C distillate yield slightly lower in the Fe-case. The Fe-case has lower C_4-199°C light distillate yield but higher 199-524°C heavy distillate yield than the standard case. The Mo-case has higher relative C_4-199°C light distillate yield and lower 199-524°C heavy distillate yield. The relative C_1-C_3 gas yield is slightly higher for the Mo-case than that for the Fe-case.

In overall performance comparison, the Mo-case is slightly better than the Fe-case particularly in terms of resid conversion and light distillate yield.

Run 227-75-8T used predispersed iron catalyst in the first stage and Shell S317 catalyst in the second stage, and the Run 227-77-7T (CMSL-1) used molybdenum slurry catalyst as well as predispersed iron catalyst in the first stage and Shell S-317 catalyst in the second stage. The D* values for these runs compares the relative performance of iron/moly catalyst (Fe-Mo Case) catalyst and iron catalyst (Fe Case) in the first stage for the two stage coal liquefaction process. For the convenience of discussion, the relevant D* values for Fe-Mo-Case and Fe-Case are presented below:

	D* For Fe-Mo-Case	D* For Fe-Case
C_4-524°C, W% MAF	-0.64	0.72
Coal Conversion, W% MAF	8.02	6.17
Resid, W% MF	1.94	3.18
C_1-C_3, W% MF	2.44	1.69
C_4-199°C, W% MF	0.3	-3.03
199-524°C, W% MF	-1.17	3.68
H_2O, W% MF	2.36	-0.97
Hydrogen Consumption, W%	0.94	1.02

The above table shows that coal conversions are significantly higher in both Fe-Mo-Case and Fe-case than that in the standard case. At least 2-4 W% of coal conversion can be credited to the effects of Fe-Mo and Fe catalysts in the first stage. The C_4-524°C distillate yields are more or less equivalent in all cases considering experimental uncertainty.

Resid yield and gas yield are higher in both Fe-Mo-case and Fe-Case than those in the standard case. Hydrogen consumptions are also higher for Fe-Mo-Case and Fe-Case than that in the standard case.

The above comparison shows that except for coal conversion, the performance of the Fe-Mo-Case or Fe-Case are not in any respect superior to that of the standard case.

Comparison of the Fe-Mo-Case with the Fe-Case shows that resid yield and 199-524°C heavy distillate yield are higher for the Fe-case, and C_4-199°C light distillate yield and C_1-C_3 gas yields are higher for the Fe-Mo-Case. Water yield is almost 3.3 W% higher for the Fe-Mo-Case than that for the Fe-Case, which is possibly not truly the case.

Apparently, the overall performances of these two cases are not significantly different from each other. It appears that the presence of molybdenum catalyst in the first stage improves resid conversion and light distillate yield. Considering higher coal conversion and higher resid conversion for the Fe-Mo-Case, the overall performance of the Fe-Mo-Case is somewhat superior to the Fe-Case.

Run 227-75-5T used predispersed iron catalyst in the first stage and Shell S317 catalyst in the second stage, and the Run 227-77-5T used molybdenum slurry catalyst as well as predispersed iron catalyst in the first stage and Shell S317 catalyst in the second stage. The D* values for these runs compares the relative performance of iron-molybdenum (Fe-Mo-Case) catalyst and iron (Fe-Case) catalyst in the first stage for the two stage coal liquefaction process. For the convenience of discussion, the relevant D* values for Fe-Case and Fe-Mo-Case are presented below:

	D* For Fe-Case	D* For Fe-Mo-Case
C_4-524°C, W% MAF	2.2	-0.76
Coal Conversion, W% MAF	7.11	6.84
Resid, W% MF	2.93	1.34
C_1-C_3, W% MF	1.74	1.32
C_4-199°C, W% MF	-2.6	0.3
199-524°C, W% MF	4.68	-0.99
Water, W% MF	-1.75	2.83
Hydrogen Consumption, W%	1.26	0.74

The coal conversion, hydrogen consumption, resid yield, and C_1-C_3 gas yield are higher for the Fe-Case and Fe-Mo-Case than those for the standard case. C_4-524°C distillate yield is higher for the Fe-Case than those for the Fe-Mo-Case and the standard case. However, the difference in distillate yield is still within the experimental uncertainty range. Beside coal conversion, the overall performance of the Fe-Case and Fe-Mo-Case are not in any way better than that of the standard case. Comparison of the Fe-Case with the Fe-Mo-Case shows that relative C_4-524°C yield, resid yield, and hydrogen consumption are higher for the Fe-Case than those for the Fe-Mo-Case. In Fe-Mo-Case, the resid yield is lower and C_4-199°C distillate yield is higher. Again, the presence of molybdenum catalyst in the first stage seem to improve the resid conversion and light distillate yield. Again the water yield for the Fe-Mo-Case is almost 5 W% higher than that for the Fe-Case, which is eliminating the beneficial effects of the Fe-Mo-Case. The overall performance of these two cases are not significantly different from each other.

3.3.2 Conclusions

1. The Fe-Case, Mo-Case, and Fe-Mo-Case have at least 2-4 W% higher coal conversion than that for the standard case.

2. The hydrogen consumption, C_1-C_3 gas yields and resid yield are lower for the standard case than those for the Fe-Case, Mo-Case, and Fe-Mo-Case.

3. In terms of distillate yield and hydrogen consumption, cases using the additives are not in any respect superior to the standard case.

4. The presence of molybdenum catalyst in the first stage seems to improve resid conversion and C_4-199°C distillate yield.

5. The Fe-Case has higher resid yield and 199-524°C yield than the Mo-Case. The Mo-Case has higher C_4-199°C distillate yield than the Fe-Case. In terms of C_4-524°C distillate yield and hydrogen consumption, the performance of these two cases are not significantly different from each other.

6. The performance of Fe-Case and Fe-Mo-case are more or less equivalent except that the presence of molybdenum in the first stage improves resid conversion and C_4-199°C distillate yield. High apparent water yield in Fe-Mo-Case is eliminating the beneficial effects of this case.

7. The overall performance of the Fe-Case, Mo-Case, and Fe-Mo-Case are not significantly different from each other. Beside coal conversion, the overall performance of the cases with additives are not in any respect superior to the standard case.

3.4 Evaluation Of Performance Of Different First Stage Catalysts--Part II

3.4.1 ASB Recycle And Dispersed First Stage Catalysts

The Run 227-83 (CMSL-6) with ASB recycle used Fe/Mo dispersed catalyst in the first stage and partially deactivated Shell 317 extrudate catalyst in the second stage with Black Thunder Mine subbituminous coal. The D* values in the first column of the following Table represent the difference in values between the actual case of Run 227-83-12/13 and the standard projected case for conditions of Run 227-83-12/13.

W% MAF	D*	D* (Forced Carbon Balance)
C_1-C_3	2.28	1.87
C_4-199°C	-10.51	-11.52
199-524°C	13.31	10.49
H_2O	-8.29	-4.11
CO_x	4.11	3.93
NH_3	0.32	0.32
H_2S	-0.08	-0.08
Resid	0.54	0.84
Unc. Coal	-2.03	-2.03
H_2 Consumption	2.82	-0.45
C_4-524°C	-0.32	-0.29
Coal Conversion	2.02	2.02

The significant differences in H_2O and CO_x yields are noteworthy. Consideration of carbon and oxygen contents indicates a possible error in collected, and normalized, water yields. The forced carbon balanced yields in the second column show the impact of this factor. The D* values for the carbon balanced case will be used in this discussion.

It appears that due to the effect of ASB recycle, the significant difference (4 to 8 W%) in coal conversion as observed for earlier runs that used catalyst additives has narrowed down to only 2 W%. However, this difference is principally due to the increase in conversion in the standard operation because of ASB recycle. The use of ASB recycle in Run 227-83-12/13 caused at most a small increase in conversion compared to the other runs that used catalyst additives in place of extrudate catalysts in the first stage. The standard case has higher resid conversion, higher light distillate yield, and lower heavy distillate yield compared to the Run 227-83 case. The standard case appear to have higher catalytic hydrocracking activity than the Run 227-83 case.

In terms of total distillate yield, the overall performance of the projected standard case is somewhat superior to that of the Run 227-83 case, although the Run 227-83 case has 2 wt% higher coal conversion.

For the purpose of comparing the results of Run 227-83 with the results of earlier runs using dispersed Fe/Mo and Fe catalysts in the first stage, the following table presents the D* values for these cases.

W% MAF	CMSL - 6 D* 227-83-12/13T Fe/Mo Catalyst (Carbon Balanced)	CMSL-1 D* 227-77-7T Fe/Mo Cat.	CC-15 D* 227-75-8T Fe Catalyst	D* CMSL-1 227-77-5T Fe/Mo Cat.
C_1-C_3	1.87	2.59	1.8	1.40
C_4-199°C	-11.52	0.32	-3.22	0.32
199-524°C	10.49	-1.24	3.92	-1.05
H_2O	-4.11	2.51	-1.03	3.0
CO_x	3.93	1.31	0.87	0.91
NH_3	0.32	2.21	2.01	2.15
H_2S	-0.08	-0.63	-0.49	-0.61
Resid	0.84	2.06	3.38	1.42
Unc. Coal	-2.03	-8.06	-6.15	-6.78
C_4-524°C	-0.45	-0.64	0.72	-0.76
H_2 Consump.	-0.29	1.0	1.09	0.79
Coal Conv.	2.02	8.02	6.17	6.84

A comparison of the data in this table leads to the following comments.

a) With ASB recycle and the first stage catalyst additive in Run 227-83-12/13, the D* value for coal conversion was only 2 W% compared to 6 to 8 W% in earlier similar runs without ASB recycle.

Although the actual coal conversion value for Run 227-83-12/13 was either the same or slightly higher than the other cases, it appears that ASB recycle in this case did not have any contribution to coal conversion.

b) The Run 227-83 case has higher heavy distillate yield and lower light distillate yield compared to the earlier cases.

c) The H_2O yield is much lower and CO_x yield much higher in Run 227-83 case than those in earlier cases.

d) C_1-C_3 gas yields are more or less equivalent.

e) The C_4-524°C yield in Run 227-83 case is more or less equivalent to the earlier cases.

f) Hydrogen consumption is approximately 1 W% lower due to low yield of light distillates.

g) Overall performance of the Run 227-83 case is nominally inferior to that of the other cases, primarily because of the low light-distillate yield, which would require a higher cost for downstream processing.

3.4.2 Slurry Catalyst Recycle

The recycled catalyst in Run CMSL-6, i.e., the slurry catalyst in the ashy CAS bottoms recycle was not found to have any significant impact on the overall activity of the total dispersed catalyst system (fresh + recycled together). This is based on the similar yields and conversion numbers obtained during conditions when the amount of CAS bottoms recycle was varied to vary the total dispersed catalyst concentration in the system to correspond to 133, 166, and 216% of the fresh catalyst added with the feed.

These results indicate that the recycled catalyst did not have any significant residual catalytic activities. It is apparent that the slurry catalyst additives deactivates at a much faster rate than the extrudate catalysts would.

3.5 Product Quality

Different product fraction (SOH, ASOH, PFS and PFL) from periods 5, 7, 14, and 15A of Run CMSL-1 were analyzed for their elemental composition, boiling point ranges, solubilities and API gravities. The pressure filter liquids (recycle oils) were separated into various boiling point range fractions, and these fractions were also analyzed.

3.5.1 Atmospheric Still Overheads

The results of the various analyses performed on the atmospheric still overheads (ASOH) is presented in *Table 2.1.5*. As this table shows, the quality of the ASOH did not change over the course of the run. The only noticeable trend was a slight increase in the sulfur level as the catalyst deactivated.

3.5.2. Separator Overheads

The results of the various analyses performed on the separator overheads (SOH) are presented in *Table 2.1.6*. As this table shows, the hydrogen content and gravities of the SOH did not change much over the course of the run. However, as the second stage and hydrotreater catalysts deactivated, the sulfur and nitrogen levels slowly increased.

Table 2.1.7 presents the results of a proton analysis on the SOH for periods 5, 7 and 14 broken down into three different cuts. The total level of aromatics present in the SOH increased as the catalyst aged. The level of aromatic protons and cyclic protons increased as the run progressed, while the level of paraffinic protons decreased. *Table 2.1.8* presents the results of the PONA Analysis on the SOH for Periods 5,7, and 14. This shows little variation except for Period 14 having a decrease in dicycloparaffins and an increase in alkybenzenes.

In addition to the effect of catalyst deactivation, the higher reactor and hydrotreater space velocity in Condition 2 resulted in generally lower product quality. With only a slightly higher catalyst age, the sulfur and nitrogen levels doubled and the aromatics and cyclics increased significantly.

3.5.3 Pressure Filter Liquid

The results of the various analyses performed on the pressure filter liquids (PFL) is presented in *Table 2.1.8.* The atomic H/C ratio slowly decreased as the catalyst deactivated. The nitrogen content was influenced by both the catalyst aging and the nitrogen in the feed coal. The PFL nitrogen content in Condition 3, using untreated coal, was about the same as the nitrogen content in Condition 1, using the treated coal which had a higher nitrogen content.

The changes in PFL analyses during a run are indicative of the of the catalyst deactivation. Resid content increases as the hydrocracking activity declines. *Figure 2.1.13* shows the resid content as a function of catalyst age for the three runs. Run CC-1 data is not appropriate to this comparison past a catalyst age of 168 kg dry coal/kg catalyst due to various recycle schemes that were used. Both CC-15 with the iron catalyst and CC-1 with the supported Shell S-317 catalyst demonstrated the same trend of resid buildup in the PFL. Run CMSL-1 with the molybdenum catalyst initially showed this same trend until a catalyst age of 300 kg dry coal/kg catalyst was reached, after which the resid content of the PFL was approximately constant at 27 W%. The leveling of the catalyst deactivation could be due to the benefits of continuously adding fresh Mo catalyst, but it might also have been influenced by the effect of the shutdown, catalyst wash, and restart with lighter during in Run CMSL-1.

3.5.4 Pressure Filter Cake

The results of the various analyses performed on the pressure filter cake (PFC) are presented in *Table 2.1.9.* This table shows similar quality of PFS for periods 5 and 7 and similar qualities for periods 14 and 15A. The difference between these two groups is in their ash and sulfur contents. For periods 14 and 15A the untreated coal was used. Without the iron impregnated in the coal matrix to add to the ash content, as well as binding to some of the sulfur, it would be expected that there would be lower ash and sulfur contents.

3.6 First Stage Slurry Analyses

Samples of the first stage slurry were obtained at the end of Conditions 1 and 3 (Periods 5 and 14) in Run CMSL-1. The analyses of the samples that were obtained were used in conjunction with the second stage net product and recycle solvent analyses to characterize the performance of the individual stages. The analyses were conventional D-1160 distillation of the filterable portion, and solvent fractionation of the 524°C+ residuum as 524°C+ Oil (cyclohexane soluble), 524°C+ Asphaltenes (toluene soluble, cyclohexane insoluble), and 524°F+ Preasphaltenes (toluene insoluble). The THF insoluble solids were characterized as ASTM ash and unconverted coal (the balance of the quinoline insoluble portion). Elemental analyses were obtained on the THF-washed solids, the total filter cake, the total filtered liquid, and the distillation fractions. *Table 2.1.10* shows these first stage analyses generally correspond to the second stage PFL and PFC analyses given in *Tables 2.1.8 and 2.1.9.*

3.6.1. Coal Conversion

With the relatively high first stage reactor temperature of 441°C (825°°F) almost of the coal conversion occurred in the first stage. The ash balance indicated that the first stage coal conversion was 92.4% (MAF) for Period 5 with the predispersed iron and 93.9% (MAF) for Period 14 with only the molybdenum additive. The respective overall coal conversions were 94.0% and 93.6%. The indicated Period 14 coal conversion was probably a little high, because realistically some additional coal should have been converted in the second stage. The presence of the predispersed iron did not affect the first stage convertibility of the Black Thunder coal, which approached its maximum conversion at 441°C (825°F) and the relatively high space velocity of 986 Kg/h/M^3 reactor.

3.6.2. Resid Formation and Conversion

The formation of residuum in the first stage was also similar for both conditions of Run CMSL-1. The total residuum formations were not different, averaging about 19 W% (dry coal). The presence of the predispersed catalyst had little effect. This residuum formation was a little higher than the 14 W% that had been formed in CC-1, Period 16 with a slightly lower 436 °C (817 °F) first stage. The 524 °C+ asphaltene and preasphaltene first stage formations were significantly higher for Run CMSL-1 with no supported catalyst and the higher temperature first stage. These higher asphaltenes and preasphaltenes in the first stage did react sufficientlyin the second stage to yield similar quantities overall.

3.6.3. Hydrogenation and Heteroatom Removal

As indicated in *Tables 2.1.8 and 2.1.10*, for both Periods 5 and 14 of Run CMSL-1 the hydrogen contents of all liquid fractions were higher in the second stage than in the first stage. This has been generally true in past runs when the first stage was at a higher temperature than the second stage. The hydrogen contents of the first stage liquid fractions were generally lower for Run CMSL-1 than for Runs CC-1 and CC-15. The operational differences that probably accounted for this hydrogenation difference include the higher first stage temperature (equilibrium shift) and the absence of supported NiMo catalyst in Run CMSL-1.

Figure 2.1.14 compares the relative differences between the hydrogen/carbon atomic ratios for the three heavier liquid fractions from this run with those obtained in the similar high temperature/low temperature operations of Runs CC-15 and CC-1. The figure indicates that the largest difference is in the hydrogenation of the VGO and HVGO. The iron and molybdenum dispersed catalysts (CMSL-1 Period 5 (Fe and Mo) and 14 (Mo only) and CC-15 Period 8 (Fe only)) promoted the hydrogenation in the second stage about equally, averaging 10.7% increase in the H/C ratio for these fractions. However, with no dispersed catalyst

(CC-15, Period 11) and with a somewhat aged NiMo catalyst in the second stage (CC-1, Period 16), these H/C ratios only increased by an average of 3.7%, demonstrating the benefit of having a fresh slurry catalyst in addition to the supported catalyst. However, the residuum fraction did not show this improvement due to the slurry catalyst, and the differences could have been influenced by the more favorable hydrogenation environment in first stage in Run CC-1 and CC-15.

As indicated in *Tables 2.1.8 and 2.1.10*, the nitrogen contents of the liquid fractions were generally higher for both the first and second stage products from Period 5 with the iron-treated coal than for Period 14 without the added iron. The process of treating the coal had involved nitrate and ammonium ions, which had combined with the coal. Such nitrogen that remained from the treatment was easier to remove than the original nitrogen in the coal. This difference is shown in *Figure 2.1.15*, which also includes the liquid-fraction nitrogen differences for Run CC-15 and CC-1. The nitrogen content of the second stage liquids averaged 42% lower than the nitrogen contents of the first stage liquids for the periods with iron-treated-coal feed. The change in nitrogen content was also relatively high for CMSL-1 Period 14 with the molybdenum additive, averaging 27%. Without any slurry catalyst in CC-15 Period 11 and CC-1 Period 16, the change in the nitrogen content only averaged 6%. The indicated additional denitrogenation effect of the slurry catalyst was greater for the VGO and the HVGO than for the residuum.

As indicated in *Tables 2.1.8 and 2.1.10*, there was a definite reduction in sulfur between the two stages, but the differences between the conditions were not significant because the absolute levels were so low (0.006 W% to 0.149 W%). For both conditions the change in sulfur content of the three heavier fractions varied between 53 and 83% and averaged 65%.

3.6.4. Solids

The extracted solids from the second stage were not analyzed for elemental composition, so the difference from the first stage solids was not determinable. However, the first stage H/C atomic ratios (0.62 and 0.64) were slightly higher than the H/C ratios of the first stage solids in CC-15 Periods 8 and 11 (0.58 and 0.59) and similar to the H/C ratios of the first stage solids in CC-1 Period 16. The presence of the iron additive (comparisons between conditions within Run CMSL-1 or CC-15) did not have an effect, but the solids from CMSL-1 operations with the molybdenum additive were significantly lower than the solids from the CC-15 operation with no molybdenum additive, despite the 13°C higher temperature in the CMSL-1 first stage.

3.7 Recovered Catalyst

The analytical results on the recovered catalyst for CMSL-1 as well as a comparison with the second stage catalyst recovered from Bench Runs CC-15 and CC-1 are presented in *Table 2.1.11.*

The catalyst recovery from stage 2 of CMSL-1 was 90.0% based on the relative volumes charged and recovered of +20 mesh oil free catalyst. An overall comparison of the analytical results for recovered catalysts from runs CMSL-1, CC-15 and CC-1 does not show any significant difference from each other except the effect of catalyst age.

A comparison of the particle density, pore volume, and surface area numbers for the recovered ignited catalysts from these runs show that they vary in the narrow range of 1.07-1.12 gm/cc, 0.605-0.636 cc/gm, and 204-218 m^2/gm, respectively. Catalyst age and experimental accuracy appear to be the main cause for the variation. Approximately 5% lower surface area in CMSL-1 case than that in CC-1 case is possibly due to slightly higher metal contaminant level in CMSL-1 case. Considering 0.697 cc/gm pore volume and 267 m^2/gm surface area for the fresh catalyst, the recovered ignited catalysts lost only <13.3% pore volume and <23.7% surface area.

Although both CMSL-1 and CC-15 were run without a supported catalyst in the first stage, there was not significant buildup of metal contaminants and surface area loss for second stage catalysts.

In summary, the catalyst contamination patterns for the runs CMSL-1, CC-15, and CC-1 were more or less similar.

The recovered catalyst from the hydrotreater is also included in this table. This catalyst had a recovery of 97.8% based on the relative volumes charged and recovered of +20 mesh oil free catalyst. This unimodal catalyst had a carbon buildup of 5.29 W%.

3.8 Hydrotreater Performance

The hydrotreater was on-line throughout the entire run. At the end of the run an extension condition was added without the hydrotreater to provide a basis of comparison to evaluate the hydrotreater. This allowed samples to be taken of the hot separator overhead, which was one of the input streams to the hydrotreater, along with atmospheric overhead obtained by distillation of the slurry phase from the second reactor stage. The hydrotreater performance is presented in *Table 2.1.12*. The total mass balance around the hydrotreater was 104.1% and the oil balance (ignoring gases and water) was 98.4%. The hydrodenitrogenation around only the hydrotreater was 73.7% and the hydrodesulfurization was 75.9%. The hydrotreater also improved the quality of the final product stream from a calculated H/C ratio (without hydrotreating) of 1.66 for the feed to a value of 1.72 in the hydrotreated product.

4.0 DETAILS OF OPERATION

This section summarizes the operational details of CMSL-1 (Bench Run 227-77). This was a CMSL run using sub-bituminous Black Thunder Mine coal both impregnated with an iron catalyst and untreated. Additional catalysts used were slurried ammonium heptamolybdate and supported Shell S-317.

4.1 Bench Unit Description

HRI's continuous Bench Unit No. 227 was used for this run. It employed two main reactors stages, a pretreater reactor and a hydrotreater. The first stage reactor, the thermal reactor, contained no supported catalyst and was operated as a back-mix reactor. The second stage reactor, the catalytic reactor, contained supported catalyst and was operated as an ebullated bed. The effluent from the second reactor was separated in a hot separator and the bottoms were sent to a continuous atmospheric still. The overhead from the hot separator and from the atmospheric still were combined and sent to the hydrotreater. The bottoms from the atmospheric still were pressure filtered off-line and separated into pressure filter liquid and pressure filter solids. The pressure filter liquid was recycled to the unit as the slurry oil for the feed coal. The gases were metered, sampled, and sent to flare.

The iron and molybdenum catalyst precursors were first activated in the pre-treater stage prior to the thermal (first) stage. The two catalyst precursors were activated with H2S (3 W% coal) at 300 °C (572 °F) in the pre-treater stage. The catalytic (second) stage consisted of Shell 317 1/32" extrudate. The hydrotreater was a 1 liter tubular reactor operated as a mixed-phase trickle bed and packed with Criterion 411 catalyst.

The tests were conducted at a space velocity of 480 kg coal/hr/m^3 reactor (30 lbs coal/hr/ft^3) for Conditions 1 and 3 and at 546 Kg coal/h/M^3 reactor (34 lbs coal/hr/ft^3) for Condition 2. The slurry reactor temperature was maintained at 441°C (825°F) and the ebullated bed reactor was maintained at 413°C (775°F).

4.2 Preoperational Procedures

Operations were started using L-789 as start-up oil. This was also the oil used whenever a make-up oil was needed during the run. The proper flows of oil and gases were adjusted in the system. The catalyst bed was sulfided using about 3 W% of H_2S added during start-up. The initial oil used to slurry the feed coal was recycle oil produced during the start-up procedure.

4.3 Operating Summary

A summary of the run plan for CMSL-1, consisting of 4 different operating conditions, is given in *Table 2.1.1*. Due to difficulties experienced during the run, condition 3 was eliminated. An extension Condition of 8 hours was added to the run so that product samples could be collected with the hydrotreater off-line allowing the performance of the hydrotreater to be evaluated. The actual Conditions of the run operation are presented in *Table 2.1.2*.

During the run, two shutdowns were experienced due to a high pressure drop across the reactors during period 8 and period 10. Other than these two problems operations were smooth as demonstrated by the very tight gross material balances for each period (averaging 99.4% over the course of the run) summarized up in *Figure 2.1.16*.

4.3.1 Condition 1 (Period 1-5)

The pressure upstream of the back pressure control valve fluctuated erratically during Period 1. These pressure control issues were corrected by reducing the high pressure cold separator liquid level. This allowed more disengaging space which was necessary due to the higher then normal gas flows and light ends in the feed.

There were four charge pump failures and four hydrotreater pump stoppages throughout Periods 1 to 5. Flushing the pump checks was necessary to remove solids which had settled out. This condition subsided as more PFL was recycled with the feed. The feed pump outages did not cause any feed stoppages as the feed system was equipped with two pumps that were used alternately.

Reactor temperatures were 439°C (823°F) for stage one, 413°C (775°F) for stage two, and 348°C (659°F) for the hydrotreater. The space velocity was held at 484 Kg/h/M^3 (30.5 lb/hr/ft^3).

4.3.2. Condition 2 (Period 6-8A)

During Period 6 and 7 all unit operations were very smooth. A differential pressure in excess of 0.34 MPa (50 psi) developed across the pretreater during Period 8A. Subsequently, feed flows to the pretreater stopped. The pretreater could not be flushed but both the first and second stage reactors were flushed via the buffer and high pressure sample systems. Smooth shutdown of operations followed. During inspection of the pretreater, significant coatings of unreacted coal were found on the external wall of the ebullating cup and plugging the bubble cap and riser tube.

Reactor temperatures were 439°C (822°F) for stage one, 413°C (775°F) for stage two, and 349°C (660°F) for the hydrotreater. The space velocity was increased to 549 Kg/h/M^3 (34.2 lb/hr/ft^3).

4.3.3 Condition 3 (Period 9-10A)

Eight charge pump stoppages were encountered during Period 9. The pump checks had to be flushed and cleaned periodically. During Period 9C, the differential pressure across the pretreater reactor fluctuated from 10 to 100 psi. Also, during this period the drum of coal being used was observed to be lumpy. The feed coal was switched to a different drum of coal and the unit differential pressure normalized.

During Period 10A, the unit differential pressure increased to more than 0.34 MPa (50 psi). As a result, feed flows to the pretreater stopped. First and second stages were flushed using the buffer and high pressure sample systems. Smooth shutdown of operations followed. During inspection of the pretreater, unreacted coal was found plugging the top of the reactor.

4.3.4 Condition 4 (Renamed Condition 3) (Period 10B-14)

Condition 4 was the first condition to use the untreated coal. All coal feed to the unit was hand screened to remove oversized particles. Condition 4 operations proceeded with some difficulties from the feed, buffer, ebullating and atmospheric still pumps, but none were severe enough to interrupt unit operation.

Reactor temperatures were 440°C (824°F) for stage one, 413°C (775°F) for stage two, and 349°C (661°F) for the hydrotreater. The space velocity was lowered to 477 Kg/h/M^3 (30 lb/hr/ft^3).

4.3.5 Extension Condition (15A)

This condition was held identical to Period 14 (Condition 4). The only change was that the hydrotreater was taken off-line so that samples could be taken that would allow an analysis of the hydrotreater performance.

5.0 MATERIALS USED

5.1 Feed Coal

The analyses of the two feed coals used during this Bench Run are given in *Table 2.1.13*. HRI-5828 is Black Thunder Mine sub-bituminous coal. L-780 is the same coal impregnated with the iron catalyst precursor. The iron catalyst precursor was impregnated on the coal matrix using an incipient wetness technique developed by Pittsburgh Energy Technology Center and previously scaled up by HRI for Bench Run CC-15. See Section 11 of "Catalytic Two-Stage Liquefaction (CTSL) Process Bench Studies and PDU Scale-Up with Sub-bituminous Coal, DE-88818-TOP-1" for a description of the coal impregnation procedure.

5.2 Startup/Makeup Oil

The analysis of the startup oil is given in *Table 2.1.14*. L-789 is the 343°C+ cut from L-769, which was a mixture of a topped Wilsonville distillate and the pressure filter liquid from PDU Run 260-03 made using sub-bituminous Black Thunder Mine coal.

5.3 Catalyst Additive

The molybdenum catalyst was added as a 5 W% solution of ammonium heptamolybdate at 300 ppm Mo on coal. The iron catalyst precursor was impregnated on the coal matrix using the incipient wetness technique developed by Pittsburgh Energy Technology Center and previously scaled up by HRI for Bench Run CC-15. Black Thunder Mine coal was impregnated with hydrated iron oxide (FEOOH) at 5000 ppm of iron using this technique.

5.4 Supported Catalyst

Shell S-317 1/32" extrudates (NiMo/A12O3) was only used in the second stage. This is the same batch of fresh catalyst, HRI 5394, used throughout the previous CTSL program and the subsequent runs in this program. It was presulfided during startup by injecting hydrogen sulfide. The detailed properties of the fresh catalyst are listed in *Table 2.2.16* of Section II Run CMSL-2.

5.5 Hydrotreater Catalyst

Criterion 411 NiMo catalyst was used.

6.0 CONCLUSIONS

Run CMSL-1 (227-77) was successfully completed with two conditions using FEOOH impregnated coal with the molybdenum additive and one condition with untreated coal and the molybdenum additive. Coal conversion for all three operating conditions ranged from 93.6 to 94.0 W% (MAF) while 524°C+ resid conversion ranged from 89.1 to 91.6 W% (MAF).

While the periods chosen from CMSL-1, CC-15 and CC-1 are not ideal for comparisons, the results for these periods still allow some conclusions to be drawn. At comparable operating conditions the use of combined molybdenum/iron slurried catalysts in the first stage of the CMSL process resulted in an improved process performance for liquefaction of a sub-bituminous coal over that obtained from the use of either iron or molybdenum catalyst alone or the use of the supported $Ni\text{-}Mo/Al_2 0_3$ catalyst in the first stage. CMSL-1 achieved a higher or equal level of resid conversion and a better or equal product distribution than either of the other two runs. This performance was achieved while maintaining a 46 to 66 W% higher throughput.

However, the impregnation procedure did introduce additional nitrogen to the coal matrix which resulted in more ammonia formation and a higher nitrogen content product. The economics of the improved process performance should be evaluated against the cost for impregnating the iron catalyst precursor as well as the additional hydrotreating costs.

The in-line hydrotreater removed about 75% of the sulfur and nitrogen from the light products and improved the H/C ratio from 1.66 to 1.74 in Condition 3. The relative economics of treating the entire light liquid effluent while still at high temperature and hydrogen pressure should be evaluated.

TABLE 2.1.1

Bench Run CMSL-1
Run Plan

Wyoming Black Thunder Mine Coal
Shell S-317 1/32" Extrudate Catalyst (HRI-5394)

Condition	1	2	3	4
Periods	1-5	6-8	9-11	12-15
Coal (HRI No.)	L-780	L-780	L-780	5828
Pressure, MPa (psig)	-------------17.2 (2,500) ----------			
Temperature °C (°F)				
Pretreater	------------- 300 (572) ------------			
I st Stage	------------- 440 (825) ------------			
2nd Stage	------------- 413 (775) ------------			
Hydrotreater	------------- 343 (650) ------------			
Hot Separator	------------- 316 (600) ------------			
Atmospheric Still	--------------329 (625) ------------			
Slurry Mix Tink	---- Minimun to maintain feed ----			
Space Velocity Per Stage				
Kg/h/M3	480	542	480	480
Lb/h/ft'	30	34	30	30
Additives				
Molybdenum, ppm	----------------300-------------			
Iron, ppm	5000	5000	5000	0
H_2S, W% MF Coal	--------------- 3%-------------			
Solvent/C,oal Ratio	----------------1.2/1-------------			
Recycles, W% Dry coal				
PFL to Slurry	-----------------120 -------------			
PFL, to Buf'fer				
Pretreater	----------------- 2.7 -------------			
First Stage	----------------- 2.7 --------------			
Second Stage	----------------- 2.7 --------------			

TABLE 2.1.2

Bench Run CMSL-1
Run Operation

Wyoming Black Thwider Mine Coal
Shell S-317 1/32" Extrudate Catalyst (HRI-5394)

Condition	1	2	3	3 ext
Period	5	7	14	15
Coal (HRI No.)	L-780	L-780	5828	5828
Pressure, Mpa	17.2	17.3	17.2	17.2
psig	2493	2503	2496	2498
Temperature °C (°F)				
Pretreater	300(572)	300(572)	300(572)	300(572)
1st Stage	439(823)	439(822)	439(824)	439(824)
2nd Stage	413(775)	413(775)	413(775)	413(775)
Hydrotreater	348(659)	349(660)	349(661)	349(661)
Hot Separator	321(609)	321(610)	321(605)	321(605)
Atmospheric Still	263(505)	261(502)	261(497)	261(497)
Slurry Mix Tank		Minimum to maintain		
Space Velocity Per Stage				
Kg/h/M^3	483	547	477	499
Lb/h/ft^3	30.1	34.2	29.7	31.1
Additives				
Molybdenum, ppm	300	300	300	300
Iron, ppm	5000	5000	0	0
H2S, W% MF Coal	2.7	2.6	2.9	2.9
Solvent/Coal Ratio		-----------1.2/1-----------		
Recycles, W% Dry Coal				
PFL to Slurry	116	120.1	100.8	105.8
PFL to Buffer				
Pretreat & 1st Stage	4.5	7.8	5.8	5.5
Second Stage	2.1	3.3	3.7	3.1
Makeup Oil	12.8	8.1	16.2	11.3

TABLE 2.1.3
RUN CMSL-1 OPERATING SUMMARY

DISPERSED IRON-BASED CATALYST W/MOLYBDENUM ADDITIVE RUN
COAL: BLACK THUNDER COAL - L-780 (FE TREATED) (PERIODS 1-10A)
HRI-5828 (UNTREATED) (PERIODS 10B-14)
CATALYST: 3rd STAGE-- SHELL S-317 NiMo CATALYST (HRI-5394)

Period Number	1	2	3	4	5
Date (Period)	02/05/93	02/06/93	02/07/93	02/08/93	02/09/93
Hours of Run	24	48	72	96	120
Stg 2 Cat Age (Kg dry coal/Kg cat)	32	72	114	155	196
Pretreat Temp (C)	301	298	309	301	301
1st Stage Temp (C)	421	438	439	439	439
2nd Stage Temp (C)	409	413	413	413	413
Unit Press (Mpa))	17.3	17.3	17.3	17.2	17.2
Hydrotreat Temp(C)	352	351	350	349	348
Pretreat DP (Mpa)	0.076	0.08	0.081	0.081	0.081
1st Stage DP (Mpa)	0.0	0.0	0.0	0.0	0.0
2nd Stage DB (Mpa)	0.008	0.003	0.002	0.001	0.001
SV, Kg Coal/h/M^3	375	463	483	473	482
SV, Lb Coal/hr/ft3	23	29	30	30	30
W% OF DRY COAL					
PFL Recycle	167.3	101.5	95.7	93.5	116.0
PFL Pretreat/Stage 1	15.8	12.7	16.5	12.8	4.5
PFL Stage 2	7.8	3.8	5.9	5.8	2.1
Make-up Oil	0.0	19.2	20.9	23.2	12.8
H2S	1.4	1.2	2.7	2.8	2.7
MATERIAL BAL (%)	98.66	100.96	98.94	100.49	99.78
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED					
C1-C3 in Gase				9.68	8.93
C4-C7 in Gases				4.76	3.87
180-199 deg-C in Liquids				20.17	16.64
199-260 deg-C in Liquids				11.51	10.87
260-343 deg-C in Liquids				22.52	24.22
343-454 deg-C in Liquids				-0.11	4.38
454-524 deg-C in Liquids				0.21	0.76
Toluene Soluble 524°C+ Oil				2.07	2.14
Toluene Insoluble 524°C+ Oil				0.02	0.04
Unconverted Coal				5.91	5.71
Ash				5.87	5.87
Water				20.45	20.48
CO				0.58	0.54
CO2				1.12	1.09
NH3				2.89	2.84
H2S				-0.11	-0.18
Total (100 + H2 Reacted)				107.53	108.19
PROCESS PERFORMANCE					
C4-975 deg-f Distillates, W% of MAF Coal				63.7	64.5
975F+ Conversion W% MAF				91.5	91.6
Coal Conversion W% MAF		93.7	93.6	93.6	94.0
HDN W%93.7				95.2	93.5

TABLE 2.1.3 (cont.d)
RUN CMSL-1 OPERATING SUMMARY

DISPERSED IRON-BASED CATALYST W/MOLYBDENUM ADDITIVE RUN
COAL: BLACK THUNDER COAL - L-780 (FE TREATED) (PERIODS 1-10A)
HRI-5828 (UNTREATED) (PERIODS 10B-14)
CATALYST: 3rd STAGE-- SHELL S-317 NiMo CATALYST (HRI-5394)

Period Number	6	7	8	9	10
Date (Period)	02/10/93	02/11/93	02/12/93	02/18/93	02/19/93
Hours of Run	144	168	176	200	221
Stg 2 Cat Age (Kg dry coal/Kg cat)	237	284	30	337	366
Pretreat Temp (C)	302	300		302	
1st Stage Temp (C)	440	439		421	299
2nd Stage Temp (C)	413	413	413	408	421
Unit Press (Mpa))	17.3	17.3	17.3	17.3	407
Hydrotreat Temp(C)	352	349	349	348	17.3
Pretreat DP (Mpa)	0.08	0.083	0.102	0.085	347
1st Stage DP (Mpa)	0.0	0.0	0.0	0	0.076
2nd Stage DB (Mpa)	0.001	0.001	0.002	0.014	0.003
SV, Kg Coal/h/M^3	474	546		423	385
SV, Lb Coal/hr/ft3	30	34		26	24
W% OF DRY COAL					
PFL Recycle	98.9	120.1		128.7	152.4
PFL Pretreat/Stage 1	12.2	7.8		8.9	13
PFL Stage 2	5.3	3.3		5.5	9
Make-up Oil	23.2	8.1		24.2	25.2
H2S	3.2	2.6		3.0	3.4
MATERIAL BAL (%)	100.19	100.34		101.38	94.91
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED					
C1-C3 in Gases		9.33			
C4-C7 in Gases		3.98			
IBP-199 deg-C in Liquids		14.53			
199-260 deg-C in Liquids		10.17			
260-343 deg-C in Liquids		23.30			
343-454 deg-C in Liquids		6.52			
454-524 deg-C in Liquids		1.24			
Toluene Soluble 524°C+ Oil		2.73			
Toluene Insoluble 524 °C+ Oil		0.04			
Unconverted Coal		6.17			
Ash		5.87			
Water		19.65			
CO		0.66			
CO2		1.32			
NH3		2.75			
H2S		-0.21			
Total (100 + H2 Reacted)		108.06			
PROCESS PERFORMANCE					
C4-975 deg-C Distill., W% of MAF Coal		63.5			
524C+ Conversion W% MAF		90.5			
Coal Conversion W% MAF		93.4		85.0	78.0
HDN W%		90.5			

TABLE 2.1.3 (cont.d)
RUN CMSL-1 OPERATING SUMMARY

DISPERSED IRON-BASED CATALYST W/MOLYBDENUM ADDITIVE RUN
COAL: BLACK THUNDER COAL - L-780 (FE TREATED) (PERIODS 1-10A)
HRI-5828 (UNTREATED) (PERIODS 10B-14)
CATALYST: 3rd STAGE-- SHELL S-317 NiMo CATALYST (HRI-5394)

Period Number	11	12	13	14	15
Date (Period)	02/24/93	02/25/93	02/26/93	02/27/93	02/28/93
Hours of Run	245	269	293	317	325
Stg 2 Cat Age (Kg dry coal/Kg cat)	408	449	489	530	545
Pretreat Temp (C)	299	*300*	300	300	*300*
1st Stage Temp (C)	438	440	440	440	441
2nd Stage Temp (C)	413	413	413	413	413
Unit Press (Mpa))	17.3	17,2	17.2	17-2	17.2
Hydrotreat Temp(C)	344	349	352	149	311
Pretreat DP (Mpa)	0,037	0,028	0-026	0,035	0,015
1st Stage DP (Mpa)	*0,006*	0,005	0,005	0,003	*0-005*
2nd Stage DB (Mpa)	0,003	0,001	0,001	0,001	0-001
SV, Kg Coal/h/M^3	478	478	469	476	499
SV, Lb Coal/hr/ft3	30	30	29	*30*	31
W% OF DRY COAL					
]'FL Recycle	83-8	99.9	104.1	100.8	105.8
PFL Pretreat/Stage 1	6.1	9,4	5-7	.1.8	5,5
PFL, Stage 2	3.8	3.8	3,7	3.7	3.1
Make-up Oil	33,2	18.8	17.9	16,2	11-3
H2S	2.3	2.9	3.0	2.9	2.9
MATERIAL BAL. (%)	99.23	98.73	100.11	99.67	98.51
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED					
Cl-C3 in Gases				10.43	10.19
C4-C7 in Gases				4.73	4.61
IBP-199 deg-C in Liquids				16.15	15.59
199-260 deg-C in Liquid				10.35	9.66
260-343 deg-C in Liquids				18.72	19.57
343-454 deg-C in Liquids				6.71	10.33
454-524 deg-C in Liquids				1.03	2.17
Toluene Soluble 524 °C+ oil				4.45	5.38
Toluene Insoluble 524 °C+ Oil				0.09	0.12
Unconverted Coal				5.84	6.04
Ash				5.13	5.13
Water				19-96	14.47
CO				1.01	1.30
C02				2.71	2.47
NH3				0.90	0.68
H2S				0.30	0.30
Total (I 00 + H2 Reacted)				108.5	108.01
PROCESS PERFORMANCE				60.7	65.2
C4-524 deg-C Distill., W% MAF Coal				89-1	87,9
524C+ Conversion W% MAF				93-9	93,6
Coal Conversion W% MAF	89.7	91.8	92.5	86.8	69.8
HDN W%					

TABLE 2.1.4

COMPARISON OF CONDITIONS AND RESULTS FOR CMSL-1, CC-15 & CC-1

RUN ID#	CMSL-1	CMSL-1	CMSL-1	CC-15	CC-15	CC-1
PERIOD (DAY)	5	7	14	8	11	16
CATALYST AGE (KGCOAL/KGCAT)	196	284	530	228	316	456
CAT 1ST STAGE	MOLY & IRON	MOLY & IRON	MOLY	IRON	NONE	SHELL S-317
2ND STAGE	SHELL S-317	SHELL S-317	SHELL S-317	SHELL S-317	SHELL S-317	SHELL S-317
TEMP (°C) RXN 1 (°F)	439 (823)	439 (822)	440 (824)	427 (801)	427 (801)	436 (817)
RXN 2	413 (775)	413 (775)	413 (775)	412 (774)	413 (775)	408 (767)
SPACE VELOCITY (SV_{REF} = 1.0)	1.46	1.66	1.45	0.91	0.96	1.00
COAL CONV, MAF	94.0	93.4	93.9	92.7	90.0	92.3
RESD CONV, MAF	91.6	90.5	89.1	87.7	84.0	89.1
C4-524 C, MAF	64.5	63.5	60.7	64.1	57.3	62.3
C1-C3 YLD, MAF	8.93	9.33	10.43	10.13	9.94	10.30
C4-199C YLD, MAF	20.51	18.51	20.88	19.27	18.61	22.36
199-343 YLD, MAF	35.09	33.47	29.07	30.89	27.20	25.86
343-524 YLD, MAF	5.14	7.76	7.74	10.66	8.32	10.35
RESD YLD, MF	2.18	2.77	4.54	4.67	5.66	3.00
H_2 CONS, MF	8.19	8.06	8.5	8.46	7.82	7.94

TABLE 2.1.5

INSPECTION OF ATMOSPHERIC STILL OVERHEAD

PERIOD	5	7	14	15A
GRAVITY °API	23.4	22.5	22.9	23.3
ELEMENTAL ANALYSIS, W%				
Carbon	87.28	87.24	87.21	87.37
Hydrogen	11.52	11.31	11.32	11.44
Sulfur	0.0077	0.0104	0.0130	0.0144
Nitrogen	0.35	0.47	0.36	0.38
H/C Ratio	1.58	1.56	1.56	1.57
GC SIMULATED DIST, °F				
IBP (0.50 V%)	202	231	208	209
5 V%	341	372	351	344
10 V%	385	416	384	390
15 V%	436	453	428	423
20 V%	469	483	459	456
25 V%	501	509	485	481
30 V%	512	519	508	505
35 V%	532	538	516	513
40 V%	549	553	534	530
45 V%	562	567	549	546
50 V%	580	583	562	558
55 V%	590	593	580	573
60 V%	601	610	590	587
65 V%	617	619	602	597
70 V%	626	629	618	614
75 V%	635	638	629	624
80 V%	644	647	639	635
85 V%	670	656	668	646
90 V%	679	665	681	674
95 V%	695	674	703	690
FBP (99.5 V%)	711	682	723	704

TABLE 2.1.6

INSPECTION OF SEPARATOR OVERHEAD

PERIOD	5	7	14	15A
GRAVITY °API	33.0	32.1	32.3	35.2
ELEMENTAL ANALYSIS, W%				
Carbon	86.80	86.85	87.23	86.41
Hydrogen	12.48	12.45	12.49	12.57
Sulfur	0.0089	0.0211	0.0107	0.0688
Nitrogen	0.0703	0.1495	0.0927	0.3356
H/C Ratio	1.72	1.72	1.72	1.74
ASTM DISTILLATION, °F				
IBP	140	140	136	124
5 V%	208	216	202	184
10 V%	241	250	235	210
20 V%	306	322	297	250
30 V%	386	396	371	298
40 V%	451	455	430	351
50 V%	500	505	486	406
60 V%	542	544	530	460
70 V%	575	574	564	518
80 V%	605	602	597	568
90 V%	638	634	636	622
95 V%	665	660	672	650
FBP	698	700	728	702
V% @ 199 °C (390 °F)	31	29	33	47
V% @ 260 °C (500 °F)	50	49	53	67
V% @ 343 °C (650 °F)	93	93	93	95
IBP-199 °C (390 °F), W%	27.3	25.3	28.5	42.4
199-260 °C (390-500 °F), W%	18.8	19.2	19.8	20.1
260-343 °C (500-650 °F), W%	45.6	46.6	41.6	29.4
343 °C (650 °F)+, W%	7.3	8.4	9.5	7.1
LOSS W%	1.0	0.5	0.6	1.0
TBP FRACTIONATION, W%				
IBP-177 °C (350 °F)	25.08	24.78	29.09	
177-343 °C (350-650 °F)	68.92	68.05	65.79	
343 °C + (650 °F+)	4.45	5.29	4.13	
LOSS	15.5	1.88	0.99	

TABLE 2.1.7

CMSL-1 SEPARATOR OVERHEAD PROTON ANALYSIS

PERIOD	BOILING FRACTION	AROMATICS (LV%)	AROMATIC PROTONS	PARAFFINIC PROTONS	CYCLIC PROTONS
5	IBP-177C	6.63	2.23	77.55	20.22
	177-343C	19.63	5.60	73.28	21.12
	343 C+	22.28	4.57	78.40	17.03
7	IBP-177C	7.50	2.44	76.42	21.14
	177-343C	22.61	6.45	67.45	26.10
	343 C+	26.52	5.50	72.93	21.57
14	IBP-177C	13.09	3.84	64.82	31.34
	177-343C	23.83	6.81	66.77	26.42
	343 C+	35.18	7.59	66.72	25.69

CMSL-1 SEPARATOR OVERHEAD PONA ANALYSIS, LV%

PERIOD	5	7	14
Paraffins	27.40	24.90	25.93
Olefins	0.40	0.40	0.40
Monocycloparaffins	58.30	61/51	59.01
Dicycloparaffins	6.96	6.93	5.01
Alkybenzenes	6.03	5.43	9.19
Indanes/Tetralins	0.30	0.61	0.37
Naphthalenes	0.61	0.22	0.09

TABLE 2.1.8

INSPECTION OF PRESSURE FILTER LIQUID

PERIOD	5	7	14	15A
TOTAL LIQUID				
Gravity °API	6.3	5.2	6.0	3.9
ELEMENTAL ANALYSIS, W%				
Carbon	89.29	89.50	89.88	88.65
Hydrogen	9.28	9.01	9.08	8.79
Sulfur	0.030	0.039	0.031	0.031
Nitrogen	0.50	0.98	0.49	0.52
H/C Ratio	1.25	1.21	1.21	1.19
IBP-343 °C (IBP-650 °F, W%)	8.86	7.83	12.23	11.01
343-454 °C (650-850 °F, W%)	54.53	51.98	47.38	48.42
454-524 °C (850-975 °F, W%)	13.44	14.40	12.14	13.59
524 °C (975 °F+, W%)	22.69	25.22	27.18	26.41
LOSS W%	0.48	0.57	1.07	0.57
LGO (IBP-343 °C)				
Carbon W%	88.15	88.46	88.30	88.10
Hydrogen, W%	11.17	11.12	11.21	11.12
Sulfur, W%	0.006	0.0134	0.0115	0.0121
Nitrogen, W%	0.31	0.45	0.29	0.34
HGO (343-454 °C)				
Carbon, W%	88.70	89.11	89.02	88.72
Hydrogen, W%	10.23	10.14	10.39	10.22
Sulfur, W%	0.023	0.0167	0.028	0.015
Nitrogen, W%	0.31	0.48	0.33	0.35
HVGO (454-524 °C)				
Carbon, W%	89.83	89.86	89.11	89.31
Hydrogen, W%	8.44	8.27	8.48	8.15
Sulfur, W%	0.034	0.015	0.032	0.035
Nitrogen, W%	0.67	0.84	0.59	0.63
RESID (524 °C+)				
Carbon, W%	90.28	90.53	90.92	90.48
Hydrogen, W%	6.71	6.54	6.34	6.19
Sulfur, W%	0.060	0.029	0.034	0.049
Nitrogen, W%	1.05	1.20	0.93	0.94
Cyclohexane Ins., W%	19.79		20.66	25.23
Toluene Ins., W%	1.62	1.38	1.69	1.94
Ash, W%	0.00	0.00	0.00	0.00
CCR, W%	47.29		45.91	49.97

TABLE 2.1.9

INSPECTION OF PRESSURE FILTER CAKE

PERIOD	5	7	14	15A
ELEMENTAL ANALYSIS, W%				
Carbon	58.05	59.90	61.77	60.80
Hydrogen	4.38	4.47	4.78	4.62
Sulfur	2.73	2.60	1.02	0.92
Nitrogen	0.56	0.68	0.52	90.58
COMPOSITION, W%				
ASTM Ash	34.52	31.60	27.70	28.33
Sulfur in ASTM Ash	5.84	5.51	3.23	3.07
Ash (SO3-Free)	29.48	27.25	25.46	26.16
QUINOLINE FILTRATION, W%				
Quinoline Insolubles	58.58	56.03	55.33	58.44
Ash	35.35	33.06	28.83	30.00
Sulfur in Quin. Ash	6.31	6.87	4.00	4.12
Ash (SO3-Free)	29.77	27.38	25.95	26.91

TABLE 2.1.10

INSPECTION OF FIRST STAGE SAMPLES

PERIOD	6A	15A
PRESSURE FILTRATION, W%		
Filter Cake	17.92	24.58
Filter Liquid	81.40	73.92
<u>FILTER CAKE ANALYSIS</u>		
TGA ANALYSIS		
524 °C-	18.99	28.62
524 °C+	81.01	71.38
ASH	35.92	32.16
THF FILTRATION		
Insolubles, W%	67.98	55.76
<u>ON THF WASHED SAMPLE</u>		
ELEMENTAL ANALYSIS, W%		
Carbon	40.95	35.37
Hydrogen	2.10	1.88
Sulfur	3.83	1.92
Nitrogen	0.81	.34
H/C Ratio	0.62	0.64
ASTM ASH, W%	51.52	50.95
Iron in Ash, W%	11.03	3.78
Molybdenum in Ash, ppm	4550	4950
QUINOLINE FILTRATION, W%		
Quinoline Insolubles	96.10	100.00
Ash	51.67	52.54
Sulfur in Quin. Ash	6.37	4.10
Ash (SO3-Free)	43.44	47.15

TABLE 2.1.10 (cont.)

INSPECTION OF FIRST STAGE SAMPLES

FILTER LIQUID ANALYSIS		
PERIOD	6A	15A
GRAVITY, °API	-2.5	-1.8
ELEMENTAL ANALYSIS, W%		
Carbon	88.76	88.76
Hydrogen	7.86	7.83
Sulfur	0.080	0.132
Nitrogen	1.12	0.82
ASTM D-1160 DISTILLATION		
IBP, °F	282	228
IBP-343 °C (IBP-650 °F), W%	6.47	14.12
343-454 °C (650-850 °F), W%	41.29	35.38
454-524 °C (850-975 °F), W%	14.49	14.02
524 °C (975+ °F), W%	37.10	35.75
LOSS, W%	0.65	0.73
IBP-343 °C (IBP-650 °F), V%	8.0	16.0
343-454 °C (650-850 °F), V%	45.0	38.0
454-524 °C (850-975 °F), V%	14.0	14.0
LGO (IBP-343 °C)		
Carbon, W%	87.21	87.07
Hydrogen, W%	10.39	10.64
Sulfur, W%	0.035	0.074
Nitrogen, W%	0.66	0.41
VGO (343-454 °C)		
Carbon, W%	88.90	88.48
Hydrogen, W%	9.18	8.99
Sulfur, W%	0.069	0.086
Nitrogen, W%	0.64	0.50
HVGO (454-524 °C)		
Carbon, W%	88.44	89.51
Hydrogen, W%	7.49	7.44
Sulfur, W%	0.073	0.092
Nitrogen, W%	1.17	0.88
RESID (524 °C+)		
Carbon, W%	88.06	89.82
Hydrogen, W%	5.97	5.83
Sulfur, W%	0.140	0.149
Nitrogen, W%	1.73	1.23
N-Heptane Insolubles, W%	79.70	80.94
Cyclohexane Insolubles, W%	73.68	71.18
Toluene Insolubles, W%	17.00	17.20
Ash, W%	0.26	0.20
CCR, W%	55.89	

TABLE 2.1.11

COMPARISON OF RECOVERED CATALYSTS CMSL-1, CC-15 & CC-1

Run Reactor Catalyst	CMSL-1 2nd Stage Shell 317	CMSL-1 Hydrotreat Criterion 411	CC-15 2nd St age Shell 317	CC-1 2nd Stage Shell 317
Cat Age, Lb Coa;/Lb Cat	545	530	403	675
Cat Recovery, V%	90.0	97.8	0.921	89.4
Bulk Density, gm/cc	0.874	0.959		0.903
ANALYSES OF OIL FREE +20 MESH CATALYST, W%				
Carbon	16.11	5.29	17.51	18.90
Hydrogen	0.57	0.47	1.01	0.99
H/C Ratio	0.42	1.07	0.69	0.63
Nitrogen	0.14	0.42	0.25	5.42
Sulfur	6.48	7.74	7.82	8.26
Molybdenum	7.664	11.613	1.70	1.57
Nickel	1.551	1.846	0.105	0.02
Titanium	0.0	0.0	0.034	0.07
Iron	0.102	0.308		0.20
Calcium	0.026	0.050		1.08
Sodium	1.452	0.100		1.37
Total Metal Contaminants	1.58	0.458		24.50
Loss on Ignition, W%	21.39	12.99	25.7	1.459
Particle Density gm/cc prt.	1.358	1.511	1.339	0.259
Pore Volume (D>30 A), cc/gm	0.337	0.286	0.325	101
cc/cc prt.	0.457	0.432	0.435	148
Surface Area (calc.), m2/gm	141.97	162.54	134.8	
m2/cc prt.	193	245	180	
Modal Pore Diameter, A**				
Macro-pores	2000		2700	
Mini-pores	70	75	76	
ANALYSES OF IGNITED CATALYST				
Particle Density gm/cc prt*	1.078	1.39	1.071	1.124
Pore Volume (D>30 A), cc/gm	0.622	0.401	0.636	0.605
cc/cc prt.	0.670	0.558	0.681	0.680
Surface Area (calc.),m2/ gm	204.33	173.85	218.1	214.0
m2/cc prt.	220	241	234	240
Modal Pore Diameter, A**				
Macro-pores	2500		2700	
Mini-pores	95	95	86	
ANALYSIS OF 20-100 MESH OIL-FREE SOLIDS				
Weight, gm	13.5	1.11		66.7
Molybdenum, W%	7.68	4.27	6.96	3.28

* In mercury at 10 psia.

** Criterion 411 is a unimodal catalyst.

TABLE 2.1.12

HYDROTREATER PERFORMANCE				
	INPUT STREAMS		PRODUCT STREAMS	
	HOT SEPARATOR OVERHEAD	INJECTED ATM STILL OVERHEAD	COLD SEPARATOR OVERHEAD	COLD SEPARATOR BOTTOMS
GAS STREAM COMPONENT FLOWS (gm/hr)				
H_2	173.1		173.8	
C1-C3	92.7		95.2	
C4-C7	41.8		43.1	
$C0_X$	34.2		33.8	
H_2S & NH_3	24.5		25.4	
TOTAL GAS	366.3		371.3	
LIQUID STREAM COMPONENT FLOWS (gm/hr)				
H_20	234.2			283.6
IBP-390F	120.8	23.6		146.1
390-500F	57.3	47.3		101.5
500-650F	83.7	130.0		213.2
650+F	23.0	35.4		51.8
TOTAL LIQUID	519.0	236.3		796.2
TOTAL FLOW	885.3	236.3	371.3	796.2
ELEMENTAL ANALYSIS OF LIQUID COMPONENT OF STREAM (W%)				
CARBON	86.41	87.21		87.23
HYDROGEN	12.57	11.32		12.49
NITROGEN	0.3356	0.3600		0.0927
SULFUR	0.0688	0.0130		0.0107
OXYGEN (diff.)	0.6156	1.0970		0.1766
H/C RATIO	1.74	1.56		1.72

TABLE 2.1.13

FEED COAL ANALYSIS
WYOMING BLACK THUNDER MINE

HRI NO	L-780	5828
COAL	IRON IMPREGNATED	UNTREATED
PERIODS	1-10	11-15A
MOISTURE, W%	7.15	12.87
PROXIMATE ANALYSIS, W% (MAF)		
Volatile Matter	44.65	43.37
Fixed Carbon	49.62	50.36
ULTIMATE ANALYSIS, W% (MF)		
Carbon	68.21	68.21
Hydrogen	4.37	3.85
Sulfur	0.37	0.48
Nitrogen	2.50	0.90
Ash	(6.68)	(5.96)
Sulfur in Ash	(4.86)	(5.62)
Ash (SO3-Free)	5.87	5.12
Oxygen (by difference)	18.68	21.44
Fe In Ash, W% Ash	9.92	2.84
Fe In Ash, W% mf Coal	0.656	0.205

TABLE 2.1.14

INSPECTION OF STARTUP/MAKEUP OIL

HRI NO.	L-789
GRAVITY °API	18.3
ELEMENTAL ANALYSIS, W%	
Carbon	88.27
Hydrogen	11.12
Sulfur	0.036
Nitrogen	0.23
H/C Ratio	1.51
ASTM DISTILLATION, °F	
IBP	438
5 V%	538
10 V%	566
20 V%	598
30 V%	626
40 V%	649
50 V%	665
60 V%	698
70 V%	728
80 V%	775
90 V%	850
95 V%	921
97 V%	975
V% @ 343 °C	42.0
V% @ 454 °C	90.0
V% @ 524 °C	97.0
IBP-343 °C, W%	39.58
343-454 °C, W%	46.56
454-524 °C, W%	8.36
524 °C+, W%	4.87
Loss W%	0.63

RUN 227-77 (CMSL-1)
COAL CONVERSION

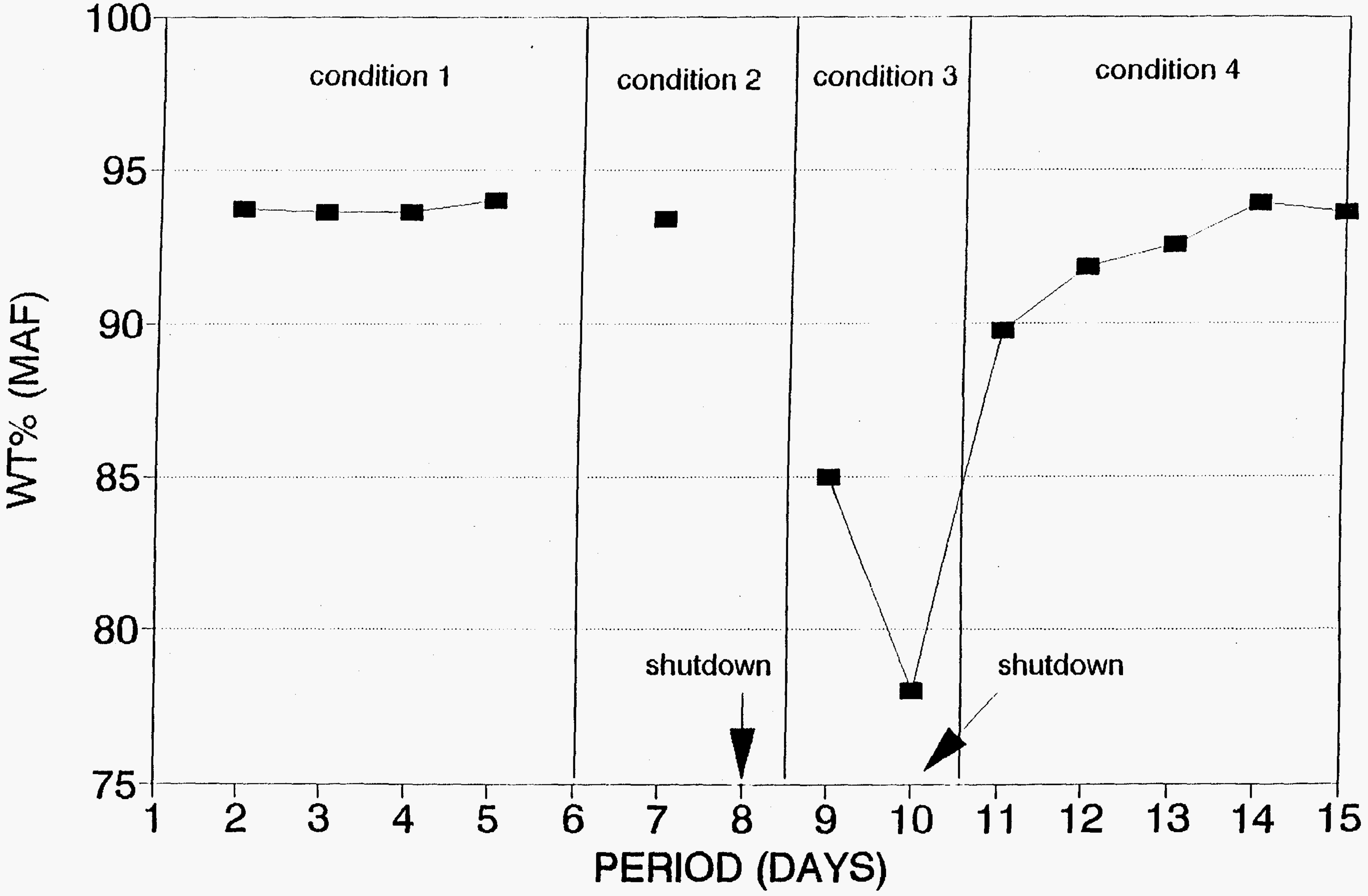


FIGURE 2.1.1

COMPARISON CMSL-1, CC-15 & CC-1 COAL CONVERSION

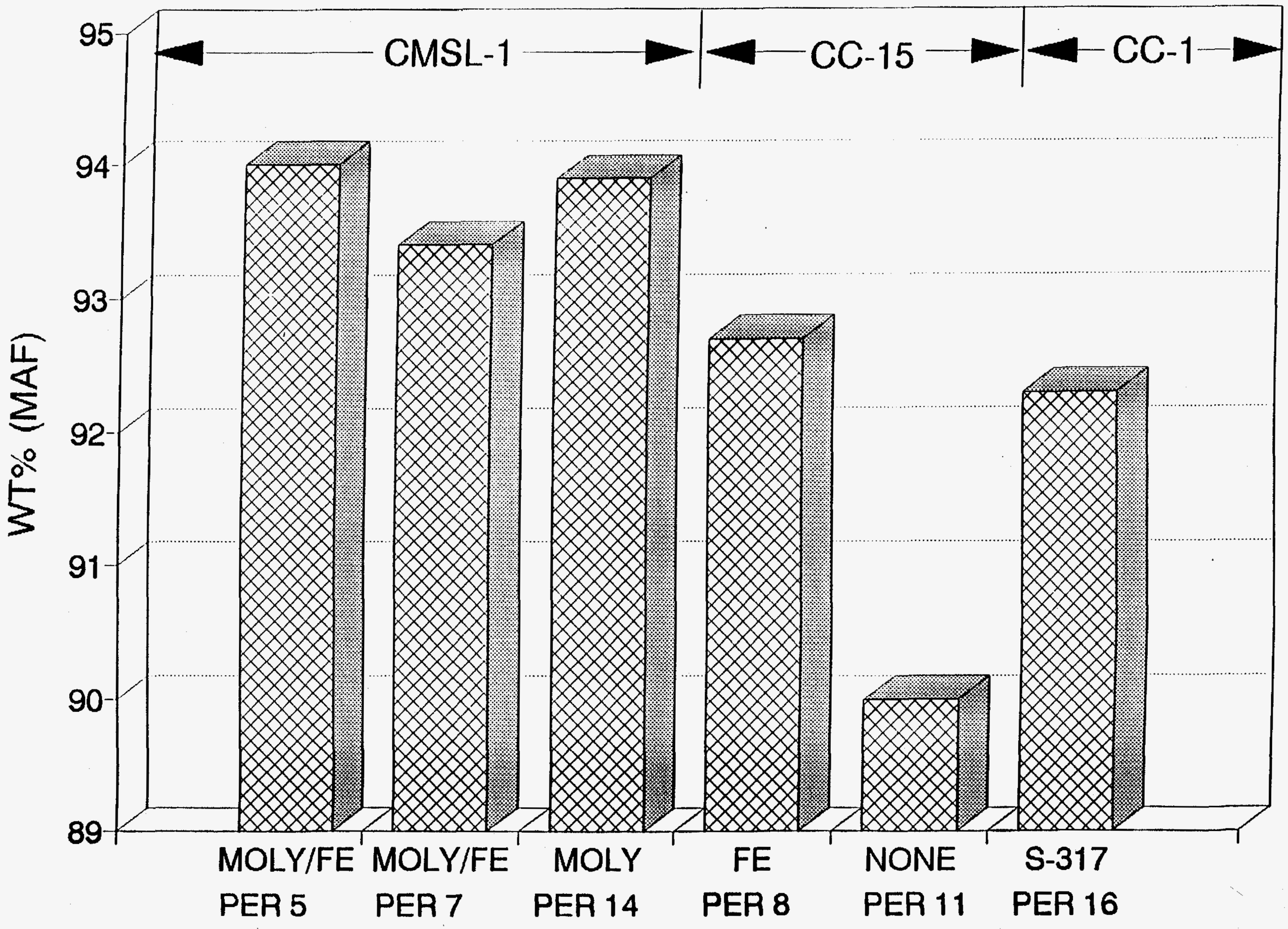


FIGURE 2.1.2

COMPARISON CMSL-1, CC-15 & CC-1
524C+ RESID CONVERSION

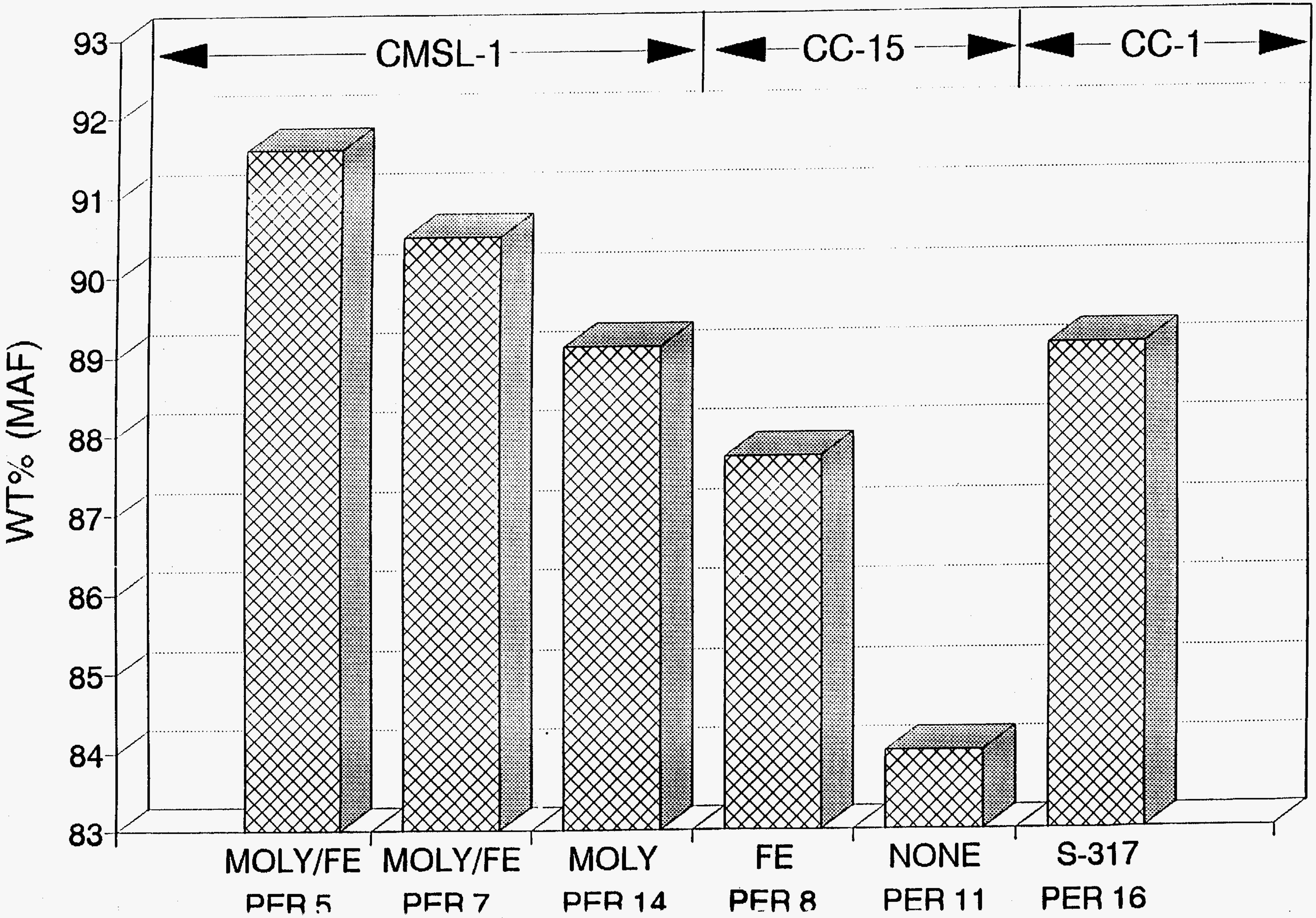
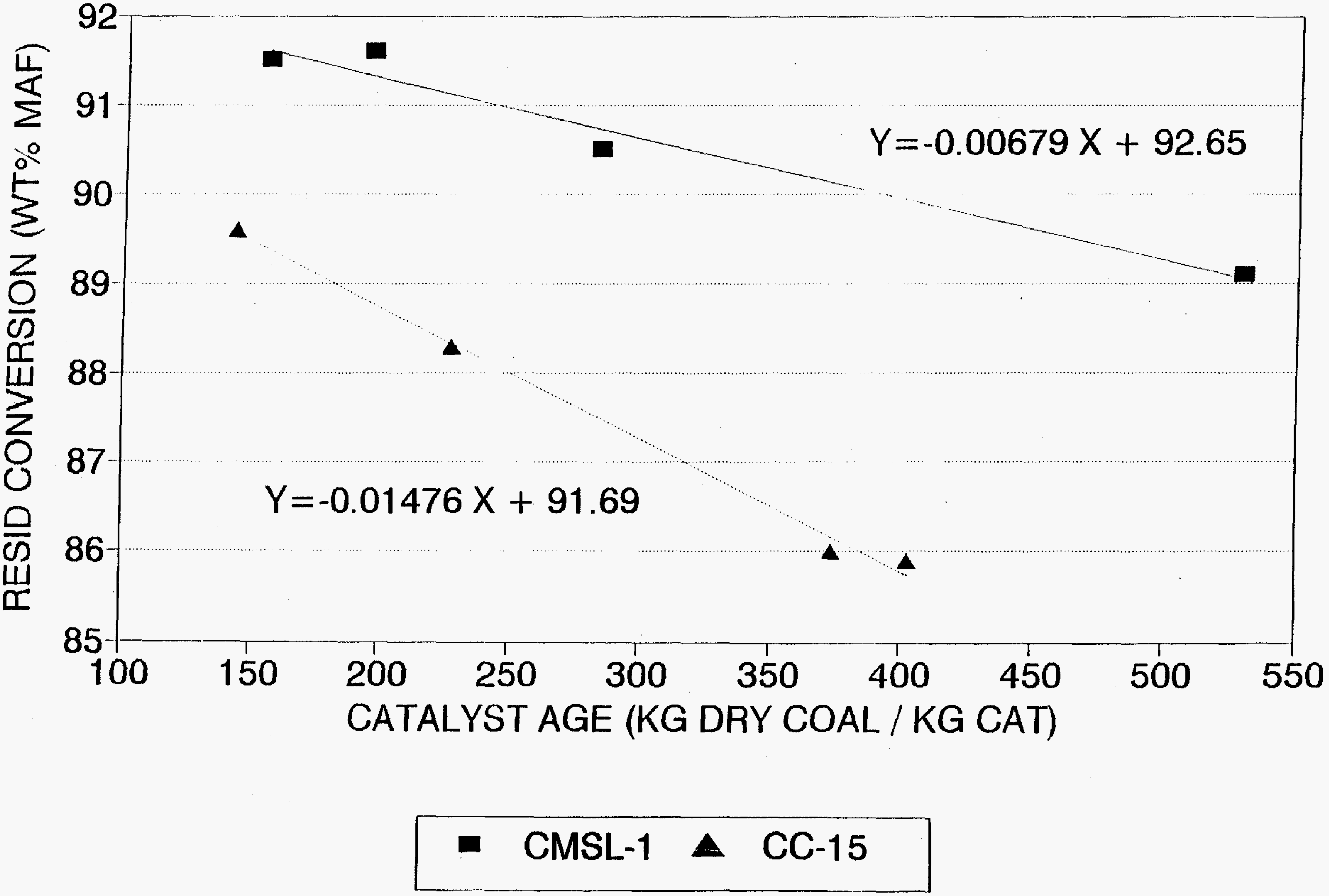


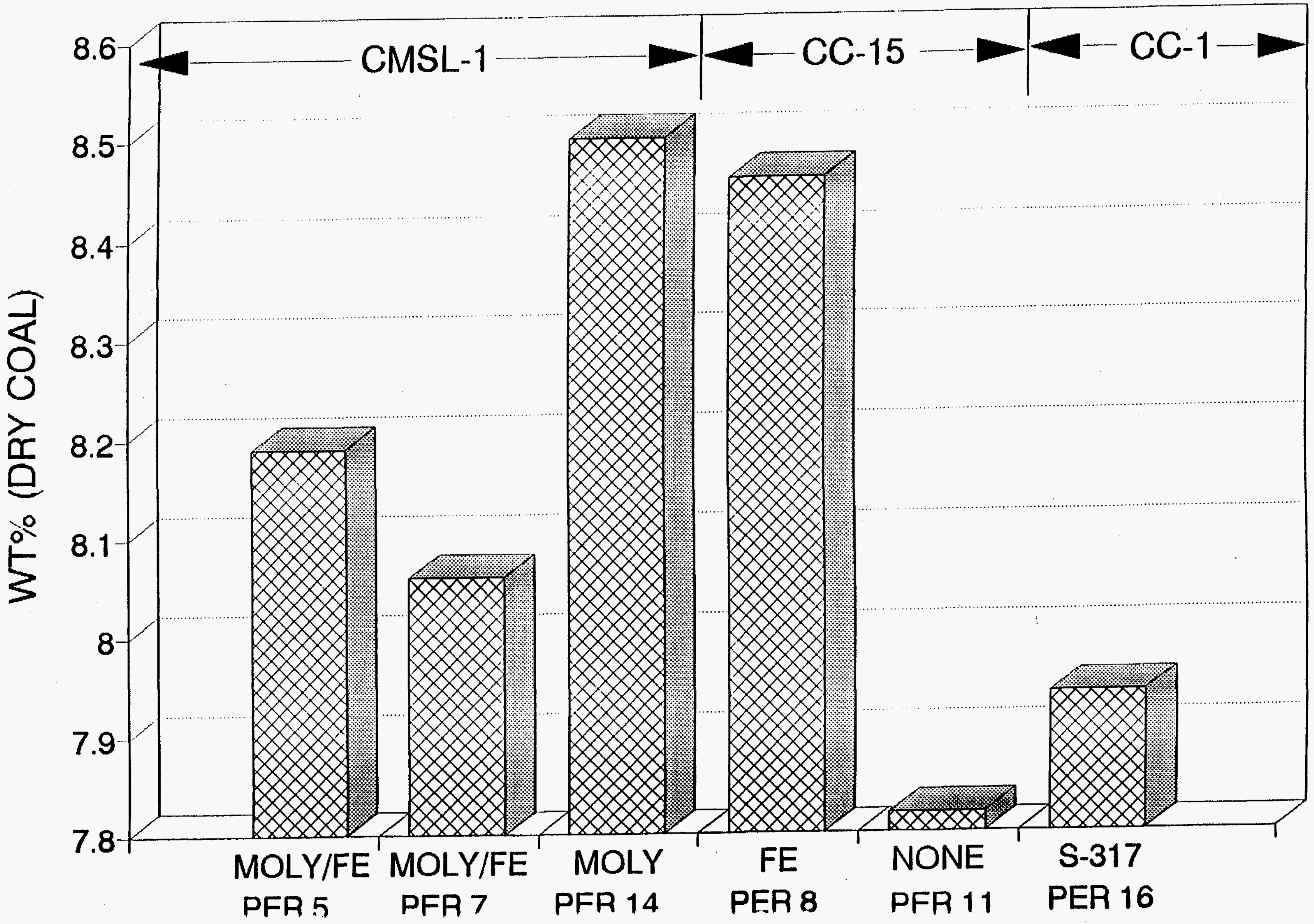
FIGURE 2.1.3



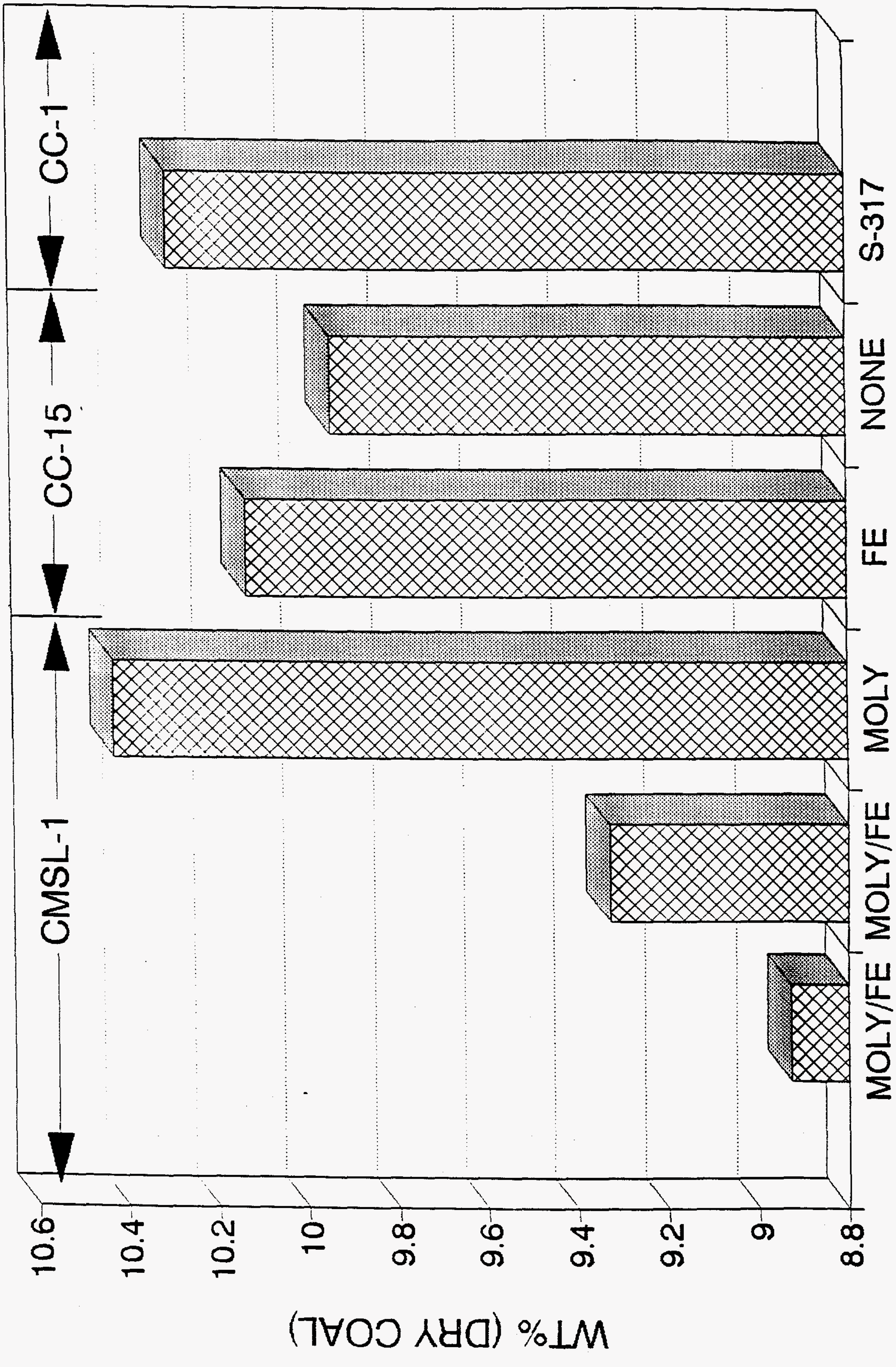
COMPARISON CMSL-1 & CC-15
RESID CONVERSION

FIGURE 2.1.4

COMPARISON CMSL-1, CC-15, CC-1 HYDROGEN CONSUMPTION



COMPARISON CMSL-1, CC-15 & CC-1
C1-C3 GAS YIELD



COMPARISON CMSL-1, CC-15 & CC-1
C4-199C NAPHTHA YIELD

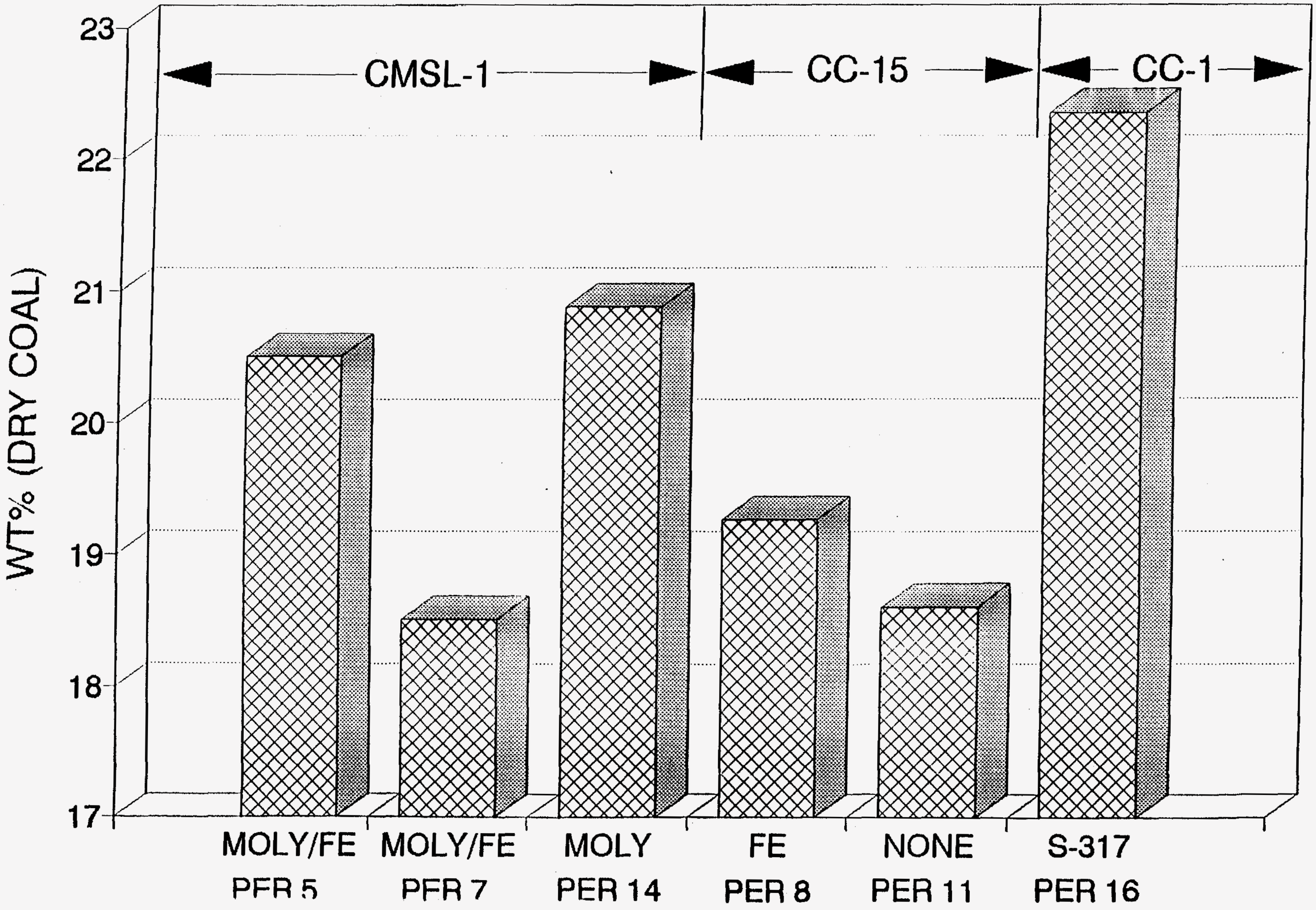
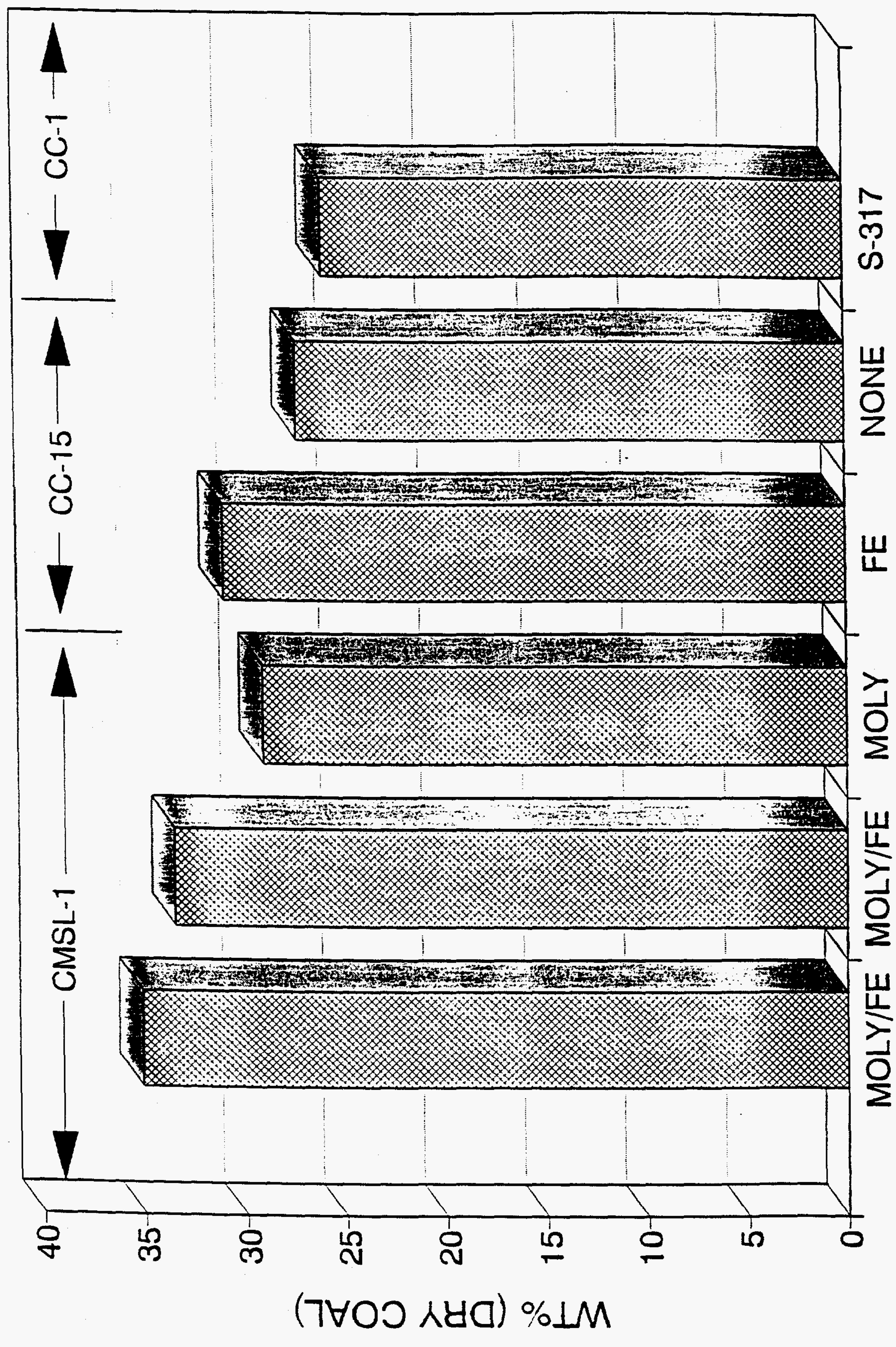


FIGURE 2.1.7



COMPARISON CMSL-1, CC-15 & CC-1 199-343C MIDDLE DISTILLATE YIELD

COMPARISON CMSL-1, CC-15 & CC-1
343-524C HEAVY DISTILLATE YIELD

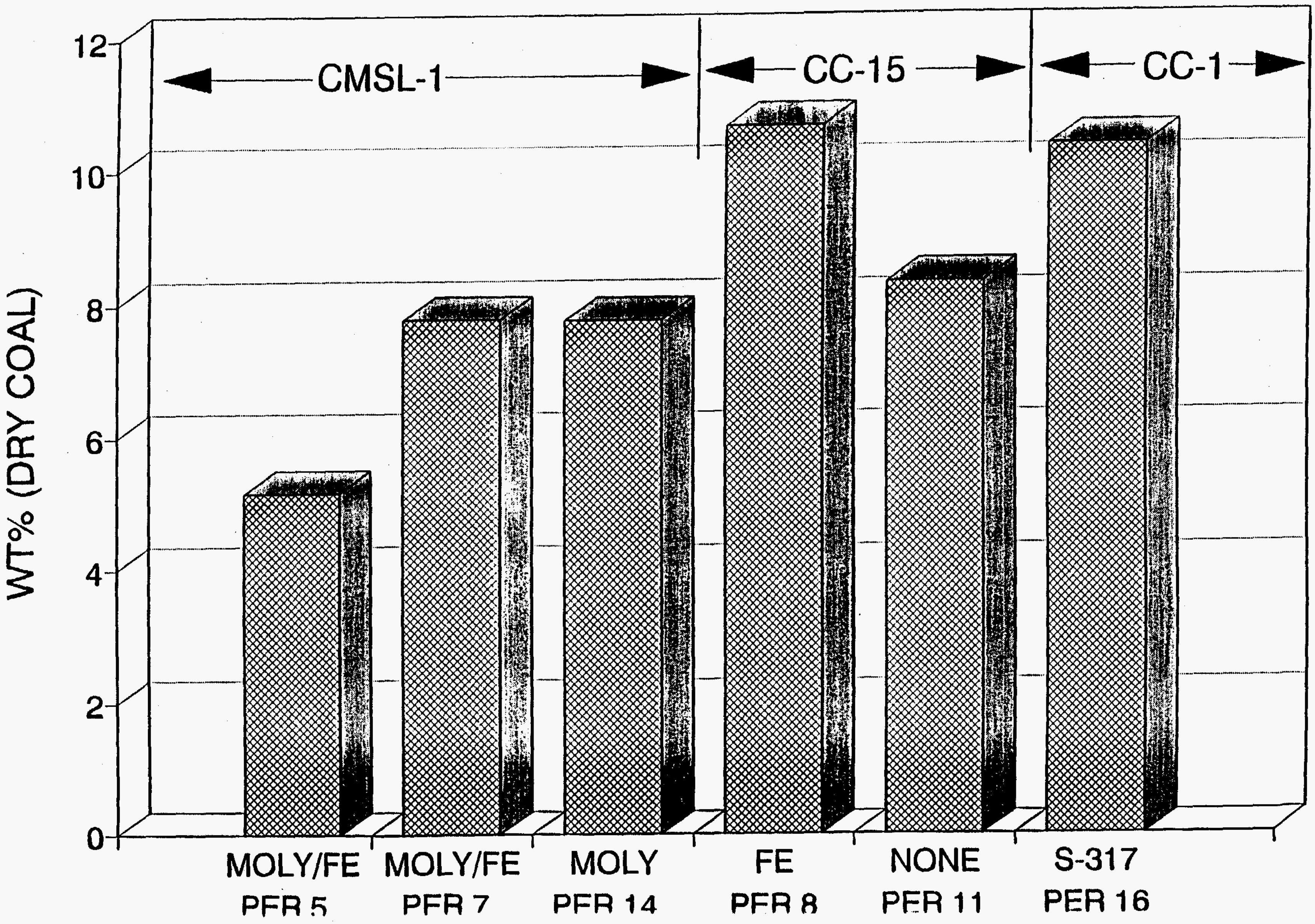


FIGURE 2.1.9

COMPARISON CMSL-1, CC-15 & CC-1
524C+ RESID YIELD

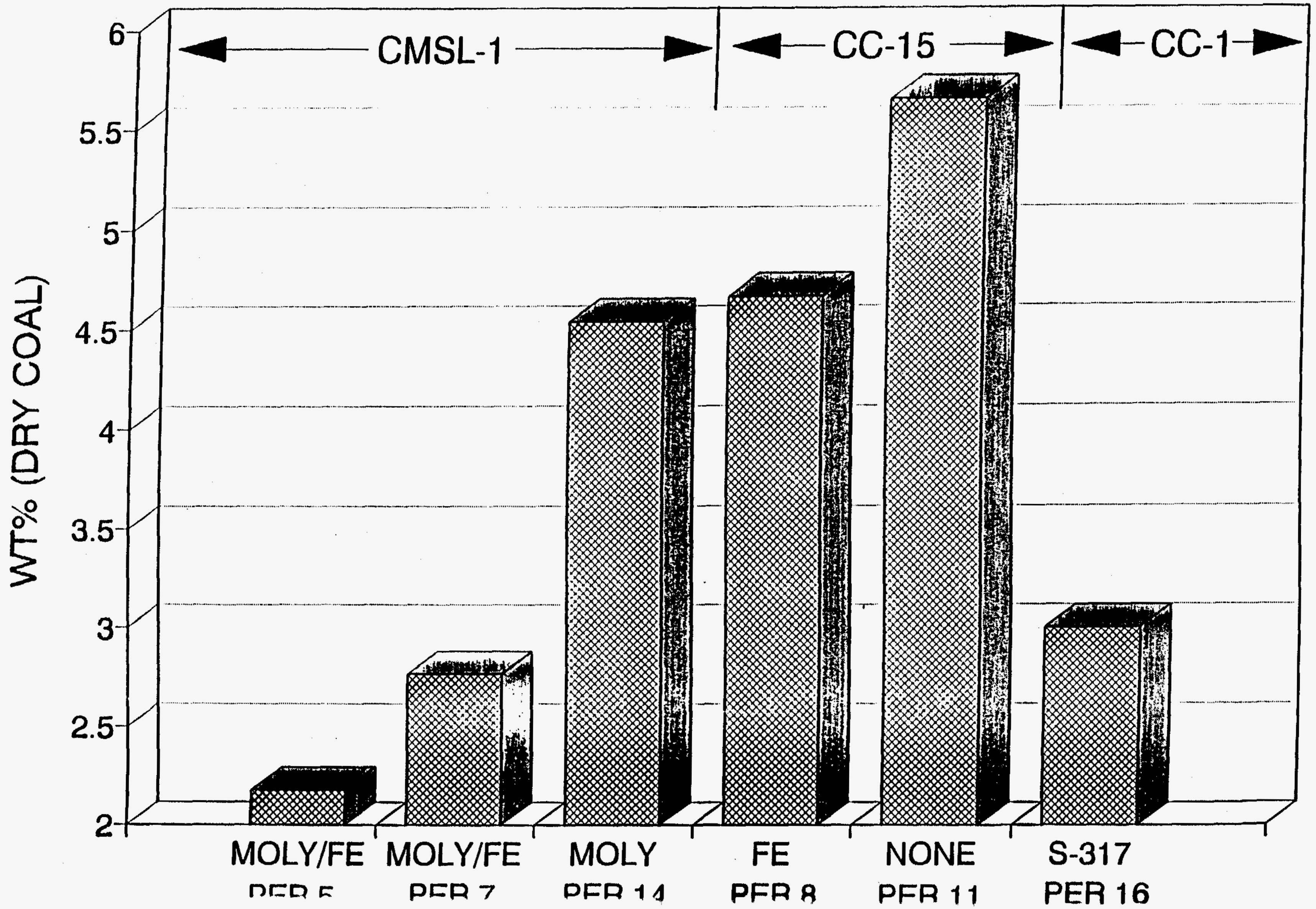


FIGURE 2.1.10

COMPARISON CMSL-1, CC-15 & CC-1
C4-524C DISTILLATE YIELD

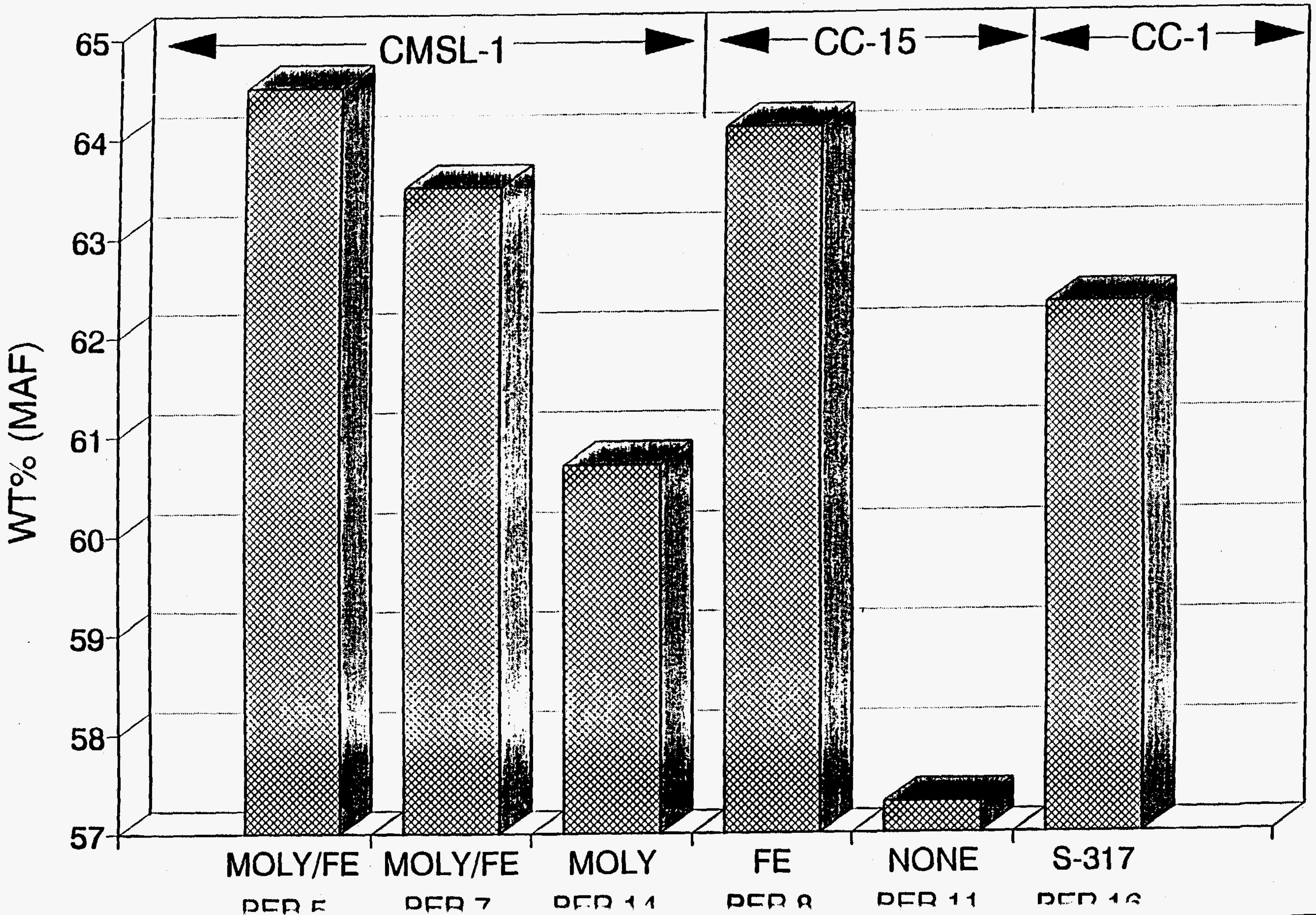
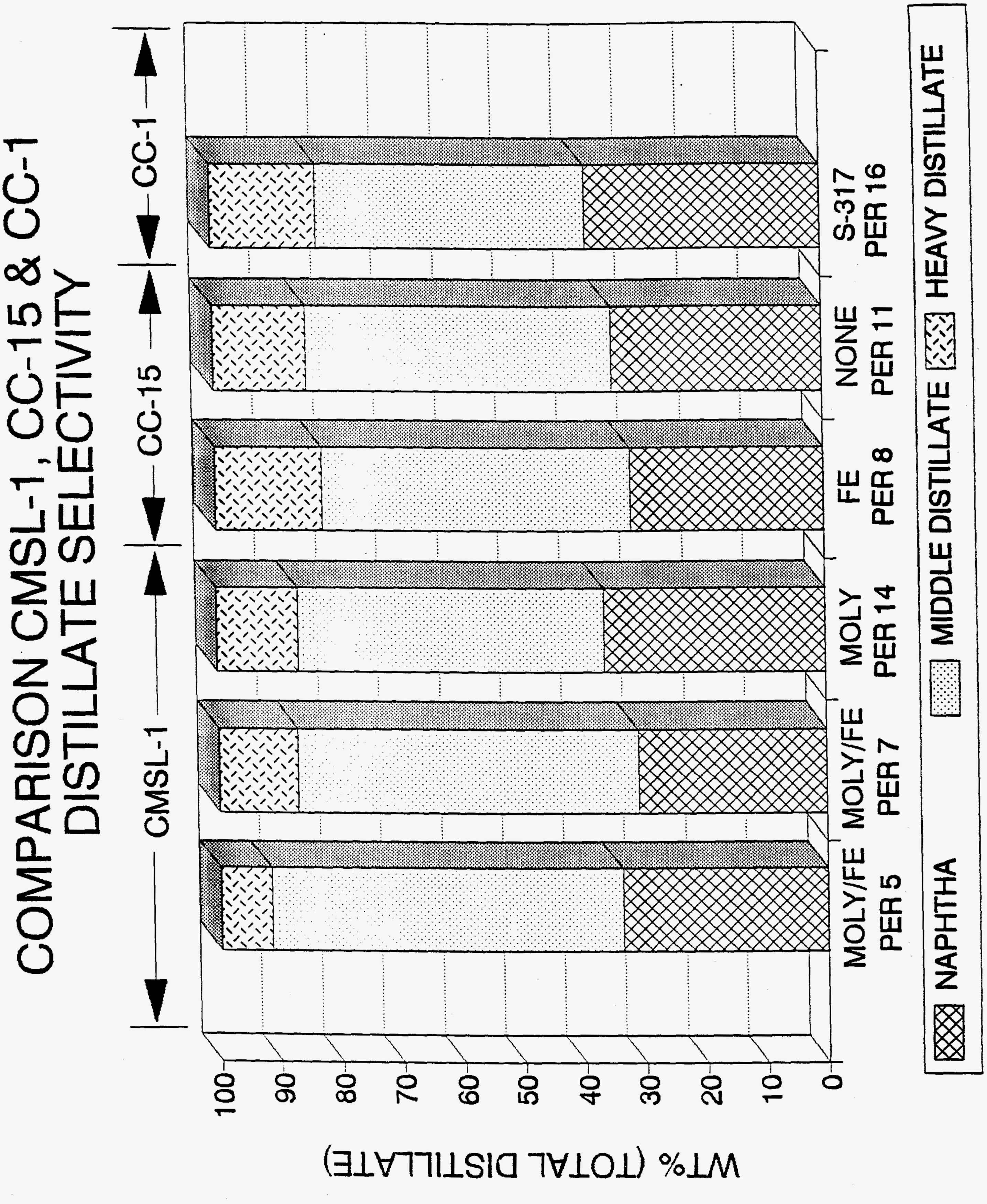


FIGURE 2.1.11

FIGURE 2.1.12


COMPARISON CMSL-1, CC-15 & CC-1
DISTILLATE SELECTIVITY
CMSL-1
CC-15
CC-1
WT% (TOTAL DISTILLATE)
100
90
80
70
60
50
40
30
20
10
0
MOLY/FE PER 5
MOLY/FE PER 7
MOLY PER 14
FE PER 8
NONE PER 11
S-317 PER 16
NAPHTHA
MIDDLE DISTILLATE
HEAVY DISTILLATE

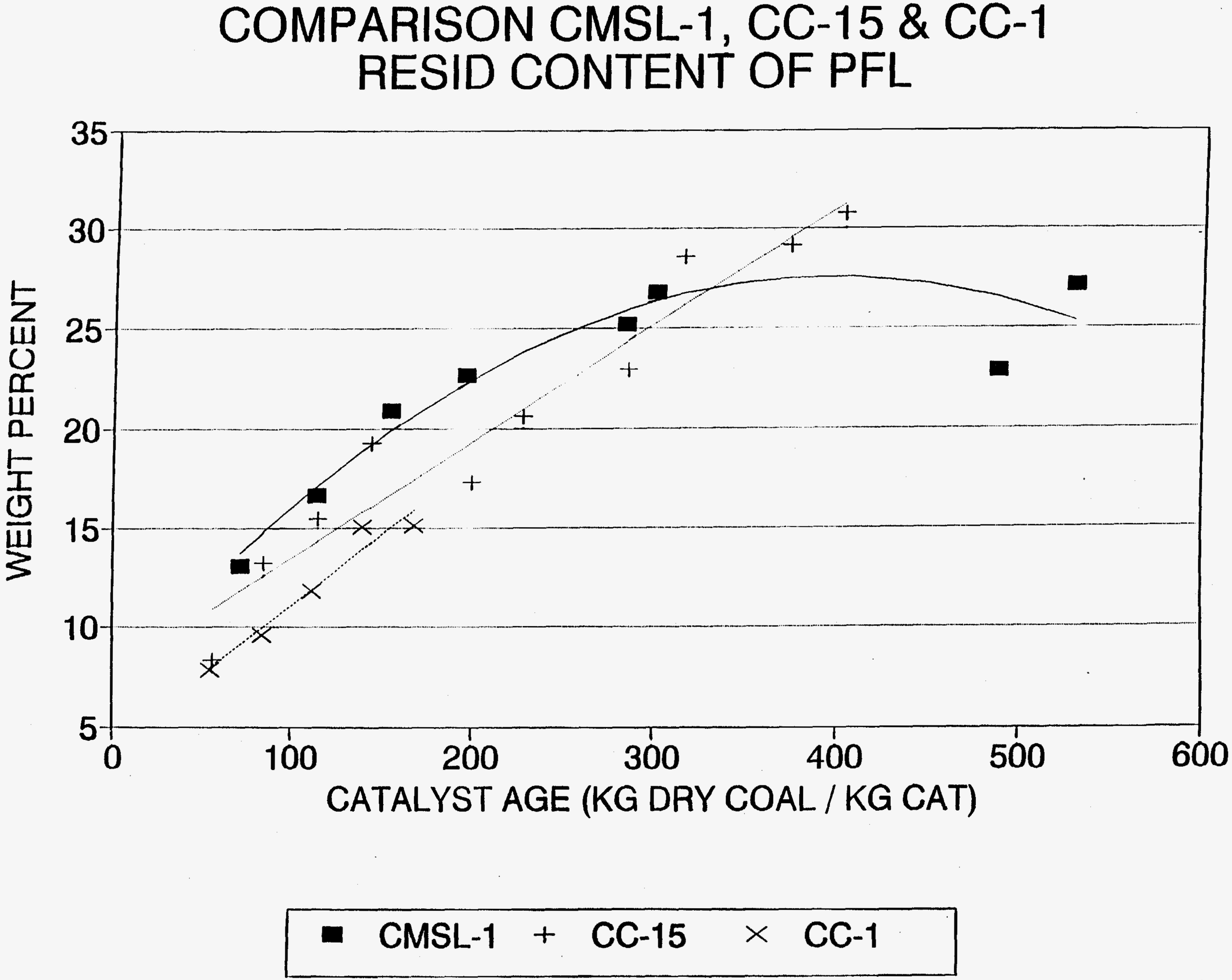

COMPARISON CMSL-1, CC-15 & CC-1
RESID CONTENT OF PFL
WEIGHT PERCENT
35
30
25
20
15
10
5
0
100
200
300
400
500
600
CATALYST AGE (KG DRY COAL / KG CAT)
■ CMSL-1
+ CC-15
× CC-1

FIGURE 2.1.13

COMPARISON CMSL-1, CC-15 & CC-1
H/C CHANGE 1ST STAGE TO 2ND STAGE

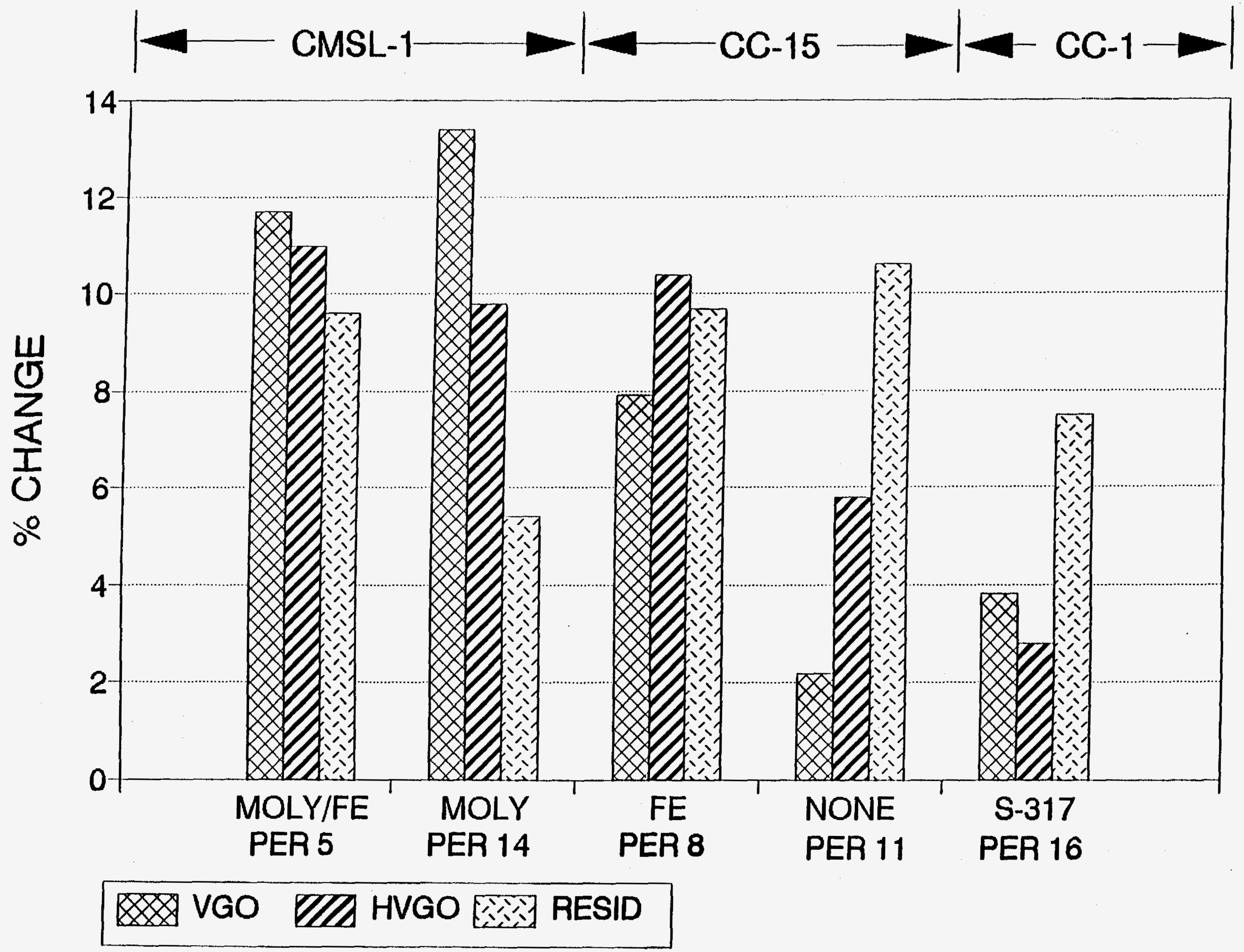


FIGURE 2.1.14

COMPARISON CMSL-1, CC-15 & CC-1
NITROGEN CHANGE 1ST STAGE TO 2ND STAGE

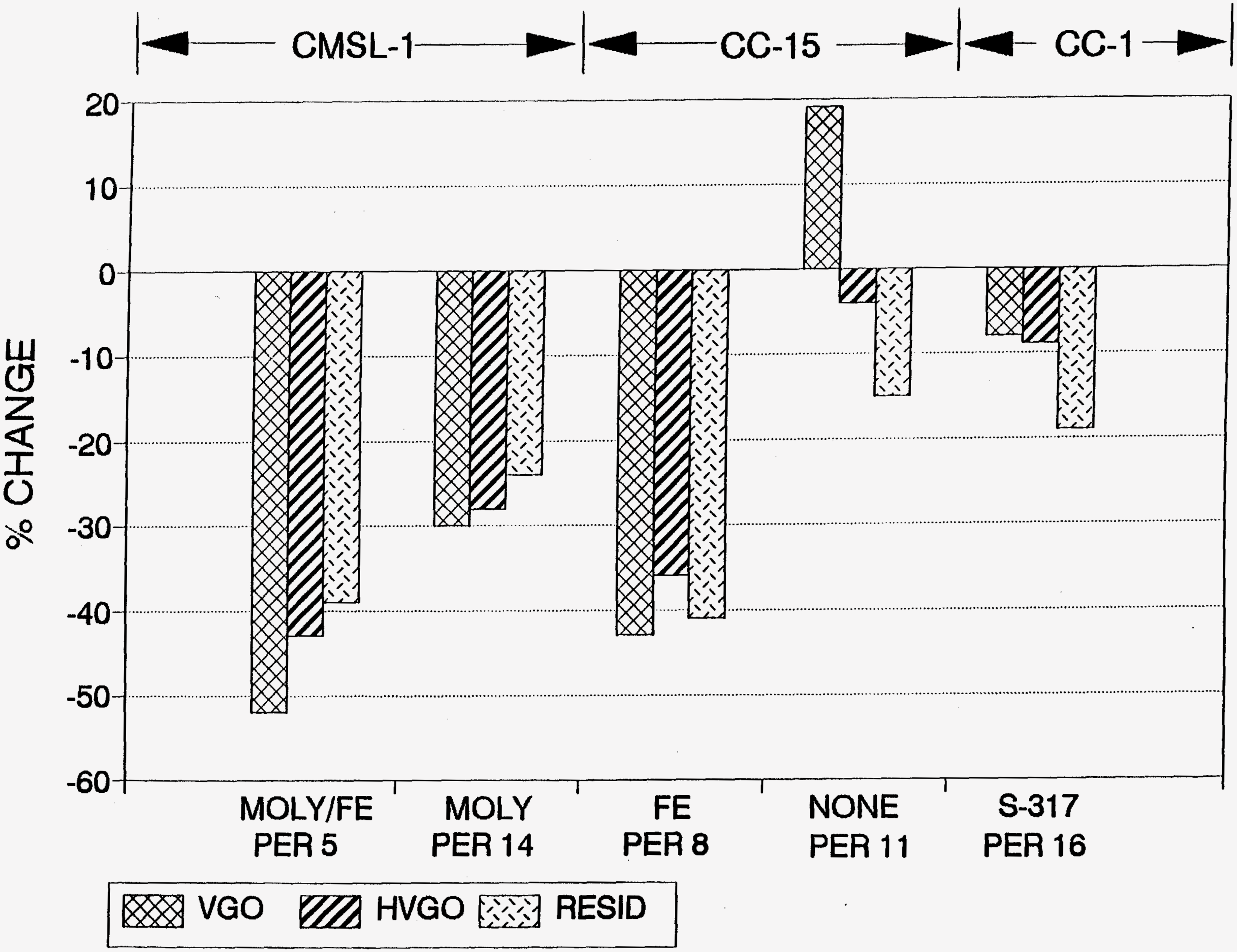


FIGURE 2.1.15

RUN 227-77 (CMSL-1)
MATERIAL RECOVERY BALANCES

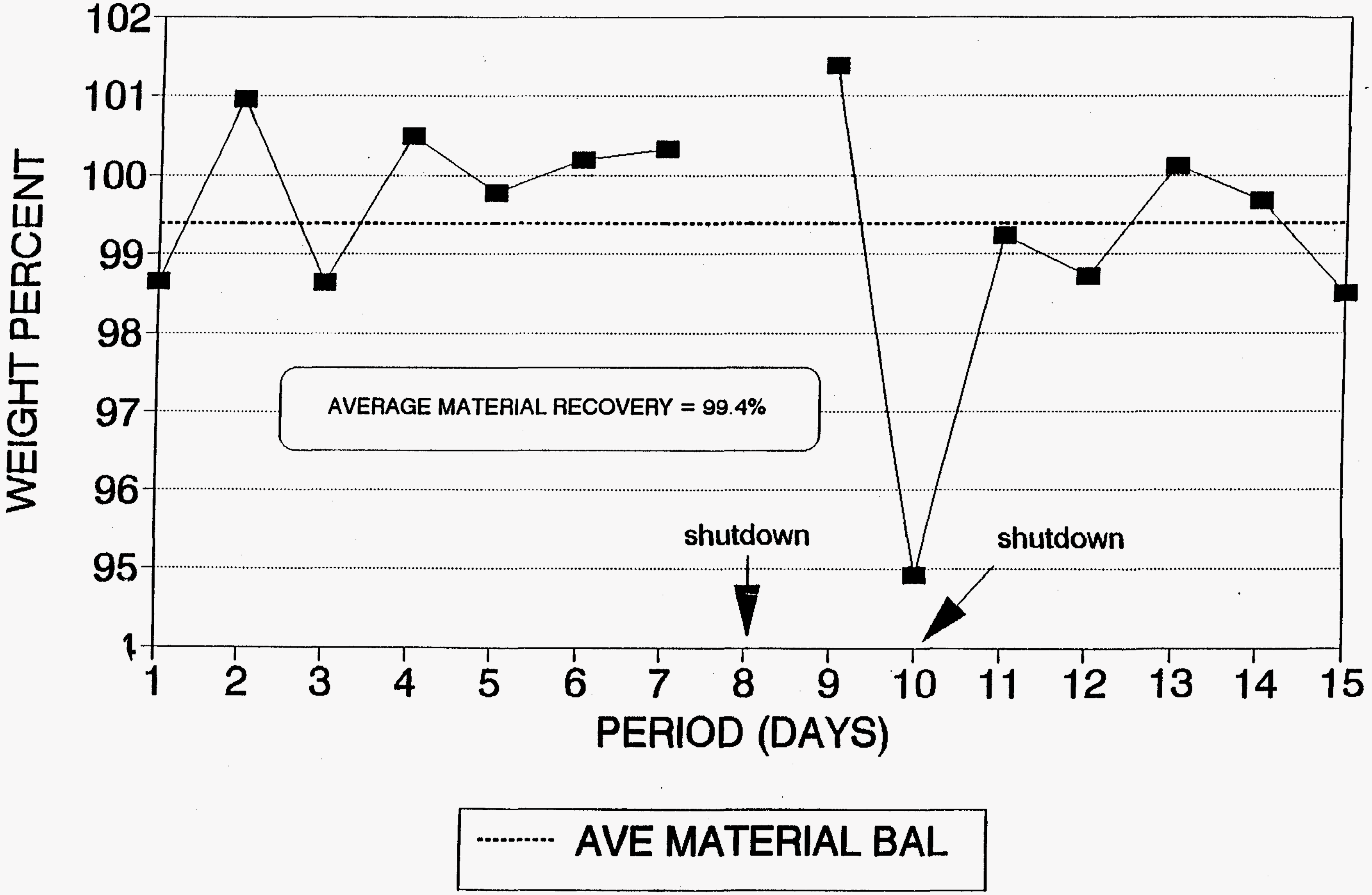


FIGURE 2.1.16

VOLUME I

SECTION II

RUN CMSL-2

EVALUATION OF LOW SOLVENT-TO-COAL RATIOS ON THE CATALYTIC TWO-STAGE LIQUEFACTION PROCESS

VOLUME I

TABLE OF CONTENTS

SECTION II - RUN CMSL - 2

Run CMSL-2 (227-78) Evaluation Of Low Solvent-To-Coal Ratios On The Catalytic Two-Stage Liquefaction Process

TABLE OF CONTENTS
(Continued)

SECTION II - RUN CMSL-2

VOLUME I

SECTION II - RUN CMSL - 2

LIST OF TABLES

VOLUME I

SECTION II - RUN CMSL - 2

LIST OF FIGURES

SECTION II - RUN CMSL-2

RUN CMSL-2 (227-78)
EVALUATION OF LOW SOLVENT-TO-COAL RATIOS ON THE CATALYTIC TWO-STAGE LIQUEFACTION PROCESS

1.0 SUMMARY

The Bench Run 227-78 (CMSL-2), carried out to evaluate the impact of lower solvent-to-coal ratios on the CTSL performance under a DOE Contract (Contract No. DE-AC22-93PC92147), was completed on May 6, 1993 after 17 and 2/3 days of operation. The overall Run CMSL-2 consisted of four different operating conditions. The first three conditions evaluated the effect of solvent-to-coal ratios of 1.1 and 0.9 on the process performance at different reaction severities (higher coal space velocities and higher reactor temperatures for Conditions 3 and 4). The last Condition of CMSL-2 (Condition 4) was carried out as an extension for the sub-contract with the Jet Propulsion Laboratory for the evaluation of a surfactant additive (2 W% of sodium lignolsulfonate relative to coal feed) on the performance of bituminous coal liquefaction. Burning Star Mine 2 Illinois No. 6 coal was used for this run with L-769 as the startup/makeup solvent and fresh Shell-317 catalyst (1/32" extrudates) which was sulfided using TNPS prior to Condition 1 of the Run.

The modified feed preparation and introduction system for CMSL-2 consisted of a slurry preparation and mixing tank that prepared coal-solvent slurries in twelve hour batches, mixed them uniformly, heated them to temperatures high enough (93-232°C or 200-450°F) to maintain a pumpable slurry viscosity, and transferred them to the feed charge pot. Prior to the beginning of CMSL-2 an off-line slurry pumping test was conducted to evaluate the pumpability of coal-solvent slurries of different coal loadings using the newly installed hot slurry preparation and feed system.

An average material recovery balance of 97.7 W% was obtained for this bench run. This value is slightly lower than what it normally is. This could be because a more involved feed preparation system was used for this bench run that allowed preparation of thicker slurries (higher coal concentrations) and transporting the same to the actual feed charge pot at high temperatures (93-232°C or 200-450 F) to maintain a proper pumpable viscosity. At the beginning of Condition 2 (as per the initial Run Plan) when solvent-to-coal ratio was about 0.8, the unit had to be shut down due to excessive plugging problems in the feed pump discharge lines. Except for this shutdown, the entire run operation went on smoothly without any major disturbances. For successful operation it appears that the solvent to coal ratio should not be lower than 0.9.

The analyses of results obtained from the Run CMSL-2 show the following ranges for product yields and conversions:

Coal Conversion, W% MAF coal: 91.7 to 93.2
524°C+ Resid Conversion, W% MAF coal: 73.4 to 91.2
C_4-524°C yield, W% MAF coal: 63 to 76.6
C_1-C_3 gas yields, W% dry coal: 4.20 to 5.89
Hydrodesulfurization, W%: 71.4 to 80.1
Hydrodenitrogenation, W%: 65.6 to 93.5

The process performance dropped sharply in going from Period 16 to 18 because of the decrease in reaction severity. The temperatures of the first and second reaction stages were dropped by 14 and 8°C (25 and 15°F), respectively, for the last two periods as per the request of the JPL. The results obtained during Condition 4 of Bench Run 227-78 (CMSL-2) indicate that the addition of sodium lignolsulfonate surfactant did not improve the performance of the CTSL process either in terms of product yields or product quality. The possibility of a positive role of the surfactant at lower temperatures (399°C or 750°F or lower) was indicated by the microautoclave testing results.

Overall, the results obtained and analyzed from CMSL-2 seem to indicate a significant advantage in terms of increased C_4-524°C distillate yields (about 8-9 W% higher on a relative basis) and 524°C$^+$ resid conversions (4 W% higher on a relative basis) for CMSL-2 using lower solvent-to-coal ratios (0.9-1.1) as compared to some of the earlier bench runs (227-37 [I-18] and 227-76 [CC-16]) on Illinois No. 6 coal liquefaction using Shell-317 1/32" extrudate catalyst (I-18) and an AO-60 Akzo 1/16" extrudate catalyst (CC-16). The solvent-to-coal ratios in these earlier runs varied between 1.5-2.0. Comparison of the recycle oil properties for CMSL-2 and for I-18, in terms of the °API gravities, H/C ratios, W% nitrogen and W% sulfur, indicates that CMSL-2 resulted in a better quality product slate. Higher °API gravities, higher H/C ratios, and lower nitrogen and sulfur contents were obtained for the recycle oil (PFL) from CMSL-2 than those for the Run I-18. Thus, the Bench Run CMSL-2 indicated improved CTSL process performance at lower solvent to coal ratios (0.9 to 1.1) i.e at higher coal loadings (47-53 W% of the feed slurry). Results from Condition 4 of this run do not reveal any effect of the addition of sodium lignolsulfonate surfactant either on the conversion levels or the product yields and product quality. The insolubility of these types of surfactant in organic media could be one of the main reasons for its failure to exhibit any influence on the CTSL process.

In summary, results from the Run CMSL-2 show that:

(i) lower solvent-to-coal ratios (0.9 to 1.1) have significant advantages in terms of distillate yield, 524°C+ resid conversion, and recycle oil properties when compared to these criteria for earlier runs with solvent to coal ratios in the range of 1. 5 to 2.0; and

(ii) the addition of sodium lignolsulfonate surfactant does not have any effect on CTSL process performance.

2.0 BACKGROUND, OBJECTIVE, AND SCOPE OF WORK

The CMSL project is set up to evaluate different novel processing concepts in catalytic coal liquefaction to complement the larger scale process demonstration "Proof of Concept" studies for the U.S. DOE. New ideas that are being explored under this program include low temperature pretreatments, more effective catalysts, on-line hydrotreating, new coal feedstocks, other (cheaper) hydrogen sources, and more concentrated feeds, etc.

The objectives of the Bench Run CMSL-2 were to evaluate the impact of lower solvent-to-coal ratios (1.1-0.9) on the liquefaction of Illinois No. 6 coal under CTSL mode of operation, and the use of surfactant. The solvent-to-coal ratio has a direct impact on the economics of CTSL. The lower this ratio, the higher is the amount of coal that can be processed at a fixed reactor volume. As coal and $524°C^+$ residuum conversions are non-zero order reactions, higher coal concentrations in the feed slurries can enhance the reaction kinetics. Most of the previous coal liquefaction work at HRI was carried out at solvent-to-coal ratios of between 1.5-2.5. The lower limit on solvent/coal ratio depends on the pumpability of the feed slurries at the selected operating conditions. Also, from the viewpoint of the chemistry of direct liquefaction, a critical amount of solvent in the liquefaction reactor is always necessary in order to provide adequate hydrogen for the stabilization of the reactive fragments generated from coal. Previous results on Wyodak coal liquefaction (Runs 227-22 and 227-25) indicate that higher conversions and distillate yields were observed when the solvent-to-coal ratio was reduced from 2.6 to 1.5. There were 2 and 3 W% improvements in coal and resid conversions, respectively. The yield of C_4-524°C distillates was also 2 W% higher at the lower solvent-to-coal ratio.

The other objectives of this bench run were to evaluate the effect of reaction severity at high coal loading conditions and to evaluate the effect of the addition of sodium lignolsulfonate (2 W% of coal feed) on the conversions and liquid yield at a solvent-to-coal ratio of 0.9.

The coal for this run was an Illinois No. 6 coal (Burning Star Mine 2) dried to about 2 W% moisture content (designated as HRI-6107). The catalyst was Shell-317 $NiMo/Al_2O_3$ 1/32" extrudates for both stages. The startup/makeup oil was L-769 (a blend of a topped distillate from Wilsonville and pressure filter liquid from the PDU 260-03 run made using Black Thunder Mine coal). The entire run was carried out at four different operating conditions designed to discretely evaluate the effect of increasing coal concentration in the feed slurry, the effect of reaction severities at high coal loadings, and the effect of a surfactant addition on the CTSL process performance. The feed flowrates (or space velocities) and stage temperatures were chosen as to allow a direct comparison of CMSL-2 with the other bench runs on Illinois No. 6 using Shell-317 catalyst that were carried out at higher solvent-to-coal ratios (lower coal concentrations).

The operating conditions for CMSL-2 are given in *Table 2.2.1*. As shown in *Table 2.2.1*, CMSL-2 consisted of four conditions each lasting for about 3-5 days. Condition 1 which was 5 days long was intended to bring the run to a steady state (to represent equilibrated results) at first and second stage reactor temperatures of 399 and 427°C (750 and 800°F), respectively, the dry coal space velocity of 332 $Kg/hr/M^3$ (21 $lbs/hr/ft^3$) (per stage) and solvent-to-coal ratio of 1.1. The Condition 2, as per the original Run Plan, was planned to be 4 days long with a solvent-to-coal ratio of 0.8 (all other parameters same as Condition 1) had to be revised after a temporary shut-down at the beginning of that condition due to excessive plugging problems. The revised Condition 2, as shown in *Table 2.2.1*, was four days long and used solvent-to-coal ratio of 0.9 with all other parameters same as Condition 1. In Condition 3, reaction severity was changed by increasing the reactor temperatures to 413 and 432°C (775 and 810°F) for the first and the second stage, respectively. The dry coal space velocity was increased to 1090 Kg/hr/M^3 (69 lbs/hr/ft^3) catalyst (per stage). The final condition (Condition 4), 4 and 2/3 days long, was an extension of this run for a sub-contract with the Jet Propulsion Laboratory (JPL) for the evaluation of the surfactant. Two weight percent of sodium lignolsulfonate was added continuously to the feed slurry; all other parameters were same as Condition 3. The last one and 1/3 day in Condition 4, the reactor temperatures were lowered to 399 and 424°C (750 and 795°F) for the first and the second stage, respectively as per the request of JPL.

3.0 PROGRAM ANALYSIS, RESULTS, AND COMPARISONS

The conversions and yields of different products, process performance, and product quality for CMSL-2 are addressed in this section. The calculations of material recovery balances, coal conversions, normalized product yields, and other process performance-related indicators were carried out using the routines available in the database. An average material recovery balance of 97.7 W%, a seemingly low value, was obtained for the entire run. The use of more involved high temperature feed preparation and slurry mixing tanks made the material balance calculations a bit difficult. *Table 2.2.2* lists the operating summary for the run CMSL-2, giving the material recovery balances, principal operating conditions for each period (day), and normalized product distributions for certain periods during the run which were considered to represent steady-state results. Periods 4, 10, 13, and 16 were chosen to represent Conditions 1 through 4 respectively during CMSL-2. The Condition 4 was later subdivided into Condition 4A (Period 16) and Condition 4B (Period 18A/B). The relative process severities, expressed as total STTUs for different Work-up Periods, are plotted in *Figure 2.2.1*.

3.1 Process Performance

3.1.1 Coal Conversion

Typical coal conversions, obtained during equilibrated Periods of different conditions of CMSL-2 are shown in *Figure 2.2 2*. The coal conversions during this run varied between 91.7 to 93.2 W% MAF coal. These conversion values are about a percentage lower than those reported for the Run CC-16 which employed a different batch of Illinois No. 6 coal (HRI-6081). The coal qualification tests, addressed in the later section, indicated the Illinois No.6 coal used in CMSL-2 (HRI-6107), was slightly less reactive than HRI-6081. HRI-6107 also contained a slightly higher amount of mineral matter (ash), 12.29 W% MF, as compared to HRI-6081 coal, 10.71 W% MF. Even though temperatures of both the reactor stages were raised during Condition 3, no apparent effect on coal conversions was observed, as the rise in temperatures was offset by the increase in the coal space velocity (lower residence time). Within the entire run, coal conversions remained essentially steady with no particular trend. It was slightly lower (91.7 W%) in Period 18 due to the lower process severity.

3.1.2 524°C$^+$ Resid Conversion

Typical resid conversion values, obtained during the equilibrated Periods of different conditions of CMSL-2 are shown in *Figure* 2.2.3. The resid conversions during this bench run varied between 73.4 to 91.2 W% (MAF coal). A typical downward trend in the resid conversion values was observed as the run progressed; an effect of the catalyst aging. The rate at which resid conversions dropped in going from Condition 1 (Period 4) to Condition 2 (Period 10) was markedly lower than that observed for the similar transition during the Bench run CC-16. This could be due to operating at a lower solvent-to-coal ratio in Condition 2 (0.9) as compared to the Condition 1 (1.1) of CMSL-2. Overall, the values of resid conversions during CMSL-2 were about 3-4 W% higher than those reported for the earlier bench runs using Illinois No. 6 coal (addressed later). This is mainly attributed to the higher coal concentration used in CMSL-2 (47-53 W% of feed slurry) as compared to I-18 (38-45 W%) and CC-16 (40 W%).

3.1.3 Hydrogen Consumption

The hydrogen consumption (the amount of H_2 reacted) in CMSL-2 varied between 5.84 and 8.38 W% of MAF coal feed (*Figure* 2.2.4). Hydrogen consumption during the run also declined at a very slow rate as the run progressed. This is in line with the slowly decreasing trend in the overall process severity. Hydrogen consumption during CMSL-2 was comparable to that during either I-18 or CC-16. This is because even though higher coal concentrations were employed during CMSL-2, as described earlier, lower light hydrocarbon gas yields were obtained which compensated for the increased coal concentration effect on the overall hydrogen consumption.

3.1.4 Hydrodesulfurization

Significant amounts of sulfur removal were achieved during CMSL-2. The HDS values of between 70 and 80 W% were obtained as shown in *Figure 2.2.5*; the HDS values for the first few periods (4 and 10) of CMSL-2 were about 3-4 W% higher than those observed for the corresponding periods with similar reaction conditions in the Bench Run CC-16. The HDS values decreased steadily towards the end of the run, as a result of catalyst aging.

3.1.5 Hydrodenitrogenation

The extent of nitrogen removal (W% HDN) during CMSL-2 varied between 69 and 93 W% (*Figure* 2.2.6). Again, these values steadily decreased with the decrease in the overall process severity and increase in the catalyst age as the run progressed. The HDN values observed during CMSL-2 were typically 3-5 W% higher than those reported for the Bench Run I-18 for periods with similar reaction conditions.

3.2. Product Distribution

3.2.1 C_1-C_3 Gas Yields

The normalized C_1-C_3 gas yields are summarized in *Figure 2.2.7* for CMSL-2. The gas yields for this run varied between 4.8 to 6.7 W% of MAF coal. As would be expected, the gas yields increased slightly upon increasing the coal concentration in the feed slurry (47 to 53 W%) and also upon increase in the reactor temperatures. The gas yields for CMSL-2 (especially after Condition 1) were lower than those reported for either I-18 or CC-16, mainly because CMSL-2 was operated at a much higher coal space velocity under similar temperature conditions than the two other bench runs.

3.2.2 C_4-199°C Naphtha Yields

The normalized naphtha yields for different Periods of CMSL-2 varied between 13-23 W% of MAF coal (*Figure* 2.2.8). These yields decreased steadily as the run progressed (in going from Period 4 to Period 18) with Period 18 resulting in the lowest yield both because of lowered reactor temperatures and higher catalyst age. Normalized naphtha yields for CMSL-2 were about 3-4 W% (holds for all four Run Conditions) higher than those reported for the Bench Run 227-37 (I-18). This is attributable to lower solvent-to-coal ratios used in CMSL-2 (0.9-1.1) as compared to I-18 (1.2-1.6).

3.2.3 199-343°C Middle Distillate Yields

The normalized yields of middle distillates for CMSL-2 varied between 26 to 46 W% of MAF coal fed (*Figure* 2.2.9). These yields typically decreased in going from Period 4 in Condition 1 to Period 16 in Condition 4 as a result, mainly of the catalyst aging. Although the reactor temperatures were increased (by 14 and 8°C or 25 and 10 F for stage 1 and stage 2, respectively) after Condition 2, the overall process severity (STTU) either remained the same or decreased as the coal and hydrogen space velocities were raised by 50% during Condition 3. The values of middle distillate yields for CMSL-2 were comparable to those obtained during Run I-18.

3.2.4 343-524°C Heavy Distillate Yields.

The normalized yields of heavy distillates varied between 8 to 26 W% of MAF coal for CMSL-2 (*Figure* 2.2.10). These yields increased steadily with the progress of the run. The yields during CMSL-2 were comparable to those reported for Bench run I-18. The highest yield of heavy distillate was obtained for Period 18 during Condition 4 as the reaction severity was lower and it was the Period with the highest catalyst age during CMSL-2.

3.2.5 524°C$^+$ Residual Oil Yields

The heavy residual oil yields for CMSL-2 varied between 1.2 and 17 W% of MAF coal. As shown in *Figure* 2.2.11, these residual oil yields increased steadily as the run progressed as a result of catalyst aging and decreasing overall reaction severity. The residual oil yields for CMSL-2 were also lower than those for either CC-16 or I-18 as indicated in *Tables 2.2.7-2.2.12*. This difference is attributed to higher coal concentrations employed in CMSL-2.

3.2.6 C_4-524°C Distillate Yields/Selectivity

The normalized yields of distillates for CMSL-2 varied between 63 and 76.6 W% of dry coal. The distillate yields also decreased steadily with the progress of the run, with Period 18 resulting in the lowest (63%) distillate yield, due to lower reaction severity conditions. The distillate yields during CMSL-2 were about 6-7 W% higher (*Tables 2.2.7 through 2.2.12*) than those reported for the Bench runs either I-18 or CC-16 (runs with higher solvent-to-coal ratios). *Figures 2.2.12 and 2.2.13* depict the distillate yields and selectivity for different fractions for CMSL-2. As expected, the selectivity for naphtha and light distillates goes down with the catalyst age.

3.3 Product Quality

Different product fractions (SOH, ASOH, PFC and PFL) from Periods 4, 10, 13, 16, and 18A/B were analyzed for their elemental composition, boiling point ranges, solubilities, and API gravity determinations. The pressure filter liquids (recycle oils) were separated into various boiling range fractions, and these fractions were also analyzed. The detailed analyses are summarized in *Tables 2.2.3, 2.2.4, and 2.2.5.*

3.3.1 Separator Overhead And Atmospheric Still Overhead Products

As shown in *Tables 2.2.3b and 2.2.3c*, the quality of the SOH fraction declined slightly as the catalyst age increased; surprisingly the quality and the properties of the ASOH fraction were maintained throughout the run (except for Period 18A/B with the lowest reaction severity and the highest catalyst age). The SOH gravity averaged about 36.5 °API and its H/C ratio around 1.75. It also contained small amounts of nitrogen and sulfur, averaging 0.07 W% and <0.01 W%, respectively. 95 V% of the SOH product boiled below 343 °C. The ASOH gravity averaged around 25 °API and its H/C atomic ratio about 1.62. It contained about 0.02 W% sulfur and about 0.10% nitrogen on an average. 95 V% of the ASOH product boiled below 343 °C.

3.3.2 Pressure Filter Liquid Properties

As shown in *Figure 2.2.14* and *Table 2.2.4*, the properties of the recycle oil (PFL) such as API gravity and H/C atomic ratio declined steadily as the catalyst age increased. Accordingly, nitrogen and sulfur contents of the product recycle oils increased with the catalyst age. Marginal improvements in the hydrogen content and the API gravity of the recycle oil could be due to the restarting of the run after a temporary shutdown during Period 7. The pressure filter liquid was further distilled into four separate fractions for analyses. These fractions were IBP-343°C Light Gas Oil (LGO), 343-454°C Vacuum Gas Oil (VGO), 454-524°C Heavy Vacuum Gas Oil (HVGO), and 524°C$^+$ Residuum. The properties of these fractions (such as gravity, H/C ratio, and heteroatom content) give generally better indications of the catalyst activity than do the overall product yields. Most of the unremoved heteroatoms are in the solid products where they are not as susceptible to catalytic conversion, and in the overall yields, the solid-phase heteroatoms obscure the more important heteroatom content of the liquid products. Also, these analyses provide good indications of catalyst activity because properties like H/C ratio are more sensitive to catalyst activity than is the shift in the boiling fractions. The analyses of these fractions are listed in *Table 2.2.5*.

3.3.3 Analyses Of TBP Fractions Of Liquid Products

The TBP fractionation of the net liquid product and the detailed analyses of the TBP fractions are presented in *Tables 2.2.6A, 2.2.6B, 2.2.6C, and 2.2.6D* for Periods 4, 10, 13, and 16 of the Run 227-78 (CMSL-2). The separator overhead (SOH) and the atmospheric still overhead (ASOH) streams were blended in the proportion of their net production rates during the selected periods of the run and this mixture was used for TBP fractionation. The results of analyses of these TBP fractions were used to calculate the net liquid product properties, by incorporating the properties of the PFL fractions for Periods where there was a net PFL formation.

3.3.4 Recovered Catalyst

The detailed analyses of the spent catalysts recovered from the first and the second stage of CMSL-2 are given in *Tables 2.2.18*. Since the first stage catalysts were replaced with new catalysts in Period 7, the catalyst age of the first stage recovered catalyst (409 kg coal/kg catalyst) was lower than the age (597 kg coal/kg catalyst) of the second stage recovered catalyst. Analyses of oil-free recovered catalysts show normal build-up of organic and inorganic matters, as well as normal loss in pore volumes and surface areas.

3.4. Comparisons Of Different Bench Runs To Establish The Effects Of Low Solvent-To-Coal Ratios In CMSL-2

As mentioned earlier, the main objective of CMSL-2 was to evaluate the impact of low solvent-to-coal ratios in feed slurries on the liquefaction performance of a bituminous coal (Illinois No. 6 Burning Star Mine No. 2) in CTSL process mode. Comparisons are made between CMSL-2 and some of the earlier bench runs (*Figures 2.2.15 through 2.2.21* and *Tables 2.2.7 through 2.2.12*) in CTSL mode with Illinois No. 6 coal and supported catalyst in both stages (either Shell-317 or Akzo AO-60). These comparisons basically allow one to clearly see the effect of high coal concentrations (or low solvent-to-coal ratios) on process performance both in terms of product yields and product quality. The comparisons are also made to delineate the effect of the added surfactant (sodium lignolsulfonate) on the process performance during the Condition 4 of CMSL-2. In these comparisons, performance during CMSL-2 has been checked against that during Bench Runs I-18 (Illinois No. 6 and 1/32" extrudate S-317 catalyst) and CC-16 (Illinois No. 6 and 1/16" extrudates Akzo catalyst) under almost similar reaction conditions, in terms of catalyst age, coal space velocity, and reactor temperatures. The activity of Akzo AO-60 catalyst was almost similar to Shell-317 catalyst and therefore, the Bench Run CC-16 is used for comparisons.

3.4.1 Conversions/Product Yields

The performance of the Bench Run CMSL-2 is compared with that of the Run I-18 in *Tables 2.2.7 through 2.2.12* and *Figure 2.2.15*. *Tables 2.2.7 and 2.2.8*, which compare the process performance at lower reaction temperatures (during some of the earlier run-periods), definitely indicate a superior process performance for CMSL-2 (with solvent-to-coal ratios between 0.9 and 1.06) than for I-18 (solvent-to-coal ratio of about 1.6), not only in terms of higher 524°C$^+$ resid conversion (4-6 W% MAF coal) but also in terms of higher C_4-524 C distillate yields (by 3-7 W% MAF coal). Also, at higher reactor temperatures, as noted in *Tables 2.2.9 and 2.2.10*, CMSL-2 results in a superior process performance. Although the yield and the conversion numbers for the two runs in *Tables 2.2.10 and 2.2.11* are comparable, CMSL-2 was operated at a much higher coal space velocity (50% higher than I-18), so the product distribution was attained with increased throughput rates. *Figure* 2.2.15 compares the C_4-524°C distillate selectivity for CMSL-2 and I-18 for selected run periods. The selectivity to light naphtha and middle distillates for both the periods during CMSL-2 shown in *Figure* 2.2.15 is higher than that for the corresponding periods during I-18.

Another Bench Run, CC-16, which was liquefaction of Illinois No. 6 coal in CTSL mode carried out for the evaluation of an Akzo AO-60 catalyst, was used for comparison of process performance (under similar reaction conditions) with CMSL-2. Since it had already been shown that Akzo AO-60 and Shell-317 catalyst performed similarly, the comparison with CC-16 was fair. As shown in Tables 2.2.11 and 2.2.12, CMSL-2 resulted in a much better overall process performance with about 7-9 W% (MAF coal) higher C_4-524°C distillate yields. Also, as shown in *Figure* 2.2.16, the run periods chosen for comparison from CMSL-2 resulted in a better product slate, in terms of distillate selectivity than the corresponding periods during Run CC-16.

3.4.2 Product Quality

As mentioned earlier, the properties of the recycle oil (pressure filter liquid) are a good measure of the overall product quality from the CTSL bench runs. *Table 2.2.13* compares the recycle oil properties for Bench Runs I-18, CC-16, and CMSL-2 for Period 9. The quality of the recycle oil was better in CMSL-2 (in terms of gravity, H/C ratio, and heteroatom content) than in either CC-16 or I-18. The amount of combined LGO and VGO fractions in the recycle oil is higher for CMSL-2 than for the two other bench runs. The amount of heavy 524°C$^+$ residuum is lower for CMSL-2 recycle oil. Analyses of the individual PFL fractions also show better properties for the recycle oil from CMSL-2. As shown in *Figure* 2.2.17, the 524°C$^+$ residuum content and even the amount of cyclohexane insolubles (asphaltene plus preasphaltene content) was much lower for the recycle oil from CMSL-2 than for the same from the other two bench runs. Thus, CMSL-2, which employed lower solvent-to-coal ratios, resulted in a better overall product quality than either CC-16 or I-18.

The main reason behind the improved performance during CMSL-2 was the higher coal concentration (lower solvent-to-coal ratio) during this bench run. The higher concentration of coal in the slurry enhances the kinetics of conversion pathways leading to the formation of different final products. CMSL-2 employed (during Conditions 1 and 2) about the same coal space velocity as the Bench Runs CC-16 and I-18 did. But because of the lower solvent throughput rates during CMSL-2, the overall residence time of the coal-solvent slurries in the reactors was higher for CMSL-2 (*Table 2.2.14*). Total reaction severity (STTU), based on the slurry residence time, was also higher for CMSL-2. These explain the improved process performance for CMSL-2, both in terms of product quality and yields, as compared to either CC-16 or I-18. Importantly, the amount of coal processed per unit time (coal throughput rate) was the same in all three bench runs.

3.5 Effect Of Addition Of Sodium Lignolsulfonate (Surfactant) On CTSL Process Performance

The last condition of this run (Condition 4) was carried out as an extension for the sub-contract with the Jet Propulsion Laboratory for the evaluation of a surfactant additive on process performance. Condition 4 (later divided into Conditions 4A and 4B) lasted for 4 and 2/3 days (Periods 14 through 18B) with the first three and 1/3 days of operation at high stage temperatures (first stage = 413°C and second stage = 432°C) and one and 1/3 day at lowered stage temperatures (first stage = 399°C and second stage = 424 C). Two weight percent (relative to coal) of sodium lignolsulfonate, a surfactant developed by the JPL, was added to the feed slurry as -70 mesh powder.

The addition of this surfactant did not seem to improve process performance to any distinguishable extent. Coal conversions of the order of 92-93% (MAF coal) were obtained with C_4-524°C distillate yields in the range of 63-69 W% (MAF coal) and°524 C resid conversions of 73-84 W% (MAF coal). These results were comparable to the values of yields and conversions obtained at the equivalent catalyst age and same reaction conditions for other bench runs for Illinois No. 6 coal carried out previously by HRI. in CTSL mode, without addition of any surfactant. Test data from this bench run utilizing the surfactant in the last 4 and 2/3 days of operation do not indicate any enhancing effect of the surfactant on the process performance. This is consistent with the observation made from previous batch microautoclave studies (especially for tests carried out at temperatures higher than 399°C). Comparisons of the process performances are made for different periods within the same run (CMSL-2) and also between two different bench runs with similar reaction conditions to assess the effect of the addition of sodium lignolsulfonate on coal liquefaction.

3.5.1 Coal Conversion

Coal conversions during Periods 12 through 18 varied between 92-93% (MAF coal). The addition of the surfactant to the slurry after Period 13 did not affect the overall coal conversions. The values reported in the operating summaries for coal conversion are based on the assumption that all of the surfactant (or its decomposition products) gets washed off by quinoline from the pressure filter cake. These values of conversions were typically a percentage (absolute) higher than those one would obtain with the assumption that all of the added surfactant goes into the pressure filter cake in the form of ash and 0.4% (absolute) lower than those one would obtain with the assumption that all of the added surfactant remains in the quinoline insolubles, but not the ash. Coal conversion dropped to 91.7% (MAF coal) for Period 18 as reactor temperatures were dropped to 399 and 424°C (750 and 795°F) for the first and the second stage reactor, respectively.

3.5.2 C_4-524°C Distillate Yields

Distillate yields from Period 12 through 18 were in the range of 63-71 W% (MAF coal), at first dropping slowly and then sharply to 63 W% for Period 18 when the reaction severity was relatively lower. As indicated in *Figure* 2.2.18, distillate yields for CMSL-2 were higher than those for the Run I-18 under similar conditions (probably due to higher coal concentrations in the feed slurry). The decrease in the distillate yields with the catalyst aging also followed the same pattern for Run I-18 and Periods 12 to 16 of Run CMSL-2. This suggests that the presence of surfactant in Periods 16 and 18 of CMSL-2 had no significant impact on the aging rate of the catalyst.

3.5.3 524°C^+ Resid Conversion

Resid conversions varied between 88.6 and 73.4 W% (MAF coal) during Periods 12 through 18 of bench run CMSL-2. The resid conversion decreased steeply (from 83.7 W% to 73.4 W%) in going from Period 16 to 18, mainly due to the lower reaction severity for Period 18 but also due to the catalyst aging effect (*Figure* 2.2.19). Addition of the surfactant additive did not have any observable effect on the residuum conversions as can be seen from *Figure 2.2.19.*

3.5.4 Heteroatom Removal

HDN was between 87.5-69 W% and HDS between 77.5-70.6 W% during Periods 12 through 18 for CMSL-2. The extent of nitrogen and sulfur removal decreased with catalyst age as shown in *Figure 2.2.20.* This behavior is consistent with that observed during most of the previous bench runs. Thus, the presence of surfactant did not affect the heteroatom removal during CMSL-2.

3.5.5 Product Quality

Figures 2.2.14 and 2.2.21 compare the characteristics of the recycle solvents (pressure filter liquids) for different periods of Bench Runs I-18 and CMSL-2 in terms of quality of products (°API gravity, H/C ratios, W% nitrogen and W% sulfur). As shown in these Figures, for both Runs I-18 and CMSL-2, the H/C ratios and API gravities decreased slowly with the catalyst age, and the nitrogen and sulfur contents of the recycle oil rose steadily with catalyst age. The addition of surfactant during the last few Periods (Periods 14 through 18A/B) of CMSL-2 did not have any positive effects on the quality of the recycle oils.

3.5.6 Ebullating Bed Recycle Rates

As the run progresses, the ebullating pump strokes (a measure of the internal recycle rates) required for bed ebullation decrease (*Figure 2.2.22).* This happens due to the slurries becoming more dense and viscous, therefore requiring less recycle rate for ebullation. No apparent effect on the internal recycle rates was observed during Condition 4 of CMSL-2 despite of continuous addition of sodium lignolsulfonate to the feed slurry. The internal recycle rate, as shown in *Figure 2.2.22*, kept on declining steadily (as it did before the addition of surfactant during CMSL-2 and as observed for most of the previous bench CTSL runs) even after addition of sodium lignolsulfonate. The inability of the added surfactant to show its effect on the slurry (or flow) properties of coal-solvent mixtures could be due to the fact that the surfactants of lignolsulfonate types, byproduct of the paper industry, are soluble only in aqueous solutions and completely insoluble in organic solvents, even alcohols[1]. Therefore, these surfactants may not affect either the surface tension or the viscosity of the non-aqueous suspensions.

3.5.7 Analysis Of Spent Catalyst For Sodium

The analysis of spent catalysts for sodium contents indicated about 0.6-0.7 W% sodium in the catalysts recovered from either the first or the second stage (*Table 2.2.18*). These levels of sodium were not much different than those reported for some of the earlier bench runs on Illinois No. 6 coal using Shell-317 extrudate catalyst. This observation rules out the possibility of any deactivation of supported catalyst by sodium deposition from the surfactant.

3.5.8 Conclusion

Thus, the results obtained during Condition 4 (Periods 14 through 18A/B) of the Bench Run 227-78 (CMSL-2) indicate that the addition of 2 W% of sodium lignolsulfonate surfactant does not have any positive effect on the CTSL process performance either in terms of product yields/conversions or product quality. Surfactant addition did not affect the ebullating recycle rates, indicating that it has little effect, if any, on the viscosity and the surface tension of the slurry reaction mixtures. Overall, no clear effect of the added surfactant was observed on process performance during CTSL operations with Illinois No. 6 coal.

---

[1] Reference: "Surfactants and Interfacial Phenomena", by Rosen, M.J., Wiley-Interscience, New York, 1978.

4.0 DETAILS OF OPERATION

This section summarizes the operational details of the Run 227-78 (CMSL-2) in the CTSL bench unit, using high concentrations (47-53 W%) of Illinois No. 6 coal in the slurry feed and a 1/32" extrudate Shell-317 catalyst in both reactors. The daily material recovery balances and reactor temperatures are presented in *Figures 2.2.23 and 2.2.24* respectively.

4.1 Bench Unit Description

HRI Continuous Bench Unit No. 227 was used for this Run (*Figure 2.2.25)*, and the run was identified as 227-78. It employed two equal-sized ebullated bed reactors in series (K-1 & K-2). Both reactors contained an equal quantity of Shell-317 1/32" extrudate catalyst. The effluent from the second reactor stage was separated in a hot separator (O-1) to obtain separator bottoms and light products. The vapors were cooled to obtain light distillate products (separator overheads, SOH) and noncondensible gases. The gases were metered, sampled, and sent to flare. The separator bottoms were sent to a continuous atmospheric still (CAS) to obtain atmospheric still overhead (ASOH) and CAS bottoms. CAS bottoms were filtered in a batch pressure filter to obtain pressure filter liquid (PFL) for recycle and pressure filter cake (PFC). PFL was recycled in required amount to slurry the feed coal.

4.2 Unit Modifications

The hot slurry mixing tank system (designated as P-6 drying tank in *Figure 2.2.26* was used during CMSL-2 for preparing the feed batches because of the requirement of transporting the high coal concentration slurries into the reactor at pumpable viscosities. This system could mix slurries and heat them to proper temperatures for maintaining pumpabilities. In general, coal and solvent were mixed and the feed batches prepared in a predetermined proportion every twelve hours and were then transferred over to the feed charge pot. The slurry was then being pumped continuously to the liquefaction reactors. A detailed drawing of this drying tank system is shown in *Figure* 26.

4.3 Preoperational Procedures

Operations were started using L-769 as a start-up oil. This was also the oil used whenever a make-up oil was needed during CMSL-2. The proper flows of oil and gases were adjusted in the system. Catalyst beds were sulfided using about 3 W% of TNPS added to the start-up feed oil. At the time of coal introduction the slurrying oil was recycle material produced during heat-up.

4.4 Operating Summary

A summary of the Run Plan for CMSL-2, consisting of four different conditions is given in *Table 2.2.1* . Beyond the normal samples taken for the in-house analyses and storage, samples of distillates (SOH and ASOH) from this run were collected and stored under a blanket of nitrogen for supplying to the Sandia National Laboratory for a DOE-sponsored secondary upgrading program.

4.4.1 Condition 1 (Periods 1 through 5)

The unit, in general, operated very well throughout this condition. Feed blends with a 1.1 oil-to-coal ratio were prepared without any process difficulty. No major mechanical problems were encountered. Reactor temperatures were 399 and 441°C (750 and 825°F) for stage one and two, respectively. A dry coal space velocity of about 303 Kg coal/h/M^3 (19 lb coal/hr/ft^3) per stage was used.

4.4.2 Condition 2 (Before & After A Shutdown: Periods 6 through 10)

The only change made in this Condition was in the oil-to-coal ratio at the feed. This ratio was changed from 1.1 to 0.8 during Condition 2. At the beginning of this Condition (Period 6), the charge pump flow interruptions became more frequent. The feed was lost from the charge pump approximately nine times. A high differential pressure of about 0.55 MPa (80 psi) developed across the first reactor. Subsequently the unit had to be shut down as the circulation of the slurry became difficult, and it was no longer possible to pump the feed into the first stage reactor. A complete turnaround and inspection of the first reactor was performed during the turnaround period. The riser tube and bubble cap were found plugged. The feed line from the charge tank to the charge pump was modified to aid in the proper suspension of coal solids by eliminating the dead space in the feed line. The catalyst was removed and new catalyst was loaded. The unit was restarted with the introduction of coal feeds (at an oil-to-coal ratio of 0.9) to the unit for Period 7B. The viscosity of the feed was controlled between 300 to 400 cps with a temperature requirement between 71 and 116°C (160 and 240°F) during Condition 2 after restart.

4.4.3 Condition 3 (Periods 11 through 13)

The reaction severity was altered by increasing the reactor temperatures to 413 and 432°C (775 and 810°F) for stage one and two, respectively. The dry coal space velocity was also increased by 50% to about 498 Kg coal/h/M^3 (31 lb coal/hr/ft^3) per stage. Operations were smooth during this condition. No mechanical problems were encountered. The viscosity of the last batch of the feed prepared in this condition was 409 cps at 186°C (366°F).

4.4.4 Condition 4 (Periods 14 through 17B) and Condition 4B (Periods 17C-18B)

The surfactant additive, sodium lignolsulfonate (2 W% relative to coal), was introduced in the feed during this condition. The viscosity of the feed increased to more than 500 cps at 196°C (385°F) by the end of Period 18B as indicated by the viscometer. The reactor temperatures were lowered to 399 and 424°C (750 and 795°F) for stage one and two respectively as per the request of JPL.

4.4.5 Shutdown

The unit was shut down and inspected following the run. Except for a few pieces of catalyst found at the top screen in the first reactor, there were no significant abnormalities found during the inspection. No significant material build-up were found either in the hot slurry mix or feed tanks during the inspection following the run.

5.0 MATERIALS USED

5.1 Feed Coal

The analyses of the Illinois No. 6, Burning Star Mine 2, coal (HRI-6107) used in this bench run are listed in *Table 2.2.16* along with the analyses of two more Illinois No. 6 coals (HRI-6081, used for Run CC-16 and HRI-5174, used for Run I-18). Coal conversions in microautoclaves were slightly lower for HRI-6107 which was used for CMSL-2; this probably explains why slightly lower coal conversions (by 1-1.5%) were obtained during CMSL-2 as compared to I-18. Although there is not much difference in the analyses of these coals, this would explain the difference in conversions.

5.2 Startup/Makeup Oil

L-769 was used as the startup or the makeup solvent. This was a mixture of a topped Wilsonville distillate and pressure filter liquid from the PDU run 260-03 made using subbituminous Black Thunder Coal. The complete analyses of this material are shown in *Table 2.2.16.*

5.3 Supported Catalyst

Shell-317 1/32" extrudate catalyst (Ni-Mo/Al_2O_3) was used in this bench run. The catalyst was presulfided during the startup by doping the startup oil with di-tertiary nonyl polysulfide (TNPS). No catalyst was added or removed on a continuous basis during the run. The detailed properties of the fresh Shell-317 catalyst are shown in *Table 2.2.17.*

5.4 Catalyst Additive

Sodium lignolsulfonate, supplied by the Jet Propulsion Laboratory, was used as an additive during the Condition 4 of this bench run. It was added as -70 mesh powder at 2 W% relative to feed coal to the slurry, prepared in the hot slurry mixing tank. The additive was water soluble, but insoluble in organic solvents.

6.0 LABORATORY SUPPORT FOR CMSL-2

6.1 Batch Microautoclave Experiments

6.1.1 Objectives:

To carry out the qualification of a new batch of Illinois No. 6 (HRI-6107) which as used in Run CMSL-2 under standard conditions. To determine the effect of addition of 2 W% (relative to coal) of sodium lignolsulfonate (a surfactant) on coal conversion levels in the presence of a recovered catalyst (with equilibrium carbon content about 15 W%)

HRI's 20 cc microautoclave system (Unit 223) was used for all of these screening tests.

6.1.2 Coal Qualification

For reference, tests were also carved out with the HRI 6081 shipment of Illinois No. 6 coal which had been used in Bench CSTL Run 227-76 (CC-16),

Common Conditions:	Catalyst :	HRI-5394P, 2.0 g
	H_2:	13.8 MPa (2000 psig)
	Coal(Dry):	2.0 g
	Solvent:	8.0 g (HRI-6002 Coal Derived Distillate 234-524C, 1.2% Residue, 14.1 API)

Ash Contents of Coals (Dry Basis)	HRI-6081	10.70 W%
	HRI-6107	12.04 W%

Run No.	**Coal**	**Temp.(°C)**	**(°F)**	**Time (min)**	**% Coal Conversion**
CL-34	HRI 6107	427	800	30.0	91.8
CL-28	HRI 6081	427	800	30.0	92.9
CL-26	HRI 6107	399	750	30.0	84.6
CL-29	HRI 6081	399	750	30.0	86.3
CL-32*	HRI 6107	427	800	30.0	85.1

* This test was carried out without any catalyst (thermal background)

Discussion:

The conversion levels at both temperatures indicate that the new Illinois No. 6 (HRI-6107) is slightly less reactive than the HRI-6081 Illinois No. 6 coal.

6.1.3 Effect of Surfactant on Conversion Levels

Common Conditions:

Catalyst :	2.0g Recovered Shell-317 from Stage 2 of Bench Run 227-77 (CMSL-1)
H_2:	13.8 MPa (2000 psig)
Coal(Dry):	2.0 g (HRI 6107)
Solvent :	8.0 g (L-769, a filtered product from an earlier PDU run 225-524 C, 26% Residue, 19.4°API)

Test No.	**Temp °C**	**°F**	**Time min**	**Surfactant gms**	**% Coal Conversion**	**% Resid Conversion**
CLS-1	399	750	30	0.04	79	45
CLS-2	399	750	30	0.00	76	41.5
CLS-3	427	800	30	0.04	90.6	46.6
CLS-4	427	800	30	0.00	88.4	46.9
CLS-5	441	825	30	0.04	91.5	52.3
CLS-6	441	825	30	0.00	92	52.6

Discussion :

The coal conversion values were calculated based on the assumption that all of the surfactant additive ends up in the THF-insoluble products. The results of these evaluation tests indicate at these conditions 2W% of the surfactant additive (sodium lignolsulfonate) does not have any significant effect (on a consistent basis) on coal and resid conversion levels. A 3% improvement in coal and resid conversion was observed in the presence of the added surfactant for tests carried out at lower temperatures (399°C), but this effect diminished at higher reaction temperatures (427 and 441°C).

6.2 Viscosity Measurements And Slurry Pumping Test

The viscosities of coal-solvent slurries of various solvent-to-coal ratios at various temperatures, with and without the added sodium lignolsulfonate surfactant, were experimentally measured. The coal feed for Run CMSL-2 , HRI 6081 Illinois NO. 6 of -70 mesh grind, was used using as solvent with PFL from Run 227-76 Period E3 (R76-E3) which contained 38.3 W% 524 C+ residual oil. The viscosities of the slurries at a solvent-to-coal ratio of 0.9 kg/kg are shown in *Figure 27*. The tests indicated that to obtain a viscosity of less than 2,000 cps the temperature would have to be about 232 C (450 F).

Other tests using a second solvent, the shutdown PFL from Run 227-76 (R76-S/D) and a second coal grind (PSD), with and without the surfactant indicated virtually no impact of the surfactant upon the viscosity. The viscosities using the L-769, 225-524 C distillate, startup oil as the solvent were about 2% of those with the R76-E3 PFL as the solvent.

The slurry pumping test was carried out prior to the run to evaluate the pumpability of several coal-solvent slurries with different coal loadings (48-63 W%) using the newly installed hot slurry preparation and mixing system. HRI 6107 Illinois No. 6 coal (-70 mesh) and PFL from Run 227-76 shutdown were used for the testing. The pumpability of the slurries was successfully checked in the temperature range of 232 to 288°C (450 to 550°F) and both with and without the added surfactant.

7.0 CONCLUSIONS

The Bench Run CMSL-2, which was a direct liquefaction of a bituminous Illinois No. 6 coal performed in the CTSL mode, indicated an improved CTSL process performance at higher coal loadings (47-53 W% of the feed slurry). Both the product yields and quality were influenced positively as an effect of processing slurries with high coal concentrations. The overall run operations also went on smoothly at these low solvent-to-coal ratios (0.9-1.1). Sodium lignolsulfonate, a surfactant additive developed by the Jet Propulsion Laboratory, did not have any effect either on the conversion levels or the product yields and quality under the conditions of the Bench Run CMSL-2.

TABLE 2.2.1

BENCH RUN CMSL-2
RUN PLAN

Condition	1	2*	3	4A	4B
Periods	1-5	6-10	11-13	14-17A	17B-18B
Temperature, °C (°F)					
First stage reactor	399 (750)	399 (750)	413 (775)	413 (775)	399 (750)
Second stage	427 (800)	427 (800)	432 (810)	432 (810)	424 (795)
reactor	316 (600)	316 (600)	316 (600)	316 (600)	316 (600)
Hot separator	329 (625)	327 (625)	327 (620)	327 (620)	327 (620)
Solvent/Coal Ratio	1.1	0.9	0.9	0.9	0.9
Space Velocity (Stg 2 vol)					
$Kg/h/M^3$	332	332	498	498	498
$Lb/h/ft^3$	20.7	20.7	31	31	31
Additive**, W% coal feed	0	0	0	2	2
Recycles (W% dry coal)					
PFL to slurry	110	90	90	90	90
PFL to Buffer					
First Stage	4.0	4.0	4.0	4.0	4.0
Second Stage	4.0	4.0	4.0	4.0	4.0

* Each period (day) is subdivided into three subperiods, A, B, and C. The Run was suspended in Period 6A due to operability problems and was restarted in Period 7B.

** Sodium lignolsulfonate, a surfactant supplied by Jet Propulsion Laboratory, was the additive.

TABLE 2.2.2

RUN CMSL-2 OPERATING SUMMARY
Evaluation of Low Solvent-To-Coal Ratios

Coal : Illinois No. 6 (HRI-6107)
Catalyst : Shell-37 (HRI-5394) Both Stages

Period Number	1	2	3	4	5
Date (Period)	04/15/9	04/16/9	04/17/93	04/18/93	04/19/93
Hours of Run	3	3 48.	72.	96.	120.
	24.				
Stage 2 Catalyst Age (Kg Dry Coal (Kg Cat)	35.	69.	98.	124.	188.
1st Stage Temperature (C)	389	399	400	400	399
2nd Stage Temperature (C)	417	427	427	427	427
Unit Pressure (Mpa)	17.2.	17.2	17.2	17.2	17.2.
SV, Kg Coal/hr/m^3	397	388	331	296	354
SV, Lb Coal/hr/ft^3	25	24	21	18	22
W% OF DRY COAL					
PFL Recycle	47.8	96.6	92.5	93.9	80.5
PFL to Buffer to Stage 1	3.6	3.8	4.4	4.4	3.9
PFL to Buffer to Stage 2	3.5	3.6	4.5	4.6	3.9
Make-up Oil	81.8	9.4	13.5	12.9	23.4
SOLVENT-TO-COAL (DRY) RATIO	1.30	1.06	1.06	1.06	1.05
MATERIAL BALANCE (%) (GROSS)	97.02	97.15	97.82	101.64	97.34
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED					
C1-C3 in Gases				4.45	
C4-C7 in Gases				3.11	
IBP-199 deg-C in Liquids				17.48	
199-260 deg-C in Liquids				13.01	
260-343 deg-C in Liquids				27.59	
343-454 deg-C in Liquids				5.69	
454-524 deg-C in Liquids				0.63	
Toluene Soluble 524C+ Oil				1.34	
Toluene Insoluble 52C+ Oil				0.01	
Unconverted Coal				6.27	
Ash				12.04	
Water				10.77	
CO				0.07	
CO2				0.04	
NH3				1.40	
H2S				3.37	
Total (100 + H2 Reacted)				107.28	
PROCESS PERFORMANCE					
C4-524 deg-C Distillates, W% of MAF Coal				76.8	
524C+ Conversion W% MAF				91.3	
Coal Conversion, W% MAF				92.9	
HDS, W%				79.2	
HDN, W%				93.5	

TABLE 2.2.2 (Cont.)

RUN CMSL-2 OPERATING SUMMARY

Period Number	6	7	8	9	10
Date (Period)	04/20/93	04/25/93	04/26/93	04/27/93	04/28/93
Hours of Run	144.	160	184	208	232
Stg 2 Cat Age, Kg dry coal/Kg cat	188	213	243	270	295
1st Stage Temp (C)	399	387	398	399	399
2nd Stage Temp (C)	427	413	427	427	428
Unit Pressure (Mpa)	17.1.	17.3	17.3	17.3	17.3
SV, Kg Coal/hr/m^3	378	422	345	305	295
SV, Lb Coal/hr/ft^3	24	26	22	19	18
W% OF DRY COAL					
PFL Recycle	78.5	90.1	89.6	90.1	90.1
PFL to Buffer to Stage 1	3.9	3.3	3.9	4.9	4.5
PFL to Buffer to Stage 2	3.9	3.0	4.0	4.8	4.4
Make-up Oil	0.0	0.0	0.0	0.0	0.0
SOLVENT-TO-COAL (DRY) RATIO	0.8	0.9	0.9	0.9	0.9
MATERIAL BALANCE (%) (GROSS)	97.43	102.02	99.28	95.46	99.25
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED					
C1-C3 in Gases					5.22
C4-C7 in Gases					3.80
IBP-199 deg-C in Liquids					15.89
199-260 deg-C in Liquids					11.13
260-343 deg-C in Liquids					27.52
343-454 deg-C in Liquids					7.36
454-524 deg-C in Liquids					1.04
Toluene Soluble 524C+ Oil					1.95
Toluene Insoluble 524C+ Oil					0.02
Unconverted Coal					6.28
Ash					12.04
Water					10.18
CO					0.10
CO2					0.04
NH3					1.40
H2S					3.40
Total (100 + H2 Reacted)					107.37
PROCESS PERFORMANCE					
C4-524 deg-C Distillates, W% of MAF Coal					75.9
524 C+ Conversion, W% MAF					90.6
Coal Conversion, W% MAF					92.9
HDS, W%					80.1
HDN, W%					91.7

TABLE 2.2.2 (Cont.)

CATALYTIC MULTISTAGE COAL LIQUEFACTION

Period Number	11	12	13	14	15
Date (Period)	04/29/93	04/30/93	05/01/93	05/02/93	05/03/93
Hours of Run	256	280	304	328	352
Stg 2 Cat Age, Kg dry coal/Kg cat	333	376	422	458	495
1st Stage Temp (C)	408	413	414	413	413
2nd Stage Temp (C)	433	433	433	433	433
Unit Pressure (Mpa)	17.3.	17.3	17.2	17.2	17.2
SV, Kg Coal/hr/m^3	434	481	535	409	414
SV, Lb Coal/hr/ft^3	27	30	33	26	26
W% OF DRY COAL					
PFL Recycle	90.1	90.1	90.2	90.1	90.0
PFL to Buffer to Stage 1	3.3	2.6	2.6	4.7	3.2
PFL to Buffer to Stage 2	3.4	2.9	2.6	4.5	3.1
Make-up Oil	0.0	0.0	0.0	0.0	0.0
Sodium Lignolsulfonate				2.0	2.0
SOLVENT-TO-COAL (DRY) RATIO	0.9	0.9	0.9	0.9	0.9
MATERIAL BALANCE (%) (GROSS)	95.63	97.91	97.28	95.81	99.3
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED					
C1-C3 in Gases		5.89	4.73		
C4-C7 in Gases		3.46	3.36		
IBP-1990 deg-C in Liquids		15.83	14.75		
199-260 deg-C in Liquids		8.61	8.09		
260-343 deg-C in Liquids		21.14	20.52		
343-454 deg-C in Liquids		10.60	12.34		
454-524 deg-C in Liquids		2.41	3.36		
Toluene Soluble 524C+ Oil		3.73	5.66		
Toluene Insoluble 524C+ Oil		0.06	0.12		
Unconverted Coal		6.28	6.69		
Ash		12.04	12.04		
Water		10.16	10.14		
CO		0.17	0.15		
CO2		1.72	0.12		
NH3		1.34	1.31		
H2S		3.29	3.29		
Total (100 + H2 Reacted)		106.74	106.67		
PROCESS PERFORMANCE					
C_4-524 deg-C Distillates, W% of MAF Coal		70.6	71.0		
524 C+ Conversion, W% MAF		88.56	85.8		
Coal Conversion, W% MAF		92.9	92.4		
HDS, W%		77.3	77.5		
HDN, W%		87.5	85.8		

TABLE 2.2.2 (Cont.)

CATALYTIC MULTISTAGE COAL LIQUEFACTION

Period Number	16	17	18A/B
Date (Period)	05/04/93	05/05/93	05/06/93
Hours of Run	376	400	416
Stg 2 Cat Age, Kg dry coal/Kg cat	535	570	597
1st Stage Temp (C)	413	406	400
2nd Stage Temp (C)	433	427	424
Unit Pressure (Mpa)	17.2	17.3	17.2
SV, Kg Coal/hr/m^3	458	412	458
SV, Lb Coal/hr/ft^3	29	26	29
W% OF DRY COAL			
PFL Recycle	88.5	90.3	88.6
PFL to Buffer to Stage 1	3	3.3	2.4
PFL to Buffer to Stage 2	3.5	4.7	2.8
Make-up Oil	0.0	0.0	0.0
Sodium Lignolsulfonate	2.0	2.0	2.0
SOLVENT-TO-COAL (DRY) RATIO	0.9	0.9	0.9
MATERIAL BALANCE (%) (GROSS)	97.69	98.96	92.96
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED			
C1-C3 in Gases	5.21		4.32
C4-C7 in Gases	3.25		3.26
IBP-1990 deg-C in Liquids	11.12		8.32
199-260 deg-C in Liquids	8.78		7.34
260-343 deg-C in Liquids	20.01		15.76
343-454 deg-C in Liquids	14.37		18.16
454-524 deg-C in Liquids	3.73		6.02
Toluene Soluble 524C+ Oil	8.15		15.58
Toluene Insoluble 524C+ Oil	0.17		0.32
Unconverted Coal	5.98		7.28
Ash	12.04		12.04
Water	8.66		2.33
CO	0.16		0.20
CO2	0.15		0.29
NH3	1.23		1.00
H2S	3.21		3.03
Total (100 + H2 Reacted)	106.21		105.24
PROCESS PERFORMANCE			
C_4-524 deg-C Distillates, W% of MAF Coal	69.6		66.9
524 C+ Conversion, W% MAF	83.7		73.6
Coal Conversion, W% MAF	93.2	93.0	91.7
HDS, W%	75.6		71.4
HDN, W%	80.1		65.6

TABLE 2.2.3 a

BENCH RUN 227-078, CMSL-2
Operational and Analytical Summary

Period	4	10	13	16	18
Date (Start of Period	04/18/93	04/28/93	05/01/93	05/04/93	05/06/9
Hours of Run	96	232	304	376	3
Dry Coal In Total Dry Fresh Feed	100	100	100	100	416
Surfactant, W% Coal Feed	0.00	0.00	0.00	2.00	100
Slurry Oil/Coal	1.05	0.90	0.90	0.88	2.00
Coal Feed, Kg/h/M^3 (Stage)	296	295	535	458	0.89
Temperatures °C					458
1st Stage	400	399	414	413	
2nd Stage	427	428	433	433	400
Slurry Mix Tank	97	100	134	167	424
Hot Separator Liquid	318	313	314	312	184
					311

TABLE 2.2.3b

SEPARATOR OVERHEAD PLUS KNOCKOUTS PRODUCT PROPERTIES

PERIOD	4	10	13	16	18
GRAVITY	40.30	39.10	36.60	33.70	30.10
ELEMENTAL ANALYSIS, W%					
Carbon	86.99	87.04	87.12	86.50	86.38
Hydrogen	13.19	13.03	12.74	12.43	12.12
Sulfur	0.01	0.00	0.01	0.01	
Nitrogen (ANTEK)	0.01	0.01	0.06	0.13	
ASTM DISTILLATION, °C					
IBP	54	39	41	81	83
5 V%	86	73	76	102	109
10 V%	98	91	92	113	123
20 V%	114	111	113	133	147
30 V%	132	131	132	158	176
40 V%	155	158	158	188	209
50 V%	183	189	190	217	237
60 V%	215	218	228	249	269
70 V%	244	250	260	281	297
80 V%	274	276	293	312	327
90 V%	303	302	324	343	360
95 V	320	319	346	369	382
END POINT	343	337	377	403	403
V% @ 177°C	54	53	53	44	37
V% @ 260°C	76	74	70	63	57
V% @ 343°C	99	99	94	90	86
IBP-177°C, W%	4.9	49.2	48.9	39.3	32.6
177-260°C, W%	23.1	21.8	17.5	19.5	20.1
260-343°C, W%	25.4	27.0	26.2	28.4	30.0
343°C+, W%	1.3	1.6	7.0	12.4	16.6
LOSS W%	0.3	0.4	0.4	0.4	0.7

TABLE 2.2.3c

ATMOSPHERIC OVERHEAD PRODUCT PROPERTIES

PERIOD	4	10	13	16	18
GRAVITY	24.80	25.60	25.10	24.00	21.80
ELEMENTAL ANALYSIS, W%					
Carbon	87.86	87.25	87.78	87.25	86.47
Hydrogen	11.96	12.02	11.87	11.53	11.41
Sulfur	0.00	0.04	0.01	0.01	
Nitrogen (ANTEK)	0.01	0.04	0.06		
ASTM DISTILLATION, °C					
IBP	108	107	87	140	149
5 V%	177	170	136	184	195
10 V%	211	199	163	208	214
20 V%	249	235	207	237	241
30 V%	272	260	239	257	254
40 V%	289	279	264	271	274
50 V%	301	291	279	287	286
60 V%	311	301	291	299	297
70 V%	322	310	302	309	308
80 V%	332	321	314	319	317
90 V%	348	333	328	333	329
95 V	357	343	337	341	336
END POINT	371	356	353	357	351
V% @ 177°C	8	10	18	8	6
V% @ 260°C	25	30	38	32	33
V% @ 343°C	88	95	98	96	98
IBP-177°C, W%	6.6	8.9	15.4	6.2	4.3
177-260°C, W%	15.7	18.4	19.7	22.3	25.5
260-343°C, W%	62.9	66.1	60.1	64.7	65.3
343°C+, W%	14.5	6.1	4.4	6.8	4.6
LOSS W%	0.3	0.5	0.4	0.0	0.3

TABLE 2.2.3d

PRESSURE FILTER LIQUID PRODUCT PROPERTIES

PERIOD	4	10	13	16	18
GRAVITY	10.90	11.20	4.00	2.10	-0.90
ELEMENTAL ANALYSIS, W%					
Carbon	89.07	89.29	89.02	89.32	89.40
Hydrogen	10.29	10.32	9.43	8.88	8.49
Sulfur	0.01	0.06	0.13	0.13	0.16
Nitrogen (ANTEK)	0.19	0.22	0.40	0.51	0.70
ASTM DISTILLATION, °C					
IBP	285	288	278	289	296
V% @ 343°C	10	12	12	7	5
V% @ 454°C	69	70	62	53	45
V% @ 524°C	84	80	78	67	62
IBP-260°C, W%	0.00	0.00	0.00	0.00	0.00
260-343°C, W%	8.95	11.29	10.34	6.52	4.61
343-454°C, W%	55.63	55.54	467.36	42.30	36.53
454-524°C+, W%	16.00	11.19	15.90	15.68	15.96
524°C+, W%	18.91	21.17	27.30	35.03	42.16
LOSS W%	0.51	0.81	0.10	0.47	0.74
524°C+ Pressure Filter Liquid					
CCR W%	29.81	28.75	44.16		
Cyclohexane Insolubles W% (inc. Ash)	5.82	7.68	28.66		
Toluene Insolubles W% (inc. Ash)	0.72	0.96	2.05	2.05	2.00

TABLE 2.2.3e

PRESSURE FILTER CAKE PRODUCT PROPERTIES

PERIOD	4	10	13	16	18
ELEMENTAL ANALYSIS, W%					
Carbon	51.47	53.33	56.00	51.12	55.08
Hydrogen	4.69	4.71	4.67	4.01	4.27
Sulfur	3.2	2.95	3.09	3.33	3.23
Nitrogen (ANTEK)	0.31	0.34	0.38	0.43	0.58
COMPOSITION, W%					
ASH (Quinoline Filtration)	39.86	37.12	37.56	39.45	32.45
ASTM ASH	39.98	38.00	38.20	38.35	34.60
SULFUR IN ASH	1.04	1.11	1.54	1.68	1.47
UNCONVERTED COAL (Adjusted)	20.83	19.81	21.22	19.95	20.93

TABLE 2.2.4

Properties of Recycle Oil (PFL) from Run 227-78

Condition	1	1	2	3	3	4	4
Period	4	5	10	12	13	16	18A/B
°API	10.9	9.9	11.2	8.3	4.0	2.1	-0.9
H/C Ratio	1.39	1.33	1.39	1.27	1.27	1.19	1.14
Nitrogen, W%	0.19	0.10	0.22	0.40	0.40	0.51	0.70
Sulfur, W%	0.012	0.043	0.065	0.128	0.128	0.128	0.157
WEIGHT PERCENT COMPOSITION							
IBP-343°C	8.95	8.88	11.29	10.97	10.34	6.52	4.61
343-454°C	55.63	53.30	55.54	49.90	46.30	42.30	36.53
454-524°C	16.0	15.2	11.2	15.22	15.90	15.68	15.96
524°C$^+$	18.91	22.10	21.17	23.91	27.30	35.03	42.16

TABLE 2.2.5

Pressure Filter Liquid Product Analysis For Run 227-78 (CMSL-2)

Condition	1	2	3	4A	4B
Period	4	10	13	16	18A/B
Catalyst Age(lb coal/lb cat)	124	295	376	535	597
Total Pressure Filter Liquid					
°API Gravity	10.9	11.2	4.0	2.1	-0.9
Boiling Fractions, W%					
IBP-343°C	8.95	11.29	10.34	6.52	4.61
343-454°C	55.63	55.54	46.36	42.30	36.53
454-524°C	16.00	11.19	15.90	15.68	15.96
524°C+	18.91	21.17	27.30	35.03	42.16
Loss	0.51	0.81	0.10	0.47	0.74
LGO (IBP-343°C)					
Elemental Analysis, W%					
Carbon	87.69	88.23	88.37		
Hydrogen	11.58	11.77	11.76		
Nitrogen	0.0114	0.0124	0.0168		
Sulfur	0.0037	0.00398	0.00779		
VGO (343-454°C)					
Elemental Analysis, W%					
Carbon	88.55	88.85	89.11		
Hydrogen	11.07	11.01	10.65		
Nitrogen	0.0144	0.0543	0.21		
Sulfur	0.0037	0.0081			
HVGO (454-524°C)					
Elemental Analysis, W%					
Carbon	89.37	90.23	90.20		
Hydrogen	9.61	9.54	9.16		
Nitrogen	0.25	0.21	0.37		
Sulfur	0.031	0.020	0.132		
RESIDUUM (524°C$^+$)					
Elemental Analysis, W%					
Carbon	90.06	90.14	89.71		
Hydrogen	8.16	7.77	7.28		
Nitrogen	0.47	0.52	0.88		
Sulfur	0.052	0.085	0.218		

TABLE 2.2.6A

RUN NO. 227-78 PERIOD 4

Detailed Analysis of TBP Fractions: The Net Liquid Product from the Process

TBP Distillation, %

IBP, °C	118
	W%
IBP-177 C	26.91
177-260 C	22.44
260-343 C	41.61
354-454	6.27
454-524 C	0.8
524 F+	0.95
Loss	1.02

TBP Fraction [C]	IBP-177	177-260	260-343	343-454	454-524	524°C +
API Gravity	51.4	32.9	22.9	NES		
Elemental Analyses, W%						
Carbon	85.53	83.66	87.05	88.24	89.37	90.06
Hydrogen	13.95	12.06	11.95	11.37	9.61	8.16
Sulfur	0.0014	0.0134	0.0315	0.018	0.031	0.052
Nitrogen	0.0015	0.0311	0.0436	0.0505	0.25	0.47
H/C Ratio	1.96	1.73	1.65	1.55	1.29	1.09
Bromine No. (g/100 g)						
Aniline Point, [C]	42	38	48			
Flash Point, [C]	-6.7	72	132			
PONA [V%]						
Paraffins	19.92	14.7				
Olefins	1	2.1				
Naphtenics	71.1	52.7				
Aromatics	7.98	30.5				
Aromatics (ASTM D2549)			46.17			

NES: Not Enough Sample

TABLE 2.2.6B

RUN NO. 227-78 PERIOD 10

Detailed Analysis of TBP Fractions: The Net Liquid Product from the Process

TBP Distillation, %

IBP, °C	126
	W%
IBP-177 C	23
177-260 C	27.72
260-343 C	44.38
354-454	3.83
454-524 C	0
524 F+	0
Loss	1.07

TBP Fraction [C]	IBP-177	177-260	260-343	343-454	454-524	524°C +
API Gravity	50.8	31.8	22.9	19.2	N/A	N/A
Elemental Analyses, W%						
Carbon	85.78	84.69	88.1	88.22	N/A	N/A
Hydrogen	14.09	12.01	11.96	11.58	N/A	N/A
Sulfur	0.0026	0.0421	0.032	0.02	N/A	N/A
Nitrogen	0.0024	0.0363	0.04	0.08	N/A	N/A
H/C Ratio	1.97	1.70	1.63	1.58	N/A	N/A
Bromine No. (g/100 g)						
Aniline Point, [C]	41	41	59			
Flash Point, [C]	-6.7	70	138			
PONA [V%]						
Paraffins	19.48	9.6				
Olefins	1	2				
Naphtenics	69.99	55.3				
Aromatics	8.83	33.1				
Aromatics (ASTM D2549)			45.63	59.76		

N/A: Not applicable, as there was no PFL formation for this Period

TABLE 2.2.6C

RUN NO. 227-78 PERIOD 13

Detailed Analysis of TBP Fractions: The Net Liquid Product from the Process

TBP Distillation, %

IBP, °C	136
	W%
IBP-177 C	24.93
177-260 C	22.47
260-343 C	36.04
354-454	9.79
454-524 C	2.38
524 F+	4.09
Loss	0.3

TBP Fraction [C]	IBP-177	177-260	260-343	343-454	454-524	524°C +
API Gravity	50.2	31	21.1	NES		
Elemental Analyses, W%						
Carbon	85.59	84.62	88.35	88.99	90.2	89.71
Hydrogen	13.97	11.82	11.6	10.74	9.16	7.28
Sulfur	0.0073	0.0585	0.06	0.042	0.032	0.22
Nitrogen	0.0124	0.08	0.11	0.2	0.37	0.88
H/C Ratio	1.95	1.68	1.58	1.45	1.22	0.97
Bromine No. (g/100 g)						
Aniline Point, [C]	102	93.5	93			
Flash Point, [C]	20	152	280			
PONA [V%]						
Paraffins	20.01	8.14				
Olefins	3	3.8				
Naphtenics	66.41	50.86				
Aromatics	10.58	37.2				
Aromatics (ASTM D2549)			51.56	51		

NES: Not Enough Sample

TABLE 2.2.6D

RUN NO. 227-78 PERIOD 13

Detailed Analysis of TBP Fractions: The Net Liquid Product from the Process

TBP Distillation, %

IBP, °C	148
	W%
IBP-177 C	23.2
177-260 C	24.66
260-343 C	25.44
354-454	16.06
454-524 C	3.14
524 F+	7.00
Loss	0.5

TBP Fraction [C]	IBP-177	177-260	260-343	343-454	454-524	524°C +
API Gravity	49.6	29.3	19.6	13.6		
Elemental Analyses, W%						
Carbon	85.9	84.63	88.2	88.94	89.96	89.47
Hydrogen	14.06	11.59	11.1	10.5	8.8	6.99
Sulfur	0.0263	0.0629	0.036	0.06	0.08	0.224
Nitrogen	0.0126	0.13	0.16	0.21	0.46	1.05
H/C Ratio	1.96	1.64	1.51	1.42	1.17	0.94
Bromine No. (g/100 g)						
Aniline Point, [C]	100.5	85.5	82			
Flash Point, [C]	20	154	290			
PONA [V%]						
Paraffins	17.25	6.51				
Olefins	4	3.6				
Naphtenics	69.75	49.59				
Aromatics	9	40.3				
Aromatics (ASTM D2549)			57.1	66.33		

TABLE 2.2.7

Comparison of Process Performance for Period No. 4 During Two Bench CTSL Runs Using Same Catalyst (Shell-317 1/32" Extrudates) but Different Solvent-to-Coal Ratios.

	Run 227-37 (I-18)			**Run 227-78 (CMSL-2)**		
SOLVENT-TO-COAL RATIO	**1.59**			**1.06**		
Catalyst Age (Lb Coal/Lb Cat)	117			124		
REACTION CONDITIONS	T:RX1	T:RX2	SV	T:RX1	T:RX2	SV
	399	427	337	400	427	296
Coal Conversion (W% MAF)	93.4			92.7		
975 °F+ Conversion (W% MAF)	87.6			91.2		
H_2 Consumption (W% dry)	6.58			7.22		
YIELDS (W% DRY BASIS)						
C_1-C_3 Gases	5.03			4.45		
C4-390 °F	15.94			20.59		
390-650 °F	33.16			40.58		
650-975 °F	16.65			6.20		
975 °F+	5.17			1.31		
C_4-975 °F Distillate Yield (W% MAF Coal)	73.6			76.6		

TABLE 2.2.8

Comparison of Process Performance Between Two Bench CTSL Runs Using Same Catalyst (Shell-317 1/32" Extrudates) but Different Solvent-to-Coal Ratios.

	Run 227-37-Period 09			Run 227-78-Period 10		
SOLVENT-TO-COAL RATIO	**1.59**			**0.90**		
Catalyst Age (Lb Coal/Lb Cat)	264			295		
REACTION CONDITIONS	T:RX1	T:RX2	SV	T:RX1	T:RX2	SV
	399	426	330	399	428	295
Coal Conversion (W% MAF)	93.7			92.9		
975 °F+ Conversion (W% MAF)	84.4			90.6		
H_2 Consumption (W% dry)	6.26			7.37		
YIELDS (W% DRY BASIS)						
C_1-C_3 Gases	5.15			5.22		
C4-390 °F	15.17			19.69		
390-650 °F	28.06			38.65		
650-975 °F	18.26			8.40		
975 °F+	8.36			1.97		
C_4-975 °F Distillate Yield (W% MAF Coal)	68.8			75.9		

TABLE 2.2.9

Comparison of Process Performance Between Two Bench CTSL Runs Using Same Catalyst (Shell-317 1/32" Extrudates) but Different Solvent-to-Coal Ratios (and Different Process Severity Conditions).

	Run 227-37-Period 18 (1-18)			**Run 227-78-Period 13**		
SOLVENT-TO-COAL RATIO	**1.12**			**0.90**		
Catalyst Age (Lb Coal/Lb Cat)	530			422		
REACTION CONDITIONS	T:RX1	T:RX2	SV	T:RX1	T:RX 2	SV
	413	433	352	414	433	535
Coal Conversion (W% MAF)	94.97			92.4		
975 °F+ Conversion (W% MAF)	85.4			85.8		
H_2 Consumption (W% dry)	6.55			6.67		
YIELDS (W% DRY BASIS)						
C_1-C_3 Gases	6.66			4.73		
C4-390 °F	18.17			18.11		
390-650 °F	28.75			28.61		
650-975 °F	15.51			15.70		
975 °F+	8.54			5.78		
C_4-975 °F Distillate Yield (W% MAF Coal)	69.8			71.0		

TABLE 2.2.10

Comparison of Process Performance Between Two Bench CTSL Runs Using Same Catalyst (Shell-317 1/32" Extrudates) but Different Solvent-to-Coal Ratios And Different Process Severity Conditions.

	Run 227-37-Period 21			**Run 227-78-Period 16** (With a Surfactant)		
SOLVENT-TO-COAL RATIO	**1.12**			**0.90**		
Catalyst Age (Lb Coal/Lb Cat)	619			535		
REACTION CONDITIONS	T:RX1	T:RX2	SV	T:RX1	T:RX 2	SV
	413	432	338	413	433	458
Coal Conversion (W% MAF)	94.7			93.2		
975 °F+ Conversion (W% MAF)	84.3			83.7		
H_2 Consumption (W% dry)	6.46			6.21		
YIELDS (W% DRY BASIS)						
C_1-C_3 Gases	6.77			5.21		
C4-390 °F	17.06			14.37		
390-650 °F	28.47			28.79		
650-975 °F	14.36			18.10		
975 °F+	9.33			8.32		
C_4-975 °F Distillate Yield (W% MAF Coal)	66.9			69.6		

TABLE 2.2.11

Comparison of Two CTSL Bench Runs: 227-76 (CC-16) with Akzo AO-60 Catalyst and 227-78 (CMSL-2) with Shell-317 Catalyst to Demonstrate the Effect of Solvent-to-Coal Ratios on Process Performance.

	Run 227-76-Period 07			Run 227-78-Period 04		
SOLVENT-TO-COAL RATIO	**1.5**			**1.1**		
Catalyst Age (Lb Coal/Lb Cat)	133			124		
REACTION CONDITIONS	T:RX1	T:RX2	SV	T:RX1	T:RX 2	SV
	399	426	332	400	427	296
Coal Conversion (W% MAF)	91.3			92.9		
975 °F+ Conversion (W% MAF)	82.9			91.3		
H_2 Consumption (W% dry)	6.37			7.28		
YIELDS (W% DRY BASIS)						
C_1-C_3 Gases	5.29			4.45		
C4-390 °F	16.29			20.59		
390-650 °F	26.88			40.60		
650-975 °F	17.39			6.32		
975 °F+	7.48			1.35		
C_4-975 °F Distillate Yield (W% MAF Coal)	67.8			76.8		
Heteroatom Removal						
HDS, W%	76.8			79.2		
HDN, W%	83.0			93.5		

TABLE 2.2.12

Comparison of Two CTSL Bench Runs: 227-76 (CC-16) with Akzo AO-60 Catalyst and 227-78 (CMSL-2) with Shell-317 Catalyst to Demonstrate the Effect of Solvent-to-Coal Ratios on Process Performance.

	Run 227-76-Period 09			**Run 227-78-Period 10**		
SOLVENT-TO-COAL RATIO	**1.5**			**0.9**		
Catalyst Age (Lb Coal/Lb Cat)	174			295		
REACTION CONDITIONS	T:RX 1	T:RX 2	SV	T:RX 1	T:RX 2	SV
	752	800	74.4	751	802	65.7
Coal Conversion (W% MAF)	92.5			92.9		
975 °F+ Conversion (W% MAF)	84.4			90.6		
H_2 Consumption (W% dry)	6.46			7.37		
YIELDS (W% DRY BASIS)						
C_1-C_3 Gases	5.76			5.22		
C4-390 °F	17.18			19.69		
390-650 °F	28.03			38.65		
650-975 °F	16.13			8.40		
975 °F+	7.28			1.97		
C_4-975 °F Distillate Yield (W% MAF Coal)	68.6			75.9		
Heteroatom Removal						
HDS, W%	76.0			80.1		
HDN, W%	83.3			91.7		

TABLE 2.2.13

Comparison of Recycle Oil Properties For Three Bench Runs, I-18, CC-16, And CMSL-2

RUN (PERIOD)	I-18 (9)	CC-16 (9)	CMSL-2 (10)
Catalyst	Shell-317	Akzo AO-60	Shell-317
Age(lb coal/lb cat)	264	174	295
Solvent/Coal Ratio	1.6	1.5	0.9
<u>PFL Properties</u>	3.7	4.9	11.2
°API Gravity	1.24	1.25	1.39
H/C Ratio	0.34	0.30	0.22
Nitrogen, W%	0.05	0.07	0.06
Sulfur, W%			
<u>Weight Percent</u>			
IBP-343°C	9.5	10.1	11.3
343-454°C	43.9	45.7	55.5
454-524°C	16.1	14.8	11.2
524°C$^+$	30.5	28.8	21.2
<u>343-454°C Fraction</u>			
H/C Ratio	1.40	1.37	1.49
Nitrogen, W%	0.09	0.13	0.05
<u>454-524°C Fraction</u>			
H/C Ratio	1.20	1.19	1.27
Nitrogen, W%	0.27	0.29	0.21
<u>524°C+ Fraction</u>			
H/C Ratio	1.03	0.98	1.03
Nitrogen, W%	0.81	0.68	0.52
Sulfur, W%	0.25	0.16	0.09
Cyclohexane Insol, W%	23.3	24.2	5.8
Toluene Insol, W%	2.2	1.8	0.7

TABLE 2.2.14

Comparison of Operating Severities for Bench Runs I-18, CC-16, and CMSL-2

Bench Run ID	I-18	CC-16	CMSL-2
Period No.	09	09	10
Solvent/Coal at Reactors (Including Buffer Oils)	1.88	1.78	0.99
Coal Space Velocity (Kg coal/h /M^3 Reactor) per stage	20.6	20.0	18.5
Total Slurry Residence Time (min) (Reactor 1 + Reactor 2)	120.0	118.1	185.7
Total Severity, STTU	22.5	24.0	38.5

TABLE 2.2.15

Feed Coal Analysis Comparison for CMSL-2, I-18, and CC-16

Feed Designation, HRI No.	6107	6081	5174
Run No.	CMSL-2	CC-16	I-18
Moisture, W%	1.16	2.97	2.57
Proximate Analysis, W% (Dry Basis)			
Volatile Matter		39.05	
Fixed Carbon		50.34	
Ash	12.04	10.61	10.55
Ultimate Analyses, W% (Dry Basis)			
Carbon	69.00	69.48	70.39
Hydrogen	4.24	4.39	4.49
Sulfur	4.00	3.68	3.60
Nitrogen	1.26	1.25	1.44
Ash	12.04	10.61	10.55
Oxygen (By Diff.)	9.46	10.59	9.54
Microautoclave Results *			
Catalytic Conversion @399°C	84.6	86.3	91.0
Catalytic Conversion @427°C	91.8	92.9	

* 30 Minutes And 13.8 MPa H_2

TABLE 2.2.16

Inspection of Startup/Makeup Oil for CMSL-2

DESIGNATION	L-769
GRAVITY, °API	19.4
DISTILLATION °C	
IBP	225
5 V%	279
10 V%	293
20 V%	308
30 V%	321
40 V%	334
50 V%	343
60 V%	361
70 V%	378
80 V%	398
95 V%	467
FBP	524
V% @ 343°C	50
V% @ 454°C	93
V% @ 524°C	99
IBP-343°C, W%	47.87
343-454°C, W%	42.64
454-524°C, W%	6.08
524°C$^+$, W%	2.56
LOSS, W%	0.85
ELEMENTAL ANALYSES, W%	
Carbon	88.38
Hydrogen	11.56
Sulfur	0.09
Nitrogen	0.07

TABLE 2.2.17

RECOVERED CATALYST ANALYSES (CMSL-2)

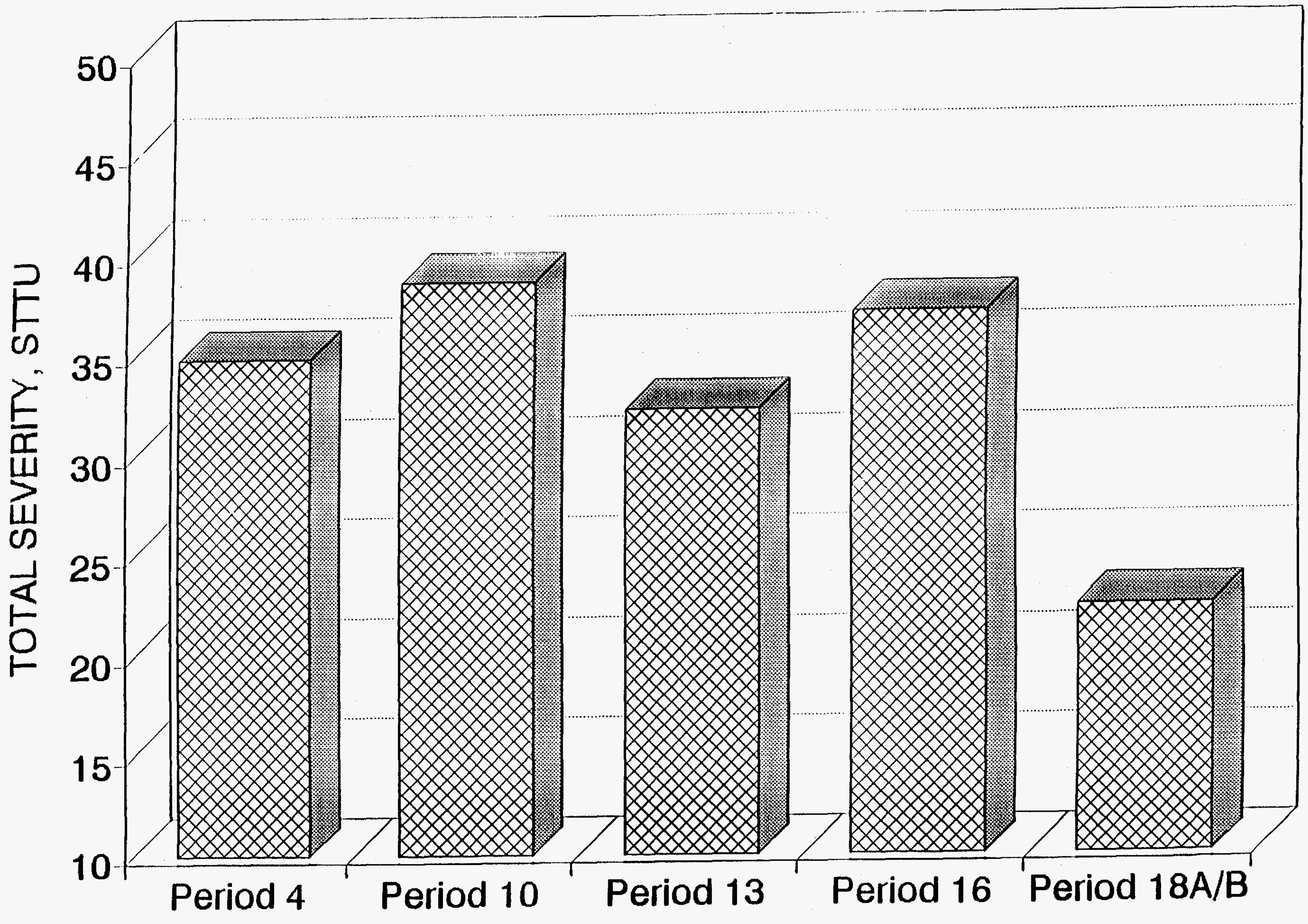
Stage	First	Second
Catalyst Age, lb coal/lb cat	409	597
Analyses of Oil Free +20 Mesh Catalyst, W%		
Carbon	15.26	16.73
Hydrogen	0.88	0.85
Nitrogen	0.25	0.17
Sulfur	5.34	6.20
Molybdenum	7.74	8.08
Nickel	1.55	1.61
Titanium	1.64	0.13
Iron	0.35	0.20
Calcium	0.027	0.006
Sodium	0.597	0.733
Loss on Ignition, W%	21.14	24.92
Bulk Density, gm/cc	0.925	0.887
Pore Volume, cc/gm	0.332	0.323
Surface Area (Calc.), m^2/gm	156.22	159.30

TABLE 2.2.18

Fresh Catalyst Properties for Bench Runs CMSL-2 and I-18

Run No.	CMSL-2	I-18
HRI No.	5394	5359
Catalyst	S-317	S-317
Nominal Size	1/32"	1/32"
CHEMICAL ANALYSIS		
Molybdenum, W%	11.41	10.76
Nickel, W%	2.21	2.86
PHYSICAL PROPERTIES		
Bulk Density, Compacted, lb/ft^3	36.7	
Particle Density, gm/cc	0.94	0.99
Surface Area (Calculated), m^2/gm	267	263
m^2/cc particle	251	260
Pore Volume, cc/gm	0.697	0.881
cc/cc particle	0.656	.674
Length, average (mm)		3.8
Diameter, average (mm)		1.0
Average Crush Strength, lb/mm		1.78
PORE SIZE DISTRIBUTION, cc/gm		
Diameter > 30 A	0.70	0.68
Diameter > 100 A	0.40	0.37
Diameter > 250 A	0.15	0.17
Diameter > 500 A	0.14	0.16
Diameter > 1500 A	0.11	0.14
Diameter > 4000 A	0.03	0.04
PORE DIAMETER (A)		
4*[Pore Volume/Calc Surf Area]	104	104

FIGURE 2.2.1



RUN 227-78 (CMSL-2)
RELATIVE PROCESS SEVERITY

FIGURE 2.2. 2

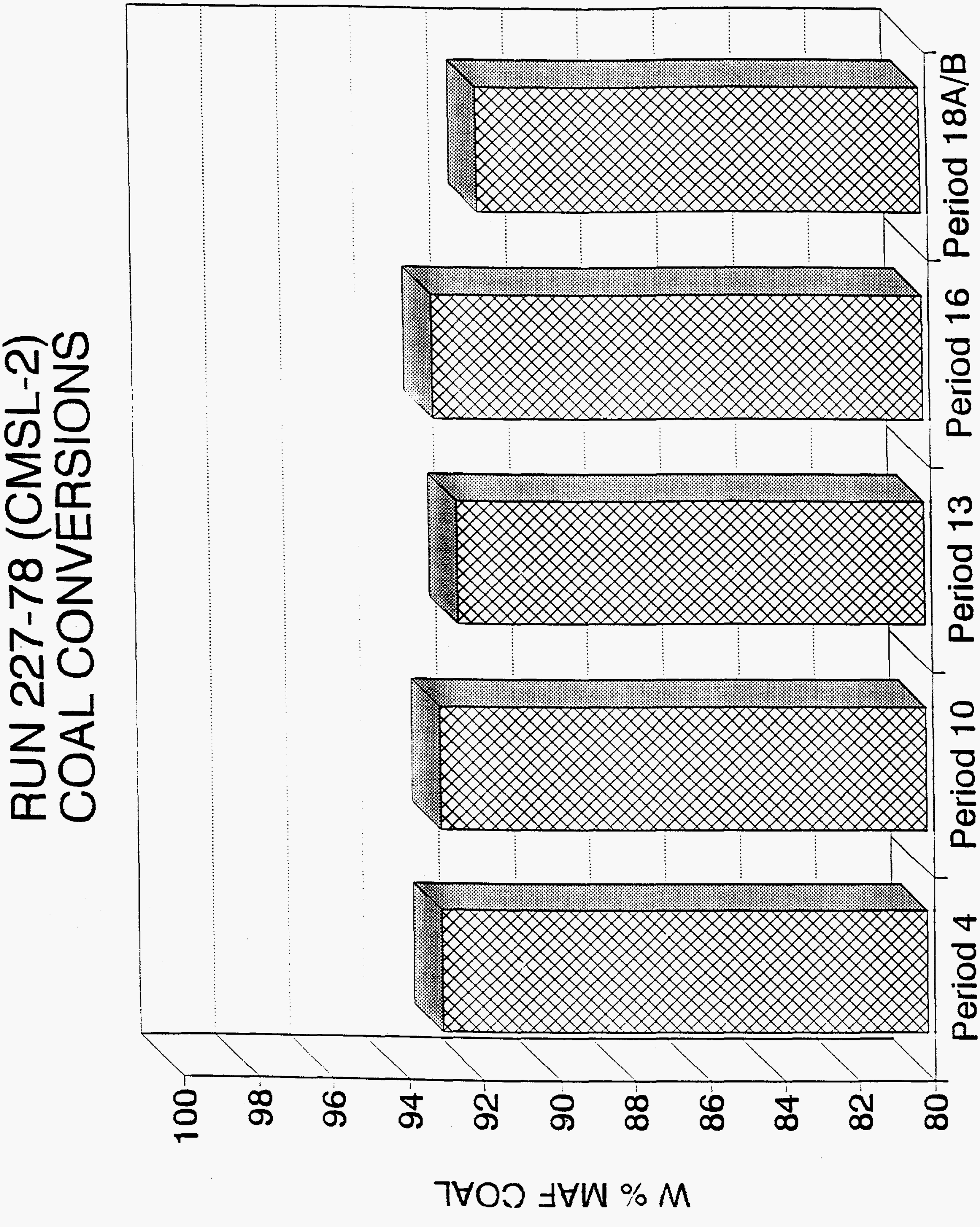
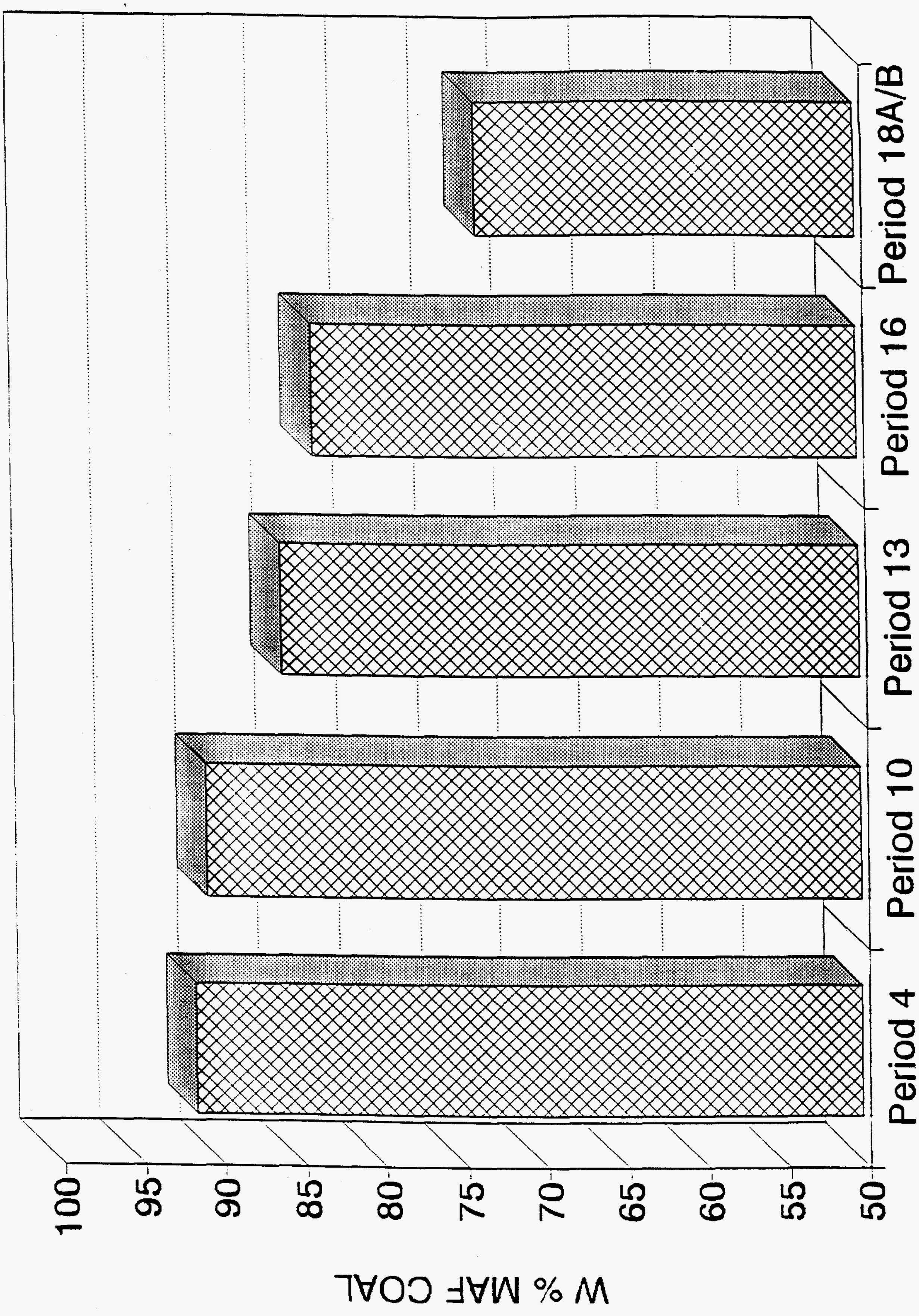

RUN 227-78 (CMSL-2)
COAL CONVERSIONS
W % MAF COAL
100
98
96
94
92
90
88
86
84
82
80
Period 4
Period 10
Period 13
Period 16
Period 18A/B

FIGURE 2.2. 3



RUN 227-78 (CMSL-2)
524 deg C+ RESID CONVERSION

FIGURE 2.2.4

RUN 227-78 (CMSL-2)
HYDROGEN CONSUMPTION

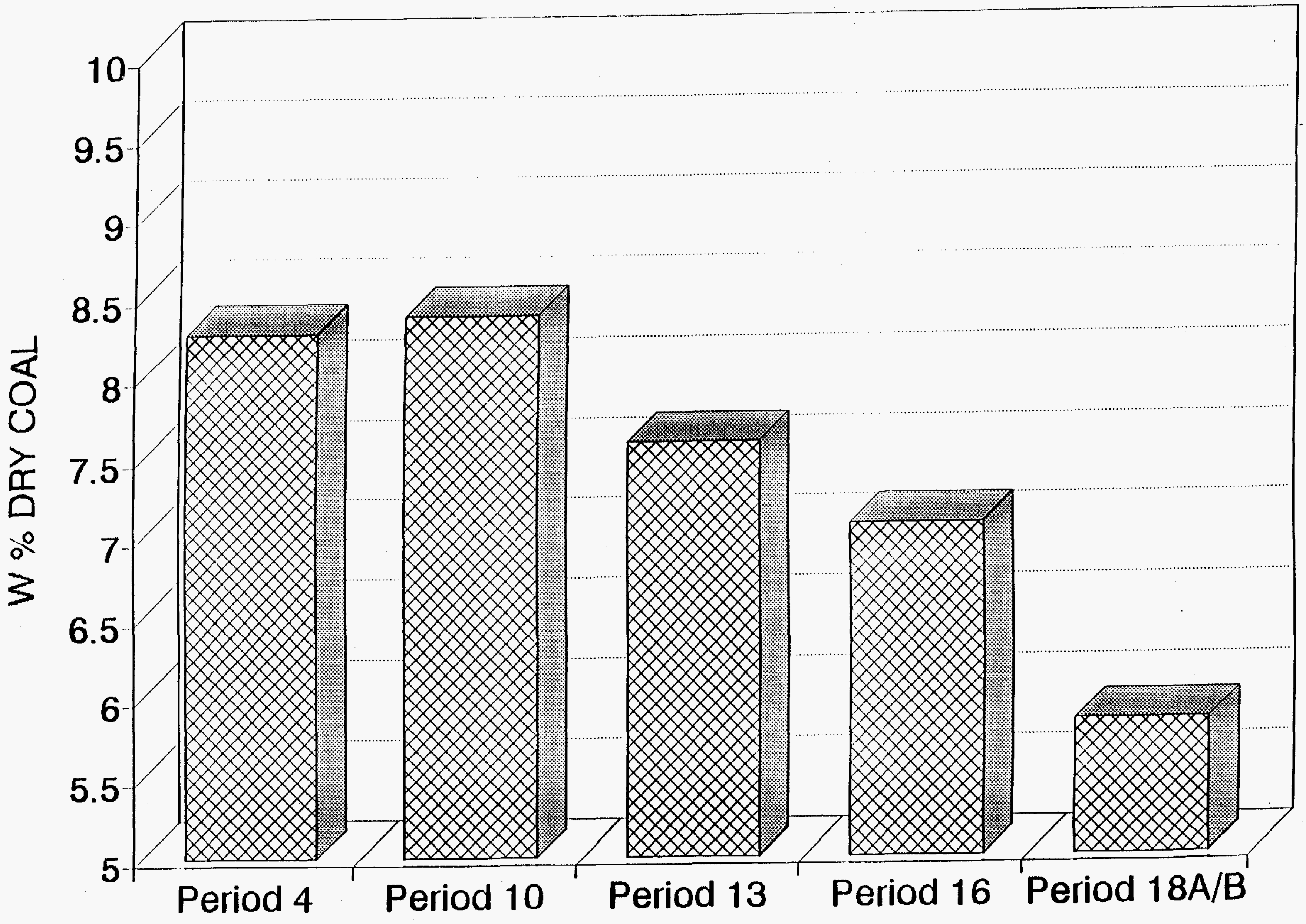


FIGURE 2.2.5


RUN 227-78 (CMSL-2)
HYDRODESULFURIZATION
HDS, W%
100
95
90
85
80
75
70
65
60
55
50
Period 4
Period 10
Period 13
Period 16
Period 18A/B

RUN 227-78 (CMSL-2)
HYDRODENITROGENATION

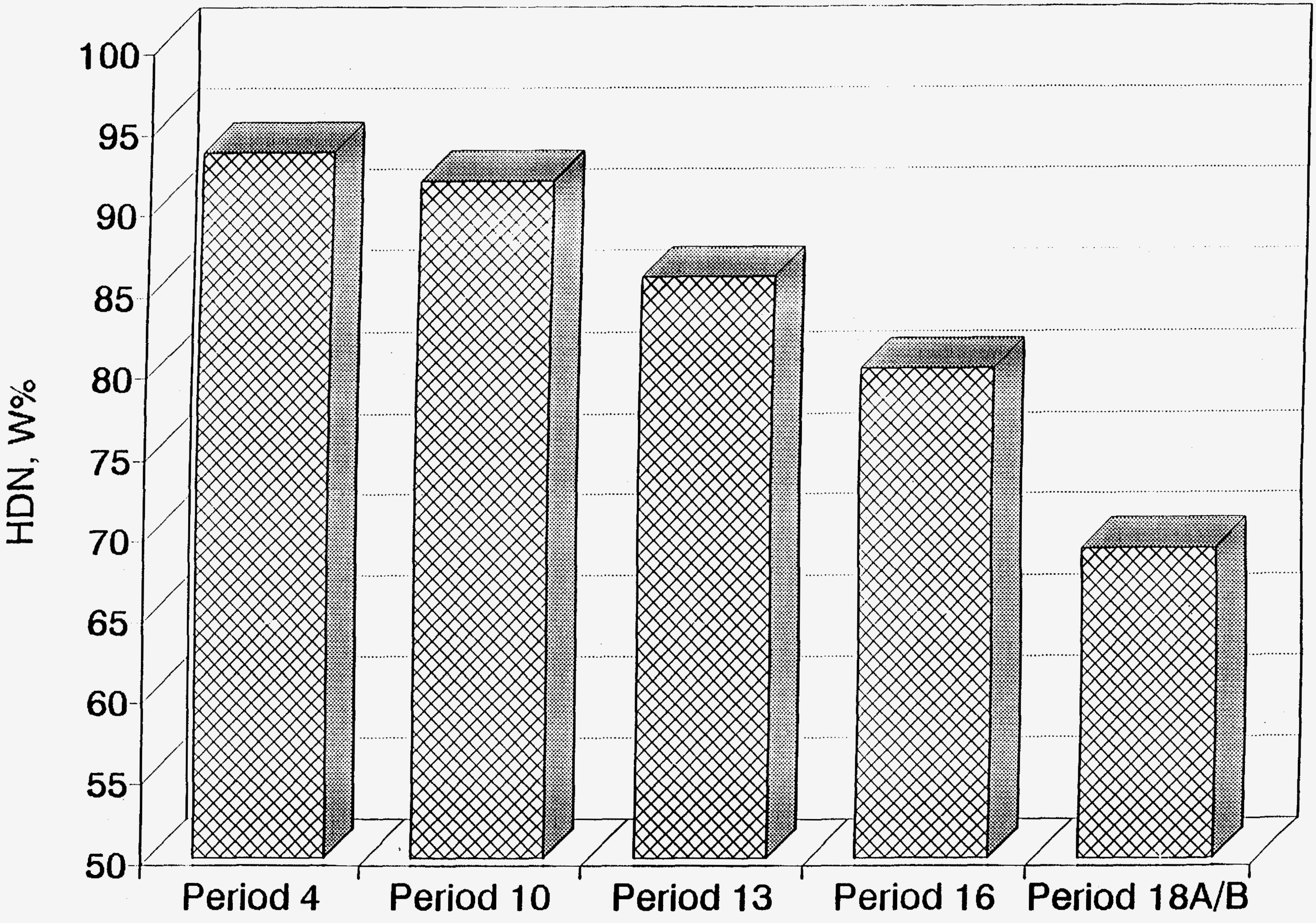
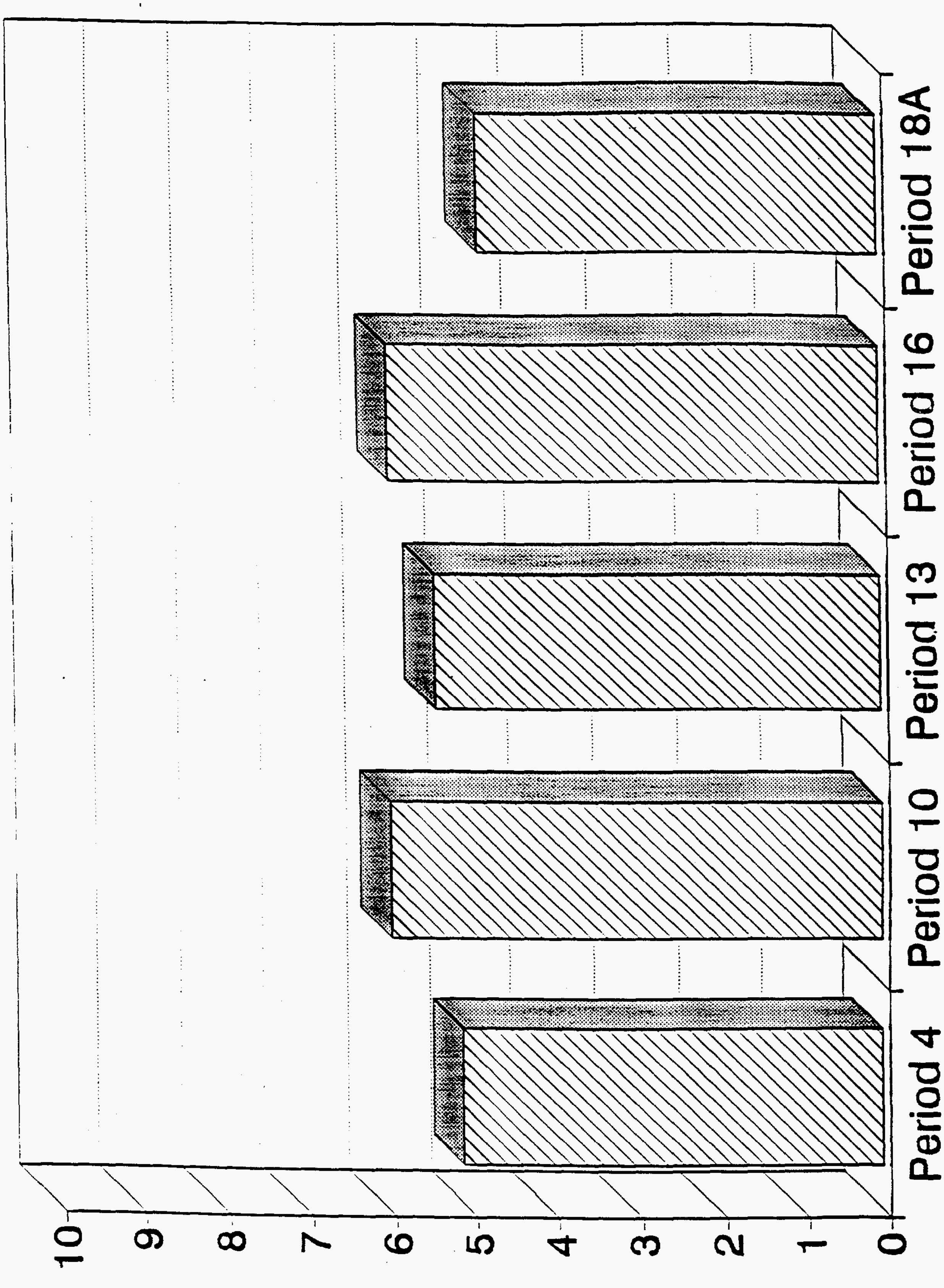


FIGURE 2.2.6

RUN 227-78 (CMSL-2)
C1-C3 GAS YIELD



RUN 227-78 (CMSL-2)
C4-199 deg C NAPHTHA YIELDS

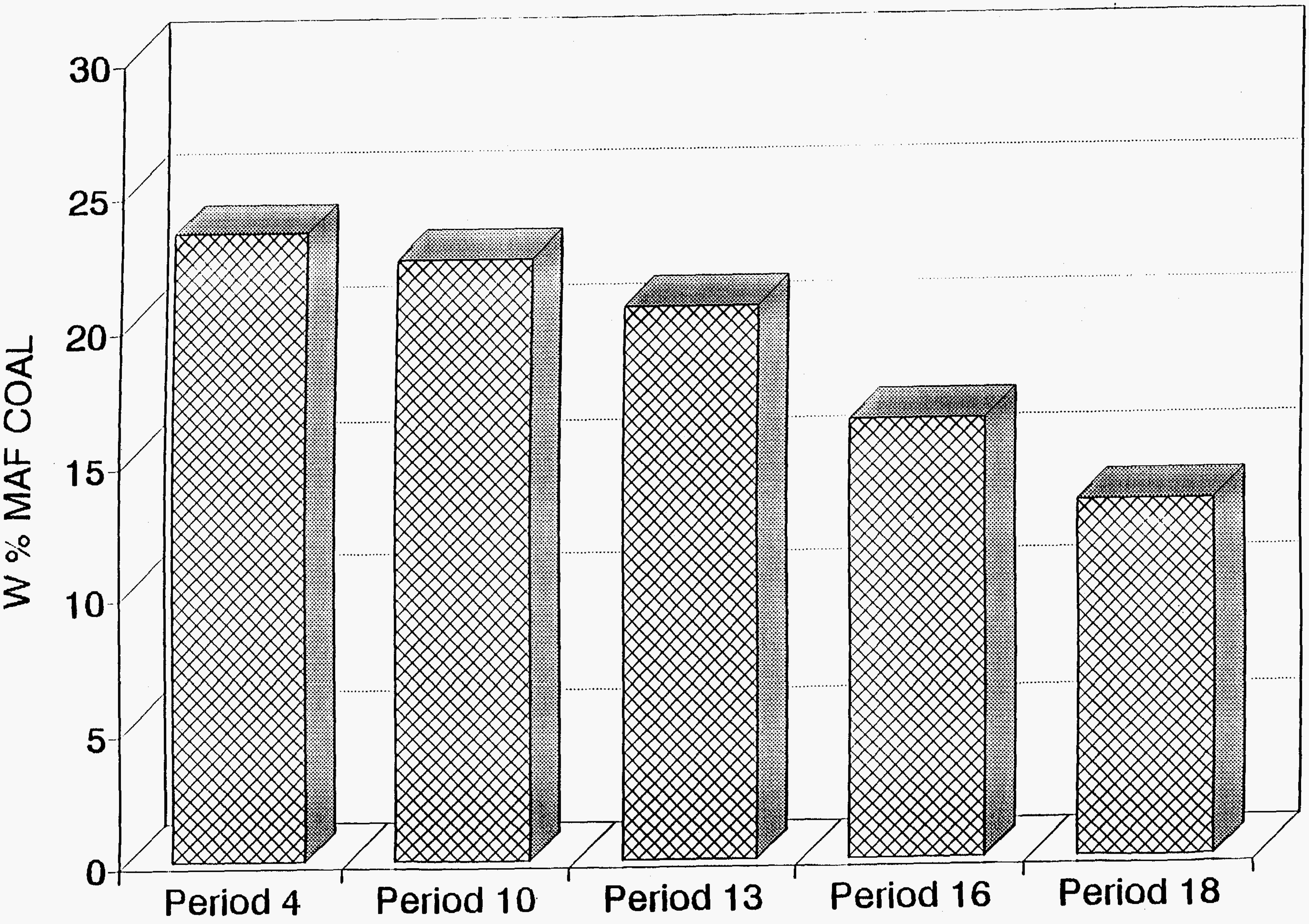


FIGURE 2.2.8

RUN 227-78 (CMSL-2)
199-343 deg C MIDDLE DISTILLATE YIELDS

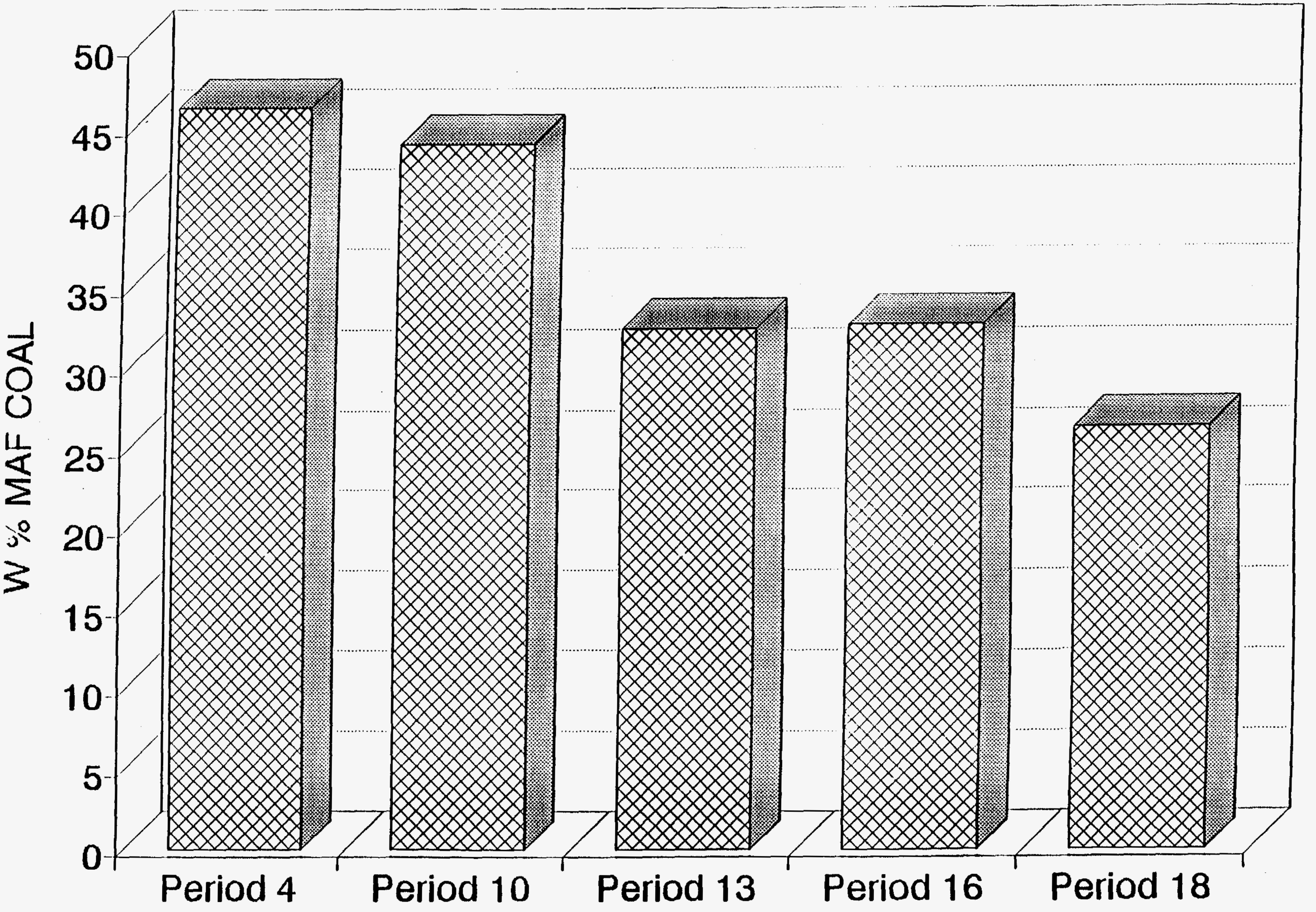


FIGURE 2.2.9

RUN 227-78 (CMSL-2)
343-524 deg C HEAVY DISTILLATE YIELDS

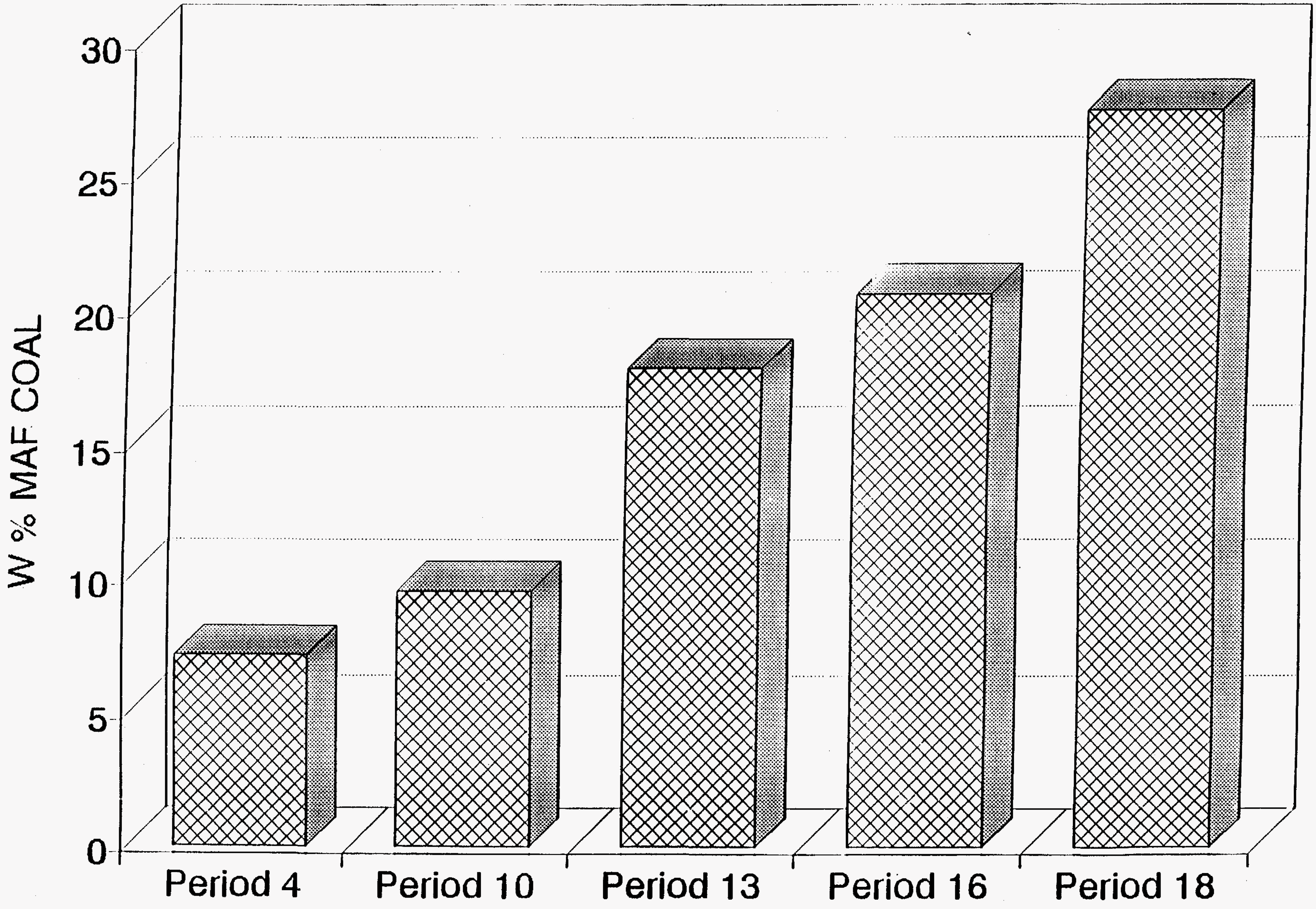
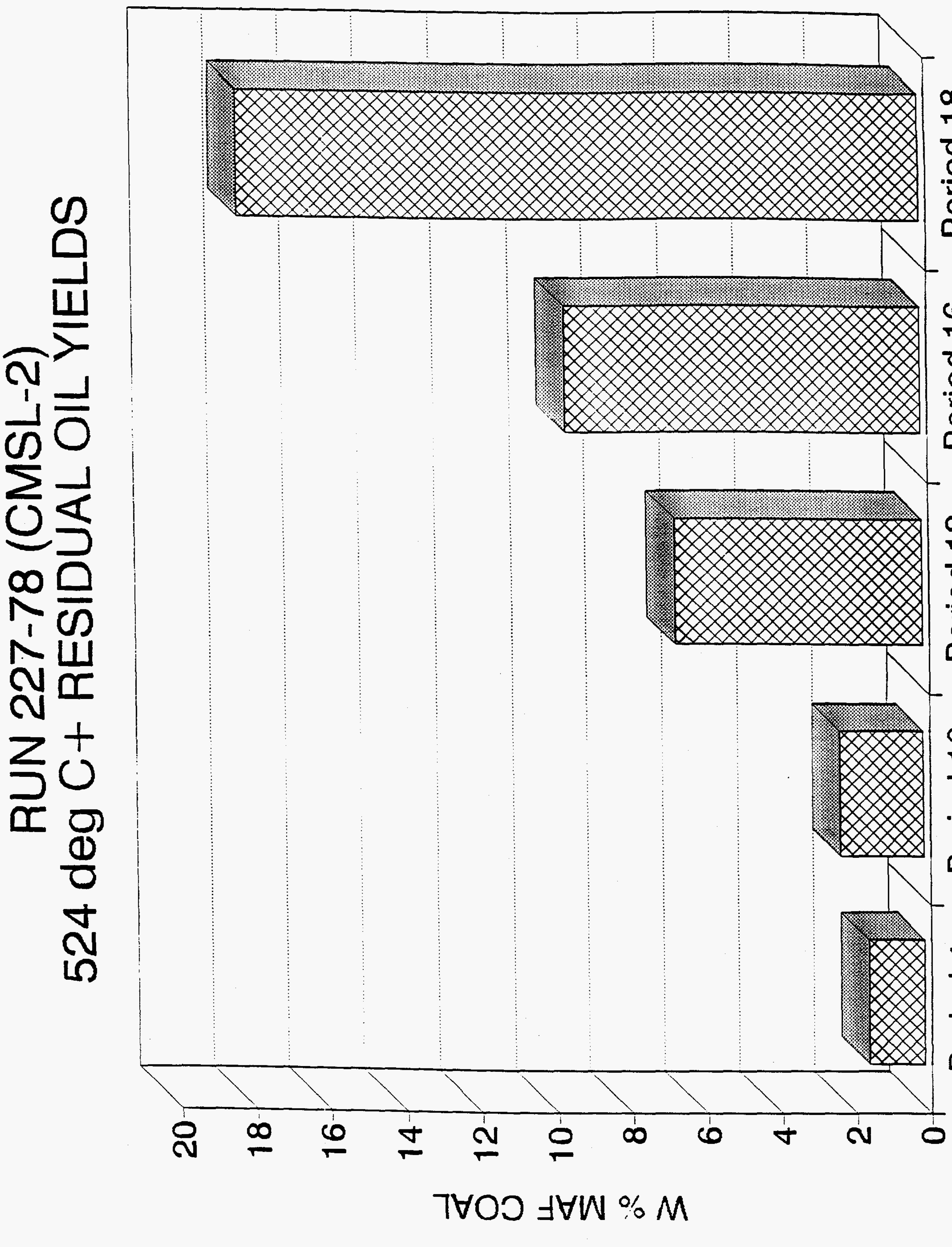


FIGURE 2.2.10

FIGURE 2.2.11


RUN 227-78 (CMSL-2)
524 deg C+ RESIDUAL OIL YIELDS
W % MAF COAL
0
2
4
6
8
10
12
14
16
18
20
Period 4
Period 10
Period 13
Period 16
Period 18

RUN 227-78 (CMSL-2)
C4-524 deg C DISTILLATE YIELD

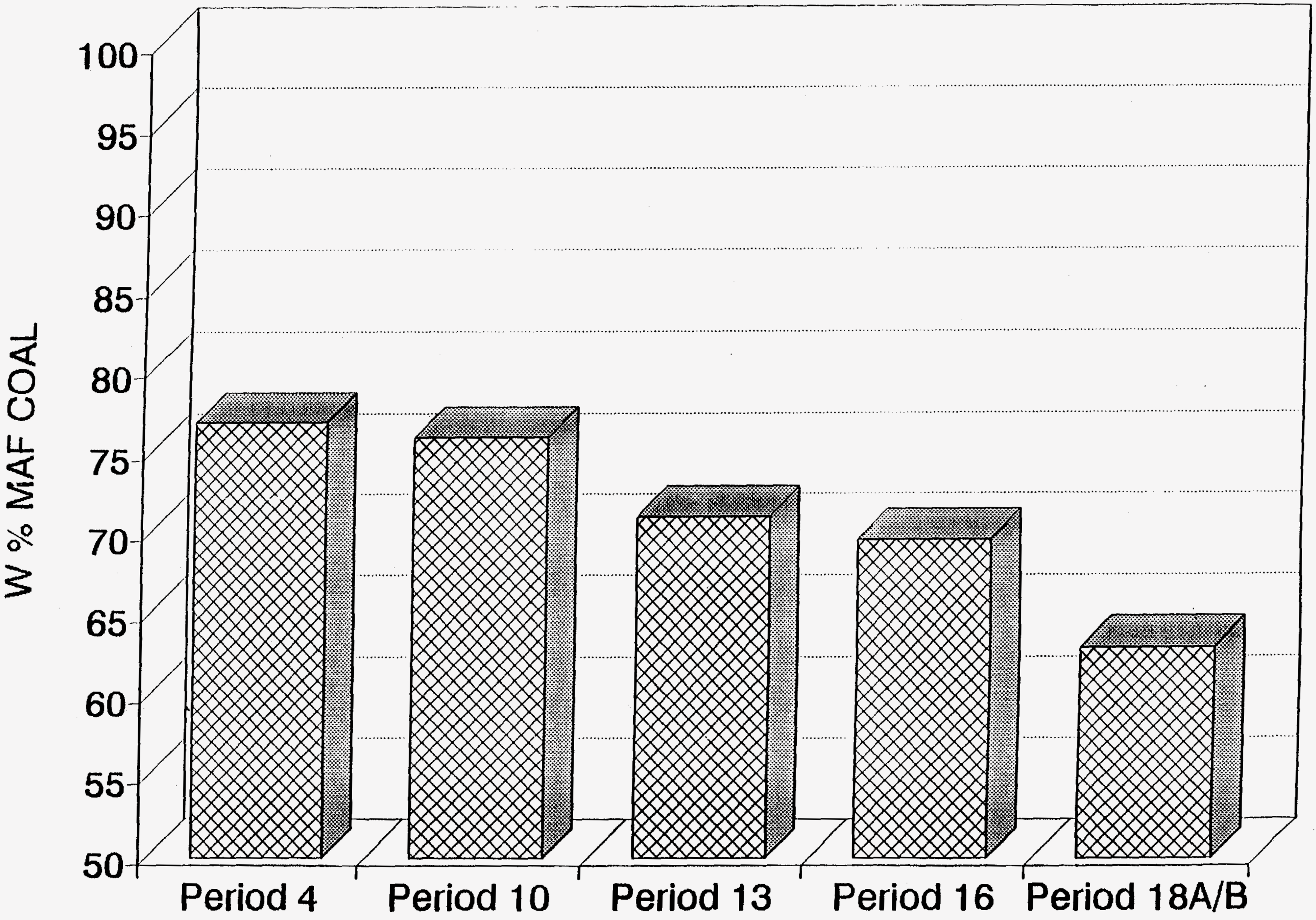
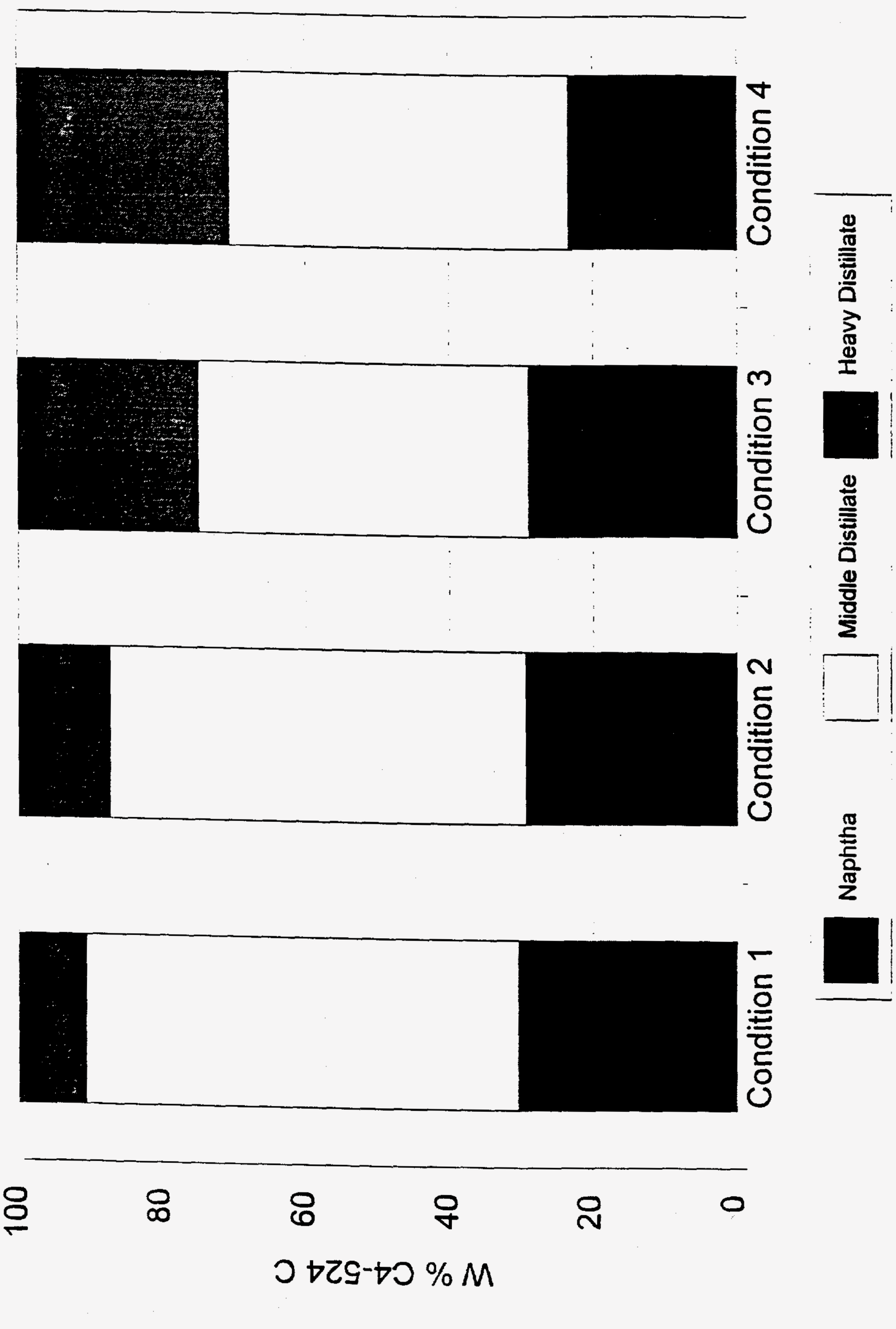


FIGURE 2.2.12

RUN 227-78 (CMSL-2)
DISTILLATE SELECTIVITY



RUN 227-78 (CMSL-2)
PFL Properties Vs. Catalyst Age

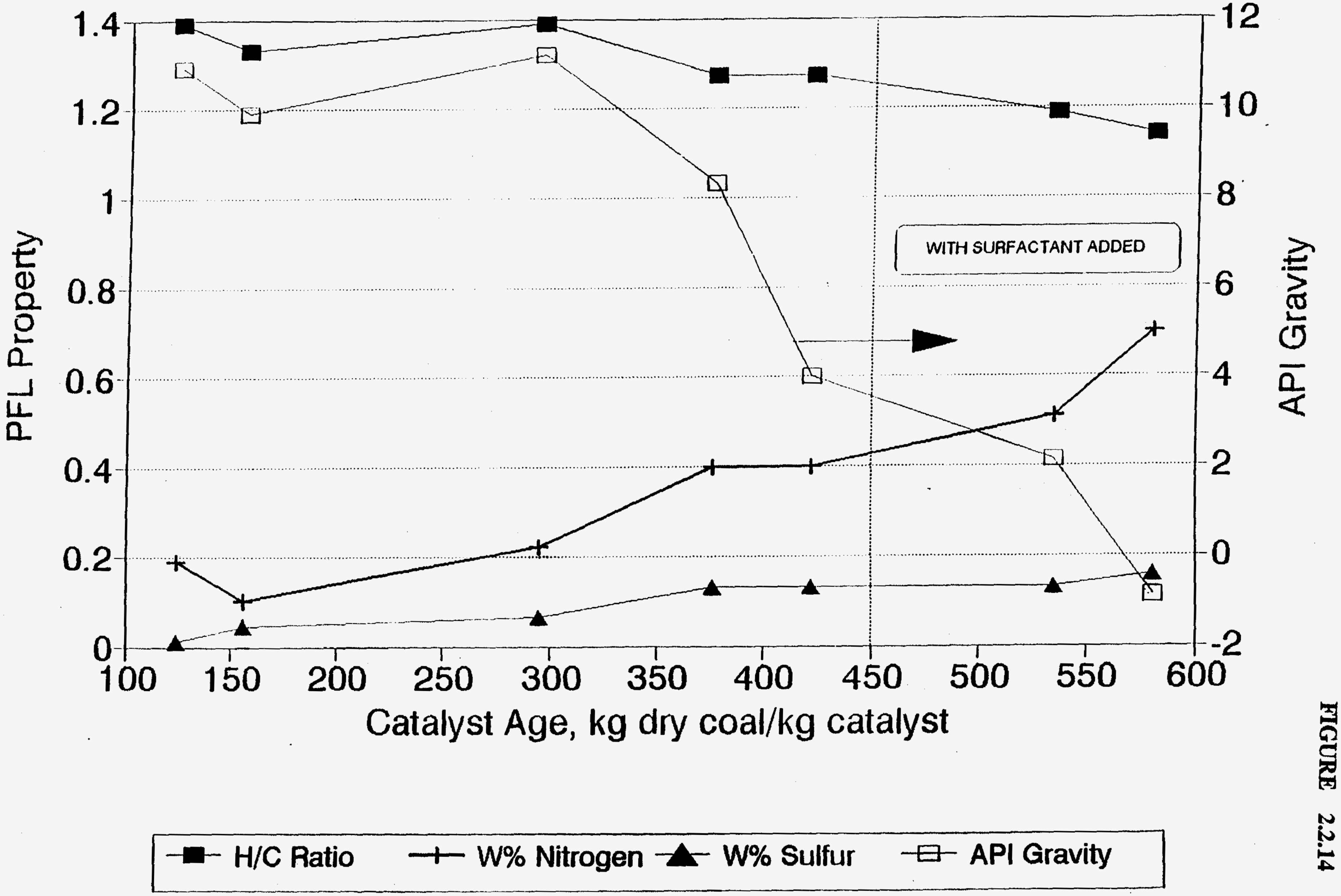


FIGURE 2.2.14

COMPARISON OF DISTILLATE SELECTIVITY FOR CMSL-2 (227-78) AND I-18 (227-37)

CMSL-2: Solvent/Coal=0.9 I-18 : Solvent/Coal=1.6

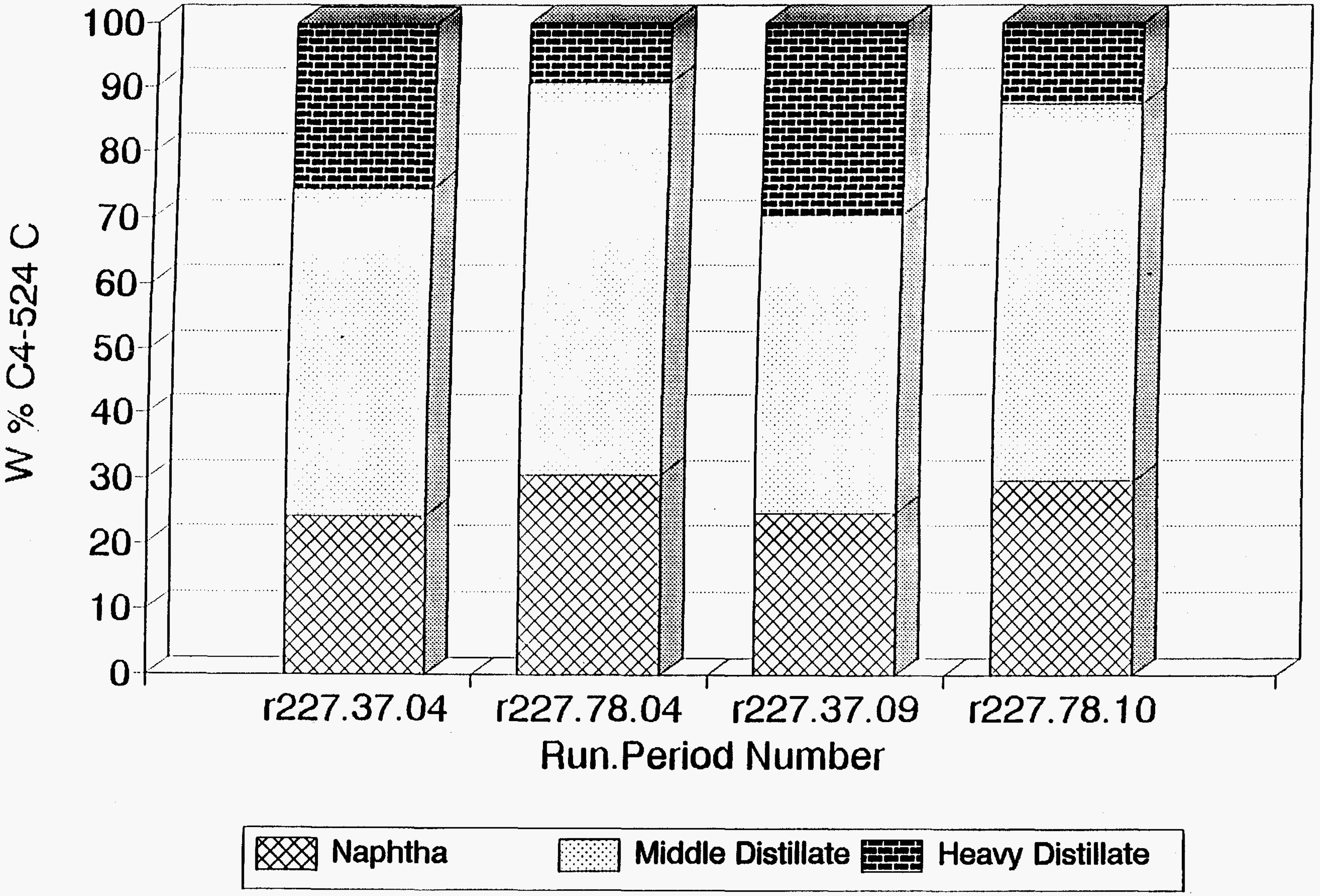


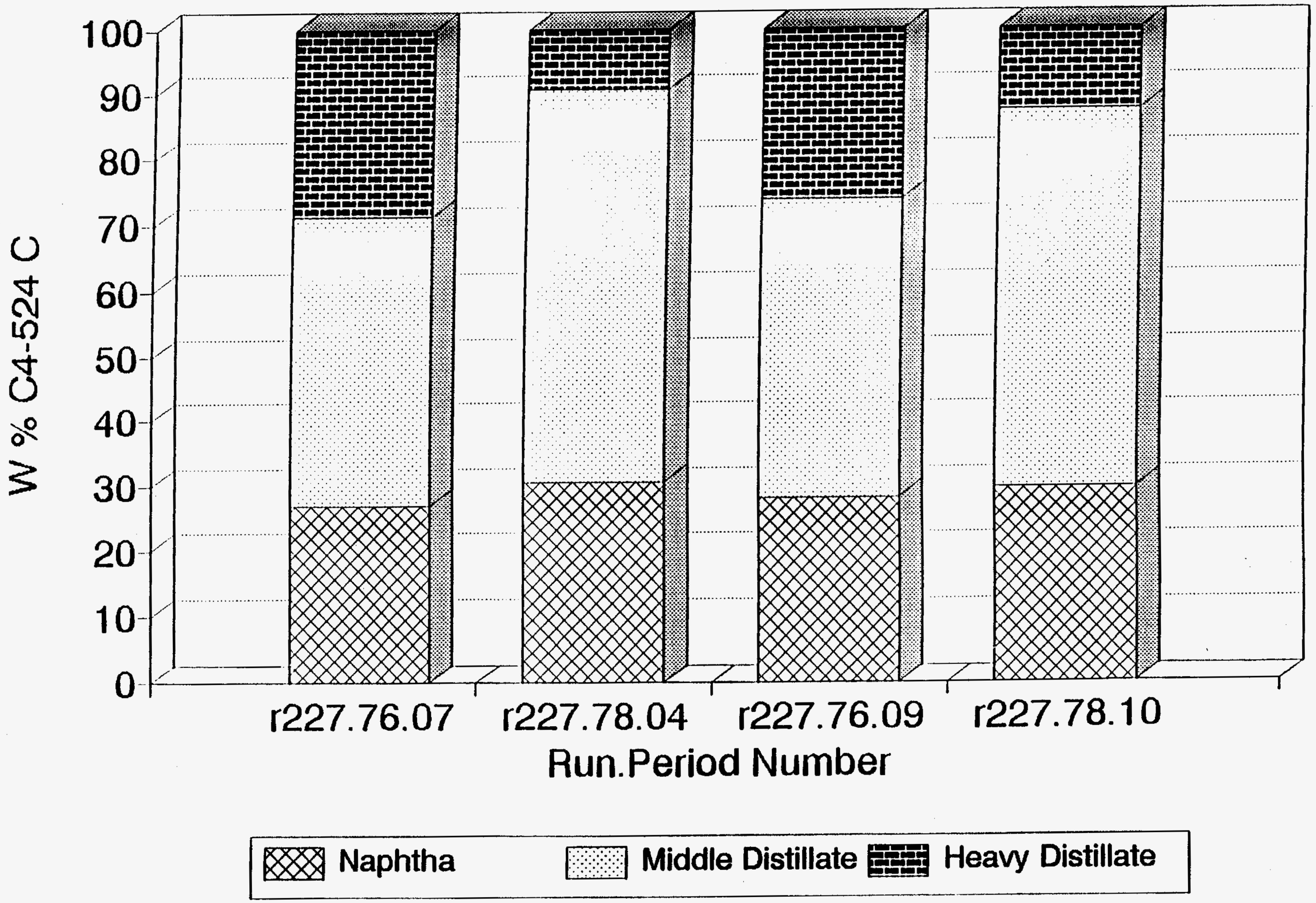
FIGURE 2.2.15

FIGURE 2.2.16

COMPARISON OF DISTILLATE SELECTIVITY FOR CMSL-2 (227-78) AND CC-16 (227-76)

CMSL-2: Solvent/Coal=0.9

CC-16: Solvent/Coal=1.5



COMPARISON OF THREE BENCH RUNS: RESID CONTENTS OF RECYCLE OILS

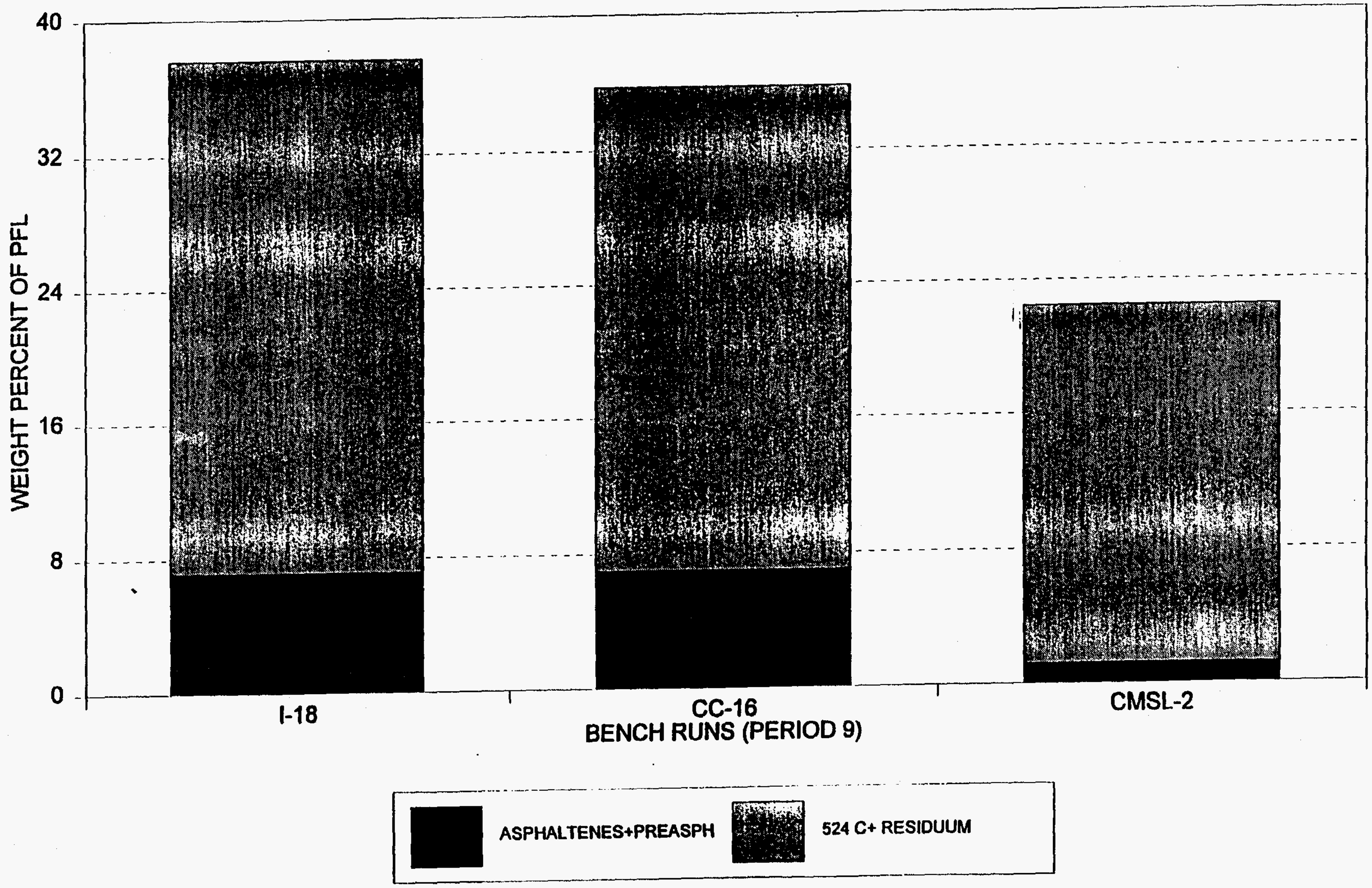


FIGURE 2.2.17

Comparison of C4-524 deg C Distillate Yields for Two Bench Runs

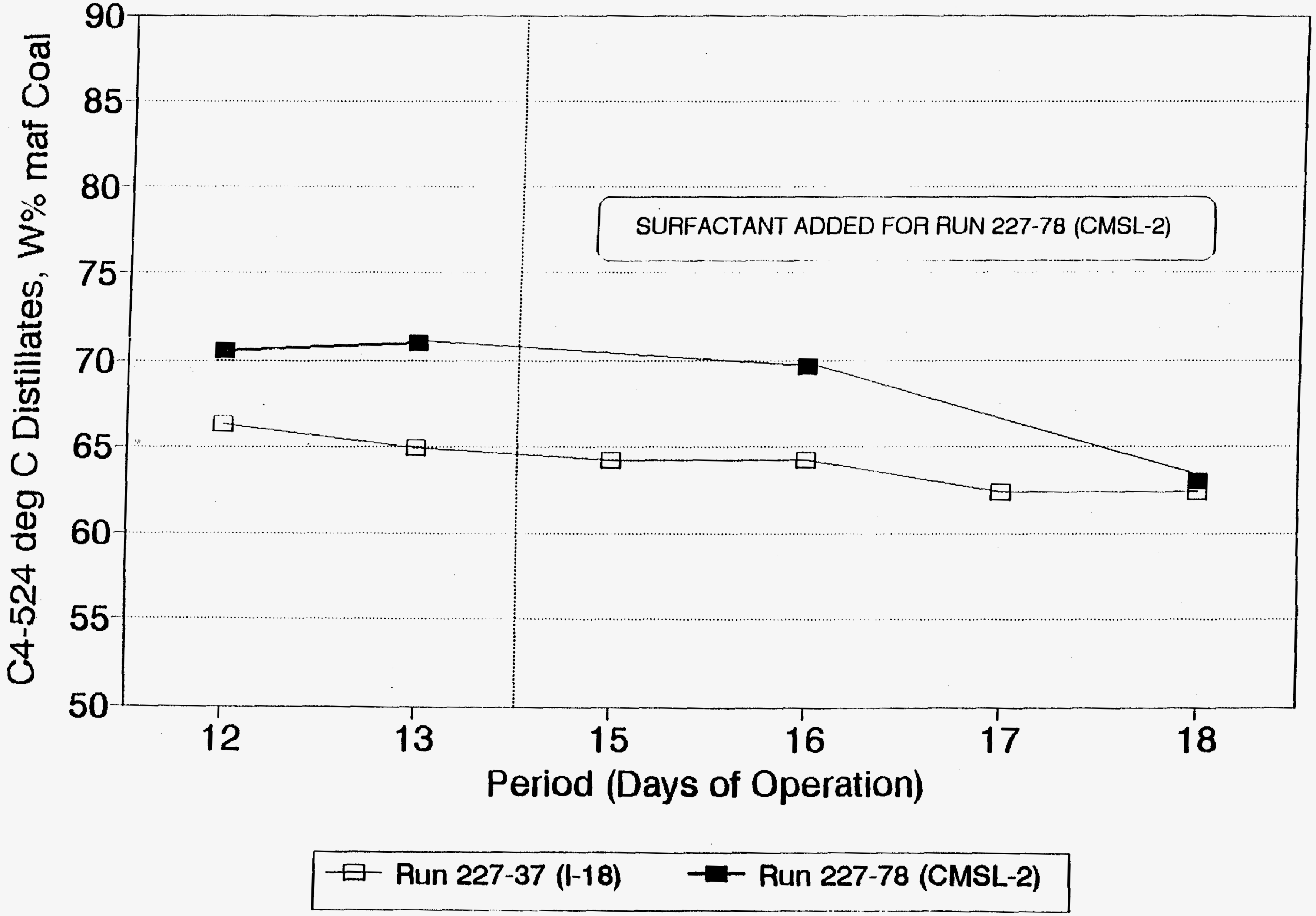
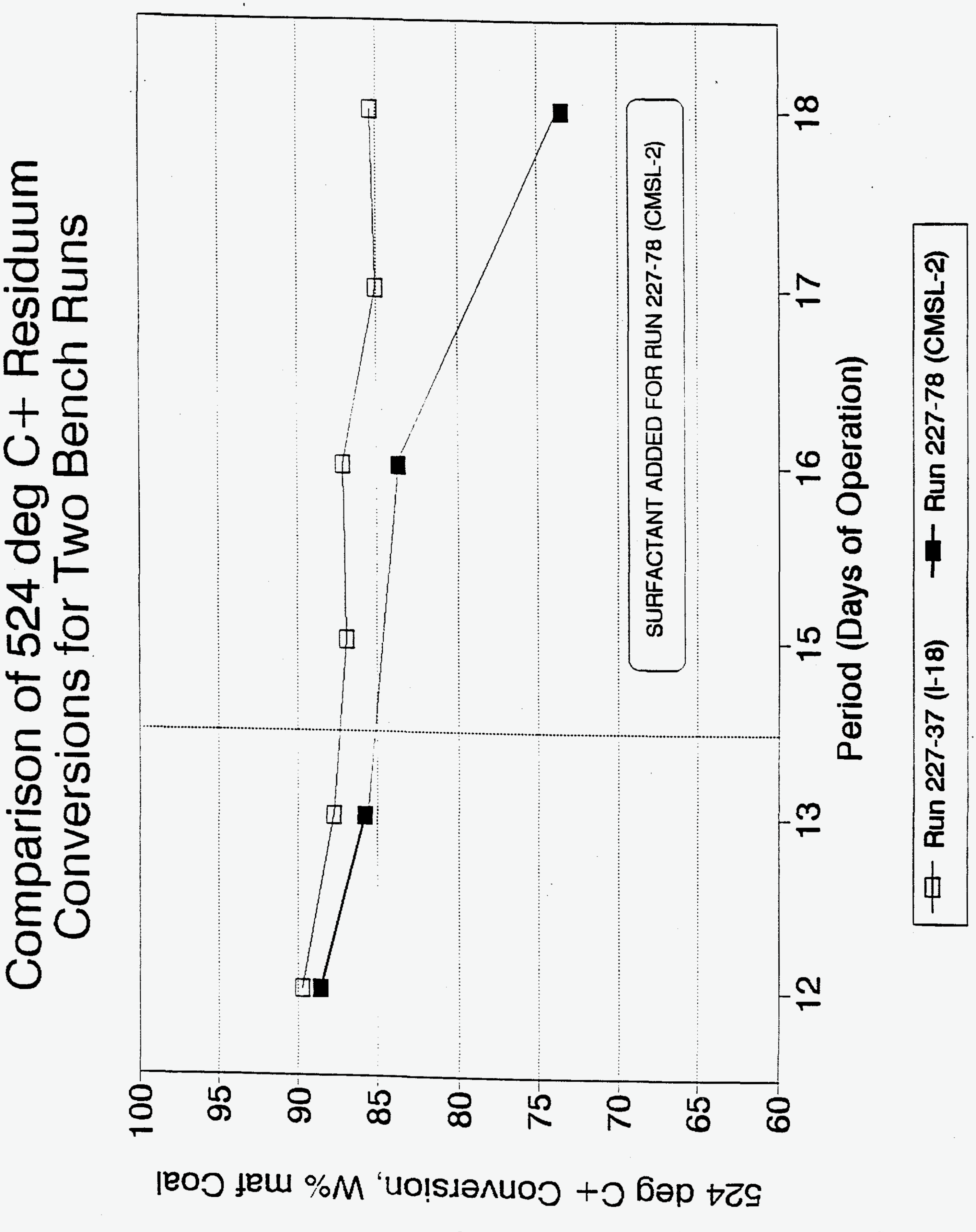
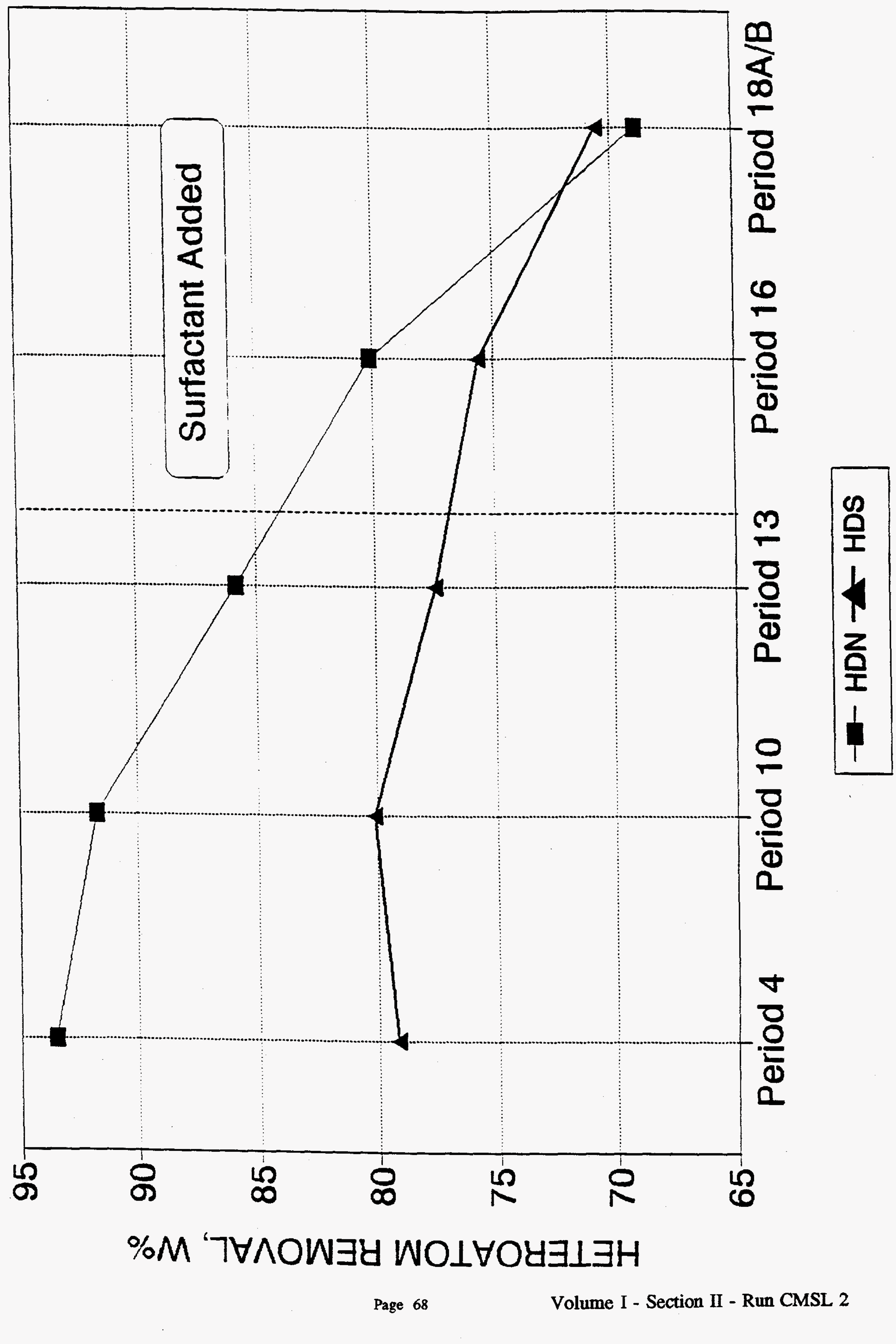


FIGURE 2.2.18

FIGURE 2.2.19


Comparison of 524 deg C+ Residuum Conversions for Two Bench Runs

RUN 227-78 (CMSL-2) HETEROATOM REMOVAL



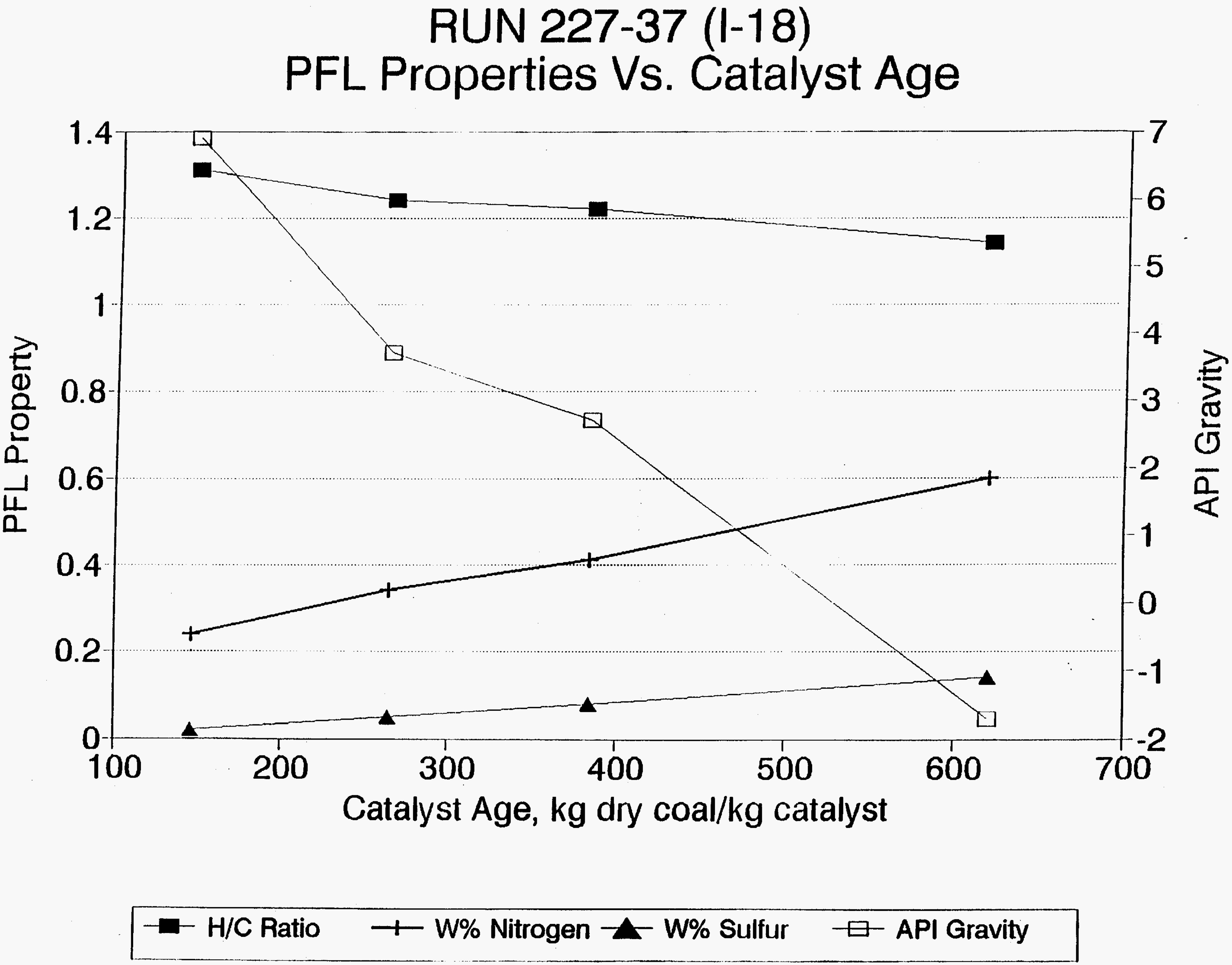
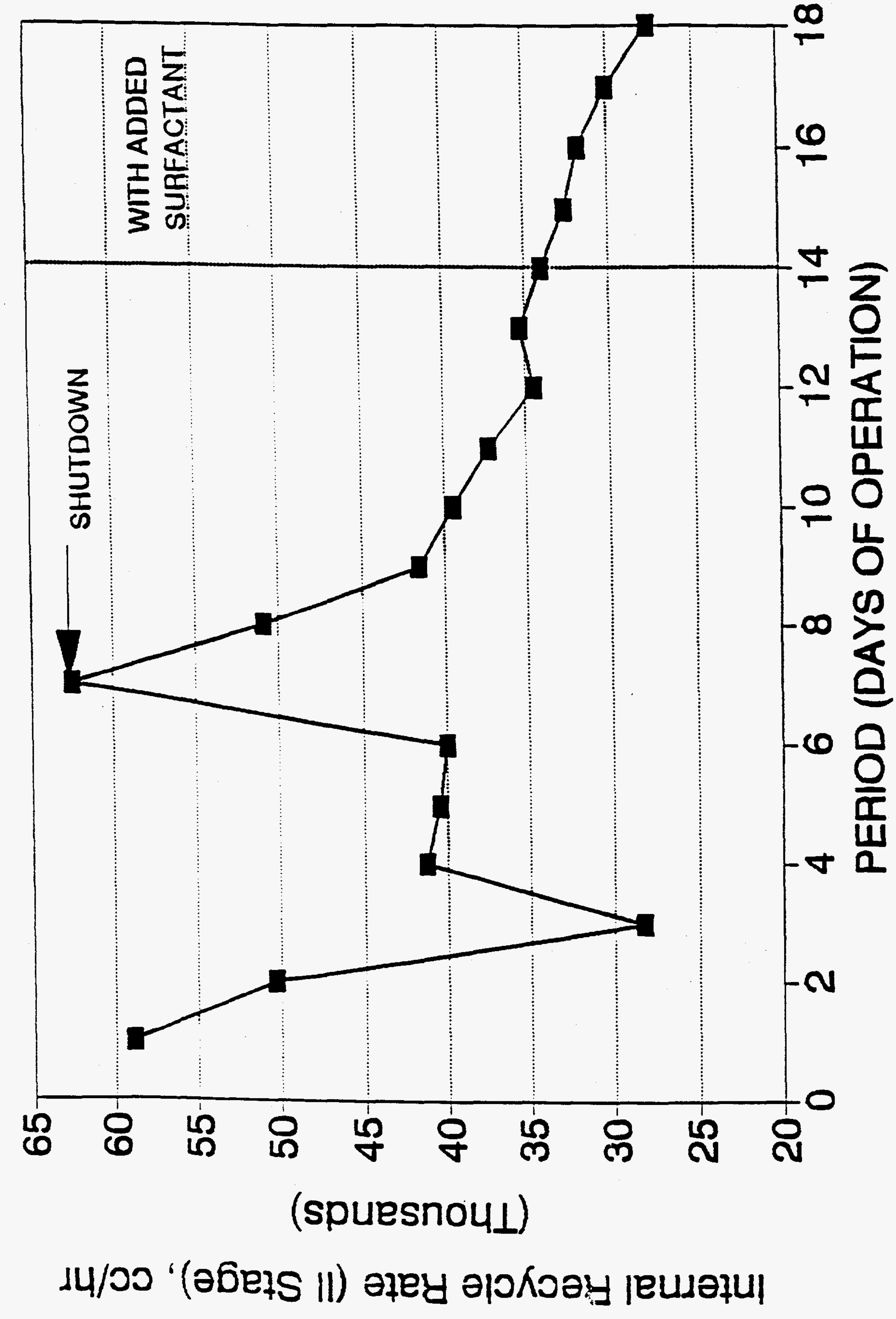
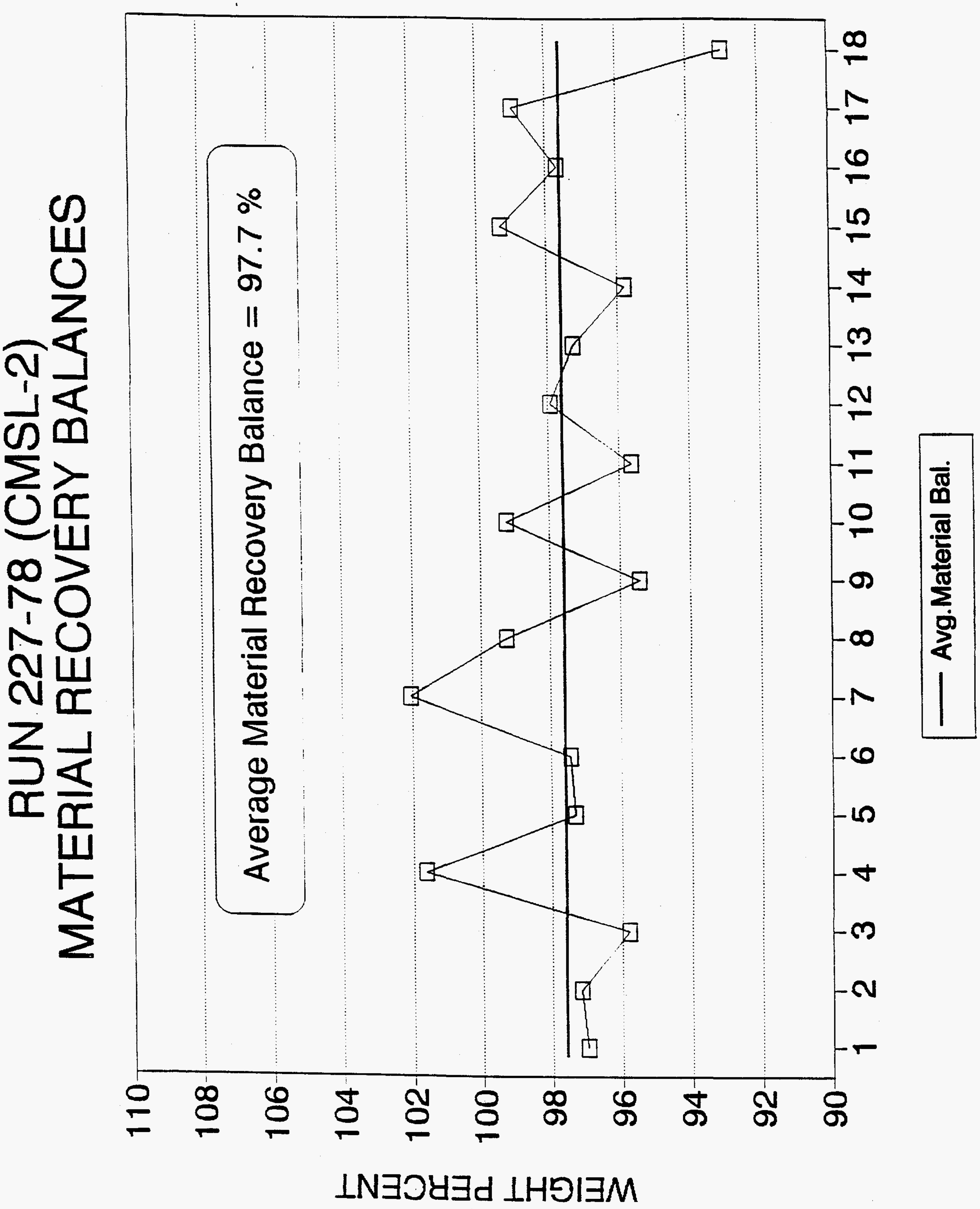

RUN 227-37 (I-18)
PFL Properties Vs. Catalyst Age
PFL Property
API Gravity
Catalyst Age, kg dry coal/kg catalyst
1.4
1.2
1
0.8
0.6
0.4
0.2
0
7
6
5
4
3
2
1
0
-1
-2
100
200
300
400
500
600
700
H/C Ratio
W% Nitrogen
W% Sulfur
API Gravity

FIGURE 2.2.21

RUN 227-78 (CMSL-2)
EBULLATING BED RECYCLE RATES




RUN 227-78 (CMSL-2)
MATERIAL RECOVERY BALANCES
Average Material Recovery Balance = 97.7 %
WEIGHT PERCENT
110
108
106
104
102
100
98
96
94
92
90
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Avg.Material Bal.

RUN 227-78 (CMSL-2)
REACTOR TEMPERATURES

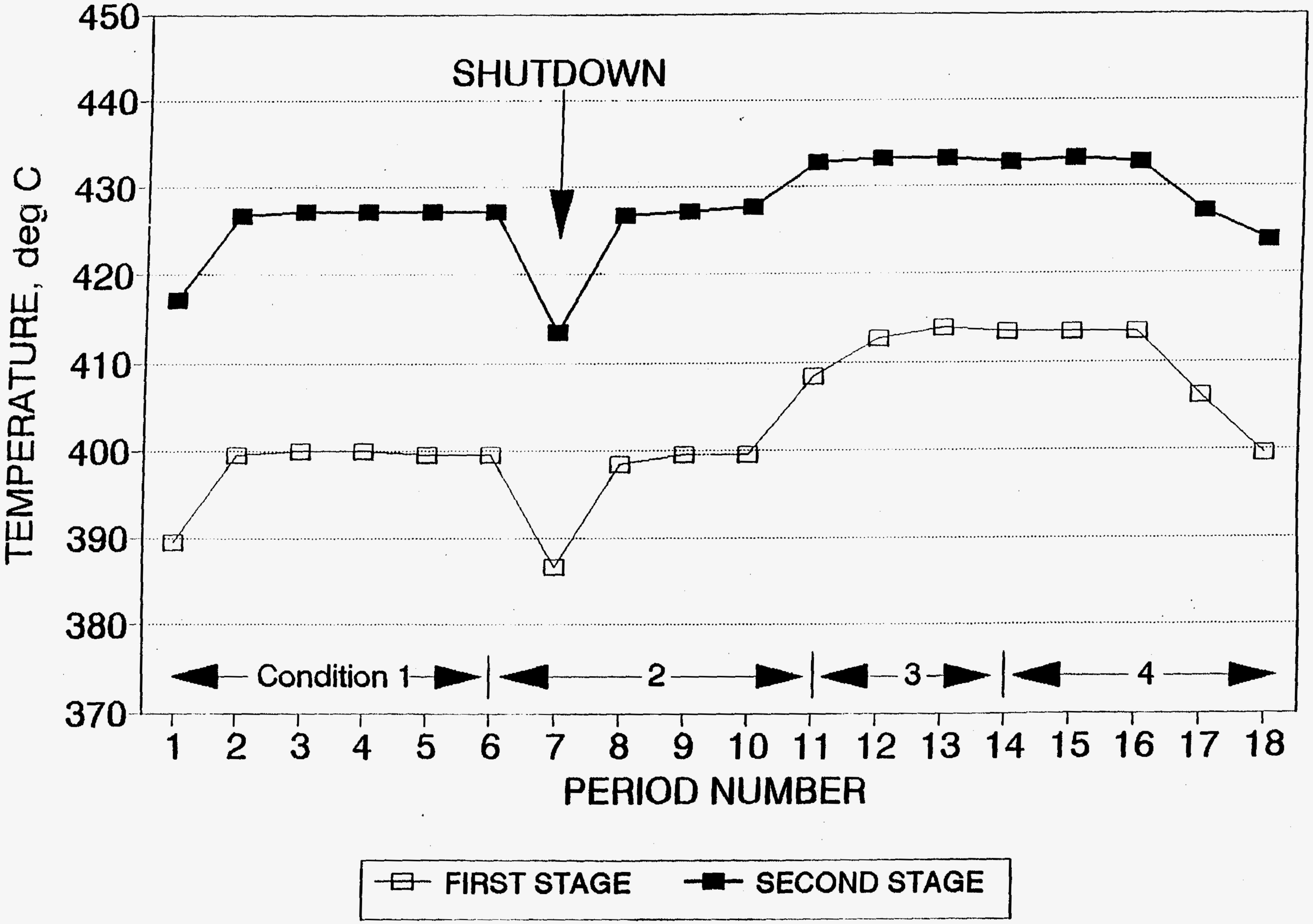
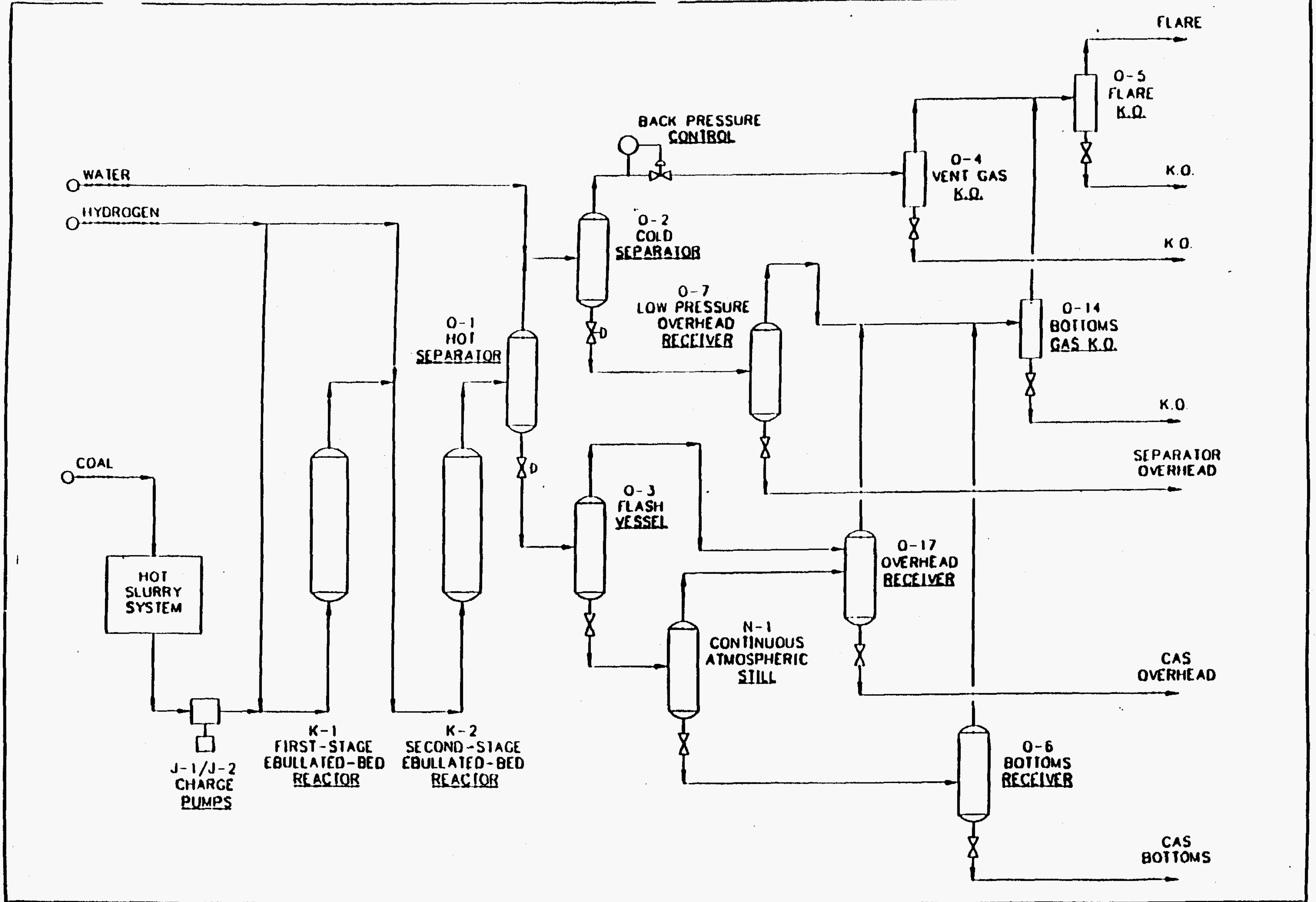


FIGURE 2.2.24

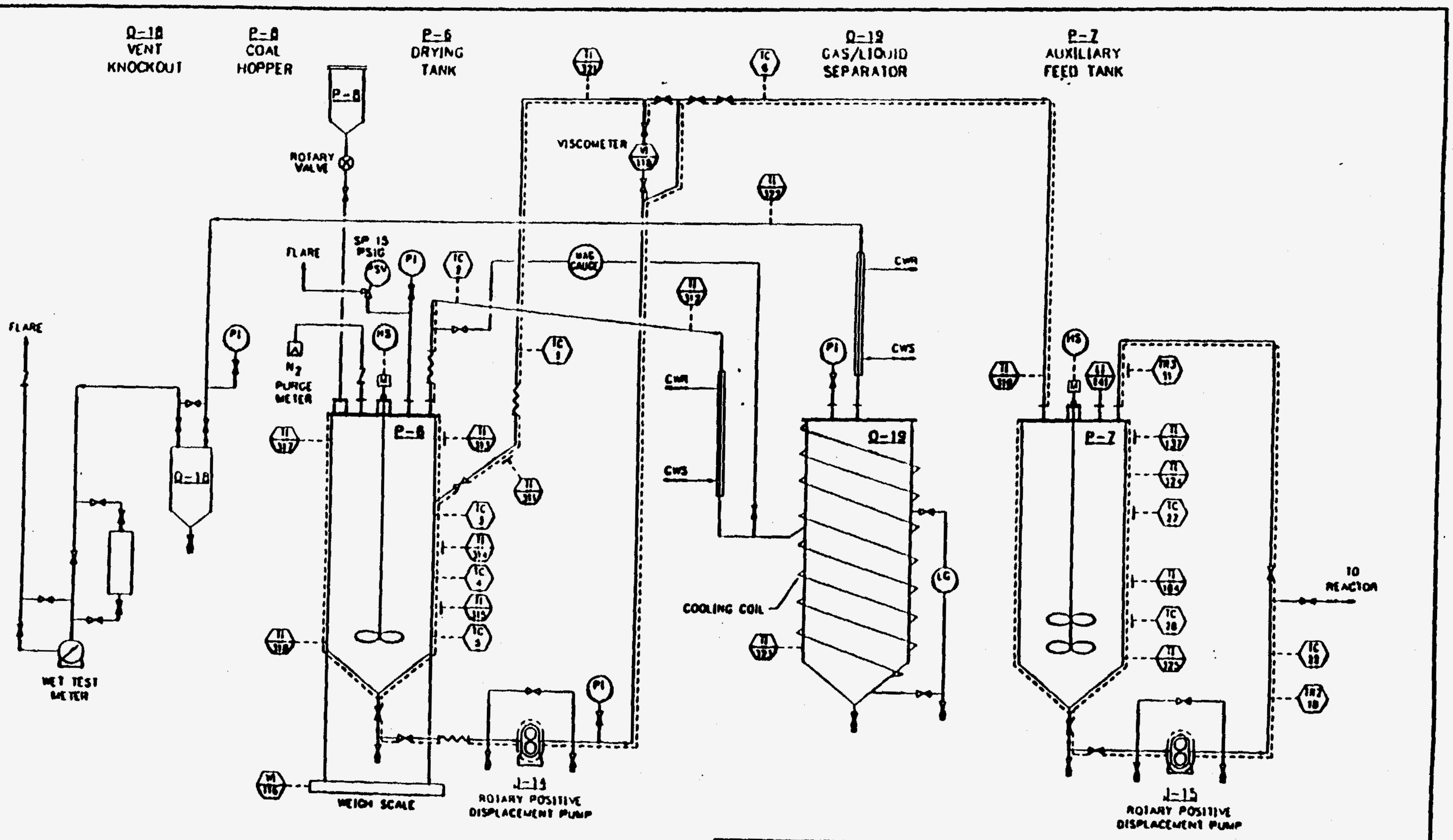
FIGURE 2.2.25



TITLE:	HYDROCARBON RESEARCH, INC.		DRAWN	DATE
227 UNIT WITH TWO STAGES, TWO GAS PRODUCTS, AND HOT SLURRY SYSTEM	JOB NO. 846	HRI DRAWING NUMBER 227SF014	DJA CHKD	03/29/93 ISSUE 1

FORM RND-AL1 (11/92)

FIGURE 2.2.26



ISS	DRAWN	CHKD	APPR	ISS	DRAWN	CHKD	APPR	ISS	DRAWN	CHKD	APPR	ISS	DRAWN	CHKD	APPR
4				3				2				1			

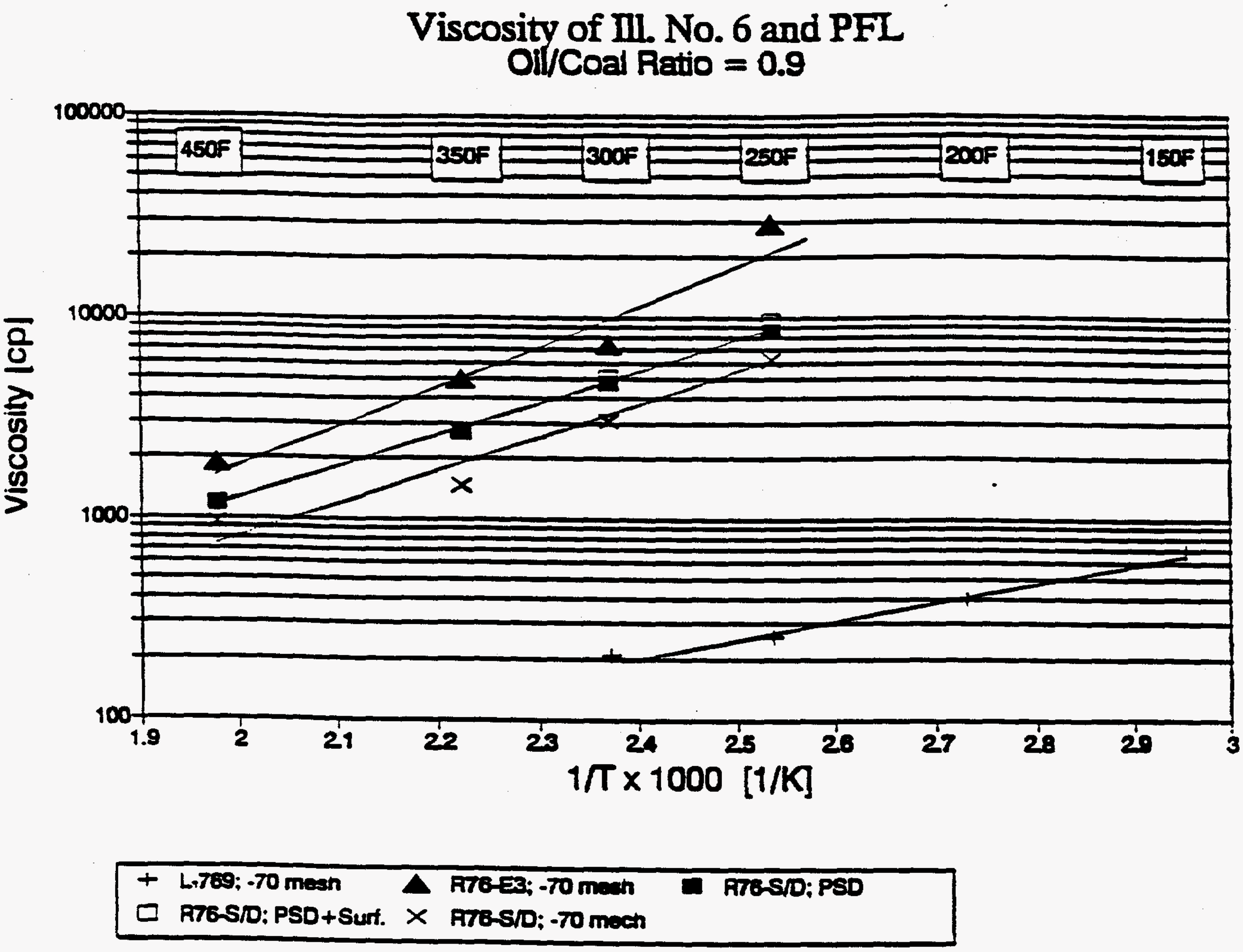
CLIENT & PLANT:
HYDROCARBON RESEARCH INC.
LAWRENCEVILLE, N.J.

AREA & UNIT:
PROCESS DEVELOPEMENT UNIT
227

TITLE:
ENGINEERING FLOW DIAGRAM
HOT SLURRY SYSTEM

HRI, INC.

JOB NO 846
DRAWING NUMBER 227PF019
ISSUE 1


Viscosity of Ill. No. 6 and PFL
Oil/Coal Ratio = 0.9
100000
10000
1000
100
450F
350F
300F
250F
200F
150F
Viscosity [cp]
1.9
2
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3
1/T x 1000 [1/K]
+ L-769; -70 mesh
▲ R76-E3; -70 mesh
■ R76-S/D; PSD
☐ R76-S/D; PSD+Surf.
× R76-S/D; -70 mech

VOLUME I

SECTION II

RUN CMSL-3

EVALUATION OF SYNGAS AS REDUCING GAS FOR LIQUEFACTION OF A SUBBITUMINOUS COAL

VOLUME I

TABLE OF CONTENTS

SECTION II - RUN CMSL-3

Run CMSL-3 (227-79) Evaluation Of Syngas As Reducing Gas For Liquefaction Of A Subbituminous Coal

VOLUME I

TABLE OF CONTENTS

SECTION II - RUN CMSL-3

Run CMSL-3 (227-79) Evaluation Of Syngas As Reducing Gas For Liquefaction Of A Subbituminous Coal

VOLUME I

SECTION II - RUN CMSL-3

LIST OF TABLES

VOLUME I

SECTION II - RUN CMSL-3

LIST OF FIGURES

SECTION II - RUN CMSL-3

RUN CMSL-3 (227-79) EVALUATION OF SYNGAS AS REDUCING GAS FOR LIQUEFACTION OF A SUBBITUMINOUS COAL

1.0 SUMMARY

The Bench Run 227-79 (CMSL-3), carried out to evaluate the use of synthesis gas (CO/H_2) as reducing gas in the first stage for liquefaction of a subbituminous Wyoming Black Thunder Mine coal, under DOE Contract (No. DE-AC22-93PC92147), was completed on July 21, 1993, after 15 days of operation. The overall run consisted of four different operating Conditions:

Condition 1 employed pure hydrogen as a reducing gas in both the reactor stages.

Conditions 2 through 4 employed a mixture of carbon monoxide and hydrogen (CO/H_2 at 75%/25% by volume) as a reducing gas in the first stage reactor (with about 40-W%-of-dry-coal water injected to the first stage with the feed for the water-gas shift reaction to occur) and pure H_2 in the second stage reactor.

Based on the results of microautoclave screening studies, the first stage reactor employed a dispersed molybdenum-containing additive (ammonium heptamolybdate), 1500 ppm Mo relative to dry coal, while the second stage was an ebullated bed of Shell-317 supported Ni-Mo catalyst. The molybdenum-containing additive, used in the first stage reactor was not only a coal hydrogenation catalyst but was found to promote the water-gas shift conversion also. Conditions 3 and 4 evaluated the effect of reaction severity (in terms of increased first stage temperature and higher space velocities) on liquefaction performance in the presence of synthesis gas in the first stage.

The entire run operation was sustained successfully without any major interruptions, using the syngas in the first stage reactor and an interstage separator. The use of syngas during Condition 2, under water-gas shift conversion atmosphere, resulted in an improved process performance in terms of coal and resid conversions, hydrogen utilization, and distillate yields as compared to Condition 1. For Period 9 (Condition 2), the coal and resid conversions improved by 2.5 W% while the distillate yields improved by 3 W% (both absolute). Water-gas shift reaction conversions during Condition 2, 28-42%, were considerably below the equilibrium conversion value (75%) under these conditions. However, the molybdenum-additive did function as a catalyst for WGS reaction. The overall process performance for the Condition 2 (as indicated by the Work-up Period 9) was better than that for the Condition 1 (Work-up Period 5). Improved process performance during Condition 2 could be partly due to these two possibilities: (i) H_2 generated *insitu* by shift reaction is in an activated form (active H. atoms for hydrogenation), i.e., it is more active than pure gas phase H_2; (ii) CO_2 produced by the shift reaction provides beneficial surfactant/slurrying properties which lead to an enhanced coal dissolution.

For Period 12 (Condition 3), the overall coal conversion is maintained at 92 W% (MAF), whereas both the resid conversion and the C_4-524°C distillate yields dropped by 3 W% (absolute). This is mainly because of the catalyst (second stage reactor) aging effects. Condition 3 (Period 15) performance shows that although the distillate yield is the same as in Period 12, the overall coal conversion and 524°C$^+$ resid conversions dropped by 2 and 1 W% (absolute) respectively. This is mainly due to higher coal space velocity (50% higher) during Condition 4 and the lower residence time of the resultant slurry.

Coal conversions in the range of 89 and 92.5 W% (MAF coal) were obtained with 524°C$^+$ resid conversions of between 87 and 90 W% (MAF coal) and C_4-524°C$^+$ distillate yields of between 61.6 and 64.6 W% (MAF coal). The C_1-C_3 gas yields were between 5 and 6.4 W% (dry coal) and H_2 consumption was between 6.4 and 7.4 W% (dry coal).

Overall, from the results obtained during this Bench Run, it is evident that, under comparable conditions of the catalyst age (second stage) and the coal space velocity, CMSL-3 shows much lower C_1-C_3 gas yield and lower H_2-consumption than most of the other bench runs on Black Thunder Mine coal (CC-series). The C_4-524°C$^+$ distillate yields were either comparable or slightly better than in the other bench runs, while coal and 524°C$^+$ resid conversions were also slightly better. Thus CMSL-3, using syngas as reducing gas, resulted in better hydrogen efficiency or utilization than some of the earlier bench runs on the subbituminous Black Thunder Mine coal.

2.0 BACKGROUND, OBJECTIVE, AND SCOPE OF WORK

The CMSL Project is set up to evaluate different novel processing concepts in catalytic coal liquefaction to complement the larger scale process demonstration "Proof-of-Concept" Studies for the U.S. DOE. The new ideas being explored in this program include low temperature pretreatments, more effective catalysts, on-line hydrotreating, new feedstocks, other (cheaper) sources of hydrogen, more concentrated coal-slurry feeds, etc.

Hydrogen (99+% pure) production constitutes one of the main operating cost components of a coal liquefaction process. Alternative sources of hydrogen such as synthesis gas (CO/H_2) mixture, coming directly out of a gasifier (coal) or a reformer (natural gas), may save about 10-15% of the operating cost if it can be employed at an equivalent process performance instead of pure hydrogen (cost of gas separation). It is known [1] that in the presence of a suitable promoter/catalyst, a mixture of $CO/H_2/H_2O$ is very effective in solubilizing high oxygen-containing low rank coals at relatively mild severity conditions of below 400°C and 30 minutes of reaction time.

The objective of the Bench Run CMSL-3 was to evaluate the performance of two-stage liquefaction of a subbituminous coal feed in the presence of a CO-rich synthesis gas (CO/H_2 of 75/25 V/V% composition) as reducing gas in the first stage, under water-gas shift conversion conditions. The secondary objective was to evaluate the impact of coal space velocity and first stage reactor temperature on process performance with synthesis gas in the first stage. Thus, the main technical objectives of the Bench Run CMSL-3 can be summarized as:

1. To evaluate the operability of an interstage separator using pure hydrogen as reducing gas for both stages.

2. To evaluate the effect of first stage temperature 388 or 399°C (730 or 750°F) with synthesis gas (CO/H_2 ratio of 75/25) as reducing gas.

3. To evaluate the impact of space velocity 318 or 477 Kg coal/h/M^3 (20 or 30 lb coal/hr/ ft^3) second stage process on process performance with synthesis gas as reducing gas in the first reactor stage.

4. Substitution of molybdenum additive for extrudate catalyst in the first stage.

This Bench run involved two liquefaction stages: one thermal and one catalytic with an interstage separator to separate/recover hot vapor product and CO_X-rich off-gases from the first stage. The volumes of both the reactor stages were equal. The first stage was a back-mixed reactor (with no supported catalyst) that essentially functioned to solubilize coal in a pure H_2 or a synthesis gas atmosphere. Gaseous product from the first stage was removed in a vapor/liquid interstage separator prior to the second catalytic hydrogenation stage.

---

[1] Amestica, L.A. and Wolf, E.E., "Catalytic liquefaction of coal with supercritical water/CO/solvent media", Fuel, Vol. 65, pp. 1226-1232, 1986.

The process variables for CMSL-3 were : composition of the reducing gas to the first stage, temperature of the first stage reactor, and coal space velocity. As there was only one catalytic stage (to provide hydrogenation and hydrocracking activities), a temperature of 800°F, at the lower end of typical range of 800-825°F, was used for the second stage reactor, to provide for maximum hydrogenation and better recycle solvent quality.

Wyoming Black Thunder Mine coal was used as received (about 20 W% moisture) for this run, with L-794 (Filtered Run 227-78 M/U oil) as start-up/make-up solvent. Shell-317 (HRI- 5394) was employed in the second stage reactor and ammonium heptamolybdate was added to the first stage thermal reactor. Tertiary nonyl polysulfide (TNPS) was added to the first stage reactor continually to maintain Mo in the active form as its disulfide. An interstage separator was used (hot and cold separators) to remove and separate CO_X-rich off gases from Stage 1; this necessitated a continuous addition of sulfur (as hydrogen sulfide) to the second stage reactor to maintain requisite partial pressure of H_2S for the supported catalyst activity. Even though this Bench run was carried out in thermal/catalytic mode, the usual pattern of high-first-stage/low-second-stage temperatures was not employed; instead, lower first stage reactor temperatures (391-399°C (736-750°F)) and a higher second stage reactor temperature (427°C (800°F)) were used to allow the thermodynamically favorable conditions to exist in the first stage reactor for the water-gas shift reaction to occur. The Run Plan for CMSL-3 is shown in *Table 2.3.1*. The run consisted of 4 conditions, one with all hydrogen and three using syngas varying temperature and space velocity.

3.0 PROGRAM ANALYSIS RESULTS, AND COMPARISONS

The conversions and yields of different products, process performance, and product quality for CMSL-3 are addressed in this Section. The calculation of daily material recovery balances, coal conversions, normalized product yields, and other process performance-related indicators were carried out using programs available in the CTSL database (some programs were also modified as per the requirement of the process schematic). An average material recovery balance of 97.7 W% was obtained (*Figure 2.3.1*) for the entire Bench Run CMSL-3. The Operating Conditions of individual Periods during CMSL-3 are shown in *Table 2.3.2. Tables 2.3.3 and 2.3.4* indicate the performance of CMSL-3 and the normalized distribution of yields, respectively, during the Work-up Periods (Periods that represent "steady-state" or equilibrium operation).

3.1 Process Performance

3.1.1 Coal Conversion

Typical coal conversions, obtained (for both the stages) during equilibrated Periods of different Conditions of CMSL-3 are shown in *Figure 2.3.2.* As shown in *Figure 2.3.2*, the coal conversions (W% MAF coal) varied between 89.5 to 92.4 W% with the highest coal conversion obtained for Period 12 (Condition 3). Coal conversions steadily increased until Period 12 as a result of the use of synthesis gas in the first stage and due to the increased first stage temperature during Condition 3. Coal conversion had increased similarly with addition of CO_2 in Run CC-13. Increased space velocity during the last Run Condition had an adverse effect on coal conversions (decreased by about 2.5 W%) as the residence time of the slurry in the reactors decreased.

3.1.2 524°C$^+$ Resid Conversion

Resid conversion values were typically between 85 and 90 W% (MAF coal), as shown in *Figure 2.3.3*. Resid conversion levels increased from 87.2 W% to 89.9 W% in going from Condition 1 to Condition 2 (syngas in the first stage). This 2.7 W% increase is about the same as the corresponding increase in coal conversion, so there was no definite effect of syngas on the conversion of residual oil to distillates. The resid conversion level dropped to 85.8 W% towards the end of the run (Period 15) as the catalyst in the second stage became more aged. The increase in temperature of Stage I reactor (Condition 3) did not have any apparent effect on resid conversions. Increase in the coal space velocity during the last Run Condition could also be another reason for a steady decline in the resid conversion levels towards the end of the run.

3.1.3 Hydrogen Consumption

Hydrogen consumption (based on the hydrogen-content of the products), calculated from the normalized yield program, varied between 6.5 to 7.3 W% MAF coal (*Figure 2.3.4*). This value was lower than the hydrogen consumption values obtained for some of the other bench runs (as illustrated later in the run comparisons). These hydrogen consumption values were close to those obtained from the metered H_2 consumption (taking into account the generation of hydrogen by shift reaction in the first stage reactor).

3.1.4 Hydrogen Efficiency

Hydrogen Efficiency, defined as the W% MAF yield of distillate (C_4-524°C) per unit W% MAF H_2 consumed, varied between 7.9 to 8.9 kg distillates/kg H_2 (*Table 2.3.3*). These values of hydrogen efficiency were higher for CMSL-3 than that for some of the other Bench runs on Black Thunder mine coal. Hydrogen efficiencies for the Work-up Periods of CMSL-3 are shown in *Figure 2.3.5*.

3.1.5 Heteroatom Removal

Significant nitrogen removal was achieved by hydrodenitrogenation during CMSL-3 (*Figure 2.3.6*). The extent of hydrodenitrogenation typically showed the same variation during the run as the $524°C^+$ resid conversion levels. The values of W% HDN varied between 72 to 85 W% during CMSL-3. The highest HDN extent was obtained for Period 9 during Condition 2, i.e., when reducing gas in the first reactor stage was a CO-rich synthesis gas. The HDS extent during this run were particularly low (between 15 to 35 W%). Possibly, the use of two sulfur sources injected separately into two reactor stages (TNPS and H_2S), maintained sufficiently high partial pressure of H_2S in the gas phase throughout the reaction to have an adverse effect on the sulfur-removal reactions. (Very small amounts of sulfur or H_2S were recovered in the off-gases from the first stage reactor, meaning most of the H_2S formed by the decomposition of TNPS added to the first stage got carried over to the second stage where HDS reactions occurred in the presence of a supported catalyst). This behavior in hydrodesulfurization has also been observed in the prior bench runs employing a slurry-phase catalyst and a sulfur addition to maintain the dispersed catalyst in the sulfided active form.

3.2 Product Distribution

3.2.1 Synthesis Gas Feed and the Effects of WGS Reactions

From Condition 2 (Period 6) onwards the feed gas to the first stage reactor, K-1, was a 75/25 V/V% mixture of CO/H_2. About 40% by weight of coal water was also injected during these Conditions with the feed slurry. CO and steam, under the prevailing reactor conditions, in the presence of an MoS_2 promoter, undergo a shift reaction to generate hydrogen *in situ.*

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad \Delta G = -3406.8\ cal/gmol\ @\ 418^\circ C\ (730^\circ f),$$

The equilibrum constant, $H_2 \times Co_2/CO/H_2O$, for this reaction at 418°C is 13.0.

The above reaction, known more commonly as the Water-Gas Shift Conversion is equilibrium limited (adversely affected by rise in temperature) although the equilibrium of this reaction is not very sensitive to temperature (low heat of reaction !). Equilibrium limiting conversion of CO by the WGS reaction for the feed containing 25 Vol% H_2 was estimated to be 75% under reaction conditions that prevailed in the first stage reactor, Period 6A onwards. The actual conversion of CO obtained during different Periods of the run was determined by the following formula:

$$\%\ COShiftConversion = 100 * \frac{GmsofCO_{Feed} - GmsofCO_{Product}}{GmsofCO_{Feed}}$$

Where $GmsofCO_{Out}$ has been corrected for the amount of CO_2 produced from the coal itself (from Condition 1: an average value over Periods 2 through 5). The amount of hydrogen generated by shift reaction can therefore be easily estimated as each mole of CO converted by shift results in one mole of hydrogen. Actual CO shift conversions of between 28 to 42% were obtained for different run Conditions during CMSL-3 (*Figure 2.3.7*), well below the value if shift reaction equilibrium were attained. The water gas ratios ($H_2 \times CO_2/CO/H_2O$) for Run CMSL-3 were 0.4-0.8.

As mentioned earlier, the process performance of CMSL-3, in terms of different conversions and yields, is shown in *Table 2.3.3*. The normalized distribution of products for the Work-up Periods are given in *Table 2.3.4.* The following section discusses normalized yields of different products, expressed as W% MAF coal basis. It is important to note here that normalized yields for Periods 9, 12, and 15 were estimated by completely isolating the effects associated with the Water-Gas Shift Reaction from the normalized yield structure as the proportions of CO, CO_2, and H_2O in the outgoing gases are high because of the high gas feed rates and the WGS reaction (*Table 2.3.5*); this leads eventually to an unrealistic normalized yield structure. To get around this problem and still get a realistic normalized yield structure, it was assumed that the composition of the gas stream after the first stage reactor was uniform for all the Periods (based on the composition data for the first stage vent gases from Period 5, i.e., it is unaffected by the Shift Conversion that involves only CO, CO_2, H_2, and H_2O). The use of synthesis gas in

Condition 2 (Work-up Period 9) definitely enhances the process performance, in terms of different conversions and product yields, as illustrated in *Figure 2.3.8.*

3.2.2 C_1-C_3 Gas Yields

As shown in *Figure 2.3.9*, the normalized C_1-C_3 gas yields for CMSL-3 varied between 5.84 to 6.76 W% MAF coal. These values are definitely much lower than some of the earlier Bench runs with Black Thunder mine coal, primarily because of the lower first stage reactor temperatures used during CMSL-3. The gas yield increased slightly in going from Condition 2 to 3 as the first stage reactor temperature was increased by 15°F; it declined again for the last Condition as the residence time of the slurry decreased during this Condition as result of increased space velocity.

3.2.3 C_4-199°C Naphtha Yields

These are shown in *Figure 2.3.10* and *Table 2.3.4*. As shown in *Figure 2.3.10*, the yields of naphtha fraction varied between 13-20 W% MAF coal. Period 9 in Condition 2 that used synthesis gas in the first stage reactor, resulted in the highest yield of naphtha fraction; the yield decreased steadily for the subsequent Conditions as the second stage catalyst became aged and the space velocity was increased.

3.2.4 199-343°C Middle Distillate Yields

As shown in *Figure 2.3.10*, the middle distillate yields varied between 25-33 W% MAF coal. The highest middle distillate yield was obtained for Period 5 (Condition 1); the yields decreased steadily as the run progressed.

3.2.5 343-524°C Heavy Distillate Yields

The heavy distillate yields for CMSL-3 varied between 12-23 W% as shown in *Figure 2.3.10* and *Table 2.3.4*. Again, the later two Conditions (3 and 4) resulted in higher yields of heavy distillates, primarily the result of catalyst aging effect coupled with increased space velocity.

3.2.6 524°C$^+$ Residual Oil Yields

These also showed similar behavior as the heavy distillate fraction. As shown in *Figure 2.3.11*, Period 12 resulted in the highest yield of residuum while Period 9 recorded the lowest yield.

3.2.7 C_4-524°C Distillate Yield/Selectivity

The normalized yield of distillates for CMSL-3 varied between 61.6 to 64.6 W% MAF coal, as shown in *Figure 2.3.12* and *Table 2.3.3*. The highest distillate yield was obtained for Period 9 in Condition 2 while as the lowest yield was recorded for Periods 5 and 12. The selectivity of different distillate boiling fractions is shown in *Figure 2.3.13*. As shown in this figure, Periods 5 and 9 resulted in better selectivity distribution (higher selectivity to naphtha and middle distillate fractions) while Periods 12 and 15 resulted in higher selectivity to the heavy distillate fraction.

3.3 Product Quality

The ASOH, SOH, PFL, and PFC products from Periods 5, 9, 12, and 15 were analyzed in detail for their composition. These analyses for different product fractions are listed in *Tables 2.3.6 through 2.3.10.*

3.3.1 Separator Overhead and Atmospheric Still Overhead Product

There were two SOH streams in CMSL-3: SOH-1st Stage and SOH-2nd Stage, as an interstage separator was used during this Bench run. The properties of the combined SOH product from the process were determined based on their relative production rates (i.e., weight percents) after adjusting for the water present in them. In all the cases, SOH oil obtained at the second reactor stage was much lighter and had better properties than the SOH oil obtained at the interstage separator after the first reactor stage (*Table 2.3.7*). The overall properties of the combined SOH fraction are shown in *Table 2.3.8.* The SOH product became steadily heavier (as indicated by the API gravity and ASTM D-86 distillation) as the run progressed. This trend corresponded to an increase in the proportion of 343°C$^+$ and an increase in the final boiling point of the SOH 1st Stage. SOH product contained small amounts of sulfur and nitrogen (< 0.2 W%). Its H/C atomic ratio varied between 1.57 to 1.70 while its API gravity varied between 24 and 32.

The atmospheric still overhead (ASOH) product (inspection shown in *Table 2.3.6*), in general, was slightly lighter (343°C$^-$ material) than the corresponding SOH product during CMSL-3. The overall properties of ASOH fraction did not vary much from Period to Period during CMSL-3. The API gravity was around 30 while H/C atomic ratio was around 1.68. It contained small amounts of nitrogen and sulfur (less than 0.2 W%).

3.3.2 Pressure Filter Liquid and Pressure Filter Solid

The API gravity of PFL varied between 1.5 and 19.0 while the 343°C$^+$ content increased from 2.5 to 38 W% as shown in *Figure 2.3.14.* The detailed inspection of PFL properties for the work-up Periods during CMSL-3 is shown in *Table 2.3.9.* The preasphaltene and asphaltene content of the PFL increased as the run progressed and the second stage supported catalyst became aged. Similar to this behavior, the light gas oil (LGO) and vacuum gas oil (VGO) fractions of the PFL decreased as the catalyst aged while the heavier fraction, HVGO and 975°F$^+$ residuum contents increased with catalyst age. The change in reducing gas from pure H_2 in Condition 1 to CO/H_2 in Condition 2 appears to have some adverse effect on the quality of the recycle oil (as shown in *Figure 2.3.15*). The analysis of the pressure filter cake from CMSL-3 is shown in *Table 2.3.10.* The preasphaltene and asphaltene contents of the recycle oil for different Work-up Periods of CMSL-3 are shown in *Figure 2.3.16.* As shown in this figure, the heavier ashphaltene and preasphaltene contents of the recycle oil increased with the progress of the run, reflecting the effect of catalyst aging.

3.3.3 Analyses of TBP Fractions of Liquid Products

The first and second stage SOH and the ASOH were combined proportionably according to the rates at which each stream was generated. The composite was fractionated into four true boiling (TBP) fractions. A series of analyses, including API gravity, elemental, compound class type (PONA) on the lighter fractions, bromine number, aniline point and flash point, was performed. The results of these analyses are reported in *Tables 2.3.11a through 2.3.11d.*

The initial and final boiling point of the composite overheads samples ranged from 46° to 57°C and 414° to 438°C, respectively. The Period 5 sample had the highest the highest initial boiling point, while the Period 15 sample had the highest final boiling point. Over 87 W% of the materials in these samples boiled below 343°C.

With the exception of the 260-343°C fraction in which hydrogen content decreased gradually as the run progressed. Process conditions seem to have minor effect on hydrogen content in the other fractions. Surprisingly, the sulfur content of the IBP-177° and 177-260° fractions decreased significantly when hydrogen was replaced by syngas as the first stage reducing gas. Also, it seems that the sulfur addition rate to the second stage reactor had a positive impact on the sulfur content in these two lighter fractions. In spite of increasing space velocity, the decline sulfur content continued from Periods 9 thru 15. Due to an equipment problem the H_2S addition rate dropped off from 2.7 W% dry coal to 1.7 and 0.4 W% in Periods 12 and 15, respectively. Process conditions had a different impact on the nitrogen level in these two fractions. The type of reducing gas had no significant impact on the nitrogen content in these two TBP fraction, Period 5 vs Period 9. However, there was considerable increase in nitrogen level in Periods 12 and 15.

The compound class type distribution (PONA) in the two lightest fractions is presented in *Tables 2.3.11a through 2.3.11d.* The largest component in the IBP-177°C fraction was naphthenics (50 to 60 V%) followed by paraffins, which constituted 25 to 30 V%, the remainder was shared equally between olefins and aromatics (less than 11 V% each). The compound class type distribution was somewhat different in the 177-260°C fraction. Although the naphthenics compound was still the largest component, its concentration had dropped to 45-50 V%, while the second largest component was shifted from paraffins to aromatics (35 to 40 V%). There were no detectable olefins in the samples from Periods 5 and 9.

3.4 First Stage Samples

The first stage samples of the product slurry from the first stage reactor were collected during Periods 6A, 10A, 13A, and 15C to represent Work-up Periods in each of the selected Run Conditions. These samples were very thick and viscous, almost sludge-like. Because of their physical form, they were not pressure filtered; instead, they were all washed and soxhlet extracted with THF. The extracted liquid was distilled by ASTM D-1160 Method after removing THF from the extracts. The samples were also washed with quinoline to determine their QI content (and the QI-ash content). Results of the analyses are reported in *Table 2.3.12.*

3.5 Comparison of Process Performance with other Bench Runs

The use of synthesis gas as reducing gas in the first stage of liquefaction of Black Thunder Mine coal definitely improved the overall performance of the process during CMSL-3 (as exemplified by the comparison between Condition 1 and Condition 2 during CMSL-3, *Figure 2.3.8*). Comparisons have also been made (at two different throughput rates or space velocities) between the process performance of CMSL-3 and some other Bench runs made earlier with the same coal and using different reactor/catalyst configurations. These comparisons, made in

Tables 2.3.13 and 2.3.14, and shown in *Figures 2.3.17 and 2.3.18*, clearly show a much improved hydrogen utilization obtained during the synthesis gas Bench run CMSL-3. *Table 2.3.15 and Figure 2.3.19* show the comparison of the recycle oil properties from Bench runs CC-1, CC-5, and CMSL-3, all with subbituminous Black Thunder Mine coal. The following observations can be made about CMSL-3 from such comparisons:

1. Lower C_1-C_3 hydrocarbon gas yield
2. Lower hydrogen consumption
3. Comparable or slightly better C_4-524°C distillate yield
4. Comparable coal and resid conversion
5. Higher hydrogen efficiency
6. Slightly inferior recycle oil properties (especially when compared to a catalytic/catalytic run CC-1)

Considering that during the Bench run CMSL-3, much lower temperatures for both the reactor stages were used (391 & 399°C or 735 & 750°F for the first stage and 427°C or 800°F for the second stage) as compared to the other Bench runs (CC-1, CC-4, CC-7, and CC-15), the process performance of this synthesis gas run warrants further investigation of using synthesis gas for catalytic/catalytic configuration and for a bituminous coal.

3.6 Evaluation Of Performance Of Syngas As Reducing Gas For Liquefaction Of A Subbituminous Coal

In order to evaluate the performance of syngas as reducing gas for liquefaction of Black Thunder Mine coal, the product yields and conversions in selected periods of runs were compared with those of projected standard cases at the same operating conditions. The differences (from actual to projected standard) in yields and conversions were then compared to evaluate relative performance. This approach is necessary because of the variation in operating conditions and catalyst age in selected periods of different runs.

The standard case is two stage liquefaction of Black Thunder Mine coal using Shell S-317 extrudate catalysts in both stages and hydrogen as reducing gas. The projection of standard case will be made by a computer simulation program developed at HTI using earlier experimental data on liquefaction runs of Black Thunder Mine coal. The projected data are compared with the actual process performance data for a few selected periods of these runs. The difference (D* = actual - projected for CTSL with extrudate catalyst in both stages) of actual and projected yields, conversion, and hydrogen consumption data for different selected periods will compare the performance of different first stage catalysts and reducing gases.

3.6.1 Effect Of Interstage Venting Of Gases

It must be recognized that in CMSL operations utilizing syngas as reducing gas in the first stage, such as Run 227-79 (CMSL-3), the gases were vented after the first stage and hydrogen gas was then added to the second stage. As a result, the CO and CO_2 formed from coal liquefaction in the first stage did not have enough reaction time to be converted into CH_x and H_2O thereby increasing C_1-C_3 gas and H_2O yields. This consideration was apparent in Run 227-79-5 (CMSL-3), with 100% hydrogen to the first stage, where the CO_2 in the first stage vent gases amounted to 7.4 W% of the coal feed. So the net effect of interstage venting of gases is increasing CO_x yield, decreasing C_1-C_3 gas and water yields, and thereby decreasing hydrogen consumption.

Before determining the effect of using syngas in coal liquefaction, it is necessary to determine the net effect of interstage venting of gases on two stage coal liquefaction using hydrogen as reducing gas. Run 227-79-5 (CMSL-3) used hydrogen as reducing gas in both stages, 1500 ppm molybdenum slurry catalyst in the first stage and Shell S-317 extrudate catalyst in the second stage. The relevant D* values, presented below for this run, compare the net effects on product yields and hydrogen consumption.

	D*	227.79-5	CTSL Correlation
C_1-C_3, W% MAF	-0.78	6.52	7.30
CO_x, W% MAF	7.98	8.78	0.80
H_2O, W% MAF	-1.49	17.09	19.58
H_2 Consumption, W% MAF	0.16	7.82	7.66

There is significantly higher CO_x production and lower C_1-C_3 gas and H_2O production. In earlier comparison for runs without interstage venting it was shown that hydrogen consumption was approximately 1 W% higher with catalyst additive in the first stage than the standard case. So with interstage venting, the hydrogen consumption is reduced by approximately 1 W%.

3.6.2 Discussion

First Stage CO_2 and C_1-C_3 gas formation with hydrogen as reducing gas and different first stage catalysts is discussed as follows:

Analyses of first and second stage gas yields for Run 227-79-5, using 1500 ppm molybdenum catalyst additive to the first stage, show the CO_2 yield was 8.21 W% MF coal. Similar analyses for Run 227-81-5 (CMSL-4), using Shell S-317 Ni-Mo extrudate catalyst in the first stage, show the CO_2 yield was 4.85 W% MF coal. The difference from the CMSL-3 result suggests the extrudate catalyst promotes some secondary reaction of CO_2 formed during the primary reaction of the coal. The first stage methane yields for the two runs were 0.43 and 1.05 W% of MF coal for Runs CMSL-3 and CMSL-4, respectively, This difference corresponds roughly to the difference in the amount of carbon in CO_2 yields.

Interstage withdrawal of gas will apparently result in an increase in CO_2 yield and decreased light gas yield, and decreased hydrogen consumption. However, the amount of this advantage is probably lower where there is extrudate catalysts in the first stage. Hydrocarbon formation from CO_x in synthesis gas used in coal liquefaction runs is discussed as follows:

Analyses of gas formation results in periods 9 to 15 of Run CMSL-3, using molybdenum slurry catalyst and synthesis gas in the first stage, show very little formation of light hydrocarbons from CO_x.

Analyses of results from Periods 10 and 12 of Run CMSL-4, using synthesis gas and Ni-Mo extrudate catalysts in the first stage, show that CH_4 yields were 4.0 to 4.9 W% MF coal compared to 1.0 W% when there was no CO in the first stage feed. Here with extrudate catalyst in the first stage there was apparently a notable amount of CH_4 formation from the CO. This difference in CH_4 yields corresponds to 7 to 8 W% of the carbon contained in the CO_2 that was formed in those tests. In other terms, for each pound of H_2 that was derived from CO (reflected by the CO_2 formation) about 0.6 pounds of CH_4 was formed from CO as well. Also, since the methane formation consumes hydrogen, the amount of syngas required will be greater than that simply needed for the hydrogenation of the coal, by about 25%. The net result of the water-gas shift and methane synthesis reactions is the following:

$$CO + 0.84\ H_2O \text{ -------->} \ 0.92\ CO_2 + 0.08\ CH_4 + 0.68\ H_2$$

To determine the effect of using syngas in the first stage, the D* values for Run 227-79-9 (CMSL-3) and Run 227-77-7 (CMSL-1) are presented below. Both these runs on liquefaction of Black Thunder Mine subbituminous coal used Shell S-317 extrudate catalysts in the second stage.

	Run 227-79-9T	Run 227-77-7T
1st Stage Catalyst:	1500 ppm Mo	300 ppm Mo + 4500 ppm Fe
1st Stage Reducing Gas:	Syngas	Hydrogen
First Stage Venting:	Yes	No
	D*	D*
C_1-C_3, W% MAF	-0.73	2.59
Water, W% MAF	-2.5	2.51
CO_x, W% MAF	8.5	1.31
Resid, W% MAF	1.65	2.06
H_2 Consumption, W% MAF	0.17	1.00
C_4-524°C, W% MAF	-0.43	-0.64
Coal Conversion, W% MAF	6.32	8.02

The D* values for Run 227-79-9T show that the C_1-C_3, water and CO_x yields, and hydrogen consumption are mainly affected by interstage venting of gases and without any major effect from using syngas.

The comparison of D* values for Runs 227-79-9T and 227-77-7T show that the relatively low C_1-C_3 yield, low hydrogen consumption, low water yield, and high CO_x yields in the syngas operation are principally associated with the interstage withdrawal of gas. Nominally, substitution of syngas for hydrogen had minimal impact on the yield and distribution of the liquid products.

When compared to the standard case, the syngas case has equivalent C_4-524°C distillate yield and hydrogen consumption, higher resid yield and coal conversion, and lower water and C_1-C_3 gas yields. In overall performance, the syngas-case with interstage venting is equivalent to the standard case and may be slightly superior to the Fe-Mo-Case, principally because of lower hydrogen consumption.

The D* values for Run 227-79-12T (CMSL-3) and Run 227-77-14T (CMSL-1) are presented in the following table for the convenience of discussion. Run 227-77-14T used low amount of catalyst additive in the first stage. Both the runs used Shell S-317 extrudate Ni-Mo catalysts in the second stage.

	Run 227-79-12T	Run 227-77-14T
1st Stage Catalyst:	1500 ppm Mo	300 ppm Mo
1st Stage Reducing Gas:	Syngas	Hydrogen
First Stage Venting:	Yes	No
	D*	D*
C_1-C_3, W% MAF	-1.02	2.72
Water, W% MAF	-4.42	1.54
CO_x, W% MAF	9.26	3.08
Resid, W% MAF	2.24	1.24
H_2 Consumption, W% MAF	-0.39	1.31
C_4-524°C, W% MAF	-0.82	-1.58
Coal Conversion, W% MAF	5.62	5.86

The D* values for Run 227-79-12T show that even after discounting the effects of interstage venting of gases, the C_1-C_3 and water yields are further reduced, and hydrogen consumption is also further reduced due to the effect of using syngas in the first stage.

The comparison of D* values for Runs 227-79-12T and 227-77-14T show that the use of syngas as reducing gas with interstage venting results in high CO_x yield, low C_1-C_3 and water yields leading to low hydrogen consumption, and slightly higher C_4-524°C distillate yield. In terms of C_4-524°C distillate yield and hydrogen consumption, the syngas-case with 1500 ppm Mo has significant advantage over the 300 ppm Mo-Case using hydrogen. In overall performance considering distillate yield, the standard case has advantage over the syngas case.

3.6.3 Conclusion

The overall results show that syngas as reducing gas in the first stage, along with interstage venting, can be used in two stage coal liquefaction processes with the net effect of reduced hydrogen consumption and improved or equivalent distillate yield. Interstage venting in itself will result in higher CO_2 yield, lower light hydrocarbon yield, lower water yield and lower hydrogen consumption; this effect is more significant with catalyst additive in the first stage than with extrudate catalyst in the first stage. Synthesis gas in place of hydrogen has small impact on liquid hydrocarbon yield and its distribution.

4.0 DETAILS OF OPERATION

This section summarizes the operational details of the Run CMSL-3, using synthesis gas for the liquefaction of a subbituminous Wyoming Black Thunder Mine coal. The daily reactor temperature profiles are shown in *Figure 2.3.20.*

4.1 Bench Unit Description

The run CMSL-3 was conducted in HRI's 50 lb/day nominal size continuous bench unit No. 227 and was designated as the Run 227-79. This run employed two identical sized, reactors: one thermal back-mixed and one ebullated catalytic-bed in series, with an interstage separator. The schematic of the unit is shown in *Figure 2.3.21.* The first reactor (K-1) was charged with coal-recycle oil slurry and additives (water, ammonium heptamolybdate, and TNPS). The effluent from the first stage reactor passed through an interstage separator (hot separator, O1A); the separator bottoms were sent to the second stage ebullated bed reactor, K-2. O-1A overhead products are collected as Stage I SOH product after they have been separated from the non-condensibles in the cold separator (O-2A). The products from second stage reactor were separated using a hot separator and a continuous atmospheric still (CAS) into separator overhead (SOH-2nd Stage), atmospheric still overhead, ASOH, and CAS bottoms. The CAS bottoms were pressure filtered in a batch-mode into pressure filter liquids (PFL) and pressure filter solids (PFS). The PFL was used as recycle solvent and as buffer liquid for the ebullating pumps. The non-condensible streams both from the interstage separator and the cold separator (O-2) from the unit were metered, sampled for GC analyses and sent to flare.

4.2 Run Plan

The Run Conditions, as planned for CMSL-3, are shown in *Table 2.3.1.* Condition 1 extended from Periods 1 through 5 using pure hydrogen as reducing gas for both reactor stages. This Condition served as a Base Case for comparing with the other Run Conditions in which synthesis gas was used in the first stage reactor. In Conditions 2 through 4, water was injected to the upstream of the preheater to obtain an overall water content of 40 W% of dry coal in the feed slurry. Condition 3 evaluated the impact of increasing the first stage temperature from 388 to 399°C (730 to 750°F) while Condition 4 evaluated the impact of higher coal space velocity (1.5 times higher than that during Conditions 1 through 3). First stage samples were taken during each run Condition to determine the performance of the first stage by itself. The actual operating conditions during the Bench run CMSL-3 are shown in *Table 2.3.2.*

4.3 Unit Modifications

The hot separator from the adjacent Unit 238 was used as an interstage separator for CMSL-3. Carbon monoxide was fed to the Stage 1 reactor instead of hydrogen during Conditions 2, 3, and 4. The pure hydrogen was still added to the recirculation line on stage I reactor during Conditions 2, 3, and 4 to maintain about 75/25 V/V% ratio of CO/H_2 in the feed gas stream to Stage 1 reactor.

4.4 Preoperational Procedures

Start-up consisted of establishing proper flows of oil and gases, ebullating and presulfiding the second reactor stage catalyst bed in the bench unit 227, modified for CMSL-3. L-794, a recycle solvent derived during CMSL-2 (Run 227-78) was used as a start-up oil for this run. It was also used as a make-up oil during the run (PFL derived in the early run Periods was also used as a make-up oil during later Periods of CMSL-3). The recycle material generated during reactor heat-up period was used as slurrying medium for coal at the beginning of Period 1A.

4.6 Operations Summary

Overall, this Bench run proceeded very smoothly without any major operational interruptions. There were a couple of occasions of feed pump problems, but those were taken care of immediately. This is how the unit performed from Condition 1 through 4:

4.6.1 Startup and Shutdown

Both startup and shutdown operations proceeded smoothly without any mechanical problems. The startup commenced in July, 1993 when the Shell-317 catalyst was charged to the second stage reactor, K-2. Coal feed to the unit commenced at 1100 hours, Wednesday, July 8th, beginning Period 1A. Shutdown commenced at the end of Period 15C. All related equipment was found to be in order except for the H_2S flow check valve which was found to be restricted with hard carbonaceous material resembling unreacted coal.

4.6.2 Condition 1 (Periods 1 through 5)

Full coal feed was achieved at 1700 hours, Period 1B. During Period 1C, the unit experienced minor charge pump problems. Again, during Periods 4A and 4B, charge pump problems led to a total feed slurry outage of about two hours. These problems were immediately taken care of and the unit operated smoothly during Period 4C. During Period 5C, the first stage reactor left side hot check buffer pump failed due to a loosened shaft collar. The pump was repaired and placed on line. The average temperature of the slurry mix tank was about 79°C (175°F). The average value of liquid closure for Condition 1 was 92.9%.

4.6.3 Condition 2 (Periods 6 through 9)

The major difference between Condition 1 and Condition 2 was the use of carbon monoxide instead of hydrogen as the main feed gas to the first stage reactor. The complete transition from Condition 1 to Condition 2 was achieved 4 hours into Period 6A. First stage overall differential pressure started oscillating between 21 and 69 kPa (3 and 10 psi) during Period 7A; this was attributed to salt formation. Water rate was increased from 500 to 600 grams per hour. This brought back the differential pressure to 14 to 34 kPa (2 to 5 psi). Smooth operations were experienced throughout Periods 8 and 9. The average liquid closure for Condition 2 was 90.2%.

4.6.4 Condition 3 (Periods 10 through 12)

The main difference between this Condition and the earlier one was the first stage temperature that was increased by 8°C (15°F) during Condition 3 (Period 10A/B). The hydrogen sulfide injection rate was low throughout Condition 3. There were a couple of minor hydrogen outages during Period 11, but these did not have any detrimental effect on the unit operation. First stage reactor slurry samples of 463 and 416 grams, respectively were taken shortly after the completion of Periods 9 and 12. Overall, operations were smooth throughout Periods 10, 11, and 12. The average liquid closure for the Condition was 90.2%.

4.6.5 Condition 4 (Periods 13 through 15)

During Condition 4, the coal space velocity was increased by 50%, from 318 Kg/h/M^3 (reactor vol.) to about 484 Kg/h/M^3 (30 lb/hr/ft^3). Unit operations proceeded smoothly during Condition 4 except for difficulties encountered with the Tuthill circulating pump for the feed slurry, which continually kicked out during Period 14B. Pump failures were eliminated when speed was maintained above 60%. During Period 15, the H_2S pump was found not pumping. A first stage sample of 528 grams was collected after Period 15C. The average liquid closure for Condition 4 was 90%.

Thus, the overall run was sustained successfully for all 15 days of operation. The daily material recovery balances and reactor operating conditions are represented in *Figures 2.3.1 and 2.3.17* respectively.

5.0 MATERIALS USED

5.1 Feed Coal

HRI-5828, which is a Black Thunder Mine Wyoming subbituminous coal, was used for CMSL-3, as received (without any drying). This coal had about 25 W% moisture under ambient conditions, and the detailed analysis is shown in *Table 2.3.16*.

5. 2 Startup/Makeup Oil

L-794, the oil derived from Run 227-78 (by extracting filter cakes and blending PFLs from the startup and shutdown), was used as the startup solvent for this bench run. The detailed analysis is shown in *Table 2.3.17*.

5.3 Additives

Ammonium heptamolybdate solution (25 W%) was used as an additive for the first stage reactor; the amount of molybdenum added was adjusted to about 1500 ppm relative to dry coal. To supplement the low sulfur in the coal, 1 W% (as S) Tert-nonyl polysulfide (TNPS) was added for sulfiding molybdenum additive to the first stage, and 3 W% H_2S was added continually to the second stage reactor, to maintain the catalyst in the sulfided state.

5.4 Supported Catalyst

Shell-317 1/32" extrudate catalyst (Ni-Mo/Al_2O_3) was used in the second stage reactor during CMSL-3. The catalyst was presulfided during the startup using TNPS. No catalyst was either added or removed from the reactor during the run.

6.0 LABORATORY SUPPORT FOR CMSL-3

6..1 Effect of Different Catalysts/Promoters on Water-Gas Shift Conversion

6.1.1 Background:

Carbon monoxide and steam mixtures have been successfully employed instead of pure hydrogen in the gas phase for liquefaction of low rank coals. The equimolar mixture of CO and steam undergoes a shift reaction to produce H_2 *in situ*. The water-gas shift reaction is known to be catalyzed by alkali like potassium, sodium, and even by metals like molybdenum added to the reaction mixture in suitable forms. The bench run 227-79 (CMSL-3) will use syngas (CO + H_2) with possibly different CO/H_2 ratios (with water injection into feed slurries). It is therefore crucial to understand the effects of $CO/H_2O/H_2$ mixtures on conversion levels of Black Thunder mine coal which is going to be used in CMSL-3.

6.1.2 Tests

(A) Microautoclave tests to evaluate the effectiveness of different WGS promoters/catalysts on Coal and Resid Conversions from Black Thunder Mine coal with a 50/50 CO/H_2 mixture.

6.1.3 Objective:

To determine the effect of different WGS promoters/catalysts on coal and resid conversions from Black Thunder Mine Wyoming coal with a synthesis gas (50/50 v/v% CO/H_2) as feed gas.

6.1.4 Reaction Conditions:

Coal:	Black Thunder Mine (HRI 5828 or L-780)
Solvent:	HRI 6002 (Wilsonville Distillate)
CO:H_2 Ratio:	50/50 by volume
Temperature:	399°C (750°F)
Time:	15 minutes
Total Pressure:	12.4 MPA (1800 psig)
Total Water:	30 W% of Dry Coal
Solvent/Coal Ratio:	4:1

6.1.5 Results:

The apparent low values of total coal and residuum conversions (as shown in *Table 2.3.18*), obtained during the microautoclave tests CL-1 thru' CL-18, are mainly because of the short reaction time (15 minute) and 50% hydrogen in the gas phase (this functions to suppress the equilibrium of the Water-Gas Shift Reaction). Based on these results it can be said that potassium carbonate and ammonium heptamolybdate (with 3 W% DMDS) gave almost comparable performance in terms of both coal and residuum conversions from Black Thunder Mine coal. The results obtained in the above tests warranted a further testing in the microautoclave of different WGS promoters at higher reaction time (30 minutes) and with pure CO as a reducing gas in the gas phase with equimolar amount of water added (for WGS Reaction) to the feed mixture to the microautoclave.

(B) Microautoclave tests to evaluate the effectiveness of different WGS promoters/catalysts on Coal and Resid Conversions from Black Thunder Mine coal with pure CO as feed gas and longer reaction time.

6.1.6 Objective:

To determine the effect of different WGS promoters/catalysts on coal and resid conversions from Black Thunder Mine Wyoming coal with a Pure CO as a feed gas/Equimolar Water added to the feed and longer reaction time.

Eleven more microautoclave tests were carried out in order to determine the effects of using pure CO in the gas phase and adding water to the reaction mixture at a concentration level that will give close to equimolar ratio of CO and steam in the gas phase under reaction conditions. The design pressure rating of the microautoclave system is 22.8 MPA (3330 psig) at 454°C (850°F). Since the water added to the coal-solvent slurry is going to generate its own partial pressure under reaction conditions, the amounts of CO and water (approximately an equimolar mixture) were estimated for a total system pressure of 17.9 MPA (2600 psig) under reaction conditions.

Typical Test Conditions:

Unit:	Microautoclave
Coal:	HRI-5828 and L-780, Black Thunder coal, 2.0 g
Solvent:	Recycle oil, HRI-6002, 8.0 g
Pressure:	17.9 MPA (2600 psig) $CO+H_2O$ at reaction temp.
CO initial pressure:	5.5 MPA (800 psig) (cold)
Temperature:	399°C (750°F)
Reaction time:	30 min
Water:	40 W% of dry coal.

6.1.7 Results:

As shown in *Table 2.3.19*, in these tests also, ammonium heptamolybdate (with DMDS) and potassium carbonate were found to result in the best coal and resid conversion values. Although, potassium carbonate, in both the reaction series (CL-1 thru' 18 and CL-37 through 47), has resulted in a slightly better performance than ammonium heptamolybdate (AHM), a judicious choice was made to select AHM as an ultimate catalyst additive for the Bench Run CMSL-3 for the following reasons:

(1) Ammonium heptamolybdate, when used at 1500 Mo relative to coal (with a proper sulfiding agent), has been proven to be an active slurry catalyst for the first stage of coal liquefaction.

(2) The use of any alkali-based promoter (such as K_2CO_3 or $NaAlO_2$) for the WGS reaction was not desirable from the point of deactivation of the supported catalyst (acid sites poisoning by the alkali in the promoter) to be used in the second stage reactor of the Bench Run CMSL-3.

(3) As exemplified by the activity data (*Table 2.3.20 & Figure 2.3.22*), discussed in the next sub-section, AHM (with DMDS) was indeed found to be a good catalyst for the WGS reaction; these reactions were carried out in the absence of any coal (only CO and water were used for these tests).

6.2 Evaluating the Effect of Different Catalysts/Promoters on Water-Gas Shift Conversion Levels in the Absence of Coal and with/without a Solvent:

The microautoclave tests series CL-74 through CL-85 were carried out in order to compare the effectiveness of different catalysts/promoters for the Water-Gas Shift conversion only, i.e., these tests were carried out in the absence of any coal; the only reactants were carbon monoxide and water besides the solvent, wherever used. The following were the common conditions employed for these tests; the product work-up included GC analysis of the product gases from such tests.

Conditions:

Solvent :	L-769, 8.0 g wherever used.
Water:	0.85 g
CO pressure (cold):	5.5 MPA (800 psig)
Temperature:	399°C (750°F)
Reaction time:	30 min
CO/H_2O molar ratio:	1:1

6.2.1 Results

The results of these tests are given inTable 2.3.20 and are compared in Figure 2.3.22 Thus, the results obtained from these series of tests indicate that molybdenum-based water-soluble slurry catalyst and the supported Co-Mo/Alumina (Amocat 1A) catalyst are the most effective catalysts for the shift conversion. Since, the use of syngas is planned only in the first stage of the CMSL-3, a slurry catalyst is more suited for use in the first stage.

7.0 CONCLUSION

The entire run operation for the Bench run CMSL-3 was sustained successfully for 15 days of operation with an interstage separator and synthesis gas (CO/H_2) in the first stage reactor. Process performance has been improved by the use of synthesis gas for the liquefaction of subbituminous Wyoming Black Thunder Mine coal. Comparisons with some of the earlier Bench runs clearly shows that while comparable or slightly better conversions and distillate yields were obtained during CMSL-3, much improved hydrogen utilization (lower gas make) was evidenced. The overall success of this Bench run warrants further investigation of the synthesis gas system with supported catalyst/catalyst configuration and bituminous coal feeds.

The operation using pure H_2 tothe first stage with interstage withdrawal of vapors showed an appreciably higher formation of CO_2 than when there had been no interstage withdrawal, which leads to lower CH_4 formation in the second stage and lower hydrogen consumption.

The AHM molybdenum-additive to the first stage promoted some conversion of CO to H_2, but considerably less than might be effected by more active shift conversion catalyst.

TABLE 2.3.1

BENCH RUN CMSL-3
RUN PLAN

Wyoming Black Thunder Mine Coal (25% Moisture)
First Stage Additive: Ammonium Heptamolybdate, 1500 ppm Mo per Dry Coal Feed
Second Stage Catalyst: Shell S-317 1/32" Extrudate Catalyst (HRI-5394)

Condition	1	2	3	4
Periods	1-5	6-9	10-12	13-16
Reducing Gas (CO/H_2				
First Stage	0/100	75/25	75/25	75/25
Second Stage	0/100	0/100	0/100	0/100
Sulfur Additive				
TNPS (First Stage)	-------1 S W% of Dry Coal------			
H_2S (Second Stage)	-------3 S W% of Dry Coal------			
Pressure, MPa	-----------------17.2------------------			
Temperature C				
First Stage	388	388	399	399
Interstage Separator	388	388	388	388
Second Stage	427	427	427	427
Hot Separator	316	316	316	316
Atmospheric Still	288	288	288	288
Space Velocity Second Stage				
Kg Coal/h/M^3	318	318	318	481
Lb Coal/h/ft^3	20	20	20	30
Recycle Solvent/Coal Ratio	------------------1.2/1--------------------			

TABLE 2.3.2

OPERATING CONDITIONS FOR RUN 227-79 (CMSL-3)

Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	15
Date (Start of Period	07/11/93	07/15/93	07/18/93	07/21/93
Hours of Run (End of Period	112	208	280	344
Second Stage Cat. Age, Kg Coal/Kg Cat	123	234	316	419
CO to First Stage, V%	0	75	75	75
Temperatures, deg C				
First Stage Reactor	388	388	399	399
Second Stage Reactor	427	427	427	427
Slurry Mix Tank	66	72	73	74
Hot Separator Liquid	302	317	317	316
Pressures, MPa				
Unit Back Pressure	17.2	17.4	17.3	17.2
First Stage Reactor DP	3.4	3.6	3.7	3.9
Overall DP	5	5	5	8.3
Stage 2 Coal Space Velocity				
$Kg/h/M^3$ react.	303	311	306	424
$lb/hr/ft^3$	19	19	19	26
W% Dry Coal				
PFL Recycle	120.1	120.2	109.2	129.8
PFL to Stage 1 Buffer	4.7	4.3	5.1	3.5
PFL to Stage 2 Buffer	4.8	4.2	4.6	3
Make up Oil	0	0	12.1	2.7
Sulfur	2.8	2.7	1.7	0.4

Note: Ammonium heptabolybdate (1500 ppm Mo relative to dry coal) and TNPS (1 W% of dry coal) were the Additives to the First Stage Reactor

TABLE 2.3.3

PROCESS PERFORMANCE OF CMSL-3: EFFECT OF SYNTHESIS GAS

Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	15
Hours of Run (End of Period)	112	308	280	344
Second Stage Cat. Age, kg Coal/kg Cat	123	234	316	419
Stage 2 Coal Space Velocity				
Kg coal/h/M^3 reactor	303	311	306	424
lb coal/hr/ft^3 reactor	18.9	19.4	19.1	26.5
Reducing Gas	H_2	CO/H_2	CO/H_2	CO/H_2
Vol. in Feed	100	75/25	75/25	75/25
Total Material Recovery % (Gross)	98.75	97.22	99.14	95.04
Water-Gas Shift Conversion, Mole % C	N/A	42.1	42.1	28.1
PROCESS PERFORMANCE				
Coal Conversion, W% MAF Coal	89.5	92	92.4	90.1
524 C+ Conversion, W% MAF Coal	87.2	89.9	86.9	85.8
C4-524 C Distillates, W% MAF Coal	61.6	64.6	61.6	62
Hydrogen Consumption, W% MAF Coal	7.82	7.73	7.14	6.97
Hydrodenitrogenation, W%	75.9	84.8	80.7	72.4
Hydrogen Efficiency, kg dist./kg H_2	7.88	8.35	8.63	8.89

TABLE 2.3.4

NORMALIZED DISTRIBUTION OF PRODUCT YIELDS FOR CMSL-3

Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	15
Date (Start of Period	07/11/93	07/15/93	07/18/93	07/21/93
Hours of Run (End of Period	112	208	280	344
Second Stage Cat. Age, Kg Coal/Kg Cat	123	234	316	419
Stage 2 Coal Space Velocity				
Kg coal/h/M^3 reactor	303	311	306	424
lb coal/hr/ft^3 reactor	18.9	19.4	19.1	26.5
ESTIMATED NORMALIZED YIELDS*, W% MAF COAL				
C1-C3 in Gases	6.52	6.56	6.76	5.84
C4-C7 in Gases	4.15	4.51	3.43	2.90
IBP-199 deg C	11.91	15.34	10.30	10.70
199-260 deg C	11.47	11.06	9.16	8.48
260-343 deg C	21.30	19.55	18.19	17.81
343-454 deg C	11.80	12.76	18.42	20.54
454-524 deg C	0.99	1.29	2.15	1.58
524 deg C+	2.31	2.07	5.48	4.29
Unconverted Coal	10.49	8.00	7.65	9.95
Water	17.09	16.14	14.47	14.12
CO	0.57	0.67	0.73	0.75
CO2	8.21	8.63	9.35	9.14
NH3	0.85	0.95	0.90	0.80
H_2S	0.16	0.12	0.17	0.07
Hydrogen Consumption	7.82	7.73	7.14	6.97

Note: The Normalized Product Yields for Periods 9, 12, and 15 were estimated by isolating the Effects of the WGS Reaction from the CTSL Yield Structure (W% MAF Coal).

TABLE 2.3.5

YIELDS OF GASES FOR RUN 227-79 (CMSL-3)

Condition	1	2	3	4
Period Number	5	9	12	15
Hours of Run	112	208	280	352
CO in First Stage Feed Gas, V%	0	75	75	75
Gas Yields (Stage 1 Vent), W% of MF Coal				
CH4	0.43	0.00	0.00	0.00
C2H4	0.00	0.00	0.00	0.00
C2H6	0.42	0.38	0.61	0.58
C3H6	0.08	0.06	0.06	0.13
C3H8	0.37	0.41	0.62	0.59
C4H8	0.07	0.04	0.04	0.13
N-C4H10	0.18	0.15	0.30	0.39
I-C4H10	0.04	0.04	0.04	0.09
C5H10	0.00	0.00	0.00	0.00
N-C5H12	0.31	0.05	0.48	0.16
I-C5H12	0.04	0.05	0.16	0.11
Methyl-Cyclopentane	0.00	0.00	0.00	0.00
Cyclohexane	0.05	0.00	0.00	0.06
N-C6H14	0.00	0.00	0.06	0.06
C6-C7	0.10	0.06	0.06	0.06
CO	0.44	68.26	69.51	97.05
CO2	7.02	64.45	83.96	39.31
H_2S	0.86	0.78	1.09	2.00
Gas Yields (Stage II Vent), W% of MF coal				
CH4	1.45	2.09	2.17	2.02
C2H4	0.00	0.00	0.00	0.00
C2H6	1.27	1.11	1.14	0.93
C3H6	0.02	0.02	0.02	9.02
C3H8	1.67	1.50	1.47	1.03
C4H8	0.00	0.00	0.00	0.00
N-C4H10	0.98	0.97	0.88	0.62
I-C4H10	0.26	0.18	0.15	0.09
C5H10	0.00	0.00	0.00	0/00
N-C5H12	0.52	0.55	0.47	0.37
I-C5H12	0.30	0.33	0.18	0.22
Methyl-Cyclopentane	0.00	0.00	0.00	0.00
Cyclohexane	0.50	0.64	0.34	0.30
N-C6H14	0.28	0.26	0.13	0.09
C6-C7	0.19	0.39	0.13	0.13
CO	0.06	0.14	0.16	0.19
CO2	0.17	0.45	0.22	0.16
H_2S	3.11	1.65	1.00	0.33

TABLE 2.3.6

INSPECTION OF ATMOSPHERIC STILL OVERHEAD (ASOH)

Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	15
Gravity, API	31	30.3	29.4	29.5
IBP, deg C	130	119	119	119
FBP, deg C	307	304	302	309
ASTM D-86 Distillation, Composition				
W% IBP-177 deg C	15.3	20.3	19.5	20.9
W% 177-260 deg C	48	46.5	48.1	46.7
W% 260-343 deg C	36.7	31.9	32.1	32.4
W% 343 deg C+	0	0.9	0	0
W% Loss	0	0.4	0.3	0
Elemental Analysis				
Carbon, W%	86.29	86.99	86.35	87.42
Hydrogen, W%	12.1	12.21	12.14	12.24
Sulfur, W%	0.01	0.02	0.02	0.01
Nitrogen (Antek), W%	0.17	0.05	0.07	0.2
H/C Ratio	1.68	1.68	1.69	1.68

TABLE 2.3.7

COMPARISON OF FIRST AND SECOND STAGE SOH DURING CMSL-3

Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	15
First Stage/Second Stage				
Gravity, API	26.9/37.0	22.9/37.2	21.4/37.3	18.9/35.7
IBP, deg C	85/61	83/48	77/49	86/64
FBP, deg C	414/390	422/396	438/395	438/406
ASTM D-86 Distillation, Composition				
W% IBP-177 deg C	14.0/41.3	11.9/45.6	11.5/45.9	9.6/44.0
W% 177-260 deg C	10.3/18.3	10.5/17.3	10.4/17.5	9.1/18.3
W% 260-343 deg C	51.6/29.8	45.6/25.6	41.0/25.3	35.2/24.8
W% 343 deg C+	24.0/9.9	31.5/10.7	36.6/10.7	45.7/12.4
W% Loss	0.1/0.7	0.5/0.8	0.5/0.6	0.4/0.5
Elemental Analysis				
Carbon, W%	85.56/85.96	86.0/87.25	86.08/86.96	86.33/86.97
Hydrogen, W%	11.74/12.52	11.37/12.8	11.11/12.74	10.76/12.67
Sulfur, W%	0.079/0.011	4	0.064/0.018	0.064/0.012
Nitrogen (Antek), W%	0.22/0.15	0.086/0.012	0.15/0.072	0.34/0.16
H/C Ratio	1.65/1.75	0.057/0.049	1.55/1.76	1.50/1.75
		1.59/1.77		

TABLE 2.3.8

INSPECTION OF COMBINED SEPARATOR OVERHEAD (SOH)

Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	15
First Stage/Second Stage				
Gravity, API	32	30.7	26.7	24
IBP, deg C	61	48	49	64
FBP, deg C	414	422	438	438
ASTM D-86 Distillation, Composition				
W% IBP-177 deg C	27.6	30.1	23	19.9
W% 177-260 deg C	14.3	14.2	12.8	11.9
W% 260-343 deg C	40.7	34.8	35.8	32.1
W% 343 deg C+	17	20.3	28	35.7
W% Loss	0.4	0.6	0.6	0.4
Elemental Analysis				
Carbon, W%	85.76	86.63	86.52	86.46
Hydrogen, W%	12.13	12.11	11.93	11.33
Sulfur, W%	0.05	0.05	0.05	0.05
Nitrogen (Antek), W%	0.19	0.05	0.07	0.29
H/C Ratio	1.70	1.68	1.65	1.57

TABLE 2.3.9

INSPECTION OF PROPERTIES OF THE PRESSURE FILTER LIQUID (2ND STAGE)

Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	15
Gravity, API	12.5	7.5	5.3	1.7
IBP, deg C	267	264	282	531
ASTM D-1160 Distillation, Composition				
W% IBP-343 deg C	18.07	12.87	12.28	8.57
W% 343-454 deg C	52.11	46.37	45.84	37.66
W% 454-524 deg F	8.8	15.42	11.7	14.31
W% 524 deg C+	20.61	24.56	29.79	39.17
W% Loss	0.41	0.78	0.39	0.29
Elemental Analysis				
Carbon, W%	89.22	89.35	89.7	89.14
Hydrogen, W%	10.45	9.6	9.34	8.75
Sulfur, W%	0.02	0.02	0.03	0.04
Nitrogen (Antek), W%	0.1	0.17	0.44	0.58
H/C Ratio	1.41	1.29	1.25	1.18
CCR, W% PFL	5.97	10.18	12.35	17.13
CYCLOHEXANE INSOLUBLES, W%	1.88	3.68	6.16	11.49
TOLUENE INSOLUBLES W%	0.18	0.38	0.66	1.17

TABLE 2.3.10

INSPECTION OF THE PRESSURE FILTER CAKE (2nd STAGE)

Unit	227	227	227	227
Run	79	79	79	79
Condition	1	2	3	4
Period Number	5	9	12	14
Elemental Analysis				
Carbon, W%	65.74	63.22	61.98	68.25
Hydrogen, W%	5.63	5.17	4.8	5.39
Sulfur, W%	1.54	1.56	1.24	1.12
Nitrogen (Antek), W%	0.63	0.52	0.59	0.74
H/C RATIO	1.03	0.98	0.93	0.95
Composition, W%				
Ash (Quinoline Filtration)	24.05	27.87	27.91	21.57
ASTM Ash, W%	23.13	26.49	27.61	20.91
S in Ash, W%	4.45	4.46	4.14	4.05
Unconverted Coal (Adj.)	36.42	31.81	31.99	30.36

TABLE 2.3.11a

DETAILED ANALYSES OF TBP FRACTIONS
Run No. 277 - 79 Period No. 05

TBP Distillation, %	IBP=57°C	EP=415° C
		W%
IBP-177°C		21.77
177-260°C		27.70
260-343°C		47.67
343°C+		2.86

TBP FRACTION [°C]	IBP-177	177-260	260-343	343+
API Gravity	52.3	30.8	23.1	11.9
Elemental Analysis [W%]				
Carbon	85.10	86.68	87.68	87.42
Hydrogen	14.15	12.41	12.07	10.71
Sulfur	0.0241	0.0350	0.0179	0.0874
Nitrogen	0.08	0.15	0.11	0.47
Antek N, ppm	214	932	N/A	N/A
Bromine No. [g/100g]	20.58	11.22	10.45	
Aniline Point, [°C]	44	31	44	
Flash Point, [°C]	<7	73	132	
PONA [V%]				
Paraffins	29.51	13.54		
Olefins	9.60	0.00		
Naphthenics	49.97	50.71		
Aromatics	10.95	35.75		
Aromatics (ASTM D2549)			47.82	

TABLE 2.3.11b

DETAILED ANALYSES OF TBP FRACTIONS
Run No. 227-79 Period No. 09

TBP Distillation, %	IBP = 48°C	EP = 421°C
		W%
IBP-177°C		23.73
177-260°C		28.70
260-343°C		37.30
343°C+		10.27

TBP FRACTION [°C]	IBP-177	177-260	260-343	343+
API Gravity	51.1	29.4	21.1	14.1
Elemental Analysis [W%]				
Carbon	84.96	86.69	87.79	87.55
Hydrogen	14.00	14.00	11.67	10.69
Sulfur	0.0202	0.0268	0.0170	0.0357
Nitrogen	0.06	0.23	0.20	0.40
Antek N, ppm	198	1224	N/A	N/A
Bromine No. [g/100g]	21.82	16.36	9.47	
Aniline Point, [°C]	42	25	33	
Flash Point, [°C]	<7	76	129	
PONA [V%]				
Paraffins	28.14	10.48		
Olefins	7.40	0.00		
Naphthenics	56.36	50.95		
Aromatics	8.10	38.57		
Aromatics (ASTM D2549)			55.63	

TABLE 2.3.11c

DETAILED ANALYSES OF TBP FRACTIONS
Run No. 227-79 Period No. 12

TBP Distillation, % IBP = 46°C EP = 438°C

	W%
IBP-177°C	21.77
177-260°C	27.70
260-343°C	47.67
343°C+	2.86

TBP FRACTION [°C]	IBP-177	177-260	260-343	343+
API Gravity	50.6	28.0	20.2	13.8
Elemental Analysis [W%]				
Carbon	85.08	86.80	87.83	88.18
Hydrogen	13.96	12.09	11.57	10.73
Sulfur	0.0194	0.0156	0.0183	0.0342
Nitrogen	0.08	0.25	0.25	0.42
Antek N, ppm	326	2688	N/A	N/A
Bromine No. [g/100g]	16.74	15.54	10.92	
Aniline Point, [°C]	43	24	28	
Flash Point, [°C]	<-7	76	141	
PONA [V%]				
Paraffins	28.52	9.55		
Olefins	6.80	4.80		
Naphthenics	58.11	45.38		
Aromatics	6.57	40.27		
Aromatics (ASTM D2549)			61.47	

TABLE 2.3.11d

DETAILED ANALYSES OF TBP FRACTIONS
Run No. 277 - 79 Period No. 15

TBP Distillation, % IBP = 54°C EP = 438°C

	W%
IBP-177°C	23.30
177-260°C	37.40
260-343°C	29.40
343°C+	9.90

TBP FRACTION [°C]	IBP-177	177-260	260-343	343+
API Gravity	50.4	28.0	18.1	12.1
Elemental Analysis [W%]				
Carbon	84.19	86.86	88.34	87.70
Hydrogen	14.11	12.30	11.27	10.43
Sulfur	0.0174	0.0152	0.0210	0.0325
Nitrogen	0.07	0.27	0.33	0.52
Antek N, ppm	273	2823	N/A	N/A
Bromine No. [g/100g]	13.9	15.3	9.7	
Aniline Point, [°C]	108.0	76.5	~ 79.0	
Flash Point, [°C]	< 20	170	290	
PONA [V%]				
Paraffins	26.44	7.00		
Olefins	6.80	6.20		
Naphthenics	60.29	48.46		
Aromatics	6.47	38.34		
Aromatics (ASTM D2549)			64.35	

TABLE 2.3.12

INSPECTION OF FIRST STAGE LIQUID SAMPLE

THF Extracted THF Removed By Vacuum Evaporation, Some Possible THF Retention

PERIODS	**6A**	10A	13A	15C
Elemental Analysis [W%]				
Carbon	86.00	85.61	87.15	84.69
Hydrogen	8.82	8.71	8.20	7.57
Sulfur	0.093	0.045	0.083	0.269
Nitrogen	0.57	0.50	0.61	0.82
Weight Distribution [%]				
IBP-343 C	10.80	6.91	6.85	4.51
343-454 C	37.40	29.21	32.13	23.94
454-524 C	8.60	11.59	12.87	12.28
524 C+	36.90	47.61	43.15	52.56
Loss	6.30	4.68`	5.00	6.71
Solubility Tests, 524 C+ Residuum				
Cyclohexane Filtration:				
Insolubles	75.04	64.16	64,00	83.48
Ash	0.85	0.04	0.07	6.19
Toluene Filtration:				
Insolubles	30.86	27.79	27.59	47.00
Ash	0.65	0.18	0.02	5.93
API Gravity	3.5	6.3	-0.5	-6.5

FIRST STAGE SOLID SAMPLE ANALYSIS

Periods	6A	10A	13A	15C
Elemental Analysis [W%]				
Carbon	41.62	50.26	48.21	55.03
Hydrogen	1.99	2.72	2.69	3.14
Sulfur	3.09	1.94	2.04	2.10
Nitrogen	0.64	0.82	0.80	0.96
ASTM Ash [W%]	46.53	34.02	38.00	33.16
Quilonine Filtration:				
QI Insoluble [W%]	98.28	100.00	100.00	95.42
Ash in QI {W%]	46.08	34.19	39.02	31.37
S in QI Ash [W%]	4.90	----	4.72	4.96
Apparent Coal Conversion, W%	91.5	86.3	86.7	85.4

TABLE 2.3.13

PROCESS PERFORMANCE FOR BENCH SCALE OPERATION
Low Space Velocity Operations

RUN	CC-1	CC-7	CC-15	CMSL-3
CONFIGURATION	C/C	T/C	T/C	T/C: Syngas
Thermal Stage Additive	None	Fe 203	FeOOHimp	AHM
CONDITIONS				
Space Velocity, Kg coal/h/M^3 reactor	328	328	301	311
Temperature RX-1, deg C	399	448	427	388
Temperature RX-2, deg F	441	399	412	301
Catalyst Age, coal/kg cat.	256	1101	228	234
RESULTS				
C1-C3 Gases, W% MAF Coal	9.19	17.41	11.79	6.56
H_2 Consumption, W% MAF Coal	8.33	8.31	9.28	7.73
Coal Conversion, W% MAF Coal	91.1	92.4	92.7	92
Resid Conversion, W% MAF	88.5	87.7	88.3	89.9
C4 To 524 C Distillates, W% MAF Coal	67.2	55.8	64.1	64.6
W% HDN	76	69	87	85
HYDROGEN EFFICIENCY, kg Distillates/kg Hydrogen	8.07	6.72	6.91	8.36

TABLE 2.3.14

PROCESS PERFORMANCE FOR BENCH SCALE OPERATION
High Space Velocity Operations

RUN	CC-1	CC-4	CC-7	CC-7	CMSL-3
CONFIGURATION	C/C	CC+Fe203	C/T	T/C	T/C: Syngas
Thermal Stage Additive	None	Fe 203	Fe203	FeOOHimp	AHM
CONDITIONS					
Space Velocity, Kg coal/hr/ft^3 reactor	497	485	473	496	424
Temperature RX-1, deg C	399	399	399	448	399
Temperature RX-2, deg C	439	442	448	399	427
Catalyst Age, coal/kg cat.	617	819	801	976	419
RESULTS					
C1-C3 Gases, W% MAF Coal	6.6	7.72	12.25	15.26	5.84
H_2 Consumption, W% MAF Coal	6.63	7.78	7.58	7.96	6.97
Coal Conversion, W% MAF Coal	88.6	86.8	93.3	91.3	90.1
Resid Conversion, W% MAF	81.5	85.4	89	89.1	85.8
C4 To 524 C Distillates, W% MAF Coal	59.2	6.1	60.5	59.4	62
W% HDN	60.7	73.9	55.1	71.2	72.4
HYDROGEN EFFICIENCY	8.93	7.85	7.98	7.45	8.9

TABLE 2.3.15

COMPARISON OF THE RECYCLE OIL PROPERTIES

Run	CC-1	CC-15	CMSL-3
Period Number	10	8	9
Second Stage Catalyst Age, kg Coal/kg Cat.	284	228	234
H_2 Consumption, W% MAF Coal	8.33	9.28	7.73
Temperature, RX-1, deg C	399	427	388
Temperature, RX-2, deg C	441	412	427
API Gravity	10.4	8.4	7.5
Composition, W% PFL			
LGO	30	24.67	12.87
VGO	44.2	42.41	46.37
HVGO	10.8	11.32	15.42
Resid (524 C+)	14.5	20.66	24.56
Elemental, W%			
Carbon	88.89	89.22	89.35
Hydrogen	10.06	9.76	9.6
Nitrogen	0.29	0.57	0.17
Sulfur	0.01	0.04	0.02
H/C Ratio	1.35	1.31	1.29

LGO is the IBP-343 C Boiling Fraction
VGO is the 343-454 C Fraction
HVGO is the 454-524 C Fraction

TABLE 2.3.16

ANALYSIS OF FEED COAL FOR CMSL-3

HRI NO.	5828
Moisture Content	25.4
Proximate Analysis, W% Dry Basis	
Volatile Matter	43.37
Fixed Carbon	50.36
Ash	6.27
Ultimate Analysis, W% Dry Basis	
Carbon	70.4
Hydrogen	3.88
Sulfur	0.44
Nitrogen	0.87
Ash	6.27
Oxygen (by diff.)	18.14
H/C Ratio	0.66
SO3-fresh Ash	5.59

TABLE 2.3.17

ANALYSIS OF START-UP SOLVENT FOR CMSL-3

HRI No.	L-794
API Gravity	14
Elemental Analysis, W%	
Carbon	88.16
Hydrogen	10.48
Sulfur	0.144
Nitrogen	0.35
ASTM D-1160 Distillation, deg F	
IBP	
5 V%	255
10 V%	298
20 V%	316
30 V%	338
40 V%	353
50 V%	371
60 V%	386
70 V%	402
80 V%	428
90 V%	471
	524
WEIGHT PERCENTS	
IBP-343 DEG C	
343-454 DEG C	22.51
454-524 DEG C	51.28
524-+ DEG C	9.97
LOSS	15.42
	0.82
TOLUENE INSOLUBLES, W%	
	1.31

TABLE 2.3.18

THE EFFECT OF PROMOTERS/CATALYSTS ON COAL CONVERSIONS IN MICROAUTOCLAVE TESTS CL-1 THROUGH CL-18 WITH 50/50 CO/H_2 FEED MIXTURE

Run No.	CO/H_2	Catalysts/Promoters	Amount	Coal Conversion	975F+ Conversion
CL-1	50/50	K2CO3	5 W%	55.2	22.8
CL-2	50/50	AHM	300 ppm Mo	50.8	19.4
CL-3	50/50	AHM	1500 ppm Mo	50.6	18.5
CL-4	50/50	AHM/3 WT% DMDS	1500 ppm Mo	52.9	20.3
CL-5	50/50	FEOOH	5000 ppm Fe	40.9	1.7
CL-6	50/50	FEOOH	5000 PPM Fe Wet Coal	34.0	18.6
CL-8	50/50	FE2O3/DMDS	5 W%	54.2	18.6
CL-9	50/50	Recovered Shell-317	5 W%	42.8	13.3
CL-10	50/50	None	----	41.0	10.8
CL-11	70/30	K2CO3	5 W%	54.7(53.7)	25.2
CL-12	70/30	Recovered Shell-317	5 W%	55.7(52.1)	19.9
CL-13	0/100	AHM	1500 ppm Mo	48.2	17.6
CL-14	0/100	Recovered Shell-317	5 W%	48.9	20.6
CL-15	50/50	Na-Aluminate	4 W%	56.1	22.6
CL-16	50/50	Na Aluminate, 3:1 H_2O:Coal	4 W%	52.7	18.6
CL-17	50/50	Na Aluminate	2 W%	54.3	19.5
CL-18	50/50	Na Aluminate/ 30 Min. Test	4 W%	62.5	26.2

TABLE 2.3.19

Effect of Different Catalysts/Promoters on Coal Liquefaction under Water-Gas Shift Conditions with Pure CO as Feed Gas.

Test No.	Catalyst	W% Added	% Coal Conv.	% Resid Conv.
CL-37	K_2CO_3	5.0	76	43
CL-38	AHM	1500ppm	63	27
CL-39	AHM+DMDS[b]	1500ppm	70	39
CL-40	DMDS	3.0	69	33
CL-41[d]	K_2CO_3	5.0	72	42
CL-42[d]	AHM/DMDS	1500ppm	64	28
CL-43	Shell-317	100	75	41
CL-44	$NaAlO_2$	4.0	77	38
CL-45[c]	K_2CO_3	5.0	75	38
CL-46	K_2CO_3	5.0	70	29
CL-47	$NaAlO_2$	4.0	78	34

[a] relative to MF coal added.

[b] the amount of DMDS added was 3 w% relative to MF coal.

[c] this run was carried out for 60 minutes of reaction time.

[d] using undried L-780 coal.

Table 2.3.20

Effect of Different Catalysts/Promoters on Water-Gas Shift Conversion

Test No.	Solvent	Catalyst/Promoter	%CO Conversion[1]
CL-74	Yes	K2CO3, 5 W% of 2.0g	14.02
CL-75	no	==same=	14.70
CL-76	yes	NaAlO2, 4 W% of 2.0 g	11.21
CL-77	no	NaAlO2, 4 W% of 2.0 g	17.50
CL-78	yes	Fe2O3, 0.1 g	3.91
CL-79	no	Fe2O3, 0.1 g	5.75
CL-80	yes	AHM+DMDS[2]	20.2
CL-81	no	AHM+DMDS	27.9
CL-82	yes	None	8.20
CL-83	no	None	12.7
CL-84	yes	Amocat 1A[3]	31.2
CL-85	no	Amocat 1A	29.6

---

[1] %CO conversion in the WGS reaction was calculated as %CO_2 in the products/(%CO+%CO_2) in the products. This definition was used for CO-conversion by the WGS reaction because there was NO contribution to product CO_2 from coal in these tests.

[2] 375 ppm Mo (relative to 8.0 g of the solvent) was used as ammonium heptamolybdate with 3% DMDS.

[3] This is a Co-Mo/Al_2O_3 catalyst.

FIGURE 2.3.1

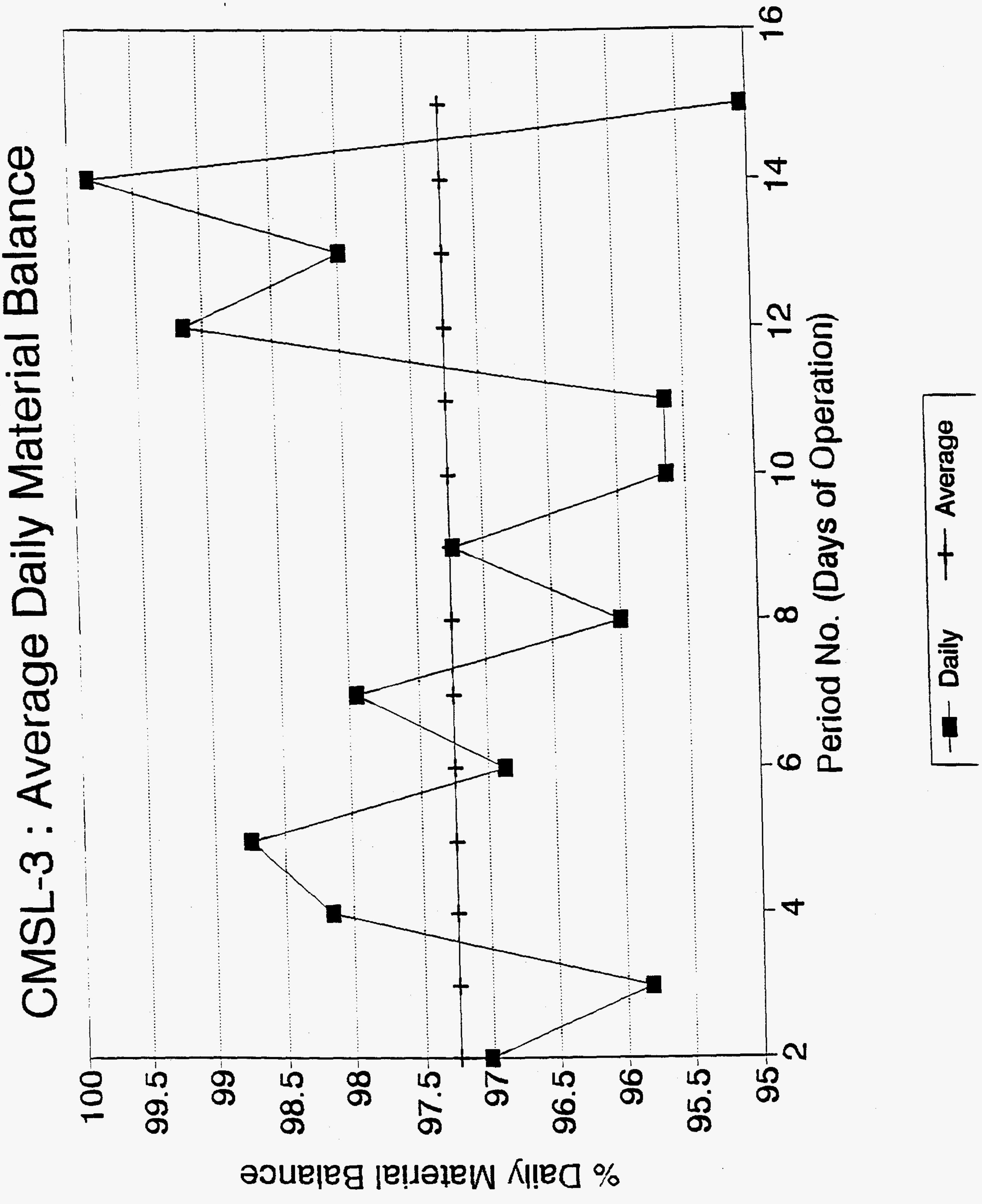
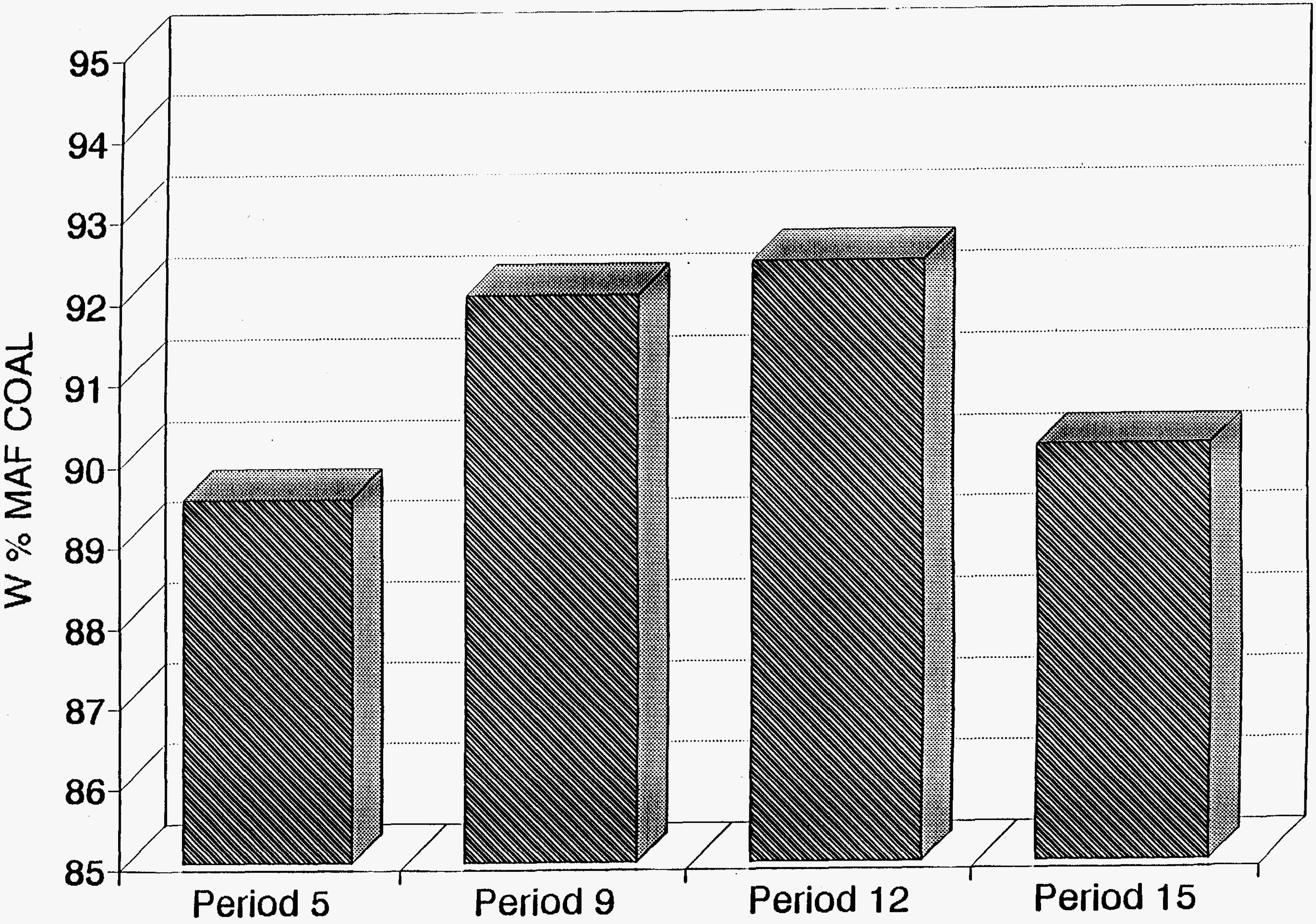
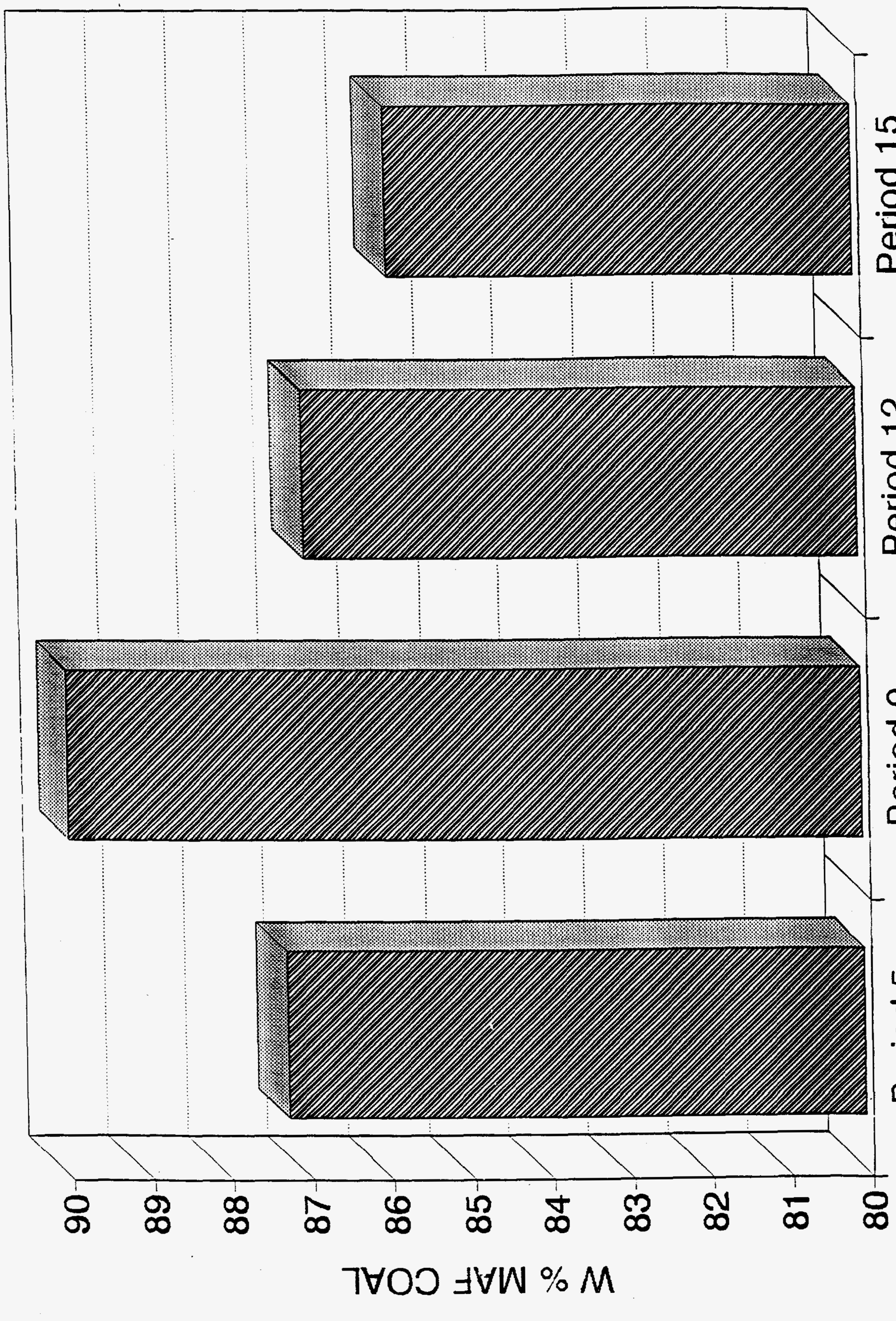

CMSL-3 : Average Daily Material Balance
% Daily Material Balance
100
99.5
99
98.5
98
97.5
97
96.5
96
95.5
95
2
4
6
8
10
12
14
16
Period No. (Days of Operation)
Daily
Average

FIGURE 2.3.2

CMSL-3 : COAL CONVERSIONS FOR WORK-UP PERIODS



CMSL-3 : 524 C+ RESID CONVERSIONS FOR WORK-UP PERIODS



CMSL-3 : HYDROGEN CONSUMPTION FOR WORK-UP PERIODS

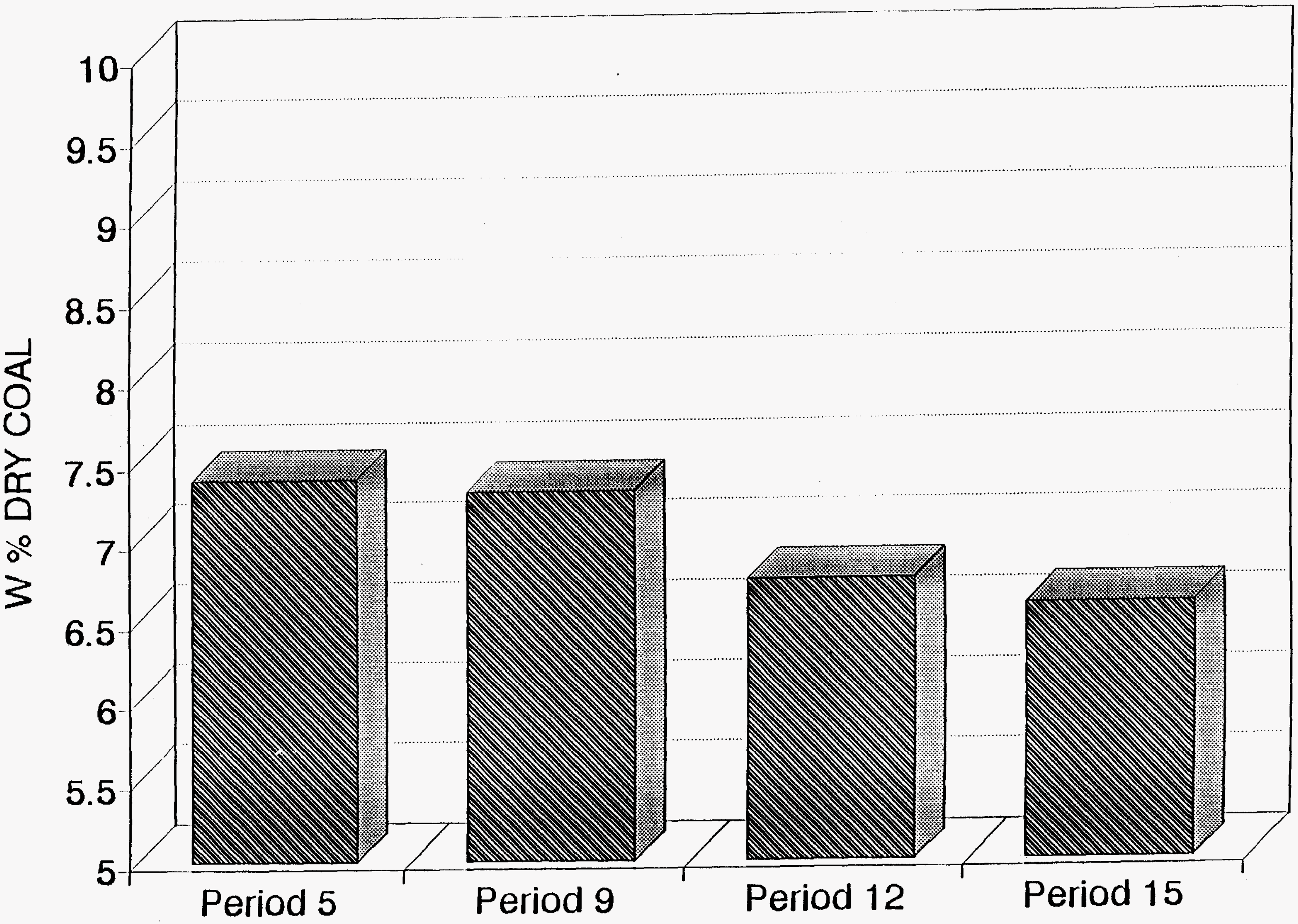


FIGURE 2.3.4

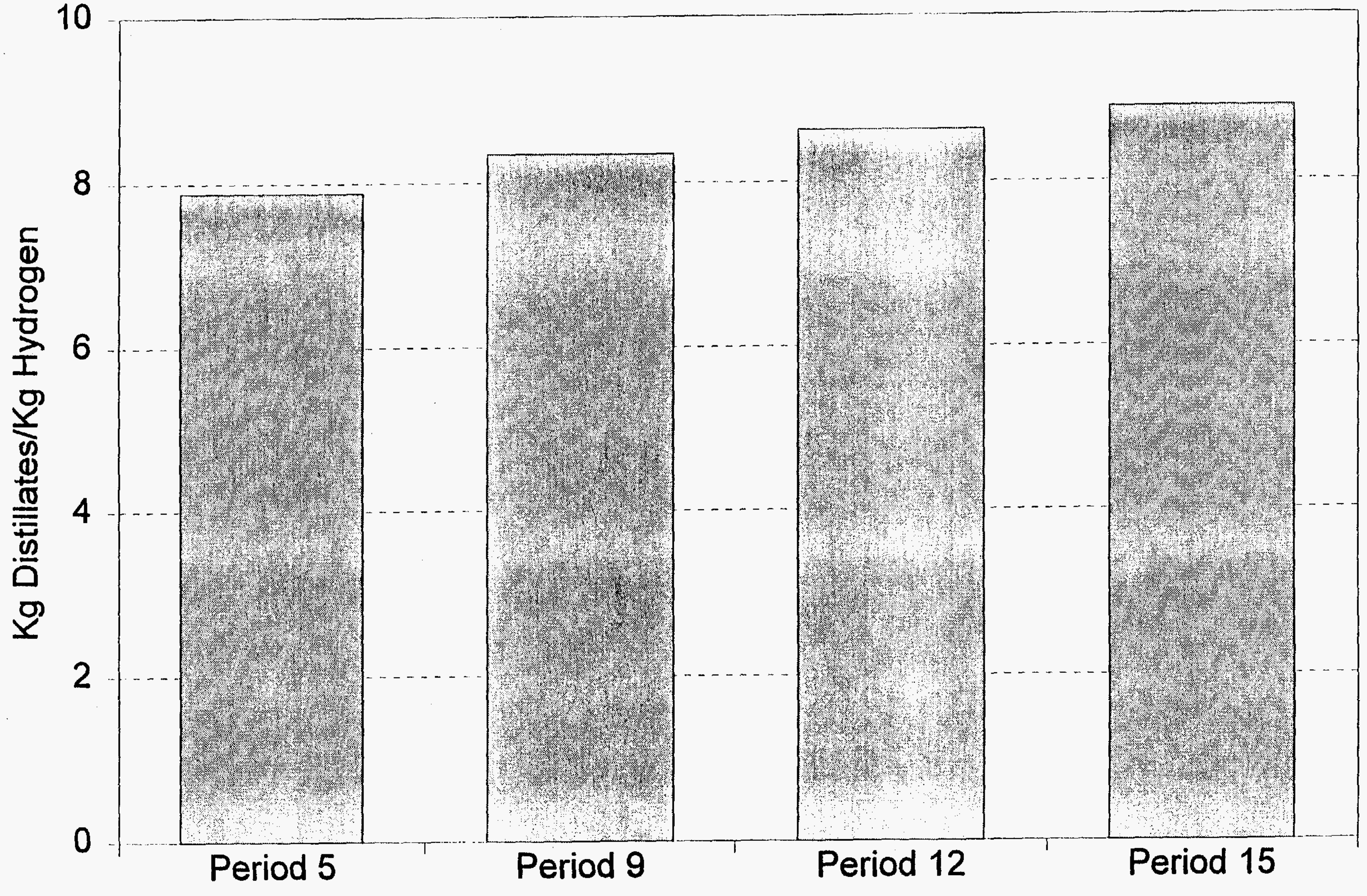

CMSL-3 : HYDROGEN EFFICIENCY
FOR WORK-UP PERIODS

FIGURE 2.3.5

CMSL-3 : HYDRODENITROGENATION FOR WORK-UP PERIODS

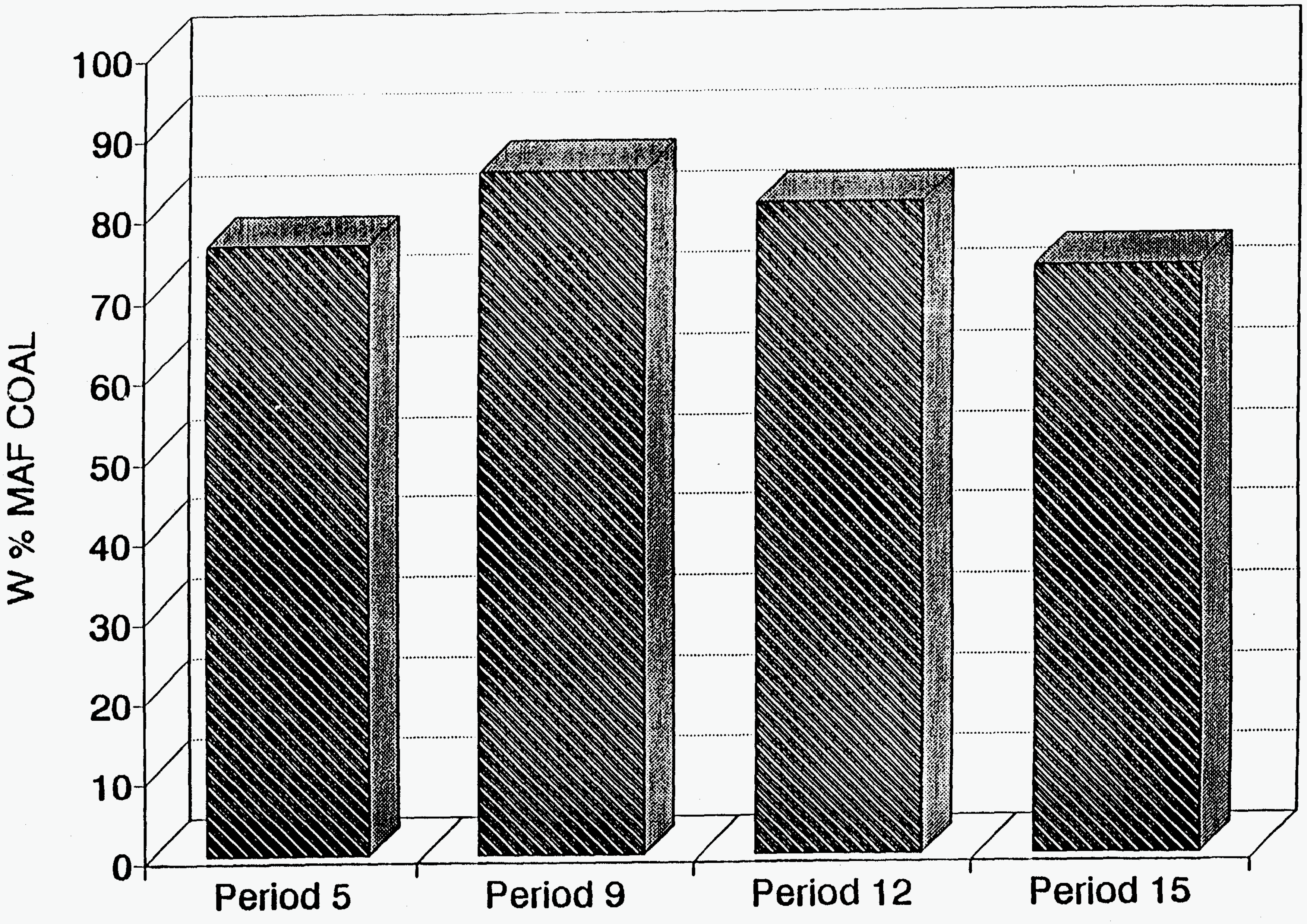


FIGURE 2.3.6

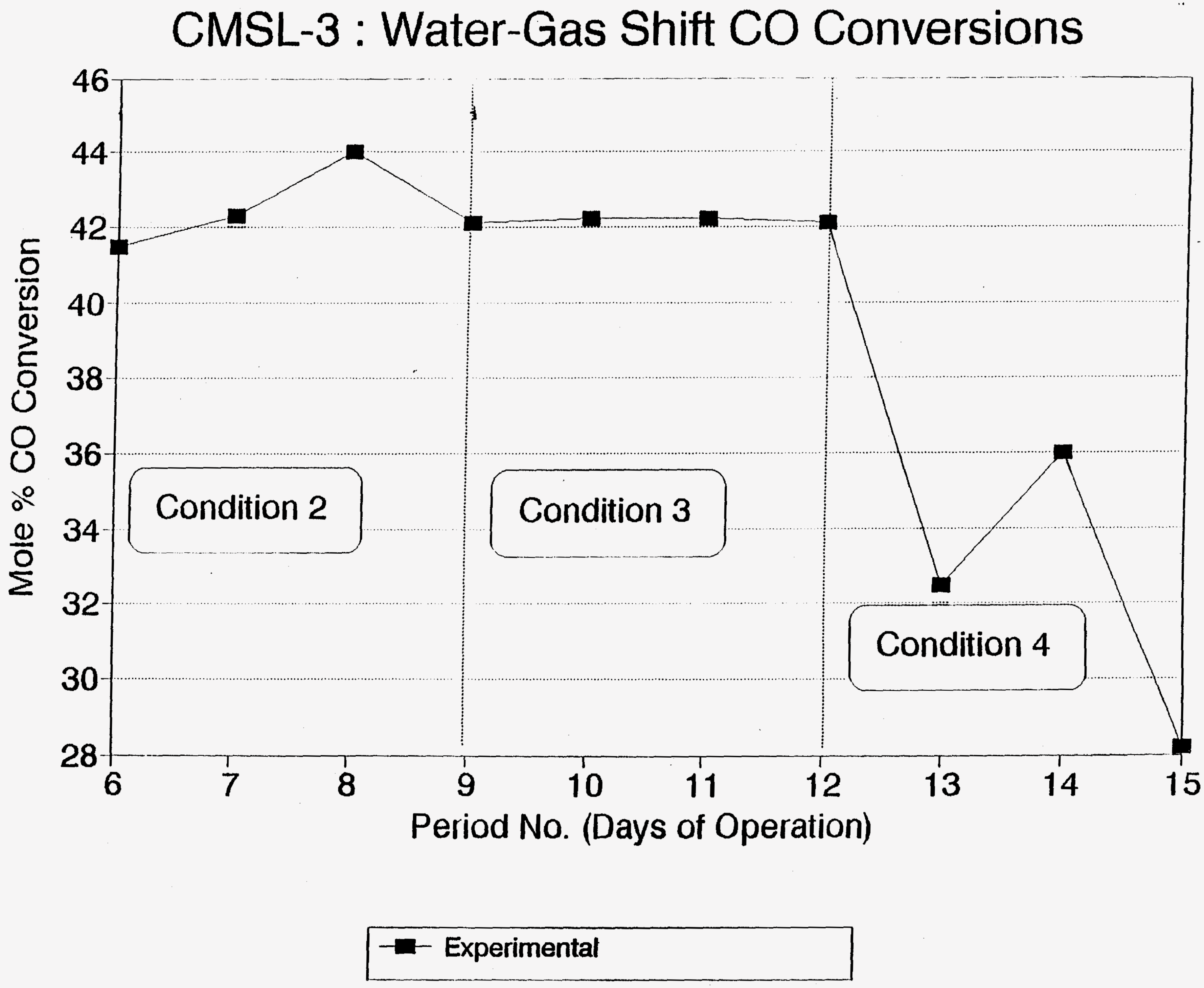
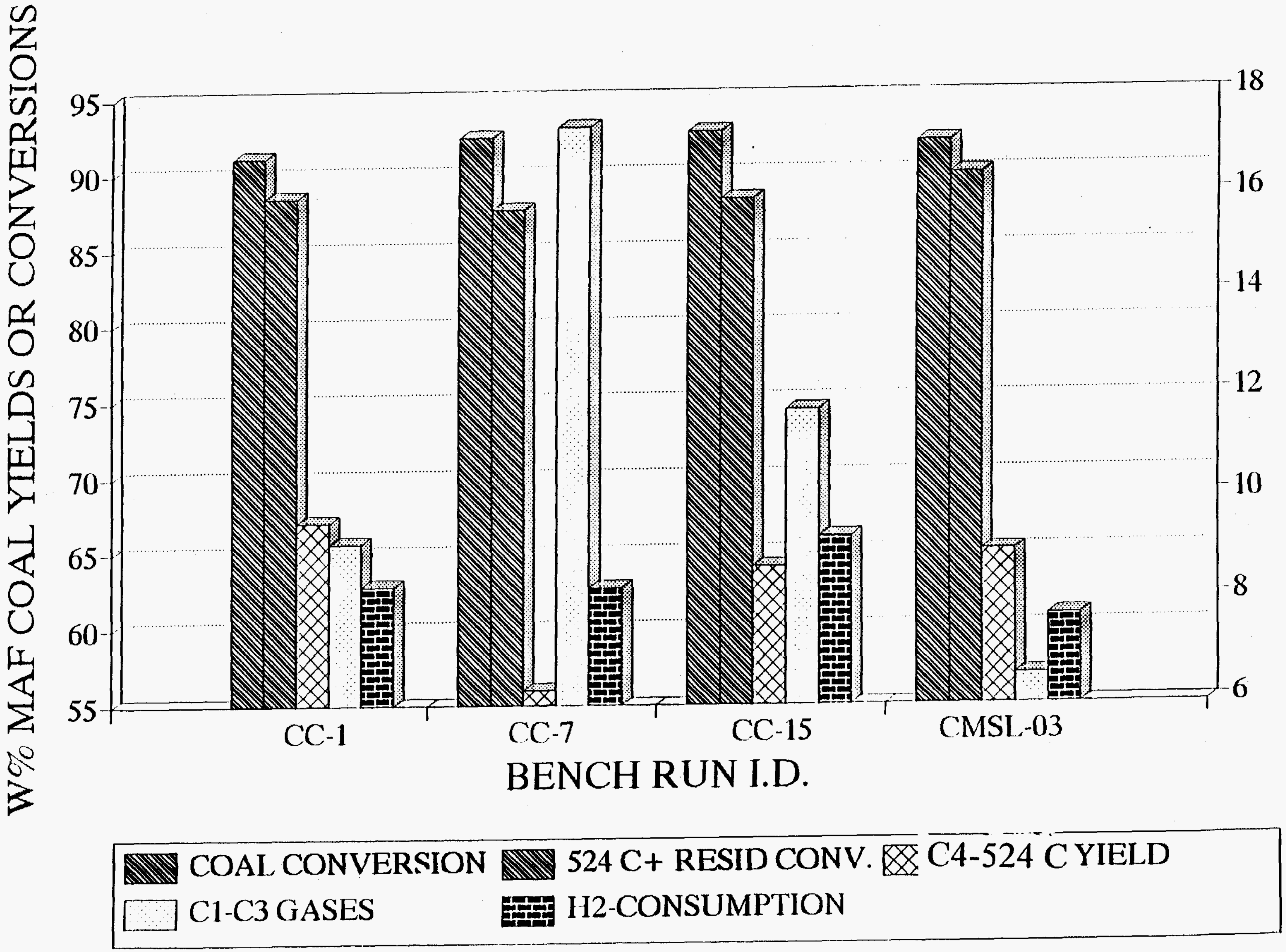

CMSL-3 : Water-Gas Shift CO Conversions
Mole % CO Conversion
46
44
42
40
38
36
34
32
30
28
6
7
8
9
10
11
12
13
14
15
Period No. (Days of Operation)
Condition 2
Condition 3
Condition 4
Experimental

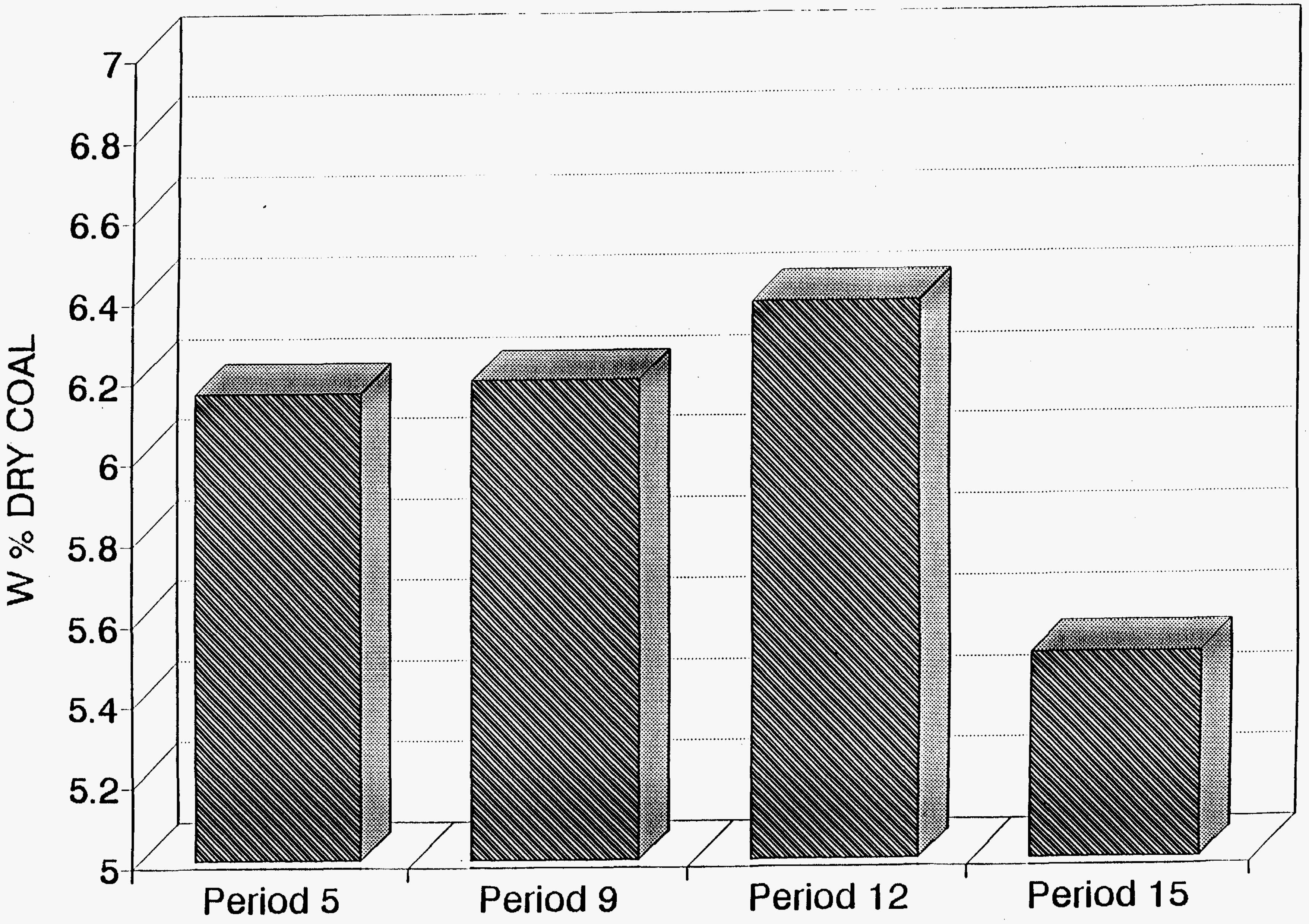
FIGURE 2.3.7

FIGURE 2.3.8

Effect of Using Synthesis Gas (CO/H2) for the CTSL of a Subbituminous Coal



CMSL-3 : C1-C3 GAS YIELDS FOR WORK-UP PERIODS



CMSL-3 : Yields of Different Boiling Fractions for Work-up Periods

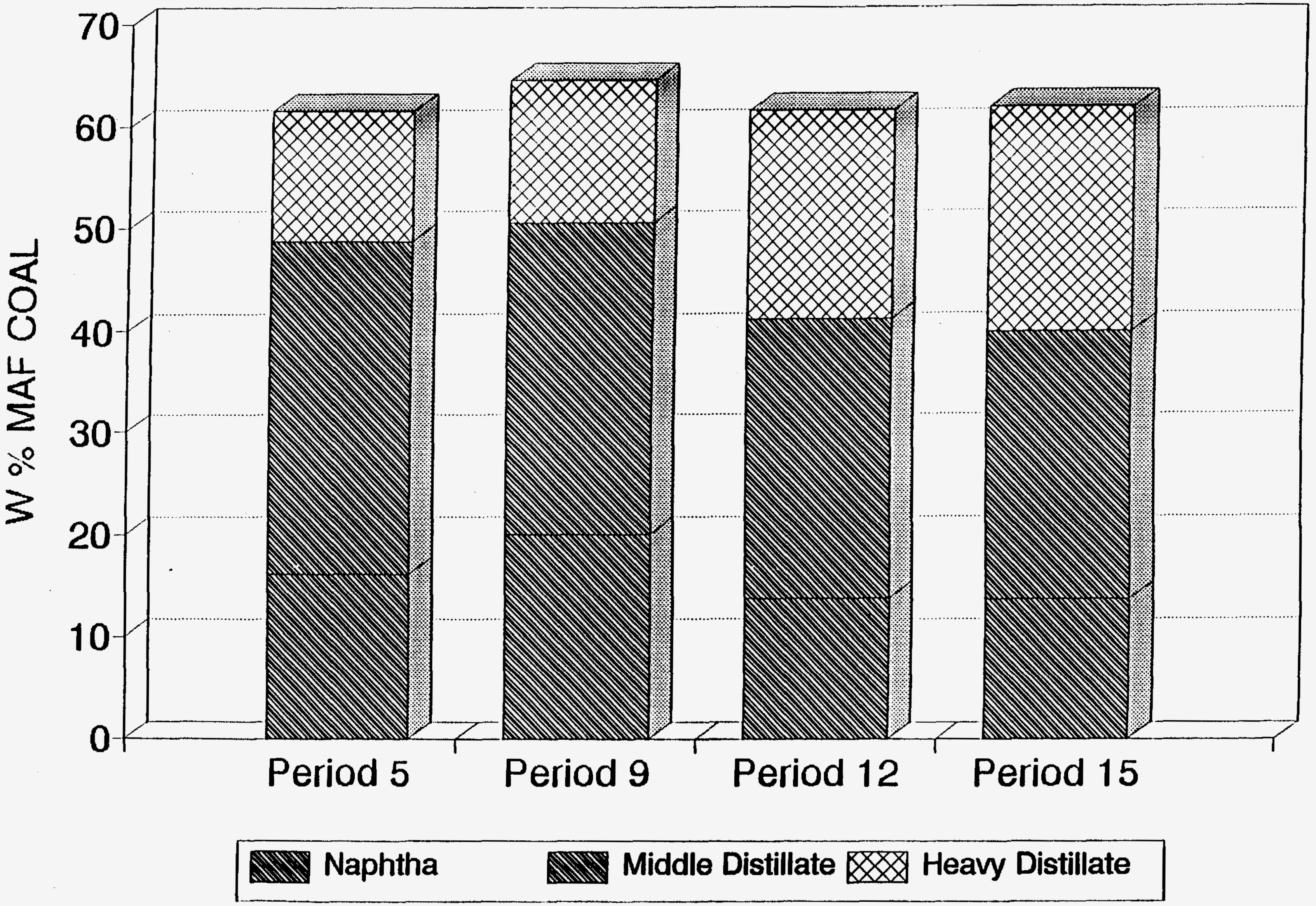
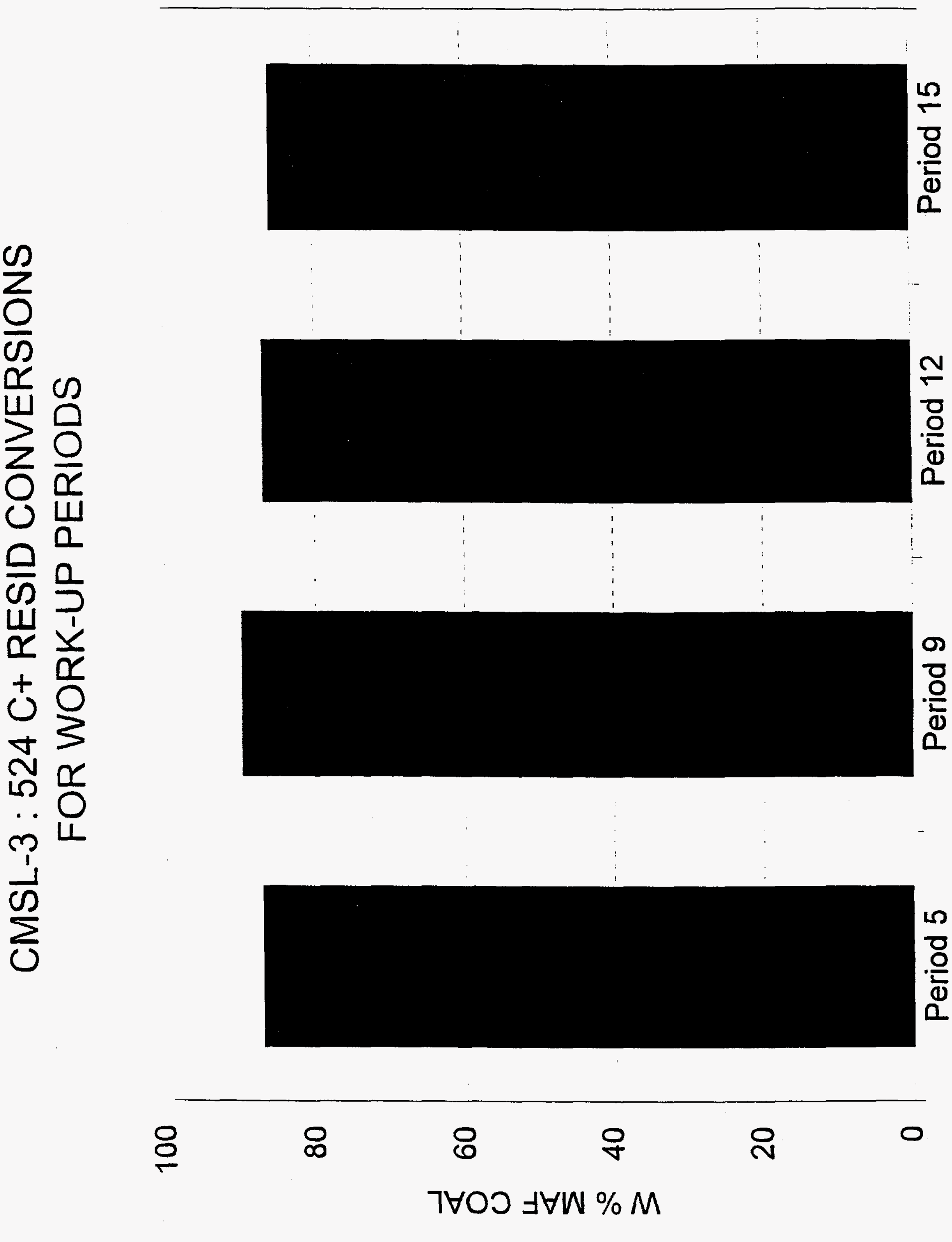


FIGURE 2.3.10

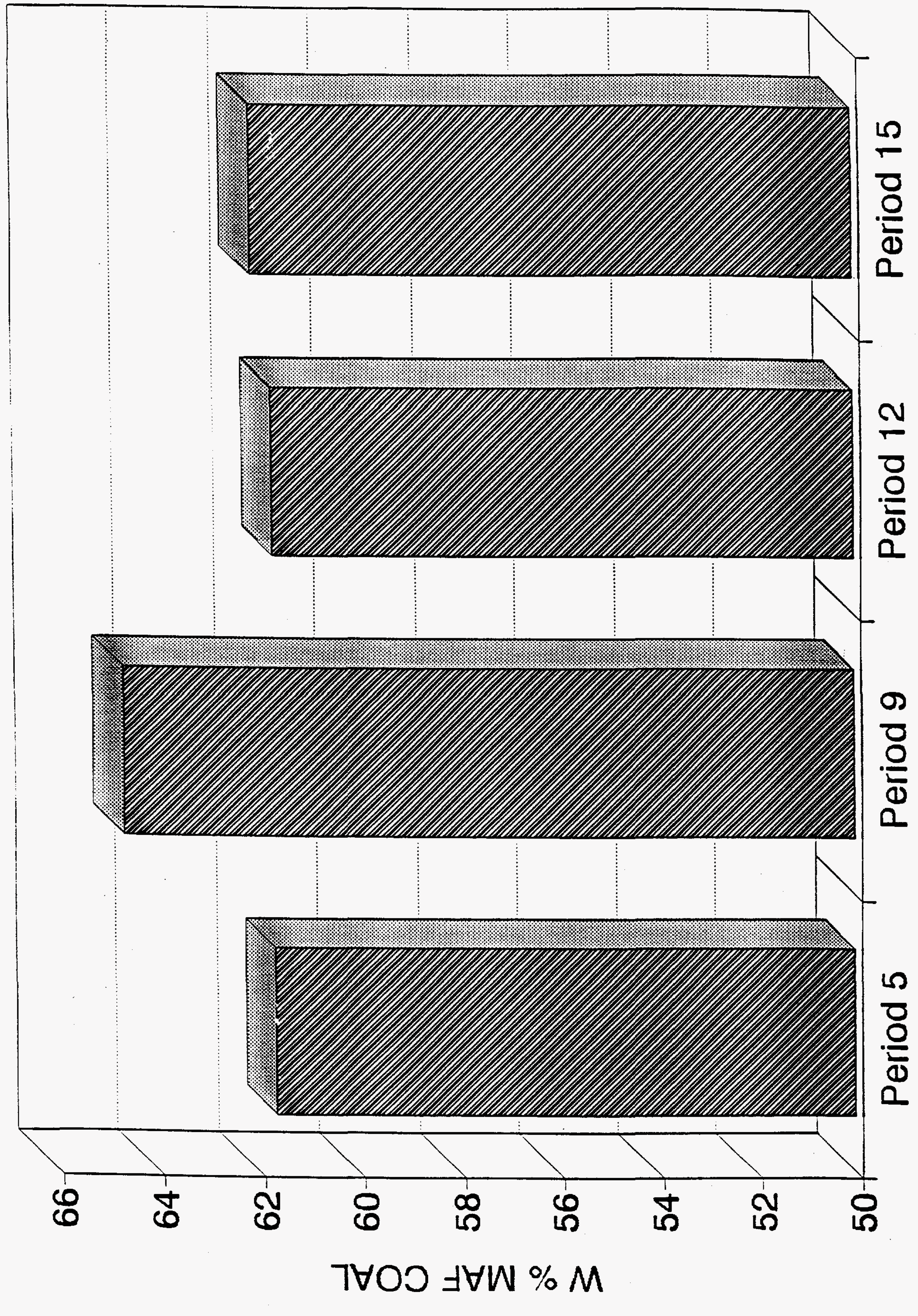
FIGURE 2.3.11



CMSL-3 : 524 C+ RESID CONVERSIONS FOR WORK-UP PERIODS

FIGURE 2.3.12

CMSL-3 : C4-524 C DISTILLATE YIELDS FOR WORK-UP PERIODS



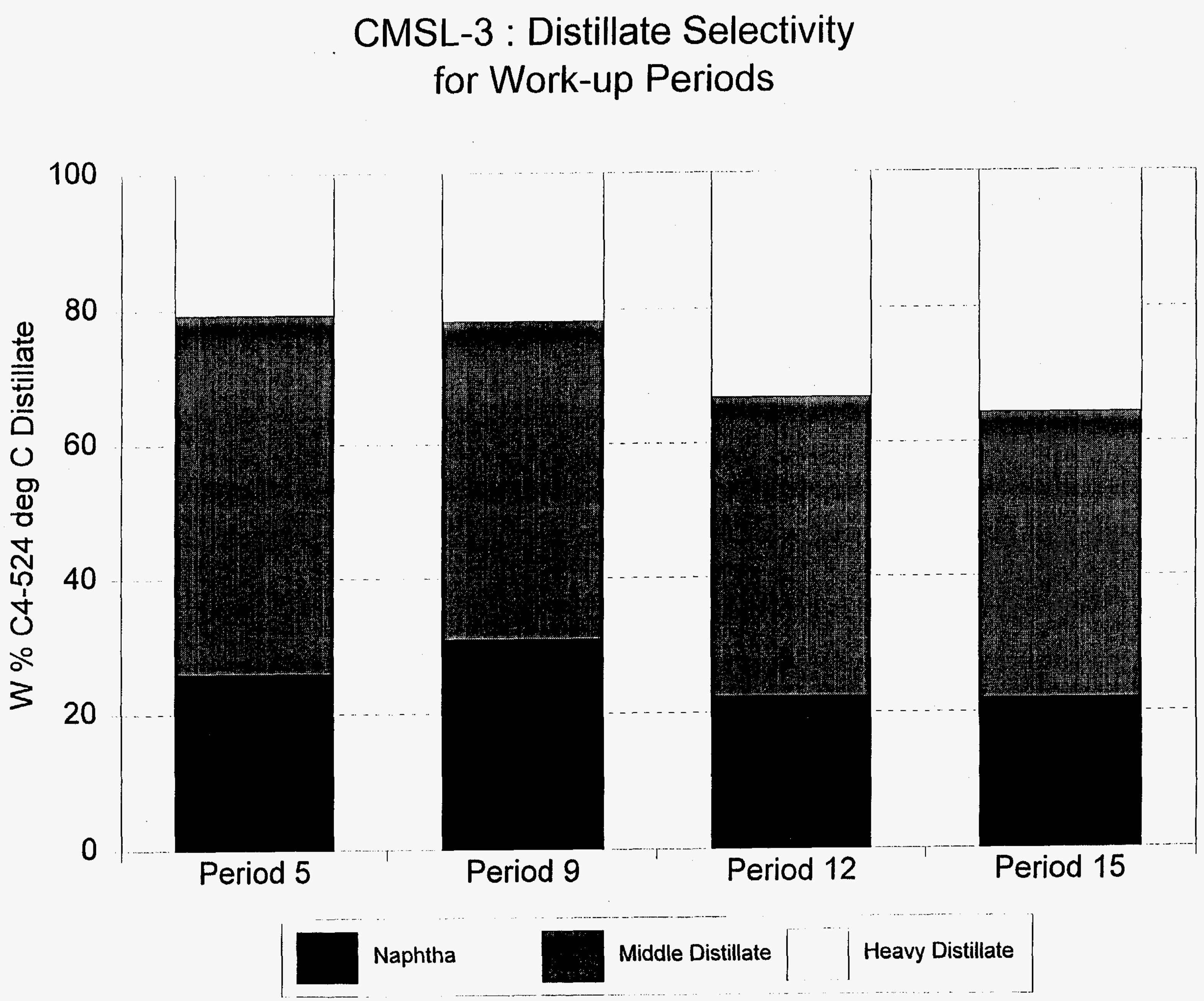

CMSL-3 : Distillate Selectivity
for Work-up Periods
W % C4-524 deg C Distillate
100
80
60
40
20
0
Period 5
Period 9
Period 12
Period 15
Naphtha
Middle Distillate
Heavy Distillate

FIGURE 2.3.13

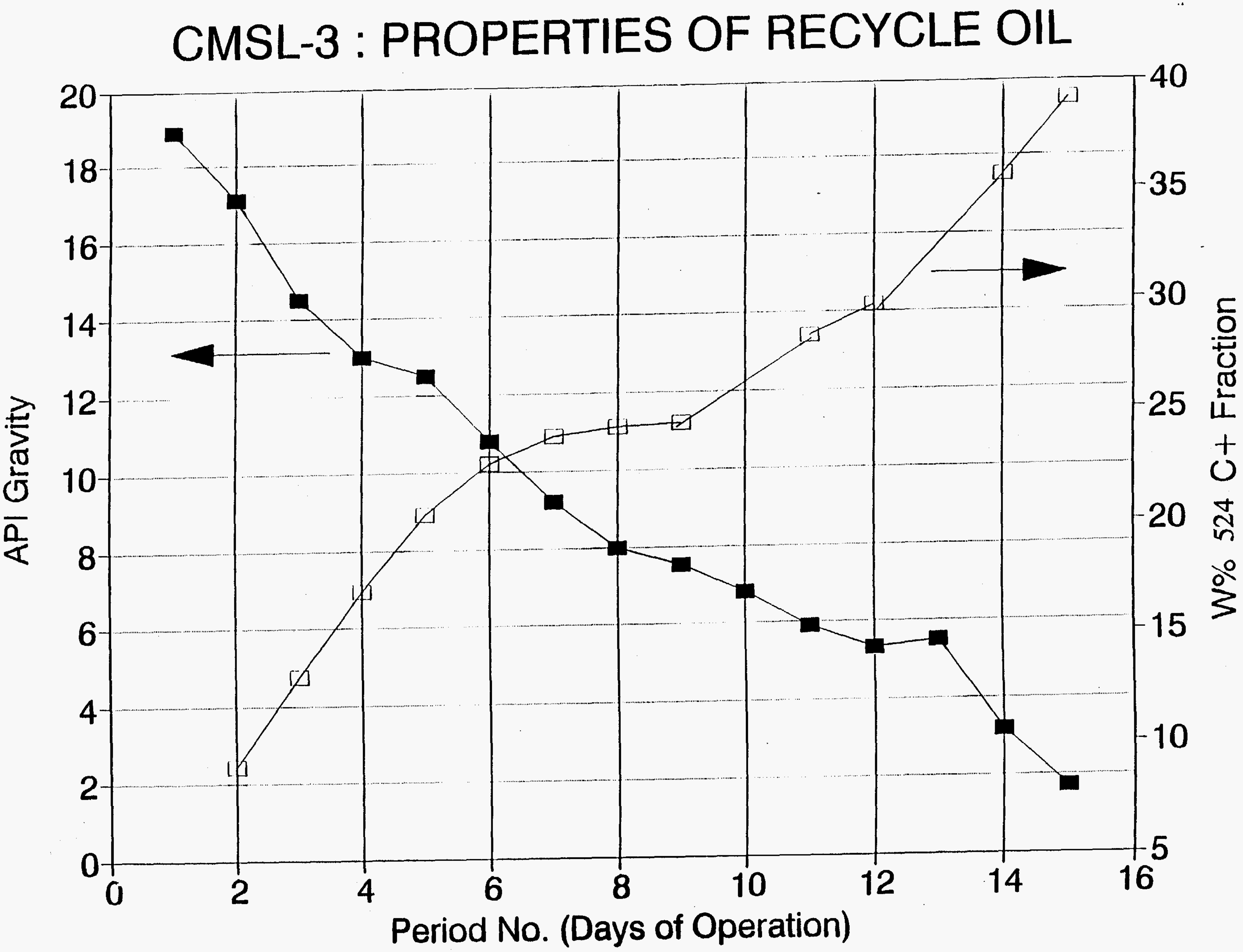

CMSL-3 : PROPERTIES OF RECYCLE OIL

FIGURE 2.3.14

CMSL-3 : EFFECT OF SYNTHESIS GAS
Comparison of Recycle Oil Properties

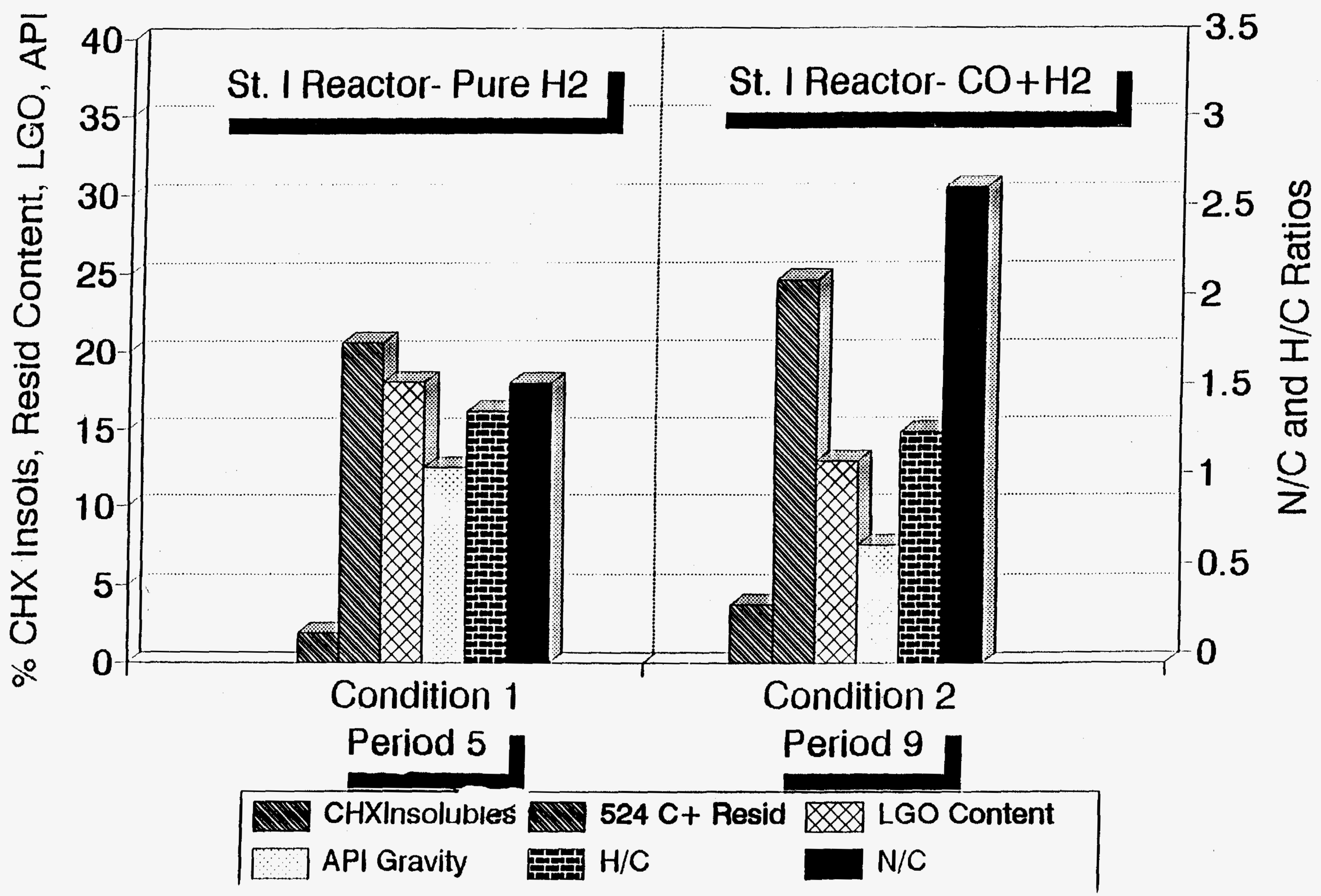
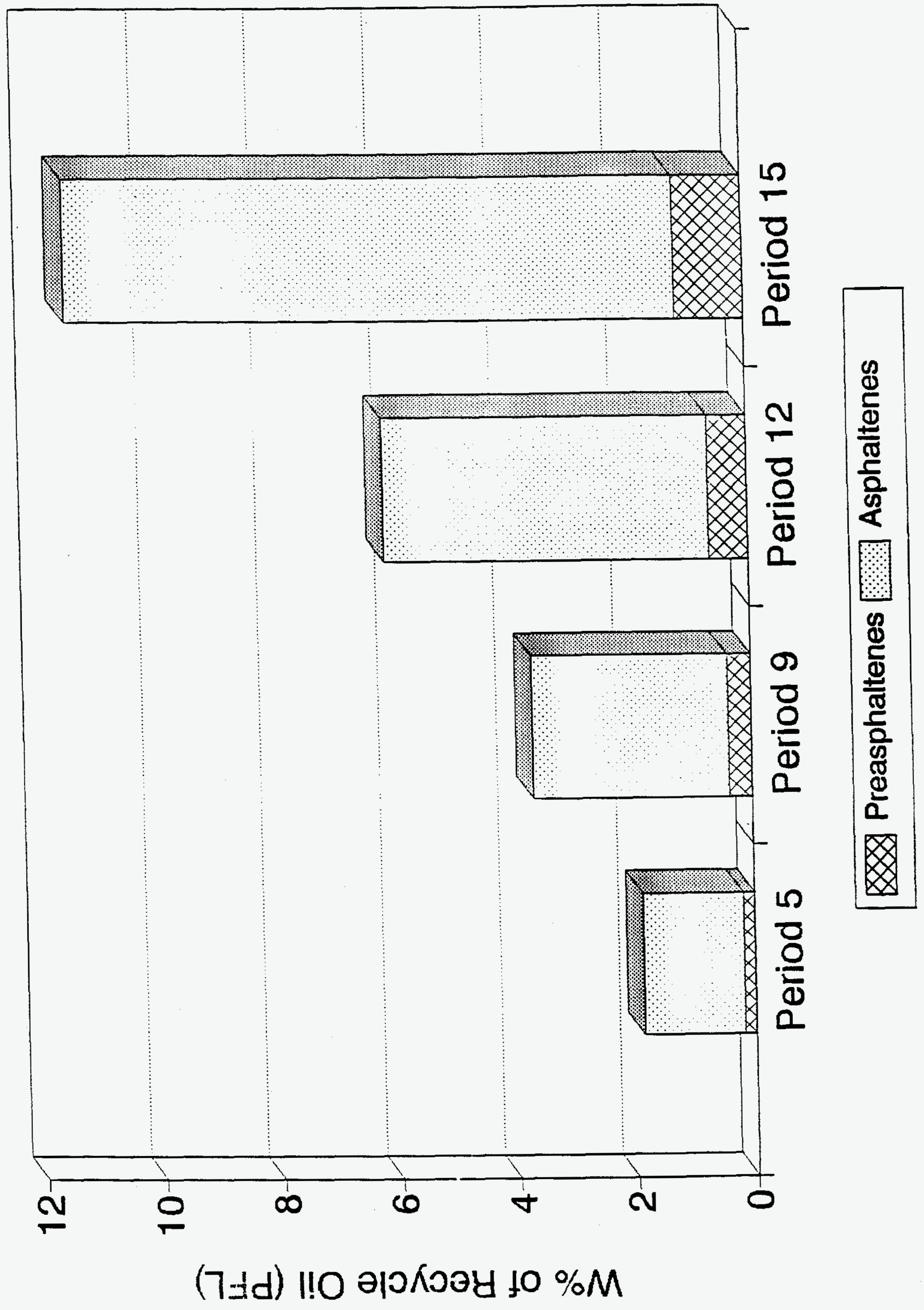


FIGURE 2.3.15



CMSL-3 : Asphaltene & Preasphaltene Contents of the Recycle Oil

COMPARISON OF PROCESS PERFORMANCE BETWEEN DIFFERENT BENCH RUNS

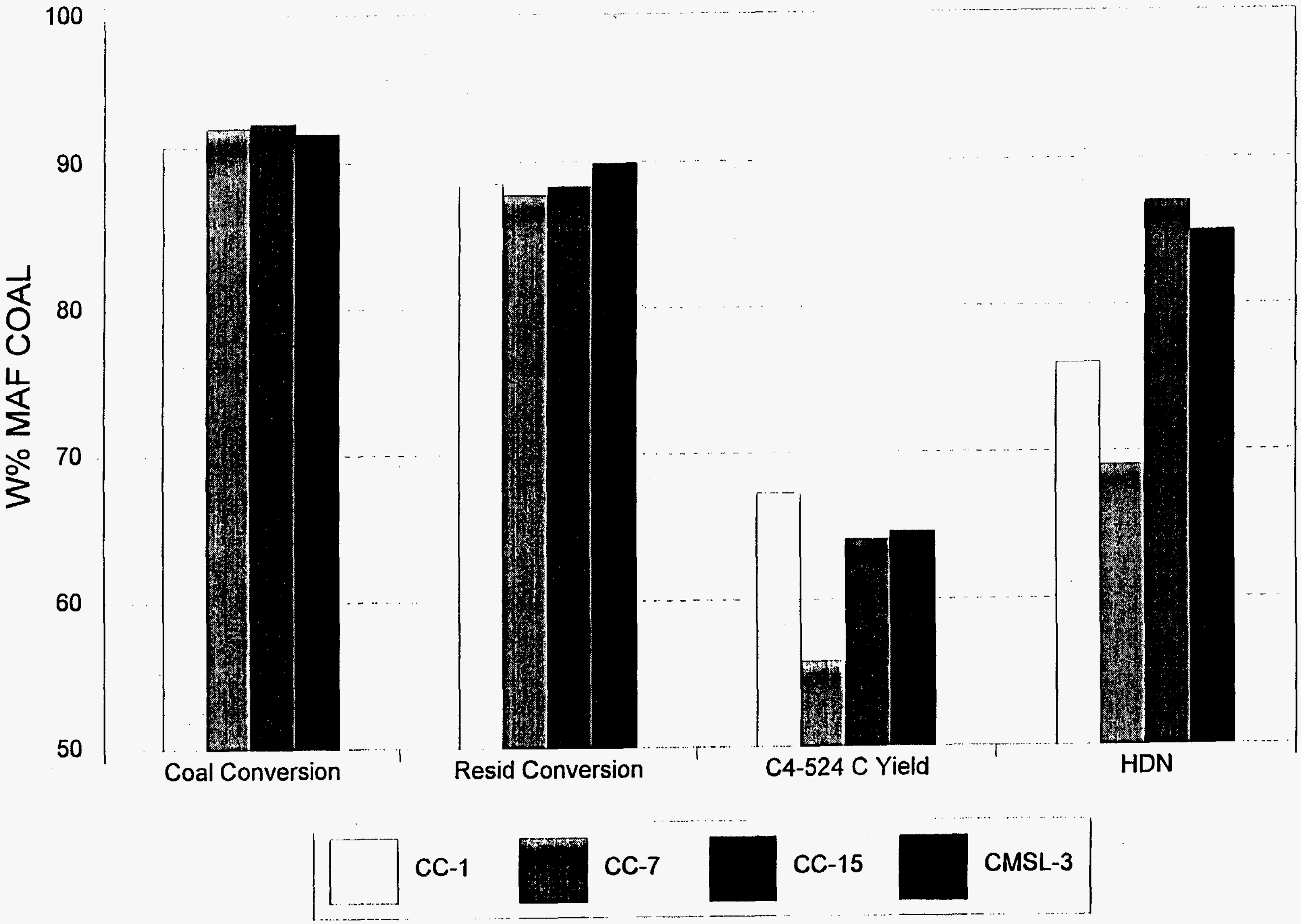


FIGURE 2.3.17

COMPARISON OF H2-UTILIZATION BETWEEN DIFFERENT BENCH RUNS

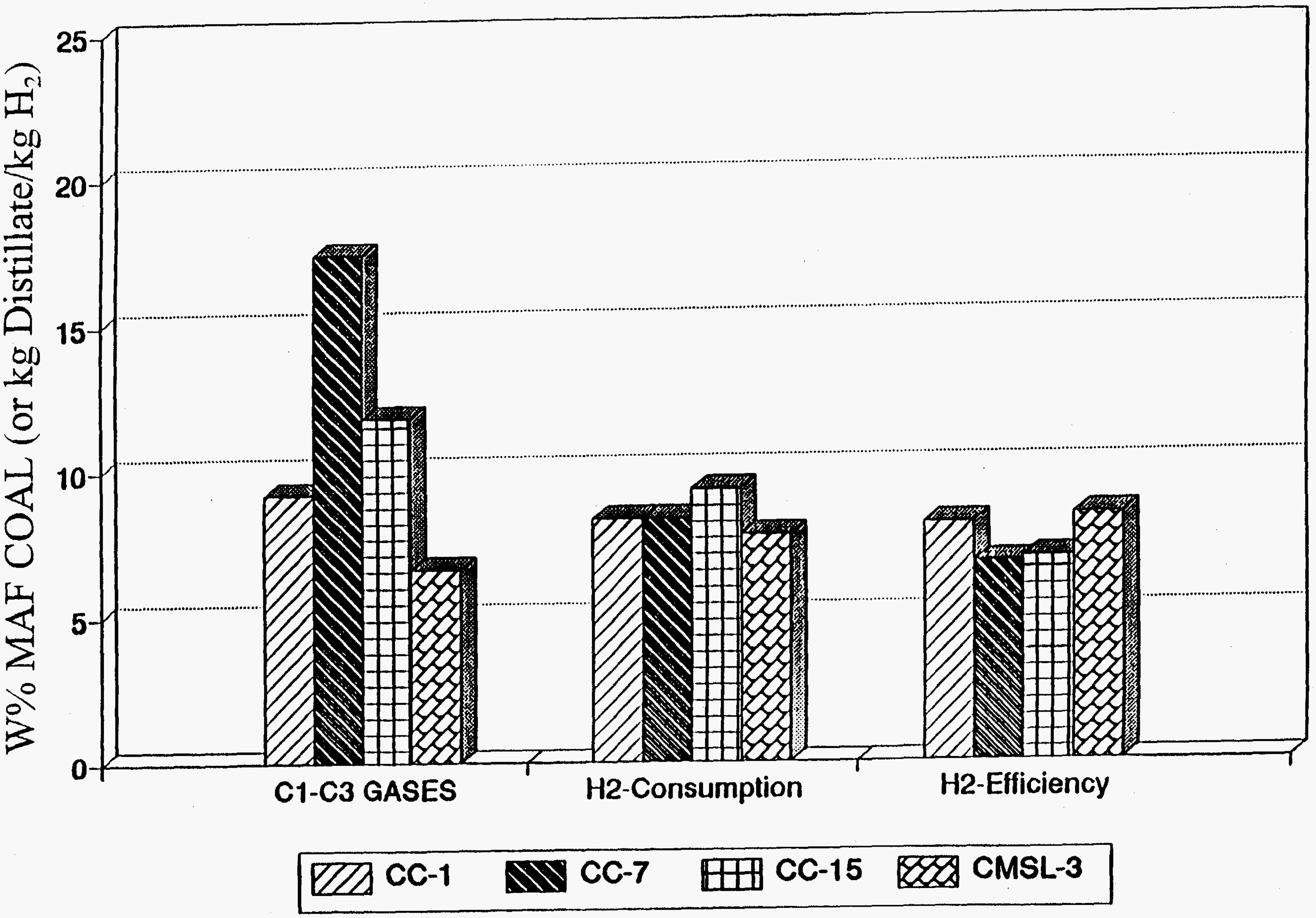
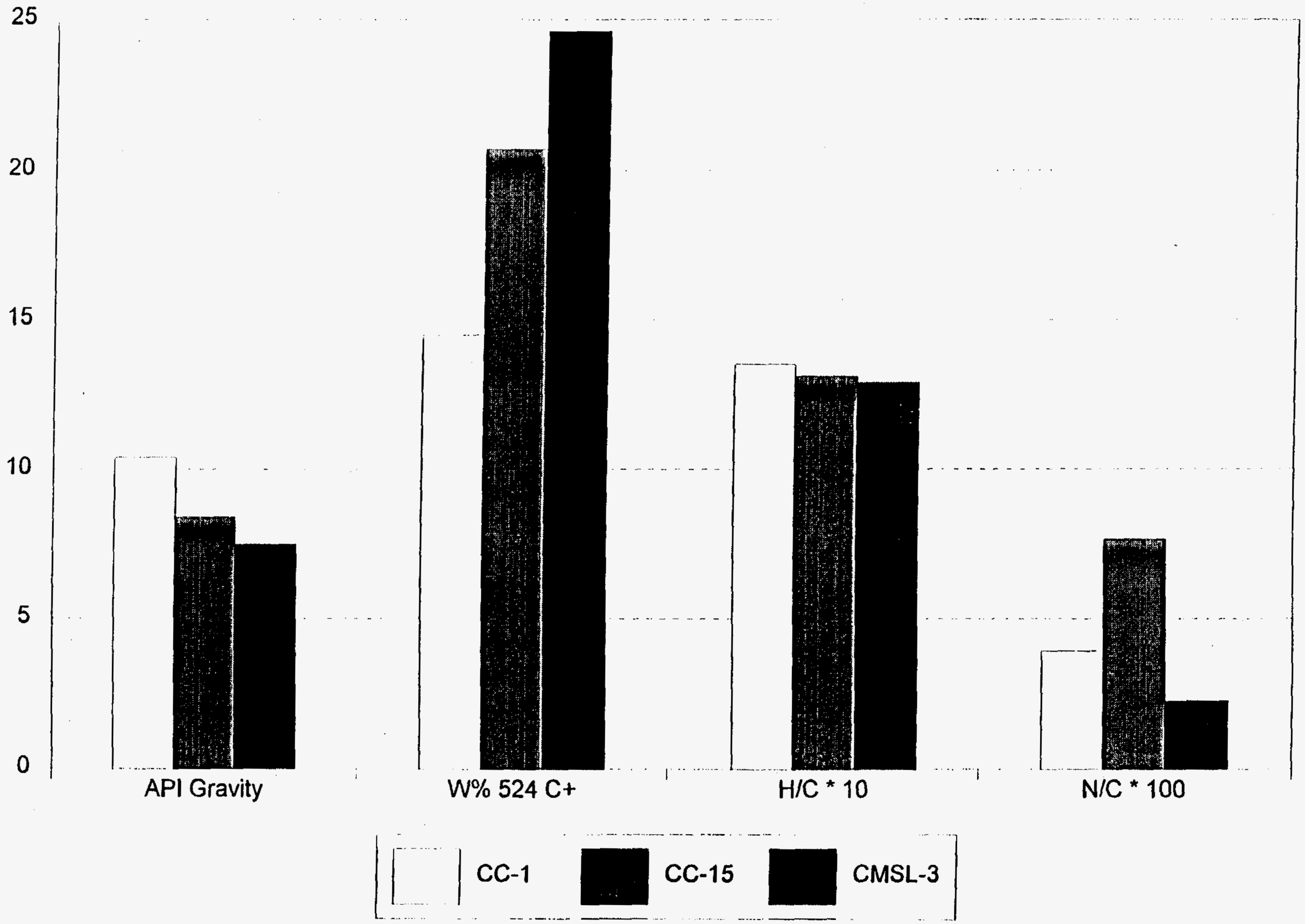


FIGURE 2.3.18

FIGURE 2.3.19

COMPARISON OF RECYCLE OIL PROPERTIES BETWEEN DIFFERENT BENCH RUNS



CMSL-3 : Daily Stage Temperatures & Coal Space Velocities

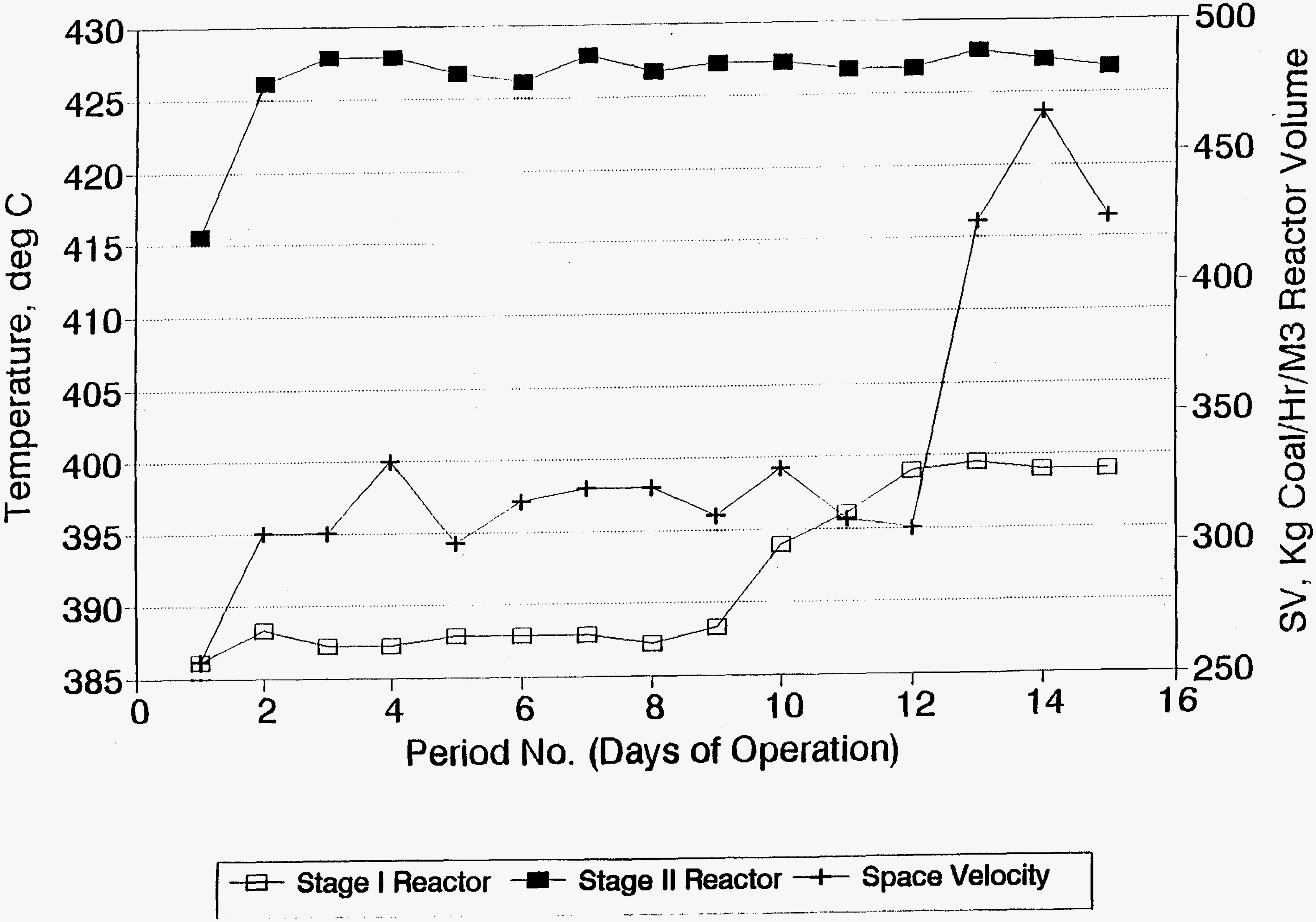
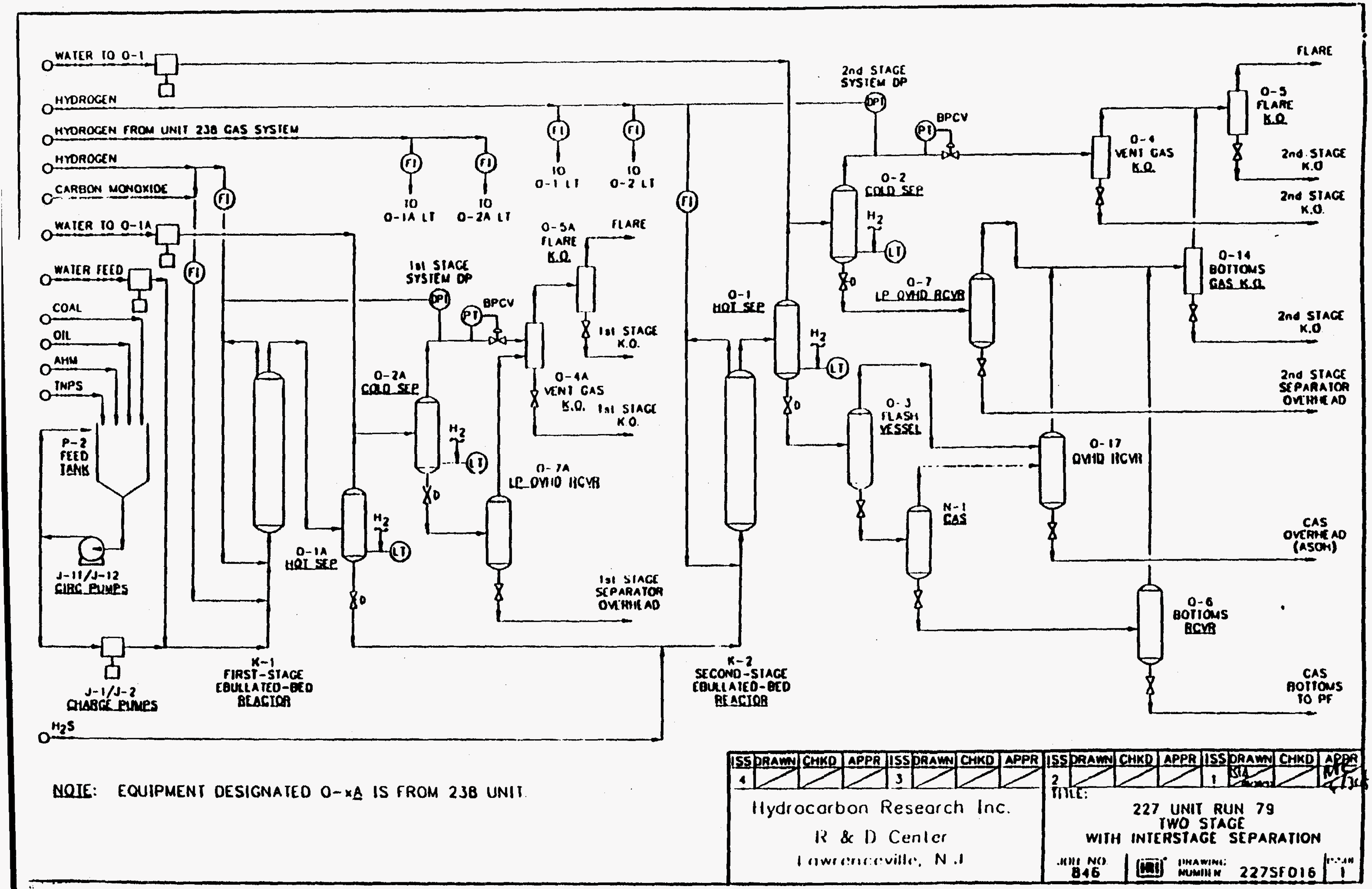


FIGURE 2.3.20



NOTE: EQUIPMENT DESIGNATED O-xA IS FROM 238 UNIT.

ISS	DRAWN	CHKD	APPR	ISS	DRAWN	CHKD	APPR	ISS	DRAWN	CHKD	APPR	ISS	DRAWN	CHKD	APPR
4				3				2				1			

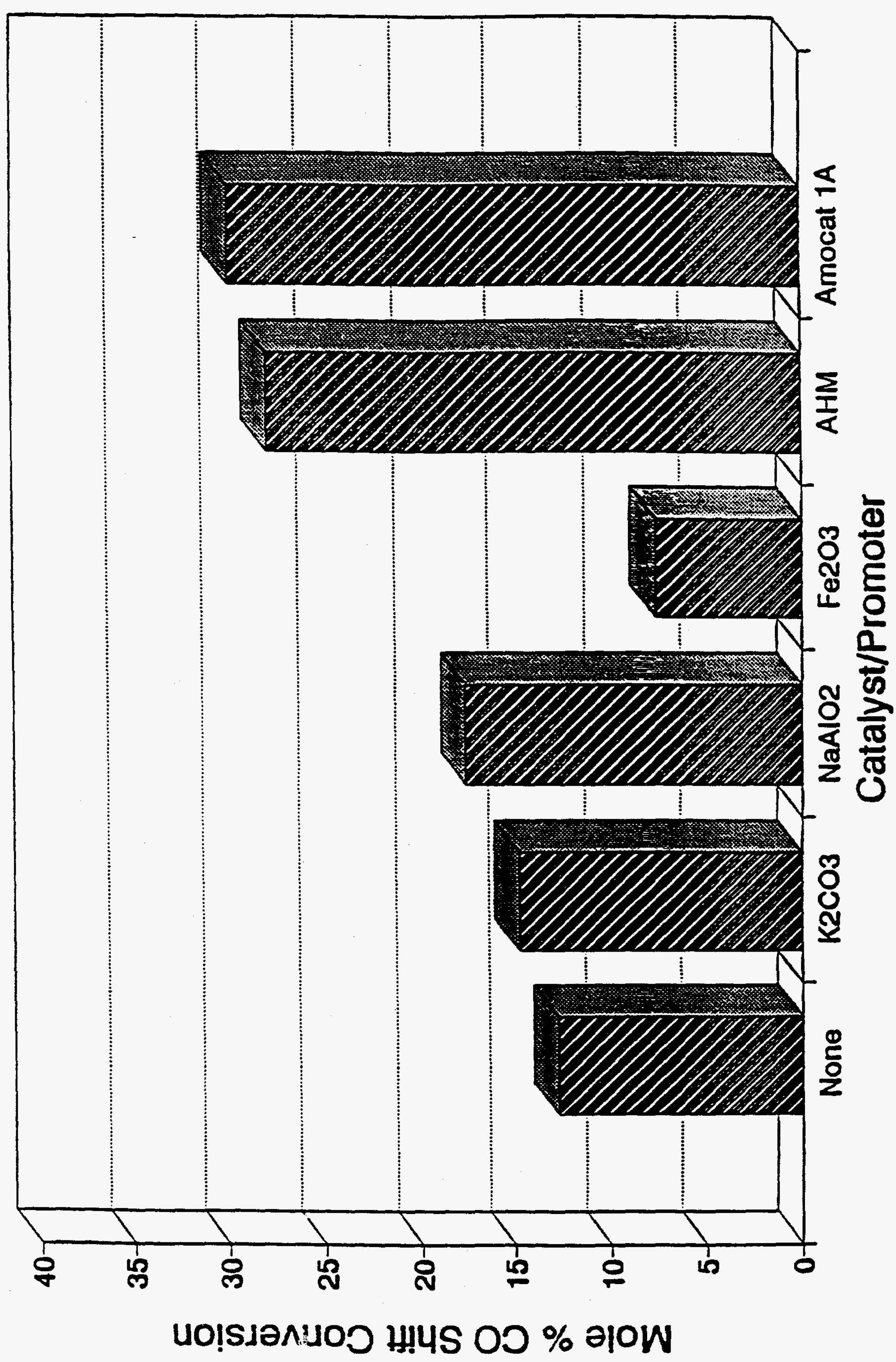
Hydrocarbon Research Inc.
R & D Center
Lawrenceville, N.J

TITLE:
227 UNIT RUN 79
TWO STAGE
WITH INTERSTAGE SEPARATION

JOB NO. 846
HRI
DRAWING NUMBER 227SF016
1

FIGURE 2.3.21

FIGURE 2.3.22



CMSL-3 : Laboratory Support
Effect of Promoters on Shift Reaction

VOLUME I

SECTION II

RUN CMSL-4

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

VOLUME I

TABLE OF CONTENTS

SECTION II - RUN CMSL-4

Run CMSL-04 (227-81) Impact Of Syngas On Liquefaction In A Catalytic/Catalytic Mode Of Operation

VOLUME I

SECTION II - RUN CMSL-4

LIST OF TABLES

VOLUME I

SECTION II - CMSL-4

LIST OF FIGURES

SECTION II - RUN CMSL-4

RUN CMSL-04 (227-81)
IMPACT OF SYNGAS ON LIQUEFACTION IN A CATALYTIC/CATALYTIC MODE OF OPERATION

1.0 SUMMARY

Under mild liquefaction conditions, first and second stage temperatures of 388°C (730°F) and 427°C (800°F) respectively, the performance of using syngas vs hydrogen as the reducing gas in the CTSL operation in catalytic/catalytic mode was compared. A mixture of syngas and water for the coal solubilization step in stage 1 resulted in an initial coal conversion 3.1% higher than with pure hydrogen and a final steady state value 0.8% higher than the pure hydrogen condition. The residuum conversion was constant for these two conditions even though the catalyst had aged by the time of the syngas condition, indicating that the effect of syngas balances the effect of catalyst aging at this time. The syngas condition also had a higher distillate yield than the hydrogen condition by 0.9 W% MAF coal. Syngas can be used as an effective reducing gas in the first stage of the CTSL process operating in the catalytic/catalytic mode.

Comparison of low and high severity operations with syngas indicates that the high severity operation results in an increase in coal conversion, by 3.2 W% MAF coal, an increase in resid conversion, by 2.7 W% MAF coal, and a shift in distillate selectivity toward the lighter products.

An initial comparison between Periods 12 and 13, performed under identical operating conditions except for Period 13 being "starved" of CO due to a low flow rate, shows the effect of CO feed on process performance. Coal conversion increased by 1.1 W% MAF coal, resid conversion increased by 3.9 W% MAF coal, light gas yield increased by 2.2 W% MAF coal, and distillate selectivity did not change. This fortuitous result should be further investigated to determine why the lower CO flow resulted in improved performance.

2.0 BACKGROUND, OBJECTIVE, AND SCOPE OF WORK

The main objective of this run was to evaluate the effect of reaction severity on the dissolution of Black Thunder Mine subbituminous coal using synthesis gas (CO/H_2) as a reducing gas in the first stage of a two-stage ebullated bed configuration. Additional technical objectives included the determination of the relative performance of using CO/H_2 vs H_2 in the first stage of a fully ebullated two-stage system and determination of the effects of interstage separation as well as on-line hydrotreating on CTSL process performance with synthesis gas.

The production of hydrogen constitutes one of the major operating cost components of a coal liquefaction process. 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 the operating cost by 10-15%. It is known that in the presence of an alkali salt, a mixture of CO/H_2 and water is very effective in solubilizing high oxygen containing low rank coals at relatively mild 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-03 (227-79). The interstage separation used during CMSL-03 was instrumental in removing CO_x off gases, thereby reducing further reforming of these gases to methane/water at the expense of the valuable hydrogen. CMSL-03 operating conditions were identical to those in the run plan for CMSL-04 except that CMSL-03 used a slurry catalyst (ammonium molybdate) instead of a supported catalyst (Shell S-317) in the first stage reactor.

The dissolution of Black Thunder Mine coal was evaluated using H_2 in the first stage at a base condition and the syngas in the first stage at the same base condition as well as at a higher reactor severity in a catalytic/catalytic two-stage operation. The impact of using syngas on liquefaction was evaluated in terms of product quality and overall process performance.

The run plan, *Table 2.4.1,* included four process conditions. The conditions were selected so that the effects of process severity and feed gas composition could be determined for this run, and similar comparisons could be made with Run CMSL-3, which contained Mo 1st Stage supported catalyst. The actual operating conditions are presented in *Table 2.4.2*. A simplified process schematic is presented in *Figure 2.4.1.*

3.0 PROGRAM ANALYSIS, RESULTS AND COMPARISONS

A summary of conditions and performance is given in *Table 2.4.3.* The product inspection of the various flow streams are given in *Tables 2.4.4-2.4.8.*

3.1 Process Performance

3.1.1. Coal Conversion

Coal conversion varied during Condition 1 from 82.8 to 86.8 W% MAF coal, *Figure 2.4.2.* It began low due to the high space velocity at which the unit was operated. When the space velocity was reduced at the end of period 3, the coal conversion increased to a steady value of 86.8 W% MAF coal. This is 2-3 W% lower than would normally be expected for Black Thunder coal at these processing condition. In Condition 2 the coal conversion initially jumped to a high value of 89.9 and then slowly decreased for the remainder of the condition to 87.6 W% MAF coal. This initial increase just as the CO was introduced to the reactor might be due to the combined benefit of the high solvent quality generated with the H_2 feed and the direct attack and in-site hydrogen formation with the CO feed. The later decrease in coal conversion could be due to a decrease in the quality of the recycle solvent. During Condition 3 the coal conversion increased to 92 W% as the temperature of both reactors was raised. This only changed at the very end of the run when it falls off, possibly due to the poor material balance experienced during the end of the run.

3.1.2 524°C$^+$ Resid Conversion and Yield

The resid conversion, the amount of maf coal that forms products other than quinoline insolubles and resid, is normally a strong function of catalyst age (*Figure 2.4.3*). Due to the aging of the catalyst in a Bench Unit, the resid conversion was expected to decrease over the course of the run as the residuum yield increased. Going from Condition 1 to Condition 2 there was no decrease in the resid conversion, indicating that the positive effect of the CO nearly balanced the effect of catalyst aging. During Condition 3, the resid conversion increased due to the effect of raising the process severity. However, in comparing Periods 12 and 13, at identical process severities, the resid conversion increased from 87.2 to 91.1 W% MAF coal. During Condition 4, the residuum conversion decreased sharply. Part of this decrease could be due to the low CO and H_2 gas flows and increasingly poor solvent quality.

3.1.3 Hydrogen Consumption

Typical hydrogen consumption (based on the hydrogen-content of different products), obtained from the normalized yield program, varied between 7.5 to 8.4 W% mf coal (*Figure 2.4.4*). This value was higher than the hydrogen consumption values obtained for some of the CMSL-3 (as illustrated later in the run comparisons). This value shows good agreement with the metered hydrogen consumption which is calculated from the hydrogen content of the inlet and outlet gases.

3.1.4 Heteroatom Removal

Denitrogenation and Organic Desulfurization was high for this run as can be seen from *Figure 2.4.5*. The desulfurization varied from 95.4 to 99.0 W% MAF coal. Typically, desulfurization drops over the course of the run as the catalyst ages. This follows that pattern except for Condition 4, with low CO flow. The denitrogenation varied from 89.5 to 96.9 W% MAF coal. This normally follows the same pattern as the desulfurization, decreasing as the run progresses. The denitrogenation also show a small rise for Condition 4.

3.2 Product Distribution

3.2.1 C_1-C_3 Gas Make

The gas made during Condition 1, using pure hydrogen as the reducing gas, was typical for Black Thunder coal - a light gas make of 6.3 to 6.6 W% and a total gas make of 9.9 to 10.0 W%(*Figure 2.4.6*). During Condition 2, the gas make increased slightly to a light gas make of 7.3 to 7.6 W% and a total gas make of 11.8 W%. This is also the gas make during the initial part of Condition 3 (Period 12) even though the temperature was increased from 388°C (730°F) to 399°C (750°F) in the first reactor and from 426°C (800°F) to 438°C (820°F) in the second reactor. During Period 13, the CO input stream was approximately 1/3 of the flow during Period 12, and the gas make increased. During Condition 4, also with the low CO flow, the light gas make was 8.9 to 9.1 W% and the total gas make was 13.7 to 14.6 W%. A correction was made to the methane production due to the reforming of H_2 and CO.

3.2.2. Liquid Yield

Condition 1, with hydrogen feed to both stages, resulted in a distillate yield of 57.6 W% MAF coal (*Figure 2.4.7 and Table 2.4.3*). This is lower than the 61 W% expected for Black Thunder Coal with these conditions at this catalyst age. Under identical processing condition, the syngas (Condition 2) gave a 0.9% higher distillate yield of 58.5 W% MAF coal. The liquid yield, however, is shifted toward the heavier fractions. As can be seen in *Figure 2.4.7*, Condition 2 gives a 2.7 W% lower IBP-177°C yield and a 4.4 W% higher 343-454°C yield. Condition 3, at a higher reactor temperature and higher space velocity, gave a distillate yield of 58.9 W% MAF coal, 0.4 W% higher than Condition 2 (*Table 2.4.3)*. Condition 3 also had a lighter yield distribution than Condition 1: 1.3 W% more IBP-177°C, 1.6 W% more 177-260°C, identical 260-343°C, 0.8 W% less 343-454°C, and 0.5 W% less 454-524°C. Condition 4 had an extremely low distillate yield of only 53.3 W% MAF coal; however, this is most likely due to the poor material balance experienced at the end of the run. The resid yield increases as the run progresses and the catalyst ages, as is expected, from a low value of 2.2 to a high of 4.8 W% MAF coal.

3.3 Product Quality

Analyses of the liquid products are presented in *Tables 2.4.4-2.4.8* and *Figures 2.4.8-2.4.12.*

3.3.1 Separator Overhead and Atmospheric Still Overhead

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 were not sampled. The second stage SOH is the product from the hydrotreater (see *Figure 2.4.1* for the simplified flow scheme). The sulfur, nitrogen and H/C atomic ratios for the first stage SOH and second stage SOH and ASOH are presented in *Figures 2.4.8-2.4.10.*

The sulfur content of the first stage SOH rose sharply from Condition 1, with H_2 to the first stage, from 147 to 428 ppm to Condition 2, with CO to the first stage. During Conditions 3 and 4, the sulfur content remained relatively high at 410-471 ppm. The ASOH sulfur rose steadily from an initial value of 38 ppm to 115 ppm. The second stage SOH, the hydrotreater product, had a low sulfur content ranging from 31 ppm to 45 ppm, showing that the hydrotreater was effectively removing the sulfur.

The nitrogen content of the first stage SOH increased steadily from an initial value of 747 ppm to about 2950 ppm in Conditions 3 and 4. The ASOH nitrogen content increased monotonically from an initial value of 435 ppm to a final value of 3412 ppm. The second stage SOH had a much lower nitrogen content than these two hydrotreater feed streams and increased from 22 ppm in Condition 1, with the H_2 feed, to 32-36 ppm in the other conditions, with the CO feed.

The H/C atomic ratio was consistently higher for the second stage SOH, ranging from 1.73 to 1.79, as compared to either the first stage SOH, ranging from 1.59 to 1.76, or the ASOH, ranging from 1.52 to 1.63. The hydrotreater increased the hydrogen content of the product.

3.3.2 Pressure Filter Liquid and Pressure Filter Solid

The pressure filter liquid (PFL) properties are presented in *Table 2.4.7* and *Figures 2.4.11 and 2.4.12.* As the catalyst aged, the resid content of the PFL increased from 22 W% to 39.7 W% and the H/C atomic ratio decreased from 1.37 to 0.98. The cyclohexane and toluene insolubles contents of residuum also increased from 0.29 to 17.63 W% and 0.10 to 1.98 W%, respectively. These indicated that levels of asphaltenes and preasphaltenes in this run with the supported catalyst were lower for the first two conditions than they had been in CMSL-3 without the first stage supported catalyst. However, the PFL levels of asphaltenes, preasphaltenes, and CCR were lower in this run with CO feed than in previous CTSL runs.

The pressure filter cake (PFC) analysis is presented in *Table 2.4.8.*

3.3.4 Analysis of TBP Fraction of Liquid Products

The light product oils were combined and sent through the hydrotreater. The product stream from the hydrotreater was fractionated into four true boiling point (TBP) fractions. A series of analyses, including API gravity, elemental, compound class type (PONA) on the lighter fractions, bromine number, aniline point and flash point, was performed. The results of these analyses are reported in *Tables 2.4.9a-2.4.9d.*

The initial boiling point of the hydrotreater product samples range from 38.3° to 50.0°C. The distribution of the four TBP fractions from these samples are compared in *Table 2.4.9a-2.4.9d.* Over 89 W% of the materials in these samples boiled below 343°C.

The compound class type distribution in the two lightest fractions are presented in *Table 2.4.9a-2.4.9d.* The largest component in the IBP-177°C fraction is the monocycloparaffins which is consistent at 49.23 to 53.41 V%. The next largest component is the paraffins which after an initial value of 37.91 V% drops to a range of 29.85 to 31.7 V%.

3.4 CO Conversion and Water Balance

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

$$CO + H_2O <====> CO_2 + H_2 + \text{heat}$$

is slightly exothermic, hence low temperature tends to shift the reaction towards the right. The equilibrium conversion for a syngas feed containing 25 vol% of H_2 is estimated as 75% under the process condition planned for the first reactor. However, this estimate does not include the decreased H_2 concentration because of its reaction with coal, allowing additional conversion of CO.

In calculating the amount of CO and CO_2 in the off gas, a small correction was made based on the amount of CO and CO_2 produced from the coal when only hydrogen was used, Condition 1. This correction was based on the average values for Periods 5 and 6.

Table 2.4.10 provides a summary of the CO conversion and water balance for all four conditions. As indicated in the Table, the water consumed in the WGS reaction is taken as the average of two different calculations. First, the amount of reacted CO and the stoichiometric equation for the water-gas shift reaction are used to calculate the amount of water consumed. Similarly, the amount of CO_2 produced is used to calculated the amount of water that was consumed. The average of these two calculations is then taken as the "true" amount of water consumed by the shift reaction.

The water balance is presented as the feed water and the collected water. The feed water includes the water injected into the first reactor, the moisture content of the coal (25.38 W%) and the water formed by the deoxygenation of the coal. The collected water is just the water collected in the SOH outlet streams. The difference between these two values gives the amount of water that was consumed in the water-gas shift reaction. The level of deoxygenation was calculated iteratively so that this calculated water consumed would exactly match that calculated from the stoichiometric equation and the CO and CO_2 balance. This results in reasonable values for the deoxygenation, ranging from 84 to 96%.

The first and second stage gas yields for Run CMSL-4 are summarized in *Table 2.4.16*. In Period 9 to 12 operations with syngas feed, the first stage CH_4 yields were 4.0-5.2 W% of mf coal feed, compared to 1.0 W% for the Period 5 operation where the first stage feed was pure hydrogen. The increase in CH_4 yield corresponded to 7-8 M% of the CO_2 formed from CO. This apparent CH_4 synthesis with extrudate catalyst in the first stage contrasts with the experience of Run CMSL-3, with no extrudate catalyst in the first stage and Mo additive, where there was virtually no increase in first stage CH_4 formation when syngas was fed to that stage. In addition to the CO directly converted to CH_4, the hydrocarbon synthesis consumes hydrogen and the amount of syngas available for hydrogenation of the coal is reduced further, so that the amount of syngas need will increase by about 25%. The combined results of the water gas shift and methane synthesis reactions is the following:

$$CO + 0.84\ H_2 \text{ ----------> } 0.92\ CO_2 + 0.08\ CH_4 + 0.68\ H_2$$

The calculated CO conversions for the Period 9 to 12 operations were 70-75%. This proportion was over 1.5 times that obtained in Run CMSL-3 which had no extrudate catalyst in the first stage. The water gas reaction equilibrium ratios, $H_2{*}CO_2/CO{*}H_20$, for the Run CMSL-4 operations were 7.0-7.2, approaching the equilibrium values of 12-13 at the first stage temperatures that were used. In Run CMSL-3, with no extrudate catalyst in the first stage, the calculated ratios were 0.4-0.8.

3.5 First And Second Stage Product Analyses For Runs CMSL-4 And CMSL-7 With SYNGAS Feed To The First Stage

3.5.1 Solids Analyses

The filter cakes from the first and second stages were filtered with quinoline, and the resulting solids were washed with THF to remove the quinoline. For Run CMSL-4 only the ash was determined and the results are presented in *Table 2.4.12*. For CMSL-7 ash and elemental analyses were determined and are presented in *Table 2.4.11.*

Figure 2.4.13 compares the first and two stage coal conversions for these two runs with 3 periods from CC-1 also with low/high catalytic/catalytic operation but with pure hydrogen feed to the first stage. The coal conversion for the first stage for Run CC-1 were lower than for any of the periods with syngas feed. This difference averaged about 15 W% MAF even though some of the syngas first stages were at the lower temperature 388°C (730°F). However, the one condition in CMSL-4 that had pure H_2 fed to the first stage had a higher first stage coal conversion of 78 W% MAF, comparable to the syngas condition. Thus, although the first stage coal conversion is not definitively increased by syngas, it is at least equally as high as when the full partial pressure of hydrogen is present. The reason for the higher first stage coal conversion in CMSL-4 Period 6 is not clear. One possible explanation is that the wet coal feed in CMSL-4 improved the conversion in the first stage.

After the second (hydrogen) stage, the coal conversions were approximately at levels that would be expected based on the corresponding severity, increasing to about 88 W% MAF for operations at 800°F and to about 92 W% MAF for operations at 825°F. It is interesting that in the last condition of CMSL-4, which was starved for CO because of a blockage, the coal conversion in the first stage was high (87.3 W% MAF), but it actually declined in the 438°C (820°F) second stage. This indicates the importance in low temperature/high temperature CTSL of preparing the coal in the first stage for further conversion in the second stage, through sufficient pressure of either syngas or hydrogen. Similarly, the coal converted in the first stage at very high levels during the 2 conditions of lowest CO and H_2 pressure in CMSL-7 (85.5 and 87.8 W% MAF), but the additional coal conversion in the second stage was only about 4 W% MAF in both cases.

Figure 2.4.14 shows the H:C atomic ratios vs. coal conversion for the comparable periods in CC-1 and CMSL-7. The hydrogen content of the first stage solids in CC-1 remained close to the initial value of the coal. This is typical for the low temperature catalytic first stage, which effectively adds hydrogen to the reacting solids, and they are not hydrogen depleted as in higher temperature thermal operations. With the syngas feed to the first stage in CMSL-7, the solids hydrogen contents were lower, suggesting a different mechanism of coal dissolution. However, after the second stage, the two operations resulted in similar solids hydrogen contents. Surprisingly, the two highest second stage solids hydrogen contents in Run CMSL-7 occurred during the last two conditions with the lowest back pressure, 10.3 MPa (1500 psig). The missing data from Run CMSL-4 would have been useful in confirming the lower solids hydrogen contents of the syngas operations because of its additional comparison data point with higher coal conversion with H_2 feed.

Figure 2.4.15 shows the solids nitrogen:carbon atomic ratios for Runs CC-1 and CMSL-7. In the first stage, these N:C ratios were higher than for the feed coal, indicating that the nitrogen was extracted more slowly than the coal was converted. Additional nitrogen was removed from the solids in the second stage. The syngas and H_2 operations generally had similar behavior with respect to nitrogen in the solids, except that less nitrogen was extracted in the second stage during the lower (hydrogen) pressure conditions. At the lowest pressure, 10.3 MPa (1500 psig), the nitrogen even increased in the solids between the first and second stages because of the insufficient hydrogen partial pressure.

3.5.2 Liquid Fraction Analyses

Tables 2.4.12 and 2.4.13 list the elemental analyses of the four liquid fractions of the slurry phase liquids for the first and second stage for Runs CMSL-4 and CMSL-7. Additionally, the CCR and cyclohexane and toluene insolubles of the resid fractions are listed.

Figures 2.4.16 through 2.4.19 compare the hydrogen contents of the liquid fractions from these two runs, using syngas feed to the first stage, with Run CC-1 Periods 6, 10, and 19, using pure hydrogen feed. Both types of operation showed the general trend of lower hydrogen content as the catalyst deactivated, but for all fractions the first and second stage fractions from Run CC-1 had higher hydrogen contents than the corresponding fractions from Runs CMSL-4 and CMSL-7. The improved hydrogenation of all liquid fractions with pure hydrogen feed was confirmed by the CMSL-4 Period 5 and 6 (also using pure hydrogen) data, which fell in line with the CC-1 data. It is not clear why the CMSL-7 hydrogen contents were consistently the lowest, even in Condition 1, with equal back pressure as the other runs.

The hydrogen contents were generally lower for the higher temperature second stage liquid fractions. This difference, however, was often less (and sometimes reversed) for the operations with syngas feed, implying that the hydrogenation environment was not as favorable in the first stage.

The liquid fraction nitrogen analyses, *Figures 2.4.20 through 2.4.23*, show the trend of increasing as the catalyst deactivated. There was generally little difference between the nitrogen of the first and second stage product fractions, commonly with just a little improvement in the second stage. The CMSL-4 liquid fraction had, on average, slightly higher nitrogen contents than the CC-1 liquid fractions, and the CMSL-7 liquid fractions were higher than the corresponding fractions from the other two runs. Possibly this lower quality with respect to hydrogen and nitrogen contents, could be due to differences in the new batch of coal used for CMSL-7.

Cyclohexane and toluene insolubles in the resid fractions (*Figures 2.4.24 and 2.4.25*) were much higher for the operations with the syngas feed, especially for Run CMSL-7, than for operations with pure hydrogen feed. They also increased more rapidly with time, inferring possible faster catalyst deactivation in the low hydrogen-pressure environment.

3.6 Evaluation Of Performance Of Syngas As Reducing Gas For Liquefaction Of A Subbituminous Coal

In order to evaluate the performance of syngas as reducing gas for liquefaction of Black Thunder Mine coal, the product yields and conversions in selected periods of runs were compared with those of projected standard cases at the same operating conditions. The differences (from actual to projected standard) in yields and conversions were then compared to evaluate relative performance. This approach is necessary because of the variation in operating conditions and catalyst age in selected periods of different runs.

The standard case is two stage liquefaction of Black Thunder Mine coal using Shell S317 extrudate catalysts in both stages and hydrogen as reducing gas. The projection of standard case will be made by a computer simulation program developed at HTI using earlier experimental data on liquefaction runs of Black Thunder Mine coal. The projected data are compared with the actual process performance data for a few selected periods of these runs. The difference (D* = actual - projected for CTSL with extrudate catalyst in both stages) of actual and projected yields, conversion, and hydrogen consumption data for different selected periods will compare the performance of different first stage catalysts and reducing gases.

3.6.1 Effect Of Interstage Venting Of Gases

It must be recognized that in CMSL operations utilizing syngas as reducing gas in the first stage, such as Run 227-79 (CMSL-3), the gases were vented after the first stage and hydrogen gas was then added to the second stage. As a result, the CO and CO_2 formed from coal liquefaction in the first stage did not have enough reaction time to get converted into CH_x and H_2O thereby increasing C_1-C_3 gas and H_2O yields. This consideration was apparent in Run

227-79-5 (CMSL-3), with 100% hydrogen to the first stage, where the CO_2 in the first stage vent gases amounted to 7.4 W% of the coal feed.

So the net effect of interstage venting of gases is increasing CO_x yield, decreasing C_1-C_3 gas and water yields, and thereby decreasing hydrogen consumption.

Before determining the effect of using syngas in coal liquefaction, it is necessary to determine the net effect of interstage venting of gases on two stage coal liquefaction using hydrogen as reducing gas. Run 227-79-5 (CMSL-3) used hydrogen as reducing gas in both stages, 1500 ppm molybdenum slurry catalyst in the first stage and Shell S-317 extrudate catalyst in the second stage. The relevant D* values, presented below for this run, compare the net effects on product yields and hydrogen consumption.

	D*
C_1-C_3, W% MAF	-0.78
CO_x, W% MAF	7.98
H_2O, W% MAF	-1.49
H_2 Consumption, W% MAF	0.16

There is significantly higher CO_x production and lower C_1-C_3 gas and H_2O production. In earlier comparison for runs without interstage venting it was shown that hydrogen consumption was approximately 1 W% higher with catalyst additive in the first stage than the standard case. So with interstage venting, the hydrogen consumption is reduced by approximately 1 W%.

3.6.2 Discussion

First Stage CO_2 and C_1-C_3 gas formation with hydrogen as reducing gas and different first stage catalysts is discussed as follows:

Analyses of first and second stage gas yields for Run 227-79-5, using 1500 ppm molybdenum catalyst additive to the first stage, show the CO_2 yield was 8.21 W% MF coal. Similar analyses for Run 227-81-5 (CMSL-4), using Shell S-317 Ni-Mo extrudate catalyst in the first stage, show the CO_2 yield was 4.85 W% MF coal. (See *Table 2.4.16*) The difference from the CMSL-3 result suggests the extrudate catalyst promotes some secondary reaction of CO_2 formed during the primary reaction of the coal. The first stage methane yields for the two runs were 0.43 and 1.05 W% of MF coal for Runs CMSL-3 and CMSL-4, respectively, which difference corresponds roughly to the amount of carbon in difference in CO_2 yields.

Interstage withdrawal of gas will apparently result in an increase in CO_2 yield and decreased light gas yield, and decreased hydrogen consumption. However, the amount of this advantage is probably lower where there is extrudate catalysts in the first stage. Hydrocarbon formation from CO_x in synthesis gas used in coal liquefaction runs was discussed above in the section on CO conversion.

To determine the effect of using syngas in the first stage, the D* values for Run 227-79-9 (CMSL-3) and Run 227-77-7 (CMSL-1) are presented below. Both these runs on liquefaction of Black Thunder Mine subbituminous coal used Shell S-317 extrudate catalysts in the second stage.

	Run 227-79-9T	Run 227-77-7T
1st Stage Catalyst:	1500 ppm Mo	300 ppm Mo + 4500 ppm Fe
1st Stage Reducing Gas:	Syngas	Hydrogen
First Stage Venting:	Yes	No
	D*	D*
C_1-C_3, W% MAF	-0.73	2.59
Water, W%	-2.5	2.51
CO_x, W% MAF	8.5	1.31
Resid, W% MAF	1.65	2.06
H_2 Consumption, W% MAF	0.17	1.00
C_4-524°C, W% MAF	-0.43	-0.64
Coal Conversion, W% MAF	6.32	8.02

The D* values for Run 227-79-9T show that the C_1-C_3, water and CO_x yields, and hydrogen consumption are mainly affected by interstage venting of gases and without any major effect from using syngas.

The comparison of D* values for Runs 227-79-9T and 227-77-7T show that the relatively low C_1-C_3 yield, low hydrogen consumption, low water yield, and high CO_x yields in the syngas operation are principally associated with the interstage withdrawal of gas. Nominally, substitution of syngas for hydrogen had minimal impact on the yield and distribution of the liquid products.

When compared to the standard case, the syngas case has equivalent C_4-524°C distillate yield and hydrogen consumption, higher resid yield and coal conversion, and lower water and C_1-C_3 gas yields. In overall performance, the syngas-case with interstage venting is equivalent to the standard case and may be slightly superior to the Fe-Mo-Case, principally because of lower hydrogen consumption.

The D* values for Run 227-79-12T (CMSL-3) and Run 227-77-14T (CMSL-1) are presented in the following Table for the convenience of discussion. Run 227-77-14T used low amount of catalyst additive in the first stage. Both the runs used Shell S-317 extrudate Ni-Mo catalysts in the second stage.

	Run 227-79-12T	Run 227-77-14T
1st Stage Catalyst:	1500 ppm Mo	300 ppm Mo
1st Stage Reducing Gas:	Syngas	Hydrogen
First Stage Venting:	Yes	No
	D*	D*
C_1-C_3, W% MAF	-1.02	2.72
Water, W% MAF	-4.42	1.54
CO_x, W% MAF	9.26	3.08
Resid, W% MAF	2.24	1.24
H_2 Consumption, W% MAF	-0.39	1.31
C_4-524°C, W% MAF	-0.82	-1.58
Coal Conversion, W% MAF	5.62	5.86

The D* values for Run 227-79-12T show that even after discounting the effects of interstage venting of gases, the C_1-C_3 and water yields are further reduced, and hydrogen consumption is further reduced due to the effect of using syngas in the first stage.

The comparison of D* values for Runs 227-79-12T and 227-77-14T show that the use of syngas as reducing gas with interstage venting results in high CO_x yield, low C_1-C_3 and water yields leading to low hydrogen consumption, and slightly higher C_4-524°C distillate yield. In terms of C_4-524°C distillate yield and hydrogen consumption, the syngas-case with 1500 ppm Mo has significant advantage over the 300 ppm Mo-Case using hydrogen. In overall performance considering distillate yield, the standard case has advantage over the syngas case.

4.0 DETAILS OF OPERATION

4.1 Bench Unit Description

This bench run was performed using two equal volume ebullated beds. A simplified process flow diagram is presented in *Figure 2.4.1.* Coal was dissolved in the first-stage in the presence of syngas and water, while the primary coal liquids were further upgraded in the second stage. An interstage separator was installed to remove gases and light distillates (as a separator overhead, SOH) generated from the first stage and to recover any unreacted CO/H_2O. 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.

4.2 Operating Summary

The run plan, *Table 2.4.1,* included four process conditions. The conditions were selected so that the effects of process severity and feed gas composition could be determined for this run, and similar comparisons could be made with Run CMSL-3, which contained no 1st Stage supported catalyst. The actual operating conditions are presented in *Table 2.4.2*. Condition 1 extended from Periods 1 to 6 using pure hydrogen as reducing gas for both reaction stages. This condition served as a base case for comparison, having identical severity and feed gas as Condition 1 of Run CMSL-3. Condition 2 was identical to Condition 1 except the reducing gas was changed from pure hydrogen to a 86%/14% mixture of CO and H_2. 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 W% of the dry coal in the feed slurry. Condition 3 was at a higher overall system severity than the initial two conditions. The space velocity was changed from 325 to 405 Kg dry coal/h/M^3 (20 to 25 lb/hr/ft^3) and the first and second stage reactor temperatures were raised from 388/427°C (730/800°F) to 399/438°C (750/820°F). Condition 4 was to vary from Condition 3 by the CO/H_2 balance in the reducing gas used in the first stage. This was to have changed from 90% CO to 75% CO. However, a problem was experienced during the run with the CO gas compressor. An internal seal leaked, allowing oil to enter the CO flow stream which then plugged the CO-flow-control mass flow meter. It did not plug the entire meter, just the main flow stream, the slip stream that is used to calculate the mass flow through the meter was still open. From the end of Period 12 on, this is the only flow of CO into the system resulting in approximately 1/3 of the designed flow.

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

The daily recovery and operating conditions are presented in *Figures 2.4. 26-2.4.29.* The daily material balance averaged 97.5 W% with the greatest variation at the beginning and end of the run, *Figure 2.4.29.* The reactor temperatures are presented in *Figure 2.4.26* and show a very small variation from target values. The space velocity is presented in *Figure 2.4.27* and shows smooth operation for the later part of Condition 1 and Condition 2 at 297 K2g dry coal/h/M^3 (18.5 lb/hr/ft^3) and smooth operations for Condition 3 and 4 at 374 Kg dry coal/h/M^3 (23.3 lb/hr/ft^3). The initial part of Condition 1 shows the original target space velocity of 441 Kg dry coal/h/M^3 (27.5 lb/hr/ft^3) but during Period 3 it was decided to lower this to 297 Kg dry coal/h/M^3 (18.5 lb/hr/ft^3). The overall process severity is presented in *Figure 2.4.28* showing an initial relative severity of 1.1 for Conditions 1 and 2 and a severity of 1.6 for Conditions 3 and 4. The first 3 periods show low severity of 0.8 due to the initial higher space velocity which was later lowered.

5.0 MATERIALS USED

5.1 Coal

Wyoming subbituminous coal, Black Thunder Mine, was used as the feedstock. The coal analyses of the feed (HRI-5828) are presented in *Table 2.4.14*. This batch of coal was previously evaluated in CC-13, CC-15, CMSL-01 and CMSL-03. This coal has approximately 25 W% moisture in the raw form and was pulverized without further drying.

5.2 Start-up/Makeup Oil

The start-up / make-up oil used during this run was the coal-derived recycle solvent generated during POC-01 (PDU RUN 260-04). The elemental analysis and boiling point distribution is shown in *Table 2.4.15*.

5.3 Catalyst

Fresh Shell S-317 1/32" extrudates ($NiMo/Al_2O_3$) were charged to both the first and second stage ebullated bed reactors. The hydrotreater was charged with Criterion C-411 trilobe catalyst. The catalysts were presulfided during normal start-up operations using TNPS.

6.0 CONCLUSION

The overall results show that syngas as reducing gas in the first stage, along with interstage venting, can be used in two stage coal liquefaction process with the net effect of reduced hydrogen consumption and improved or equivalent distillate yield. Interstage venting in itself will result in higher CO_2 yield, lower light hydrocarbon yield, lower water yield and lower hydrogen consumption; this effect is more significant with catalyst additive in the first stage than with extrudate catalyst in the first stage. Synthesis gas in place of hydrogen has small impact on liquid hydrocarbon yield and its distribution.

Extrudate catalyst was far more effective than molybdenum additive for conversion of CO to H_2, with values of the water gas shift reaction equilibrium ratio approaching the thermodynamic values at the temperatures that were used. However, the extrudate catalyst also promoted a considerable amount of CH_4 from the CO, which, in effect, consumed almost one-third of the hydrogen derived from the CO that was reacted. Also, this promotion of the hydrocarbon synthesis reaction by the extrudate catalyst lowered the net CO_2 formation in the first stage, when feeding pore H_2 to about two-thirds of that obtained with only molybdenum additive as the first stage catalyst.

TABLE 2.4.1

Run Plan For Bench Run CMSL-04 (227-81)

BLACK THUNDER MINE COAL
1st & 2nd Stage Catalyst: Shell S-317 Ni/Mo 1/32" Extrudates
Hydrotreater Catalyst: Criterion C-411 Trilobe

CONDITION	1	2	3	4
PERIOD	1-5	6-9	10-12	13-15
FEED GAS				
1st Stage	H_2	CO/H_2	CO/H_2	CO/H_2
2nd Stage	H_2	H_2	H_2	H_2
% GAS FLOW TO 1ST STAGE				
H_2	100	10	10	25
CO	0	90	90	75
TEMPERATURE, °C (°F)				
1st Stage	388 (730)	388 (730)	399 (750)	399 (750)
2nd Stage	427 (800)	427 (800)	438 (820)	438 (820)
Hydrotreater	357 (675)	357 (675)	377 (710)	377 (710)
SPACE VELOCITY (2nd Stage)				
Lb Dry Coal/Hr/Ft^3	20	20	25	25
Kg Dry Coal/Hr/M^3	325	325	405	405
SOLVENT/COAL RATIO	1.2	1.2	1.2	1.2
OVERALL PROCESS SEVERITY (1.00 at 388/427°C and 325 SV) (or at 730/800°F and 20 SV) STTU	1.00	1.00	1.45	1.45

TABLE 2.4.2

Actual Operating Conditions For Run CMSL-04 (227-81)

BLACK THUNDER MINE COAL
1st & 2nd Stage Catalyst: Shell S-317 Ni/Mo 1/32" Extrudates
Hydrotreater Catalyst: Criterion C-411 Trilobe

CONDITION	1	2	3	4
PERIOD	1-6	7-10	11-13	14-17
FEED GAS				
1st Stage	H_2	CO/H_2	CO/H_2	CO/H_2
2nd Stage	H_2	H_2	H_2	H_2
% GAS FLOW TO 1ST STAGE				
H_2	100	10	10	25
CO	0	90	90	75
TEMPERATURE, °C (°F)				
1st Stage	388 (730)	388 (730)	399 (750)	399 (750)
2nd Stage	427 (800)	427 (800)	438 (820)	438 (820)
Hydrotreater	357 (675)	357 (675)	377 (710)	377 (710)
SPACE VELOCITY (2nd Stage)				
Lb Dry Coal/Hr/Ft^3	20	20	25	25
Kg Dry Coal/Hr/M^3	325	325	405	405
SOLVENT/COAL RATIO	1.2	1.2	1.2	1.2
OVERALL PROCESS SEVERITY (1.00 at 388/427°C and 325 SV) (or at 730/800°F and 20 SV) STTU	1.00	1.00	1.45	1.45

TABLE 2.4.3

PROCESS PERFORMANCE FOR CMSL-04

CONDITION	1	2	3	4
PERIOD	5	10	12	16
HOURS OF RUN	120	240	288	384
CATALYST AGE (Kg Dry Coal/Kg Cat)	185	315	377	507
REACTOR TEMPERATURES, °C (°F)				
K-1 Temperature	388 (730)	388 (730	399 (750)	399 (750)
K-2 Temperature	427 (800)	427 (800)	438 (820)	437 (819)
SPACE VELOCITY (2nd Stage Catalyst)				
(Lb Dry Coal/Hr/Ft^3)	43.4	42.1	51.4	52.3
(Kg Dry Coal/Hr/$M^{3)}$	697	676	825	839
RELATIVE SEVERITY IND	1.06	1.06	1.59	1.52
SOLVENT/COAL RATIO	1.2	1.2	1.2	1.2
1^{ST} STAGE GAS FEED, %SCF				
H_2	100	14	16	70
CO	0	86	84	30
PROCESS PERFORMANCE, W% (MAF COAL)				
Coal Conversion	86.82	87.63	90.80	86.81
524°C+ Conversion	84.63	84.54	87.25	82.00
C4-524°C Distillate Yield	57.64	58.42	58.93	53.26
Hydrogen Consumption	8.10	9.61	9.51	8.35
Denitrogen, W%	96.90	95.15	89.53	90.02
Desulfur (Org), W%	99.03	97.20	95.43	97.28
NORMALIZED YIELDS, W% (MAF COAL)				
C_1 - C_3 Gases	6.3	7.65	7.96	9.17
C_4 - C_7 Gases	3.64	4.11	3.27	5.45
IBP-177 °C	12.78	10.07	14.07	14.36
177-260 °C	9.95	9.11	11.59	9.76
260-343 °C	21.26	20.63	21.35	15.95
343-454 °C	8.28	12.67	7.44	6.56
454-524 °C	1.73	1.93	1.21	1.18
524+ °C	2.19	3.09	3.55	4.81
Unconverted Goal	13.18	12.37	9.20	13.19
Water	22.34	21.49	23.00	21.27
CO	0.51	0.51	0.52	0.51
CO_2	4.85	5.02	5.15	5.00
NH_3	0.90	0.83	0.94	0.91
H_2S	0.20	0.14	0.26	0.23

TABLE 2.4.4

ANALYSIS OF FIRST STAGE SOH FOR CMSL-04

CONDITION	1	2	3	4
PERIOD	5	10	13	17
GRAVITY, °API	31.3	25.2	25.8	30.5
IBP, °C	88.3	95.0	81.7	67.2
FBP, °C	427	431	433	426
ASTM D-86 DISTILLATION, W%				
IBP-177 °C	34.52	23.1	25.8	40.0
177-260 °C	9.43	10.5	11.2	11.3
260-343 °C	26.70	27.5	26.6	22.0
650+ °C	28.65	38.3	36.0	26.1
Loss	0.70	0.6	0.4	0.6
ELEMENTAL ANALYSIS, W%				
Carbon	86.62	86.84	86.59	85.83
Hydrogen	12.67	11.67	11.5	11.78
Sulfur	0.0147	0.0428	0.0471	0.0410
Nitrogen	0.0747	0.1960	0.2941	0.2965
H/C RATIO	1.76	1.61	1.59	1.65

TABLE 2.4.5

ANALYSIS OF FIRST ASOH FOR CMSL-04

CONDITION	1	2	3	4
PERIOD	5	10	13	17
GRAVITY, °API	24.4	22.8	22.6	21.6
IBP, °C	160	143	137.2	132
FBP, °C	366	361	362	364
ASTM D-86 DISTILLATION, W%				
IBP-177 °C	4.85	5.1	5.9	6.9
177-260 °C	10.13	21.7	24.1	23.3
260-343 °C	70.48	64.8	62.1	50.8
650+ °C	12.45	8.1	7.7	8.5
Loss	2.09	0.3	0.2	0.5
ELEMENTAL ANALYSIS, W%				
Carbon	87.75	87.59	87.61	87.14
Hydrogen	11.89	11.59	11.24	11.06
Sulfur	0.0038	0.0079	0.0106	0.0115
Nitrogen	0.0435	0.1345	0.3067	0.3412
H/C RATIO	1.63	1.59	1.54	1.52

TABLE 2.4.6

Analysis of Second Stage SOH (Hydrotreater Outlet) For CMSL-04

CONDITION	1	2	3	4
PERIOD	5	10	13	17
GRAVITY, °API	31.9	31.1	32.1	33.5
IBP, °C	84.4	77.2	54.4	60.0
FBP, °C	389	401	407	396
ASTM D-86 DISTILLATION, W%				
IBP-177 °C	30.48	25.7	28.3	35.0
177-260 °C	19.63	18.2	20.2	20.7
260-343 °C	41.11	39.9	37.6	33.1
650+ °C	7.97	15.7	13.2	10.6
Loss	0.81	0.5	0.7	0.6
ELEMENTAL ANALYSIS, W%				
Carbon	86.65	87.19	87.07	86.31
Hydrogen	12.92	12.73	12.55	12.60
Sulfur	0.0037	0.0045	0.0041	0.0031
Nitrogen	0.0022	0.0036	0.0035	0.0032
H/C RATIO	1.79	1.75	1.73	1.75

TABLE 2.4.7

ANALYSIS OF PRESSURE FILTER LIQUID FOR CMSL-04

CONDITION	1	2	3	4
PERIOD	5	10	13	17
GRAVITY, °API	10.0	5.5	1.0	-4.7
IBP, °C	299	295	293	301
ASTM D-86 DISTILLATION, W%				
IBP-343 °C	6.2	6.87	5.14	6.09
343-454 °C	53.0	49.95	46.73	39.25
454-524 °C	18.5	17.52	17.01	14.70
524+ °C	22.0	25.36	30.65	39.70
Loss	0.3	0.30	0.47	0.26
ELEMENTAL ANALYSIS, W%				
Carbon	89.83	89.93	90.64	91.2
Hydrogen	10.22	9.16	8.39	7.46
Sulfur	0.01	0.047	0.06	0.047
Nitrogen	0.21	0.29	0.43	0.57
H/C RATIO	1.37	1.22	1.11	0.98
CCR, W%	6.60	10.32	17.16	25.97
CYCLOHEXANE INS, W%	0.29	1.92	8.94	17.63
TOLUENE INS, W%	0.10	0.18	0.88	1.98

*These filtration analyses were performed on the entire PFL samples; analyses performed on the 524°C+ fraction (*Table 2.4.6 and Table 2.4.8*) generally corresponded to higher entrie-sample insolubles.

TABLE 2.4.8

ANALYSIS OF PRESSURE FILTER CAKE FOR CMSL-04

CONDITION	1	2	3	4
PERIOD	5	10	13	17
ELEMENTAL ANALYSIS, W%				
Carbon	70.71	70.33	65.55	68.03
Hydrogen	6.09	5.46	4.69	4.65
Sulfur	0.841	1.01	1.06	0.99
Nitrogen	0.59	0.73	0.60	0.61
H/C Ratio	1.03	0.93	0.86	0.82
COMPOSITION, W%				
Quinoline Insolubles	54.78	54.59	54.26	51.42
Ash (quinoline filtration)	18.29	19.26	24.36	16.18
S in QI Ash				
ASTM Ash	17.85	18.55	23.99	22.73
S in ASTM Ash	4.15	4.13	3.80	3.87

TABLE 2.4.9a

DETAILED ANALYSIS OF TBP FRACTIONS
RUN 227-81, PERIOD 6 CMSL-04

TBP Distillation, % IBP = 49.4 ˚C

	W%
IBP-177 ˚C	22.59
177-260 ˚C	47.08
260-343 ˚C	27.33
343 ˚C+	3.00

TBP FRACTION [˚C]	IBP-177	177-260	260-343	343+
API Gravity	54.8	28.6	21.5	20.6
Elemental Analysis [W%]				
Carbon	85.4	87.75	88.47	88.26
Hydrogen	14.54	12.66	11.79	12.2
Sulfur	0.0004	0.0017	0.0019	0.0104
Nitrogen	.06	.01	0.04	.04
Antek N, ppm	<1.0	5.8	22.3	130
Bromine No. [g/100g]	2.45	0.90	1.15	
Aniline Point, [˚C]	50.6	40.8	41.1	
Flash Point, [˚C]	<-7	81	157.2	
PONA [V%]				
Paraffins	37.91	9.99		
Olefins	0.40	25.27		
Monocycloparaffins	49.23	21.65		
Dicycloparaffins	6.16	9.64		
Alkylbenzene	5.40	9.81		
Indanes/Tetralins	0.27	21.20		
Naphthalenes	0.63	2.44		
Aromatics (ASTM D2549)			51.34	44.73

TABLE 2.4.9b

DETAILED ANALYSIS OF TBP FRACTIONS
RUN 227-81 PERIOD 10 CMSL-04

TBP Distillation, % IBP = 46.1 °C

	W%
IBP-177 °C	24.05
177-260 °C	38.33
260-343 °C	26.62
343 °C+	11.00

TBP FRACTION [°C]	IBP-177	177-260	260-343	343+
API Gravity	53.1	28.5	20.7	19.9
Elemental Analysis [W%]				
Carbon	85.14	88.04	88.36	87.56
Hydrogen	14.42	12.52	12.27	12.38
Sulfur	0.0018	0.0020	0.0032	0.0072
Nitrogen	0.06	.003	0.04	0.03
Antek N, ppm	<1.0	18.0	22.0	215.5
Bromine No. [g/100g]	2.43	1.36	1.15	
Aniline Point, [°C]	47	34	53	
Flash Point, [°C]	<-7	83	166	
PONA [V%]				
Paraffins	31.70	10.14		
Olefins	0.50	22.38		
Monocycloparaffins	53.41	21.47		
Dicycloparaffins	6.10	9.47		
Alkylbenzene	6.93	10.69		
Indanes/Tetralins	0.59	23.4		
Naphthalenes	0.77	2.45		
Aromatics (ASTM D2549)			42.59	35.34

TABLE 2.4.9c

DETAILED ANALYSIS OF TBP FRACTIONS
RUN 227-81 PERIOD 13 CMSL-04

TBP Distillation, %	IBP = 38.3 °C
	W%
IBP-177 °C	25.78
177-260 °C	37.56
260-343 °C	33.33
343 °C+	3.33

TBP FRACTION [°C]	IBP-177	177-260	260-343	343+
API Gravity	53.0	29.2	19.4	18.4
Elemental Analysis [W%]				
Carbon	85.38	87.76	87.98	87.79
Hydrogen	14.15	12.35	11.45	12.2
Sulfur	0.0004	0.0011	0.0035	0.0126
Nitrogen	0.05	0.05	0.07	0.08
Antek N, ppm	<1.0	9.2	22.7	185.4
Bromine No. [g/100g]	2.43	1.36	0.71	
Aniline Point, [°C]	45.3	30.3	38.9	
Flash Point, [C]	<-7	81.1	154	
PONA [V%]				
Paraffins	31.31	10.57		
Olefins	0.40	23.91		
Monocycloparaffins	51.22	16.15		
Dicycloparaffins	6.39	4.56		
Alkylbenzene	9.23	11.26		
Indanes/Tetralins	0.77	31.6		
Naphthalenes	0.68	1.95		
Aromatics (ASTM D2549			55.72	43.81

TABLE 2.4.9D

DETAILED ANALYSIS OF TBP FRACTIONS
RUN 227-81 PERIOD 17 CMSL-04

TBP Distillation, % IBP = 50.0 °C

	W%
IBP-177 °C	25.78
177-260 °C	37.56
260-343 °C	33.33
343 °C+	3.33

TBP FRACTION [°C]	IBP-177	177-260	260-343	343+
API Gravity	52.1	27.8	19.5	18.1
Elemental Analysis [W%]				
Carbon	85.57	87.99	88.77	88.54
Hydrogen	13.86	12.14	11.32	11.67
Sulfur	0.0002	0.0004	0.0027	0.0100
Nitrogen	0.04	0.03	0.05	0.03
Antek N, ppm	<1.0	23.1	22.2	134.5
Bromine No. [g/100g]	1.55	1.35	0.71	
Aniline Point, [°C]	42.8	27.8	33..3	
Flash Point, [C]	<-7	77.8	162.8	
PONA [V%]				
Paraffins	29.85	11.99		
Olefins	0.50	23.95		
Monocycloparaffins	51.09	14.47		
Dicycloparaffins	6.00	4.74		
Alkylbenzene	11.35	11.20		
Indanes/Tetralins	0.85	31.73		
Naphthalenes	0.36	1.92		
Aromatics (ASTM D2549			60.50	50.48

TABLE 2.4.10

CO CONVERSION AND WATER BALANCE
Grams/24 Hours

PERIOD	5	10	12	16
WATER BALANCE				
Water Injected	22670	16498	20351	19849
Moisture in Coal	5087	4936	6046	6133
Coal Oxygen W%	18.74	18.74	18.74	18.74
Calc. Deoxygen (%)	85.6	96.0	86.0	84.0
Water from Oxygen	2699	2937	3223	3193
Total Feed Water	30456	24371	29620	29175
SOH H_2O Collected	304.56	17171	21544	27500
Water Consumed	0	7200	8076	1675
WATER CONSUMED IN SHIFT				
CO Reacted	0	11173	11834	3227
Equivalent Water	0	7182	7607	2074
CO_2 Produced	0	17637	20892	3167
Equivalent Water	0	7215	8547	1296
Average Water Cons	0	7199	8077	1685
CO CONVERSION	N/A	68.5	74.5	93.2

TABLE 2.4.11

COMPARISON OF FIRST AND SECOND STAGE PRODUCT FRACTION ANALYSES RUN CMSL-7 (227-84)

	Second Stage (PFC)					First Stage			
Condition	1	2	3	4	4	1	2	3	4
Period Number	7	11	14	18	19	7	11	14	19
Catalyst Age, Kg Coal/Kg Catalyst	157	269	352	460	488	157	269	352	488
Solids (THF-Washed Filter Cake)									
Ash, W%	45.31	43.43	37.22	43.58	41.28	22.92	26.48	29.34	32.87
Elemental Analyses, W% (Ash-Free Basis)									
Carbon	68.92	70.59	70.59	70.41	67.84	71.01	70.32	77.22	76.53
Hydrogen	3.02	3.08	3.65	3.50	3.48	3.61	3.46	4.16	3.19
Sulfur	2.85	2.54	1.00	2.39	2.49	1.72	1.39	1.76	2.34
Nitrogen	1.12	1.16	1.55	1.17	1.12	1.52	1.32	1.54	1.19
Total	75.91	77.37	76.79	77.47	74.93	77.86	76.49	84.68	83.25
Sulfur in Ash, W%	2.80	2.66	3.46	3.03	3.05	4.17	2.98	3.07	2.78
Sample Filtration									
Filter Cake W% of Sample						43.88	41.62	52.86	13.56
Quinoline Insolubles, W% of Filter Cake	53.43	54.94	41.40	48.48	44.84	53.79	54.54	48.37	45.70
Coal Conversion, %	92.6	92.1	89.6	93.0	91.3	80.0	83.4	85.5	87.8

TABLE 2.4.12

COMPARISON OF FIRST AND SECOND STAGE PRODUCT FRACTION ANALYSES
Run CMSL-04 (227-81)

	---Second Stage (PFL)-----				--------First Stage--------			
Condition	1	2	3	4	1	2	3	4
Period Number	5	10	13	17	6	10	13	17
Catalyst Age, Kg	185	315	410	540	211	315	410	540
TOTAL LIQUID								
Gravity, °API	10.0	5.5	1.0	-4.7	9.6	5.2	-2.4	-5.3
Elemental Analyses Analyses, W%								
Carbon	89.83	89.93	90.64	91.20	88.65	89.13	89.48	89.42
Hydrogen	10.22	9.16	8.39	7.46	10.03	9.30	7.96	7.53
Sulfur	0.010	0.047	0.060	0.047	0.030	0.090	0.104	0.127
Nitrogen	0.21	0.29	0.43	0.57	0.22	0.35	0.54	0.62
Total	100.1	99.43	99.52	99.28	98.93	98.87	98.08	97.70
IBP-343 °C-, W%	6.20	6.87	5.14	6.09	8.08	6.28	5.02	5.62
343-454 °C, W%	53.00	49.95	46.73	39.25	47.36	45.51	37.50	34.26
454-524 °C, W%	18.50	17.52	17.01	14.70	17.05	17.59	14.78	14.01
524 °C+, W%	22.00	25.36	30.65	39.70	27.12	30.14	41.97	45.58
Loss, W%	0.30	0.30	0.47	0.26	0.39	0.48	0.72	0.53
LGO (IBP-343 °C)								
Carbon, W%	89.41	88.68	88.98	88.92	87.88	88.04	87.59	87.62
Hydrogen, W%	11.61	10.78	10.58	10.10	11.73	11.25	10.59	10.39
Sulfur, W%	0.004	0.017	0.017	0.018	0.021	0.058	0.057	0.066
Nitrogen, W%	0.047	0.151	0.255	0.329	0.084	0.247	0.258	0.357
VGO (343-454 °C)								
Carbon, W%	89.27	89.35	89.83	90.02	88.59	89.17	89.19	88.98
Hydrogen, W%	10.91	10.06	9.60	9.06	10.81	10.39	9.56	9.09
Sulfur, W%	0.009	0.038	0.045	0.041	0.029	0.071	0.074	0.123
Nitrogen, W%	0.078	0.178	0.257	0.297	0.108	0.251	0.260	0.377
HVGO (454-524 °C)								
Carbon, W%	89.81	89.95	90.61	91.32	88.75	90.06	89.64	89.52
Hydrogen, W%	9.91	8.94	8.20	7.64	9.83	8.95	7.97	7.79
Sulfur, W%	0.019	0.041	0.042	0.037	0.039	0.079	0.081	0.142
Nitrogen, W%	0.17	0.31	0.43	0.57	0.21	0.29	0.42	0.52
RESIDUUM (524 °C+)								
Carbon, W%	90.16	90.58	91.43	91.50	88.88	89.21	89.28	89.42
Hydrogen, W%	8.61	7.22	6.34	5.64	8.61	7.38	6.05	7.53
Sulfur, W%	0.060	0.050	0.043	0.056	0.070	0.082	0.132	0.127
Nitrogen, W%	0.31	0.55	0.73	0.92	0.43	0.64	0.84	0.62
CCR, W%	30.00	40.72	55.98	65.42	25.90	41.70	59.16	64.85
CHX Insols., W%	1.79	12.41	31.54	71.11	2.19	25.44	74.16	74.76
Tol. Insols., W%	0.08	1.04	1.84	18.57	0.36	1.67	23.13	35.15
Ash, W%	0.00	0.01	0.00	0.03	0.00	0.00	0.03	0.01
Quinoline Ext. Solids								
SO_3 -Free Ash, W%	29.31	31.66	40.28	28.30	23.22	18.32	26.31	30.16
Coal Conversion	86.8	87.0	91.9	86.2	78.3	75.6	84.7	87.3

TABLE 2.4.13

COMPARISON OF FIRST AND SECOND STAGE PRODUCT FRACTION ANALYSES
Run CMSL-07 (227-84)

	---Second Stage (PFL)-----				--------First Stage--------			
Condition	1	2	3	4	1	2	3	4
Period Number	7	11	14	19	7	11	14	19
Catalyst Age, Kg Coal/Kg	157	269	352	488	157	269	352	488
TOTAL LIQUID								
Gravity, °API	1.8	4.4	-8.0	-5.1	-0.5	-5.2	-3.8	-2.6
Elemental Analyses Analyses, W%								
Carbon	91.13	90.46	90.29	90.18	89.01	89.06	88.75	89.96
Hydrogen	8.10	7.36	6.88	7.18	8.26	7.29	7.71	7.45
Sulfur	0.048	0.050	0.166	0.1043	0.123	0.190	0.560	0.271
Nitrogen	0.36	0.44	0.61	0.62	0.51	0.67	0.56	0.75
Total	99.64	98.31	97.95	98.08	97.90	97.21	97.58	98.43
IBP-343 °C-, W%	7.25	4.76	4.19	2.99	57.96	4.91	5.69	14.85
343-454 °C, W%	51.32	47.44	44.24	47.68	44.72	38.55	47.74	33.42
454-524 °C, W%	15.44	15.81	15.88	16.61	16.30	15.45	15.70	15.03
524 °C+, W%	25.52	31.81	34.99	32.14	30.19	40.54	30.33	35.98
Loss, W%	0.47	0.18	0.70	0.62	0.83	0.44	0.54	0.72
LGO (IBP-343 °C)								
Carbon, W%	89.98	89.56	89.61	89.63	87.86	87.92	87.85	87.23
Hydrogen, W%	10.31	9.82	9.54	9.70	10.62	10.21	10.11	11.33
Sulfur, W%	0.033	0.058	0.101	0.035	0.056	0.091	0.168	0.199
Nitrogen, W%	0.19	0.35	0.41	0.42	0.29	0.36	0.32	0.29
VGO (343-454 °C)								
Carbon, W%	90.62	90.23	90.22	90.64	89.85	89.17	89.62	89.74
Hydrogen, W%	8.87	8.52	8.04	9.31	9.11	8.54	8.40	8.48
Sulfur, W%	0.056	0.051	0.141	0.110	0.128	0.181	0.516	0.354
Nitrogen, W%	0.26	0.36	0.48	0.53	0.27	0.36	0.32	0.48
HVGO (454-524 °C)								
Carbon, W%	91.46	89.96	90.76	91.23	89.47	90.26	88.98	90.24
Hydrogen, W%	7.73	7.13	6.44	6.95	7.55	7.37	7.10	6.67
Sulfur, W%	0.067	0.0474	0.183	0.140	0.182	0.295	0.719	0.463
Nitrogen, W%	0.45	0.56	0.71	0.70	0.50	0.59	0.50	0.69
RESIDUUM (524 °C+)								
Carbon, W%	92.25	91.73	90.88	91.71	88.77	88.48	88.32	91.06
Hydrogen, W%	6.12	5.59	4.92	5.42	6.64	5.96	5.92	5.16
Sulfur, W%	0.028	0.038	0.108	0.056	0.195	0.256	0.441	0.186
Nitrogen, W%	0.45	0.56	0.71	0.70	0.50	0.59	0.50	0.69
CCR, W%	53.72	60.82	70.85	62.93	50.86	57.66	59.74	
CHX Insols., W%	29.03	70.14	86.85	61.19	58.92	72.91		81.27
Tol. Insols., W%	2.64	11.33	27.04	10.19	14.81	28.70		30.31
Ash, W%	0.00	0.00	1.020	0.00	0.03	0.12		0.00

TABLE 2.4.14

ANALYSIS OF FEED COAL FOR CMSL-04

HRI No.	58.28
MOISTURE CONTENT	25.38
PROXIMATE ANALYSIS, W% Dry Basis	
Volatile Matter	43.48
Fixed Carbon	50.49
Ash	6.03
Sulfur in Ash	5.62
SO_3 - Free Ash	5.18
ULTIMATE ANALYSIS, W% Dry Basis	
Carbon	70.4
Hydrogen	3.88
Sulfur	0.44
Nitrogen	0.87
Ash	6.03
Oxygen (by. diff.)	18.38
H/C RATIO	0.66

TABLE 2.4.15

ANALYSIS OF START-UP SOLVENT FOR CMSL-04

HRI NO.	L-809
°API Gravity	6.3
ELEMENTAL ANALYSIS, W%	
Carbon	88.62
Hydrogen	9.32
Sulfur	0.58
Nitrogen	0.18
H/C RATIO	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%	435
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 2.4.16

YIELDS OF GASES FOR RUN 227-81 (CMSL-4)

CONDITION	1	2	2	3	4
PERIOD NUMBER	5	9	10	12	15
HOURS OF RUN	120	228	240	288	260
CO IN FIRST STAGE FEED, V%	0	90	90	90	75
GAS YIELDS (STAGE 1 VENT), W% of MF Coal					
CH_4	1.05	5.16	4.86	4.04	1.04
C2H4	0.00	0.00	.00	0.00	0.00
C2H6	0.49	0.70	0.69	0.66	0.79
C3H6	0.00	0.00	0.06	0.05	0.02
C3H8	0.52	0.51	0.88	0.75	1.07
C4H8	0.00	0.00	0.00	0.00	0.01
N-C4H10	0.29	0.27	0.30	0.34	0.70
I-C4H10	0.03	0.04	0.04	0.08	0.13
C5H10	0.00	0.00	0.00	0.00	0.00
N-C5H12	0.16	0.17	0.21	0.19	0.30
I-C5H12	0.08	0.11	0.11	0.09	0.16
Methyl-Cyclopentane	0.00	0.00	0.00	0.00	0.00
Cyclohexane	0.09	0.13	0.25	0.22	0.25
N-C6H14	0.05	0.07	0.06	0.11	0.22
C6-C7	0.00	0.13	0.13	0.11	0.07
CO	0.45	35.50	36.96	26.25	0.65
CO_2	4.31	135.87	125.69	121.05	23.90
H_2S	1.53	2.07	2.00	1.68	2.05
GAS YIELDS (STAGE II VENT), W% OF MF COAL					
CH_4	1.21	3.24	2.66	3.16	2.58
C2H4	0.00	0.00	0.00	0.00	0.00
C2H6	0.99	1.31	1.82	1.51	1.71
C3H8	0.00	0.00	0.01	0.00	0.00
C3H8	1.38	1.71	3.31	1.82	2.05
C4H8	0.00	0.00	0.04	0.00	0.00
N-C4H10	1.03	1.22	2.38	1.03	1.36
I-C4H10	0.17	0.22	0.45	0.21	0.26
C5H10	0.00	0.00	0.00	0.00	0.00
N-C5H12	0.34	0.39	1.34	0.21	0.36
I-C5H12	0.26	0.27	0.66	0.16	0.29
Methyl-Cyclopentane	0.00	0.00	0.39	0.00	0.00
Cyclohexane	0.30	0.45	1.28	0.09	0.30
N-C6H14	0.30	0.33	0.91	0.09	0.19
C6-C7	0.10	0.19	0.33	0.00	0.12
CO	0.00	0.20	0.16	0.15	0.04
CO_2	0.03	0.57	1.68	0.32	0.08
H_2S	2.40	4.22	5.24	2.20	0.20

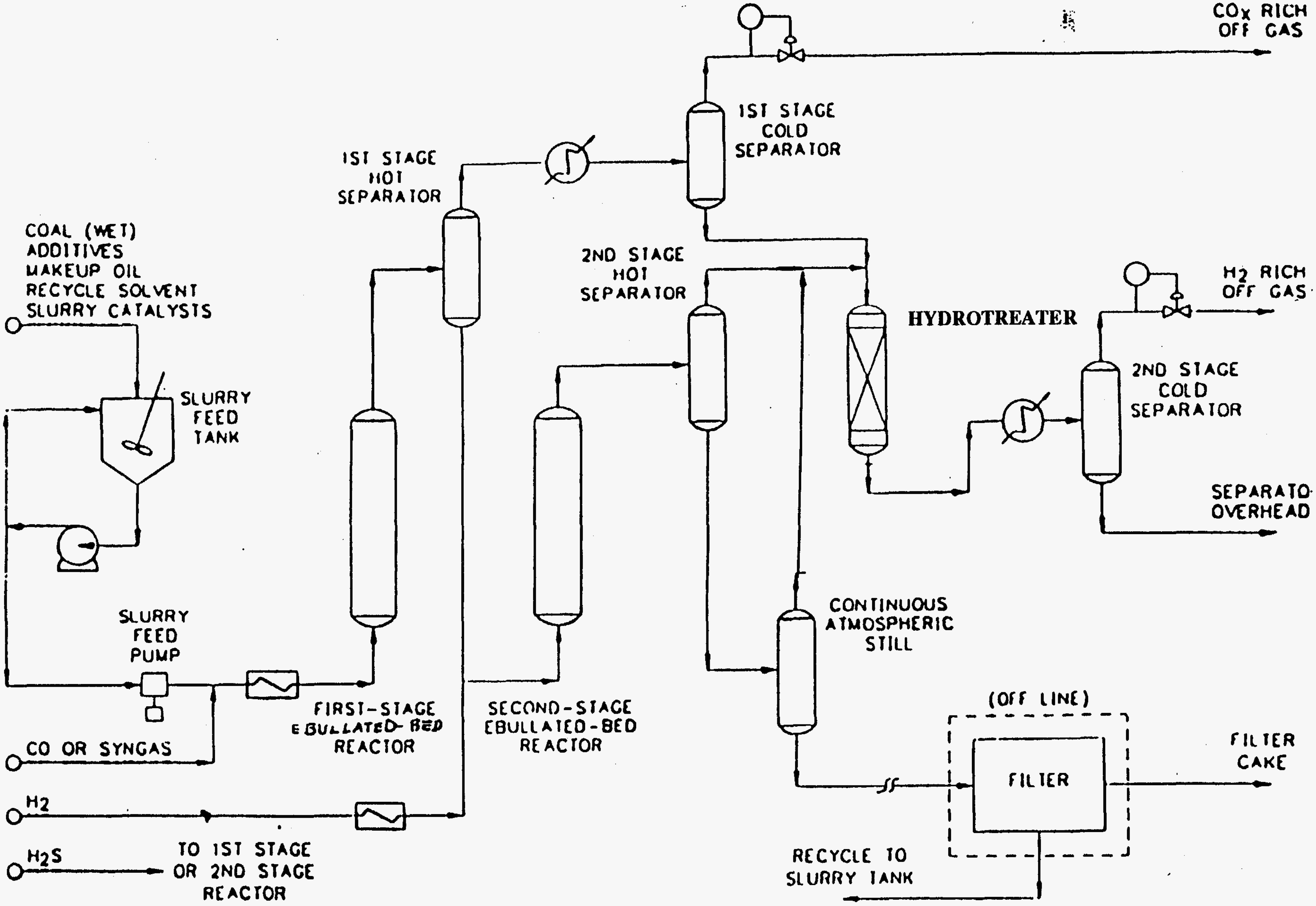


FIGURE 2.4.1

HTI SYNGAS - H2 TWO-STAGE COAL LIQUEFACTION SCHEME

CMSL-04 (RUN 227-81)
COAL CONVERSION

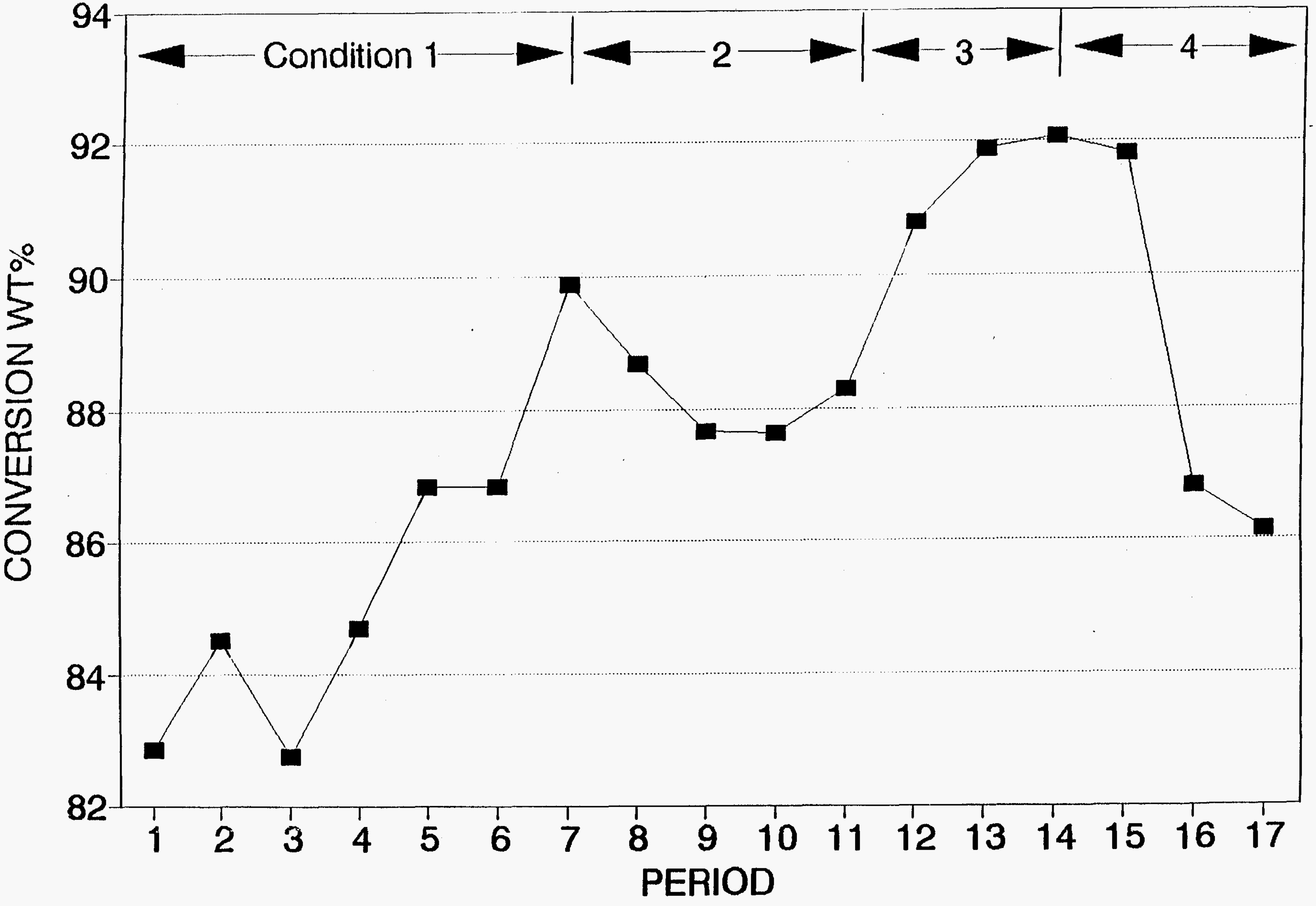


FIGURE 2.4.2

CMSL-04 (RUN 227-81)
RESID CONVERSION

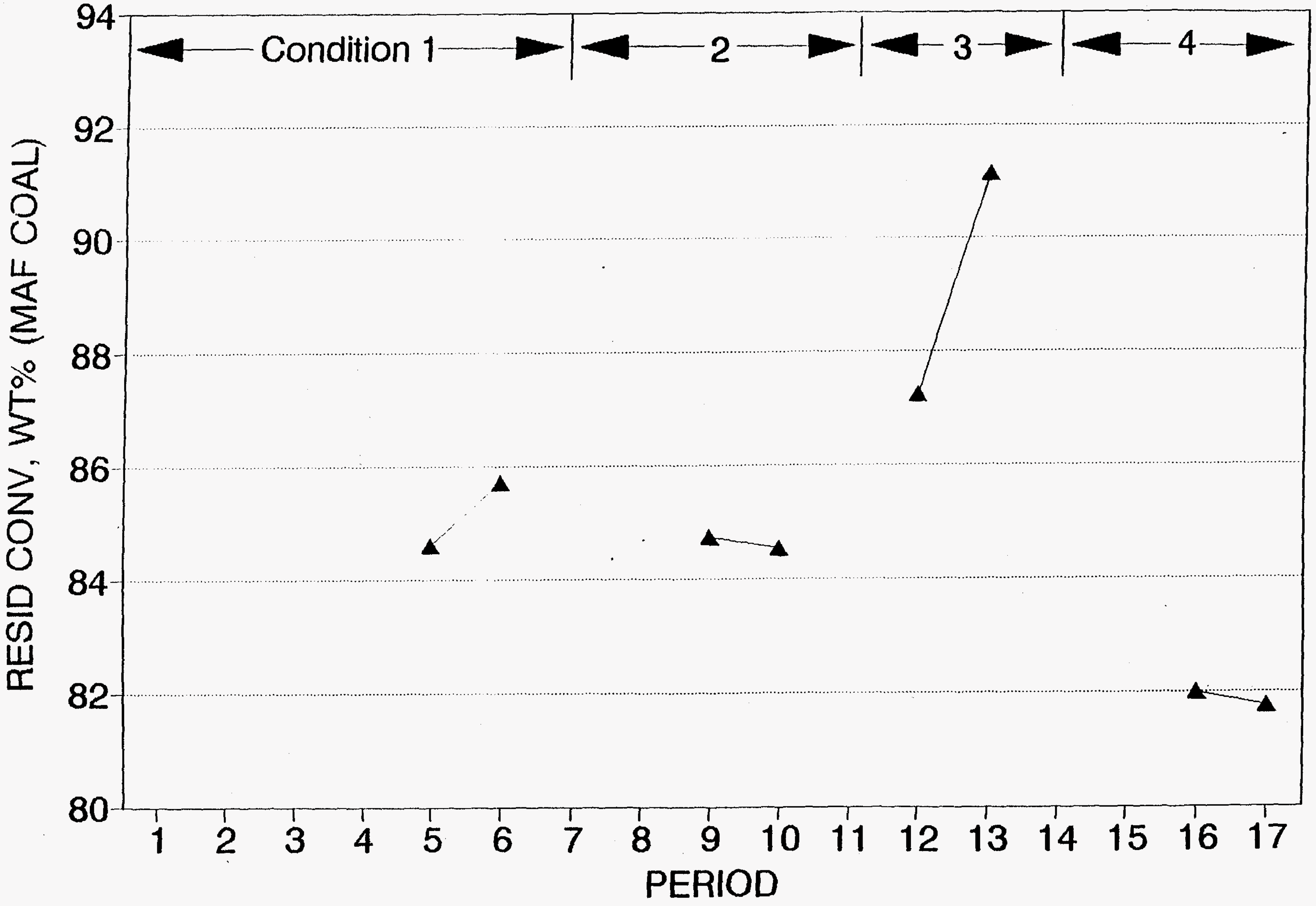


FIGURE 2.4.3

CMSL-04 (RUN 227-81)
HYDROGEN CONSUMPTION

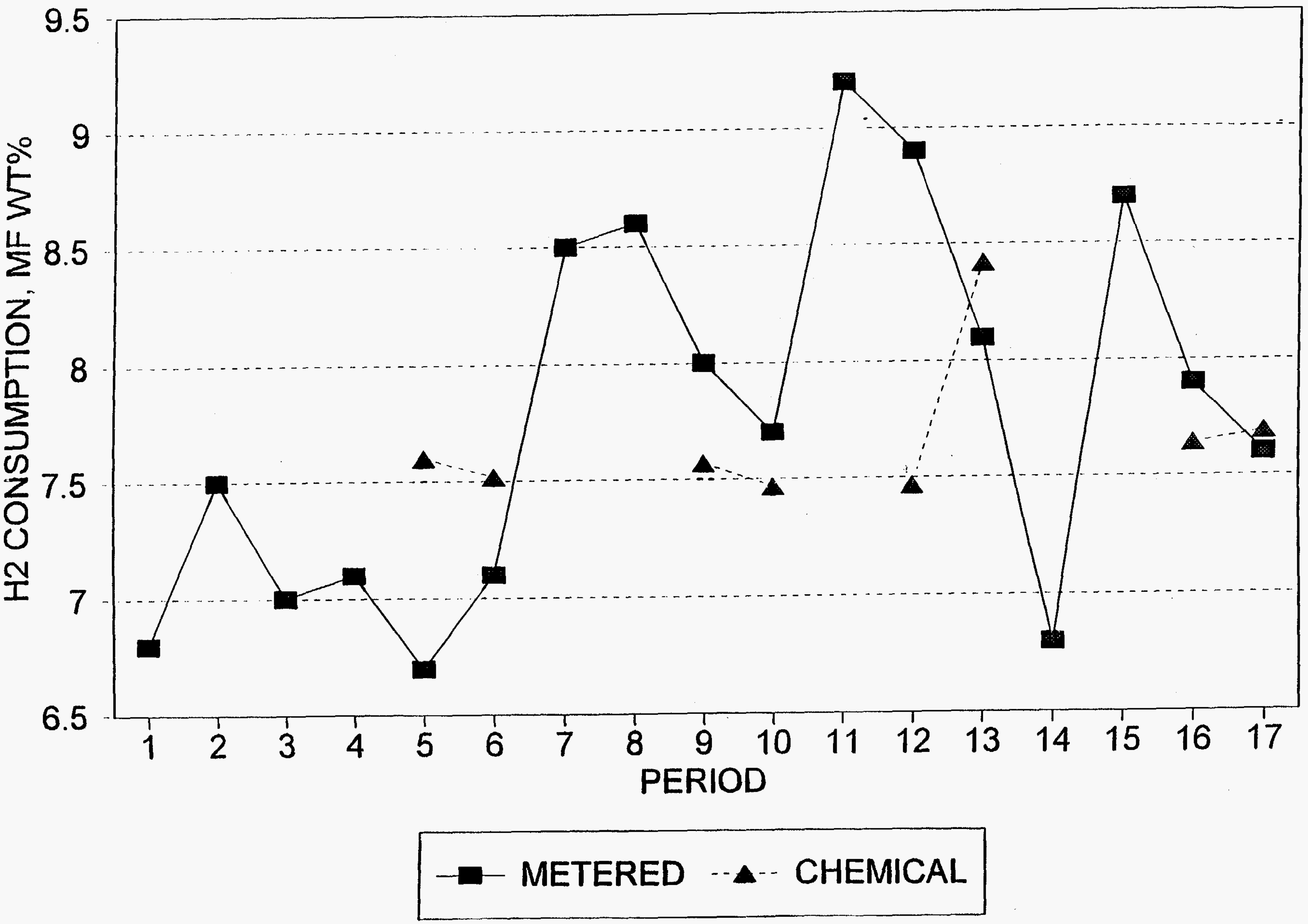
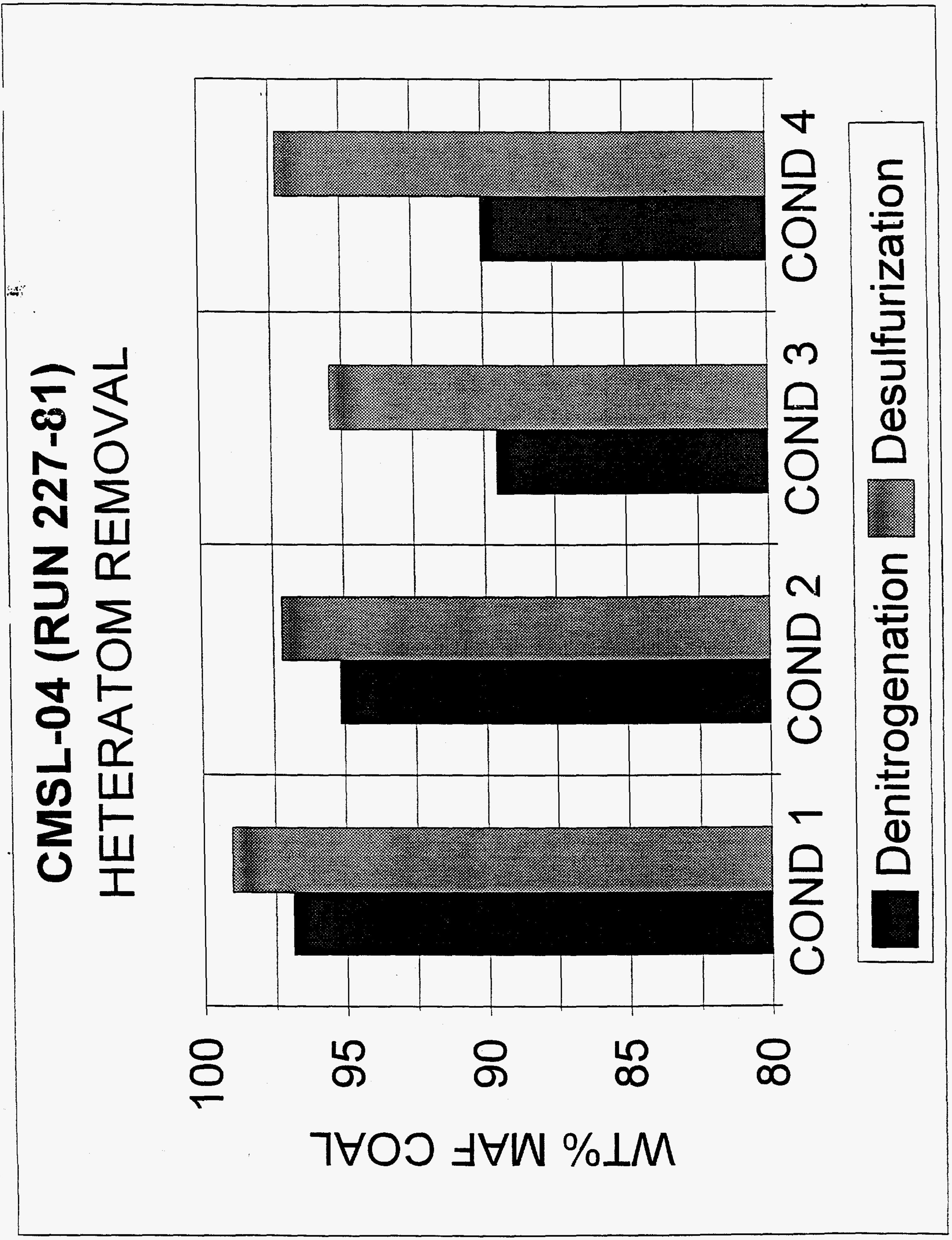
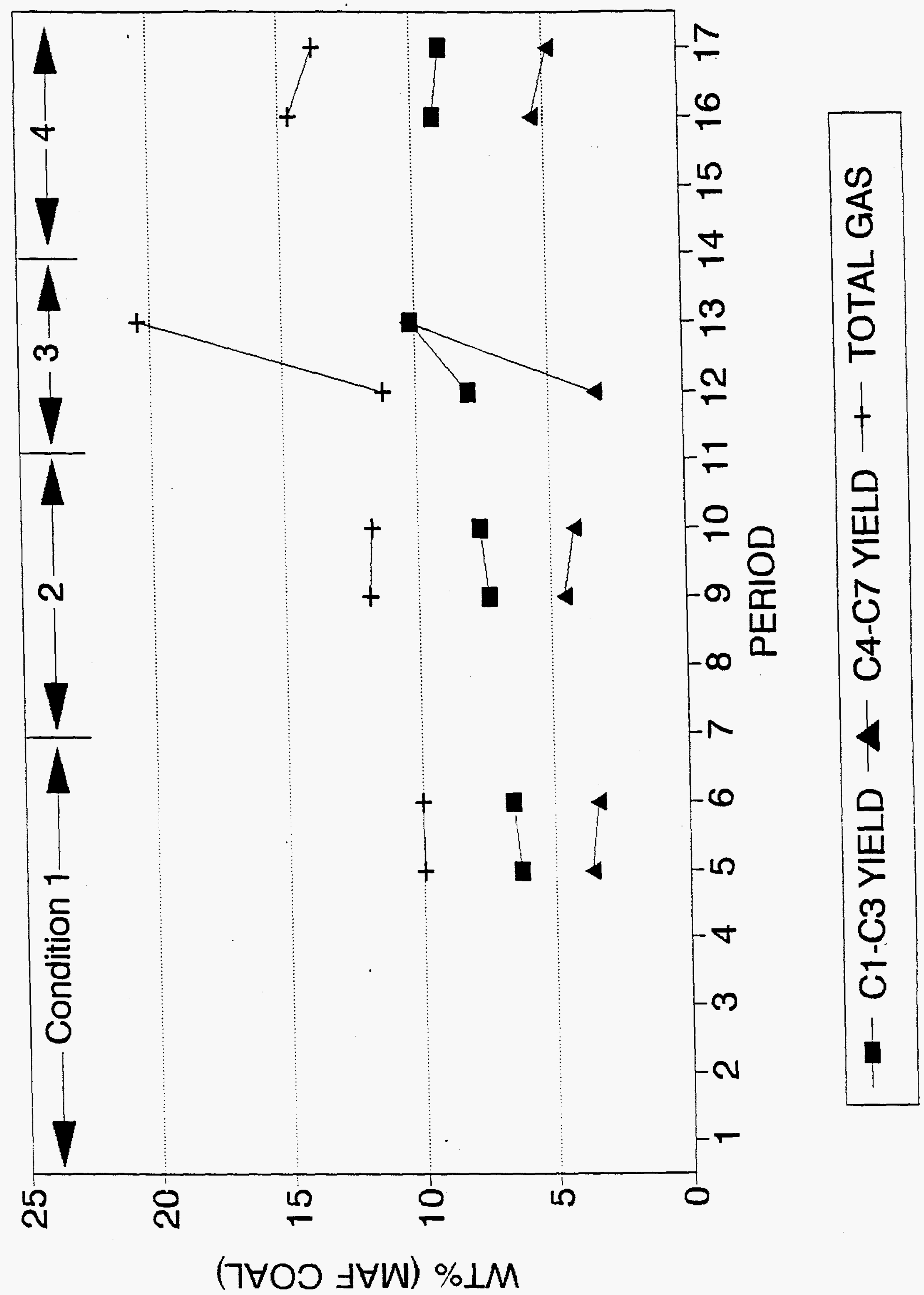


FIGURE 2.4.4



CMSL-04 (RUN 227-81)
HETERATOM REMOVAL

CMSL-04 (RUN 227-81)
GAS YIELDS



CMSL-4 (RUN 227-81)
DISTILLATE YIELD

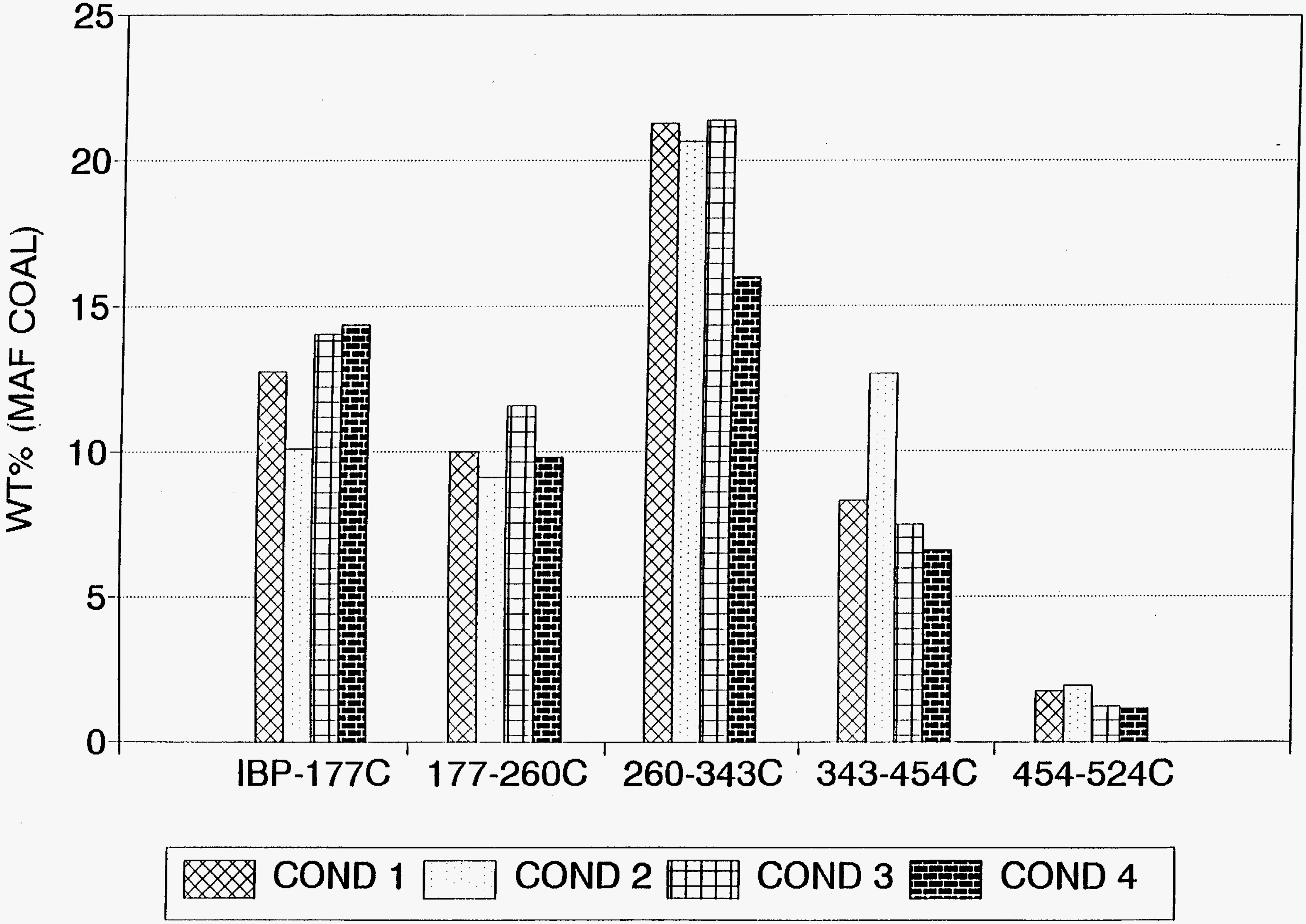


FIGURE 2.4.7

CMSL-04 (RUN 227-81)
SULFUR CONTENT

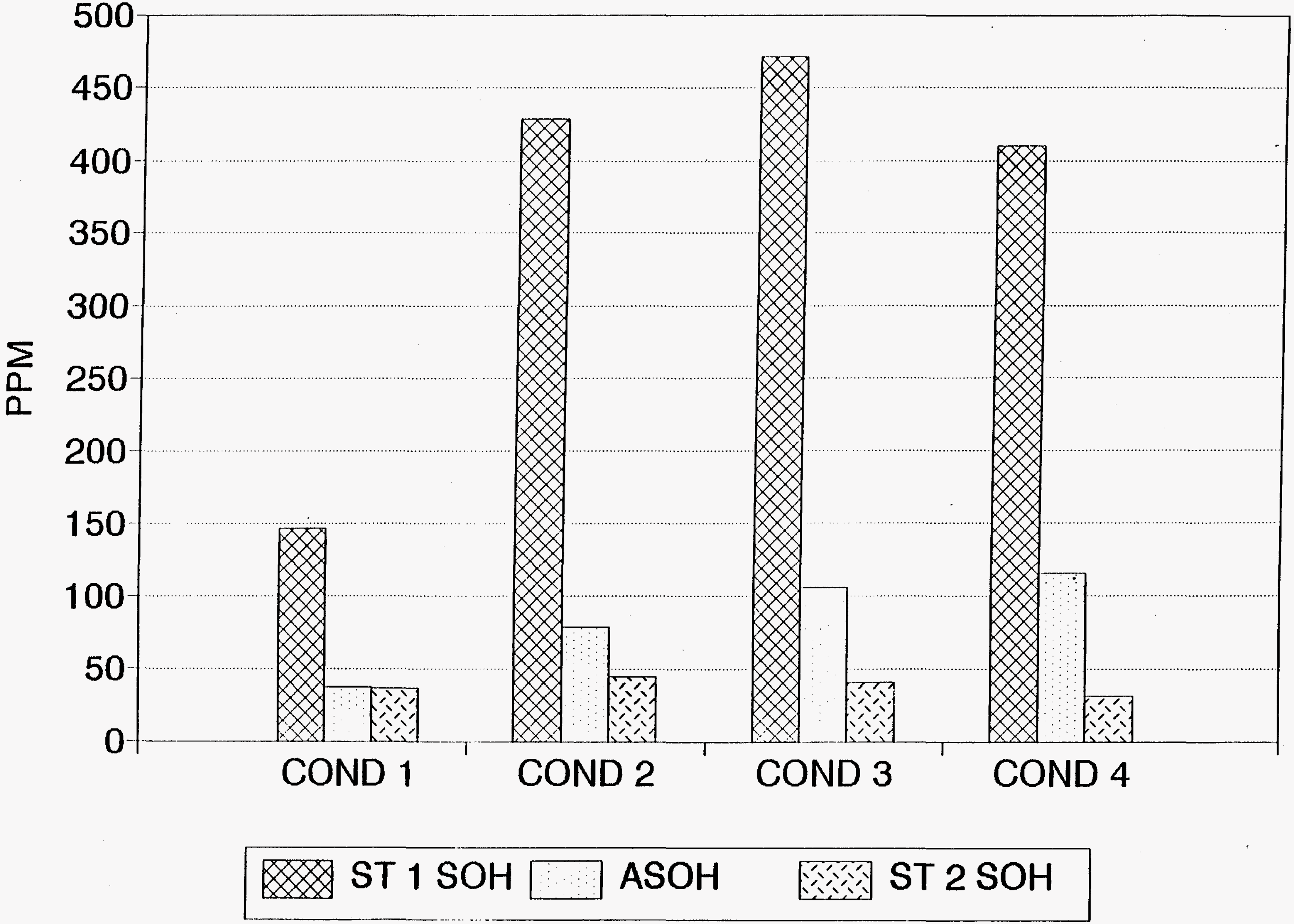


FIGURE 2.4.8

CMSL-04 (RUN 227-81)
NITROGEN CONTENT

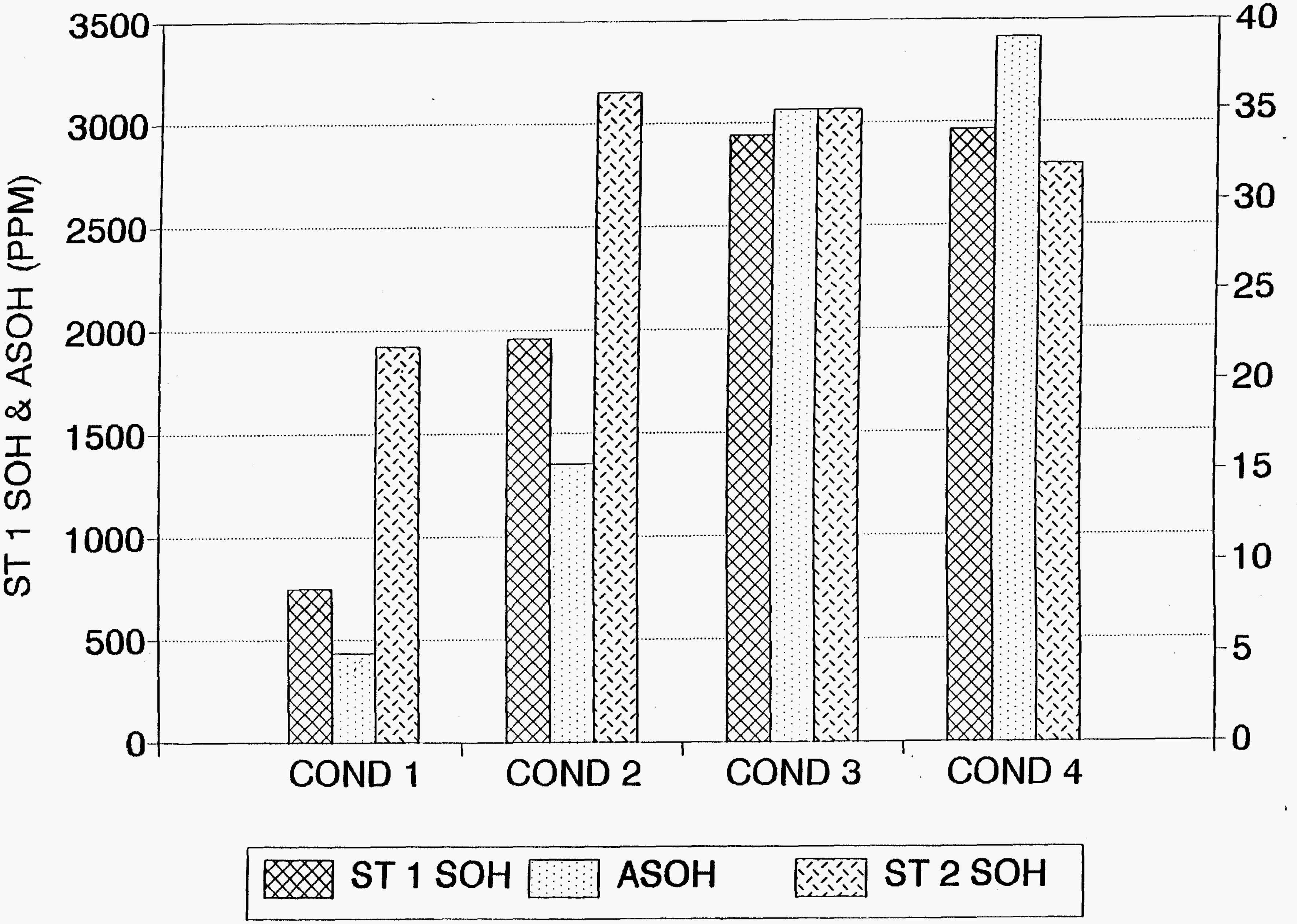


FIGURE 2.4.9

FIGURE 2.4.10

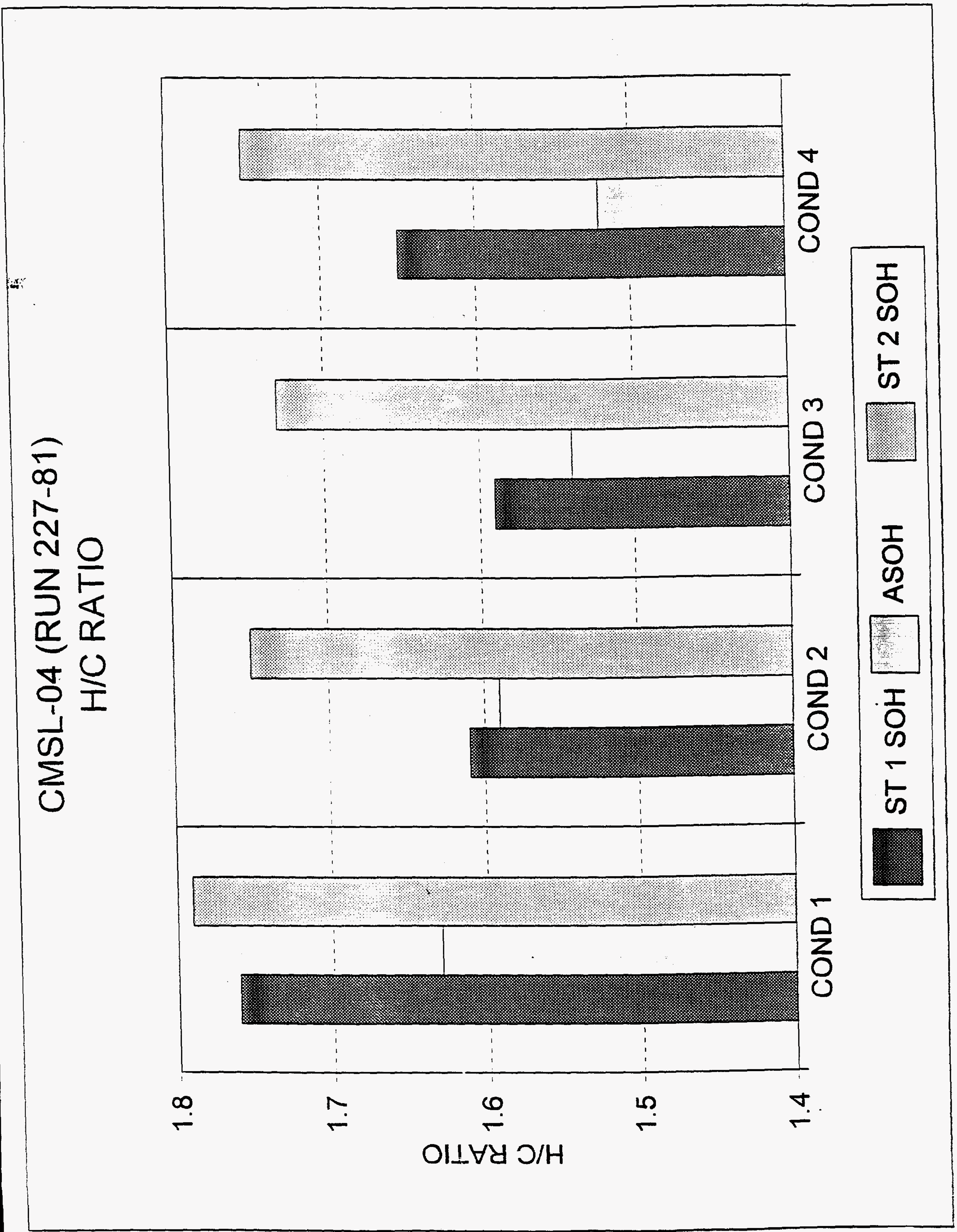
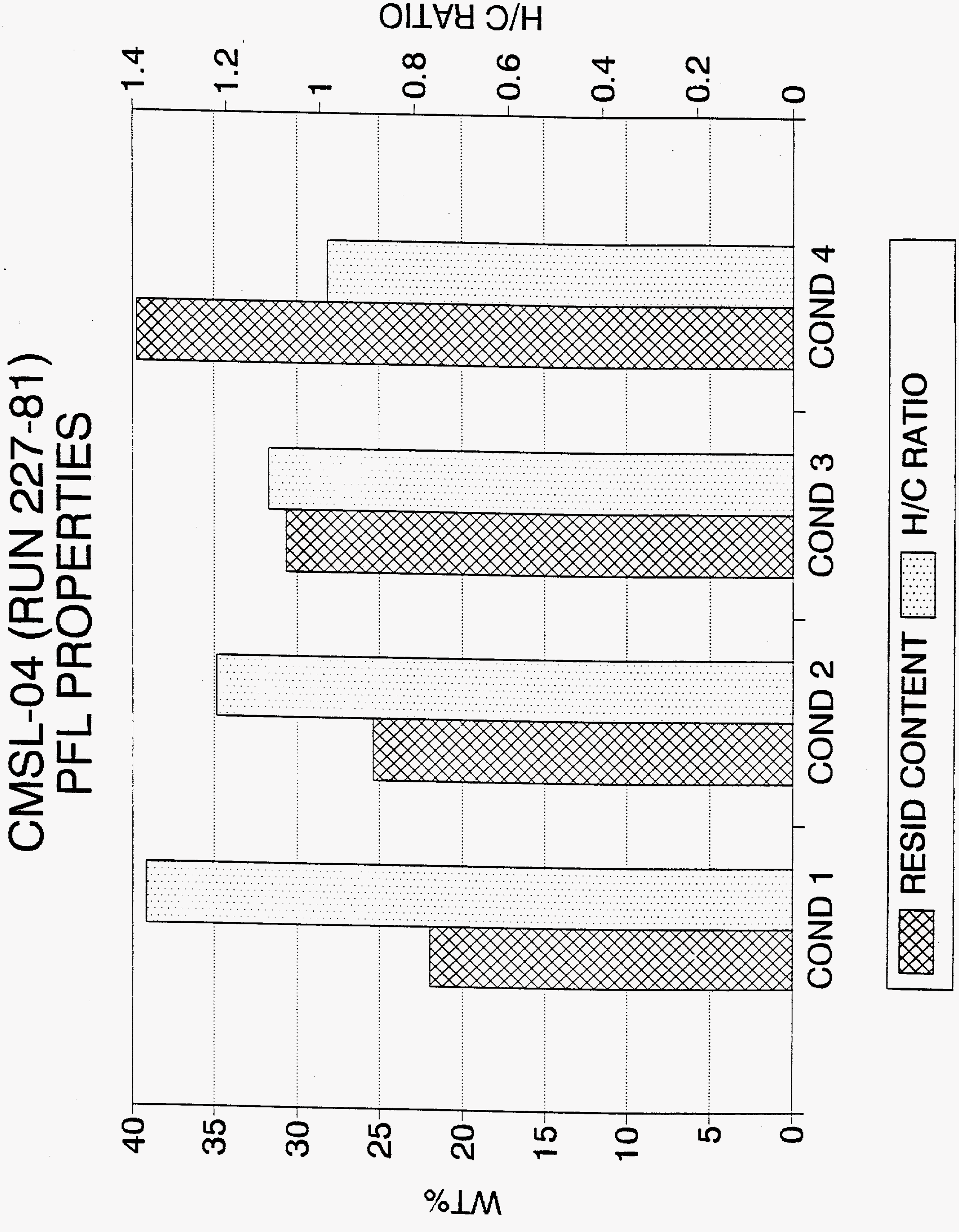

CMSL-04 (RUN 227-81)
H/C RATIO
H/C RATIO
1.8
1.7
1.6
1.5
1.4
COND 1
COND 2
COND 3
COND 4
ST 1 SOH
ASOH
ST 2 SOH

FIGURE 2.4.11


CMSL-04 (RUN 227-81)
PFL PROPERTIES
WT%
0
5
10
15
20
25
30
35
40
H/C RATIO
0
0.2
0.4
0.6
0.8
1
1.2
1.4
COND 1
COND 2
COND 3
COND 4
RESID CONTENT
H/C RATIO

CMSL-04 (RUN 227-81)
PFL INSOLUBLES

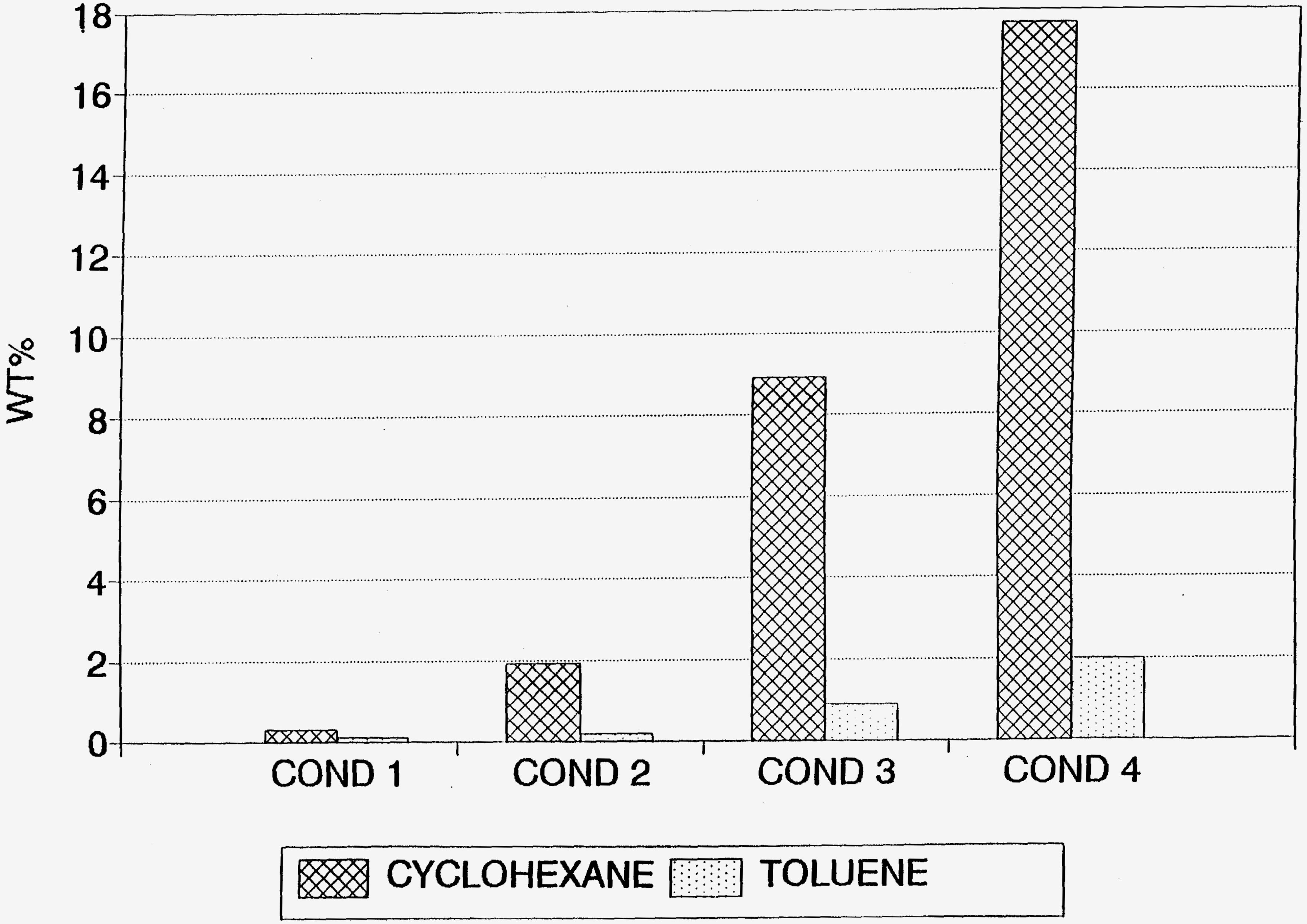


FIGURE 2.4.12

FIRST- AND TWO-STAGE COAL CONVERSION COMP. OF SYNGAS (CMSL-4,-7) & H2 (CC-1)

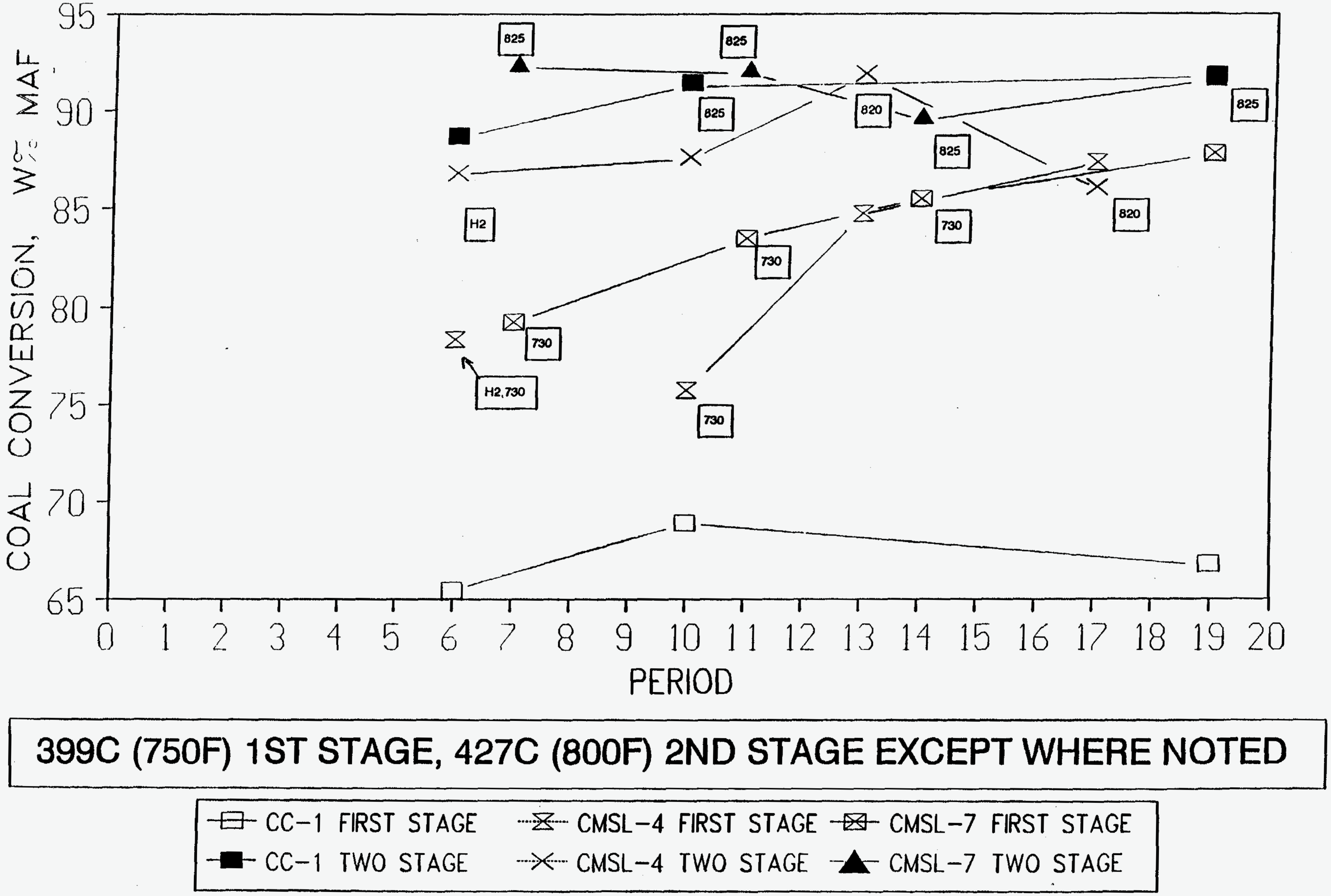


FIGURE 2.4.13

SOLIDS H:C RATIO VS. COAL CONVERSION RUNS CC-1 AND CMSL-7

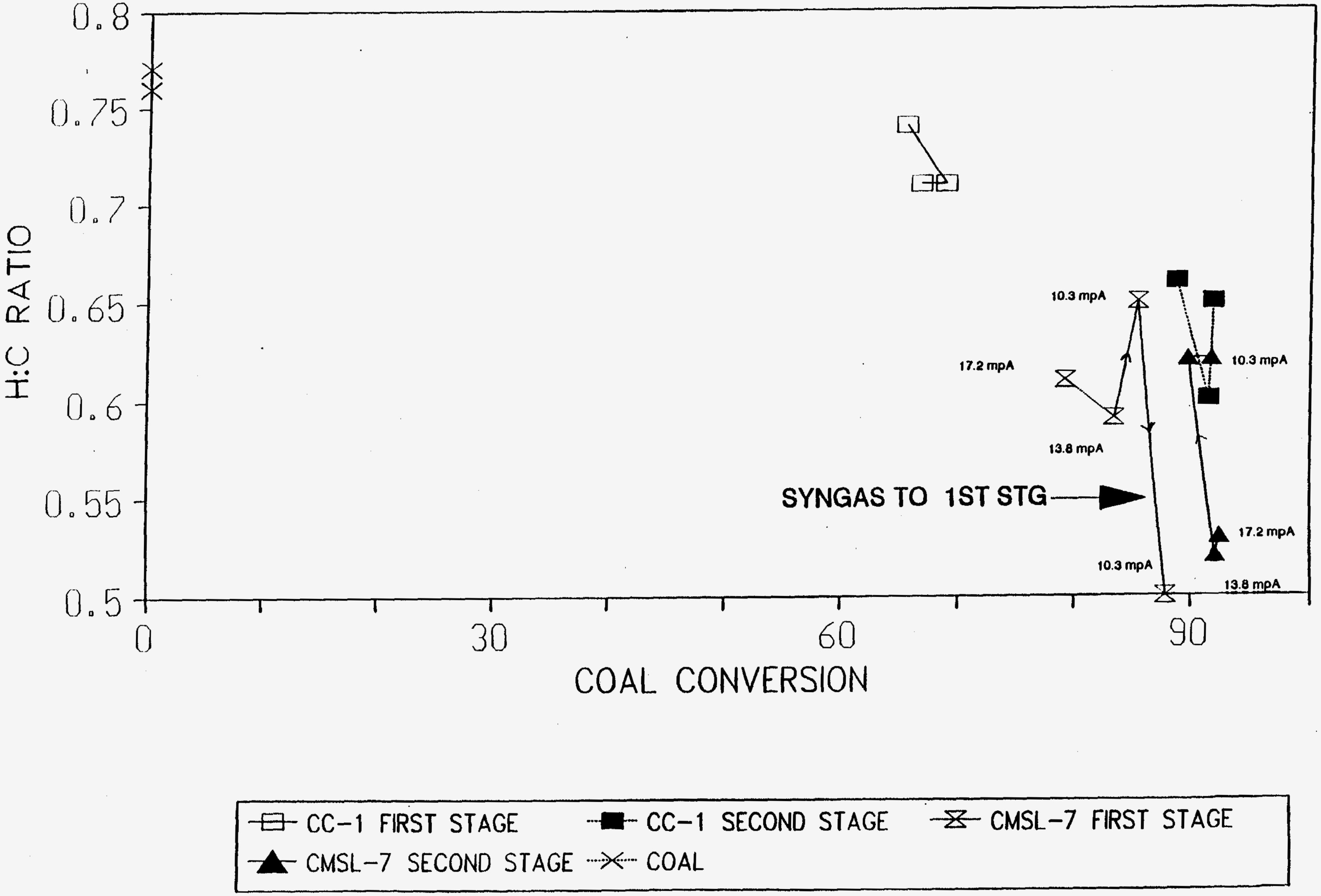


FIGURE 2.4.14

SOLIDS NITROGEN/CARBON RATIO
RUNS CC-1 AND CMSL-7

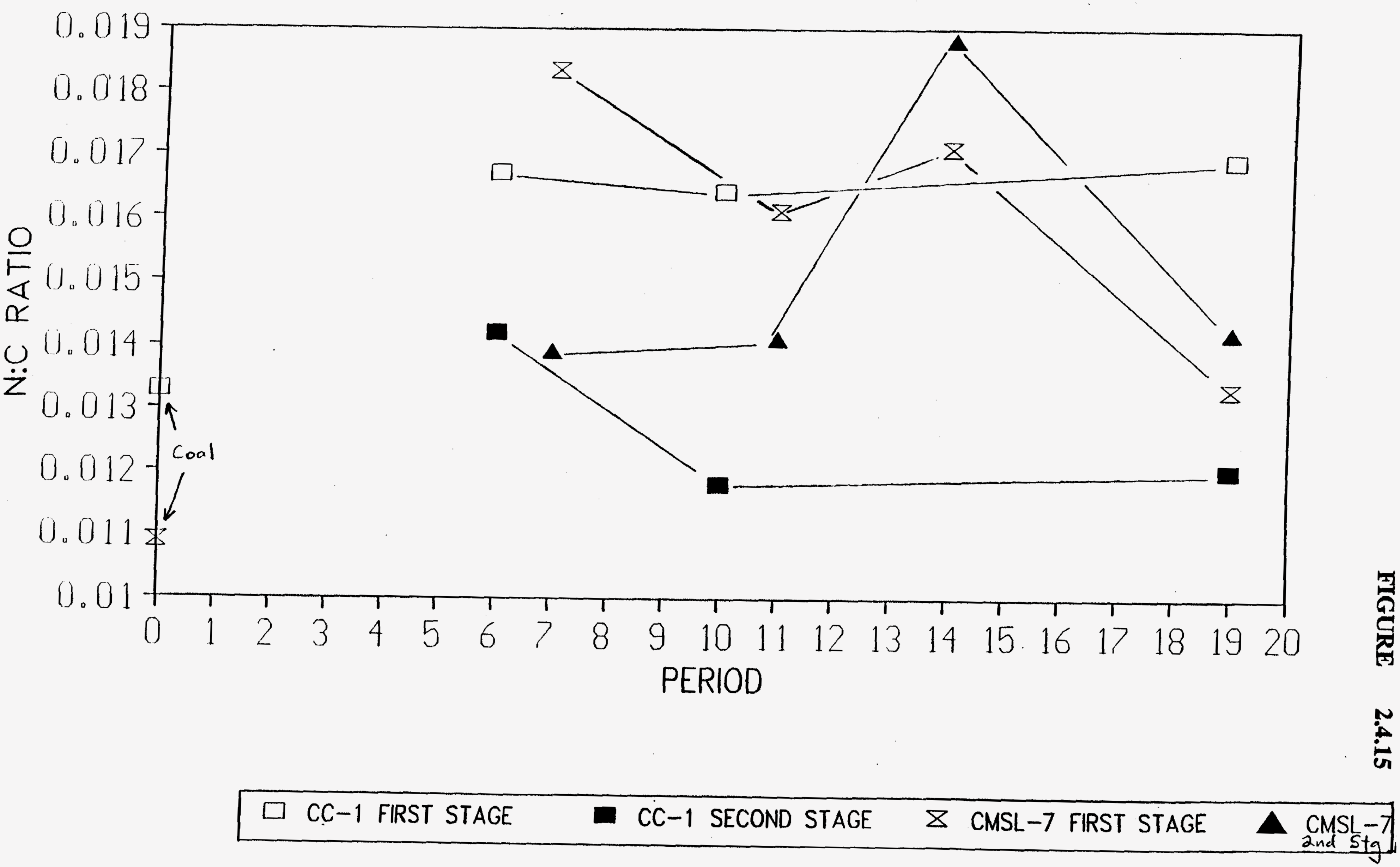
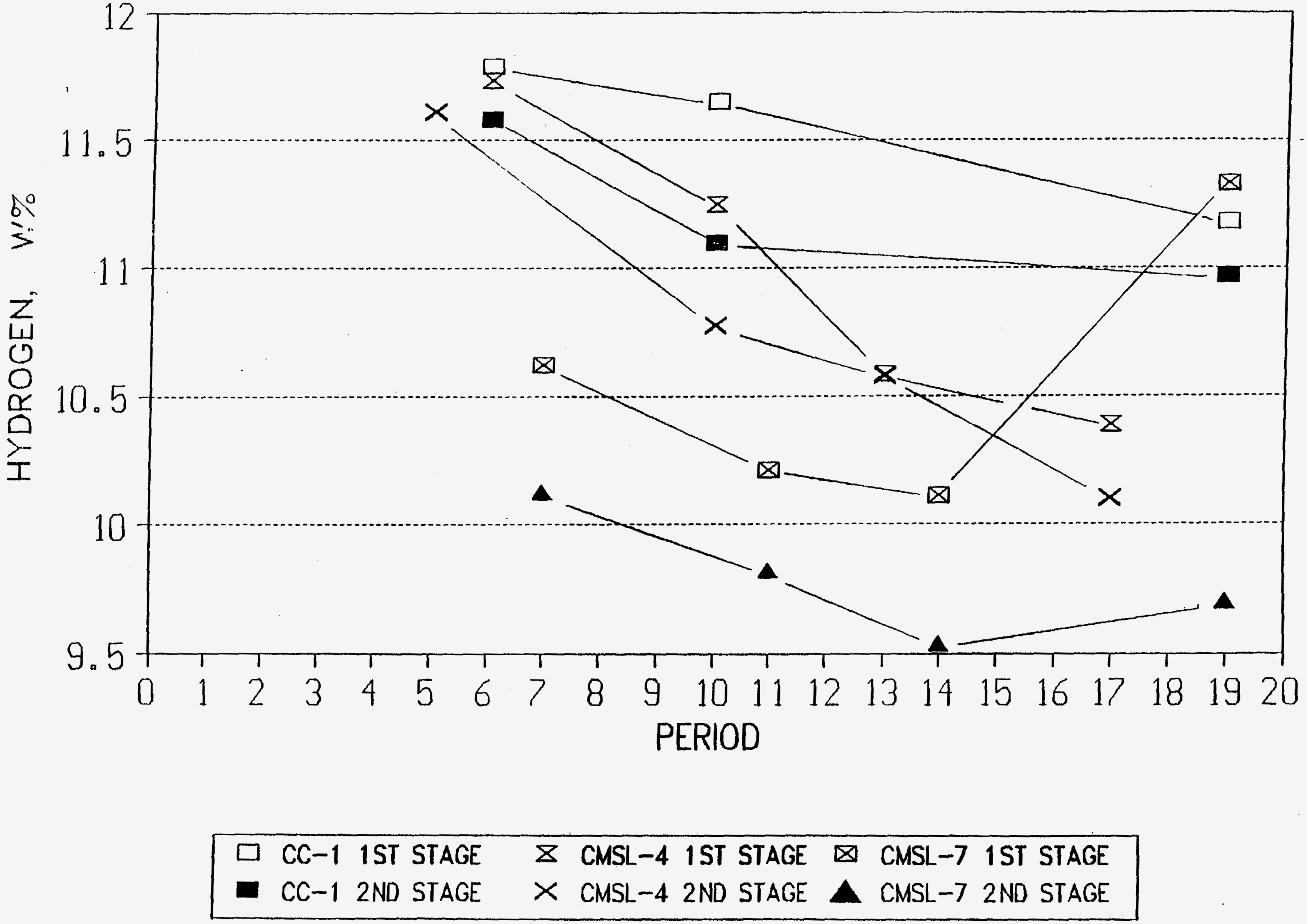


FIGURE 2.4.15



HYDROGEN CONTENT OF 1ST & 2ND STAGE LGO
RUNS CC-1, CMSL-4, & CMSL-7

FIGURE 2.4.16

HYDROGEN CONTENT OF 1ST & 2ND STAGE VGO
RUNS CC-1, CMSL-4, & CMSL-7

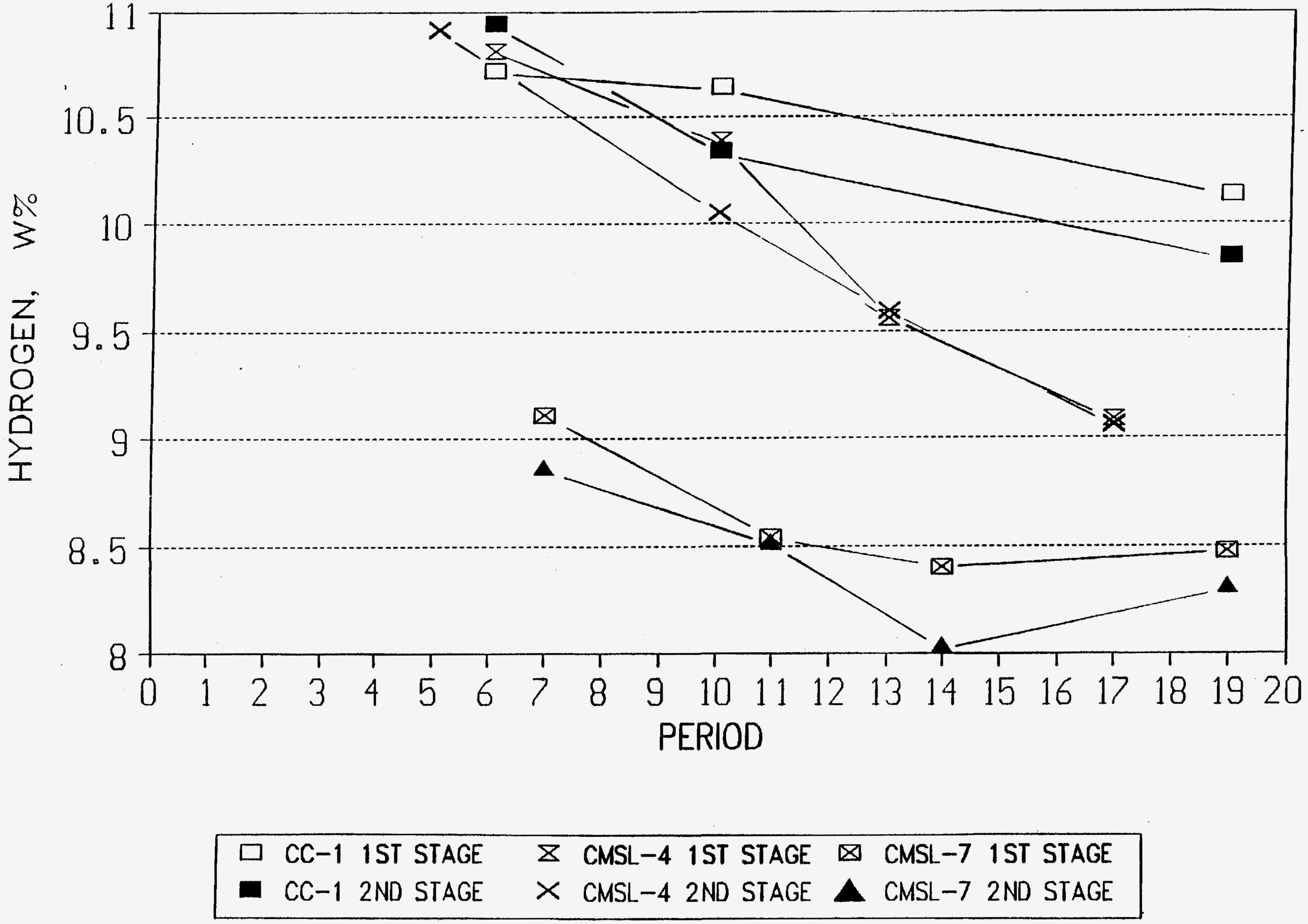
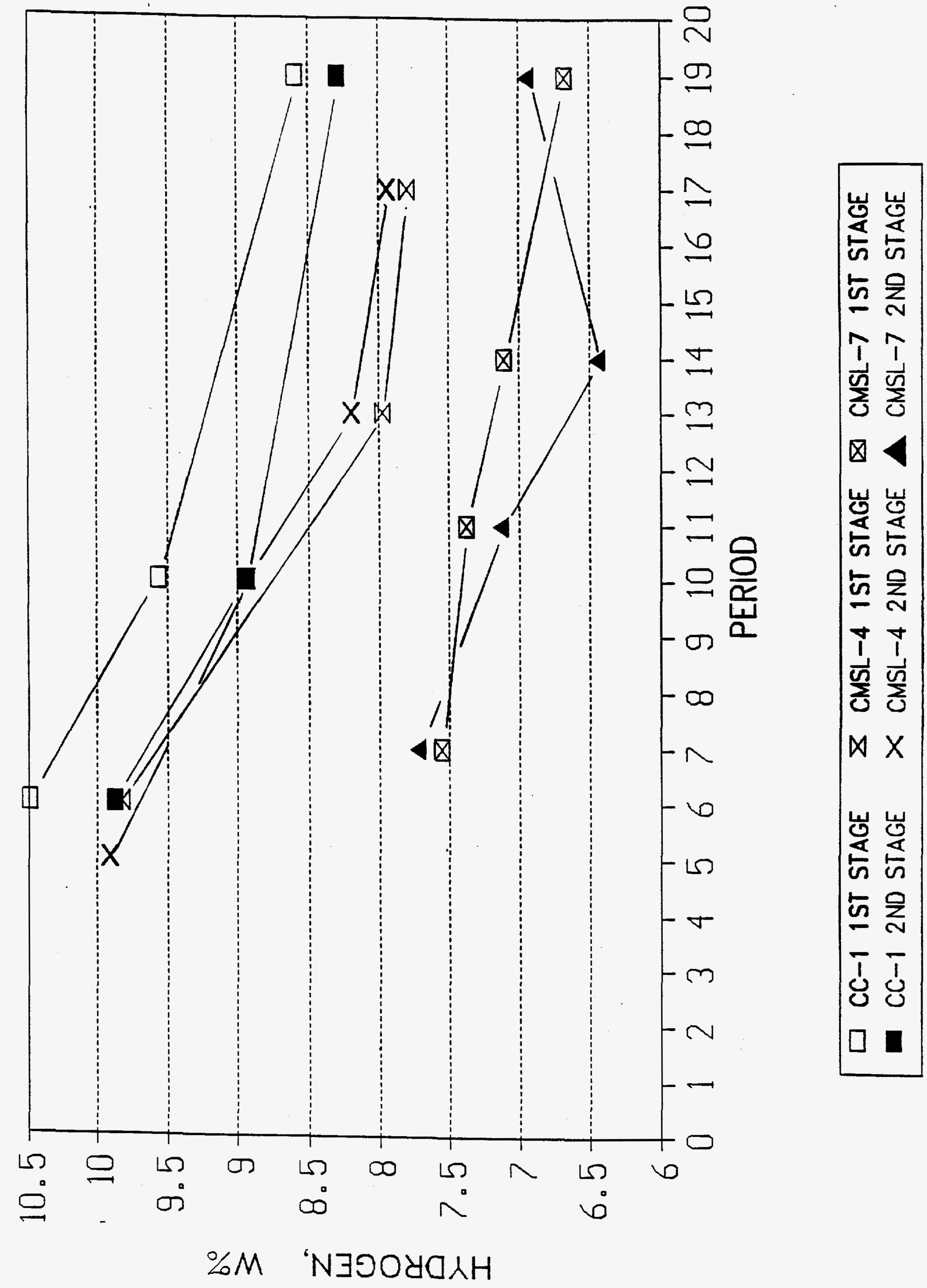


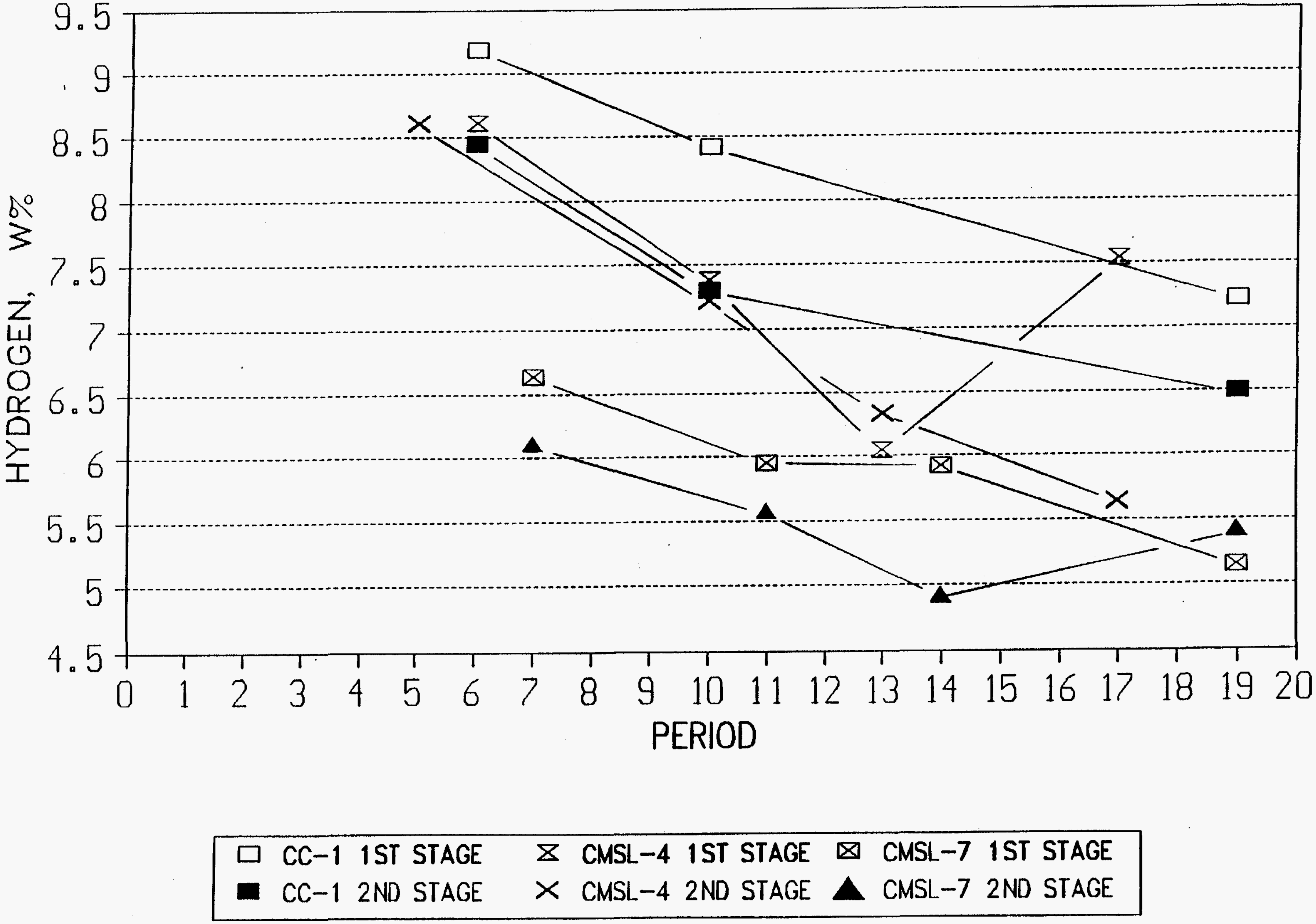
FIGURE 2.4.17

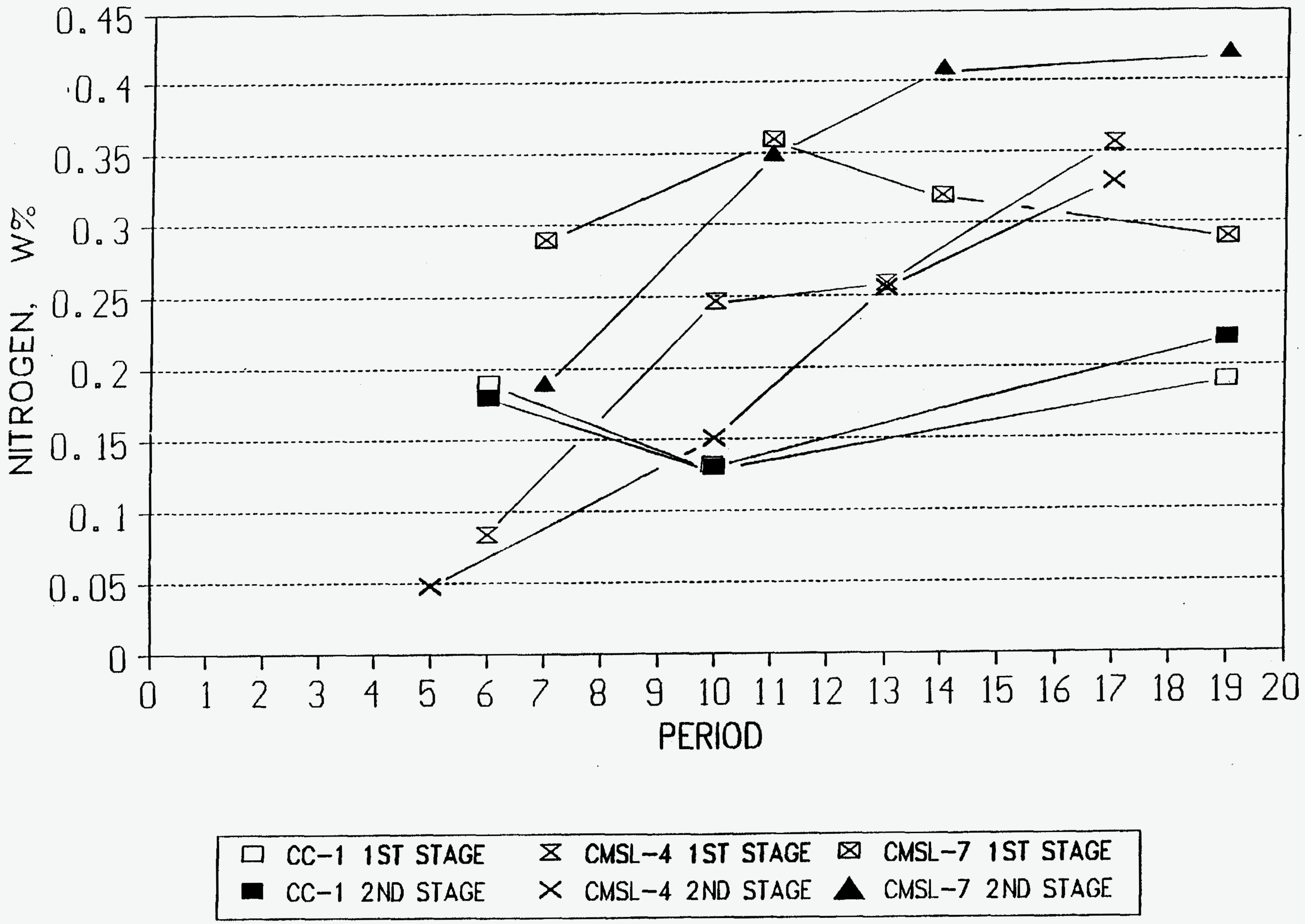


HYDROGEN CONTENT OF 1ST & 2ND STG HVGO
RUNS CC-1, CMSL-4, & CMSL-7

FIGURE 2.4.19

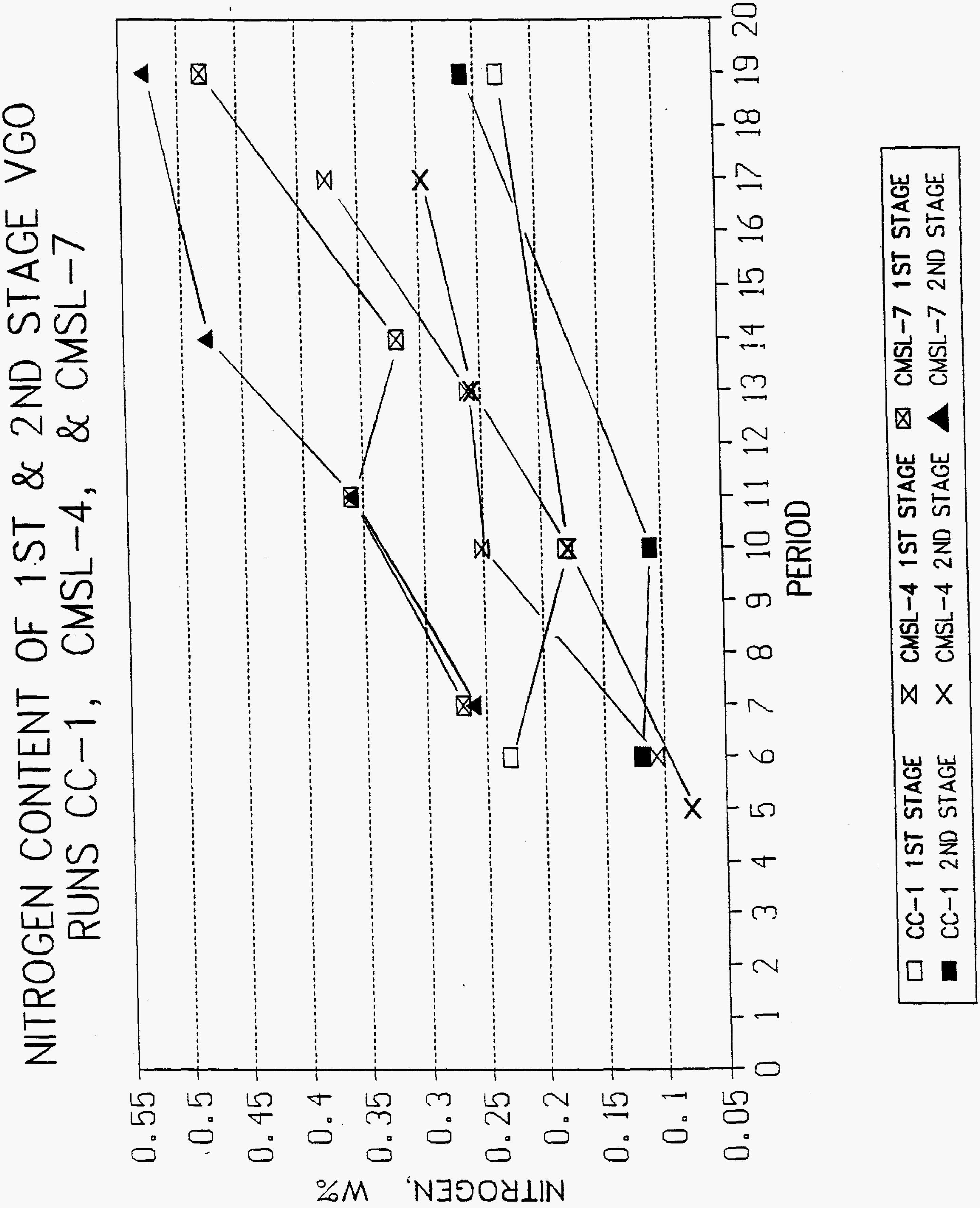
HYDROGEN CONTENT OF 1ST & 2ND STG RESID
RUNS CC-1, CMSL-4, & CMSL-7





NITROGEN CONTENT OF 1ST & 2ND STAGE LGO
RUNS CC-1, CMSL-4, & CMSL-7

FIGURE 2.4.20


NITROGEN CONTENT OF 1ST & 2ND STAGE VGO
RUNS CC-1, CMSL-4, & CMSL-7
NITROGEN, W%
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
PERIOD
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
□ CC-1 1ST STAGE
■ CC-1 2ND STAGE
☒ CMSL-4 1ST STAGE
X CMSL-4 2ND STAGE
☒ CMSL-7 1ST STAGE
▲ CMSL-7 2ND STAGE

NITROGEN CONTENT OF 1ST & 2ND STG HVGO
RUNS CC-1, CMSL-4, & CMSL-7

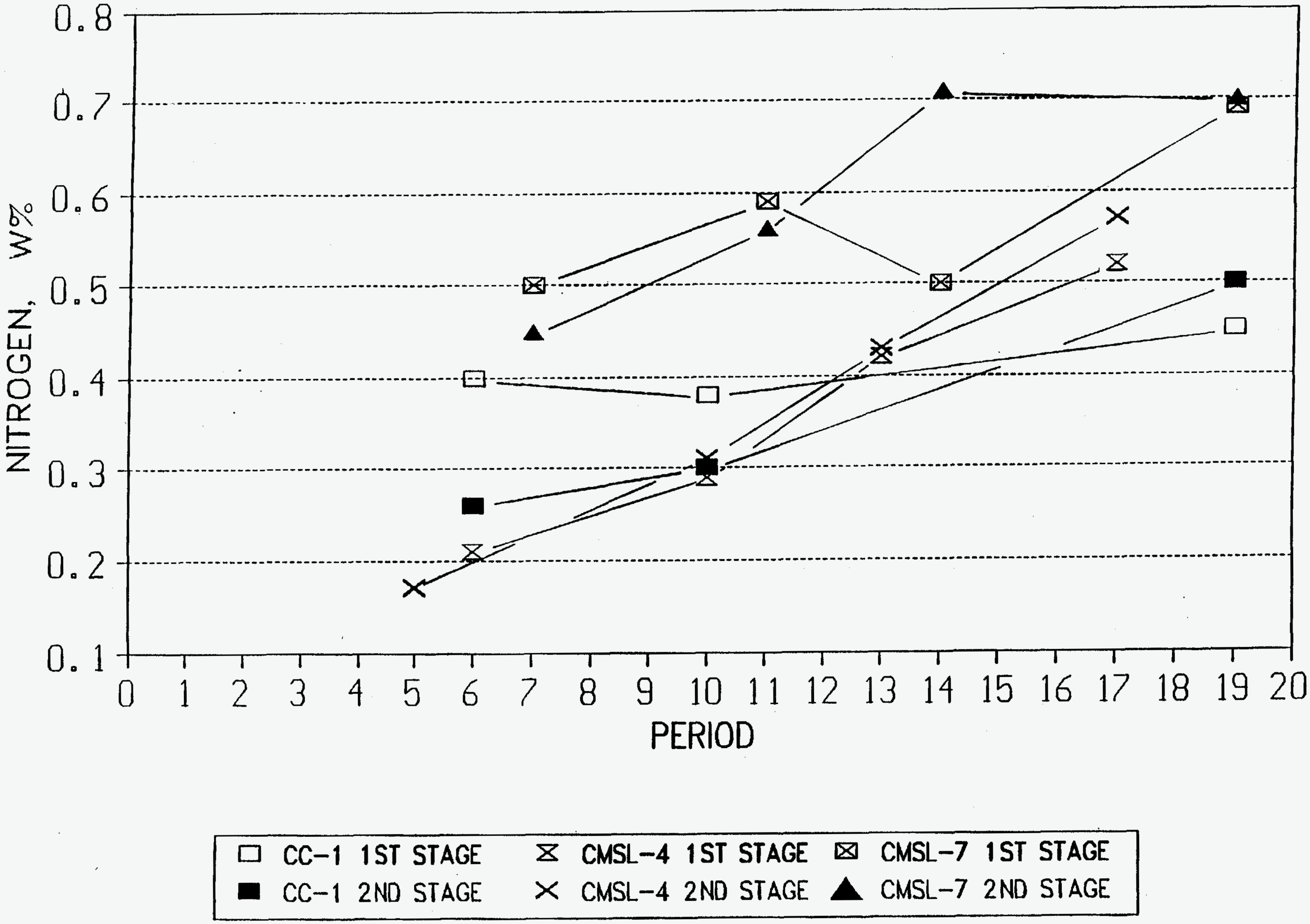


FIGURE 2.4.22

NITROGEN CONTENT OF 1ST & 2ND STG RESID
RUNS CC-1, CMSL-4, & CMSL-7

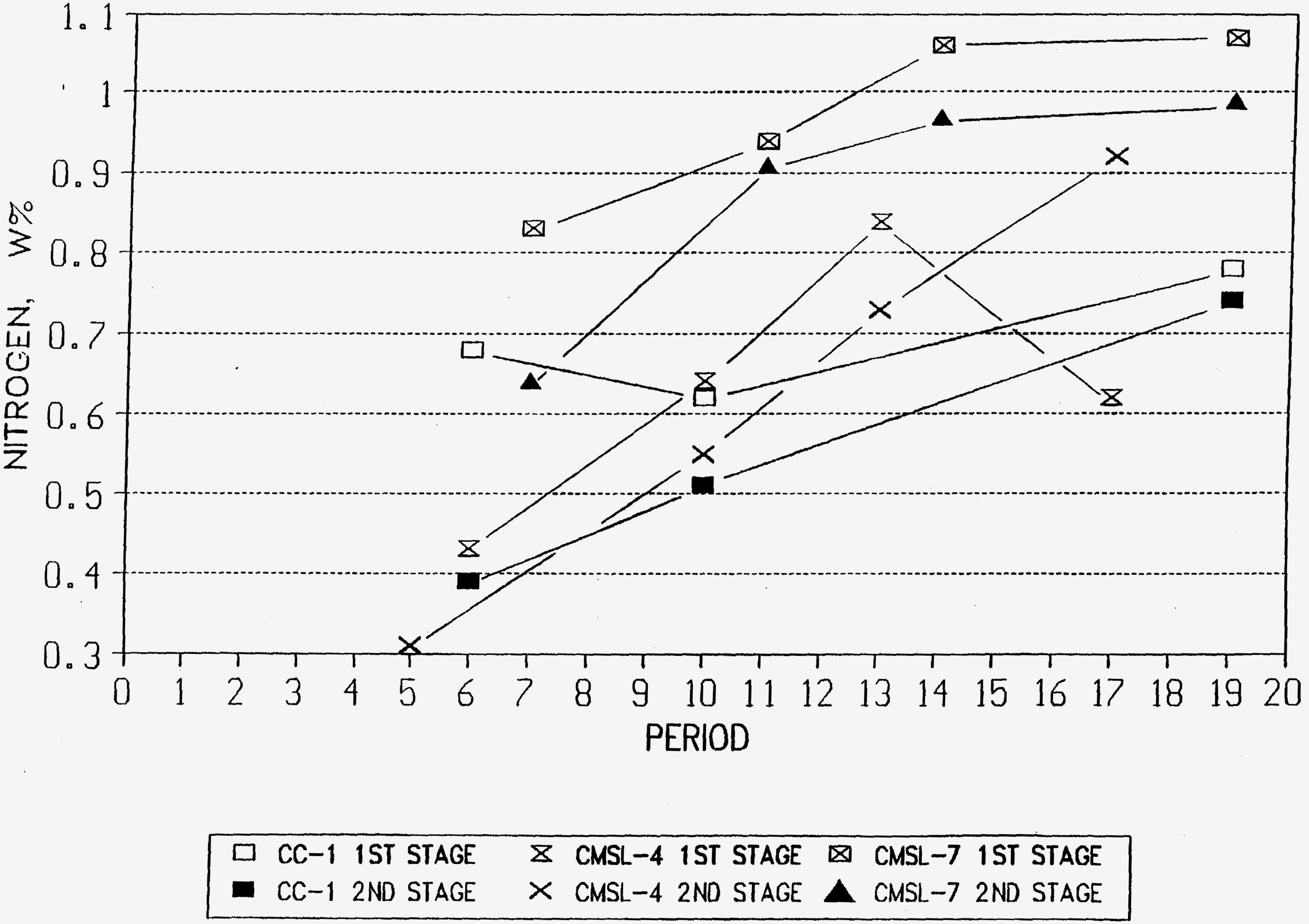


FIGURE 2.4.23

CYCLOHEXANE INSOLS IN 1ST&2ND STG RESID
RUNS CC-1, CMSL-4, & CMSL-7

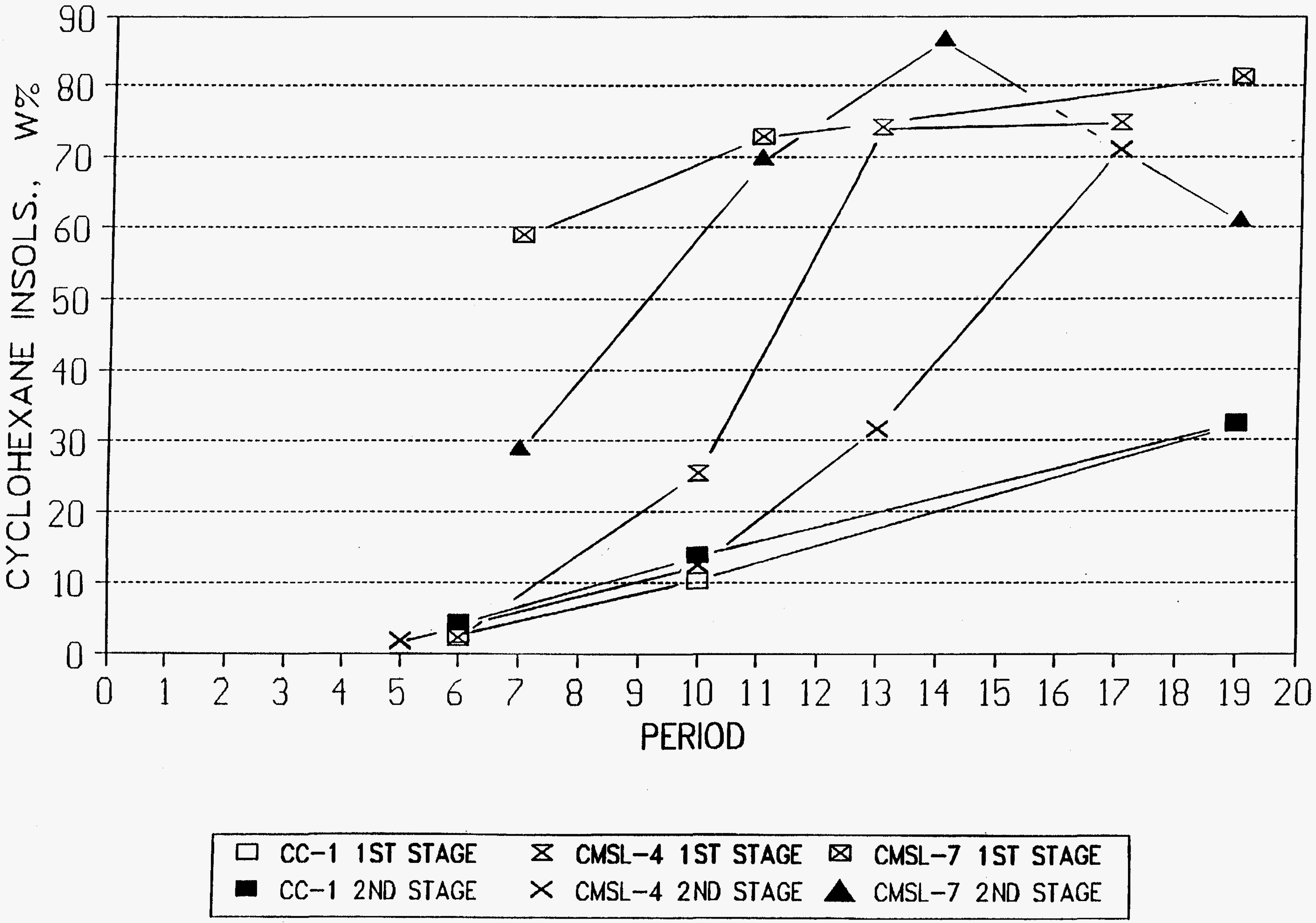


FIGURE 2.4.24

TOLUENE INSOLS IN 1ST & 2ND STG RESID
RUNS CC-1, CMSL-4, & CMSL-7

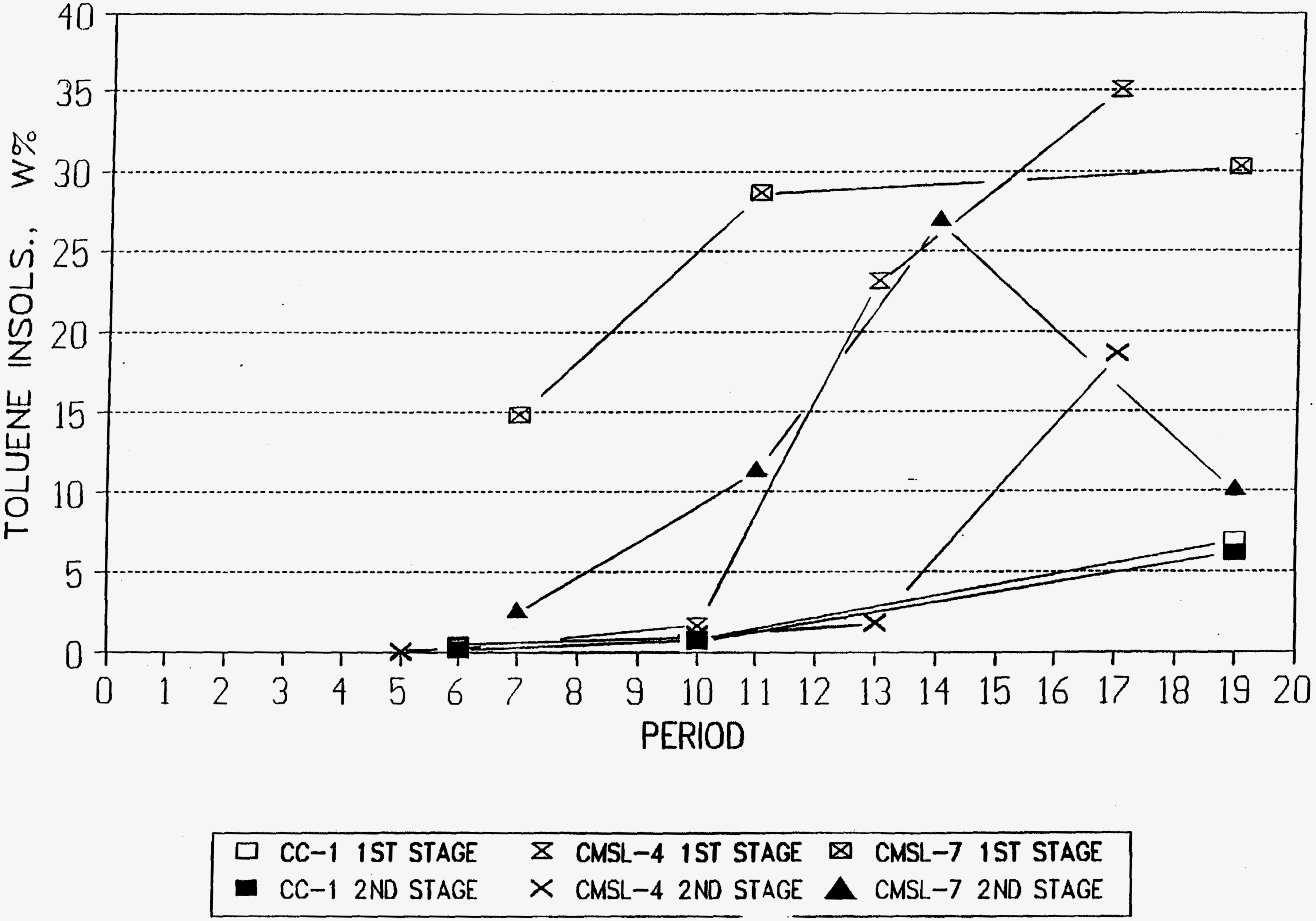


FIGURE 2.4.25

CMSL-04 (RUN 227-81)
TEMPERATURE VS PERIOD

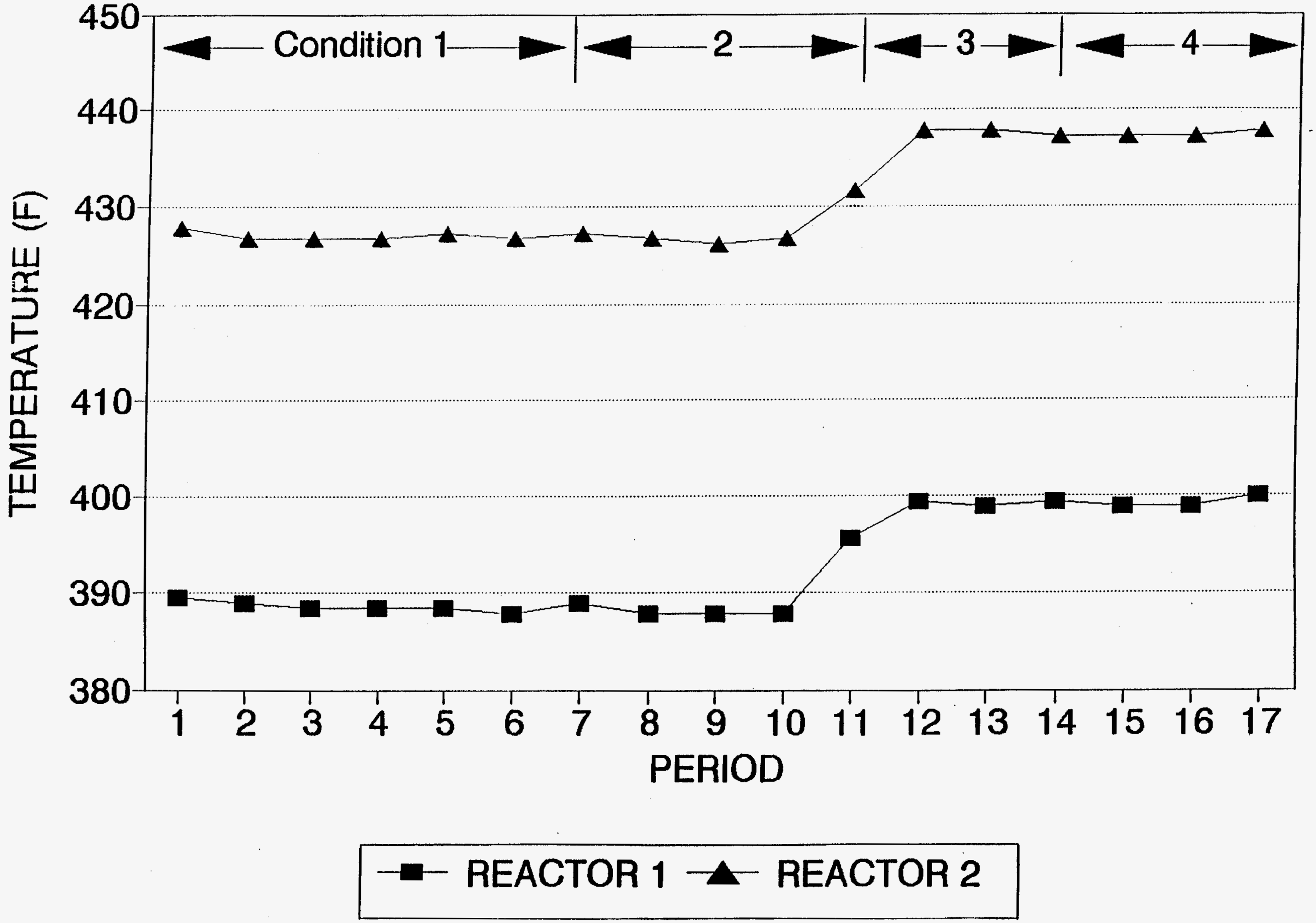
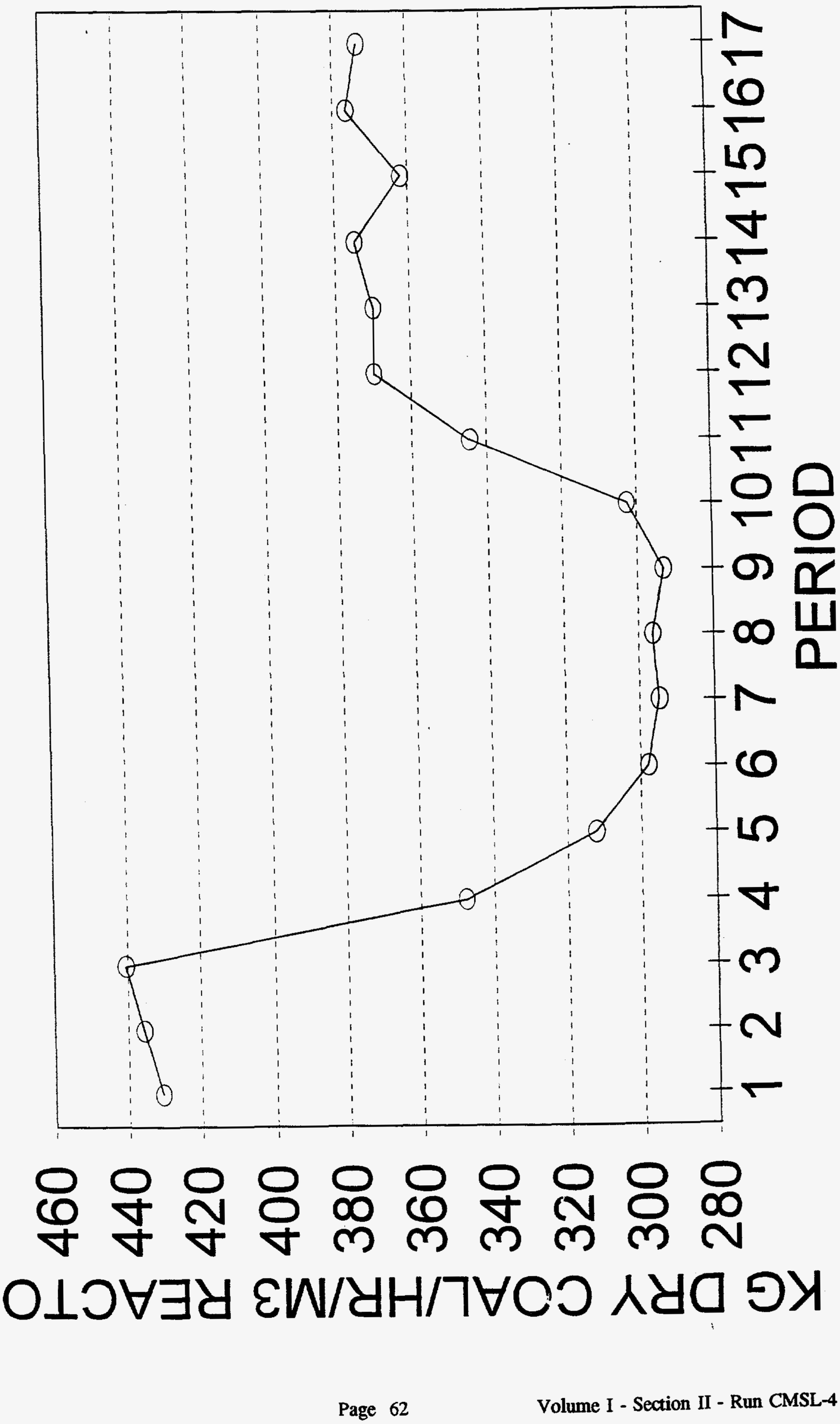


FIGURE 2.4.26

CMSL-04 (RUN 227-81)
SPACE VELOCITY



CMSL-04 (RUN 227-81)
OVERALL PROCESS SEVERITY

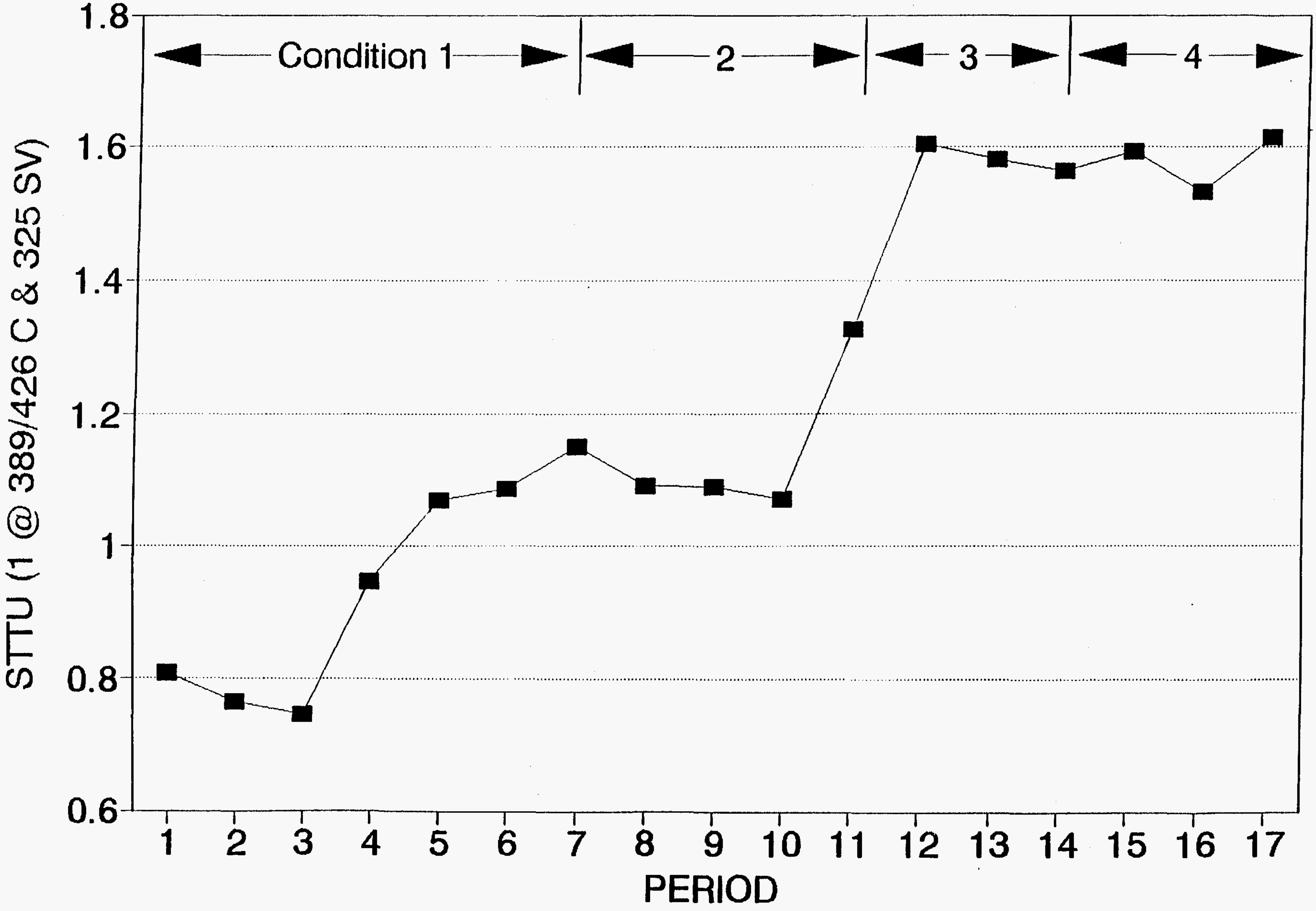


FIGURE 2.4.28

CMSL-04 (RUN 227-81)
DAILY MATERIAL BALANCE

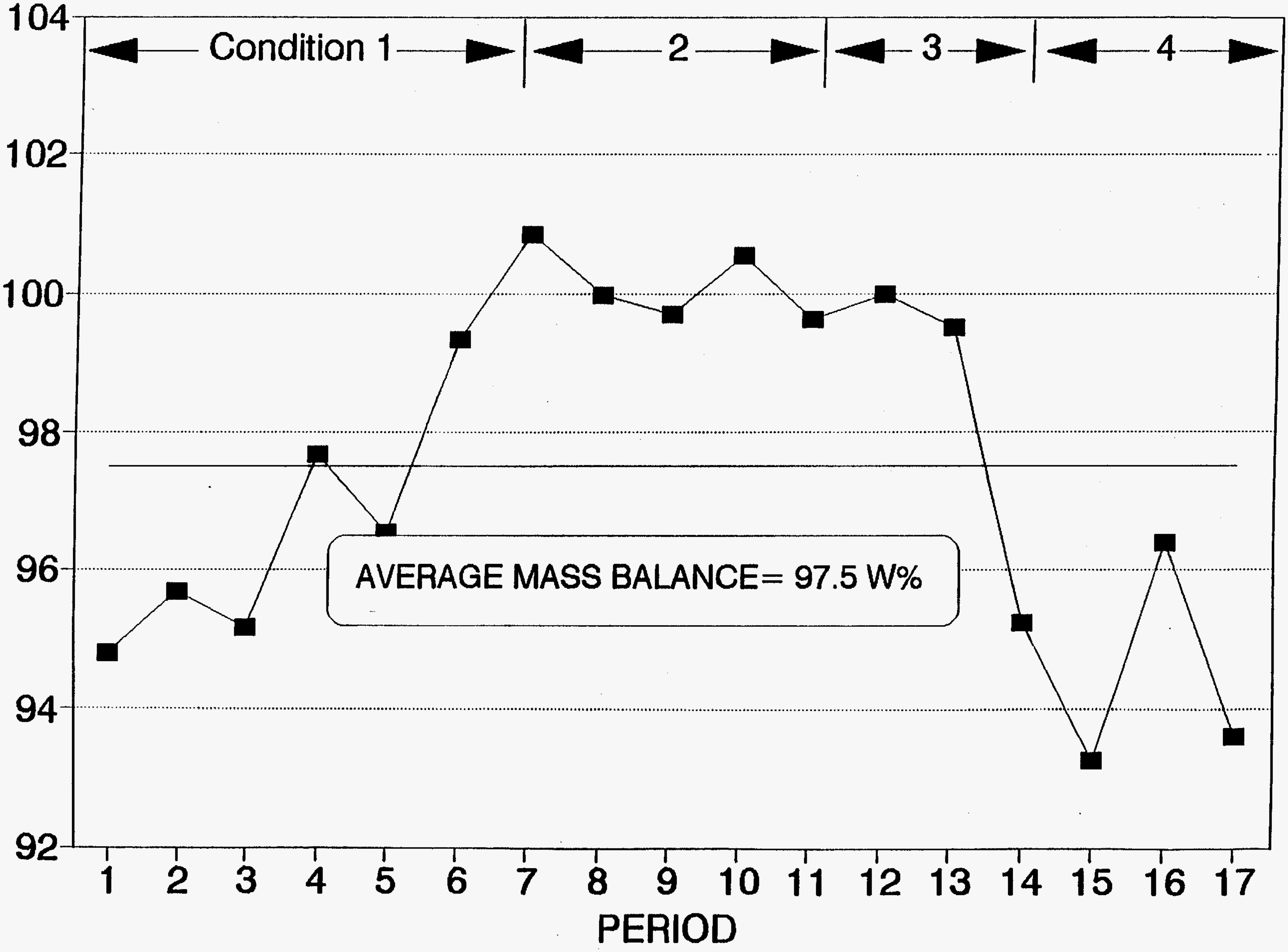


FIGURE 2.4.29

VOLUME I

SECTION II

RUN CMSL-5

EVALUATION OF INTERSTAGE PRODUCT SEPARATION, SYNGAS AND IN-LINE HYDROTREATING ON THE CMSL PERFORMANCE

VOLUME I

SECTION II - RUN CMSL-5

TABLE OF CONTENTS

Evaluation of Interstage Product Separation, Syngas and In-line Hydrotreating On The CMSL Performance

VOLUME I

SECTION II - RUN CMSL-5

LIST OF TABLES

VOLUME I

SECTION II - RUN CMSL-5

LIST OF FIGURES

VOLUME I

SECTION II - RUN CMSL-5

RUN CMSL-05 (227-82)

EVALUATION OF INTERSTAGE PRODUCT SEPARATION, SYNGAS, AND IN-LINE HYDROTREATING ON THE CMSL PERFORMANCE

1.0 SUMMARY

Run CMSL-05 (227-82) was carried out for 16 continuous days spread over four Conditions to investigate the effects of interstage product separation, in-line hydrotreating, and synthesis gas feed (75/25 V/V% of CO/H_2) in the first stage reactor as a reducing gas on the CMSL Process performance using Illinois No. 6 coal and Shell S-317 Ni-Mo extrudate catalysts, in back stages.

The first two run conditions, carried out at high coal space velocities of 480 $Kg/h/M^3$ (30 $lbs/hr/ft^3$) and reactor temperatures of 413 and 441°C (775 and 825°F) were very successful, resulting in over 93 W% resid conversions, over 95 W% coal conversions, with about 80 W% (all MAF coal basis) C_4-524°C distillate liquid yields. The in-line hydrotreating, achieving light product heteroatom levels of 17-50 ppm sulfur and 10 ppm or less of nitrogen, turned out to be fairly successful at both 357 and 379°C (675 and 715°F) operating temperatures.

Condition 3 was at lower space velocity of 325 Kg/h/M3 (20 lb/hr/ft3) and lower temperatures of 399° C and 427° C (750 and 800° F) which corresponded to an overall process severity 84% of that during the first two conditions. During Condition 3 there was an increase in residual oil yield, and a decline in distillate yield, from those of previous operations that was about twice that would have been projected from the apparent rate of catalyst deactivation indicated during the earlier operations, reflecting the impact of the lower severity. Still, the resid conversions of over 85% and distillate yields of over 72 W% of maf coal were obtain during Condition 3 operations. Coal conversions during Condition 3 were about 1% lower than during earlier operations

The last run Condition (Condition 4) was with the same reactor temperatures and space velocities as in Condition 3, but with a 75/25 V/V% mixture of CO/H_2 as a reducing gas, along with water for an H_2O/CO ratio of 0.4, instead of pure H_2 in the first stage reactor. Unfortunately, some problems were encountered in the CO-handling system causing progressive plugging of the CO-meter past Period 14B; this cause reduced CO flow to Stage 1 reactor during Periods 14, 15, and even parts of 16 (estimated CO flow being only 20-30 V% of the desired value that was used during Periods 12 and 13).

The yields and heteroatom removal during Period 13 of Condition 4 with the planned CO flow, continued the trends during the earlier operations, although with greater changes than manifest by the earlier patterns of catalyst deactivation for residual oil yields. However, coal conversion was higher by 1 W% than during the earlier comparable operation with pure hydrogen feed.

The distillate yield was 69.7 W% of maf coal and resid conversions with 81% during this operation. During Periods 14 and 15 when there was partial failure of the CO flow, to 37% CO and 40% as much combined H2 + CO flow, there was only a moderate decline in performance with 0-2% lower distillate yield than in previous syngas operation and about the same resid conversion.

Throughout this run, excellent heteroatom removals were obtained, with HDS (organic) of about 97-98 W% and HDN of between 91.4 to 96.3 W%.

The interstage withdrawal of vapors in the operations with pure H_2 feed gas to first stage resulted in a CO_x yield that was no greater than that yield for two stage operations without interstage withdrawal. This pattern was different from that of Run CMSL-4 which processed subbituminous coal. In the syngas operations of Run CMSL-4, the conversion of CO to H_2 was high approaching the amounts to be expected if thermodynamic equilibrium was attained. However, there was a considerable formation of CH_4 from CO, which corresponded to utilization of about 50% of the hydrogen generated from the conversion of CO. These patterns are the same as those in the syngas operations of Run CMSL-4, which also used extrudate catalyst in the first stage.

Overall CMSL-05 was a technical/operational success, demonstrating the advantages of the interstage product separation, in-line hydrotreating, and establishing that even though the use of syn-gas as a reducing gas in the first stage reactor does not significantly improve process performance with high rank bituminous coals (as it does with low rank subbituminous coals), the performance is well maintained at a lower cost of the reducing gas.

2.0 BACKGROUND, OBJECTIVE, AND SCOPE OF WORK

The CMSL Project is set up to evaluate different novel processing concepts in catalytic coal liquefaction to complement the larger scale process demonstration "Proof-of-Concept" Studies for the U.S. DOE. The new ideas being explored in this program include low temperature pretreatments, more effective catalysts, on-line hydrotreating, new feedstocks, other (cheaper) sources of hydrogen, more concentrated coal-slurry feeds, etc.

This bench run was carried out using Illinois No. 6 bituminous coal with Shell-317 extrudate catalyst in two ebullated bed reactors. It had the following technical objectives:

1. To investigate the effect of interstage separation of light gases and hydrocarbons (distillates) from the heavier product stream going from the first stage to the second stage reactor on the overall process performance. Interstage separation of light ends $343^{\circ}C^{-}$ (650°F) material from the products of the first stage reactors can improve the effective hydrogen partial pressure in the second stage reactor; it can also enhance the kinetics of conversions in the second stage by concentration of the heavy resid components in the feed to the second stage. The interstage separation can also increase the residence time of the slurry in the second stage reactor without lowering the overall coal throughput of the entire process.

2. To determine the effects of using an in-line hydrotreater on the quality of the distillates obtained from coal liquefaction. An in-line hydrotreater uses the available high temperature and high hydrogen partial pressure in the product stream exiting the second stage reactor; thus, no additional processing investment is incurred in such hydrotreating of light ends, generating premium distillates with less than 10 ppm nitrogen and sulfur. This concept had been successfully tested for the processing of subbituminous coals at HTI but never before was it investigated for high sulfur and nitrogen containing bituminous coals.

3. To determine the effect of using synthesis gas as a reducing gas (first time at HTI with a bituminous coal) in the first stage ebullated bed reactor on the process performance. The use of synthesis gas as a reducing gas instead of pure H_2 was found to result in about the same or slightly better process performance with subbituminous Black Thunder coal in the earlier bench runs. The cost reduction that can be brought about by replacing the expensive hydrogen in the first stage reactor with a cheaper alternate source such as a gasifier-obtained synthesis gas was the main motivation behind testing this concept during the bench run CMSL-05.

Both the separator overheads from the first stage and the second stage were sent through the hydrotreater along with the atmospheric still overheads obtained by distillation of the product slurry.

3.0 PROGRAM ANALYSIS, RESULTS AND COMPARISONS

The conversions and yields of different products, process performance, and product quality for CMSL-05 are addressed in this Section. The calculation of daily material recovery balances, coal conversions, normalized product yields, and other process performance-related indicators were carried out using programs available in the CTSL database (some programs were also modified as per the requirement of the process schematic). An average material recovery balance of 98.8 W% was obtained (*Figure 2.5.1*) for the entire Bench Run CMSL-05. The run plan is presented in *Table 2.5.1*. The Operating Summary of individual Periods during CMSL-05 is shown in *Table 2.5.2*. *Figures 2.5.2 and 2.5.3* show the operating conditions during CMSL-05 in terms of coal space velocities, reactor temperatures, and the overall process severity (relative STTUs) respectively.

3.1 Process Performance

3.1.1 Coal Conversion

Typical coal conversions, obtained (for both the stages) during equilibrated Periods of different Conditions of CMSL-05 are shown in *Figure 2.5.4*. As shown in *Figure 2.5.5*, the coal conversions (W% MAF coal) were steady with a little variation between 95 and 96 W% throughout the course of the Run. The last run condition, using synthesis gas in the first stage reactor, saw a marginal increase (0.5-1.0 W%) in coal conversions.

3.1.2 524°C$^+$ Resid Conversion

Resid conversion values were typically high, varying between 85 to 95 W% (MAF coal), as shown in *Figure 2.5.4*. Resid conversion levels decreased from 95 to 80 W% from the beginning to the end of the run. This downward trend in the resid conversion level was due to the lower process severity in the later half of the run, along with catalyst deactivation.

3.1.3 C_4-524°C Distillate Yields

High distillate liquid yields were obtained during CMSL-05. These varied typically between 67 to 80 W% MAF coal during the course of the run. The first two run conditions with high process severity yielded 78-80 W% distillates while the yields during last two run conditions dropped to about 70-73 W% as the reaction severity was reduced and low rates of CO and H_2 were provided to the first stage reactor during the last two Periods. As shown in *Figure 2.5.4*, the trend in distillate yields paralleled the resid conversion levels.

3.1.4 Hydrogen Consumption

Typical hydrogen consumption (based on the hydrogen contents of the feed and products), calculated using the normalized yield program, varied between 6.0 to 7.8 W% MAF coal (*Figure 2.5.5*). This value of hydrogen consumption was in good agreement with that obtained from the metered hydrogen flows. Although hydrogen consumption was slightly higher in the first half of the run, higher distillate yields were also obtained. *Figure 2.5.5* also shows hydrogen utilization and hydrogen efficiency, defined as pounds of C_4-524°C distillate yield per pound of hydrogen used. Hydrogen consumptions between 7-8 W% MAF coal and hydrogen efficiencies of between 9 to 11 were obtained during CMSL-05.

Hydrogen efficiency, defined as the W% MAF yield of distillate (C_4-524°C) per unit W% MAF H_2 consumed, varied between 9 to 11 kg distillates/kg$_2$ H (*Figure 2.5.5*). This value of hydrogen efficiency was higher for CMSL-05 than that for some of the other Bench Runs on Illinois No. 6 coal.

3.1.5 Heteroatom Removal

The use of an in-line hydrotreater (that was operational through Period 8) resulted in light distillates with very low levels of heteroatoms. Typically separator overhead nitrogen and sulfur contents of about 10 ppm or less were obtained. As shown in *Figure 2.5.6*, HDN varied between 91.5 W% to over 96 W% during the course of the run; the HDN value dropped by 4% towards the end of the run as catalyst aged, the hydrotreater went off-line, and the process severity was reduced. Similar trends, as shown in *Figure 2.5.6*, were observed with the organic sulfur removal also (HDS = 96.7-98.7 W%).

3.2 Product Distribution

3.2.1 C_1-C_3 Gas Yields

As shown in *Figure 2.5.5*, the normalized C_1-C_3 gas yields for CMSL-05 varied between 5.0 to 7.0 W% MAF coal. The light gas yields were typically higher during the first two run conditions due to high overall severity. The lower, 5.0 W%, C_1-C_3 gas yields in Condition 3 increased slightly to 5.5 W% when CO/H_2 was introduced in Condition 4, mainly due to some CO in the feed converting to CH_4.

3.2.2 C_4-177°C Naphtha Yields

These yields are shown in *Figure 2.5.7* and *Table 2.5.2*. As shown in *Figure 2.5.8*, the yields of naphtha fraction varied between 10 and 22 W% MAF coal. The run Condition 2, where H_2S was injected into the second stage reactor, resulted in the highest light naphtha yield. The yields went down as the reaction severity was reduced and catalyst became deactivated towards the end of the run.

3.2.3 177-343°C Middle Distillate Yields

As shown in *Figure 2.5.7*, the middle distillate yields were the highest yields among the distillate products. These varied between 33 and 50 W% MAF coal. The highest middle distillate yield was obtained for Period 4 (Condition 1); the yields decreased steadily as the run progressed in the same fashion as the light naphtha yields.

3.2.4 343-524°C Heavy Distillate (Gas Oil) Yields

The heavy distillate yields for CMSL-05 varied between 8-25 W% as shown in *Figure 2.5.7* and *Table 2.5.2*. The later two Conditions (3 and 4) resulted in higher yields of heavy distillates, primarily the result of catalyst aging effect coupled with reduced reaction severity.

3.2.5 524°C$^+$ Residual Oil Yields

The 524 C+ residual oil yields, shown in *Figure 2.5.8*, had an upward trend, from 1 to 13.5 W% during the run similar to that of the heavy distillates. In part, this trend reflects the deactivation of the extrudate catalyst, but the higher yields of Condition 3 (lower process severity) and Condition 4 (syngas operations) appear to reflect an additional impact of the changes in the operations. The concentration of residual oil in the recycled PFL solvent, also shown in *Figure 2.5.8,* (which follows the actual concentration in the reactor environment) is indicative of the catalyst deactivation. In Conditions 1 and 2 this concentration increased steadily from 21.2 W% in Period 4 to 26.7 W% in Period 8, an increase of 1.4 W% per day. In Periods 10 and 11 (Condition 3 at the lower severity) this concentration increased to 33.9 W% and 34.5W%, an increase of about 3.8 W% higher concentrations than would have been expected if the Condition 1 and 2 trends had continued. In Period 13 (Condition 4 syngas operations) this concentration in Period 11, a rate of increase which was over three times that at the beginning of the run and a concentration that was 6.9 W% higher than if the earlier trends and continued into Period 13. The conclusions that the results of Conditions 3 and 4 are not solely due to catalyst deactivation have statistical confidence levels of 95% and greater. Subsequent operations in Period 14 and 15, with lower amounts of CO fed to the first stage, actually appeared to reverse the increase that was apparent in Period 13.

3.2.6 C_4-524°C Distillate Yield

The normalized yield of distillates for CMSL-05 varied between 67-80 W% MAF coal, as shown in *Figure 2.5.7* and *Table 2.5.2*. The highest distillate yield was obtained for Period 5 in Condition 1, whereas the lowest yield was recorded for Periods 15. The selectivity of different distillate boiling fractions is also shown in *Figure 2.5.7.* 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.

3.3 Product Quality

Different product fractions (First-Stage/Second-Stage Vent Gases, ASOH, SOH, PFL, and PFC) from Periods 5, 8, 11, and 15 were analyzed in detail for their composition. These analyses for different product fractions are listed in *Tables 2.5.3 through 2.5.7.*

3.3.1 Separator Overhead and Atmospheric Still Overhead Product

There were two SOH streams in CMSL-05: SOH-1st Stage and SOH-2nd Stage, since an interstage separator was used during this Bench run. While the hydrotreater unit was on-line during the first two run conditions, the only net distillate stream out was the SOH-2nd stage because the SOH-1st stage oil, ASOH, and the second stage hot separator overheads were being fed directly to the hydrotreater. The properties of the combined SOH product for the last two run conditions from the process were determined based on their relative production rates (i.e., weight percents) after adjusting for the water present in them. In all the cases, SOH oil obtained at the second reactor stage (*Table 2.5.4*) was always lower boiling and had better quality than the SOH oil obtained at the interstage separator after the first reactor stage (*Table 2.5.3*). The overall properties of the combined SOH fraction are shown in *Table 2.5.4.* The SOH product became steadily heavier (as indicated by the API gravity and ASTM D-86 distillation) as the run progressed. SOH products contained small amounts of sulfur and nitrogen. Their H/C atomic ratio varied between 1.59 and 1.93 while their API gravities varied between 25 and 44.

The properties of the atmospheric still overhead product (*Table 2.5.5*), in general, did not vary much from Period to Period during CMSL-05. The API gravity was around 23 while H/C atomic ratio was around 1.60. It contained small amounts of nitrogen and sulfur (less than 0.2 W%).

3.3.2 Pressure Filter Liquid and Pressure Filter Cake

The detailed inspection of PFL properties for the work-up Periods during CMSL-05 are shown in *Table 2.5.6 and 2.5.8.* The API gravity of PFL varied between -1.9 and 5.4 while the 524°C$^+$ resid content increased from 22 to 44 W% as shown in *Figure 2.5.8.* The preasphaltene (toluene insolubles) and asphaltene (cyclohexane insolubles) contents of the PFL increased as the run progressed and the supported catalyst became aged. The effect of catalyst age on resid yield and PFL resid content is shown in *Figure 2.5.8.* Reflecting this behavior, the light gas oil (LGO) and vacuum gas oil (VGO) fractions of the PFL decreased as the catalyst aged while the heavier fraction, HVGO and 524°C$^+$ residuum contents increased with catalyst age. The detailed analysis of all these PFL fractions is shown in *Table 2.5.8.* The analysis of pressure filter cake from CMSL-05 is shown in *Table 2.5.7.* Operationally, as the resid content of the PFL increased with the progress of the run, the temperature of the slurry mix tank had to be increased steadily to maintain a pumpable feed slurry viscosity at a 47 W% coal concentration in the feed slurry (*Figure 2.5.9*).

3.3.3 First Stage Samples

The first stage samples are the samples of the 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 coal and resid conversions. The first stage samples of the product slurry were collected during Periods 6A, 9A, 12A, and 16A to represent Work-up Periods in each of the selected Run Conditions. The first stage samples were pressure filtered hot, and both the filtered liquid and the cake were analyzed and worked-up separately. Filter liquids were distilled (ASTM D-1160), and cakes were extracted with quinoline to determine the coal conversions. *Table 2.5.9* lists all the information that was derived from the first stage samples analyses. *Tables 2.5.10 and 2.5.11* also show the detailed inspections of the liquids and cake obtained from the first stage samples.

3.4 Hydrotreater Performance:

As seen from the results in *Table 2.5.12*, the in-line hydrotreater did a good overall job. For both the Run Conditions, over 95 W% of sulfur and nitrogen removal (overall) were achieved. The feed to the hydrotreater until Period 7B was an on-line O-1 separator overhead plus off-line feed consisting of the first stage separator overhead oil, unit knockouts, and the ASOH. The off-line feed line was plugged after Period 7B, and until Period 9A the only feed going to the hydrotreater was the O-1 separator overheads. Hydrotreater was taken off-line completely as of Period 9B. As shown in *Table 2.5.12*, the hydrotreater did an excellent job of heteroatom removal, mainly nitrogen removal (over 98 W%) as indicated by the nitrogen contents (1-10 ppm) and the sulfur contents (10-65 ppm) of the distillate products.

3.5 Comparisons And Analysis Of Results

3.5.1 Effect of using H_2S as an Additive for Stage II Reactor

As the high rank bituminous coals contain high amounts of both organic and pyritic sulfur, under normal circumstances, it is not deemed necessary to provide the supported catalyst with an external source of sulfur for maintaining its activity during the course of the reaction. During CMSL-05 it was thought that H_2S produced in the first stage reactor would be removed with other off-gases from the first stage reactor at the interstage separator. As this would lead to a possible deficiency of sulfur in the second stage reactor, one of the run conditions during CMSL-05, Condition 2, was designed to investigate the effect of providing H_2S as a source of sulfur to the second stage reactor. As shown in *Table 2.5.13*, this extraneous addition of H_2S to the second stage reactor did not do much in terms of improving the process performance, although it seemed to have accelerated hydrocracking, in the second stage reactor. Using H_2S during Condition 2, gave higher yields of light gases, and also lighter distillates (more naphtha yields). However, the addition of H_2S to the second stage reactor did not appear to moderate the rate of deactivation in the supported catalyst activity as indicated by the trends in residual oil concentrations during Conditions 1 and 2.

3.5.2 Effect of using Synthesis Gas as a Reducing Gas in Reactor I

Condition 4 (Periods 12 through 15) during CMSL-05 used a mixture of 75/25 V/V% of CO/H_2 as a reducing gas instead of pure H_2 in the first stage reactor with 30% as much water injected for the water-gas shift reaction. Unfortunately, some problems were encountered in the CO-handling system causing progressive plugging of the CO-meter after Period 14B; this manifested itself in reduced CO flow to first stage reactor during Periods 14, 15, and even parts of 16. (Estimated CO flow was only 20-30 V% of the desired value that prevailed during Periods 12 and 13.) The yields, conversions, and heteroatom removal during Period 13, with proper CO flow, were similar to those during Periods 10 and 11, except for the effects of catalyst deactivation (*Table 2.5.14*). Interestingly, Periods 14 and 15, with possible hydrogen starvation in first stage reactor due to low CO flow and one fourth of the H_2 flow during Condition 1 through 3, also show similar process performance as Period 13, except for minor catalyst deactivation effects (*Table 2.5.15*). Between 67-70 W% distillate yields and 80-83% resid conversions were obtained with coal conversion holding its level at about 95.5% (MAF). The first stage coal conversion during Period 15 with CO in the first stage was about 4 W% higher than all other Periods with pure H_2 in the first stage.

Table 2.5.21 summarizes the yields of gases from the first and second stage for the operations of Run CMSL-5. Throughout Conditions 1 to 3, with pure hydrogen fed to the first stage, the first stage methane yield averaged 0.79W% of mf coal, while the Condition 4 operation, with synthesis gas feed, this yield was 4.55 W% of mf coal reflecting CH_4 synthesis from the CO that was fed. The increase in CH_4 yield corresponded to 11.8 M% of the CO that had been converted to CH_4 and CO2, so that, considering the H_2 reacted in forming the CH_4 , the H_2 available for coal hydrogenation was only 53% of the CO consumed, following the net reaction of:

$$1.000\ CO + 0.764\ H_2O \dashrightarrow 0.118\ CH_4 + 0.882\ CO_2 + 0.528\ H_2$$

Possibly, with syngas feed there were slightly higher yields of C_2 hydrocarbon, by 0.35 W%, and C_3 hydrocarbons, by 0.27 W% in the first stage. With syngas feed to first stage, second stage C_1, C_2, and C_3 gas yields were slightly higher than in the Condition 3 operation with pure hydrogen and comparable conditions by 0.76W%, 0.10 W%, and 0.14 W%, respectively, although such differences are probably in the range of the experimental uncertainty. These patterns of hydrocarbon synthesis are similar to those Run CMSL-4 which also had extrudate catalyst in the first stage.

The CO conversion indicated by the first stage yields presented in *Table 2.5.21* was 44 M%, which is considerably lower than the level of 75% obtained in Run CMSL-4. This difference was caused by lower proportion of H_2O fed to the first stage in Run CMSL-5, 0.39 moles per mole CO, so that a much higher proportion of the H_2O was reacted. A value of 5.2 was calculated for the water gas shift reaction ratio, $H2*CO2/CO*H_2O$, for the Run CMSL-5 operation, which compares to an equilibrium value of 11.8 at the first stage temperature, indicating that the extrudate catalyst is a fairly effective catalyst for the shift reaction.

It is to be noted in *Table 2.5.21*, that for operations in Conditions 1 through 3 with pure hydrogen feed to the first stage, the first stage yield of CO_x was only 0.3 W% of MF coal. This contrasts with the high first stage CO_x yields obtained in Run CMSL-4 with subbituminous coal feed. With bituminous coal feed in Run CMSL-5 there appeared to no advantage of interstage separation with respect to conservation of hydrogen consumption by first stage elimination of oxygen as CO_2.

3.5.3 Comparison with CMSL-02 & POC-01

A comparison is shown (*Tables 2.5.16 & 2.5.17*) between the process performance of CMSL-02 (Run 227-78) Period 10 with similar overall severity (STTU) and Periods 7-8 of CMSL-05 with identical catalyst ages. CMSL-05 with the interstage separation shows a much improved process performance, indicated mainly by about 3-4 W% (absolute) higher resid conversionS and distillate yield. However, the higher resid conversion can be partly attributed to the higher coal conversion of the more active Crown II Mine Illinois No.6 coal. There is a distinct kinetic advantage of interstage product separation and also the in-line hydrotreater results in a very clean distillate product slate (N: <=10 ppm and S: 10-60 ppm). Similarly, comparison between the Periods 10-11 process performance during CMSL-05 and Period 13 of CMSL-02 (*Table 2.5.17*), under similar relative severities and catalyst ages, shows that there is distinct benefit of interstage separation of products as manifested by the marginally higher yields and conversions during CMSL-05. *Table 2.5.16* includes data from one of the steady-state conditions during the PDU run POC-01, which used the same Illinois No. 6 coal from the Crown II Mine (under similar severity conditions). The yields and conversions during CMSL-05 definitely stand out in this comparison, and it could be attributed to the beneficial effects of the interstage product separation.

4.0 DETAILS OF OPERATION

The Run Plan (*Table 2.5.1*) includes four Run Conditions that were selected to meet the technical objectives specified above. Only the last Run Condition was to be with synthesis gas in the first stage reactor. The conditions were chosen so that comparisons could be made with the results obtained during CMSL-2 bench run (with low solvent/coal ratio and no interstage separation). Also, the condition with synthesis gas going to the first stage was similar to the previous condition with only H_2 gas feed so that these could be compared.

4.1 Bench Unit Description

The simplified flow sheet for Run CMSL-5 is shown in *Figure 2.5.10.* HTI's continuous flow Bench Unit No. 227 was used for this run. It employed two liquefaction reactors, an interstage separator and an in-line hydrotreater. Both reactors were ebullated beds of supported Ni-Mo catalysts. The effluent from the second reactor was separated in the second stage hot separator and the bottoms were sent to a continuous atmospheric still. The vapor overhead from the hot separator and the overhead from the atmospheric still (through Period 6 only) went to the in-line hydrotreater along with the condensate from the interstage separator. The bottoms from the atmospheric still were pressure filtered as a batch operation and separated into pressure filter liquid and pressure filter solids. The pressure filter liquid was recycled to the unit as slurry oil for the feed coal. The uncondensed gases were metered and sampled and sent to flare.

4.2 Operating Summary

The first two run conditions were chosen to have high reactor temperatures 413 and 441°C (775 and 825°F) and high coal throughput rates (space velocities of 481 Kg/h/M^3 [30 lbs/hr/ft^3] reactor volume). The difference between these two conditions was the hydrotreater temperatures and the injection of hydrogen sulfide to the second stage reactor. It was felt that interstage product separation would remove most of the H_2S generated from coal in the first stage reactor and hence during Condition 2 about 2 W% of dry coal of H_2S was injected to the second stage reactor to maintain the activity of sulfided catalyst therein. The last two run conditions were at a slightly reduced severity (lower reactor temperatures but lower space velocities as shown in *Table 2.5.1*). The first stage reducing gas feed was changed to synthesis gas for Condition 4. Two eight-hour-long extensions of CMSL-05 were also planned as shown. These were designed to study the effect of the type of reducing gas in the first stage reactor on the type of off-gases obtained from the process, so that the effects of CO-shift conversion could be studied in the absence of any coal in the unit. The solvent to coal ratio for the entire run was maintained at 0.9.

5.0 MATERIALS USED

5.1 Feed Coal

L-811, which is an Illinois No. 6 bituminous coal from the Crown II Mine (also used for the POC-01 PDU operations), was used for CMSL-05 as received (without any drying). It had about 4 W% moisture under ambient conditions. Detailed analyses of this coal is shown in *Table 2.5.18*, and compared with those of the Burning Star Mine Coal used in Run CMSL-2.

5.2 Startup/Makeup Oil

L-809, a hydrotreated cat cycle oil mixed with small amounts of coal-derived oil during POC-01, was used as the startup solvent for this bench run. The detailed analysis is shown in *Table 2.5.19.*

5.3 Hydrotreater Catalyst

Hydrotreater unit (HTU) was charged with a trilobe-shaped Criterion C-411 catalyst that is believed to be of Ni-Mo on alumina formulation.

5.4 Fresh and Recovered Catalyst

Shell-317 1/32" extrudate catalyst (Ni-Mo/Al_2O_3) was used for both the first and the second stage reactor during CMSL-05. The catalyst was presulfided during the startup using TNPS. No catalyst was either added or removed from the reactor during the run.

6.0 CONCLUSIONS

CMSL-05 was a very successful bench run both from the technical and operational standpoint. The main technical objectives of the run were achieved over a span of 16 continuous days of operations. A Solvent/Coal ratio of 0.9 was maintained successfully throughout the run. The following conclusions can be drawn based on the results obtained during CMSL-05:

- Interstage product separation is very effective in enhancing the liquefaction kinetics in the second stage reactor, thereby giving very high levels of resid conversion and light distillate yields.

- In addition of a sulfiding agent to the second stage reactor, when added to compensate for the removal by the interstage separator of H2S generated in the first stage, did not appear to moderate the apparent rate of deactivation of the catalyst for residual oil conversion. However, an increase in light distillate yield was indicated.

- In-line hydrotreating is very effective for producing premium distillate with less than 10 ppm each of sulfur and nitrogen, especially when about a third of the distillate product is obtained as a first reactor stage overhead during the interstage product separation.

- Replacing expensive pure hydrogen in the first stage reactor with an alternate cheaper source such as synthesis gas, improves both the first stage and overall coal conversion levels. However, the overall process performance was possibly slightly poorer than that expected for operations using pure hydrogen feed.

- The process performance obtained during the last periods of CMSL-05 with low hydrogen flow indicates a potential for lower hydrogen pressure coal liquefaction, but the sustainability of such operations is questionable because of the declining product quality.

- The low H2O/CO ratio used during the syngas operations of the run probably did not make full use of CO in the syngas and the potential of syngas operations should be viewed in this light.

- Syngas operations using extrudate catalyst, although effectively promoting the water gas shift reaction, have the disadvantage of the synthesis of a considerable amount of C_1-C_3 hydrocarbons from the CO.

TABLE 2.5.1

CMSL -05 Run Plan: **EFFECT OF INTERSTAGE SEPARATION AND AN IN-LINE HYDROTREATING**
ILLINOIS NO. 6 CROWN II MINE COAL (HRI L-811)
Back Pressure: 17.2 MPa
Catalyst: Shell-317, HRI-5394 Both Stages
Hydrotreater: HRI-6135 (Criterion C-411 Trilobe)

Condition		1	2	3	4	4-EXT*	4-EXT
Period		1-5	6-8	9-11	12-15	16B	16C
Feed Gas:	1st Stage	H2	H2	H2	CO/H2	CO/H2	H2
	2nd Stage	H2	H2	H2	H2	H2	H2
Temperature [F]	1st Stage	413	413	399	399	399	399
	2nd Stage	441	441	427	427	427	427
	HTU	357	379	379	N/A	N/A	N/A
Space Velocity (Kg coal/h/M3 react.)		480	480	320	320	320	320
Solvent/Coal Ratio		0.9	0.9	0.9	0.9	Infinity	Infinity
Sulfur Additives:							
H2S to Stage 2:2 W% of dry coal		No	Yes	No	No	No	No

*No coal was to be used during these Conditions

TABLE 2.5.2
RUN CMSL-5 OPERATING SUMMARY
CTSL WITH INTERSTAGE PRODUCT SEPARATION AND AN IN-LINE HYDROTREATER
COAL: ILLINOIS NO. 6 (HRI L-811)
CATALYST: SHELL-317 (HRI-5394) BOTH STAGES, CRITERION C-411 (HRI-6135) HYDROTREATER

Period Number	**1**	**2**	**3**	**4**	**5**
Date (Period)	04/04/94	04/05/94	04/06/94	04/07/94	04/08/94
Hours of Run	24	48	72	96	120
Stage 2 Catalyst Age (Kg dry coal/Kg cat)	32	75	118	159	200
1st Stage Temp (C)	399	413	413	412	412
2nd Stage Temp (C)	416	437	441	441	440
Unit Press (Mpa)	17.2	17.2	17.2	17.2	17.3
SV, Kg Coal/h/M^3	362	479	484	466	461
SV, Lb Coal/hr/ft^3	22.6	29.9	30.2	29.1	28.8
W% of Dry Coal					
PFL Recycle	209.3	90.8	89.5	90.0	89.5
PFL to Buffer Stage 1	6.1	2.8	3.2	3.4	3.2
PFL to Buffer Stage 2	6.9	3.1	2.8	2.9	3.0
Make-up Oil	0.0	0.0	0.0	0.0	0.0
H_2S	0.0	0.0	0.0	0.0	0.0
SOLVENT TO COAL RATIO (DRY)		0.9	0.9	0.9	0.9
MATERIAL BAL (%) (GROSS)	100.47	97.64	98.92	98.48	100.62
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED					
C1-C3 in Gases				6.77	5.30
C_4-C7 in Gases				4.49	3.43
IBP-199 deg-C in Liquids				13.29	12.48
199-260 deg-C in Liquids				16.65	15.69
260-343 deg-C in Liquids				27.62	26.39
343-454 deg-C in Liquids				7.82	11.41
454-524 deg-C in Liquids				0.32	2.04
Toluene Soluble 524C+ Oil				0.60	2.39
Toluene Insoluble 524C+ Oil				0.01	0.02
Unconverted Coal				3.58	3.54
Ash				10.40	10.40
Water				9.70	7.96
CO				0.17	0.16
CO2				0.38	0.19
NH3				1.53	1.56
H2S				4.37	4.38
Total (100 + H2 Reacted)				107.60	107.33
PROCESS PERFORMANCE					
C_4-524 deg-C Distillates, W% of MAF Coal				78.3	7.97
524C+ Conversion, W% MAF				95.3	93.4
Coal Conversion W% MAF		95.7	96.0	96.0	96.0
HDS W%				98.7	98.8
HDN W%				94.6	96.3

TABLE 2.5.2
(Continued)
RUN CMSL-5 OPERATING SUMMARY

Period Number	6	7	8	9	10
Date (Period)	04/09/94	04/10/94	04/11/94	04/12/94	04/13/94
Hours of Run	144	168	324	216	240
Stage 2 Catalyst Age (Kg dry coal/Kg cat)	243	283	324	359	388
1st Stage Temp (C)	413	413	414	404	399
2nd Stage Temp (C)	440	441	441	431	427
Unit Press (Mpa)	17.2	17.2	17.2	17.1	17.1
SV, Kg Coal/h/M^3	481	442	461	399	328
SV, Lb Coal/hr/ft^3	30.0	27.6	28.8	24.9	20.5
W% of Dry Coal					
PFL Recycle	89.5	89.5	89.5	89.1	89.4
PFL to Buffer Stage 1	2.9	3.7	3.2	3.5	4.5
PFL to Buffer Stage 2	3.1	4.0	2.7	3.2	4.2
Make-up Oil	0.0	0.0	0.0	0.0	0.0
H_2S	1.9	2.2	2.0	0.0	0.00
SOLVENT TO COAL RATIO (DRY)		0.9	0.9	0.9	0.9
MATERIAL BAL (%) (GROSS)	97.81	100.81	99.34	99.22	100.06
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED					
C1-C3 in Gases		6.68	7.08		4.97
C_4-C7 in Gases		3.77	3.65		3.06
IBP-199 deg-C in Liquids		17.85	12.96		9.51
199-260 deg-C in Liquids		16.66	15.60		11.47
260-343 deg-C in Liquids		22.76	24.64		20.67
343-454 deg-C in Liquids		8.68	11.01		16.52
454-524 deg-C in Liquids		0.66	1.53		4.00
Toluene Soluble 524C+ Oil		1.10	2.65		8.35
Toluene Insoluble 524C+ Oil		0.02	0.05		0.18
Unconverted Coal		3.54	3.54		4.12
Ash		10.40	10.40		10.40
Water		7.81	7.60		6.48
CO		0.18	0.15		0.15
CO2		0.21	0.13		0.19
NH3		1.54	1.54		1.49
H2S		4.37	4.37		4.29
Total (100 + H2 Reacted)		107.32	106.89		105.85
PROCESS PERFORMANCE					
C_4-524 deg-C Distillates, W% of MAF		79.7	77.4		72.8
Coal		94.8	93.0		85.9
524C+ Conversion, W% MAF		96.0	96.0		95.4
Coal Conversion W% MAF		98.7	98.6		96.8
HDS W%		95.3	95.1		92.4.
HDN W%					

TABLE 2.5.2
(Continued)
RUN CMSL-5 OPERATING SUMMARY

Period Number	**11**	**12**	**13**	**14**	**15**
Date (Period)	04/14/94	04/15/94	04/16/94	04/17/94	04/18/94
Hours of Run	264	288	312	336	360
Stage 2 Catalyst Age (Kg dry coal/Kg cat)	417	448	475	504	532
1st Stage Temp (C)	399	399	399	398	398
2nd Stage Temp (C)	428	428	428	428	428
Unit Press (Mpa)	17.1	17.1	17.0	17.1	17.1
SV, Kg Coal/h/M^3	325	346	309	328	312
SV, Lb Coal/hr/ft^3	20.3	21.6	19.3	20.5	19.5
W% of Dry Coal					
PFL Recycle	87.5	91.4	91.4	91.4	91.4
PFL to Buffer Stage 1	4.3	4.0	5.4	10.5	5.9
PFL to Buffer Stage 2	3.8	3.6	4.1	3.8	4.3
Make-up Oil	0.0	0.0	0.0	00	0.0
H_2S	0.0	0.0	0.0	0.0	0.0
H_2 to Stage 1	0.0	14.1	30.5	14.9	18.9
SOLVENT TO COAL RATIO	0.9		0.9	0.9	0.9
H_2+CO Stage 1, SCM/kg	1.246	1.129	1.308	0.619	0.515
CO, V%	0.00	74.1	74.7	50.2	37.5
MATERIAL BAL (%) (GROSS)	99.85	99.64	101.99	94.77	91.94
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED					
C1-C3 in Gases	4.95		5.58	5.08	6.03
C_4-C7 in Gases	2.62		2.36	2.74	2.63
IBP-199 deg-C in Liquids	9.66		11.19	9.01	7.43
199-260 deg-C in Liquids	11.61		11.63	10.75	9.84
260-343 deg-C in Liquids	20.87		17.69	19.07	18.96
343-454 deg-C in Liquids	16.37		15.31	16.51	16.55
454-524 deg-C in Liquids	4.06		4.25	4.54	4.95
Toluene Soluble 524C+ Oil	8.86		11.04	11.51	13.19
Toluene Insoluble 524C+ Oil	0.19		1.63	0.25	0.29
Unconverted Coal	4.47		4.38	3.60	4.14
Ash	10.40		10.40	10.40	10.40
Water	5.67		5.27	6.39	5.50
CO	0.16		0.16	0.17	0.16
CO2	0.14		0.14	0.15	0.14
NH3	1.49		1.23	1.48	1.48
H2S	4.28		3.59	4.30	4.31
Total (100 + H2 Reacted)	105.80		105.86	105.97	106.00
PROCESS PERFORMANCE					
C_4-524 deg-C Distillates, W% of MAF Coal	72.8		69.7	69.9	67.4
524C+ Conversion, W% MAF	84.9		81.0	82.8	80.3
Coal Conversion W% MAF	95.0		95.1	96.0	95.4
HDS W%	96.7		81.0	97.1	97.3
HDN W%	92.3		76.2	91.5	91.5

TABLE 2.5.3

CMSL-05: SEPARATOR OVERHEAD STAGE I (SOH-I) INSPECTION

Unit	227	227	227	227
Run	82	82	82	82
Condition	1	2	3	4
Period Number	5	8	11	15
Gravity, API	30.6	30.3	30.1	25.3
IBP, deg C	68	75	76	76
FBP, deg C	414	423	420	427
ASTM D-86 Distillation, Composition				
W% IBP-177 deg C	30.6	28.5	29	22.3
W% 177-260 deg C	21.1	23	22.9	21.7
W% 260-343 deg C	28.8	28.5	27.5	28.8
W% 343 deg C	19.1	19.5	20.1	26.7
W% Loss	0.4	0.5	0.5	0.5
Elemental Analysis				
Carbon, W%	86.74	86.68	86.53	86.02
Hydrogen, W%	12.17	12.19	12.32	11.4
Sulfur, W%	0.036	0.04	0.04	0.084
Nitrogen (Antek), W%	0.1	0.13	0.14	0.25
H/C RATIO	1.68	1.69	1.71	1.59

TABLE 2.5.4

CMSL-05: SEPARATOR OVERHEAD STAGE II (SOH-II) INSPECTION

Unit	227	227	227	227
Run	82	82	82	82
Condition	1	2	3	4
Period Number	5	8	11	15
Gravity, API	30.6	40.9	43.9	43.8
IBP, deg C	69	82	72	63
FBP, deg C	414	344	263	252
ASTM D-86 Distillation, Composition				
W% IBP-177 deg C	20.9	44.6	61.5	64.1
W% 177-260 deg C	26.3	33.4	36.3	35.2
W% 260-343 deg C	42.6	20.7	1.7	0
W% 343 deg C	9.8	1.1	0	0
W% Loss	0.4	0.2	0.5	0.7
Elemental Analysis				
Carbon, W%	86.67	85.89	85.92	85.73
Hydrogen, W%	11.78	13.8	13.38	13.37
Sulfur, W%	0.005	0.001	0.013	0.034
Nitrogen (Antek), W%	10 ppm	<1 ppm	0.017	0.028
H/C RATIO	1.68	1.93	1.87	1.87

TABLE 2.5.5

CMSL-05: ATMOSPHERIC STILL OVERHEAD (ASOH) INSPECTION

Unit	227	227	227	227
Run	82	82	82	82
Condition	1	2	3	4
Period Number	5	8	11	15
Gravity, API	23.8	23.0	23	21.4
IBP, deg C	119	126	269	108
FBP, deg C	373	373	363	363
ASTM D-86 Distillation, Composition				
W% IBP-177 deg C	5.2	4.0	2.9	3.1
W% 177-260 deg C	23.7	24.3	22.9	23.5
W% 260-343 deg C	59.1	59.0	64.7	63.9
W% 343 deg C	11.4	12.3	9.4	9.1
W% Loss	0.6	0.4	0.1	0.4
Elemental Analysis				
Carbon, W%	87.55	87.92	87.49	87.31
Hydrogen, W%	11.59	11.64	11.68	11.17
Sulfur, W%	0.004	0.011	0.01	0.036
Nitrogen (Antek), W%	0.057	0.087	0.093	0.23
H/C RATIO	1.59	1.59	1.6	1.54

TABLE 2.5.6

CMSL-05: PROPERTIES OF PRESSURE FILTER LIQUID (2nd STAGE)

Unit	227	227	227	227
Run	82	82	82	82
Condition	1	2	3	4
Period Number	5	8	11	15
Gravity, API	5.4	3.1	2.6	-1.9
IBP, deg C	278	266	304	308
ASTM D-86 Distillation, Composition				
W% IBP-343 deg C	7.06	10.75	5.47	6.5
W% 343-454 deg C	51.35	46.91	44.34	39.93
W% 454-524 deg C	18.86	15.13	15.47	14.74
W% 524 deg C	22.34	26.74	34.53	38.19
W% Loss	0.39	0.47	0.19	0.64
Elemental Analysis				
Carbon, W%	90.00	90.23	89.31	89.23
Hydrogen, W%	9.32	8.83	9.2	8.04
Sulfur, W%	0.023	0.034	0.107	0.198
Nitrogen (Antek), W%	0.21	0.35	0.39	0.78
H/C RATIO	1.24	1.17	1.24	1.08
CCR, W% PFL	7.6	10.58	12.03	19.74
CYCLOHEXANE INSOLUBLES, W%	2.52	6.77	8.03	21.87
TOLUENE INSOLUBLES, W%	0.23	0.5	0.76	4.93

TABLE 2.5.7

CMSL-05: INSPECTION OF THE PRESSURE FILTER SOLIDS (2ND STAGE)

Unit	227	227	227	227
Run	82	82	82	82
Condition	1	2	3	4
Period Number	5	8	11	15
Elemental Analysis				
Carbon, W%	51.36	51.57	55.88	54.45
Hydrogen, W%	4.36	4.31	4.78	4.34
Sulfur, W%	2.77	2.74	2.55	2.7
Nitrogen (Antek), W%	0.2	0.34	0.43	0.57
H/C RATIO	1.02	1.00	1.03	0.96
Composition, W%				
Ash (Quinoline Filtration)	40.03	38.55	35.05	33.32
ASTM Ash, W%	39.64	38.55	35.31	35.18
S in Ash, W%	1.04	1.11	1.16	1.41
Unconverted Coal (Adj.)	14.01	14.44	15.24	14.04

TABLE 2.5.8

PRESSURE FILTER LIQUID INSPECTIONS FROM CMSL-05

FILTER LIQUID ANALYSIS

Condition	1	2	3	4
Period Number	5	9	11	15
Catalyst Age, kg coal/kg cat	200	325	417	532
Gravity, °API	5.4	3.1	2.6	-1.9
Boiling Fractions, W%				
IBP-343°C	7.06	10.75	5.47	6.5
343-454°C	51.35	46.91	44.34	39.9
454-524°C	18.86	15.13	15.47	14.74
524°C+	22.34	26.74	34.53	38.19
Loss	0.39	0.47	0.19	0.64
Elemental Analysis. W% LGO (IBP-343°C)				
Carbon				
Hydrogen	89.17	89.11	88.5	88.65
Nitrogen	11.13	10.78	11.38	10.72
Sulfur	0.07	0.15	0.08	0.18
	0.006	0.014	0.016	0.05
VGO (343-454°C)				
Carbon	89.77	90.43	88.94	89.74
Hydrogen	9.99	9.69	10.17	8.23
Nitrogen	0.13	0.18	0.16	0.59
Sulfur	0.014	0.023	0.026	0.14
HVGO (454-524°C)				
Carbon	90.44	90.86	89.64	89.23
Hydrogen	8.94	8.55	9.21	6.27
Nitrogen	0.24	0.37	0.31	1.34
Sulfur	0.037	0.05	0.022	0.38
Resid (524°C+)	90.7	90.74	89.16	
Carbon	7.42	6.91	7.58	
Hydrogen	0.44	0.75	0.79	
Nitrogen	0.064	0.198	0.23	
Sulfur				

TABLE 2.5.9

CMSL-05: INTERSTAGE SAMPLES INFORMATION

Period No.	Coal Conversion %maf	Resid Conv. %maf	W% PFS	W% PFL	Resid in PFL	H/C of PFL
6A	90.1	78	42.6	57.4	30%	1.26
9A	91.3	76.5	41.2	58.8	33%	1.23
12A	91.1	74	39.9	60.1	40%	1.25
16A	95.1	70	20	80	44%	1.09

TABLE 2.5.10

CMSL-05: PROPERTIES OF THE PRESSURE FILTER LIQUID (1st STAGE)

Unit	227	227	227	227
Run	82	82	82	82
Condition	1	2	3	4
Period Number	5	8	11	15
Gravity, API	4.6	2.7	2.7	-3.1
IBP, deg C	247	222	262	262
FBP, deg C				
ASTM D-1160 Distillation, Composition				
W% IBP-343 deg C	10.29	12.33	6.83	6.44
W% 343-454 deg C	42.12	37.95	38.52	34.85
W% 454-524 deg C	16.63	16.22	14.28	14.07
W% 524 deg C+	30.38	32.83	39.94	44.01
W% Loss	0.58	0.67	0.48	0.63
Elemental Analysis				
Carbon, W%	88.99	88.56	88.52	88.71
Hydrogen, W%	9.33	9..04	9.25	8.04
Sulfur, W%	0.153	0.214	0.19	0.302
Nitrogen (Antek), W%	0.31	0.45	0.41	0.82
H/C RATIO	1.26	1.22	1.25	1.09
CCR, W% PFL	9.3	11.8	12.12	21.47
CYCLOHEXANE INSOLUBLES, W%	6.37	10.63	17.6	24.33
TOLUENE INSOLUBLES, W%	0.64	1.17	2.87	5.21

TABLE 2.5.11

CMSL-05: INSPECTION OF THE PRESSURE FILTER SOLIDS (1st STAGE)

Unit	227	227	227	227
Run	82	82	82	82
Condition	1	2	3	4
Period Number	5	8	11	15
Elemental Analysis				
Carbon, W%	68.82	67.78	69.72	43.86
Hydrogen, W%	6.1	5.87	6.34	2.92
Sulfur, W%	1.94	2.06	1.88	4.33
Nitrogen (Antek), W%	0.54	0.63	0.65	0.47
H/C RATIO	1.02	1.04	1.09	0.80
Composition, W%				
Ash (Quinoline Filtration)	20.14	19.5	18.05	45.99
ASTM Ash, W%	20.53	20.6	18.81	48.32
S in Ash, W%	2.74	2.38	2.54	3.18
Unconverted Coal (Adj.)	15.47	14.6	15.44	19.44

TABLE 2.5.12

HYDROTREATER PERFORMANCE DURING CMSL-05

Period No.	Feed To HTU	Flow, g/h	N, ppm	S, ppm	HTU Temp °C	Product of HTU	Flow, g/g	N, ppm	S, ppm
4	ASOH	275	473.7	34.7	357	SOH-II Oil	562	9.3	17.5
	SOH-I Oil	163	866.3	310.8					
	0-1-II Ovhd	150	100	40					
5	ASOH	250	568	45	357	SOH-II Oil	532	10	54
	SOH-I Oil	138	1016	362					
	0-1-II Ovhd	150	100	40					
7A	ASOH	252	655	66	379	SOH-II Oil	538	12.7	74.7
	SOH-I Oil	137	1088	434					
	0-1-II Ovhd	150	150	50					
8	0-1-II Ovhd	150	150	50	379	SOH-II Oil	150	<1	10

TABLE 2.5.13

CMSL-05 Effect Of Interstage Separation/In-Line Hydrotreater
Effect Of H2S Added To The Second Stage Reactor During CMSL-05

	CMSL-05	CMSL-05
Unit Run	227-82	227-82
Condition	1	1
Period Number	4 & 5	7 & 8
Hours of Run (End of period)	120	192
Stage 1 Temp (C)	412	413
Stage 2 Temp (C)	441	441
H2S to Stage 2 Reactor, g/h	0	20
Stage 2 Cat Age, kg coal/kg cat	200	324
Stage 2 Space Velocity, Kg coal/h/M^3 reactor	465	452
lb coal/h/ft3 reactor	29	28.2
Solvent/Coal Ratio (Feed Slurry)	0.9	0.9
Oil/Solids Ratio (Reactor)	0.96	0.96
Total Material Recovery % (gross)	99.55	100.1
Relative Severity Index	1.18	1.19
ESTIMATED NORMALIZED YIELDS, W% MAF COAL		
C1-C3 in Gases	6.74	7.73
C_4-C7 in Gases	4.42	4.14
IBP-199 deg-C in Liquids	14.38	17.19
199-260 deg-C in Liquids	18.05	18.56
260-343 deg-C in Liquids	30.14	26.45
343-454 deg-C in Liquids	10.73	10.99
454-524 deg-C in Liquids	1.31	1.22
524C+	1.68	2.13
Unconverted Coal	3.97	3.95
Water	9.85	8.60
CO	0.18	0.18
CO2	0.31	0.19
NH3	1.72	1.72
H2S	4.87	4.88
PROCESS PERFORMANCE		
Coal Conversion W% MAF	96.0	96.0
C_4-524 deg-C Distillates, W% of MAF Coal	79.0	78.6
524C+ Conversion, W% MAF	94.3	93.9
Hydrogen Consumption, W% Maf Coal	8.35	7.93
Hydrogen Efficiency, kg distillates/kg H2	9.46	9.91
HDS W%	98.7	98.6
HDN W%	95.5	95.2

TABLE 2.5.14

CMSL-05: Effect Of Interstage Separation/In-Line Hydrotreater Process Performance Comparison With/Without Syngas

	CMSL-05	CMSL-02	CMSL-05 WITH CO/H2
Unit-Run	227-82	227-78	227-82
Condition	3	3	4
Period Number	10 & 11	13	13
Hours of Run (End of period)	264	304	312
Stage I Temp (C)	399	414	399
Stage 2 Temp (C)	427	433	428
H2S to Stage 2 Reactor, g/h	0	0	0
Stage 2 Cat Age, kg coal/kg cat	417	422	475
Stage 2 Space Velocity, Kg coal/h/M3 reactor	327	516	309
lb coal/h/ft3 reactor	20.4	32.2	19.3
Solvent/Coal Ratio (feed slurry)	0.9	0.9	0.9
Oil/Solids Ratio (reactor)	0.96	0.95	1.01
Total Material Recovery % (gross)	99.95	97.91	101.99
Relative Severity Index	0.99	1.03	0.99
ESTIMATED NORMALIZED YIELDS, W% MAF COAL			
CI-C3 in Gases	5.53	5.82	6.21
C_4-C7 in Gases	3.17	3.82	2.62
IBP-199 deg-C in Liquids	10.69	16.77	12.43
199-260 deg-C in Liquids	12.87	9.2	13.08
260-343 deg-C in Liquids	23.17	23.33	20.63
343-454 deg-C in Liquids	18.32	14.03	18.03
454-524 deg-C in Liquids	4.48	3.82	4.75
524C+	9.57	6.57	12.31
Unconverted Coal	4.79	7.6	4.02
Water	6.77	11.52	5.84
CO	0.17	0.17	0.17
C02	0.19	0.14	0.16
NH3	1.72	1.49	1.65
H2S	4.86	3-74	4.78
PROCESS PERFORMANCE			
Coal Conversion, W% MAF Coal	95.2	92.4	96.0
C_4-524 deg-C Distillates, W% of MAF Coal	72.7	71.0	71.5
524C+ Conversion W% MAF	85.4	85.8	83.7
Hydrogen Consumption, W% MAF Coal	6.3	7.58	6.68
Hydrogen Efficiency, kg distillates/kg H2	11.54	9.37	10.7
HDS W%	96.7	96	97
HDN W%	92.3	85.8	91.4

TABLE 2.5.15

CMSL-05 Condition 4: Process Performance Under "H2-Starved First Stage Reactor" Condition

Period Number	13	14	15
Hours of Run (end of period)	312	316	360
Stage I Temp (C)	399	398	398
Stage 2 Temp (C)	428	428	428
Stage 2 Cat Age, kg coal/kg cat	475	504	532
Stage 2 Space Velocity, Kg coal/h/M3 reactor	309	328	312
lb coal/h/ft3 reactor	19.3	20.5	19.5
Solvent/Coal Ratio (feed slurry)	0,9	0.9	0-9
Oil/Solids Ratio (reactor)	1.04	1.04	1.01
Total Material Recovery % (gross)	101.99	94.77	91.94
Relative Severity Index	1.02	1.01	1.02
Gas Rates, % of Target			
CO	100	34	20
H2	100	100	100
% Volume of feed			
CO	74.6	50	37.3
H2	25.4	50	62.7
Estimated H_20/CO Ratio in Stage	0.4	2	3
Mole % CO Conversion	40.6	73.8	04.1
PROCESS PERFORMANCE			
Coal Conversion, W% MAF Coal	95.1	96.0	95.4
C_4-524 deg-C, Distillates, W% of MAF Coal	69.7	69,9	67.4
524C+ Conversion W% MAF	81.0	82,8	80,3
Hydrogen Consumption, W% MAF Coal	6.54	6.68	6.70
Hydrogen Efficiency, kg distillates/kg H2	10.7	10.5	10.1

TABLE 2.5.16

CMSL-05: Effect of Interstage Separation/In-Line Hydrotreater Process Performance Comparison

	CMSL-05	POC-01	CMSL-02
Unit-Run	227-82	260-4	227-78
Condition	2	2	2
Period Number	7 & 8	18-20	10
Hours of Run (end of period)	192	432	232
Stage I Temp (C)	413	407	399
Stage 2 Temp (C)	441	412	428
H2S to Stage 2 Reactor, g/h	20	0	0
Stage 2 Cat Age, kg coal/kg cat	324	493	295
Stage 2 Space Velocity, Kg coal/h/M3 reactor	452	332	285
lb coal/h/ft3 reactor	28,2	20,7	17.8
Solvent/Coal Ratio (feed slurry)	0.9	1.26	0.9
Oil/Solids Ratio (reactor)	0.96	1.3	0.99
Total Material Recovery % (gross)	100.1	99.1	99.25
Relative Severity index	1.19	1.29	1.0
ESTIMATED NORMALIZED YIELDS, W% MAF COAL			
C I -C3 in Gases	7.73	5.66	5.93
C_4-C7 in Gases	4.14	2.38	4.32
IBP-199 deg-C in Liquids	17.19	16.65	18.06
199-260 deg-C in Liquids	18.56	29.04	12.65
260-343 deg-C in Liquids	26.45	17.25	31.29
343-454 deg-C in Liquids	10.99	2.49	8.37
454-524 deg-C in Liquids	1.22	6.12	1.18
524C+	2.13	8.45	2-24
Unconverted Coal	3.95	4.97	1.14
Water	8.60	9.91	11.57
Co	0.19	0.04	0.11
C02	0.19	0.02	0.04
NH3	1.72	1.45	1.59
H2S	4.99	2.45	3.87
PROCESS PERFORMANCE			
Coal Conversion, W% MAF Coal	96	95	92.9
C_4-524 deg-C Distillates, W% of MAF Coal	78.6	74.2	75.9
524C+ Conversion W% MAF	93.9	86.6	90.6
Hydrogen Consumption, W% MAF Coal	7.93	7.14	8.36
Hydrogen Efficiency, kg distillates/kg H2	9.91	10.4	9-08
HDS W%	98.6	97.7	98
HDN W%	95.2	82.5	91.7

TABLE 2.5.17

CMSL-05.- Effect of Interstage Separation In-Line Hydrotreater Process Performance Of CMSL-05

	CMSL-05	CMSL-05	CMSL-02	CMSL-05	CMSL-02	CMSL-05 With CO/H2
Unit-	227-82	227-82	227-78	227-82	227-78	227-82
Condition	1	2	2	3	3	4
Period Number	4&5	7&8	10	10 & 11	13	13
Hours of Run (end of period)	120	192	231	264	104	312
Stage I Temp (C)	412	413	399	399	414	399
Stage 2 Temp (C)	441	441	428	427	433	428
H2S to Stage 2 Reactor, g/h	0	20	0	0	0	0
Stage 2 Cat Age, kg coal/kg cat	200	324	295	417	422	475
Stage 2 Space Velocity						
Kg coal/h/M3 reactor	465	452	285	327	516	309
lb coal/h//ft3 reactor	29	28.2	17.8	20-4	32,2	19.3
Solvent (Coal Ratio (feed slurry)	0.9	0.9	0.9	0.9	0.9	0.9
Oil/Solids Ratio (reactor)	0.96	0.96	O.99	0.96	0.95	1.04
Total Material Recovery % (gross)	99.55	100.1	99.25	99.95	97.91	101.99
Relative Severity index	1.18	1.19	1.0	0.99	1.03	1.02
ESTIMATED NORMALIZED YIELDS, W% MAF COAL						
Cl -C3 in Cases	6.74	7.73	5.93	5.53	5.38	6.21
C_4-C7 in Gases	4.42	4.14	4.32	3.17	3.82	2.62
IBP-199 deg-C in Liquids	14.08	17.19	18.06	10.69	16.77	12.43
199-260 deg-C in Liquids	18.05	18.56	12.65	12-97	9.2	13.08
260-343 deg-C in Liquids	30.14	26.45	31.29	23.17	23.33	20.63
343-454 deg-C in Liquids	10.73	10.99	8.37	18.32	14.03	18.03
454-524 deg-C in Liquids	1.31	1.22	1.18	4.48	3.82	4.75
524C+	1.68	2.15	2.24	9.57	6.57	12.31
Unconverted Coal	3.97	3.95	7.14	4.70	7.6	4.02
Water	9.85	8.60	11.57	6.77	11.52	5.84
CO	0.18	0.19	0.11	0.17	0.17	0.17
C02	0.31	0.19	0.04	0.19	0.14	0.16
NH3	1.72	1.72	1.59	1.72	1.49	1.65
H2S	4.87	4.88	3.87	4.86	3.74	4.78
PROCESS PERFORMANCE						
Coal Conversion, W% MAF Coal	96	96	92.9	95.2	92.4	96
C_4-524 deg-C Distillates, W% of MAF Coal	79	78.6	75.9	72.7	71	71.5
524C+ Conversion W% MAF	94.3	93.9	90.6	85.4	85.8	83.7
Hydrogen Consumption, W% MAF Coal	8.35	7.93	8.36	6.3	7.58	6.68
Hydrogen Efficiency, kg distillates/kg Coal	9.46	9.91	9.08	11.54	9.37	10.7
HDS W%	98.7	98.6	98	96.7	96	97
HDN W%	95.5	95.2	91.7	92.3	85.3	91.4

TABLE 2.5.18

FEED COAL ANALYSES

RUN	CMSL-5	CMSL-2
HRI NO.	HRI L-811	HRI 6107
MINE	Crown II	Burning Star No. 2
MOISTURE, W%	3.98	1.16
PROXIMATE ANALYSIS, W% (Dry)		
Volatile Matter	41.48	
Fixed Carbon	49.08	
Ash	10.4	12.04
ULTIMATE ANALYSIS, W% (Dry)		
Carbon	70.28	69.00
Hydrogen	4.73	4.24
Sulfur	4.17	4.00
Nitrogen	1.33	1.26
Oxygen (by difference)	91.0	9.46
Ash	10.40	12.04
MICROAUTOCLAVE CONVERSIONS @ 427 °C/30 Min Reaction		
Thermal	89.6	84.6
Catalytic	95.2	91.8

TABLE 2.5.19

INSPECTION OF STARTUP/MAKEUP OIL

HRI NO,	L-809
GRAVITY °API	6.3
ELEMENTAL ANALYSIS, W%	
Carbon	88.62
Hydrogen	9.32
Sulfur	0.58
Nitrogen	0.18
H/C Ratio	1.26
ASTM 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
524oC+	15.15
LOSS	0.39

TABLE 2.5.20

ANALYSES OF RECOVERED CATALYSTS

Reactor Stage	K-1	K-2
Percent Oil	24.4	23.7
W % of Dried Catalyst		
+ 20 mesh	88.9	92.9
20 - 100 mesh	6.94	4.95
-100 mesh	4.16	2.15
For +20 Mesh Catalyst		
Bulk Density, g/cc	0.92	0.94
Ignition Loss (W%)	37.7	22.64
Surface Area, m2/g (BET)	99.69	113.54
Pore Volume, cc/g	0.238	0.309
Particle Density, g/cc	1.256	1.254
Weight percents,		
Carbon	22.86	13.00
Hydrogen	0.90	0.75
Sulfur	5.24	5.63
Nitrogen	0.22	0.18
Molybdenum	7.16	7.60
Nickel	1.39	1.48
Iron	0.26	0.34
Sodium	0.8	0.74
Calcium	0.09	1.86
Titanium	0.28	1.62
Ignited +20 Mesh Catalyst		
Pore Volume, cc/g	0.542	0.565
Particle Density, g/cc	1.101	1.082
Surface Area, M^2/g (BET)	157.3	149.4

TABLE 2.5.21

YIELDS OF GASES FOR RUN 227-82 (CMSL-05)

CONDITION	1	2	3	4
Hours of Run	120	192	264	312
Period Number	5	8	11	13
CO In First Stage Feed Gas, V%	0	0	0	75
Gas Yield (Stage I Vent), W% of mf Coal				
CH4	0.86	0.80	0.71	4.55
C2H4	0.00	0.01	0.00	0.00
C2H6	0.70	0.63	0.56	0.91
C3H6	0.02	0.02	0.02	0.06
C3H8	0.00	0.68	0.57	0.80
C_4H8	0.00	0.00	0.00	0.00
N-C_4H10	0.48	0.42	0.33	0.31
I-C_4H10	0.08	0.06	0.03	0.04
C5H10	0.00	0.00	0.00	0.00
N-C5H12	0.14	0.14	0.11	0.11
I-C5H12	0.11	0.07	0.08	0.05
Methyl-Cyclopentane	0.00	0.00	0.00	0.00
Cyclohexane	0.16	0.20	0.22	0.13
N-C6H14	0.08	0.07	0.04	0.07
C6-C7	0.04	0.04	0.04	0.07
CO	0.16	0.15	0.16	71.90
CO2	0.17	0.13	0.14	77.22
H2S	2.42	1.74	1.98	2.44
Gas Yields (Stage II Vent), W% of mf Coal				
CH4	1.17	1.29	0.98	1.74
C2H4	0.00	0.00	0.01	0.01
C2H6	1.14	1.47	0.88	0.98
C3H6	0.00	0.00	0.06	0.08
C3H8	1.47	2.13	1.10	1.22
C_4H8	0.00	0.00	0.00	0.03
N-C_4H10	1.16	1.48	0.83	0.90
I-C_4H10	0.18	0.31	0.11	0.13
C5H10	0.03	0.00	0.00	0.00
N-C5H12	0.31	0.32	0.25	0.16
I-C5H12	0.28	0.29	0.18	0.16
Methyl-Cyclopentane	0.00	0.00	0.00	0.00
Cyclohexane	0.15	0.04	0.21	0.11
N-C6H14	0.22	0.15	0.17	0.12
C6-C7	0.00	0.00	0.00	0.04
CO	0.00	0.00	0.00	0.28
CO2	0.02	0.00	0.00	0.16
H2S	0.38	2.00	0.75	0.37

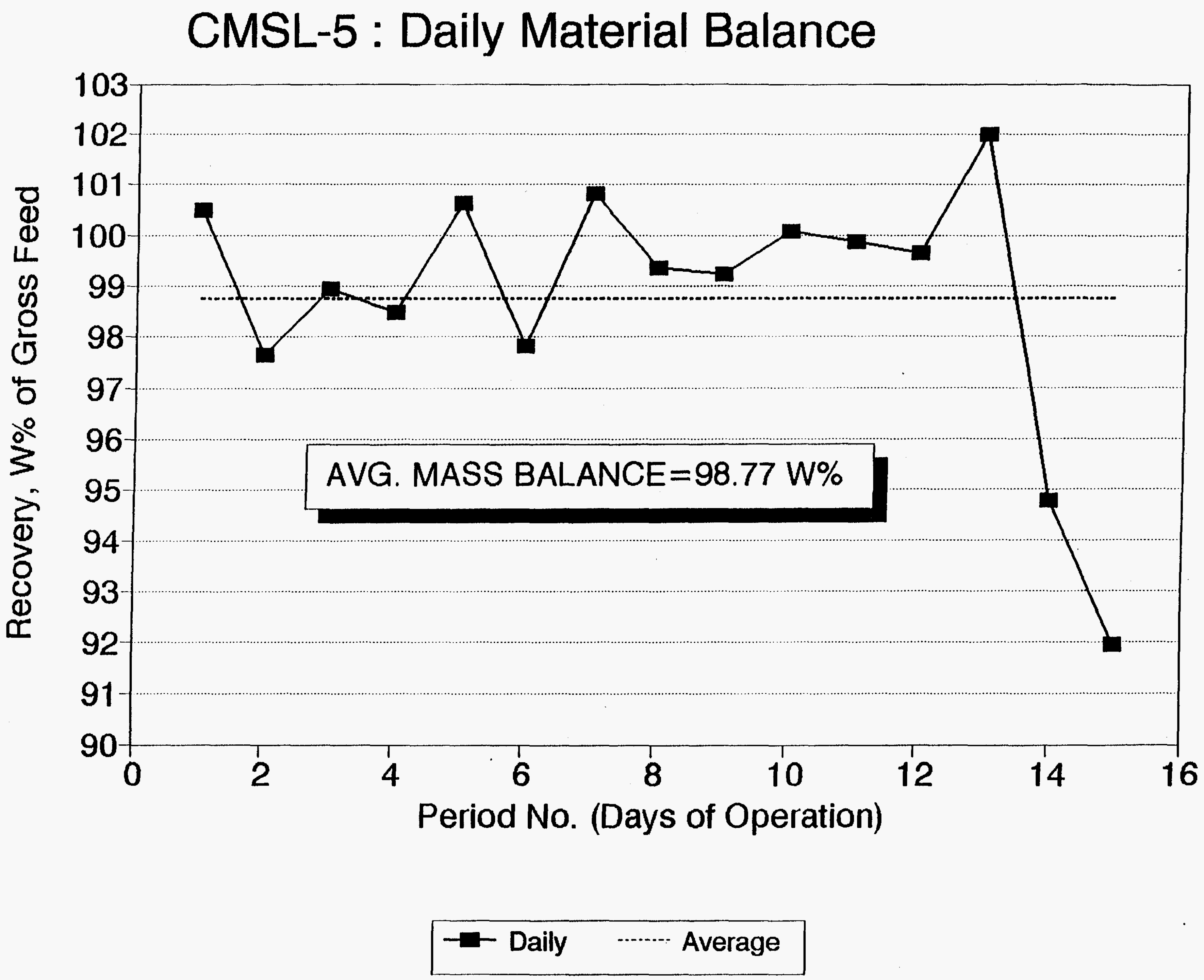

CMSL-5 : Daily Material Balance
Recovery, W% of Gross Feed
103
102
101
100
99
98
97
96
95
94
93
92
91
90
0
2
4
6
8
10
12
14
16
Period No. (Days of Operation)
AVG. MASS BALANCE=98.77 W%
Daily
Average

FIGURE 2.5.1

CMSL-5 : Daily Stage Temperatures & Coal Space Velocities

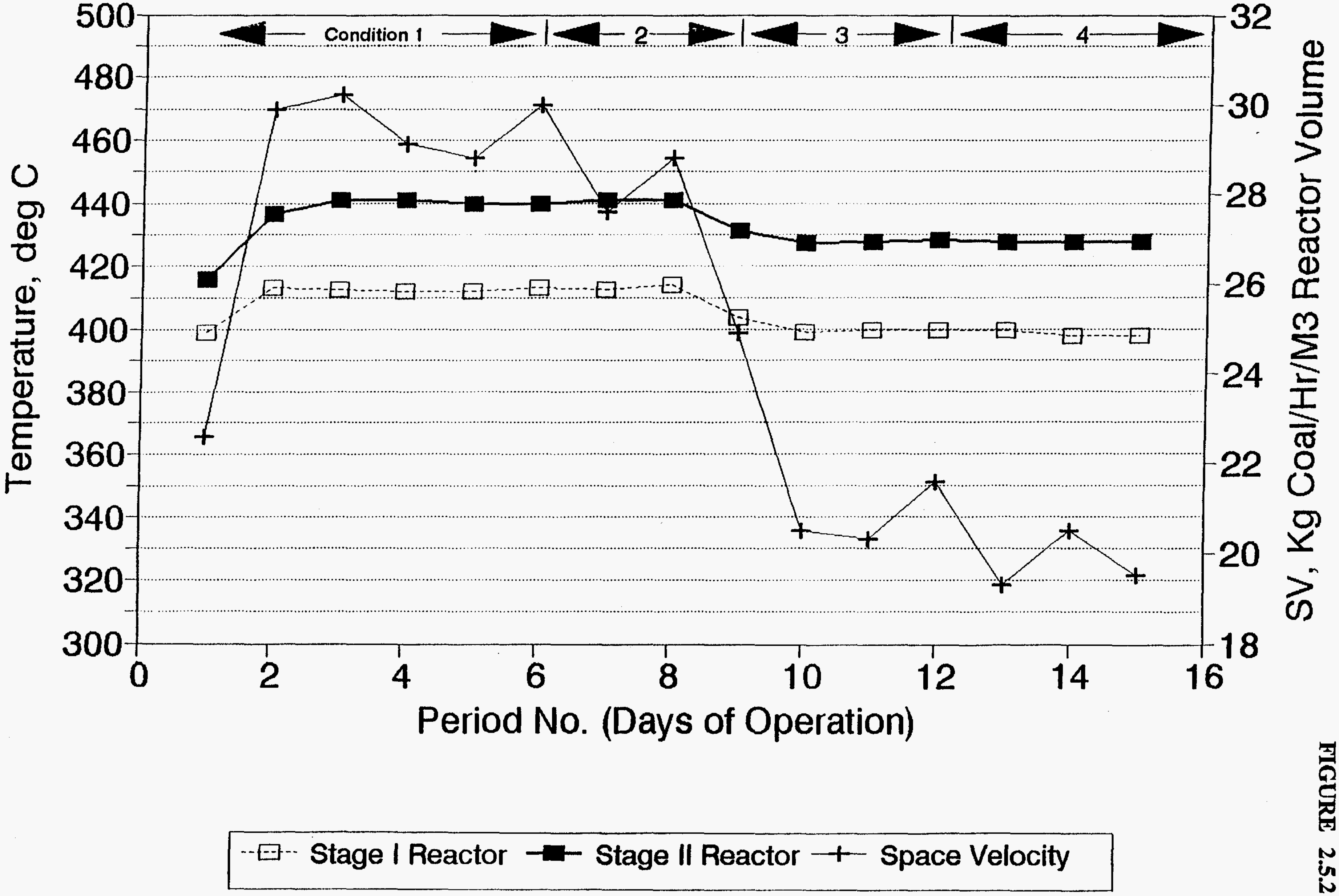
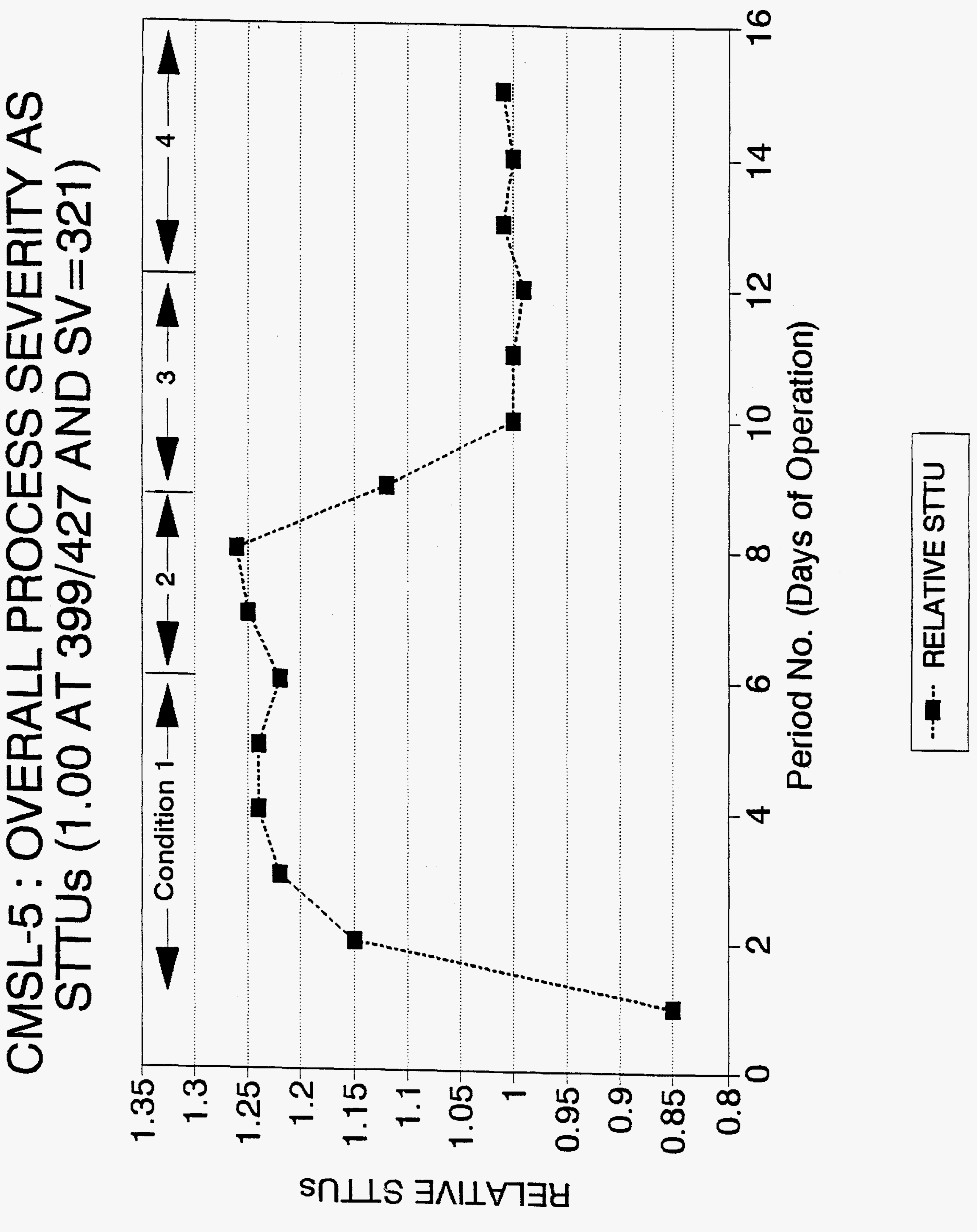


FIGURE 2.5.2

FIGURE 2.5.3



CMSL-5 : OVERALL PROCESS SEVERITY AS STTUs (1.00 AT 399/427 AND SV=321)

CMSL-5 : PROCESS PERFORMANCE- COAL, RESID CONVERSIONS & C4-524 C YIELDS

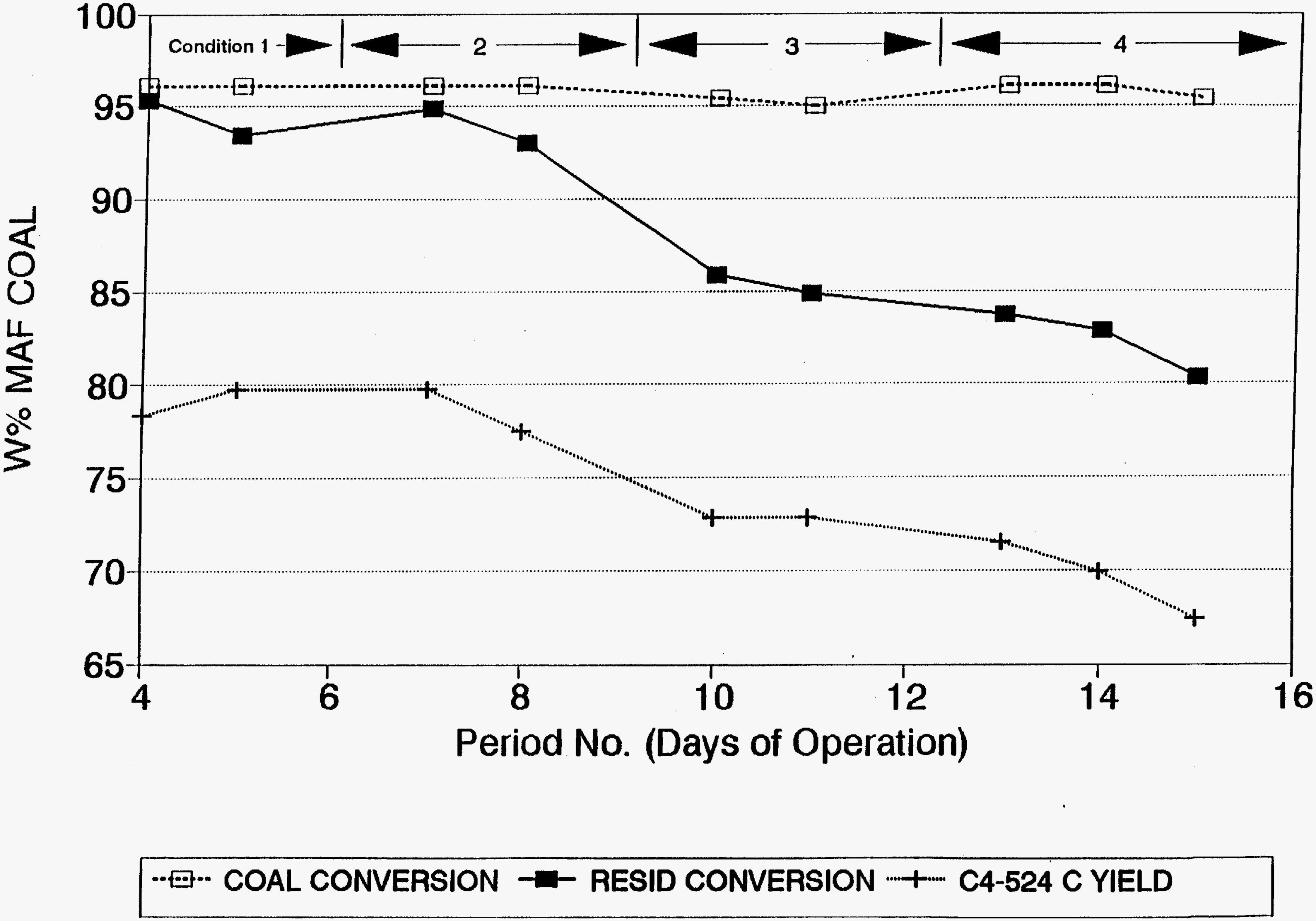


FIGURE 2.5.4

CMSL-5 : PROCESS PERFORMANCE- GAS YIELDS & H2-UTILIZATION

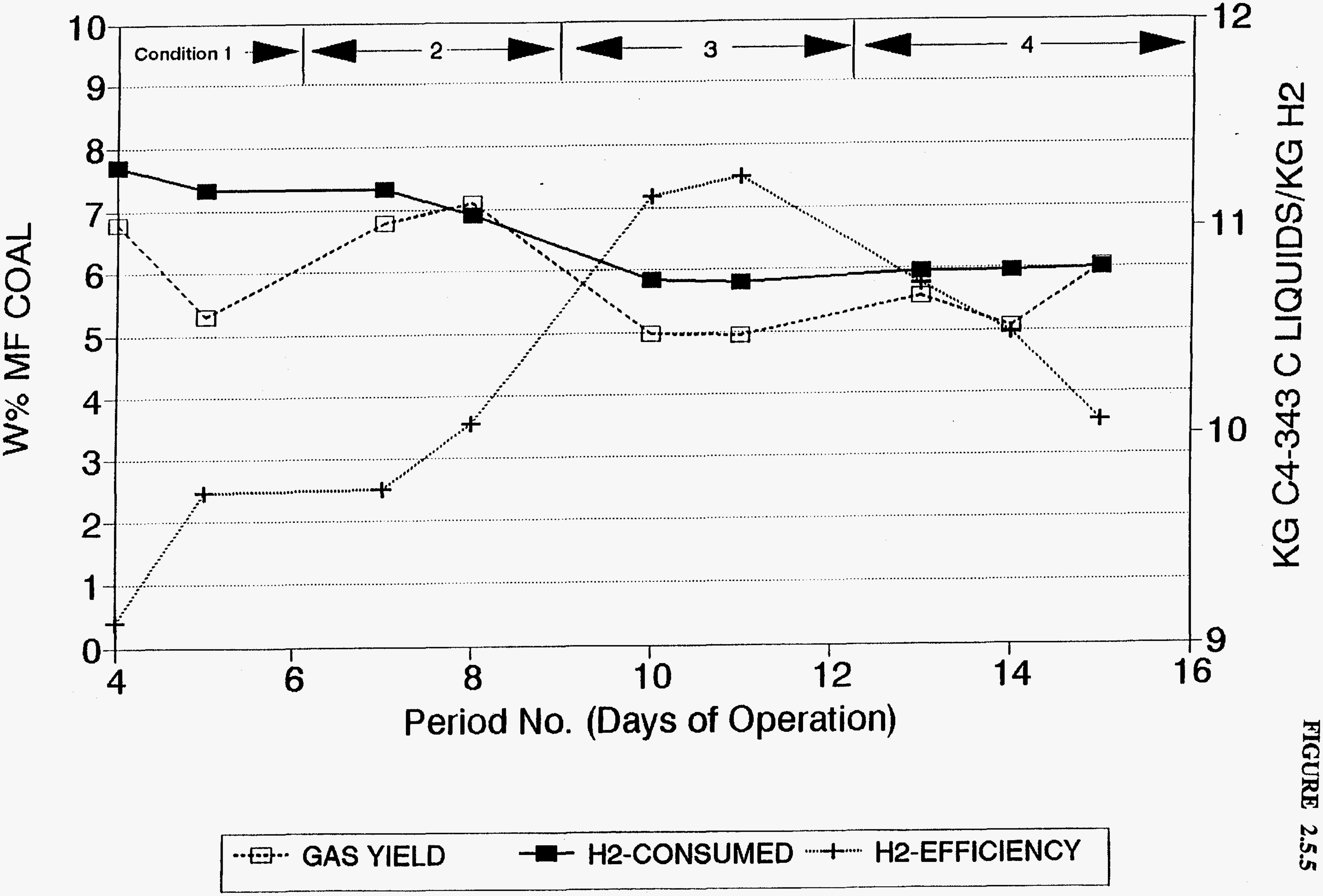


FIGURE 2.5.5

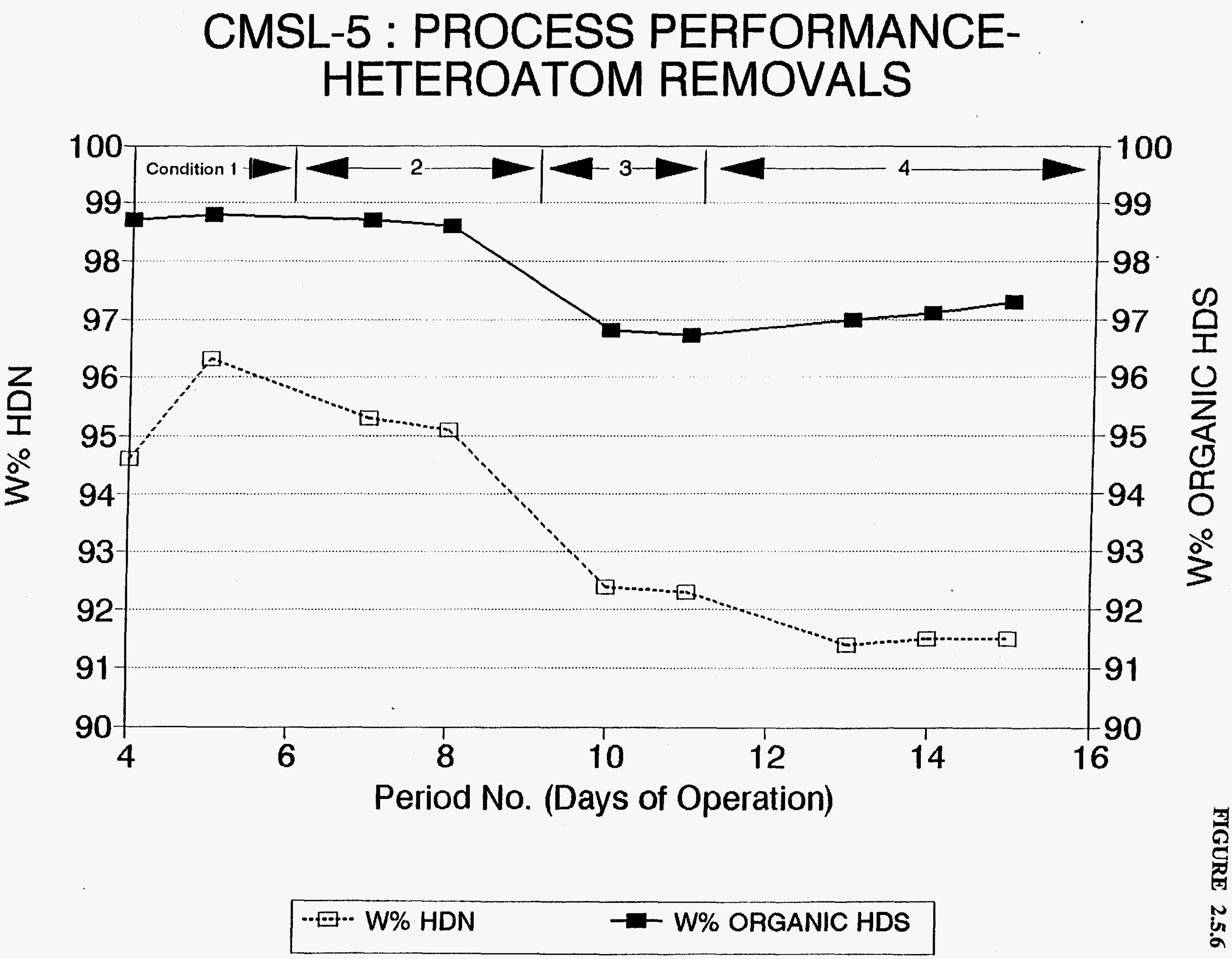

CMSL-5 : PROCESS PERFORMANCE-
HETEROATOM REMOVALS
Condition 1
2
3
4
W% HDN
W% ORGANIC HDS
100
99
98
97
96
95
94
93
92
91
90
4
6
8
10
12
14
16
Period No. (Days of Operation)
W% HDN
W% ORGANIC HDS

FIGURE 2.5.6

CMSL5: PROCESS PERFORMANCE
C4-524°C: YIELD & SELECTIVITY OF DISTILLATES

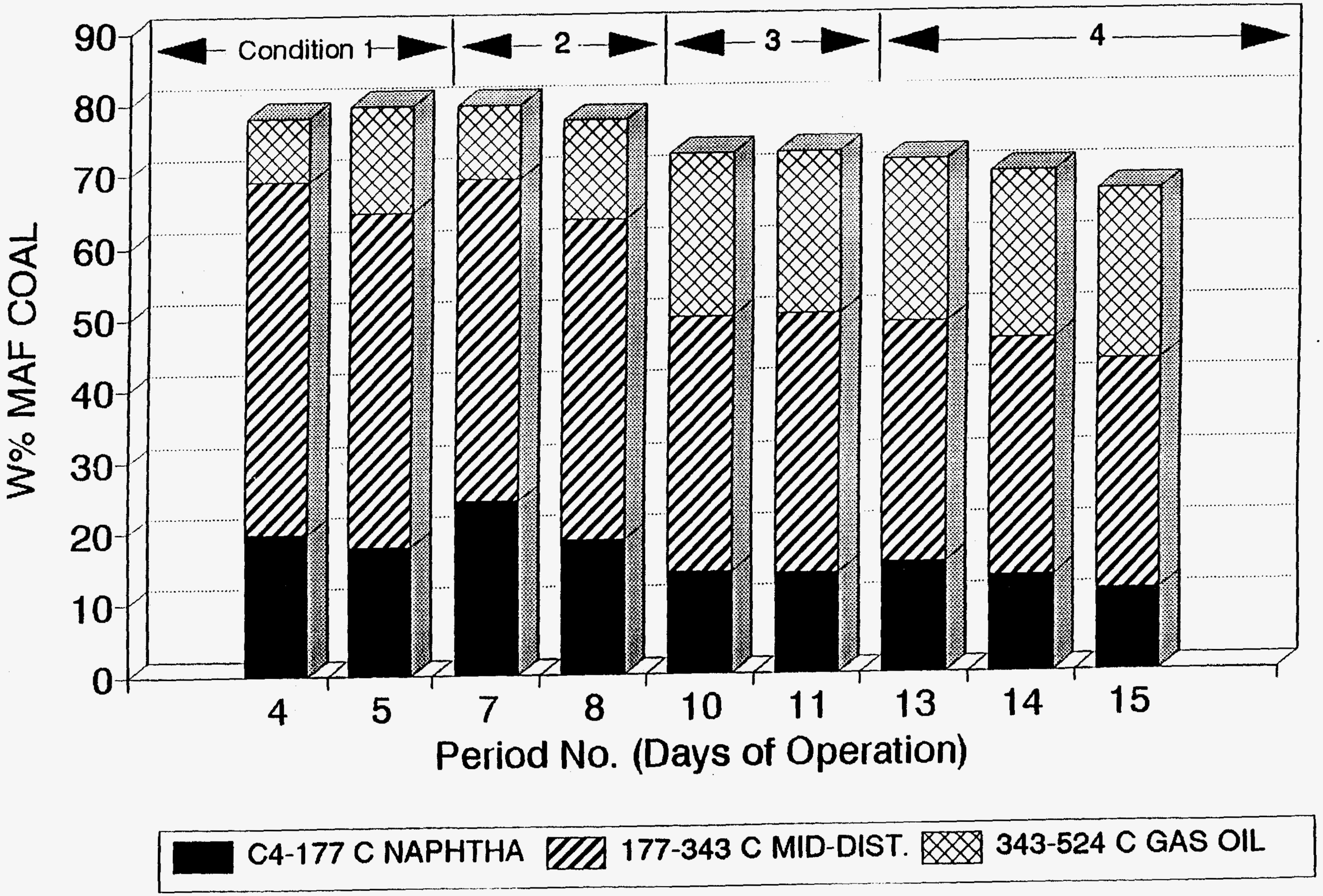


FIGURE 2.5.7

CMSL-5 : PROCESS PERFORMANCE- RESID YIELDS & PFL RESID CONTENT

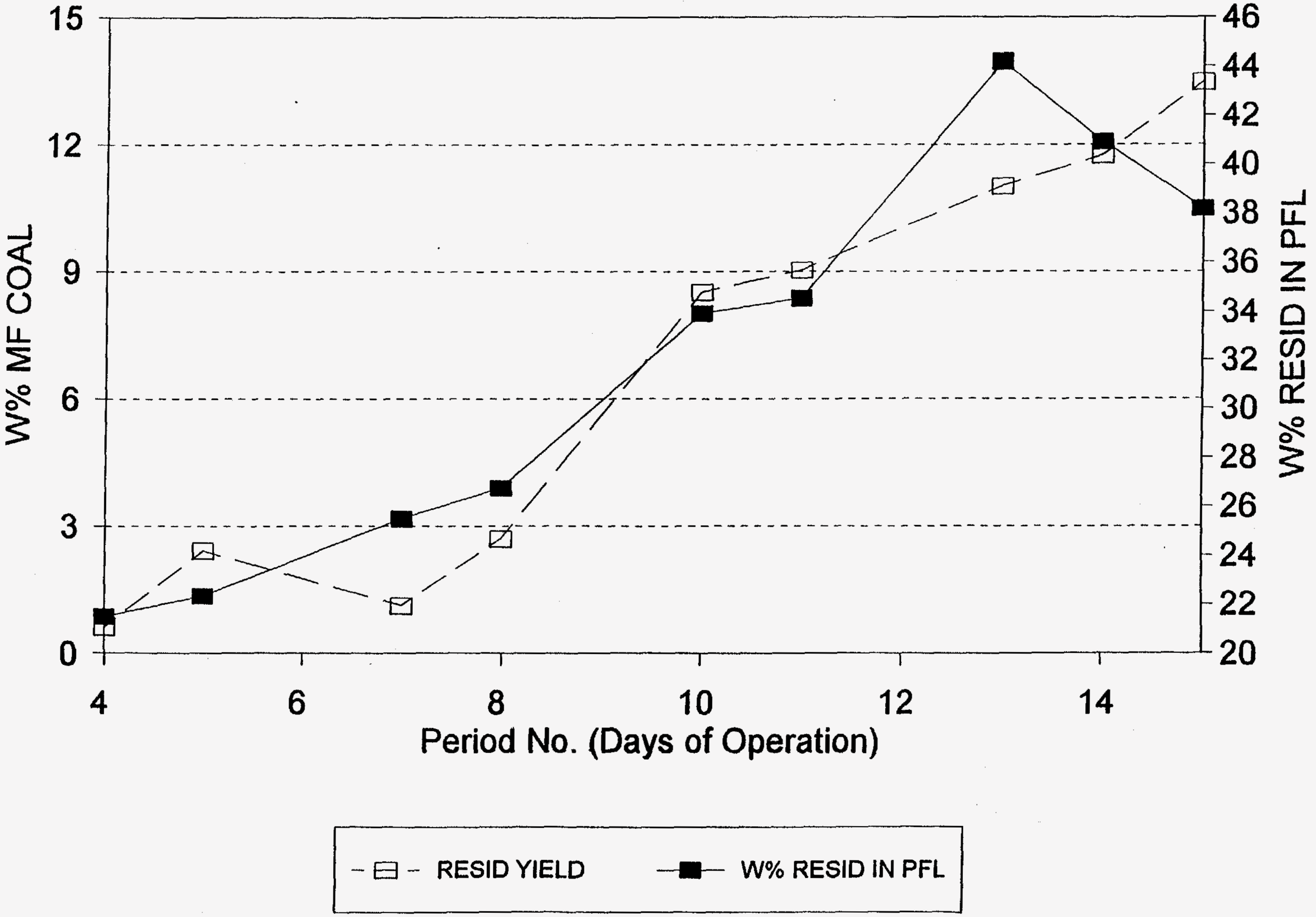


FIGURE 2.5.8

FIGURE 2.5.9

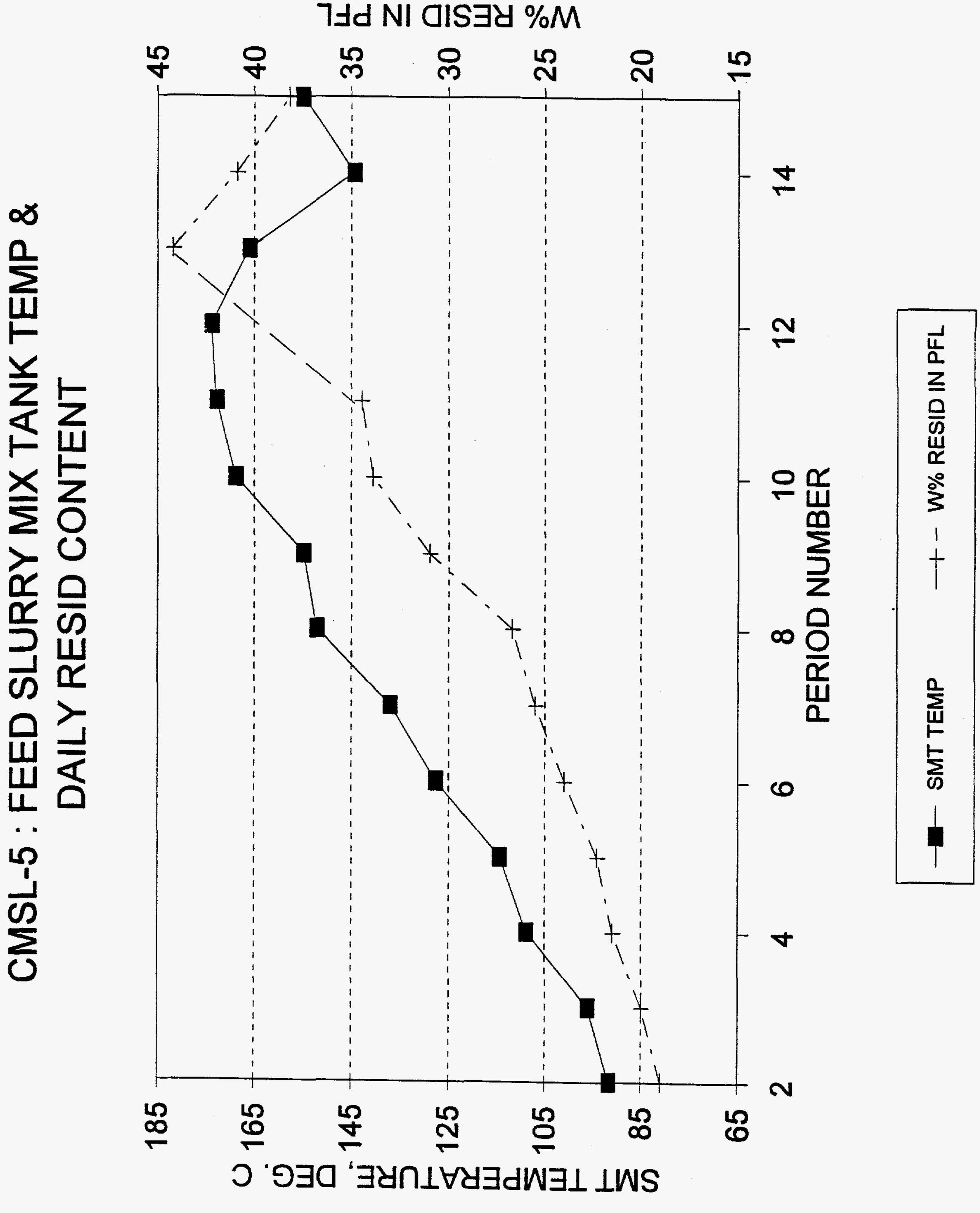
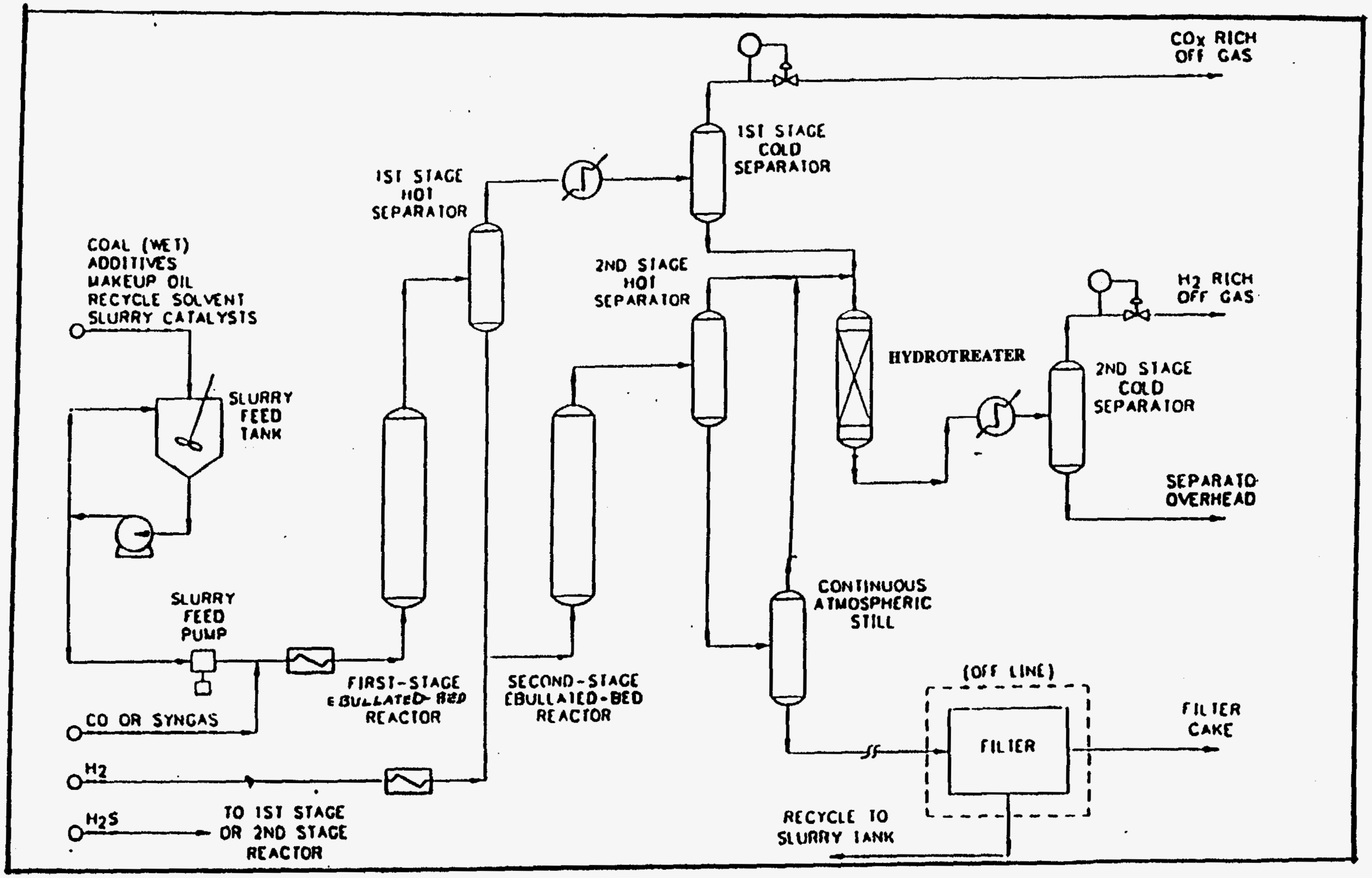

CMSL-5 : FEED SLURRY MIX TANK TEMP &
DAILY RESID CONTENT
SMT TEMPERATURE, DEG. C
185
165
145
125
105
85
65
W% RESID IN PFL
45
40
35
30
25
20
15
PERIOD NUMBER
2
4
6
8
10
12
14
SMT TEMP
W% RESID IN PFL

FIGURE 2.5.10



HTI SYNGAS - H2 TWO-STAGE COAL LIQUEFACTION SCHEME