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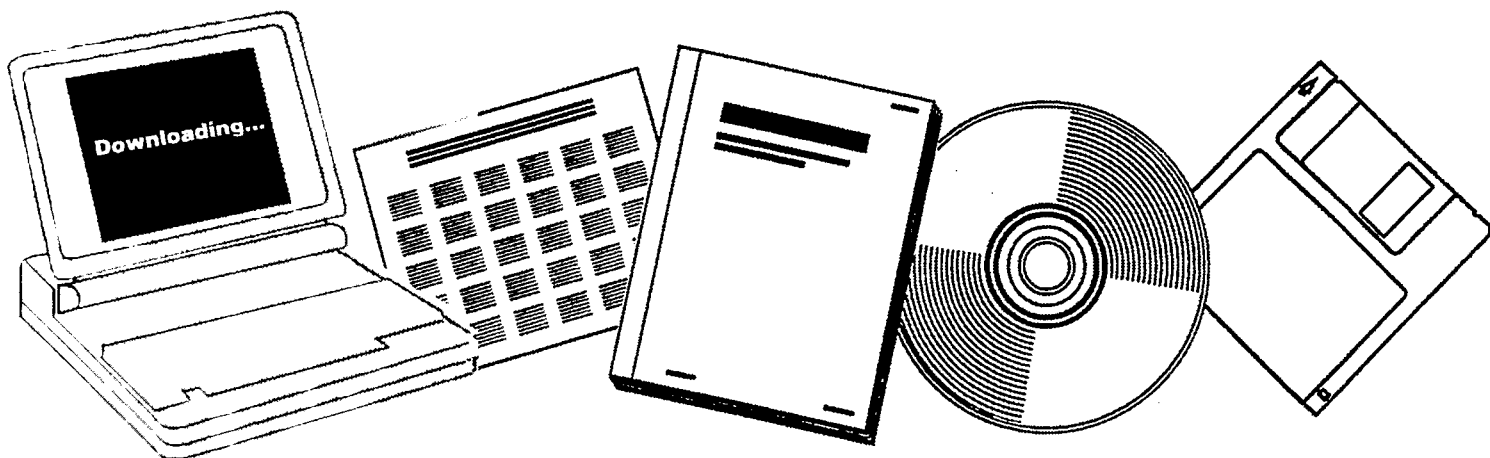
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**EXXON CATALYTIC COAL GASIFICATION PROCESS:
PREDEVELOPMENT PROGRAM. MONTHLY REPORT,
AUGUST 1977**

EXXON RESEARCH AND ENGINEERING CO.
BAYTOWN, TX

26 SEP 1977



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EXXON CATALYTIC COAL GASIFICATION PROCESS
PREDEVELOPMENT PROGRAM

Monthly Report for the Period
August, 1977

N. C. Nahas - Project Manager

Exxon Research and Engineering Company
Baytown, Texas 77520

September 26, 1977

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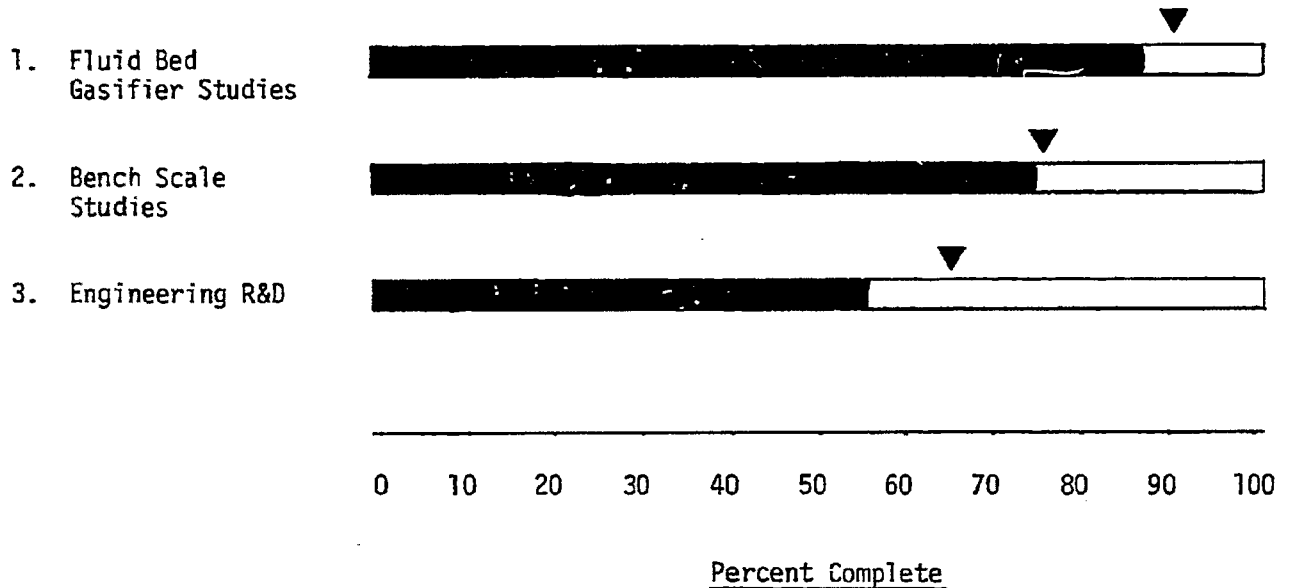
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SUMMARY OF PROGRESS THROUGH August 31, 1977 FOR PREDEVELOPMENT
WORK ON EXXON CATALYTIC COAL GASIFICATION PROCESS

Technical Reporting
Category



Legend

Shaded area = Percent of activity actually completed

▼ = Percent of activity scheduled for completion

ABSTRACT

The FBG was operated during the first two weeks of August to produce an inventory of char for subsequent catalyst recovery studies. Approximately 134 hours of material balanced operations were logged during the first two weeks of August with good material balance closures. Operations of the FBG as specified in the current contract are now complete and the unit has been shut down.

Construction of the pilot scale digester unit was completed and initial operations begun. Preliminary results show approximately the same recoveries as achieved in the bench scale unit for operations at the same conditions. Experiments were initiated to determine the mechanism by which air exposure of char decreases the amount of potassium catalyst which can be recovered by water washing. The data clearly indicate that there is a reaction between char and wet air, and that this reaction reduces the fraction of potassium which is water-soluble. Work continued on the use of $\text{Ca}(\text{OH})_2$ digestion to recover potassium from gasifier ash/char residue. Most of the experiments conducted this month employed a reduced liquid:char ratio of 4:1 in the digestion step. Work has indicated that acceptable recoveries may be possible at a temperature as low as 300°F with 4 hours residence time. Further work will be done to determine the effect of residence time and calcium loading on potassium recoveries.

Work has continued on the development of the process basis for the catalytic Gasification Commercial Plant Study Design. Preparation of this study design will involve the major share of the engineering effort under the Predevelopment contract during the latter part of 1977. The basis has been set for a screening study of catalyst recovery using "digestion" with $\text{Ca}(\text{OH})_2$ (also called "hydrothermal treatment"), and onsite equipment lists are being prepared for investment cost estimating.

DISCUSSION

FLUID BED GASIFICATION STUDIES (REPORTING CATEGORY 1)

FBG Operations

The FBG was operated during the first two weeks of August to produce an inventory of char for subsequent catalyst recovery studies. Since catalyst recycle operations had been completed in July, the coal was impregnated with fresh potassium carbonate solution.

For the first week FBG operations continued at high coal and steam feed flow rates. These conditions were employed to produce an inventory of gasified char which will be used for continuing work on catalyst recovery methods. In the second week of operation the gasifier bed temperature and feed flow rates were reduced to obtain data useful for development of the reactor model. Data from four material balanced operations are summarized in Table I.

Approximately 134 hours of material balanced operations were logged during the first two weeks of August with good material balance closures. The longest continuous run lasted over 72 hours.

It was necessary to empty the gasifier and pull the bottom when a feed line plug, which could not be cleared externally, occurred. The gasifier internal surface was also inspected at that time and was found to be clean and free of deposits with the exception of a minimal wall coating at the very bottom. This coating was very friable and disintegrated when touched. Because of this downtime and earlier electronic problems in the analog/digital conversion system the service factor for the two weeks was 54%.

Operations of the FBG as specified in the current contract are now complete and the unit has been shut down. Work is continuing on the analysis of the FBG data that has been accumulated during the past year.

Digester Operations

Construction of the pilot scale digester unit was completed and initial operations begun. The purpose of these runs was to determine recovery of the potassium from the gasifier ash/char residue by hydrothermal digestion with calcium hydroxide at various operating conditions.

The digestion procedure involved first adding the solution (water or KOH), then adding solid lime and mixing, and finally charging the ash/char residue. The digester was kept under a nitrogen blanket during these steps to minimize air exposure. When charging was complete agitation was maintained and the unit was sealed, heated to 400°F and controlled at

TABLE I

SUMMARY OF FBG MATERIAL BALANCE DATA FOR AUGUST, 1977

Material Balance Period:	47	48	49	50
Duration, hours	24	24	24	24
Reaction Conditions				
Temperature, °F	1310	1305	1287	1289
Pressure, psig	99.0	100.2	98.7	98.6
Input, lbs/hr (ExN ₂):				
Coal + Catalyst	16.3	15.2	8.9	6.9
Steam	24.3	24.0	14.4	15.0
Syngas	11.8	13.8	14.0	12.7
Total	52.4	53.0	37.3	34.6
Output, lbs/hr (ExN ₂):				
Product Gas	35.2	35.1	22.7	22.8
Water	12.3	12.3	10.2	9.4
Carryover	1.4	2.5	1.3	0.7
Withdrawn	3.5	3.6	3.0	1.1
Total	52.4	53.5	37.2	34.0
Accumulation, lbs/hr.	(.26)	(.60)	(1.05)	.03
Material Balance, %				
Overall	99.5	99.8	96.9	98.4
Oxygen	102.0	99.3	99.8	100.6
Hydrogen	96.9	98.3	97.2	98.9
Syngas, SCFH				
CO + H ₂ in Unit	434	467	508	452
CO + H ₂ in Product Gas	646	657	439	462
Syngas Balance, %	149	141	86	102
Steam Conversion, %				
By Water Balance	50.4	50.0	30.8	38.1
By Oxygen Balance	53.0	49.0	30.5	39.0
Product Gas, Mol % (dry, ExN ₂)				
H	56.1	56.7	57.4	59.4
CO	17.4	17.5	15.4	16.0
CO ₂	16.9	16.6	15.3	15.6
CH ₄	8.6	8.2	11.0	8.2
H ₂ S	1.0	1.0	0.9	0.8
Approach to Methanation Equilibrium, °F				
	54	70	28	74
Carbon Conversion (by Solids Analysis), %	79.2*	76.5	52.6*	73.5*

*Carbon Conversion by gas analysis

that temperature for four hours.

Vessel pressure was determined by the vapor pressure of steam over the solution. At the end of the reaction time, the vessel was cooled and the slurry effluent filtered to recover the solution. Additional recovery was obtained by a series of crosscurrent wash steps in which the filter cake was reslurried with two or three times its weight of fresh water and filtered again.

The results of the initial shakedown operations are shown in Table II. The wash steps in runs 3 and 4 used a 3:1 weight ratio of water to wet filter cake. Runs 5 and 6 used a 2:1 weight ratio of water to wet filter cake. The negative recoveries shown for the digestion step in runs 5 and 6 resulted from a portion of the KOH in the solution charge being heldup as rich solution in the filter cake. This is removed by subsequent wash steps.

These preliminary results show approximately the same recoveries as achieved in the bench scale unit for operations at the same conditions.

During September studies on the effect of reduced temperature, holding time, and calcium:potassium ratio will be conducted.

TABLE II
RECOVERY OF POTASSIUM CATALYST BY HYDROTHERMAL DIGESTION WITH Ca(OH)₂

Run No.	Conditions				Digestion Step	Cumulative Percent Potassium Recovered				
	Reaction Time (hrs)	Temperature (°F)	Moles Ca Moles K	Solution Weight Per lb. Char		First Wash	Second Wash	Third Wash	Fourth Wash	Fifth Wash
2	4	400	0.61	3 lb. H ₂ O	30.2					
3	4	400	0.0	3 lb. H ₂ O	27.4	47	52.2			
4	4	400	0.60	4 lb. H ₂ O	36.5	77.2	84.9	88.2		
5	4	400	0.39	4 lb. 8.79% KOH	-84.4	47.4	71.9	76.7	81.2	83.4
6	4	400	0.37	4 lb. 9.34% KOH	-21.9	62.9	77.9	82.5	84.7	

BENCH SCALE STUDIES (REPORTING CATEGORY 2)

Catalyst Recovery Via Water Washing

Experiments were initiated to determine the mechanism by which air exposure of char decreases the amount of potassium catalyst which can be recovered by water washing. In order to identify whether the char reacts with oxygen or with water vapor in the air, identical portions of char were exposed to streams of wet air, dry air, wet nitrogen and dry nitrogen for a 24 hour period. At the end of the reaction period, the weight change of each char sample was noted, and two samples of that char were analyzed for water soluble and total potassium. The ratio of water soluble to total potassium was used as an indicator to determine how each gas affects the leachability of the char. The char initially had a water soluble to total potassium ratio of .71. The results of the experiments are as follows:

<u>Reactant Gas</u>	<u>Weight Change</u>	<u>Water Soluble K (% of Total K)</u>
Dry Air	+1%	77
Dry N ₂	0	74
Wet Air	+18	66
Wet N ₂	-	73

The data clearly indicate that there is a reaction between char and wet air, and that this reaction reduces the fraction of potassium which is water-soluble. This supports previous observations in the laboratory that exposure of char to humid air significantly decreases catalyst recovery by cross-current water washing.

Any reaction between char and the other gas mixtures, however, is not as obvious. On the basis of the consistently higher ratios of water soluble to total potassium, it appears that char leachability might actually be improved by treatment with the appropriate gases. The usefulness of these data, however, are somewhat limited by the analytical technique used for determination of water soluble potassium. A revised experimental procedure is now being developed, and will be used for further investigation of this behavior.

Recovery of Water Insoluble Catalyst

Work continued on the use of Ca(OH)₂ digestion to recover potassium from gasifier ash/char residue. As reported last month, there is an incentive to operate the digestion step with a concentrated slurry in a commercial catalyst recovery system. Therefore, most of the experiments conducted this month employed a reduced liquid:char ratio of 4:1 in the

digestion step. Temperature and residence time were maintained at 400°F and 4 hours, respectively.

The procedure used for most runs has included rinsing the treated char with an excess of distilled water to remove potassium solution held in the moist char. In the commercial process, there is the incentive in this step to also keep the slurry concentrated. In order to estimate possible recoveries with minimal water rinsing, the usual procedure was slightly modified for several runs.

To avoid the use of excess water, the treated slurry was removed from the tubing bomb and separated by filtration without adding water and the filtrate was used to rinse the bomb. The moist char was washed three times with distilled water added at a liquid/char ratio of ~3.0. Each wash was held at 212°F for 15 minutes. This washing procedure is similar to that used to determine the recovery of water soluble potassium by water washing. The data for the runs made with this modified procedure are shown below:

<u>Molar Ratio</u> <u>Ca/K</u>	<u>Total K</u> <u>Recovered</u>
0.85	83%
0.73	87%
0.65	84%
0.48	85%

The recoveries for all of these runs are in the range of 85%, similar to runs made under similar process conditions and washed with an excess of water.

A series of experiments to investigate the effect of temperature on potassium recoveries was initiated in August. The runs were made with the usual procedure, including an excess of water to rinse the treated char. Recent work has indicated that acceptable recoveries may be possible at a temperature as low as 300°F with 4 hours residence time. These data are summarized below:

<u>Run</u> <u>Temperature</u>	<u>Molar Ratio</u> <u>Ca/K</u>	<u>% Total K</u> <u>Recovered</u>
200°F	0.78	74%
300°F	0.81	87%
350°F	0.80	86%
400°F	0.68	89%
450°F	0.84	90%

Further work will be done to determine the effect of residence time and calcium loading on potassium recoveries.

ENGINEERING RESEARCH AND DEVELOPMENT (REPORTING CATEGORY 3)

Catalytic Gasification Commercial Plant Study Design

Work has continued on the development of the process basis for the catalytic Gasification Commercial Plant Study Design. The study design will reflect the current conception of a commercial catalytic gasification plant producing approximately 250 MSCF/SD of SNG from Illinois coal. Estimates will be made of both investment and operating cost. Preparation of this study design will involve the major share of the engineering effort under the Predevelopment contract during the latter part of 1977.

As in July, efforts have focused on studies needed to set the process bases for the catalytic gasifier and recycle synthesis gas loop. As discussed in the July Report, gasifier conditions for the new study design will be 500 psia and 1275°F. In order to provide key inputs to the gasifier heat balance, studies by the Exxon Engineering Technology Department are in progress in the areas of coal feeding methods and gasifier lining design. Data from FBG material balance periods are under review to develop bases for gasifier solids carryover and gasifier char withdrawal rates and properties. These bases will be used in designing solids recovery equipment for the gasifier effluent gas stream, and in designing the catalyst recovery system. Data on properties of the "mid-char" from the FBG fluid bed will also be reviewed to serve as a basis for gasifier volume calculations using the catalytic gasifier reactor model.

Studies are also underway to define the flow sequence for the gasifier effluent solids recovery and heat recovery train. In addition, a screening study of acid gas scrubbing alternatives for use with catalytic gasification has begun. Vendor contracts are planned early in September.

Evaluation of Catalyst Recovery Alternatives--Screening Study of Hydrothermal Treatment

The basis has been set for a screening study of catalyst recovery using "digestion" with $\text{Ca}(\text{OH})_2$ (also called "hydrothermal treatment"), and onsite equipment lists are being prepared for investment cost estimating. As mentioned in the July Monthly Report, this study will define the facilities and quantify the investment and operating costs required for this catalyst recovery system. This information will help to measure the incentive for the use of $\text{Ca}(\text{OH})_2$ digestion.

The process basis for this screening study reflects recent laboratory data on hydrothermal treatment and water-washing. The important basis items for the present study are summarized below:

- Feed catalyst loading is 15% K_2CO_3 -equivalent on dry coal.
- 27% of this total potassium ties up with the coal ash as water-insoluble KAlSiO_4 , and thus only 73% of the feed potassium can be

recovered by water washing alone.

- In contrast, after hydrothermal treatment 90% of the potassium fed to catalyst recovery is water-soluble and thus recoverable.
- The hydrothermal treatment step replaces one stage of the water-wash sequence. Based on bench lab studies to date, the operating conditions for the digestion vessels are set at 250 psia, 400°F, 4 hours residence time, and a lime (CaO) rate which reflects a molar ratio of calcium to the total potassium feed of 0.6/1. (CaO hydrolyzes to $\text{Ca}(\text{OH})_2$ in aqueous solution.)
- The makeup catalyst (30% KOH solution) is added to the hydrothermal treatment step to take advantage of probable enhanced recovery at higher pH.
- The recovered rich catalyst solution is stripped with CO_2 before returning to the catalyst addition facilities in order to minimize recycle of K_2S , which may oxidize to catalytically less active K_2SO_4 in the catalyst addition step.
- The forms of water-soluble potassium in the stripped rich catalyst solution are mostly K_2CO_3 and KHCO_3 , with about 1% each of K_2S , K_2SO_4 , and $\text{K}_2\text{S}_2\text{O}_3$.

These bases will be reexamined after experimental work at reduced severity. Equipment lists for this screening study of hydrothermal treatment will be completed and submitted for cost estimating in September.

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