

DE84003530



EXXON CATALYTIC COAL-GASIFICATION-PROCESS DEVELOPMENT PROGRAM. FINAL PROJECT REPORT



EXXON RESEARCH AND ENGINEERING CO. BAYTOWN, TX

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DE84003530

COR.17.KW-P.81

DOE/ET/13005--T12

FE-2777-31 Dist. Category UC-90c

DE84 003530

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FINAL PROJECT REPORT

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Baytown, Texas 77520

November, 1981

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY UNDER Contract No. ET-78-C-01-2777



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ABSTRACT

The Exxon Catalytic Coal Gasification (CCG) Development Program began in July 1978 and was completed in March of 1981. The program was a coordinated effort involving bench scale R&D, operation of a one ton-per-day Process Development Unit (PDU), and engineering support. The PDU was being operated with bituminous Illinois No. 6 coal catalyzed with potassium hydroxide. This work was aimed at advancing the catalytic coal gasification technology through the development stage to make it ready for further scaleup in a large pilot plant.

This report covers the activities for the Exxon Catalytic Coal Gasification Development Program during the period July 1978 through March 1981. This work was performed by the Exxon Research and Engineering Company (ER&E) and was supported by the United States Department of Energy under Contract No. ET-78-C-01-2777 and by the Gas Research Institute.

The highlights of this report are summarized below:

Bench Scale Research and Development

An experimental program was carried out to quantify the amounts of various potassium species present in catalyst recovery operations. New titration methods were developed to correct for anion interferences inherent in determination of catalyst forms. The pulse polarography method was also revised to eliminate polysulfide interferences with analysis or other sulfur species. Some catalytically inactive forms were found in the recovered catalyst solution such as potassium silicates, sulfate, and chloride. Treatment of recovered catalyst solution with CO_2 removes about 90% of the dissolved silicate and strips sulfide and polysulfide ions out of solution as H₂S.

Comparison of the visible spectra of catalyst recovery solutions with pure compound solutions identified the sources of color in the aqueous char extracts. The blue-green color of water-washed catalyst recovery solution is apparently due to potassium iron sulfide (KFeS₂). The yellow color of digested catalyst recovery solution is due to polysulfide species.

Other results indicate that air exposure of the PDU char reduces the efficiency of catalyst recovery, that leaching temperatures above 200°F improve catalyst recovery, and that the overall efficiency of a multistep leaching operation is not greatly dependent upon the water-to-char ratio used.

Catalyst recovery studies also indicated that $Ca(OH)_2$ digestion in dilute KOH (0.1 M) solutions may be as effective as in concentrated solutions (1.0 M). The lack of adequate mixing of char, lime, and process solution prior to digestion was found to increase the amount of inactive potassium silicates in the recovered catalyst solution. This result may be due to agglomeration of lime prior to digestion, preventing the full utilization of the calcium in the lime for the digestion reaction. Experiments have shown that soluble potassium can be extracted from flocculant treated chars. Furthermore, flocculant pretreatment was found to increase sedimentation and filtration rates by a factor of 2 to 5 depending on process conditions of temperature, pH, and weight percent solids in the slurry. A combination of a cationic and an anionic flocculant gave even better filtration and sedimentation rates and liquid clarity than the use of either one of them alone. Bench tests of flocculant treated water washed chars showed that the flocculant remains effective for multiple settling cycles. Flocculant pretreatment was also found to increase both sedimentation and filtration rates for digested char slurries; however, the potential is not as great for digested material as for water washed materials.

Bench scale devices were used to measure the cake resistance and critical settling time of char from the PDU. Data from this unit will help in studies of the CCG catalyst recovery system. A variety of PDU char and fines samples were tested in the bench scale filtration and settling devices.

A bench scale recycle gas furnace simulator was operated to study the extent of the water-gas shift reaction at commercial conditions. Operation of this reactor was troubled with some deposition of carbon in the heated zone during operation. Neither SO_2 pretreatment of the reactor internals nor use of a quartz sleeve were effective in completely eliminating the carbon deposits. Deposition of carbon in the apparatus was traced to the ceramic mullite beads used as filling in the tube. Carbon deposition was eliminated by removing the ceramic beads. Some water-gas shift reaction was observed at temperatures above 1000°F, but the reaction rate is slow, indicating that the CO_2 concentration in the recycle gas from the commercial furnace should be small.

Process Development Unit Operations

Guidelines and recommendations for the safe operation of the PDU gasifier were formulated and carried out. The gasification section of the PDU was operated at 500 psia and 1200°F using nitrogen and steam as the fluidizing gases for short periods of up to 14 hours while the feed and withdrawal systems were debugged. During August 1979, a sustained operation of 165 hours at conditions of 1200-1250°F and 500 psia was completed. Feed rates were 150 lbs/hour steam, 3500 SCFH total nitrogen, and 90 lbs/hour catalyzed Illinois coal. Material balances were in the 95-98% range.

Syngas (H₂ and CO) was introduced into the gasifier for the first time during October 1979. The unit ran for seven days with steam and syngas as feed to the bottom of the reactor. During November 1979, the Process Development Unit (PDU) completed two sustained periods of operation of 144 hours and 110 hours with syngas (75% H₂ and 25% CO) in the reactor. During December 1979, a 146-hour run was made with carbon conversions of 80 to 90%. The dry nitrogen-free product gas contained 20 to 30% methane.

Initial operations in the PDU were hampered by chunk formation and low fluid bed density. By increasing the gas flow through the coal feed line and ensuring that the initial bed height is above the feed line, chunk formation was essentially eliminated. Bed density was improved by lowering reactor pressure and by mild oxidation of the feed coal. In May 1980, an 811-hour PDU gasification section run period was completed. The gasifier operated at temperatures of 1260 to 1290°F and a pressure of 265 psia. Carbon conversions ranged from 61 to 92%. Steam conversions from 25 to 37% and fluid bed density from 5 to 17 lb/ft^3 . For about 300 hours during this period, some of the synthesis gas and catalyst were recovered and recycled to the gasifier, though not at design target rates.

During the third quarter of 1980, the PDU gasifier was run successfully at 500 psia. The reactor fluid bed char density was increased to 18-20 lbs/ft³ when the coal preoxidizer temperature was closely controlled between 180-200°C. It was determined that CO_2 was causing recurrent freeze-out problems in the cryogenic tower. The problem was corrected by making improvements in the molecular sieves which remove trace quantities of CO_2 .

In the last quarter of 1980, a number of cracks were discovered in the bottom flange and the char withdrawal lines of the Process Development Unit (PDU). The cracks appear to be the result of caustic stress corrosion cracking. The damaged metal was removed and replaced with a more resistant alloy. As a further precaution, care was taken to monitor and control temperatures at the bottom portion of the gasifier and avoid potential steam condensation.

During the first quarter of 1981, the PDU successfully achieved 23 days of smooth, lined-out operation at conditions demonstrating operability of the CCG Sasifier. Fluid bed density was controlled at about 15 lbs/ft³ with 16 mesh Illinois No. 6 coal. The carbon conversion level was controlled at about 85-90%.

In parallel with the operation of the gasifier as described above, the PDU Catalyst Recovery Unit (CRU) was designed, constructed, and operated. Final equipment specifications and detailed diagrams were completed early in 1979 for the CRU. Construction began in October 1979. Before completion of the CRU, preliminary experiments were carried out using a rental filter to gain experience in filter operation. By mid-1980, all major equipment items were in place and process piping was completed. Operation of the CRU was relatively trouble free.

The CRU recovered 70-75% of the total potassium on the gasifier char in two-stage water-wash operations. Material balances around the CRU were generally in the range of 99-106%.

During the last quarter of 1980, a CO_2 stripping system was added to the CRU. Operation of this system reduced the concentration of silicate in the recovered catalyst stream by 40% to 95%.

Data Acquisition and Correlations

The CCG Reactor Model is a tool which is used to correlate and understand pilot plant data and to predict the performance of larger scale gasifiers. It includes expressions to model the complex interactions of reaction kinetics at the coal particle and the hydrodynamic behavior of the fluidized bed. This model was first developed in 1976 and has undergone updating since then as understanding has improved. The model uses correlations which are based on bench scale studies of kinetics and devolitization and on proprietary and literature correlations for fluidization and contacting.

During this contract, many material balances have been obtained in the PDU at 265 and 500 psia operating pressures, including the demonstration run. This data, along with earlier data at 100 psia, has been used to validate the model. The data cover a broad range for each of the important process variables. Based on this evaluation of the model, it has been concluded that the model has a good fit for pilot unit data over a broad range of conditions.

A cold model of the PDU gasification reactor was built to help troubleshoot solids flow problems in the PDU operation. This cold model has essentially the same dimensions as the PDU gasifier except that it is about onesixth of the height. A series of experiments was carried out to evaluate the performance of the solids feed and the fines return systems of the PDU and recommendations were made regarding purge locations and gas rates through them.

A system was designed to monitor PDU temperatures, flow rates, pressures, gas analyses, and weights which is capable of monitoring 600 process variables. A computer program was written to use this data to calculate an on-line material balance and identify possible operating problems such as faulty instrument readings or process leaks.

An off-line data reconciliation program for the PDU was also developed, debugged, and used. This program provided a tool for obtaining consistent and reliable data from PDU operations.

Advanced Study of the Exxon Catalytic Coal Gasification Process

Two bench scale gasification reactors were used in this study. One unit was a mini-fluidized bed reactor that operated at atmospheric pressure and the second unit was fixed bed reactor that operated at 500 psia. Both reactors were used to study gasification kinetics over a broad range of conditions to screen process conditions for further PDU study as well as expand the data base for the kinetic model.

Work was aimed at further defining the effect of catalyst loading, temperature, gas composition, gas flow rate, and pressure on the gasification rate. Results from minibed experiments indicate that gasification rate increases with increasing potassium-to-carbon ratio even beyond the region where this effect was previously believed to saturate. The apparent activation energy was found to be highly sensitive to the ratio of H₂O to H₂ in the feed gas. From fixed bed experiments, the gasification rate was found to be rather insensitive to pressure changes but highly sensitive to the ratio of H₂O to H₂ in the feed gas.

Study of the devolatilization process at atmospheric pressure showed that oxidation level of catalyzed coal accounted for variations in the density of gasifier chars in the FBG. Catalyst form and coal soak time were shown not to be significant factors in the char density. Bench scale studies also showed that changing the devolatilization pressure from 100 psia to 500 psia significantly alters the char properties. Operation at 100 psia produced chars similar to chars from the atmospheric test units; however, 500 psia operation produced both finer particles and lower density chars. Results indicate that a mild oxidation at about 350°F or extraction of humic acid from fresh coal with hot KOH may eliminate swelling of KOH catalyzed Illinois coal.

A bench! scale program was completed which determined the amounts and forms of mineral matter in the solids streams in the PDU. Samples were taken of raw coal, wet catalyzed coal, dry catalyzed coal, oxidized coal, gasifier char, entrained char, withdrawn char, and spent filter cake from catalyst recovery.

• Engineering Research and Development

A revised offsites facilities definition and cost estimate were prepared to update the CCG Commercial Plant Study Design done during the Predevelopment Program. This update included a more detailed study of water treatment and reuse options and a flue gas desulfurization (FGDS) study design for a lime scrubbing system. For a pioneer commercial plant feeding Illinois No. 6 coal and producing 257 billion Btu/SD SNG, the updated investment estimate was 1,530 MS and the updated gas cost was 6.18 \$/MBtu. These economics are on a January, 1978 cost basis, and reflect 100% equity financing and a 15% current dollar DCF return. The investment was down 7% and the gas cost was down 4% from the Predevelopment Program Study Design. Revised cost estimating tools for materials handling equipment and the use of lime scrubbing for FGDS were the main factors leading to cost reductions.

The key process basis items for a heat input study evaluating integral steam reforming were a reformer coil outlet temperature of 1500°F and a steam conversion of 48%. This study showed a gas cost savings of about 3% compared to the CCG Study Design. Most of the cost savings for this study resulted from designing for higher steam conversion than the Study Design. This is possible because of the greater flexibility provided by the use of steam reforming for heat input. Carbon laydown was identified as a potential problem for this system.

A second heat input study, which is called supplemental steam reforming and evaluated the use of a small conventional steam reformer operating in parallel with a preheat fired heater for heat input to the gasifier, avoided the potential problem of carbon laydown. The process basis for this study was a coil outlet temperature of 1500°F for the preheat fired heater and 1400°F for the supplemental steam reformer and a steam conversion of 48%. Supplemental steam reforming was shown to result in a 1% gas cost savings while providing much greater heat input flexibility than the preheat fired heater specified in the CCG Study Design. A gas cost sensitivity to this study with a steam conversion equal to that of the CCG Study Design was a standoff with the CCG Study Design.

A brief incentive study of an alternative two-stage gasification concept was completed. Preliminary economics indicate an incentive for staged gasification, but additional laboratory data are required to develop a better estimate of the incentive.

Inquiries were made to numerous American and European manufacturers as part of a study to determine the types and performance of coal crushing/ drying equipment appropriate for commercial CCG plants. Preliminary replies

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were received from most of the manufacturers. Only one American design appears to satisfy the requirements specified. Systems proposed by two European vendors may also be satisfactory. Testing of all three systems in small-scale equipment is desirable.

A screening study was conducted to identify and evaluate potential commercial techniques to prepare a gasifier coal feed with a top size of 30 mesh while minimizing 325 mesh fines. Previous studies for CCG coal crushing/drying were based on 8 mesh top size. Based on early indications from PDU operations, reducing coal feed top size may help to increase gasifier fluid bed density. Preliminary economics based on cost information from an American vendor indicated that the cost debit for preparing coal with a top size of 30 mesh rather than 8 mesh is small.

A study was initiated to identify mixing systems which are potentially suitable for adding catalyst solution to crushed and dried coal feed on a commercial scale. A range of process conditions for the coal/catalyst solution mixer was tentatively defined and several potentially applicable mixer types were identified.

An early laboratory guidance study was conducted to estimate the potential effects of oxygen consumption in coal/catalyst preoxidation on the CCG system material and energy balance. Pretreatment via air oxidation is one approach under investigation for increasing gasifier fluid bed density. The study indicated that "mild" preoxidation, with 2-4 wt% O_2 consumption (on dry coal), is a potentially low cost method of increasing density. However, "severe" preoxidation, with greater than 10 wt% O_2 consumption, results in a significant loss in SNG product yield per ton of coal and is not likely to be economically attractive. To provide further guidance to the CCG program, a screening study was carried out to evaluate the potential economic impact of coal/catalyst preoxidation. The results of this screening study showed that adding a preoxidation step to the front of a commercial CCG plant may lead to a 4-8% gas cost increase over the base CCG Study Design.

An additional laboratory guidance study was carried out to identify potential commercial operating ranges for coal/catalyst preoxidation process variables, and thus help to focus the continuing development work on conditions of commercial interest. Initial results based on available kinetic data showed that residence times of 2-4 hours and bed heights of 10-25 feet are likely to be preferred in commercial operation.

A lab guidance study was carried out on the impact of uncertainties in carbon devolatilization yield on gasifier volume, and on the risks and benefits of alternative coal feed point elevations. If the coal devolatilization yield was double the kinetic model yield, with the rest of the kinetic model unchanged, the gasifier volume requirement could be reduced by 18%. Raising the coal feed point above the bottom of the fluidized bed could reduce gasifier volume by up to 15%, but tar breakthrough which would foul the high level heat recovery must be avoided. A series of laboratory guidance studies were carried out to determine the effects of alternative gasifier operating conditions on the CCG material and energy balance. Reducing gasifier pressure below the CCG Study Design level of 500 psia was tested in the PDU to increase gasifier fiuid bed density. Based on material and energy balances, it appeared that reducing gasifier pressure to 300 psia was potentially a low cost method of increasing gasifier fluid bed density. However, gasifier operation at 100 psia is not likely to be economically attractive. Material and energy balances were also developed to help select gasifier conditions for both the PDU process variable studies and more detailed engineering screening studies on gasifier process conditions. The effects of catalyst loading, gasifier temperature, gasifier feed steam rate, and carbon conversion were investigated.

A detailed screening study to evaluate the potential economic impact of reduced gasifier operating pressure was completed. Operating the CCG gasifier at 300 psia instead of 500 psia (assuming the same solids properties at both pressures) resulted in a 1% investment increase and a 2% gas cost increase.

A lab guidance study was conducted to measure the economic impact of methanation kinetics slower than were predicted by the gasifier model used for the CCG Study Design. Methanation kinetics in the range of current PDU operations showed a gas cost increase of 3-10% over the CCG Study Design.

A series of CCG reactor system material and energy balances were developed to quantify the potential effects of basis changes and uncertainties regarding catalyst forms. Enthalpy basis revisions and the heat of hydration of feed potassium carbonate had only minor impacts on preheat requirements and SNG yield. However, the effects of reduced oxygen content and increased potassium carbonate in the solids leaving the gasifier were significant. Although these effects are partially offsetting, they introduce substantial uncertainty into current CCG material and energy balances. In addition, a small percentage error in feed coal heating value can also change the preheat fired heater duty and net SNG yield fairly significantly.

A brief screening study showed that there are incentives (e.g., 17% lower recycle rate) to reduce the methane content of the gas stream recycled to the catalytic gasifier below the 10% level used in the CCG Study Design.

A study to develop a more optimum process basis for the gas separations sections of the CCG process was completed. This effort was based on work by Air Products and Chemicals, Inc., under contract to DOE. For methane recovery, Air Products proposed a system which included a low pressure stripping tower and autorefrigeration. Material and energy balances showed this system required 26% less horsepower than the system used in the CCG Study Design. The improvements in the gas separation sections of the CCG process were shown to yield a 6% gas cost savings. This savings was due to lower investments, lower product losses, and lower power requirements. A study was initiated to identify trace components which might be present in the CCG gas loop and to assess their potential impacts on the CCG process. This information was used to assist in planning an appropriate series of analyses for the PDU gasifier effluent.

An engineering screening study to evaluate the economic incentive for cryogenic distillation for acid gas removal resulted in a gas cost 3.2% less than the Study Design gas cost. However, studies by Air Products and Chemicals, Inc., under contract to DOE, concluded that the selective heavy glycol solvent absorption process specified in the CCG Study Design can be optimized to save about 1-2\% in gas cost. This reduced the incentive for cryogenic acid gas removal to only 1-2%. This incentive is small relative to the probable problems in handling CO₂ freeze-out. Optimization of the cryogenic acid gas removal system would likely reduce its cost, but would make it more difficult to deal with CO₂ freeze-out. Thus, there is little incentive for research on the cryogenic acid gas removal system as defined by this study.

A laboratory guidance study was made to estimate the economic impact of evaporating dilute catalyst solutions from catalyst recovery to concentrations suitable for direct addition to the gasifier feed coal. The incremental gas cost for concentrating a 10% (wt) KOH solution is about 0.12-0.19 \$/MBtu, or 2-3% of the CCG Study Design gas cost. The use of dilute catalyst solutions would reduce the number of stages required for catalyst recovery.

An early guidance study was carried out to evaluate the cost of additives which may be used to improve filtration performance. Use of a filter aid as a body feed appears prohibitively expensive, but use as a precoat may be acceptable. Flocculating chemicals offer the most promise as an economical approach to increasing filtration rates.

A series of six catalyst recovery screening studies to evaluate the economic impacts of alternative processing approaches and solid-liquid separation techniques were completed. These studies were based on data from early bench-scale filtration and settling tests. The results indicated that Case 2, Water Wash with Rotary Drum Filters, has a significant advantage over Case 1, Lime Digestion with Rotary Drum Filters, because of greater difficulty in filtering lime-digested solids. Because of this result, emphasis in the program was shifted away from lime digestion to water wash only. Case 3, Water Wash with Gravity Settlers, may have a moderate economic advantage over Case 2. Case 4, Water Wash with Hydroclones, is approximately breakeven with Cases 2 and 3. However, Case 5, Water Wash with Centrifuges, is considerably more expensive and it is recommended that centrifuges be dropped from further consideration in the CCG process development program. Case 6, Water Wash with Vacuum Belt Filters and Cake Washing, is about as expensive as Case 5. However, incorporation of data collected since the bases were set for these studies would improve Case 6 relative to the other cases. Therefore, Case 6 will not be dropped at this time.

A catalyst chemistry study was initiated to determine the impact of current catalyst chemistry data on the catalyst recycle loop. A preliminary commercial flow plan for CO_2 treatment was devised. Its effects on material balance and on catalyst recovery system equipment were evaluated. In addition, buildup of various inert compounds in the catalyst recycle loop was evaluated.

Systems modeling work was included in the CCG Process Development Program to develop material and energy balance tools which reduced the effort required to do many of the engineering studies. A material balance computer model was developed for the catalyst recovery system to assist in the extensive screening studies carried out in that area. A material and energy balance computer model was also completed for the CCG reactor system. The latter model consists of four major blocks and a process simulation network which links them together. This new model provided accurate, consistent and cost-efficient material and energy balances for several reactor system screening studies.

A coordinated set of engineering technology programs was carried out to develop fundamental process and equipment technology to support the overall laboratory and engineering process development effort. These activities included:

- A five-part materials evaluation program for the PDU to assemble a data base on materials in CCG process services. The program consisted of corrosion rack exposure testing, corrosion probe monitoring, process stream analyses, non-destructive testing inspection, and component examination (failure analysis). Corrosion rate data were obtained for two sets of corrosion racks. In addition, analyses were conducted of several equipment components which failed in PDU service.
- Completion by Wilco Research Company of a subcontract to obtain data needed for modeling vapor-liquid equilibrium in sour water/catalyst systems containing ammonia, carbon dioxide, hydrogen sulfide, and potassium hydroxide. Three computer programs modeling vapor-liquid equilibrium in sour water systems were tested against the experimental data.
- Completion of a program to collect physical and thermodynamic property information for catalyst recovery solutions. An extensive literature survey was carried out to obtain available property data for aqueous solutions of potassium hydroxide, potassium carbonate, potassium bicarbonate, potassium sulfide, and potassium bisulfide. Graphs were developed of density, enthalpy, viscosity, and boiling point for potassium hydroxide and potassium carbonate solutions.
- Extensive bench filtration tests on CCG char slurries as part of a program to identify and evaluate alternatives for the solid-liquid separations needed in catalyst recovery. Filtration rates for limedigested char slurries were well below desirable commercial rates.

"Undigested" water/char slurries showed acceptable filtration rates. Rates were improved significantly by the use of a flocculant. Cake washing and char slurry attritability experiments were also conducted.

- A comprehensive environmental control program to characterize wastewaters, spent solids, and solids slurries produced in the PDU. PDU streams corresponding to waste streams expected in a commercial CCG plant were selected for sampling and analysis. A first-stage program was completed consisting of analysis of grab samples and time series samples. CCG wastewater pollutant levels were indicated to be about one order of magnitude lower than corresponding levels found in literature sources for other gasification processes.

 An atmospheric environmental control program to identify and quantify potential air emissions from a commercial CCG plant. A preliminary commercial emissions inventory was developed covering particulates, SO₂, NO_x, C2 and hydrocarbons, based on the CCG Study Design facilities.

 Development of dynamic models of the CCG gasification reactor and the recycle loop to gain an understanding of CCG plant dynamics. Emphasis in the recycle loop model was concentrated on the cryogenic methane recovery section. Dynamic simulations using the recycle loop model have shown that the recycle loop is stable to temperature, flow rate, and composition upsets.

Development of a single species gasifier solids balance model for a first pass assessment of the effects of variables such as solids attrition, particle density and gasification on equilibrium bed size distributions and fines losses. Validation of the model was carried out using preliminary data from the Process Development Unit (PDU). A good match of predicted and measured PDU gasifier distributions and fines losses for the first two yield periods was obtained by adjusting the char attrition rate constant and using a tentative entrainment correlation for low superficial velocities. Simulations of PDU operations with cyclone underflow return predicted finer bed size distributions and lower bed densities than with no cyclone return as the PDU currently operates. A two-solids species model for distinguishing between char and high conversion "ash" particles was then developed.