LIQUID PHASE METHANOL PROCESS DESIGN/EVALUATION STUDIES

R. L. Mednick and J. P. Romeo

Chem Systems Inc.
303 South Broadway
Tarrytown, NY 10591

Presented at the

DOE/FE Indirect Liquefaction Contractors'
Review Meeting

Pittsburgh, PA
15-17 November, 1988

Preceding page blank

INTRODUCTION

In September 1981, the United States Department of Energy awarded Air Products and Chemicals, Inc. (Air Products) a contract which was the first phase of a program aimed at further developing the LPMEOH* process in a representative engineering-scale Process Development Unit (PDU). A second contract was awarded in July 1985. The third, currently active contract entitled "Liquid Phase Methanol LaPorte PDU: Modification, Operation, and Support Studies" began on 9 April 1987 to complete the final phase of the development work. Air Products is the prime contractor providing overall program management and is responsible for engineering design, procurement, construction, and operation of the PDU. Chem Systems, as the key subcontractor in the program is involved with assisting Air Products on LaPorte and with the conceptualization of LPMEOH process flowschemes, development of commercial-scale process designs, economic evaluations of the commercial designs, and optimization of the LPMEOH process through parametric sensitivity studies. Results of these analysis are used to guide the research and development program in the most economic direction.

During the past year, Chem Systems has updated its base case commercial-scale evaluation of CO-rich operation based on an integrated gasification-combined cycle (IGCC) facility with once-through methanol (OTM). The LPMEOH process configuration has been compared with conventional vapor phase technology and with developmental vapor phase higher alcohol technology. Furthermore, sensitivity analyses have been performed to study the effect of varying the fraction of the coal higher heating value which is converted into methanol rather power. In the area of all-methanol production, a conceptual flowsheet has been assembled based on coal gasification and a novel two-stage high-pressure LPMEOH configuration utilizing nearly balanced gas. This concept shows promise and now requires laboratory verification.

This paper will briefly review the results of the CO-rich process evaluations, including the sensitivity analyses, and the conceptual all-methanol flowsheet based on a two-stage LPMEOH design.

CO-RICH EVALUATIONS

Overview

The CO-rich evaluation consists of updating LPMEOH process case studies performed under previous contracts and developing vapor-phase cases with commercial or developmental technologies for comparison. The following section is an update of the LPMEOH base case originally developed under a previous contract(1). This is followed by a comparable analysis based on conventional vapor-phase technology and then by a once-through mixed-alcohol scenario developed from published information. The economics of the three cases are developed in the context of an IGCC facility.

---

* LPMEOH is a trademark of Chem Systems Inc.

LPMEOH Base Case Design

The LPMEOH base case design is configured to fit into an intermediate-sized Texaco-based IGCC facility design developed by Fluor, producing 658 megawatts of electricity at 20°F ambient(2). A radiant plus convective design was chosen as the basis for this study because of its high thermal efficiency.

Insertion of an LPMEOH unit between the acid gas removal system and the gas turbine generator requires the gasification pressure to be raised from a nominal 600 psia to 950 psia to accommodate an average pressure of 765 psia in the methanol synthesis reactors without intermediate synthesis gas compression. A COS hydrolysis unit must be added between raw gas scrubbing and acid gas removal to convert carbonyl sulfide into hydrogen sulfide. Methanol feed gas must be heated and sent to guard beds for removal of carbonyls, sulfur compounds, and other potential poisons prior to entering the synthesis converters. Unconverted synthesis gas must be cooled to condense methanol, reheated, and expanded to 390 psia before being sent to the fuel gas saturator. The end result is extensive reliance on heat exchange to conserve energy.

Design assumptions for the once-through methanol unit are summarized in Table 1 based on LaPorte PDU results with CO-rich gas(3,4). The base case process design was developed for an once-through LPMEOH unit capable of converting approximately 20 percent of the synthesis gas energy from a Texaco gasifier into fuel-grade methanol with a purity of greater than 97 weight percent. A flowsheet for the LPMEOH unit is shown in Figure 1. This unit is designed to fit between the gas cleanup and the fuel gas saturation sections of the IGCC facility.

Cleaned synthesis gas from acid gas removal is preheated in a series of exchangers to about 600°F and then passed through a series of guard beds. The gas is then cooled to 460°F for injection into the LPMEOH reactors.

The required heat removal equipment is contained within the LPMEOH reactor and the unconverted syngas is disengaged from the slurry in a separate vessel. Temperature control is achieved by regulating the steam pressure in the steam drum. Other configurations, such as external cooling of the slurry and slurry/gas separation within the LPMEOH reactor, are also possible.

The unconverted synthesis gas from the slurry separator at about 482°F is cooled first in the feed/effluent exchanger and then in the BFW heater to about 300°F. The majority of the evaporated hydrocarbon oil is condensed at this point and separated from the gas stream.

The essentially oil-free gas is cooled first in a series of gas/gas exchangers and finally in a cooling water exchanger to 100-110°F. Unconverted gas is sent to a fuel gas expander (not shown) after exchanging heat with the reactor effluent. About 89 percent of the methanol produced is condensed and removed in the vapor/liquid separator. Dissolved gases are removed from the methanol product in a two-stage flash system before being sent to storage. The methanol produced contains about

1.4 percent water, 0.7 percent ethanol and higher alcohols, and about 600 ppm of oil. This methanol could be easily purified to chemical-grade methanol in a single-tower system.

Figure 2 is a simplified block diagram of the IGCC facility with once-through methanol coproduction (IGCC/OTM). Raw synthesis gas exiting the convective cooler at 650°F is exchanged with methanol guard bed feed and then sent to scrubbing. The scrubbed gas containing approximately 26 weight percent water is reheated by exchange with 1545 psia saturated steam to 430°F and passed through a COS hydrolysis reactor, reducing the carbonyl sulfide to 14 ppm. This is further reduced to 10 ppm in acid gas removal and the remainder is absorbed in the methanol guard beds.

The depleted fuel gas from the LPMEOH unit is expanded from 725 psia and 164°F to 390 psia and 85°F, generating 5.3 megawatts of electricity. It is then saturated and heated to about 353°F by countercurrent contact with hot boiler feedwater in a tower to give a gas with a water content of about 29 weight percent. The saturated gas water content is further increased to about 36 percent by injecting medium-pressure steam from the LPMEOH unit and is reheated to about 400°F by exchange with hot gas from COS hydrolysis. The introduction of steam to the depleted fuel gas before being burned in the gas turbine combustor has the effect of reducing NO_x emissions in addition to providing additional power in the gas turbine. A summary of IGCC/OTM operating performance is found in Table 2.

Capital costs and cost of production estimates have been developed for the IGCC/OTM facility. The methodology chosen for this analysis involves developing a cost of production for each plant segment. Thus, a syngas cost is developed for the gasification, gas cleanup, and oxygen plant facilities. This syngas value is then used to generate a methanol price for the LPMEOH unit and an electricity price for the power facilities.

Aftertax discounted cash flow (DCF) returns of 7.5 percent based on total equity financing were assumed for syngas, methanol, and electricity products instead of the more complex utility financing generally applied to projects of this type. The net result is similar.

A breakdown of total fixed investment for the IGCC/OTM facility, by plant section, is shown in Table 3. The total facility has been split into a gasification section at $485 million, a methanol facility at $36 million, and a power generation section at $297 million. The total fixed investment is $818 million. This is only slightly less than the cost of an IGCC-only facility. Both units would be identical in syngas generation size, but vary in power facility size and other plant sections.

Costs of production for the IGCC/OTM case are summarized in Table 4. Syngas production is handled as a separate cost item with return on capital investment included. The syngas cost plus return is used as a raw material price in methanol and electricity production. Thus, the capital investment in the gasification facility is recovered through the transfer of syngas to the methanol unit and the combined-cycle facility.

All utilities are transferred internally among the three plant sections at their cash costs of production. For electricity, this is 3.66 cents per kilowatt-hour. The cash costs for various steam levels and 550°F boiler feedwater are proportional to their enthalpy, using 240°F boiler feedwater as the reference. Absolute values for the steam and boiler feedwater costs are determined from their equivalent cash costs in a coal-fired steam boiler. Based on the resultant steam values, the gasification and combined-cycle units have slight positive utility costs whereas the methanol unit has a net utility credit. Steam is a valuable export for both the gasification and the LPMEOH units, but, in the case of gasification, the potential credit is offset by electricity demand in the oxygen plant.

The IGCC/OTM facility produces syngas at a cost plus return of $4.83 per MMBtu, fuel methanol at 45.3 cents per gallon, and power at 4.64 cents per kWh. The fuel methanol price is equivalent to $7.12 per million BTU.

Sensitivity Analysis and Enhancement

Over the years a number of methods have been used for the development of the LPMEOH process to represent the conversion of synthesis gas into methanol in a manner useful as a predictive tool. The simplest method for predicting the expected methanol yield in an LPMEOH process involves correlating the synthesis gas conversions in terms of approach to methanol equilibrium.

In order to develop methanol conversions over a pressure range of 515-1265 psia and a space velocity range of 4,000-12,000 standard liters per hour per kilogram of catalyst, simultaneous methanol and water-gas shift equilibria were computed. Using end-of-run conditions from a 40-day test at the LaPorte LPMEOH PDU with carbon monoxide-rich gas, an approach to equilibrium curve was developed that represented the operating range under investigation in this study.

The resultant methanol productivities at various average reactor pressures and space velocities are depicted in Figure 3. Carbon monoxide conversions vary from 5.9-10.3 percent at 515 psia to 19.8-24.5 percent at 1265 psia compared to the base case value of 13.2 percent. Accordingly, methanol productivities vary from 8.7-15.5 gram moles per hour per kilogram of catalyst at 515 psia to 20.4-49.7 gram moles per hour per kilogram of catalyst at 1265 psia as compared to the base case value of 22.3.

Process designs, capital cost estimates, and costs of production were developed for a range of pressures and space velocities. Only the LPMEOH unit itself was investigated in this sensitivity analysis. Thus, all information relating to the gasification and combined cycle systems was held identical to the base case design, including capital investments, steam and electricity production levels, and syngas and electricity costs. Although this assumption can result in some differences in the methanol cost of production calculations, the trends observed over the range of pressures and space velocities should be indicative of those that would result from a more thorough analysis that includes the economic effects on gasification and power generation.

A series of cases was developed for a gasifier pressure of 700 psia. Compression was added to boost the syngas from 595 psia at the inlet to the LPMEOH unit to 845, 1095, and 1345 psia, allowing methanol synthesis at exit reactor pressures of 765, 1015, and 1265 psia, respectively. Each pressure level was evaluated at space velocities of 4,000, 8,000, and 12,000.

Total capital investment for the LPMEOH unit including compression and expansion is summarized as a function of space velocity in Figure 4 and as a function of methanol production in Figure 5. In each of these figures, the reactor exit pressure varies from 515 psia, where no compression is needed, to 1265 psia. Methanol cost plus return as a function of space velocity is depicted in Figure 6 and as a function of methanol production in Figure 7.

A two-reactors-in-series configuration was also studied, but is not discussed here.

Conventional Vapor-Phase Methanol Synthesis

A conventional vapor-phase methanol (CVPM) design was also configured to fit into a Texaco-based IGCC facility. A design containing both radiant plus convective and radiant plus quench trains was chosen as the basis. The quench train is used to saturate a portion of the raw gas stream with water to aid in promoting the CO shift reaction. The convective train is used to maximize the thermal efficiency of the remaining gas in the system. The conventional methanol unit was sized to produce the same amount of methanol as in the LPMEOH process, 977.9 tons per day.

As shown in Figure 8, insertion of a CVPM unit after the acid gas removal system requires a nominal gasifier pressure of 950 psia to accommodate an exit reactor pressure of 735 psia. This eliminates the need for any intermediate reactor feed gas compression. In the convective train the raw gas is scrubbed for removal of any ash particles, cooled to 101°F to condense out water and remove heat that is supplied to the saturator, and sent to acid gas removal for sulfur cleaning. On the quench side the raw gas is scrubbed free of any ash particles, enters a CO shift reactor to adjust the hydrogen to carbon monoxide molar ratio, cooled to 101°F to remove water and supply heat to the saturator, and sent to acid gas and carbon dioxide removal.

The raw gas exiting the radiant boilers is split into two streams - 12.2 percent enters the quench unit and the remaining 87.8 percent passes through convective boilers producing 1545 psia steam. This split is determined by the methanol production of the conventional vapor-phase methanol facility. The quenched raw gas enters a CO shift reactor producing a gas with a hydrogen to carbon monoxide ratio of 12.9 to 1.0. In order to achieve a hydrogen to carbon monoxide ratio of 2.4 to 1.0, a criterion set by an existing Stone and Webster design,(5) 11.3 percent of the scrubbed gas from the convective train is split off, sent to a COS hydrolysis unit, and combined with the scrubbed gas exiting the carbon monoxide shift reactor. The converted gas exiting the CO shift reactor is highly hydrogen rich and must be combined with carbon monoxide-rich gas in the convective train. This blending produces a gas with the proper hydrogen to carbon monoxide ratio. A COS hydrolysis unit is necessary to convert carbonyl sulfide into hydrogen sulfide. The acid gas removal units will then selectively remove sulfur compounds and carbon dioxide. The catalyst used to perform CO shift will also promote the COS hydrolysis reaction; therefore, no additional COS hydrolysis unit is necessary in the quench train.

The cleaned and conditioned gas from the quench train is sent to a conventional Lurgi methanol reactor shown in Figure 9. The fresh reactor feed gas is sent through guard beds to remove any remaining sulfur compounds and any carbonyl compounds, which may poison the methanol catalyst. This stream is combined with the pressurized recycle gas and passed through feed/effluent exchangers to heat the feed stream to 460°F. This unit has the catalyst present on the inside of the tubes and the steam production occurring on the shell side of the reactor. The effluent from the reactor is cooled through a series of exchangers to produce a two-phase mixture. This mixture is separated so that the vapor stream is pressurized up to reactor pressure and combined with the fresh reactor feed gas. The liquid, composed mainly of methanol, is sent to distillation columns for purification of the product to 98.3 weight percent methanol and 1.7 weight percent water. The exothermic heat of reaction produces 565 psia steam, which is sent to an intermediate pressure steam turbine that produces electricity.

Because the CVPM system has a recycle stream, only 22.1 percent of the cleaned syngas is required. The remaining portion passes through the convective side cooling train and on to the fuel gas saturator. A small purge stream from the methanol unit is combined with the fuel gas from the convective train. The purge is required to eliminate any buildup of inerts in the system. The carbon dioxide removed in the acid gas removal unit is simply purged because over 99.8 weight percent of this stream is carbon dioxide. It is not worth recovering this stream for only 0.2 weight percent of hydrogen and carbon monoxide.

Some design assumptions for the conventional vapor-phase methanol case are summarized in Table 5. The net operating performance data for the IGCC/CVPM facility are shown in Table 6.

The breakdown of total fixed investment for all sections of the plant is given in Table 7. Here, the total plant investment for the gasification front-end, which includes the convective and quench trains, CO shift, and carbon dioxide removal, is $504 million. The power requirements for this section are 87.1 megawatts. The total plant investment for the methanol section is $40 million with a power consumption of 1.2 megawatts. The total fixed investment of the power generation section is $304 million. The power production is 630.2 megawatts with an internal power consumption of 10.4 megawatts. Total plant investment is $848 million, with a net power generation of 532.5 megawatts and 977.9 tons per day of methanol.

The vapor phase methanol production facility is more expensive than the LPMEOH unit because of the type of reactor studied, the presence of a recycle compressor, and the requirement of purification columns to achieve a fuel-grade methanol product.

Speculative Once-Through Vapor-Phase Technology

Under carbon monoxide-rich conditions as opposed to hydrogen-rich conditions employed commercially, vapor-phase methanol processes tend to produce considerably more higher alcohols. To capitalize on this phenomenon, several organizations have been developing cosolvent alcohol processes based on modifications to vapor-phase methanol technology where the objective is to produce a mixed alcohol product that can be used as a motor fuel additive. These processes generally rely on modifications to methanol synthesis catalysts and higher reactor temperatures to further enhance the proportion of higher alcohols. By-product water is also produced. Carbon dioxide levels in the feed gas must be limited in order to maintain high reaction rates and to reduce water formation since water must be removed in the motor fuel application.

Based on feed gas requirements, it could be speculated that a carbon monoxide-rich vapor-phase process would fit into an IGCC facility in a manner very similar to Liquid Phase Methanol. Although such a design would be interesting to compare against Liquid Phase Methanol, it must be pointed out that there are a number of uncertainties associated with a speculative once-through vapor-phase design. First of all, the resultant methanol/higher alcohol product has not yet been tested as a turbine fuel. Water removal may or may not be necessary. Although Liquid Phase Methanol produces some higher alcohols and other by-products, the quantity is only a small fraction of that produced in the vapor-phase processes under carbon monoxide-rich conditions. Finally, reaction rates, catalyst longevity, and process flexibility under IGCC conditions are issues requiring further scrutiny before the viability of a once-through vapor-phase scheme can be placed on the same level of certainty as Liquid Phase Methanol. Despite this, development of a speculative design for carbon monoxide-rich vapor-phase technology for comparison against Liquid Phase Methanol helps to complete the assessment of options for IGCC/methanol facilities.

In order to develop a design basis for vapor-phase carbon monoxide-rich methanol synthesis, available data were examined.(6-8) Alcohol productivity versus space velocity is shown graphically in Figure 10. Inspection of information of this type makes it possible to develop a basis for the vapor-phase design.

One of the more interesting aspects of the vapor-phase design involves the permissible level of carbon dioxide in the synthesis gas. Since evidence points to the necessity of maintaining relatively low carbon dioxide levels for optimal productivity, a kinetic model proposed by Klier et al.(7) was implemented to study the effects of carbon dioxide concentration on carbon monoxide conversion. Although use of this model involves extrapolation from its original hydrogen-rich basis, the results for a Texaco synthesis gas at 250°C and 3,000 liters/hour-kilogram catalyst space velocity show a maximum at 4 percent carbon dioxide in the feed as indicated in Figure 11. The predicted maximum reaction rate is about 10 gmol per hour per kilogram of catalyst.

From the Anderson data (6), a temperature of 285°C in a doped catalyst would result in about 15 weight percent higher alcohols. The high temperature is required to simultaneously have high productivities and to deplete by-product water, provided the carbon dioxide concentration in the syngas is low.

A vapor-phase reactor system would have the disadvantage of a low inlet carbon dioxide concentration requirement. This involves additional energy consumption in the form of low-pressure steam for carbon dioxide stripping in the acid-gas removal system. At this point, it is difficult to determine the optimum inlet carbon dioxide level for vapor-phase alcohol synthesis. A carbon dioxide level of 1 mol percent was chosen for this analysis.

The developmental vapor-phase alcohol (VPA) design was configured to fit into a Texaco-based IGCC facility. A radiant plus convective design was chosen as the basis for this study because of its high thermal efficiency. The VPA unit was sized to produce an alcohol product with the same heat availability (or Btu content) as in the LPMEOH product.

As shown in Figure 12, insertion of a VPA unit between the acid gas removal system and the gas turbine generator follows the same general setup as the LPMEOH-based facility. The only difference is that a carbon dioxide removal unit is added to reduce the carbon dioxide level to 1 mol percent which is necessary to achieve the maximum alcohol productivity. The removed carbon dioxide stream is compressed to 390 psia and combined with the unconverted synthesis gas being sent to fuel gas saturation.

Design assumptions for the once-through developmental vapor-phase alcohol (OTVPA) unit are summarized in Table 8. The net operating performance data for the IGCC/OTVPA facility are shown in Table 9.

A flowsheet for the VPA unit is shown in Figure 13. Cleaned synthesis gas from acid gas removal is preheated in a series of exchangers to about 600°F and then passed through a series of guard beds before being sent to the VPA reactor. The gas is then cooled to 460°F for injection into the VPA reactor. The VPA reactor is a fixed-bed unit with the catalyst present in the shell side of the reactor and a spiral tube bundle present for removing the exothermic heat of reaction, thereby producing steam. Temperature control is achieved by regulating the pressure in the steam drum. The steam produced can be as high as 705 psia due to the reactor effluent temperature of 545°F. The reactor effluent, at about 545°F, is first cooled in the feed/effluent exchanger to 202°F, and then in the effluent coolers to about 100°F. About 90 percent of the alcohol product is condensed at this point and separated from the gas stream in the vapor/liquid separator. Unconverted gas is sent to a fuel gas expander (not shown) after exchanging heat with the reactor effluent.

Dissolved gases are removed from the alcohol product in a two-stage flash system before being sent to storage. The alcohol produced contains about 84.3 percent methanol, 6.9 percent ethanol, 3.1 percent propanol, 3.5 percent butanol, 1.3 percent ethyl acetate, 0.1 percent pentane, and 0.8 percent water. It is assumed here that most of the water formed from the production of higher alcohols is consumed in the shift reaction producing carbon dioxide and hydrogen. If this is not the case, azeotropic distillation would be required to produce a fuel-grade alcohol product.

A breakdown of total fixed investment for the IGCC/OTVPA facility, by plant section, is shown in Table 10. The total facility has been split into a gasification section at $499 million, an alcohol facility at $25 million, and a power generation section at $311 million. The total fixed investment is $835 million. This is about 2 percent higher than the cost of the IGCC/OTM facility.

Comparison of OTM Process Economics

As in the case of LPMEOH facility design, the economics of each of the vapor phase processes was analyzed in terms of its three facility segments. However, process comparisons are more discernable using an overall cost of production analysis for each process where fuel alcohol is considered the prime product and electricity is considered a by-product. For ease of comparison, all three fuel alcohol products are considered on a higher heating value basis and electricity is valued at the price developed by the LPMEOH facility base case analysis of 4.64 cents per kilowatt-hour. The methanol/alcohol sales costs for the conventional vapor-phase methanol facility and for the developmental vapor-phase alcohol facility are 10.5 percent and 5.7 percent higher than for the LPMEOH facility, respectively. From these results a clear distinction is evident. The IGCC/OTM plant is the most economical, followed by the IGCC/OTVPA plant, which is followed by the IGCC/CVPM plant. A summary of the economics for each facility is given in Table 11.

ALL-METHANOL EVALUATION

A conceptual design developed for an all-methanol Liquid Phase Methanol (ALLPMEOH) facility based on natural gas feedstock, revealed quite encouraging results.(9) The conceptual ALLPMEOH design utilized a two-stage system in which a large percentage of carbon monoxide was converted to methanol in the first stage and the remainder of the carbon monoxide and unconverted carbon dioxide was converted in the subsequent stage utilizing a recycle stream to the second stage in order to obtain high carbon efficiencies.

To further assess the commercial potential for an all-methanol process it was decided to determine the economic feasibility of utilizing a front-end based on Texaco coal gasification in conjunction with a two-stage liquid-phase all-methanol back-end. In this evaluation, the material balance around the ALLPMEOH process based on the natural gas design was retained to facilitate comparison. This unit has the potential for approximately 5,200 STPD of methanol product from a single train.

Since an objective of this evaluation was to develop a conceptual design that would achieve all-methanol production with maximum thermal efficiency, the design includes both quench and convective trains as shown in Figure 14. The quench train is needed to sufficiently saturate the gas stream with water to allow a CO shift reaction to be carried out. The shift reaction along with a carbon dioxide purge allows control of the syngas feed composition to the LPMEOH unit. The convective train allows maximum heat recovery. A COS hydrolysis unit must be added between raw gas scrubbing and acid gas removal in the convective train section to convert carbonyl sulfide into hydrogen sulfide. An acid gas removal unit is required to selectively remove sulfur and carbon dioxide from the syngas. Prior to entering the LPMEOH reactor, feed gas must be heated and sent to guard beds for removal of carbonyls, sulfur, and other potential poisons. Finally, compression is required to deliver the clean syngas to the first stage at a pressure of approximately 1530 psia.

The conceptual design of the all-methanol LPMEOH process is partly based on a U.S. patent, which describes a Liquid Phase Methanol reactor staging process for the production of methanol from a syngas feed.(10). Reaction conditions, summarized in Table 12, are maintained so that the reactor in the first stage favors the conversion of carbon monoxide over carbon dioxide relative to the reactor in the second stage. Conversely, conditions are maintained in the second-stage that favor the conversion of carbon dioxide over carbon monoxide relative to the first stage.

Figure 15 depicts the two-stage ALLPMEOH design with interstage carbon dioxide removal. Synthesis gas from the coal gasification section enters the first-stage LPMEOH reactor, after being heated by the feed/effluent exchanger. Boiler feedwater is used to cool the reaction thereby generating medium-pressure steam. After the feed/effluent exchanger, reactor effluent is further cooled to condense the crude methanol product. Crude methanol product is collected in a vapor/liquid separator, and sent to methanol stabilization. The uncondensed gases from the vapor/liquid separator are sent to a carbon dioxide absorber column after being further cooled in the feed/effluent heat exchanger.

The gas stream is introduced at the bottom of the carbon dioxide absorber column. Carbon dioxide is removed by introducing cold methanol at the top of the column. By maintaining a 40°F temperature for the cold methanol feed, the removal of carbon dioxide can be controlled. Condensed methanol from the bottom the column, containing carbon dioxide is sent to a hydraulic power recovery turbine. The power generated is used to partly meet the power requirements of the methanol circulation pump. The carbon dioxide rich methanol stream is then sent to the carbon dioxide stripper column. Nitrogen, recovered from the air separation unit in the gasification section of the process, is used as a stripping gas. The regenerated methanol is then recycled to the top of the carbon dioxide absorber column.

The synthesis gas leaves the carbon dioxide absorber column and is compressed to approximately 2200 psia in a booster compressor. After being combined with gases from the recycle compressor and cooled by the feed/effluent exchanger, the gas is introduced into the bottom of the second-stage reactor. Again boiler feedwater is used to control the reaction temperature and to generate medium-pressure steam. Effluent from the second-stage reactor is cooled to condense methanol from the effluent stream. The liquid/gas mixture is separated in a vapor/ liquid separator. Crude methanol product is sent to stabilization and gases are recycled via the recycle compressor.

All plant power requirements are met by generating electricity from the steam accumulated from gasification, CO shift, methanol synthesis, etc. The total steam generation exceeds the amount needed for in-plant purposes. Therefore, surplus electric power can be generated and exported. Total electricity generated is 144.1 megawatts. The gasification section steam production accounts for 88.9 megawatts and the LPMEOH section for 55.2 megawatts. Total energy requirements for the IG/ALLPMEOH design are 131.5 megawatts, resulting in a net export of 11.8 megawatts.

The capital cost breakdown for the high-pressure two-stage LPMEOH facility with a Texaco gasifier front-end producing 5,227 STPD of methanol is summarized in Table 13. The total fixed capital investment is $810 million dollars, with $124 million (15 percent) attributed to the methanol synthesis/purification (LPMEOH) section, $597 million (74 percent) to the gasification section and $89 million (11 percent) to the power-generation facility.

The cost of production for the IG/ALLPMEOH case has been developed and is presented in Table 14. The basis for this cost of production estimate is a non-utility, investor-owned facility.

The IG/ALLPMEOH facility produces methanol at a full cash cost of production of 33.5 cents per gallon. Depreciation charges add 26.9 cents per gallon, giving a net cost of production of 60.4 cents. A sales price of 67.3 cents is required to achieve a 10 percent discounted cash flow. This is significantly higher than a natural gas based design due primarily to capital investment and related factors.

FUTURE WORK

As implied above, a coal-to-methanol facility cannot currently compete cost effectively with a design based on natural gas. However, it would be useful to compare the ALLMEOH process economics with an equivalent conventional vapor-phase methanol synthesis route from coal. This will be accomplished in the near future. If, as expected, the two-stage LPMEOH concept is more attractive than conventional coal to all-methanol, the next step would involve laboratory verification of the process assumptions.

With regard to once-through LPMEOH process evaluations, it is intended to update the base case IGCC/OTM design and economics upon completion of the current LaPorte run. Preliminary indications are that incorporation of all current process and catalyst performance improvements will result in a 5-10 percent decrease in methanol selling price compared to the already favorable values reported herein.

REFERENCES

1. "Liquid Phase Methanol Process Development Unit: LaPorte PDU Research and Engineering Support Studies" Final Report under DOE Contract No. DE-AC22-85PC80007, by Air Products and Chemicals, Inc. and Chem Systems Inc. (1987).

2. "Cost and Performance for Commercial Applications of Texaco-Based Gasification Combined-Cycle Plants" EPRI AP-3486 (Vol. 1 and 2), by Fluor Engineers, Inc. (1984).

3. "Liquid Phase Methanol Process Development Unit: Installation, Operation, and Support Studies" Final Report under DOE Contract No. DE-AC22-81PC30019, by Air Products and Chemicals, Inc. and Chem Systems Inc. (1985).

4. "Liquid Phase Methanol Process Development Unit: Installation, Operation and Support Studies, Topical Report, Task 10: Liquid-Entrained Operations in LaPorte LPMEOH PDU" DOE Contract No. DE-AC22-81PC30019, by Air Products and Chemicals, Inc. and Chem Systems Inc. (1986).

5. "H-Coal and Coal-to-Methanol Liquefaction Processes: Process Engineering Evaluation" EPRI AP-3290, by Stone and Webster Engineering Corporation (1983).

6. Anderson, R.B. and Smith, K.J., "The Higher Alcohol Synthesis Over Promoted Cu/ZnO Catalysts," The Canadian Journal for Chemical Engineering, 61, 40-45, February 1983.

7. Klier, K. et al. "Catalytic Synthesis of Methanol From CO/H_2, IV. The Effects of Carbon Dioxide," Journal of Catalysis, 74, 343-360, 1982.

8. German Patent No. 3,403,492 to Metallgesellschaft (Lurgi), August 8, 1985.

9. "Optimization of LPMEOH Configurations of IGCC/OTM", EPRI RP-2771-1 Final Report by Chem Systems Inc., to be published.

10. U.S. Patent 4,766,154 (to Air Products and Chemicals, Inc.), August 23, 1988.

Table 1

LPMEOH UNIT DESIGN ASSUMPTIONS

Space velocity, L/hr-kg catalyst	8,000
Temperature, °F	482
Pressure, psia	765
CO conversion, %	13.2
CO_2 conversion, %	1.1
Selectivity to methanol, mol %	99.58
Catalyst concentration, wt %	30
Catalyst replacement rate, %/day	0.37
Net methanol production, TPD (pure)	961
Net fuel methanol production, TPD	978

Table 2

OPERATING PERFORMANCE DATA FOR IGCC/OTM FACILITY*
(Megawatts)

	Power Produced	Electricity Generated
Gas turbine power	759.0	
Air compressor power	374.1	
Net shaft power	384.9	377.2
Steam turbines power		
High pressure	66.3	
Intermediate pressure	54.8	
Medium pressure	131.6	
Net shaft power	252.8	247.7
Expansion turbine power	5.4	5.3
Total power generated in combined cycle		630.2
Electricity consumed in the complex		96.9
Net power produced		533.3

*Net fuel methanol production: 977.6 STPD.

Table 3

PLANT FACILITIES INVESTMENT FOR IGCC/OTM
(Mid-1987, Millions of Dollars)

	Gasification	LPMEOH	Power Gener.	Total Plant
Power generated, MW	-	-	630.2	630.2
Power consumed, MW	85.8	0.4	10.7	96.9
Net power generated, MW	**(85.8)**	**(0.4)**	**619.5**	**533.3**
Methanol production, TPD	-	977.6	-	977.6
Coal receiving, grinding and slurry preparation	38.9	-	-	38.9
Oxidant feed	103.6	-	-	103.6
Gasification, high-temperature gas cooling, particulate removal and ash removal	164.9	-	-	164.9
Low-temperature gas cooling and fuel gas saturation	11.6	-	5.3	16.9
COS hydrolysis, acid gas removal sulfur recovery, and tail gas treating	36.9	-	-	36.9
Steam, condensate and BFW	-	-	5.6	5.6
Combined-cycle system	-	-	207.2	207.2
General facilities	63.2	4.7	38.7	106.6
Methanol unit	-	26.2	-	26.2
	419.1	30.9	256.8	706.8
Project contingency	62.9	4.6	38.5	106.0
Initial catalyst and chemicals	3.1	1.0	1.4	5.5
Total plant investment	**485.1**	**36.5**	**296.7**	**818.3**

Table 4

SUMMARY ECONOMICS FOR IGCC/OTM FACILITY

	Texaco Gasification (¢/MMBtu)	LPMEOH Unit (¢/Gal)	Combined Cycle (¢/kWh)
Raw materials			
Coal @ $35/ST	205	-	-
Syngas @ $4.83/MMBtu	-	33.8	3.21
Catalysts/chemicals	3	2.3	0.02
Total raw materials	208	36.1	3.23
Utilities	2	(2.7)	0.06
Direct cash costs	55	2.2	0.20
Allocated cash costs	39	1.3	0.19
By-product credits			
Sulfur @ $75/ST	(15)	-	-
Ash disposal @ $10.50/ST	6	-	-
Total by-product credit	(9)	-	-
Cash cost of production	295	36.7	3.68
Cost plus return @ 7.5 percent DCF	483	45.3	4.64

TABLE 5

CVPM UNIT DESIGN ASSUMPTIONS

Space velocity, hr^{-1}	9,000
Temperature, °F	510
Pressure, psia	735
Feed H_2/CO (molar)	2.40
Feed CO_2 concentration, mol %	3.04
Selectivity to methanol, mol %	100.0
Net methanol production, TPD (pure)	961.2

TABLE 6

OPERATING PERFORMANCE DATA FOR IGCC/CVPM FACILITY*
(Megawatts)

	Power Produced	Electricity Generated
Gas turbine power	772.9	
Air compressor power	394.9	
Net shaft power	378.0	370.4
Main steam turbine power		
High pressure	63.6	
Intermediate pressure	53.1	
Medium pressure	136.9	
Secondary steam turbine power	12.6	
Net shaft power	266.1	260.8
Total power generated in combined cycle		631.2
Electricity consumed in the complex		98.7
Net power produced		532.5

* Net methanol fuel production: 977.9 STPD.

Table 7

PLANT FACILITIES INVESTMENT FOR IGCC/CVPM
(Mid-1987, Million Dollars)

	Gasification	CVPM	Power Gener.	Total Plant
Power generated, MW	-	-	631.2	631.2
Power consumed, MW	87.1	1.2	10.4	98.7
Net power generated, MW	**(87.1)**	**(1.2)**	**620.8**	**532.5**
Methanol production, TPD	-	977.9	-	977.9
Coal receiving, grinding and slurry preparation	38.9	-	-	38.9
Oxidant feed	103.6	-	-	103.6
Gasification, high-temperature gas cooling, particulate removal and ash removal	161.9	-	-	161.9
COS hydrolysis and CO shift	4.6	-	-	4.6
Low-temperature gas cooling and fuel gas saturation	18.9	-	4.9	23.8
Acid gas removal, sulfur recovery, and tail gas treating	41.5	-	-	41.5
Steam, condensate and BFW	-	-	5.7	5.7
Combined-cycle system	-	-	212.7	212.7
General facilities	65.6	5.2	39.7	110.5
Methanol unit	-	29.1	-	29.1
	435.0	34.3	263.0	732.3
Project contingency	65.3	5.1	39.5	109.9
Initial catalyst and chemicals	3.8	1.0	1.4	6.2
Total plant investment	**504.1**	**40.4**	**303.9**	**848.4**

TABLE 8

VPA UNIT DESIGN ASSUMPTIONS

Space velocity, hr^{-1}	3,000
Temperature, °F	545
Pressure, psia	795
Feed H_2/CO (molar)	0.77
Feed CO_2 concentration, mole %	1.00
CO conversion, percent	13.6
Selectivity to methanol, mol percent	78.64
Selectivity to ethanol, mol percent	8.54
Selectivity to propanol, mol percent	4.28
Selectivity to butanol, mol percent	5.34
Selectivity to ethyl acetate, mol percent	2.23
Selectivity to pentane, mol percent	0.97
Net alcohol production, TPD (pure)	887.6

TABLE 9

OPERATING PERFORMANCE DATA FOR IGCC/OTVPA FACILITY*
(Megawatts)

	Power Produced	Electricity Generated
Gas turbine power	768.4	
Air compressor power	386.8	
Net shaft power	**381.6**	374.0
Main steam turbine power		
High pressure	65.0	
Intermediate pressure	54.6	
Medium pressure	137.2	
Secondary steam turbine power	13.5	
Net shaft power	**270.3**	**264.9**
Expansion turbine power	5.3	5.2
Total power generated in combined cycle		**644.1**
Electricity consumed in the complex		106.0
Net power produced		**538.1**

* Net fuel alcohol production: 895.9 STPD.

TABLE 10

PLANT FACILITIES INVESTMENT FOR IGCC/OTVPA
(Mid-1987, Millions of Dollars)

	Gasifi-cation	OTVPA Unit	Power Gener.	Total Plant
Power generated, MW	-	-	644.1	644.1
Power consumed, MW	88.4	0.1	17.5	106.0
Net power generated, MW	**(88.4)**	**(0.1)**	**626.6**	**538.1**
Alcohol production, TPD	**-**	**895.9**	**-**	**895.9**
Coal receiving, grinding and slurry preparation	38.9	-	-	38.9
Oxidant feed	103.6	-	-	103.6
Gasification, high-temperature gas cooling, particulate removal and ash removal	164.9	-	-	164.9
Low-temperature gas cooling and fuel gas saturation	11.6	-	5.3	16.9
COS hydrolysis, acid gas removal, CO_2 compression, sulfur recovery, and tail gas treating	47.1	-	5.2	52.3
Steam, condensate and BFW	-	-	5.8	5.8
Combined-cycle steam	-	-	212.3	212.3
General facilities	65.0	3.0	40.6	108.6
Alcohol unit	-	17.2	-	17.2
	431.1	20.2	269.2	720.5
Project contingency	64.7	3.0	40.4	108.1
Initial catalyst and chemicals	3.5	1.7	1.4	6.6
Total plant investment	**499.3**	**24.9**	**311.0**	**835.2**

TABLE 11

SUMMARY ECONOMICS FOR ONCE-THROUGH PROCESSES
($/MM Btu)

	IGCC/ LPMEOH	IGCC/ CVPM	IGCC/ OTVPA
Raw Materials			
Coal @ $35/ST	11.70	11.76	12.02
Catalyst/Chemicals	0.71	0.48	0.80
Total Raw Materials	12.41	12.24	12.82
Utilities	(31.42)	(31.60)	(32.63)
Direct Cash Costs	4.85	5.00	5.04
Allocated Cash Costs	3.71	3.85	3.88
By-product Credits			
Sulfur @ $75/ST	(0.85)	(0.86)	(0.87)
Ash Disposal @ $10.50/ST	0.33	0.33	0.34
Total by-product credit	(0.52)	(0.53)	(0.54)
Cash cost of production	(10.98)	(11.00)	(11.44)
Cost plus return @ 7.5 percent DCF	7.12	7.87	7.53

TABLE 12

ALLPMEOH UNIT DESIGN ASSUMPTIONS

	STAGE 1	STAGE 2
Space velocity, L/hr-Kg cat	8,500	10,000
Exit temperature, °F	482	500
Exit pressure, psia	1,490	2,130
Carbon monoxide conversion, %	60.6	65.2
Carbon dioxide conversion, %	0.0	7.3
Net crude methanol produced, STPD	3,143	2,084

TABLE 13

ALL-METHANOL LPMEOH PLANT INVESTMENT
(Mid-1987, Millions of Dollars)

	Gasification	LPMEOH	Power Generation	Total Plant
Power generated, MW	-	-	144.1	144.1
Power consumed, MW	113.9	15.7	1.9	131.5
Net power generated, MW	(113.9)	(15.7)	142.2	11.8
Methanol production, STPD	-	5,227.0	-	5,227.0
Coal Receiving, grinding and slurry preparation	43.1	-	-	43.1
Oxidant Feed	132.6	-	-	132.6
Gasification, high-temperature gas cooling, particulate removal and ash removal	169.9	-	-	169.9
COS hydrolysis and CO shift reactor	11.3	-	-	11.3
Low-temperature gas cooling	28.1	-	-	28.1
Acid gas removal, sulfur recovery, and tail gas treating	53.0	-	-	53.0
Steam, condensate and BFW	-	-	5.2	5.2
Power system	-	-	60.7	60.7
General facilities	77.3	15.3	11.6	104.2
Methanol unit	-	62.9	-	62.9
Distillation	-	27.7	-	27.7
Subtotal	515.3	106.5	77.6	699.3
Project Contingency	77.4	16.0	11.6	105.0
Initial catalyst and chemicals	4.5	1.3	0.0	5.9
TOTAL PLANT INVESTMENT	597.2	123.8	89.2	810.2

TABLE 14

ALL METHANOL COST OF PRODUCTION

Capacity, MM gals methanol/yr	527
On-stream time, hrs/yr	8,000
Capital Cost, MM $	
ISBL	606.3
Offsites	203.9
Total Fixed Investment	810.2
Working Capital	61.4
Total Investment	871.6
Production Cost Summary, cents/gal	
Net Raw Materials	17.9
Total Utilities	(0.7)
Variable Cost of Production	17.2
Total Direct Cash Cost	8.0
Total Allocated Cash Cost	8.3
Full Cash Cost of Production	33.5
Depreciation	26.9
Net Cost of Production	60.4
Required Sales Price at 10% DCF	67.3

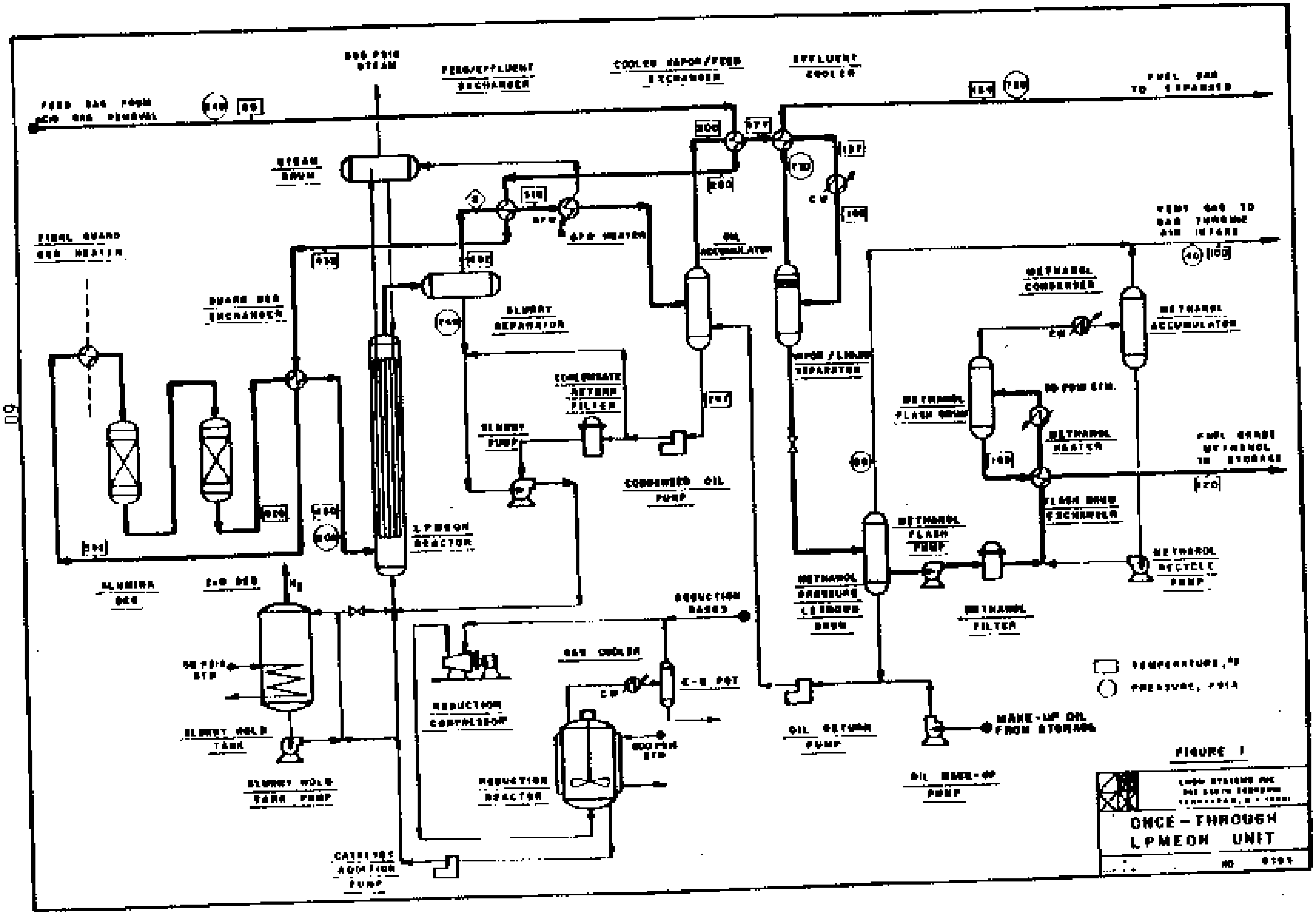


FIGURE 1

ONCE-THROUGH
LPMEOH UNIT

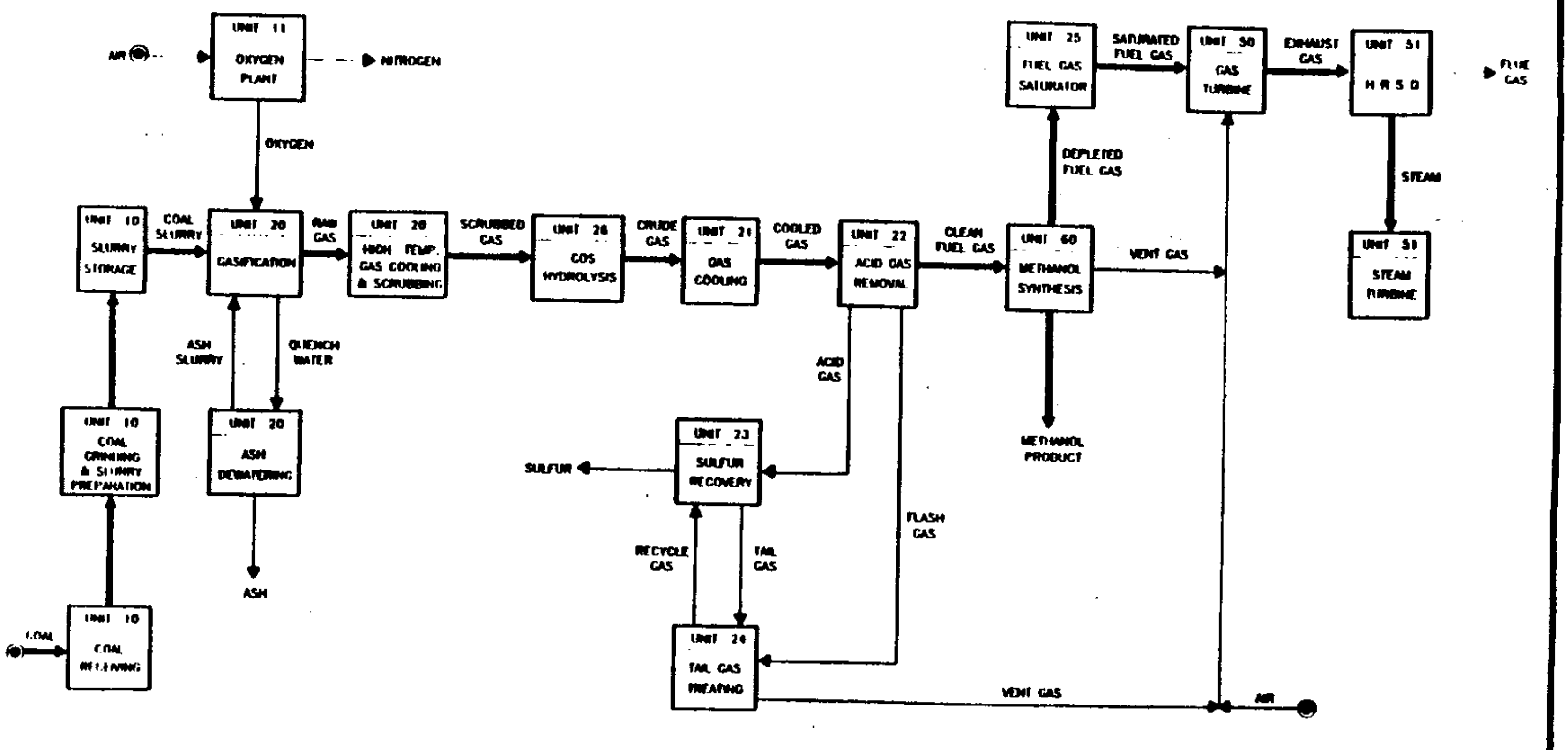


FIGURE 2

CHEM SYSTEMS INC.
303 SOUTH BROADWAY
TARRYTOWN, NEW YORK 10591

TITLE I G C C WITH LIQUID PHASE METHANOL COPRODUCTION

PROJECT NO 6185

FIGURE 3

PRODUCTIVITY ESTIMATES AT VARIOUS REACTOR PRESSURES AND 250°C WITH CO-RICH GAS

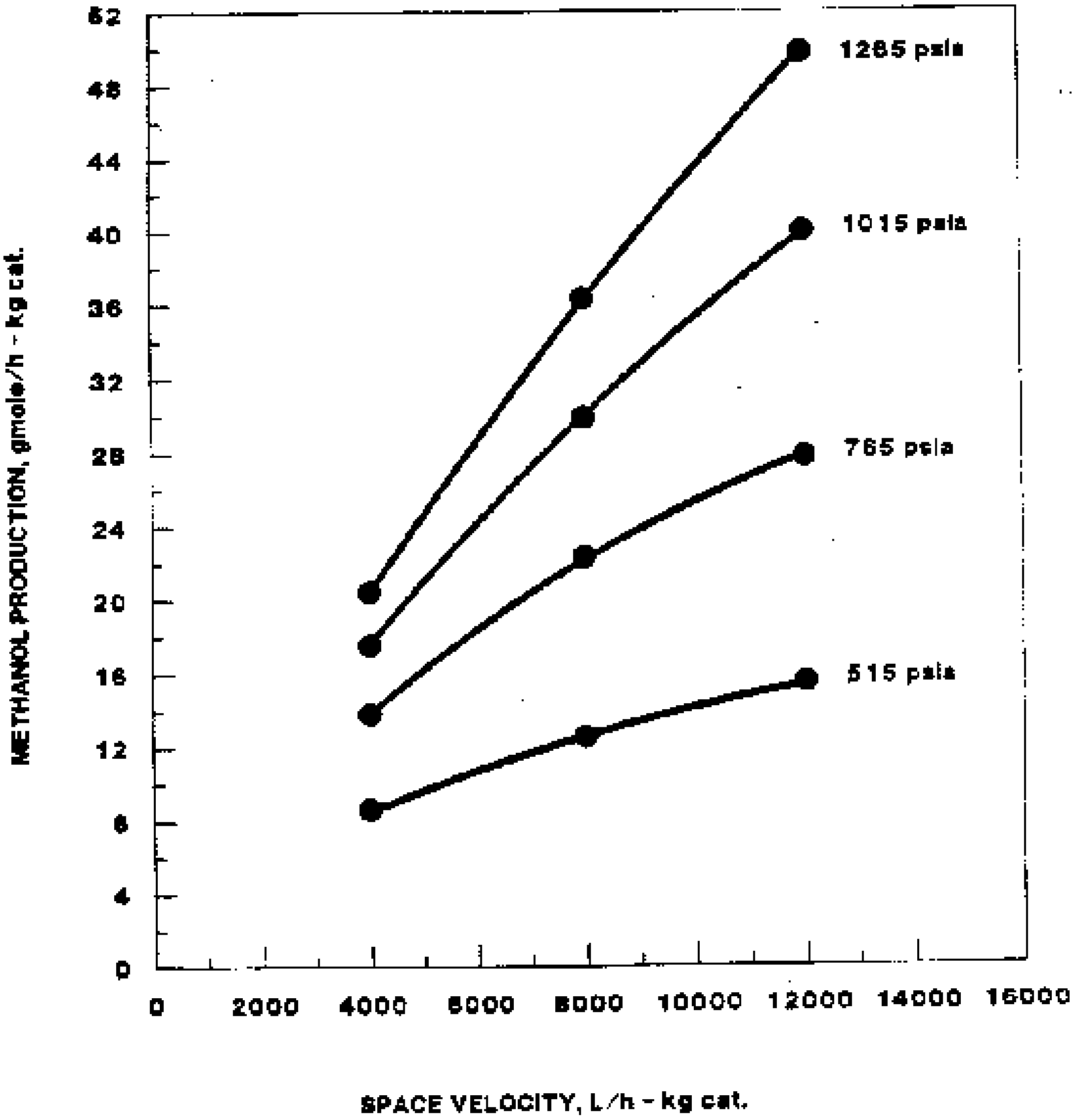


FIGURE 4

METHANOL FACILITY INVESTMENT FOR LPMEOH INLET PRESSURE OF 595 PSIA AS A FUNCTION OF SPACE VELOCITY AND COMPRESSION TO VARIOUS REACTOR PRESSURES

BASIS: MID-1987

FUEL GAS EXPANDER INCLUDED

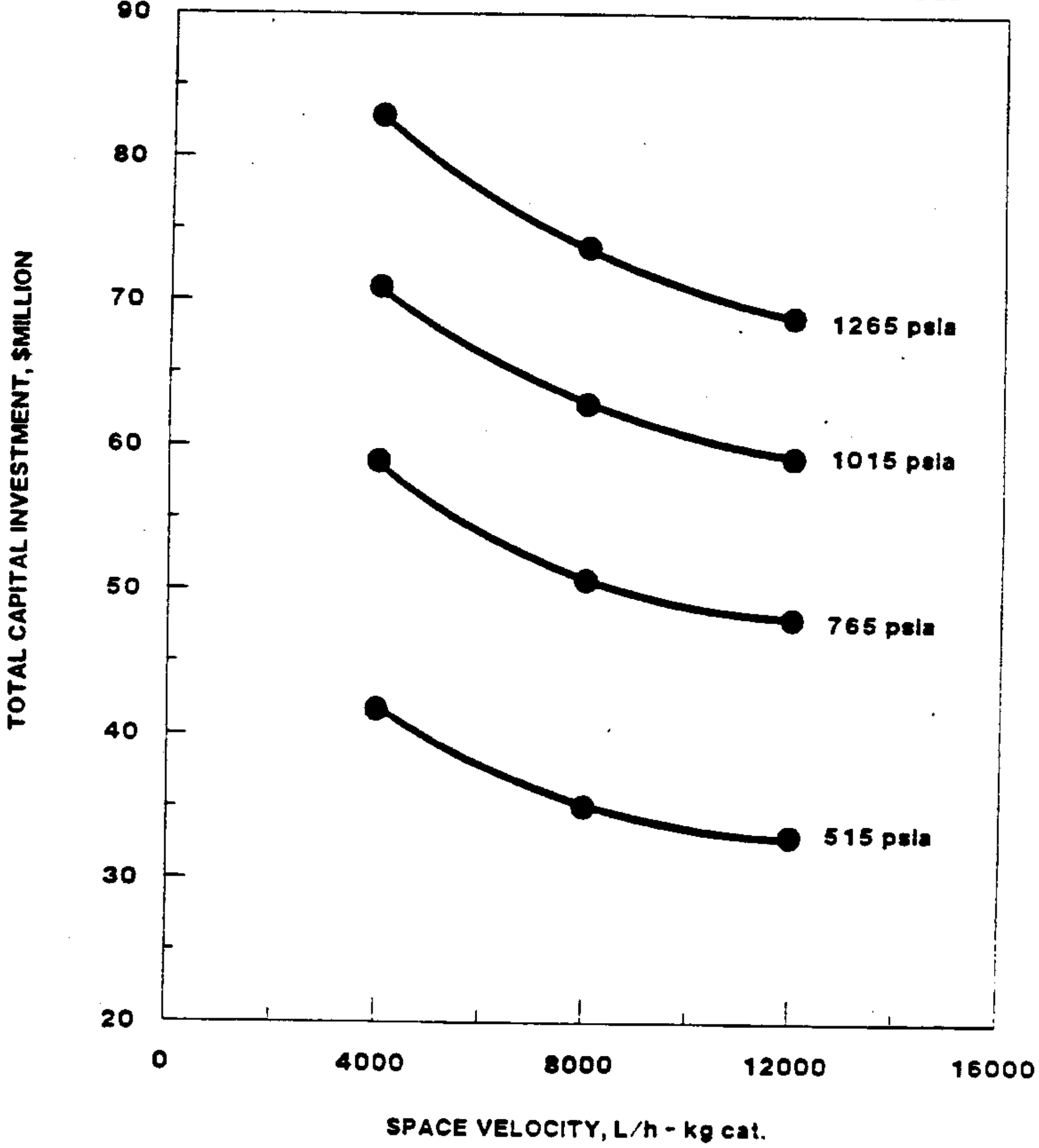


FIGURE 5

METHANOL FACILITY INVESTMENT FOR LPMEOH INLET PRESSURE OF 595 PSIA AS A FUNCTION OF SPACE VELOCITY AND COMPRESSION TO VARIOUS REACTOR PRESSURES

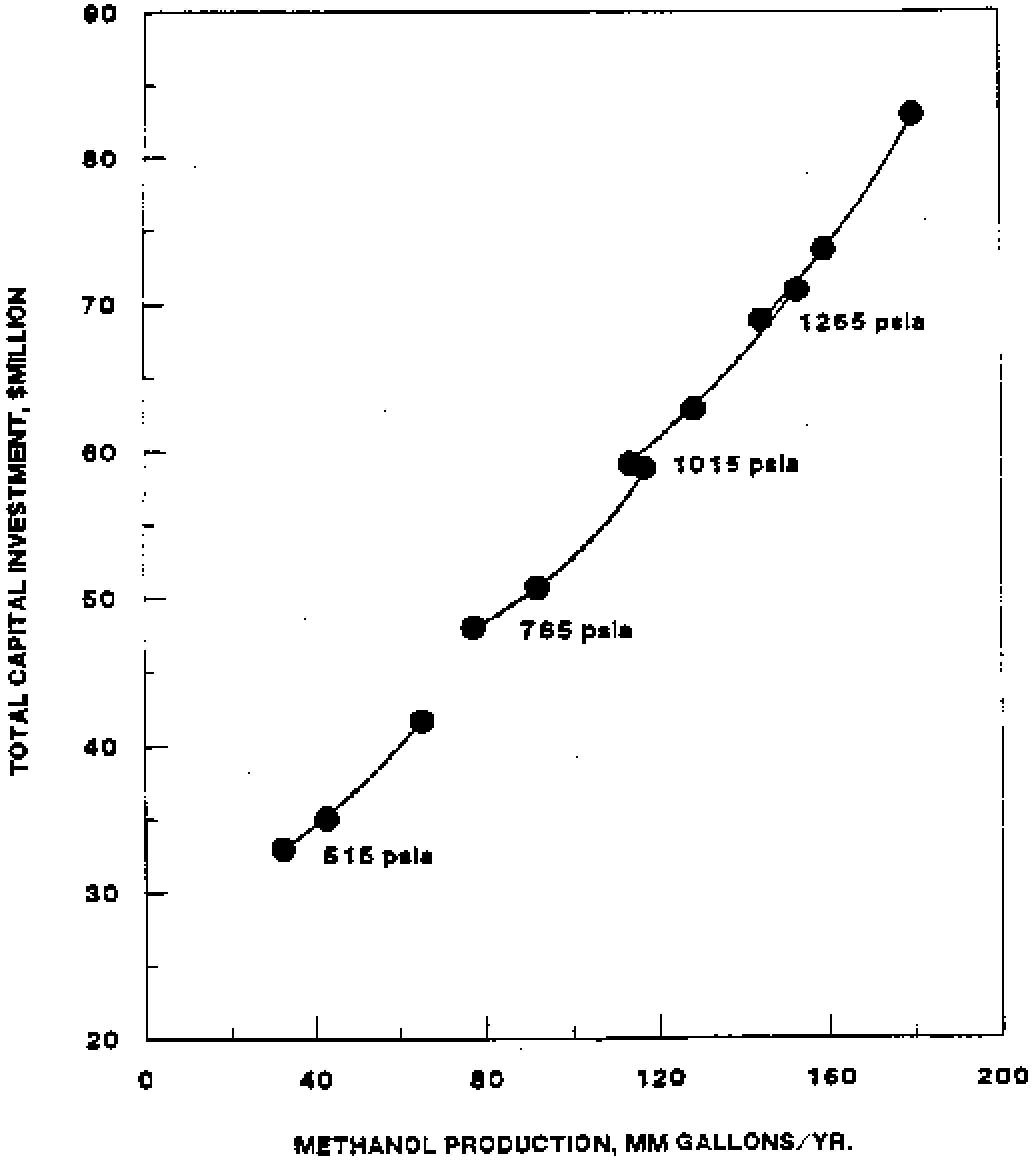

BASIS: MID-1987
FUEL GAS EXPANDER INCLUDED

FIGURE 6

METHANOL COST PLUS RETURN FOR LPMEOH INLET PRESSURE OF 595 PSIA AS A FUNCTION OF METHANOL PRODUCTION AND COMPRESSION TO VARIOUS REACTOR PRESSURES

BASIS: MID-1987
7.5% DCF RETURN
SYNGAS AT $4.83/MM BTU
POWER AT 3.68 CENTS/kWh
FUEL GAS EXPANDER INCLUDED

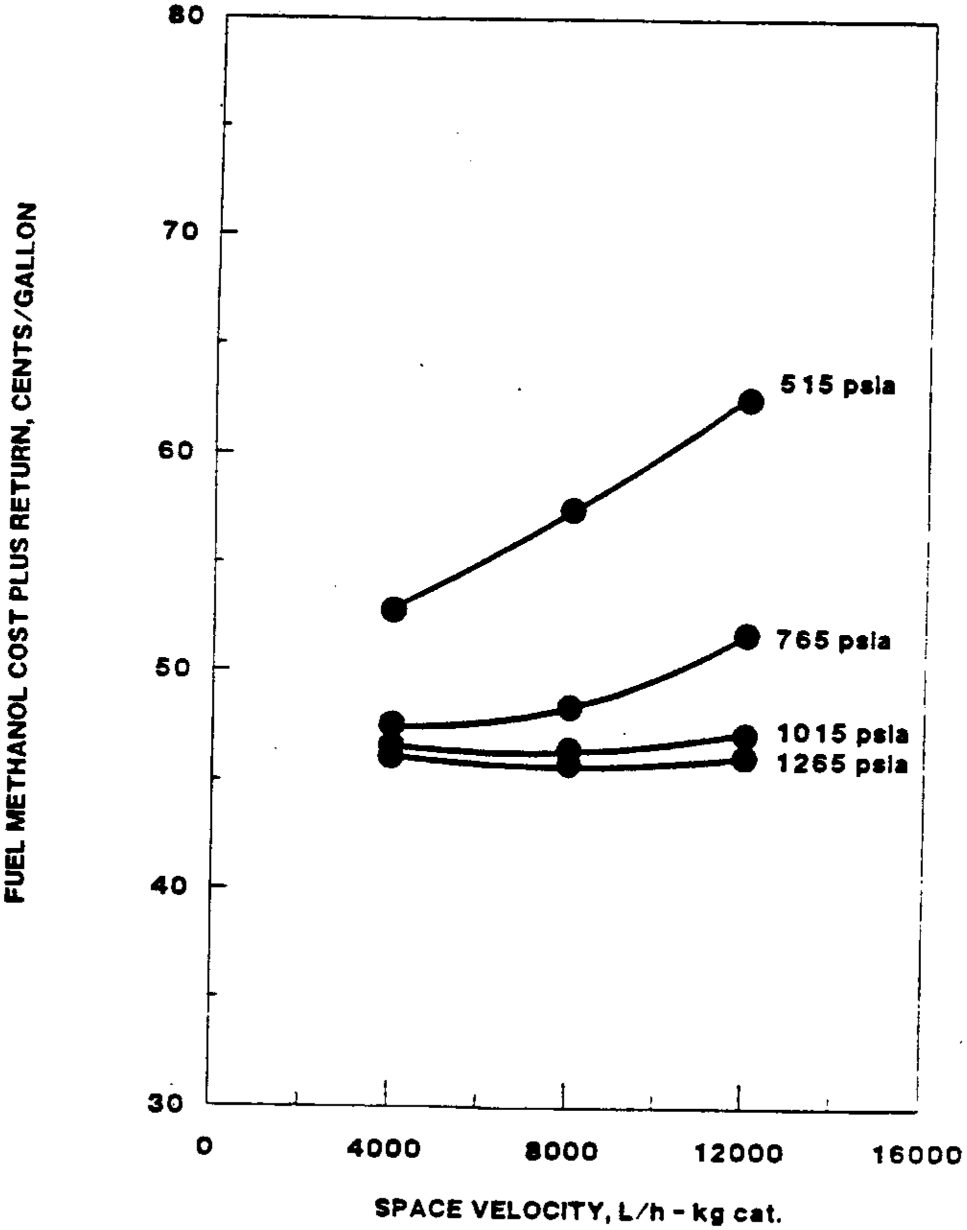
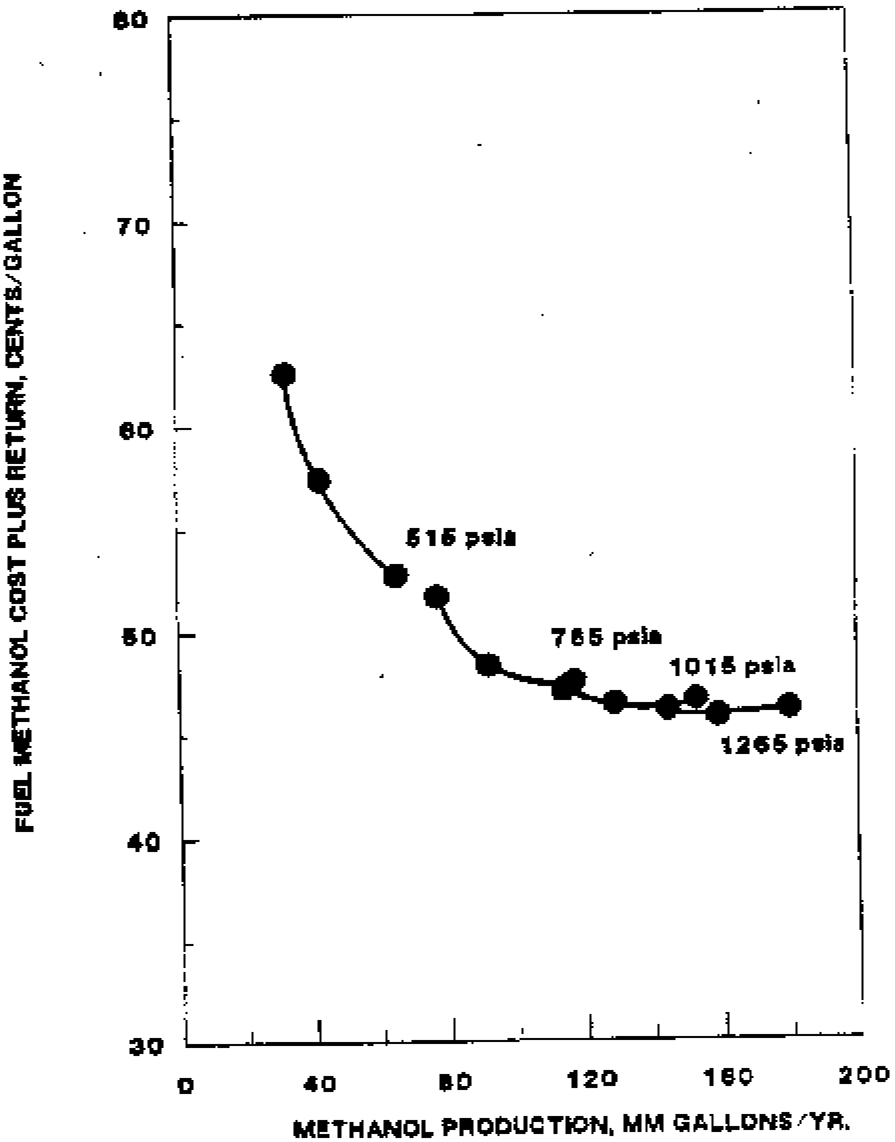
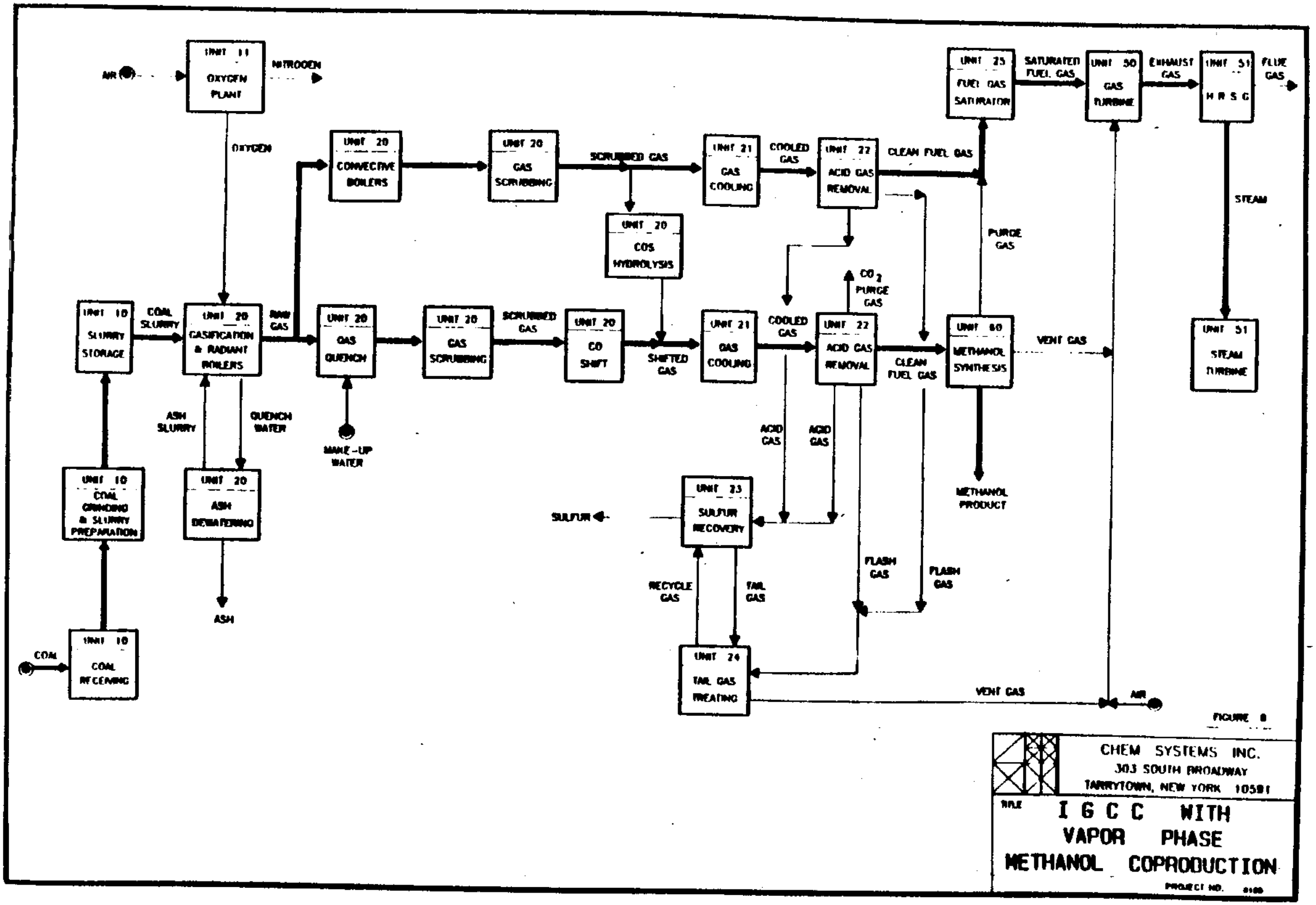


FIGURE 7

METHANOL COST PLUS RETURN FOR LPMEOH INLET PRESSURE OF 595 PSIA AS A FUNCTION OF METHANOL PRODUCTION AND COMPRESSION TO VARIOUS REACTOR PRESSURES

BASIS: MID-1987
7.5% DCF RETURN
SYNGAS AT $4.83/MM BTU
POWER AT 3.68 CENTS/kWh
FUEL GAS EXPANDER INCLUDED




AIR
UNIT 11 OXYGEN PLANT
NITROGEN
OXYGEN
COAL
UNIT 10 COAL RECEIVING
UNIT 10 COAL GRINDING & SLURRY PREPARATION
UNIT 10 SLURRY STORAGE
COAL SLURRY
UNIT 20 GASIFICATION & RADIANT BOILERS
ASH SLURRY
QUENCH WATER
UNIT 20 ASH DEWATERING
ASH
RAW GAS
UNIT 20 CONVECTIVE BOILERS
UNIT 20 GAS SCRUBBING
SCRUBBED GAS
UNIT 20 COS HYDROLYSIS
UNIT 21 GAS COOLING
COOLED GAS
UNIT 22 ACID GAS REMOVAL
CLEAN FUEL GAS
UNIT 20 GAS QUENCH
MAKE-UP WATER
UNIT 20 GAS SCRUBBING
SCRUBBED GAS
UNIT 20 CO SHIFT
SHIFTED GAS
UNIT 21 GAS COOLING
COOLED GAS
UNIT 22 ACID GAS REMOVAL
CO2 PURGE GAS
CLEAN FUEL GAS
ACID GAS
ACID GAS
UNIT 23 SULFUR RECOVERY
SULFUR
RECYCLE GAS
TAIL GAS
UNIT 24 TAIL GAS TREATING
FLASH GAS
FLASH GAS
VENT GAS
AIR
UNIT 60 METHANOL SYNTHESIS
METHANOL PRODUCT
PURGE GAS
VENT GAS
UNIT 25 FUEL GAS SATURATOR
SATURATED FUEL GAS
UNIT 30 GAS TURBINE
EXHAUST GAS
UNIT 51 H R S G
FLUE GAS
STEAM
UNIT 51 STEAM TURBINE
FIGURE 8
CHEM SYSTEMS INC.
303 SOUTH BROADWAY
TARRYTOWN, NEW YORK 10591
TITLE
I G C C WITH
VAPOR PHASE
METHANOL COPRODUCTION
PROJECT NO.

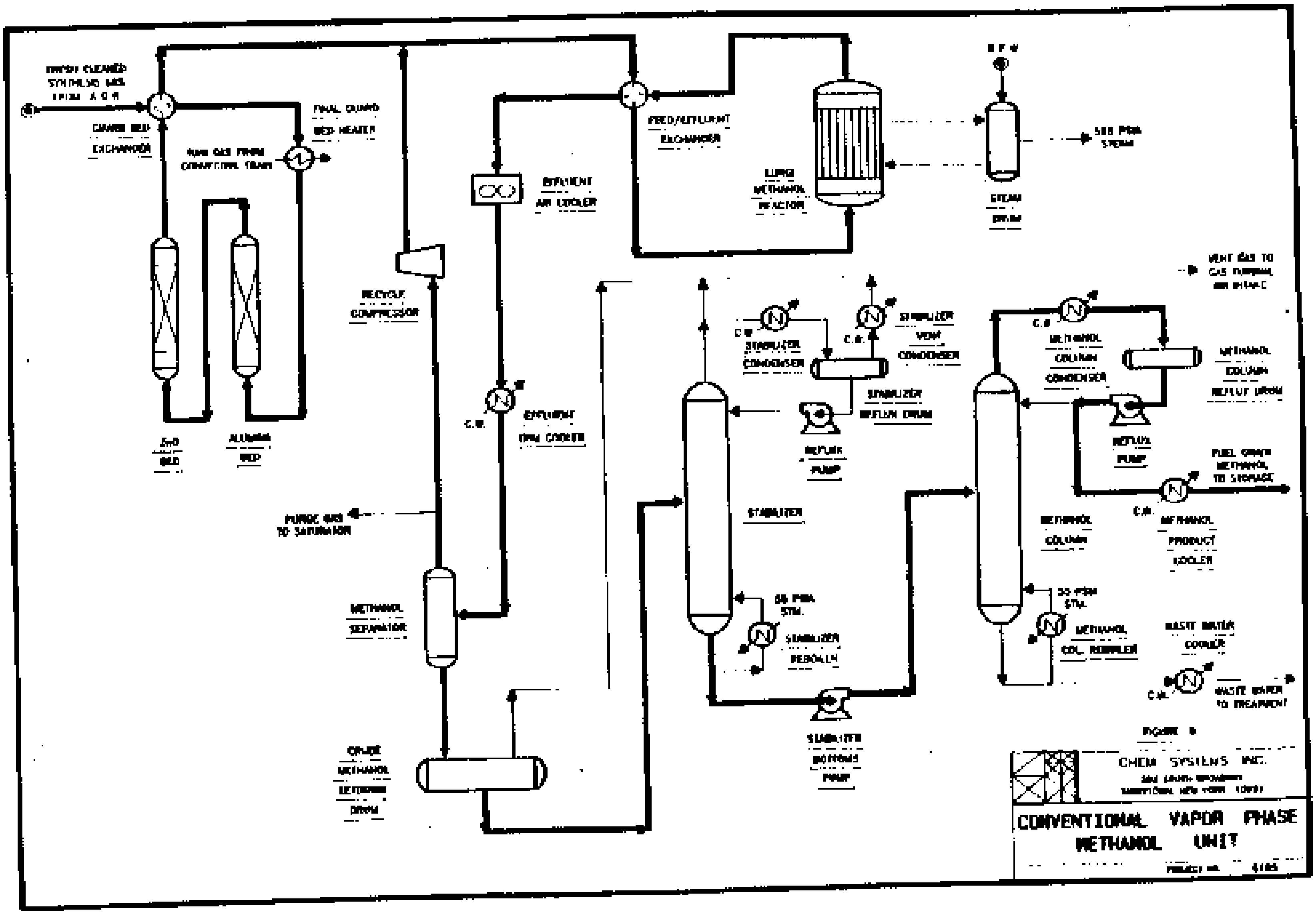

FRESH CLEANED SYNTHESIS GAS FROM A G R
GUARD BED EXCHANGER
RAW GAS FROM COMPRESSION TRAIN
FINAL GUARD BED HEATER
ZnO BED
ALUMINA BED
RECYCLE COMPRESSOR
PURGE GAS TO SATURATOR
EFFLUENT AIR COOLER
C.W.
EFFLUENT C.W. COOLER
METHANOL SEPARATOR
CRUDE METHANOL LETDOWN DRUM
FEED/EFFLUENT EXCHANGER
LURGI METHANOL REACTOR
B F W
STEAM DRUM
580 PSIA STEAM
C.W.
STABILIZER CONDENSER
C.W.
STABILIZER VENT CONDENSER
STABILIZER REFLUX DRUM
REFLUX PUMP
STABILIZER
50 PSIA STM.
STABILIZER REBOILER
STABILIZER BOTTOMS PUMP
VENT GAS TO GAS TURBINE AIR INTAKE
C.W.
METHANOL COLUMN CONDENSER
METHANOL COLUMN REFLUX DRUM
REFLUX PUMP
FUEL GRADE METHANOL TO STORAGE
C.W.
METHANOL PRODUCT COOLER
METHANOL COLUMN
50 PSIA STM.
METHANOL COL. REBOILER
WASTE WATER COOLER
C.W.
WASTE WATER TO TREATMENT
FIGURE
CHEM SYSTEMS INC.
CONVENTIONAL VAPOR PHASE METHANOL UNIT
PROJECT NO. 4185

FIGURE 10

Cu/ZnO CATALYST PERFORMANCE WITH CO-RICH GASES PRODUCTIVITY vs. SPACE VELOCITY

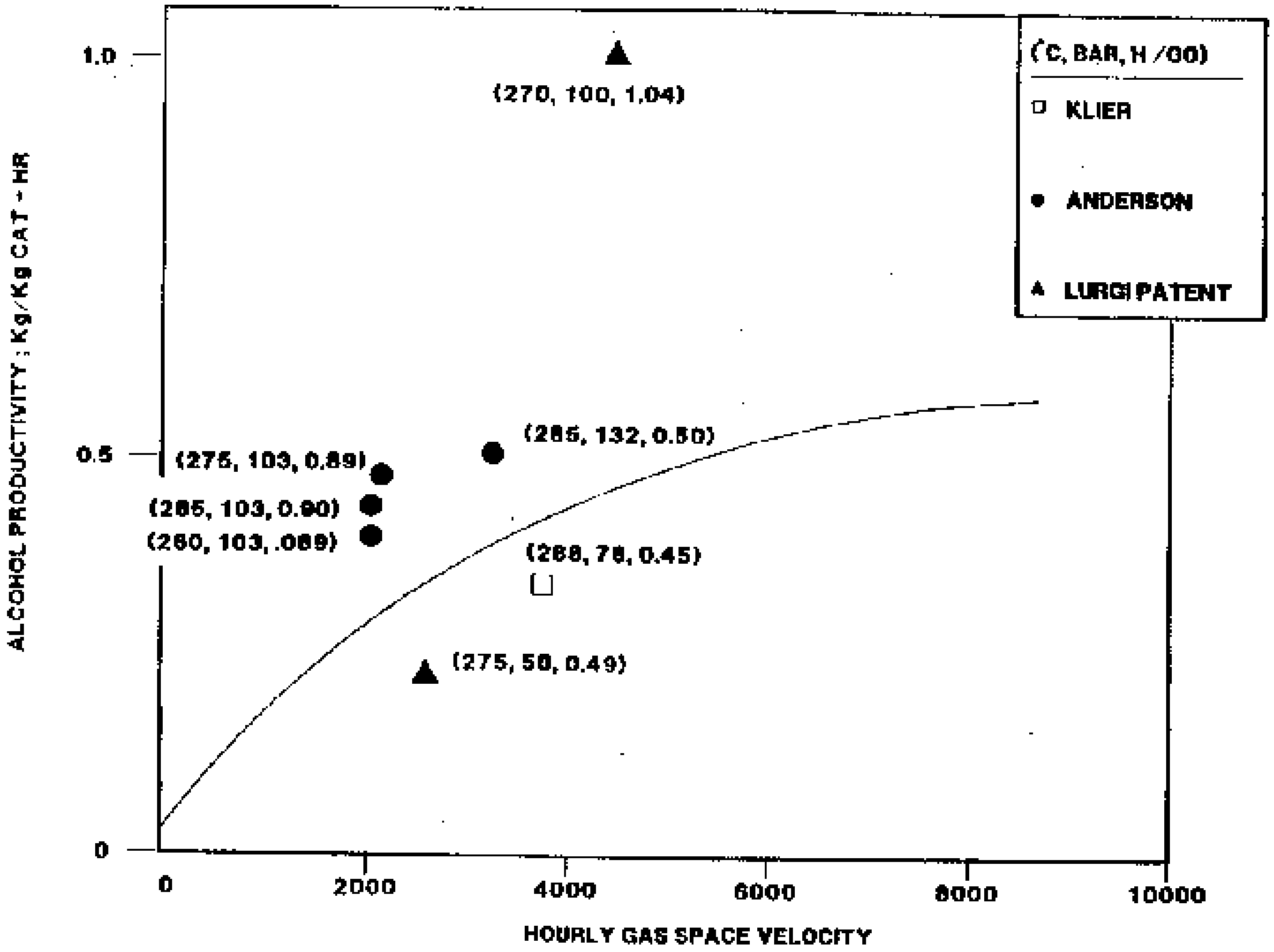
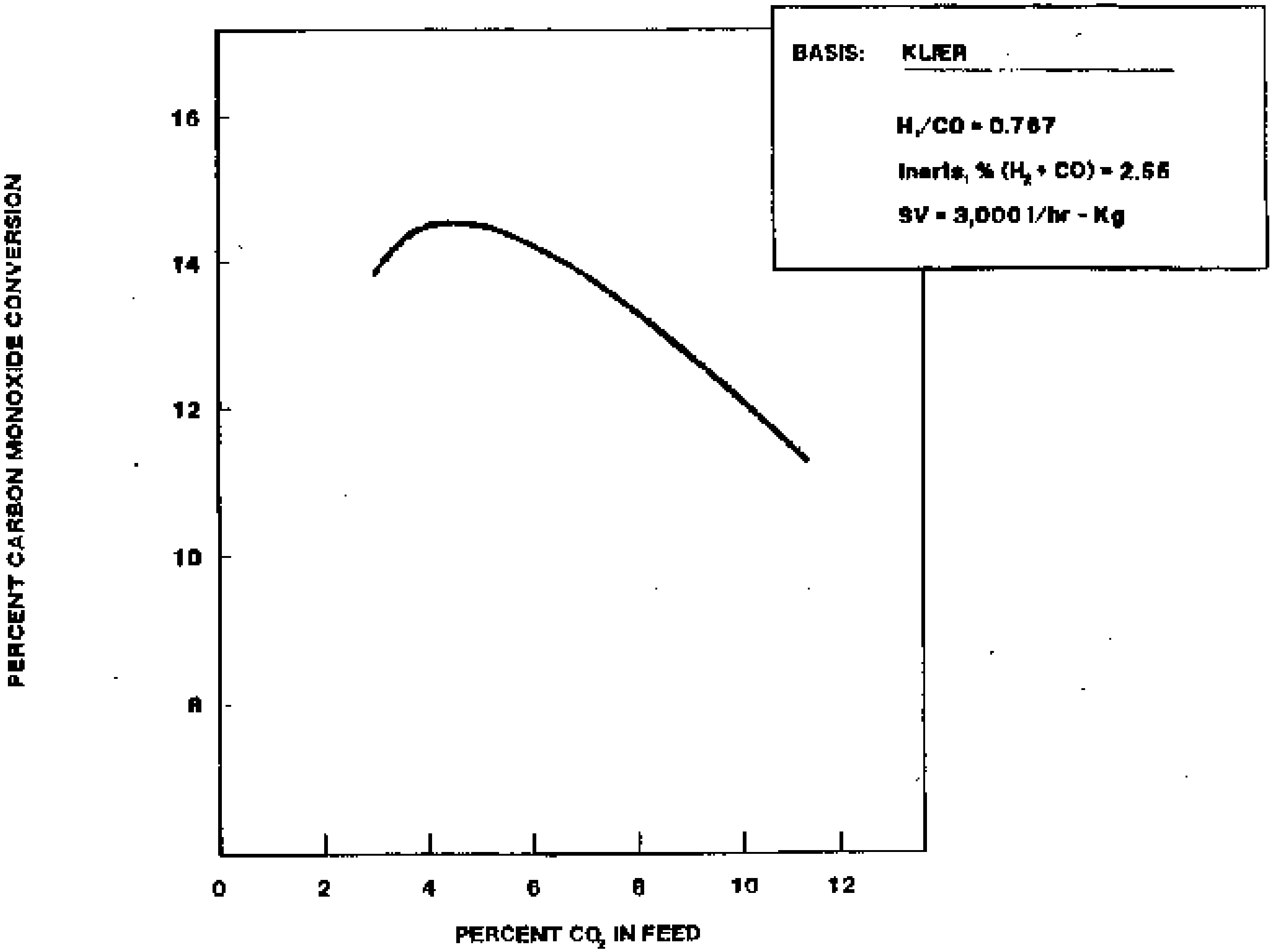


FIGURE 11

EFFECT OF CO_2 CONCENTRATION ON CO CONVERSION AT 250 C°



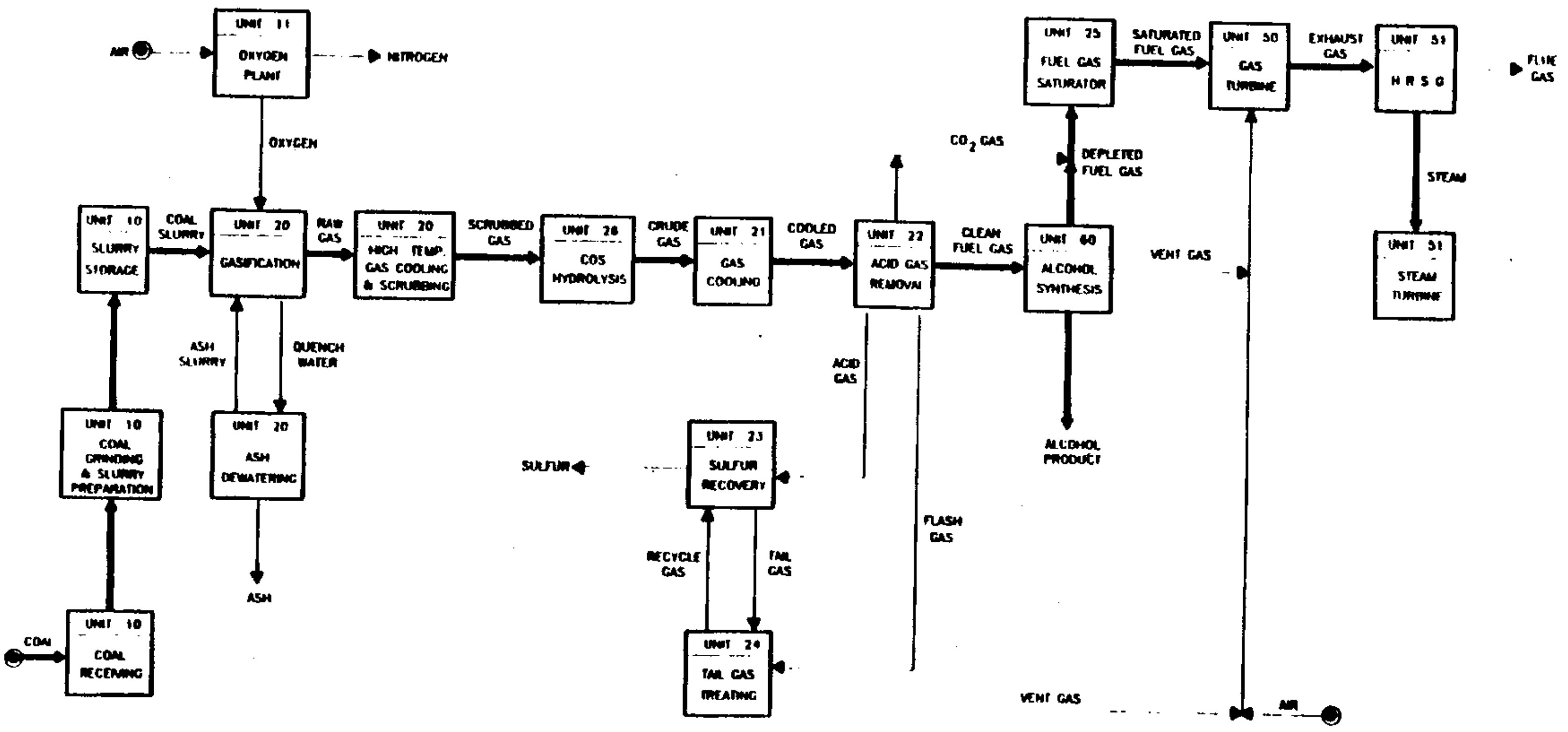
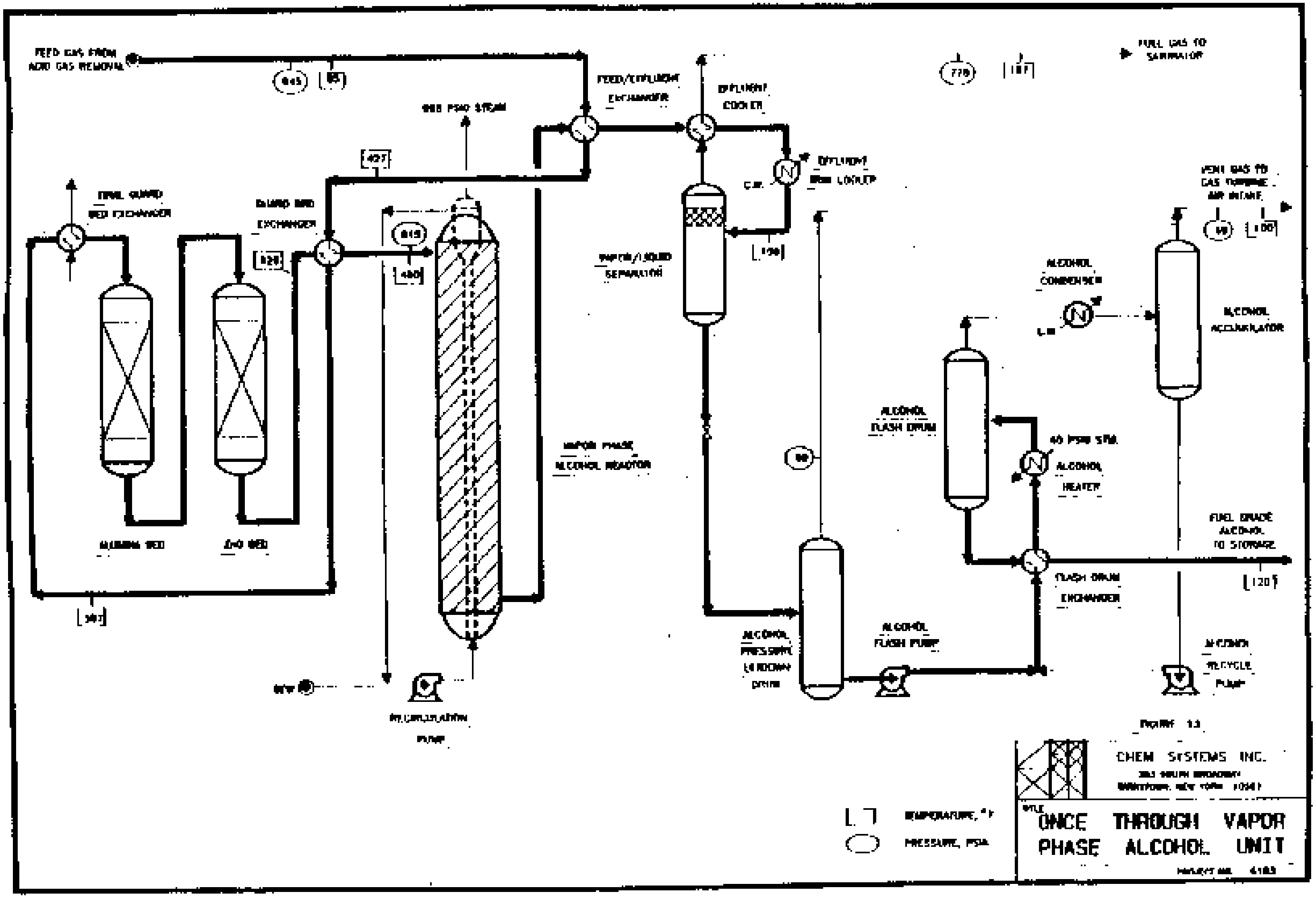


FIGURE 12

CHEM SYSTEMS INC.
303 SOUTH BROADWAY
TARRYTOWN, NEW YORK 10591

TITLE I G C C WITH VAPOR PHASE ALCOHOL COPRODUCTION

PROJECT NO. 6185


FEED GAS FROM
ACID GAS REMOVAL
645
85
FEED/EFFLUENT
EXCHANGER
600 PSIG STEAM
427
FINAL GUARD
BED EXCHANGER
GUARD BED
EXCHANGER
820
615
480
ALUMINA BED
ZnO BED
307
BFW
RECIRCULATION
PUMP
VAPOR PHASE
ALCOHOL REACTOR
EFFLUENT
COOLER
EFFLUENT
TRIM COOLER
C.W.
130
VAPOR/LIQUID
SEPARATOR
ALCOHOL
PRESSURE
LETDOWN
DRUM
ALCOHOL
FLASH PUMP
ALCOHOL
FLASH DRUM
40 PSIG STM.
ALCOHOL
HEATER
FLASH DRUM
EXCHANGER
ALCOHOL
CONDENSER
C.W.
ALCOHOL
ACCUMULATOR
VENT GAS TO
GAS TURBINE
AIR INTAKE
100
FUEL GAS TO
SATURATOR
778
107
FUEL GRADE
ALCOHOL
TO STORAGE
120
ALCOHOL
RECYCLE
PUMP
TEMPERATURE, °F
PRESSURE, PSIA
FIGURE 13
CHEM SYSTEMS INC.
TITLE
ONCE THROUGH VAPOR
PHASE ALCOHOL UNIT

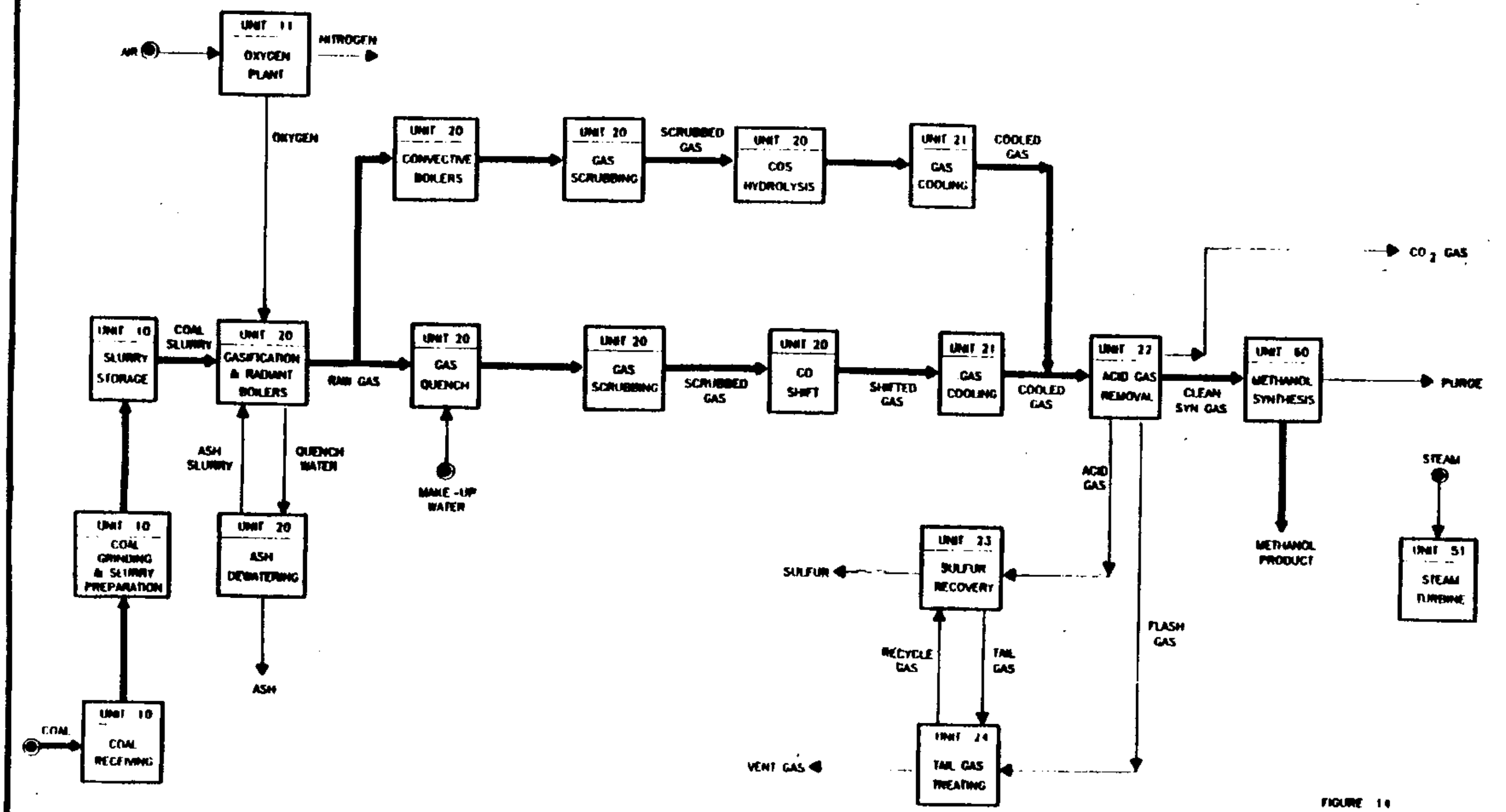


FIGURE 14

CHEM SYSTEMS INC.
303 SOUTH BROADWAY
TARRYTOWN, NEW YORK 10591

2 STAGE LPMEOH DESIGN
WITH TEXACO GASIFIER
FRONT END

PROJECT NO. 6185

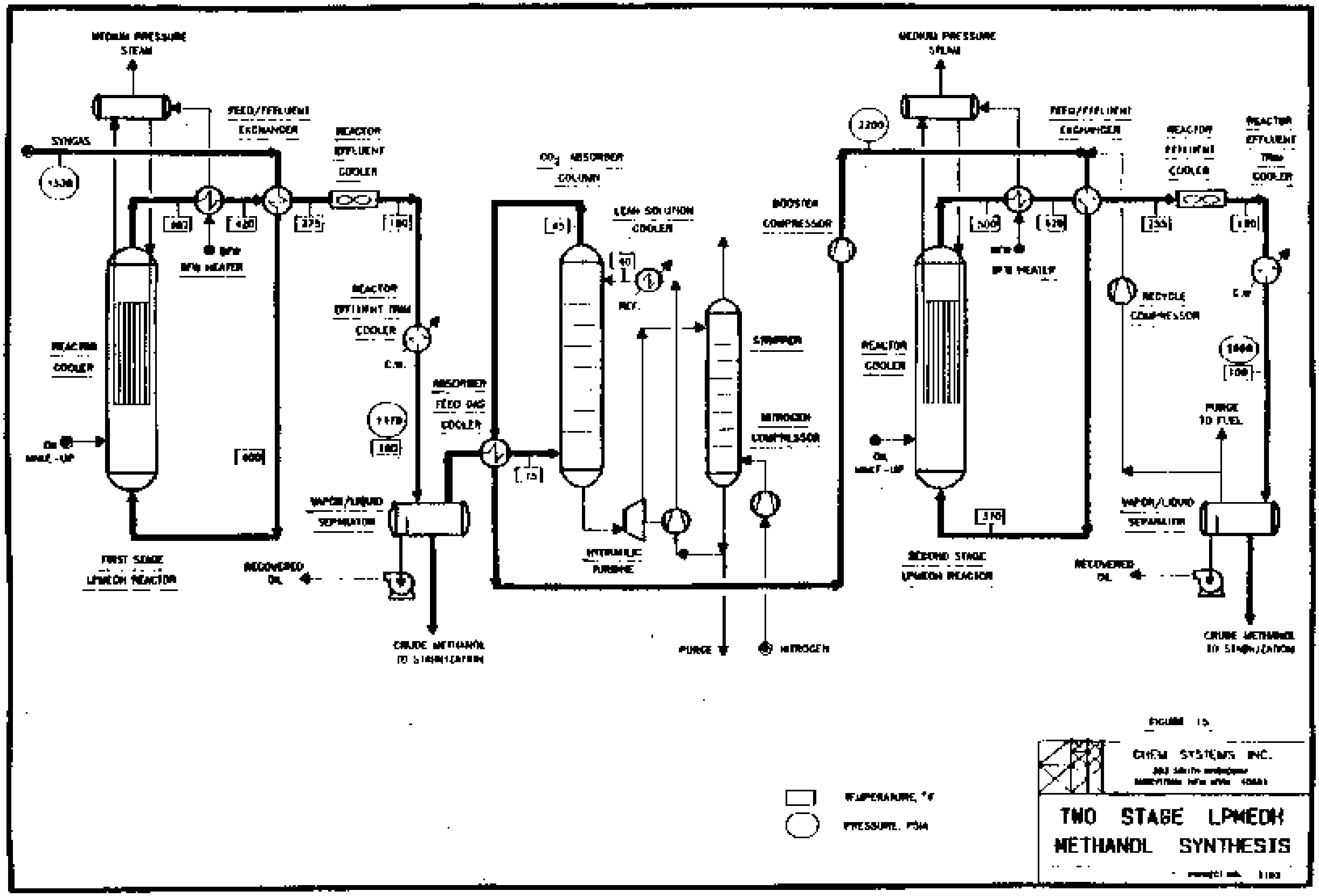


FIGURE 15

CHEM SYSTEMS INC.

TWO STAGE LPMEOH METHANOL SYNTHESIS