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LIQUID-PHASE METHANOL PDU-PROJECT STATUS AND PLAN

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ABSTRACT

In September 1981, the U.S. DOE and Air Products and Chemicals, Inc. began a 42-month R&D program to prove the feasibility of the Liquid Phase Methanol (LPMeOH) technology. Chem Systems Inc., inventor of the LPMeOH technology, is performing as a key subcontractor in the program. Cost sharing participants are DOE, Air Products, Fluor Engineers, Inc. and the Electric Power Research Institute. LPMeOH technology has the potential to be a more efficient, lower-cost conversion route to methanol-from-domestic coal than current gas-phase processes. Laboratory work to date shows LPMeOH technology particularly suited to coal-derived synthesis gas rich in carbon monoxide because: it is capable of processing feed gas of varying CO and H_2 contents; it results in higher CO conversion per pass; and it permits more effective recovery of heat liberated during reaction. In this program, a DOE-owned skid mounted process development unit is being transferred from Chicago, refurbished, expanded for service as the LPMeOH Process Development Unit (PDU), and then relocated to Air Products' LaPorte, TX facility. Synthesis feed gas from the facility will be used to test the unit for a planned 15-month period. The PDU operation is supported by an extensive 42-month laboratory program, conducted principally at Chem Systems' labs, with a complementary research effort at Air Products. Chem Systems is providing technical management for the project. Air Products is providing overall program management and is responsible for engineering design, construction, and operation.

During Phase I of the program, Air Products conducted the detailed engineering review of the originally proposed plan for installation of the LPMeOH PDU adjacent to Air Products' existing commercial facilities in LaPorte. The LPM unit was transferred from Chicago to Houston, and is now being refurbished and expanded for LPMeOH service. The review included: establishment of the LaPorte LPMeOH PDU process design basis and a process flowsheet; review of existing equipment from the LPM unit; evaluation of permit requirements and exemption from an environmental air permit; performance of a process hazards review; preparation of process equipment specifications, mechanical purchase specifications, a preliminary engineering flowsheet, and semi-final equipment arrangement and plot plan drawings compiling much of the review data. The latter engineering drawings and documents formed the basis for a detailed cost

estimate for engineering, equipment, and renovation/installation of the LaPorte LPMeOH PDU.

In the laboratories, Chem Systems completed successful testing and optimization of liquid phase (in-situ) catalyst reduction procedures. A major milestone was accomplished with completion of a 540-hour liquid-fluidized (ebullated bed) run in the Lab PDU at Fairfield, using a new, improved catalyst. The activity of the successful catalyst was 25-80% higher than the best prior catalyst, and the resistance to activity loss over the short term was approximately 3 times better. The apparent catalyst attrition was still high, but was 25-30% less than that observed in earlier work. Progress was made on the modifications to the Lab PDU to allow liquid-entrained operation, with specification, bid tab analysis, and purchasing activity. A number of equipment items were ordered. In the Air Products' laboratories, the Gas Phase Screening Reactor was assembled and successfully commissioned. Baseline tests are now in progress. The Stirred Autoclave (Slurry) Reactor system was assembled and is undergoing final leak checking. The first 5 new slurry catalyst preparations were completed and analyzed. The fundamental modeling work progressed with definitive plans to develop a dispersed-flow model to describe the LPMeOH reactor. A two-phase CSTR model was modified to include liquid/solid mass transfer and the methanol synthesis and water-gas shift reactions; this is being used to treat data from the Stirred Autoclave Reactors and obtain parameters on LPMeOH intrinsic reaction kinetics.

INTRODUCTION

In September 1981, the U.S. DOE and Air Products and Chemicals, Inc. began a 42-month R&D program to prove the feasibility of the Liquid Phase Methanol (LPMeOH) technology. The contract is entitled, "Liquid Phase Methanol Process Development Unit: Installation, Operation, and Support Studies." The contract number is DE-AC22-81PC30019. Chem Systems Inc., inventor of the LPMeOH technology, is performing as a key subcontractor in the program. Cost sharing participants are DOE, Air Products, Fluor Engineers, Inc. and the Electric Power Research Institute. This paper provides an overview of this program. The history of the development of LPMeOH technology is reviewed following this introduction, in order to provide some background perspective to the program. After the historical review, the current program is described. The tasks and objectives of the program are outlined. The achievements over the first 11 months of contract performance and the current program status are then reviewed. Finally, some comments are offered on the upcoming program milestones.

Before going on to the history of LPMeOH technology development, it may be helpful to discuss how the LPMeOH project fits into DOE's plan of basic, long-range research in the area of indirect liquefaction.

In recent years, the U.S. government has made a strong commitment to research aimed at the conversion of our nation's abundant coal resources into liquid fuels which can be substituted for products derived from imported petroleum. The creation of new technologies that can efficiently convert a wide range of domestic coals into liquid fuels is critical to the nation's national security. DOE's overall program in indirect coal liquefaction, and the Liquid Phase Metharol project in particular, is consistent with this objective.

Indirect coal liquefaction is recognized as being more flexible than direct liquefaction with respect to the types of coal that can be used and the end products that can be produced, e.g., jet fuel, gasoline, diesel and methanol. However, it is also recognized that fundamental technical improvements are essential for indirect liquefaction technology to achieve its full potential.

It was in recognition of the need for basic, long-range research in the area of indirect liquefaction, that DOE initiated several programs, including the LPMeOH project. Methanol, the end-product of this technology, holds promise as a clean, premium fuel with a variety of potential applications. Methanol from domestic coal could become an important substitute for products derived from imported petroleum.

Liquid Phase Methanol technology has the potential to be a more efficient, lower-cost means of producing methanol from coal than the current commercial processes, which must be licensed from foreign firms and which were designed to produce methanol from natural gas — a premium fuel itself. Based on laboratory work to date, it appears that LPMeOH technology is particularly advantageous when the starting raw material is coal rather than natural gas. Early laboratory results suggest that the LPMeOH process is capable of accepting synthesis gas of varying carbon monoxide and hydrogen contents, and in particular, gases with the low H_2/CO ratios that are typical of modern, thermally efficient coal gasifiers. It also appears that LPMeOH produces a higher CO conversion per pass, and permits more effective recovery of the heat liberated during the H_2/CO reaction. However, this potential must be verified and expanded through additional research. More specifically, long-range, high-risk research on catalysts and on novel concepts is required.

The LPMeOH process was originally conceived by Chem Systems Inc. Early development work was carried out by Chem Systems under the sponsorship of the Electric Power Research Institute. The current LPMeOH program calls for continued research at Chem Systems' laboratories in Fairfield, New Jersey. Additional research is being carried out at the Air Products laboratories in Allentown and Linwood, Pennsylvania. Larger-scale testing will be conducted at LaPorte, Texas, adjacent to a synthesis gas plant owned by Air Products. An existing DOE process development unit will be revamped and relocated from Chicago to LaPorte. Use of this unit, which represents a previous investment of $2.1 million by DOE, is an important feature of the LPMeOH program. The availability and suitability of the unit presents a unique opportunity for the government to conduct engineering research on indirect coal liquefaction in a timely and cost-effective manner.

The LPMeOH project contains elements of generic technology development that will be applicable to problems in both direct and indirect coal liquefaction. The project involves exploratory research on new families of catalysts that are very different from "conventional" commercial methanol catalysts. These new catalysts may have performance features that are of interest in other reactions involving synthesis gas. The project also involves fundamental engineering research on the behavior of three-phase (gas/liquid/solid) reactors. This research will lead to an improved understanding of the fluid mechanics of three-phase systems, which should have implications for other coal conversion processes. Lastly, the project involves the creation of a test facility that is large enough to permit the study of the engineering variables that affect process performance. Upon conclusion of the LPMeOH project, this facility will be useful for similar research on other indirect liquefaction technologies. Thus, it constitutes an important element of DOE's long-range research strategy in fossil energy.

The LPMeOH program can be viewed as the foundation for a basic, long-range, generic research program in indirect liquefaction. Despite the speculative and long-range nature of this technology, the fundamental attractiveness of the technical approach has led to strong industrial participation in the LPMeOH program. Air Products, Fluor Engineers, Inc., and the Electric Power Research Institute are providing a total of $1.8 million cost share. Chem Systems Inc., the originator of the technology, contributes as a key partner in the research program. The broad private participation indicates that this research, if successful, will not languish for lack of interest or capability.

HISTORY OF LPMeOH TECHNOLOGY DEVELOPMENT

Description of the Process

The Liquid Phase Methanol process differs significantly from presently available gas phase technologies for methanol synthesis. In gas phase processes, the reaction of synthesis gas to methanol is carried out over a packed bed of catalyst. The liquid phase process utilizes a catalyst fluidized by a circulating inert hydrocarbon liquid, usually a mineral oil. The presence of this liquid serves to control the reacion temperature much better than in gas phase processes, allowing a closer approach to equilibrium and permitting better recovery of the heat of reaction.

Figure 1 illustrates the function of the three-phase, fluidized-bed (ebullated bed) reactor within the synthesis section of a LPMeOH plant. Synthesis gas containing CO, CO_2, and H_2 is passed upward into the reactor cocurrent with the inert hydrocarbon liquid which absorbs the heat liberated during reaction. Phase separation between solids, liquid and vapor occurs at the top of the reactor. The liquid-fluidized catalyst (typically 2 mm x 6 mm extrudates) remains in the reactor. The inert hydrocarbon liquid, separated from both catalyst and vapor, is recirculated to the bottom of the reactor via a heat exchanger, where cooling occurs by steam generation. The reactor effluent gases are cooled to condense the products and any inert hydrocarbon liquid which may have been vaporized. Methanol and the inert hydrocarbon liquid are immiscible and exist as separate liquid phases. The methanol stream produced is suitable for fuel use directly or can be sent to a distillation system (not shown) to produce chemical grade product. Unconverted gases are recycled back to the reactor. A small purge stream is taken off to limit the buildup of inerts which may be present in the synthesis gas feed.

An alternative type of three-phase reactor system that can be utilized in the LPMeOH process is termed the liquid-entrained (slurry) catalyst reactor. In this system, the objective is to use much smaller catalyst particles (typically 50 micron) and intentionally suspend the catalyst in the process liquid. The catalyst-liquid slurry is circulated through the reactor. Contact with the synthesis gas is provided by feeding the gas countercurrent or cocurrent to the flow of the liquid-entrained catalyst solution. Figure 2 illustrates a cocurrent reactor system. Other reactor designs are also possible. The reactor product gas is treated in the same manner as with a liquid-fluidized reactor.

LPMeOH Technology Development by Chem Systems

Development work on the Chem Systems LPMeOH process with a liquid-fluidized bed reactor started in early 1975 and continued through 1978. Most of this work was funded by the Electric Power Research Institute [References (1), (2), and (3)]. The major areas of the development program included the demonstration of concept feasibility, design and construction of a three-phase bench scale unit, catalyst modifications for the LPMeOH Process, process variable studies, scale-up in a larger laboratory process development unit, and engineering studies.

In December 1979, Chem Systems initiated a development effort on the liquid-entrained reactor concept which continued until September 1981. This effort was funded by Air Products and Fluor Engineers, Inc. in order to lay a stronger foundation for the technology and to allow acceleration into the upcoming DOE program. The major areas of this laboratory program included powdered catalyst reduction procedures, reaction studies in an autoclave and design of a liquid-entrained laboratory PDU [Reference (4)].

Demonstration of Concept Feasibility

One of the original incentives for developing a new, more efficient methanol process was to provide for the conversion of a certain percentage of coal-derived synthesis gas to a storable form such as methanol with minimal effect on the overall efficiency of both the coal conversion and methanol conversion processes. The results of initial tests in a fixed bed reactor using the liquid phase system proved that commercial methanol catalyst could operate effectively in the presence of an inert liquid phase. Also, methanol conversions could be obtained from a high CO-containing feed gas ($H_2/CO = 0.6$) as well as from a more "balanced" ($H_2/CO = 2$) methanol synthesis feed gas. Finally, the methanol product could be phase separated from the hydrocarbon process liquid. The product purity remained consistently high.

Design and Construction of a Three-Phase Bench Scale Unit

While the initial feasibility tests were being conducted, an automated bench scale unit (BSU) was designed for three-phase liquid-fluidized bed operation. The system was constructed of 316 stainless steel and was capable of 10,400 kPa (103 atm = 1510 psia) operation at 350°C (662°F) with a nominal synthesis gas feed rate of 1,200 liter/hr (45 scfh). The process liquid superficial velocity could be varied from 0.012-0.07 m/sec (0.039-0.23 ft/sec) and gas space velocity could be varied from 1,000 to 10,000 hr.$^{-1}$. The reactor was a nominal 25 mm (0.98 in) diameter tube by 1.84 m (6 ft) long.

Catalyst Modifications for the LPMeOH Process

In the first half of the development program, experimental runs were performed in the BSU using commercial methanol catalyst which was physically crushed from its original tablets to irregular particles and sieved to give a size range of either 12 to 16 mesh (0.99 to 1.4 mm) or 16 to 20 mesh (0.83 to 0.99 mm). A considerable number of process variable scans were conducted in the BSU program which was concerned with producing a catalyst particle that would have acceptable activity and attrition resistance for use in a liquid-fluidized three-phase reactor. A catalyst vendor tried extruding and spheroiding small diameter catalysts from a powder, but the extrudates produced were not of acceptable crush strength to warrant testing. An alternative approach was to produce 2.4 mm x 2.4 mm tablets in a variety of crush strengths. Several of these catalyst samples were run in the BSU. The results indicated that the activity was not as high as obtained with the crushed commercial catalysts. In addition, an extended run in a larger laboratory process development unit (Lab PDU at Fairfield) indicated that attrition resistance of the tablets was not acceptable for a commercial process. It was recognized that additional work needed to be done to develop a catalyst suitable for the liquid-fluidized reactor. This was subsequently pursued under a separate contract between the Electric Power Research Institute and United Catalysts, Inc.

Process Variable Studies

The experimental program conducted in the BSU investigated a number of process variables. The results are discussed below.

Three different types of process liquids were tested: aliphatic, aromatic and oxygenated. The first two were found to be suitable. The aliphatic oil used in the experiments was a mineral oil with a predominant carbon number range of C_{14} to C_{21}. The composition was 72 percent paraffinic and 28 percent naphthenic with an ASTM boiling range of 270° to 350°C (518° to 662°F). The aromatic oil had a composition of 73 percent C_{10}, 18 percent C_{11} and some lighter and heavier aromatic components. The boiling range of the aromatic oil was 180° to 210°C (356° to 410°F).

Most of the experimental work was done with feed gases simulating either a Koppers-Totzek coal gasifier after acid gas removal ($H_2/CO = 0.6$) or a Lurgi coal gasifier after complete H_2S removal and partial CO_2 removal ($H_2/CO = 2.0$, 10% CO_2). Other feed gas compositions were examined to investigate the reactivity of both CO and CO_2. For gas compositions where equilibrium calculations indicated that only CO should react to form methanol, a minimum amount of CO_2 is required in the feed gas to the synthesis reactor, similar to vapor-phase methanol processes. The CO_2 appears to behave as a catalyst promoter, passing through without measurably reacting itself. On the other hand, with feed gases containing high levels of CO_2 (7 to 14%) and high H_2 concentration, a substantial conversion of CO_2 to methanol is achieved; i.e., 60 to 90 percent of that predicted by equilibrium.

The methanol product composition produced in the LPMeOH process is slightly affected by the feed gas composition. Feed gases with a H_2 to CO ratio less than the stoichiometric 2/1 ratio tend to produce larger amounts of higher alcohols. Table 1 shows typical BSU crude methanol compositions for Lurgi-type and K-T-type feed gases.

A physical means was investigated as one of several methods of increasing methanol productivity. This involved removal of dissolved methanol from the process liquid stream before it was recirculated to the reactor by reducing its pressure to allow the methanol to flash. This methanol was then condensed and combined with the methanol product that would normally exit in the reactor vapor effluent. The lean process liquid was pumped to reactor pressure to absorb additional methanol. Several experiments were performed confirming that this flash vaporization scheme can indeed work. However, a considerable amount of dissolved synthesis gas is flashed along with the methanol. An economic analysis of this scheme indicated that it has advantages in certain situations where the flashed synthesis gas need not be recompressed to reaction pressure.

Since the initial process variable scans indicated that catalysts of nominal 0.8 mm diameter were more active than catalyst of nominal 1.6 mm diameter, several runs were performed in the BSU with even smaller catalyst particles, 0.21 to 0.30 mm diameter. The results indicated a 30 to 40 percent increase in catalyst activity.

Scale-Up in a Larger Laboratory Process Development Unit

A laboratory Process Development Unit (PDU) built as part of the Liquid Phase Methanation development program funded at Chem Systems by DOE was used for larger-scale testing of the LPMeOH process. The Lab PDU at Fairfield has a 92 mm (3.6 in) inside diameter by 2.1 m (7 ft) high reactor and can handle a nominal 42,000 liter/hr (1500 scfh) synthesis gas feed rate. Operation in the Lab PDU represents approximately a 40-fold capacity scale-up from the BSU.

Three long-term continuous runs were performed. The first one was in the BSU and lasted for 645 hours. A Lurgi-type feed was used with 2.4 mm diameter "mini-tablets". Catalyst activity declined slowly throughout the run, from an initial CO conversion of 40 percent to a final value of 30 percent.

The second and third long-term runs were performed concurrently in the BSU and Lab PDU during October-November 1978. Again, the 2.4 mm diameter catalyst mini-tablets were used. The feed for these runs was a K-T-type gas ($H_2/CO = 0.6$). The BSU run lasted for 720 hours. CO conversion declined slowly from 16 percent initially to 11.5 percent. The catalyst recovered from the BSU reactor was 95 percent of that initially loaded, with only slightly reduced catalyst dimensions.

The Lab PDU run lasted for 645 hours. Process conditions were maintained at 250°C (482°F), 7,000 kPa (69 atm = 1015 psia), and 3,000 liters/kg cat-hr space velocity. Initial results from the Lab PDU were equivalent to the BSU results. However, catalyst attrition occurred throughout the run. The catalyst recovered was only 64 percent of that loaded. Inspection of individual recovered catalyst particles showed a physical reduction in size. The results of this run indicated that the catalyst mini-tablets did not possess sufficient strength for the liquid-fluidized process, and additional catalyst development work was initiated as mentioned earlier.

Powdered Catalyst Reduction Procedures

Late in 1979, work resumed on the LPMeOH process with the construction at Fairfield of a 2-liter Stirred Autoclave (Slurry) Reactor system for studying the liquid-entrained reactor concept. This equipment was first used to test several methods of reducing commercial methanol catalysts in powder form for use in liquid-entrained reactors. Catalyst powder was reduced in-situ while slurried in an inert hydrocarbon liquid. Catalyst powder was also reduced in the vapor phase prior to slurrying in the hydrocarbon liquid. Finally, a granular form of the commercial catalyst was reduced in the vapor phase and then reduced in size by agitation once placed in the liquid-filled autoclave. The two methods employing vapor phase reduction yielded equivalent results. Since catalyst activity utilizing vapor phase reduction was excellent, these procedures formed the basis for developing and comparing in-situ reduction techniques.

Reaction Studies in a Stirred Autoclave Reactor

Process variable scans were performed in the Stirred Autoclave Reactor utilizing catalyst powder reduced externally in the vapor phase. Feed gases simulating Lurgi-type and K-T-type gasifier products were utilized in these investigations. The results of varying temperature, pressure, flow rate and solids loading were correlated in terms of conversion as a function of space velocity and approach to methanol reaction equilibrium. In terms of the specific rates of methanol production, the autoclave system, as compared to the liquid-fluidized bed, is 1.5-2 times more productive at lower synthesis gas flow rates (1,000-

3,000 liters/kg cat-hr) and 2-3 times more productive at higher synthesis flow rates (5,000-6,000 liters/kg cat-hr). Productivity here is defined as mass of methanol produced per mass of catalyst per unit time.

A summary of the data for process variable scans with a Lurgi-type feed is presented graphically in Figure 3. Over the range of pressures and flow conditions investigated, the highest methanol conversions occur in the temperature range around 225°C (437°F). This is the same as the results obtained in the earlier liquid-fluidized program. At low temperature, catalyst reactivity is low, but the maximum obtainable equilibrium conversion is high. Thus, at very low flow rates, the conversion will be high, approaching equilibrium. However, at higher flow rates, the conversion will drop rapidly due to the low reactivity. On the other hand, at high temperatures, the maximum conversion is low and the activity is high. Thus, the conversion versus flow rate curve is fairly flat. This is reflected by the experimental data. Similar results are obtained with K-T-type gases.

An activity maintenance test, lasting 619 hours, was performed in the Stirred Autoclave Reactor utilizing a Lurgi-type feed gas. The catalyst activity remained essentially constant throughout the test, comparable to vapor phase fixed bed results, but at a higher productivity. Figure 4 contains a graphic summary of this test along with results of a similar one-month continuous run in the LPMeOH fluidized bed BSU and the early part of a seven-month fixed bed vapor phase reaction test. The data have been correlated on a cumulative feed gas basis. It can be clearly seen that there is a striking difference between the present autoclave results and the previous BSU fluid bed results. The autoclave results, at worst, indicate a very shallow rate of activity decline over the duration of the test, while there is a marked decline in activity for the three-phase fluid bed test. A comparison of the present autoclave results with the earlier fixed bed vapor-phase tests indicates that the activity behavior of the two systems is quite similar. This, in itself, is important. So much is known about effective catalyst life in the vapor phase, that to be able to show the activity behavior patterns for the autoclave rector are essentially equivalent to the vapor phase reactor, is a very positive finding for the liquid phase process.

LAPORTE LPMeOH PDU PROJECT DESCRIPTION

Objective

The overall objective of this program is to demonstrate the technical feasibility of the Liquid Phase Methanol (LPMeOH) process at the Process Development Unit (PDU) scale of operation.

Strategy

A key element of the program strategy is to use the existing Liquid Phase Methanation (LPM) process development unit. This DOE-owned, skid mounted unit has been transferred from Chicago, and is being refurbished and expanded for service as the LPMeOH PDU. The revamped PDU will be relocated and commissioned at Air Products' LaPorte, Texas facility. Air Products will supply synthesis feed gas to the LPMeOH PDU and operate the unit for a planned 15-month period. Chem Systems is performing the major portion of the laboratory support R&D and is providing technical management for the project. Air Products is performing complementary research. Air Products is providing overall program management and is responsible for engineering design, construction, and operation.

At LaPorte it is planned to test both the liquid-fluidized (ebullated bed) and the liquid-entrained (slurry) modes of operation. The liquid-fluidized mode will be run first as the present data base is larger and the original LPM unit was designed for this mode. Laboratory support of the liquid-fluidized mode consists principally of screening catalyst candidates in the Lab PDU at Fairfield prior to advancement of one catalyst candidate to LaPorte. A larger part of the research effort is directed at establishing the data base to support the liquid-entrained mode of operation. To establish this base, Air Products will synthesize and screen 23 new slurry catalyst candidates. Chem Systems will further screen the best Air Products catalysts. Chem Systems will also screen several catalysts prepared by outside manufacturers or developers. The final catalyst candidates will be screened in the Lab PDU at Fairfield prior to selection of one catalyst for advancement to LaPorte. A major early task in the Chem Systems effort is to modify the current liquid-fluidized Lab PDU to make it suitable for liquid-entrained operation. Chem Systems also has responsibility to optimize the in-situ catalyst reduction technique for slurry catalysts. Both Chem Systems and Air Products will work on data treatment and correlation. Chem Systems will correlate LPMeOH performance in terms of their empirical approach-to-equilibrium model, while Air Products will concentrate on developing a fundamental model to describe LPMeOH behavior.

Tasks and Phases

The program is divided into 11 major tasks which are phased to allow progress review and approval to proceed. The 11 major tasks are listed in Table 2. The tasks are phased as shown in Table 3. The schedule is shown graphically in Figure 5.

For the purposes of this review, it is convenient to consolidate tasks under the broad headings of Engineering (Tasks 2, 3, 4, 5, and 8), Operations (Tasks 6, 9, and 10) and Research (Tasks 7 and 11). The objectives of these broad activities are summarized below:

Engineering

A prime early objective of the engineering effort is the performance of a process engineering/design review and safety examination of the existing LPM unit at its original location in Chicago. Concurrent with this review is the development of detailed plans and specifications for the repair, modification, and expansion of the LPM unit to enable liquid-fluidized (ebullated bed) and, subsequently, liquid-entrained (slurry) methanol production. Permits will be obtained to install and operate the LPMeOH PDU at LaPorte. New equipment and systems which are needed will be purchased or leased, or obtained from DOE inventories.

The LPM unit has been transferred from Chicago to a vendor's facility for inspection. The unit will be renovated as necessary to become the LaPorte LPMeOH PDU. Following the preparation of the site the PDU is to be transferred and installed at LaPorte. There, final interconnections will be made and components tested. A final shakedown test will consist of an integrated run without catalyst. The engineering, procurement, renovation, installation, and shakedown effort is scheduled for completion by October 1983.

Operations

Operations of the LPMeOH PDU at LaPorte will be conducted over a 15-month period. Table 4 outlines the operating program. The PDU will operate first in the liquid-fluidized (ebullated bed) mode. The initial tests will assess the effect of the liquid-fluidized reactor distributor/offtake design. Following this, process variables will be evaluated in a series of "scans" to determine the effects of temperature, pressure, space velocity, gas superficial velocity, and feed gas composition. Two principal feed gas compositions will be tested, reflecting the principal applications of LPMeOH technology (all-methanol production and methanol/fuel gas coproduction). The 7-month liquid-fluidized operating campaign will culminate in a short-term continuous run of 45 days duration.

The liquid-entrained (slurry) mode of operation is scheduled to begin in June 1984. Process variable scans will be performed to determine the effects of temperature, pressure, space velocity, gas superficial velocity, feed gas composition, and slurry concentration. Again, two principal feed gas compositions will be tested. The liquid-entrained operating program will also end with a short-term continuous run of 45 days duration. The operating program at LaPorte is scheduled to conclude by January 1985.

Research

The catalyst effort in the Air Products' laboratories is outlined in Table 5. The Linwood laboratories will synthesize 23 new catalyst preparations for the liquid-entrained mode. The nature of the catalysts is indicated in Table 6. The Allentown laboratories will screen these catalysts using a fixed bed, Gas Phase Screening Reactor. This is a tubular reactor, 12.7 mm (0.5 in) diameter by 0.228 m (9 in) in length. From the gas phase results, 6 of the new catalysts will be selected for testing in a 1-liter Stirred Autoclave (Slurry) Reactor. These 6 catalysts will be gas phase reduced and performance tested in the slurry phase. From these results, 3 catalysts will advance for further testing. These 3 candidates will be liquid phase reduced (in-situ) and performance tested in the slurry phase. Finally, 2 of these catalysts will be advanced to Chem Systems' Fairfield laboratory. Prior to the start of screening of new catalysts, baseline data will be established for 2 commercial methanol catalysts in powder form. The lab program also includes a study of the effect of CO_2 content of the feed gas. There are also some "mini-life" tests of the best catalysts.

The modeling effort at Air Products is outlined in Table 7. The key three-phase hydrodynamic relationships important to scaleup of the liquid-entrained (slurry) reactor will be developed principally from an analytical review of available data and correlations. The fundamental model which will be developed will separate kinetic and mass transfer/hydrodynamic effects in the LPMeOH reactor.

The major elements in Chem Systems' Fairfield laboratory program are highlighted in Table 8. Screening of a liquid-fluidized catalyst was already accomplished in February-March of this year. While Air Products is preparing and screening new slurry catalysts, Chem Systems will in parallel be screening 7 slurry catalyst candidates from outside sources. The 2-liter Stirred Autoclave (Slurry) Reactor at Fairfield will be used to optimize liquid phase reduction (in-situ) techniques and performance test the catalysts. When the modified Lab PDU is ready for liquid-entrained operation in August 1983, 1 catalyst from the Chem Systems autoclave screening effort will be selected and run at that time. This run will provide early data to anticipate LaPorte slurry operation and will confirm that the modified Lab PDU is operable. Later the 2 Air Products-selected catalyst preparations will be tested in the Fairfield Stirred Autoclave Reactor. Following these screening tests, 1 additional catalyst will be selected for testing in the Lab PDU. When this second run in the Lab PDU is complete, 1 of the 2 catalysts tested in the Lab PDU will be advanced to LaPorte.

The Chem Systems modeling effort will concentrate on the approach-to-equilibrium which has been used successfully by Chem Systems in the past.

The flow of the catalyst screening work from the laboratories of Air Products to the laboratory at Chem Systems and finally to LaPorte is seen in Figure 6. This is a (very) simplified technical logic diagram for the program.

PROGRAM RESULTS AND STATUS

Engineering

During Phase I of the program, Air Products conducted the detailed engineering review of the originally proposed plan for installation of the LPMeOH PDU adjacent to Air Products' existing commercial facilities in LaPorte. The LPM unit was transferred from Chicago to Houston, and is now being refurbished and expanded for LPMeOH service. The review included: establishment of the LaPorte LPMeOH PDU process design basis and a process flowsheet; review of existing equipment from the LPM unit; evaluation of permit requirements and exemption from an environmental air permit; performance of a process hazards review; preparation of process equipment specifications, mechanical purchase specifications, a preliminary engineering flowsheet, and semi-final equipment arrangement and plot plan drawings compiling much of the review data. The latter engineering drawings and documents formed the basis for a detailed cost estimate for engineering, equipment, and renovation/installation of the LaPorte LPMeOH PDU. Table 9 gives a capsule summary of the engineering status. Highlights of results from the engineering program are given below:

Process Flowsheet

A simplified process flowsheet for the LaPorte LPMeOH PDU is shown in Figure 7. The scheme is relatively straight-forward and self-explanatory.

The detailed process design of the LPMeOH PDU and the inspection of the Chicago LPM unit revealed a number of modifications necessary in order to use the existing unit. The extent of these modifications lead to a different design approach than that originally envisioned. The original concept was to first revamp the LPM unit to permit liquid-fluidized (ebullated bed) operation, and later design add-on equipment to allow liquid-entrained (slurry) operation. The alternative approach which was adopted is labeled the "unified" design concept and is discussed in the modification comments below:

1. Feed/Recycle Compressor

The LPM unit did not have a Recycle Compressor. Early in the preparation of heat and mass balances for the LaPorte LPMeOH PDU, it became necessary to consider a Recycle Compressor. Recycle boost compression avoids imposing highly variable conditions to the final stage of feed gas compression or assuming the penalty in power costs of recompressing the recycle flow from inlet feed gas pressure.

Feed gas and recycle compression will be performed on a single reciprocating compressor frame having three cylinders. Two cylinders will perform the two stages of feed gas compression and the third will provide the necessary compression for the recycled process gas.

2. Reactor

The existing Reactor from the LPM unit is suitable for utilization in both the liquid-fluidized and liquid-entrained modes of operation required in the LaPorte LPMeOH PDU. This differs from the original concept which considered the addition of a new reactor skid as part of later liquid-entrained modifications.

3. Vapor-Liquid Separation

Due to concern with the oil-methanol separation originally planned for the Product Separator, the existing V/L Separator from the LPM unit was relocated to an intermediate point in the product gas cooling circuit to perform as a Secondary V/L Separator. It is calculated that 75% to 80% of the oil vapor leaving the Primary V/L Separator will be collected at this point.

A new, larger Primary Vapor/Liquid Separator was required for both the normal and maximum methanol production cases. This vessel was sized to accommodate the variable process oil volume from cold start through various hot operating modes, since it is impractical to impose open-loop control over the process oil inventory.

4. Feed/Product Exchanger

The Product Gas Coolers from the LPM facility could not accommodate the increased duty required for methanol production. For this reason, reactor product gas is precooled against incoming feed gas in a new Feed/Product Exchanger.

5. Steam Generating Circulating Oil Cooler Replacement With Oil Cooler

Based on operating experience with the LPM facility, it was known that the existing Steam Generating Circulating Oil Cooler was not appropriately sized for this scale of operation. This unit acted as a large heat sink and eventually had to be bypassed during operation in Chicago. Because the methanol synthesis reaction produces less of an exotherm than the methanation reaction, it was expected that this situation would worsen in the LaPorte LPMeOH PDU. There is also a lack of available boiler feed water at LaPorte. Therefore, it was necessary to substitute a different heat exchanger (Utility Oil Cooler) in this service.

6. Unified Design Concept

Due to the effects of the changes noted above and additional considerations, listed below, it was apparent that retaining the LPM piping arrangement was, in large part, inappropriate. These additional considerations were as follows:

- The Reactor and Primary Vapor/Liquid Separator were so tightly positioned within a structural steel frame that access to head flange areas for routine maintenance procedures was not possible.

- The various circulating oil pumps and filters were positioned such that inaccessibility not only hindered routine maintenance, but presented a hazard. This had been manifested in the LPM program by a disabling fire at Chicago.

- Catalyst reduction flow for LPMeOH service is preferred downflow rather than upflow as piped for the existing skidded equipment.

In light of these items, and the desirable technical benefits of a full consideration of all modes of operation for such a development unit during its initial design, the "unified design" concept was proposed and adopted. By considering both fluidized and entrained modes of operation at the start, this modification is being made in the most cost-effective manner.

Heat and Mass Balances

Air Products received basic process design information from Chem Systems, and developed this further. Based on the recommendations of Chem Systems, an awareness of potential commercial operating conditions, and the practical constraints of the existing LPM unit, a range of operating variables for the LaPorte LPMeOH PDU was defined, as given in Table 10.

The LaPorte LPMeOH PDU flowsheet was set up on Air Products' process simulator program. This program is capable of calculating the detailed point-by-point heat and mass balance for the flowsheet. A number of heat and mass balances were developed using the basic reactor mass balances provided by Chem Systems.

The final process design basis for the LaPorte LPMeOH PDU considers 8 design cases, 4 for the liquid-fluidized mode and 4 for the liquid-entrained mode. These were selected to provide a wide design range, but do not necessarily reflect "normal" operating conditions which will be run at LaPorte. The operating conditions for these design cases are given in Tables 11 and 12. As seen, the design methanol production rate ranges from 0.2 to 9.7 short tons per day. Normal operation is more likely between these extremes, and the PDU nominal capacity is considered to be 5 tons per day.

The principal feed gas compositions of interest are defined in Table 13. The Unbalanced Type feed (high CO content) is representative of Texaco gasification without shift, suitable for single-pass methanol production with coproduction of CO-rich fuel gas. This application integrates with a coal gasification combined cycle power facility where the CO-rich fuel gas is burned in gas turbines to produce electric power [Reference (5)]. The Balanced Type feed is representative of Texaco gasification with shift and CO_2 removal, suitable for all-methanol production with recycle in the LPMeOH synthesis loop. The Balanced Type feed definition here is not optimized, but is thought to be reasonable at this time. For example, the optimum CO_2 content is presently unknown. This information will be available later from the lab program, and could lead to revision of the Balanced Type composition.

Equipment

There are 32 main equipment items in the LaPorte LPMeOH PDU. Half of these items are from either the Chicago LPM unit or the Bruceton Synthoil facility. Process specification activity is complete on 31 items, mechanical specification work complete on 26, bid evaluation requirements satisfied on 21, and vendor drawings are in hand on 16 items. The Feed/Recycle Compressor and the Slurry Circulation Pump have been ordered, as well as 5 other equipment items.

Process Hazards Review

A formal process hazards review was conducted and the findings were reported. Among the events considered were: vessel rupture, seal failure of the Slurry Circulation Pump, process fluid and utility oil leakage, tube failure in the Slurry Heat Exchanger, tube failure in the compressor intercooler, methanol product storage and loading area spills, and slurry blockage in the flare header. The review confirmed the LaPorte LPMeOH PDU has been adequately designed to satisfy the safety requirements for this facility.

LPM Relocation/Inspection

The Chicago LPM unit was disassembled and shipped to a vendor shop in Houston, where the equipment was inspected and rehabilitated. Generally, all equipment items of interest will be reusable. The equipment has now left the shop and is on-site at LaPorte.

Research

Air Products Labs

1. Catalyst Preparation

Five new slurry catalyst preparations (Type I) were completed and analyzed. Four of these preparations were submitted for activity testing. Selected properties of these candidates are given in Table 14. The fifth preparation, Cu/Mg on alumina, was not released because it separated into two color fractions while screening.

2. Catalyst Screening and Testing

The Gas Phase Screening Reactor system was assembled and a shakedown test was successfully accomplished. Baseline runs are now in progress with ICI commercial methanol catalyst in powder form.

The Stirred Autoclave (Slurry) Reactor system was assembled and is presently undergoing final leak checking. This will be followed by shakedown and baseline runs with the ICI commercial methanol catalyst in powder form.

3. Modeling

Exploratory work on a fundamental model was performed using a computer version of a liquid phase Fischer-Tropsch reactor model developed by Professor W. D. Deckwer [Reference (6)]. This model was studied to determine its applicability to the LPMeOH process, and to identify the changes which would be required to adopt the F-T computer program to describe the LPMeOH reactor. It was determined that due to the major differences between the processes, substantial modifications to the Deckwer program model would be required. It was decided to alternatively modify an existing Air Products' model for a single-phase tubular dispersed-flow reactor. This work is presently underway.

The successful development of the dispersed-flow model requires an understanding of the LPMeOH intrinsic reaction kinetics. Data obtained from the Stirred Autoclave (Slurry) Reactors will be used to determine the kinetics. The analysis of these data will be performed with an existing (Air Products') two-phase CSTR model which has been modified. The modifications allow inclusion of the liquid/solid mass transfer resistance, and the methanol and water-gas shift reactions.

A literature survey was completed which identified kinetic expressions which have been used in the past to model the methanol synthesis reaction. Although the published expressions are principally for gas phase kinetics, they provide a starting point for the study of liquid phase kinetics.

Chem Systems Lab

1. Stirred Autoclave (Slurry) Reactor Tests

The program for optimizing in-situ reduction techniques for methanol catalyst powders suspended in inert hydrocarbon liquids continued. A series of evaluation tests were completed covering a wide range of in-situ reduction conditions with a single catalyst candidate. This program was successful in yielding a set of in-situ reduction conditions which activate the methanol catalyst powder to the same level as obtained from vapor phase reduction. A long-term activity maintenance test utilizing catalyst reduced by this in-situ procedure revealed that its time-dependent stability was also equivalent to vapor phase reduced material. Thus, it is now anticipated that catalyst for the liquid-entrained mode of the LPMeOH process will be reduced in the inert hydrocarbon liquid.

2. Liquid-Fluidized (Ebullated Bed) Catalyst Screening

As noted earlier, the Electric Power Research Institute contracted with United Catalysts, Inc. (UCI) to develop a more attrition-resistant liquid-fluidized catalyst for the LPMeOH process. United Catalysts completed their work in the Fall of 1981. Out of 68 catalysts prepared and tested by United Catalysts, two were identified as most promising candidates.

Since the properties of the two catalysts were similar, United Catalysts recommended testing one candidate. This catalyst is a Cu/Zn catalyst in the form of extrudates, with a diameter of 2.0 mm, an average length of 6.4 mm, and a side crush strength of 2.34 kg (5.16 lb).

Since a successful liquid-fluidized methanol program in the LaPorte LPMeOH PDU is dependent upon finding an attrition-resistant catalyst, a thorough screening of this catalyst candidate was undertaken in the Lab PDU at Fairfield during February-March 1982. The objectives of this run were two-fold:

- Determine whether this catalyst had better attrition resistance characteristics than those utilized in earlier EPRI-funded work.

- Determine the methanol productivity and activity maintenance characteristics of this catalyst candidate.

This investigation was conducted in a 540-hour run where, in addition to operating at steady conditions to satisfy the primary objectives of the experiment, a number of process variables were examined including feed gas composition, space velocity, reactor temperature, and pressure.

Depending upon the reactor conditions, the activity of this UCI catalyst was found to be 25-80 percent higher than the best prior liquid-fluidized catalyst, the 2.4 mm diameter mini-tablets, and approximately three times as resistant to catalyst activity losses over the short term. An overview of the catalyst activity in terms of CO conversion and apparent attrition in terms of settled bed height decay for the entire test is shown in Figure 8. Comparing end-of-run conversions with those obtained at 100 hours, which is after the initial period of catalyst hyperactivity, indicates an activity loss of only ten percent despite the inclusion of some process variable scans at relatively extreme conditions within that time. Catalyst attrition, as measured by settled bed height and by weight of catalyst recovered from the reactor at the end of the run, seems to be approximately 25-30 percent less than that observed with mini-tablets during earlier work. Approximately 67-74 percent of the catalyst charged remained in the reactor as finite-size extrudates at the end of the run. Most of the rest of the catalyst accumulated as micron-size particles in the downstream liquid vessels including the vapor/liquid separator and the circulating oil filters.

Despite the favorable statistics achieved in this run, the apparent attrition rate still seems high for this catalyst candidate to be considered as commercially viable, unless fines are recirculated. Additionally, some mechanical improvements to the Lab PDU might be possible, which would improve the hydrodynamics and, thus, decrease the apparent attrition rate.

3. Lab PDU Modifications

Progress was made on modifications to the Lab PDU at Fairfield to make it suitable for liquid-entrained operation. Specification, bid tab analysis, and purchasing activity continued. A number of the equipment items were ordered.

Future Events

In the upcoming months, the LaPorte LPMeOH PDU design effort will intensify as the emphasis shifts from process engineering to detailed mechanical, civil, and electrical engineering. All engineering and design specification activity is scheduled for completion by March 1983. The LaPorte site will have been made ready and nearly all equipment will either be in-hand or on-order.

In the Air Products' laboratories, 15 additional new slurry catalysts will be synthesized by March 1983. The Gas Phase Screening Reactor will have screened 10 of these catalysts, as well as 2 commercial catalysts for baseline purposes. Feedback from the gas phase results will be used to better focus on the remaining types of new catalysts to be prepared. The Stirred Autoclave (Slurry) Reactor will have provided baseline data on 2 commercial catalysts and quantitative data on the optimum CO_2 content for LPMeOH synthesis. Three new catalysts will have been selected for slurry phase testing, and one slurry test completed by March 1983. The fundamental modeling effort is targeted to be well along with a preliminary working model by February 1983.

In the Chem Systems' laboratories, the dominant effort will be performance of the Lab PDU modifications. Shakedown of the modified Lab PDU is scheduled to begin in May 1983. The screening and in-situ reduction testing of 3 more outside catalysts is expected to be completed by March 1983. The data acquisition system for the LaPorte LPMeOH PDU will be tested at Fairfield in early 1983, prior to shipment to LaPorte.

In summary, the upcoming months require the accomplishment of a number of significant program milestones. It is expected that the aggressive schedule and the demands of this research venture will continue to challenge the project team.

REFERENCES

(1) "Liquid Phase Methanol", EPRI Report AF-202, prepared by Chem Systems Inc. (August 1976).

(2) "Liquid Phase Methanol", EPRI Report AF-693, prepared by Chem Systems Inc. (May 1978).

(3) "Liquid Phase Methanol", EPRI Report AF-1291, prepared by Chem Systems Inc. (December 1979).

(4) "Liquid-Entrained LPMeOH, Advance Funded Work, Technical Data", Topical Report prepared by Chem Systems Inc. for the U.S. DOE under Contract No. DE-AC22-81PC30019 (December 1981).

(5) "Economic Evaluation of the Coproduction of Methanol and Electricity with Texaco Gasification - Combined-Cycle Systems", EPRI Report AP-2212, prepared by Fluor Engineers, Inc. (January 1982).

(6) Deckwer, W. D., et al, "Modeling the Fischer-Tropsch Synthesis in the Slurry Phase," IEC Proc. Des. Dev., Vol 21, No. 2, 231-241 (1982).

TABLE 1

CRUDE METHANOL PRODUCT COMPOSITIONS

	LURGI TYPE GAS	KOPPERS-TOTZEK TYPE GAS
Methanol	95.99 Wt. %	91.32 Wt. %
Methyl Formate	0.17	0.24
Ethanol	0.32	2.54
i-Propanol	tr	tr
Methyl Acetate	0.07	0.78
n-Propanol	0.14	1.23
C_4 Alcohols	0.23	1.43
C_5 Alcohols	0.33	1.40
C_6 Alcohols	0.06	0.55
Water	2.69	0.51

TABLE 2
LPMeOH PROGRAM TASKS

1. Program Planning
2. Engineering and Design Specifications
3. Equipment Procurement
4. LPM Unit Relocation/Inspection
5. LaPorte LPMeOH PDU Renovation, Installation, and Shakedown
6. Liquid-Fluidized (Ebullated Bed) Operation
7. Laboratory Support Program
8. Conversion of LaPorte LPMeOH PDU from Liquid-Fluidized (Ebullated Bed) to Liquid-Entrained (Slurry) Mode
9. Shakedown of Liquid-Entrained (Slurry) Operation
10. Liquid-Entrained (Slurry) Operation
11. Project Evaluation

TABLE 3
LPMeOH PROGRAM PHASES

Phase	Tasks	Schedule
I	1,2,4,7,11	28 Sept 1981 - 28 Mar 1985 (Mon 1-42)
II	3,5	1 July 1982 - 30 Sept 1983 (Mon 10-24)
III	6	1 Oct 1983 - 30 Apr 1984 (Mon 25-31)
IV	8	1 Jan 1984 - 31 Mar 1984 (Mon 28-30)
V	9,10	1 Apr 1984 - 31 Dec 1984 (Mon 31-39)

TABLE 4

OPERATING PROGRAM AT LAPORTE

LIQUID-FLUIDIZED (EBULLATED BED) MODE	**1 OCT 83 - 1 MAY 84**
• Distributor/Internals Test	2 Mons
• Process Variable Scans	2 Mons
- 1 Catalyst	
- 2 Principal Feed Gas Compositions	
- 25 Variable Conditions Each	
• Short-Term Continuous Run	3 Mons
- 45 Days	
LIQUID-ENTRAINED (SLURRY) MODE	**1 JUNE 84 - 1 JAN 85**
• Process Variable Scans	4 Mons
- 1 Catalyst	
- 2 Principal Feed Gas Compositions	
- 2 Slurry Concentrations	
- 25 Variable Conditions Each	
• Short-Term Continuous Run	3 Mons
- 45 Days	

TABLE 5
AIR PRODUCTS' LAB PROGRAM

• Gas Phase & Stirred Autoclave (Slurry) Reactors Assembled	1 July 82
• Baseline Data With Commercial Catalyst Powders	1 Feb. 83
• Preparation 23 New Slurry Catalysts	1 May 83
• Gas Phase Screening of 23 Catalyst	1 Aug. 83
• Slurry Phase Screening of 6 Catalysts	1 Sep. 83
• Slurry Phase Screening of 3 Catalysts	1 Dec. 83
• Advance 2 Catalysts to Chem Systems Lab	1 Dec. 83

TABLE 6

NEW SLURRY CATALYST PREPARATIONS

Type I:	Cu/Zn	Cu/Mg	Cu/Ce
30/70 Wt. Ratio, as Oxides	X	X	X
30/70 + 50 Wt% Al_2O_3	X	X	X
30/70 + 50 Wt% SiO	X	X	X
30/70 + 50 Wt% Cr_2O_3	X	X	X
30/70 + 50 Wt% ZnO	-	X	X

Type II:

Cu/Mo, Cu/W, and Cu/Ta

Type III:

Alloys of Types I & II

Type IV:

Raney Alloys of Types I & II Elements

TABLE 7
AIR PRODUCTS' MODELING

• Cold-Flow Data/Reactor Scaleup Evaluation	1 Jan. 83

FUNDAMENTAL MODEL

• Kinetic Rate Expressions	1 Sep. 82
• Prior Data Analysis	1 Dec. 82
• Model Refinement	1 Jan. 83
• Followup Data Analysis	1 Apr. 85

TABLE 8
CHEM SYSTEMS' LAB PROGRAM

• Liquid-Fluidized (Ebullated Bed) Catalyst Screening in Lab PDU	15 Mar. 82
• In-Situ Reduction Optimization, Outside Catalyst Screening in Stirred Autoclave (Slurry)	1 Mar. 83
• Mods to Lab PDU for Slurry Operation	1 May 83
• Stirred Autoclave (Slurry) Screening of First 6 Outside Catalysts	1 Aug. 83
• Lab PDU Run With 1st Slurry Catalyst Candidate	1 Oct. 83
• Stirred Autoclave (Slurry) Screening of 1 Additional Outside Catalyst + 2 Air Products' Catalysts	1 Mar. 84
• Lab PDU Run With 2nd Slurry Catalyst Candidate	1 Apr. 84
• Advance 1 Slurry Catalyst to LaPorte	1 Apr. 84

TABLE 9

LAPORTE LPMeOH PDU ENGINEERING STATUS

• Process Flowsheet	Complete
• Engineering Flowsheet	Rev. 1 issue, Aug. 82
• Heat & Mass Balances	Complete
• Process Equipment Specs	95% Complete
• Mechanical Equipment Specs	80% Complete
• Long Lead Equip. Purchase	Slurry Pump, Compressor Complete
• Equipment Arrangement	Prelim. Complete
• Plot Plan	Prelim. Complete
• Instrumentation & Valve Specs	In Progress
• Process Hazards Review	Complete
• LPM Unit Relocation/Inspection	Complete
• Permits	In Progress

TABLE 10

RANGE OF OPERATING VARIABLES FOR LAPORTE LPMeOH PDU

	Minimum	"Normal"	Maximum
Reactor Pressure, psig	500	700	900
(kPag)	(3,448)	(4,827)	(6,206)
Reactor Temperature, °C	220	250	270
(°F)	(428)	(482)	(518)
Liquid-Fluidized Space Velocity, liter/hr-kg cat.	1,000	2,500	4,000
Liquid-Entrained Space Velocity, liter/hr-kg cat.	2,000	6,000	10,000
Liquid-Fluidized Catalyst Loading, Settled Bed Height, ft	5	7	7
(m)	(1.5)	(2.1)	(2.1)
Liquid-Entrained Catalyst Loading, kg. cat/liter cold oil	0.1	0.2	0.4
(kg. cat/kg cat-oil slurry)	(0.11)	(0.20)	(0.33)

NOTES:

1. LaPorte LPMeOH PDU design pressure 1000 psig (6,896 kPag).
2. Liter at standard conditions 20°C (68°F), 14.696 psia (101 kPa).
3. Catalyst kg based on catalyst in oxide state, prior to reduction.

TABLE 11

DESIGN CASES FOR LIQUID-FLUIDIZED MODE:
OPERATING CONDITIONS FOR LAPORTE LPMeOH PDU

Case No.	Space Velocity 1/hr kg	Press, psig	Temp. °C	Catalyst Bed. Ht. ft	Catalyst Loading kg/l	%CO Conv. (Single pass)	%CO_2 Conv. (Single pass)	% CH_3OH Select.	% C_2H_5OH Select.	% CO_2 Select.	Reactor Feed lb-Mol/hr	Liq./Vapor Linear Velocity ft/sec	Fresh Feed lb-Mol/hr	Recycle Flow lb-Mol/hr	Purge Flow lb-Mol/hr	MeOH Product Rate ST/D
FB-4930.8	4,000	900	230	7	-	25	3	98	2	0	247	0.16/0.26	53	194	1	6.5
FL-3750.8	2,500	700	250	7	-	20	2	98	2	0	155	0.16/0.22	30	125	10	2.6
FK-2750.6	2,000	700	250	7	-	10	0	83	12	6	124	0.16/0.18	46	78	20	3.3
FK-1570.3	1,000	500	270	7	-	7	0	83	12	5	61	0.16/0.13	41	20	36	0.6

TABLE 12

DESIGN CASES FOR LIQUID-ENTRAINED MODE: OPERATING CONDITIONS FOR LAPORTE LPMeOH PDU

Case No.	Space Velocity l/hr kg	Press, psig	Temp. °C	Catalyst Bed. Ht. ft	Catalyst Loading kg/l	%CO Conv. (Single pass)	%CO_2 Conv. (Single pass)	% CH_3OH Select.	% C_2H_5OH Select.	% CO_2 Select.	Reactor Feed lb-Mol/hr	Liq./Vapor Linear Velocity ft/sec	Fresh Feed lb-Mol/hr	Recycle Flow lb-Mol/hr	Purge Flow lb-Mol/hr	MeOH Product Rate ST/D
EB-X954.8	10,000	900	250	-	0.4	30	3	98	2	0	350	0.20/0.40	77	273	0.8	9.7
EL-6762.7	6,000	700	260	-	0.2	24	2	98	2	0	107	0.16/0.16	27	80	10	2.3
EK-4762.7	4,000	700	260	-	0.2	12	0	83	12	5	72	0.16/0.10	22	50	10	1.6
EK-2571.0	2,000	600	270	-	0.1	7	0	83	12	5	18	0.16/0.04	18	0	17	0.2

TABLE 13

LAPORTE LPMeOH PDU PRINCIPAL FEED GAS COMPOSITIONS

(Texaco Gasifier)

	Methanol + Fuel Gas Coproducts	All-Methanol Product	
	Unbalanced Type Reactor Feed	Shifted Fresh Feed*	Balanced Type Reactor Feed*
H_2	34.8 mole %	66.4 mole %	54.9 mole %
CO	51.2	30.7	18.8
CO_2	13.1	2.0	4.9
CH_4, C_2H_6	0.1	0.1	2.1
N_2, Ar, Inerts	0.8	0.8	19.3
Total	100.0	100.0	100.0
H_2/CO	0.68	2.16	2.92
$\frac{H_2}{(CO+1.5CO_2)}$	0.49	1.97	2.10
$\frac{(H_2-CO_2)}{(CO+CO_2)}$	0.34	1.97	2.11

*Not optimized.

TABLE 14
SELECTED PROPERTIES OF NEW LPMeOH SLURRY CATALYSTS

Identification	974X1-3X1	1813JX1-1X1	975X1-4X1	1812JX2-21
Wt% CuO*	29.8	20.5	45.2	26.9
Wt% ZnO	68.9	30.1	-	-
Wt% Ce_2O_3	-	-	52.5	22.8
Wt% Na_2O	0.035	0.20	0.30	0.05
Support	-	Al_2O_3	-	Al_2O_3
Bulk Density, kg/L	0.473	0.551	0.649	1.004
Surface Area, m^2/gm	10	103	65	182
Ave. Particle size, microns	3.4	4.1	4.8	52

*All Wt%, Ignited Basis

FIGURE 1
THE LPMeOH PROCESS WITH A LIQUID-FLUIDIZED CATALYST REACTOR

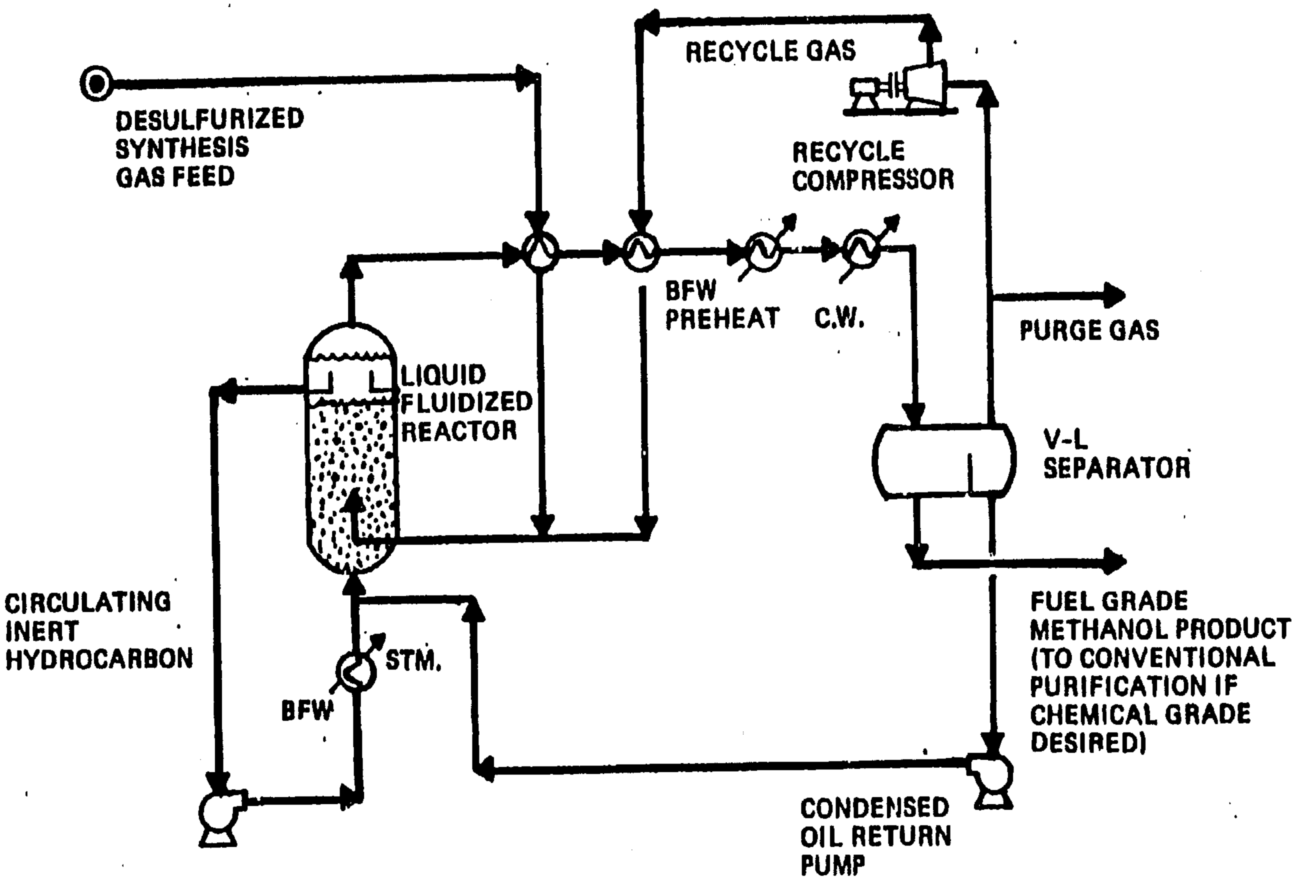


FIGURE 2
THE LPMeOH PROCESS WITH A LIQUID-ENTRAINED CATALYST REACTOR

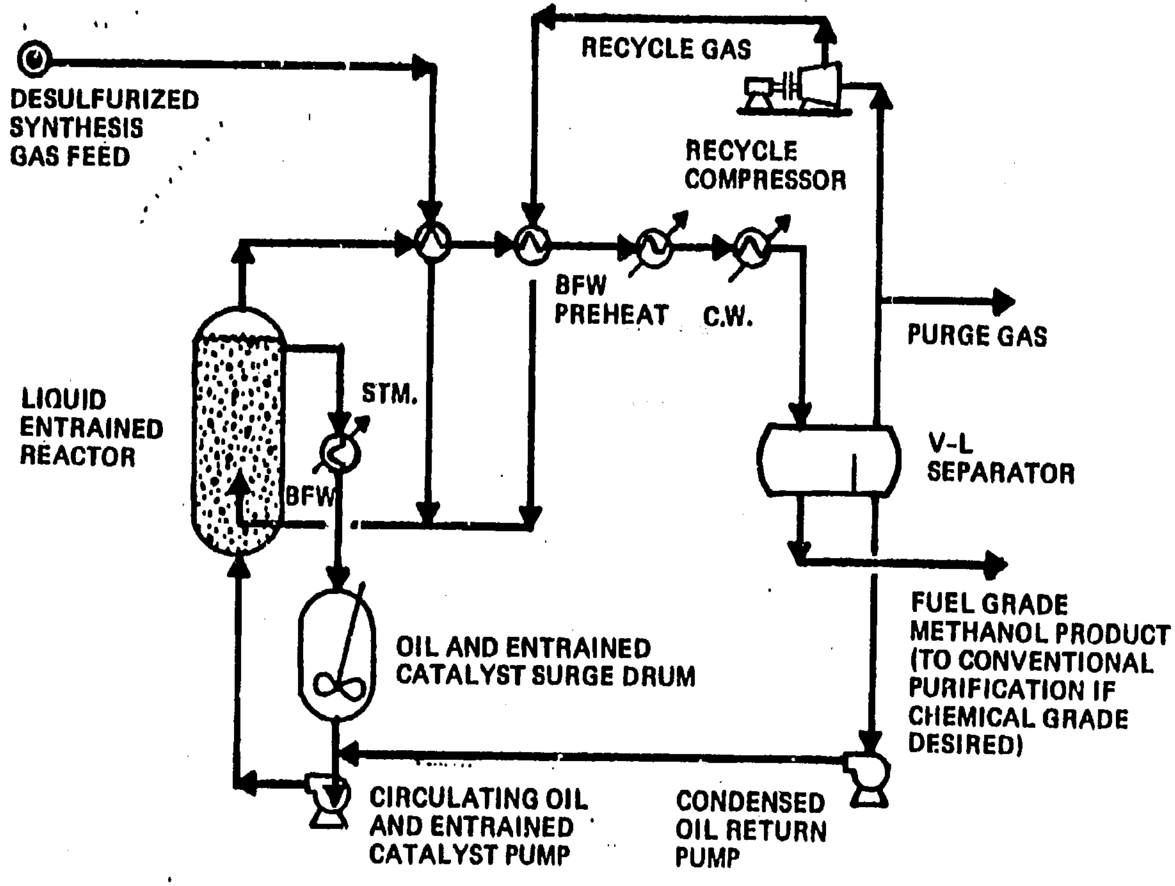


FIGURE 3

STIRRED AUTOCLAVE PROCESS VARIABLE SCANS WITH 2/1 H_2/CO GAS

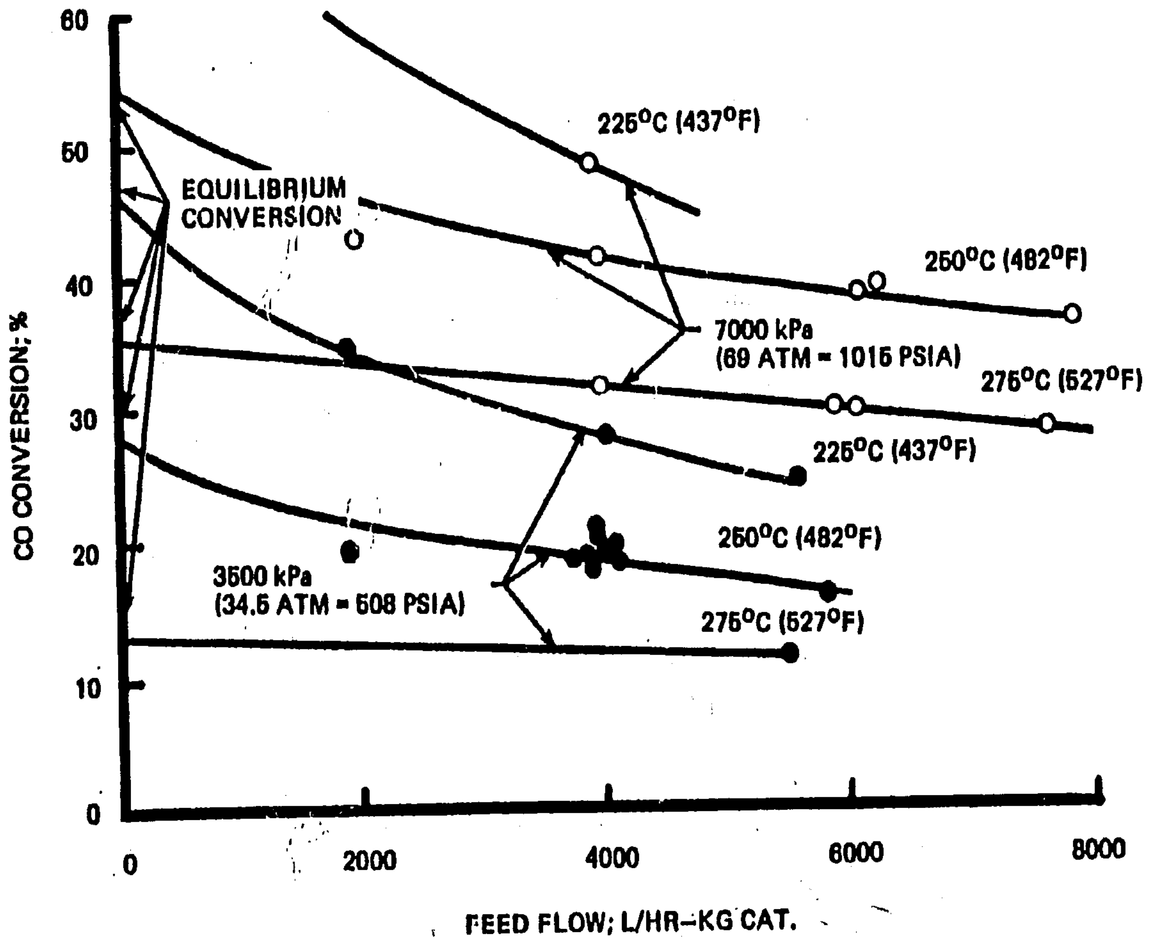
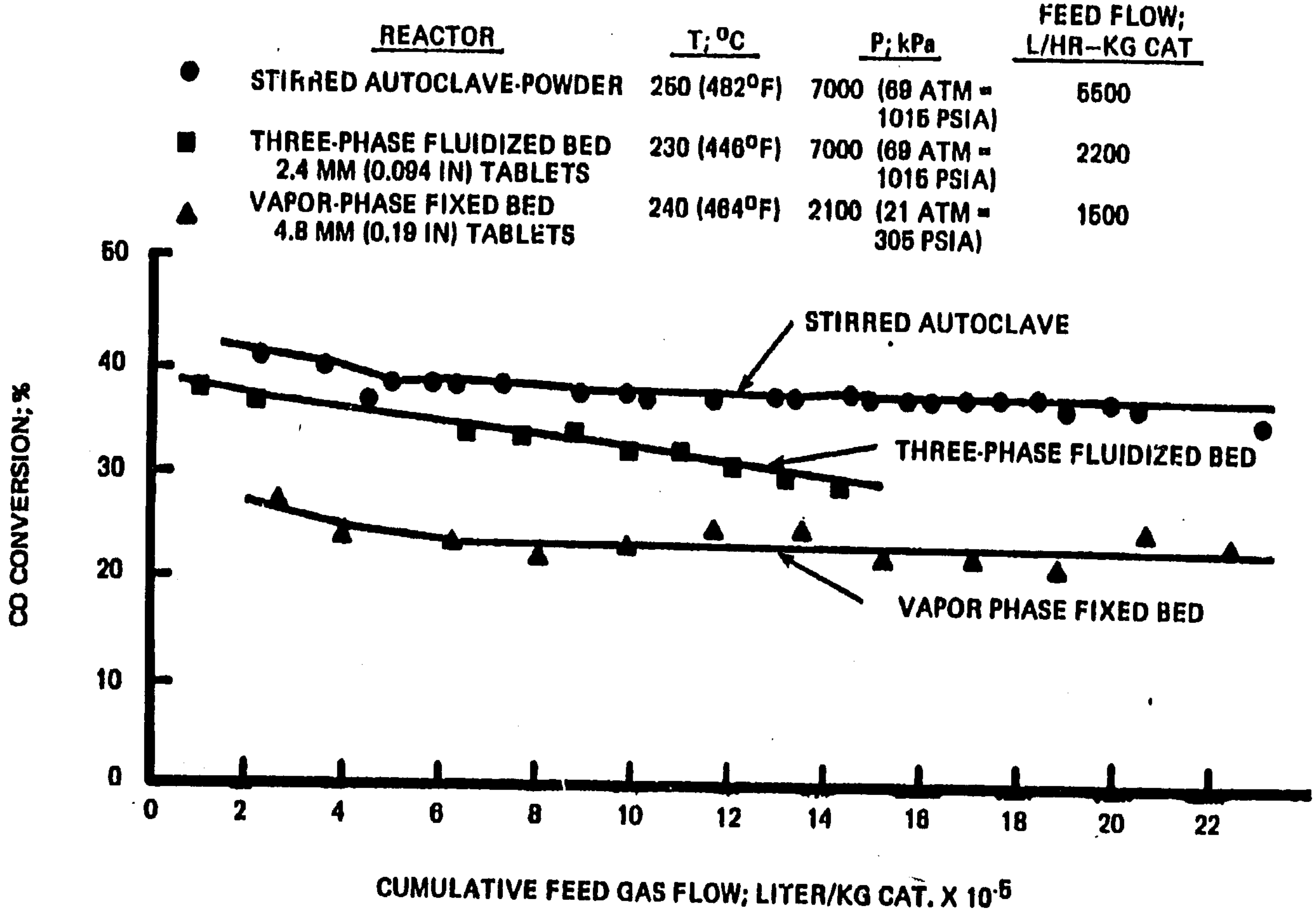


FIGURE 4
COMPARISON OF ACTIVITY MAINTENANCE RUNS WITH 2/1 H_2/CO FEED GAS



	REACTOR	T; °C	P; kPa	FEED FLOW; L/HR–KG CAT
●	STIRRED AUTOCLAVE-POWDER	250 (482°F)	7000 (69 ATM = 1015 PSIA)	5500
■	THREE-PHASE FLUIDIZED BED 2.4 MM (0.094 IN) TABLETS	230 (446°F)	7000 (69 ATM = 1015 PSIA)	2200
▲	VAPOR-PHASE FIXED BED 4.8 MM (0.19 IN) TABLETS	240 (464°F)	2100 (21 ATM = 305 PSIA)	1500

FIGURE 5
PROGRAM SCHEDULE

1 JUNE 1982

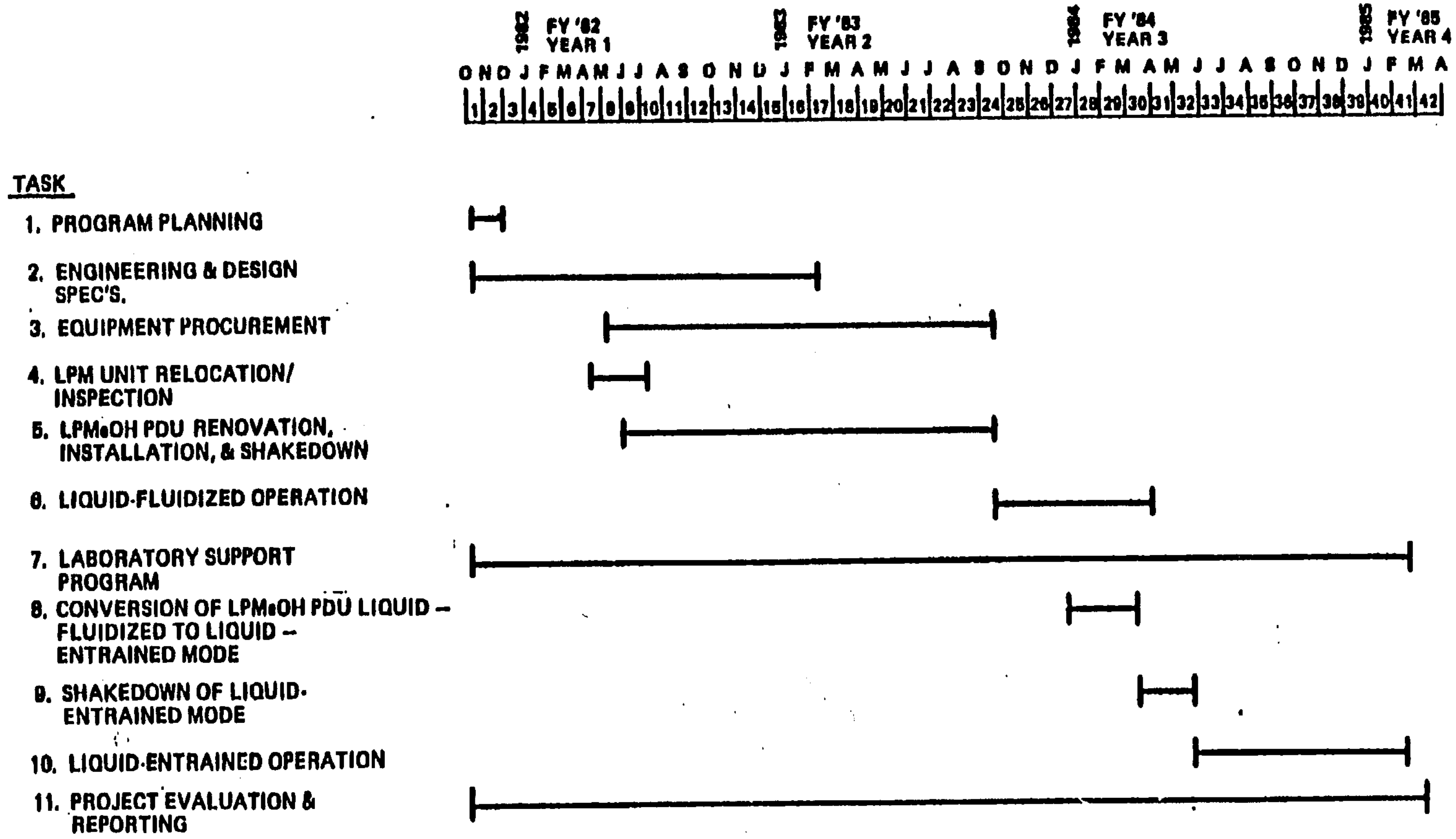


FIGURE 6
SIMPLIFIED TECHNICAL LOGIC DIAGRAM

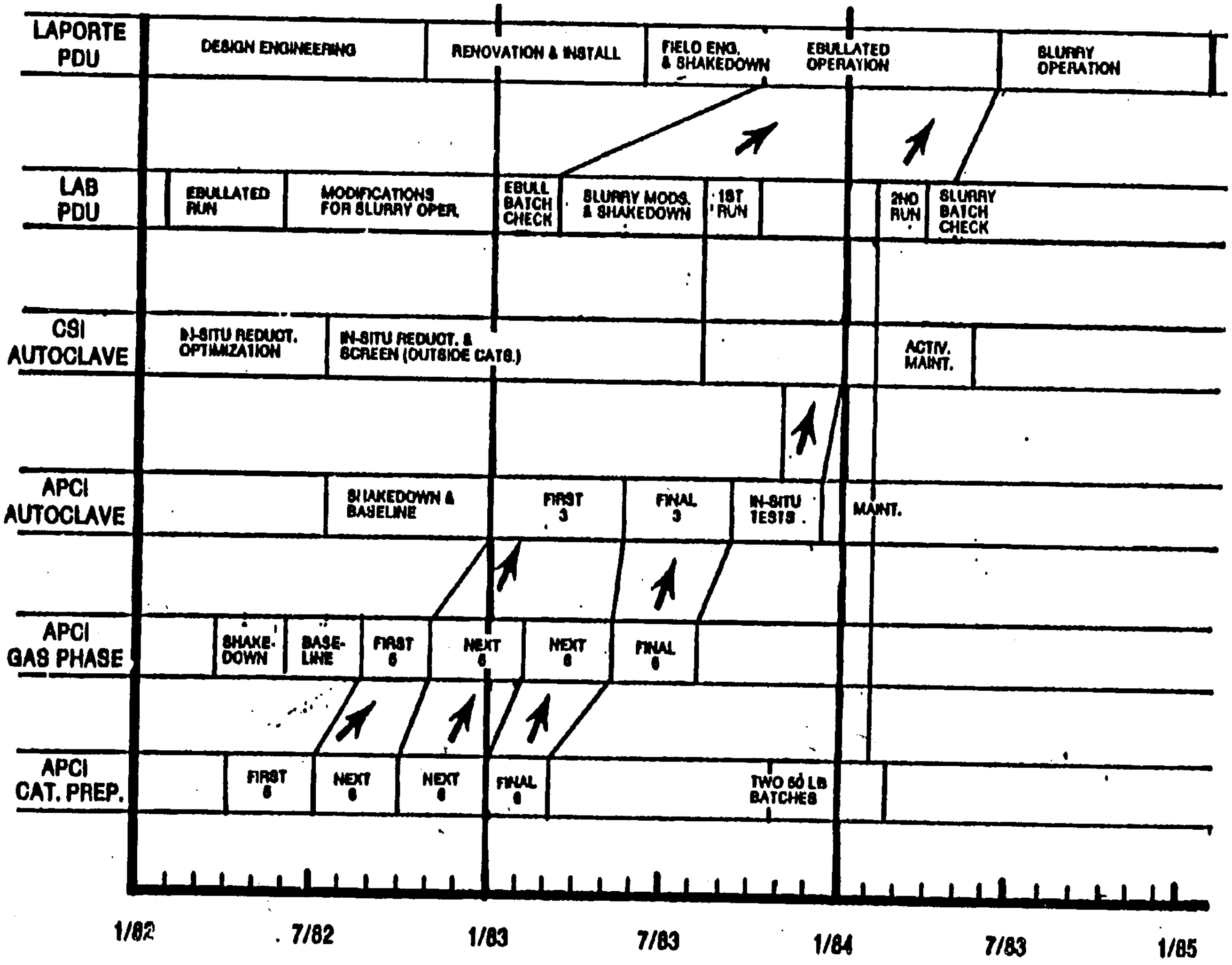


FIGURE 7

SIMPLIFIED PROCESS FLOWSHEET FOR LAPORTE LP MeOH PDU

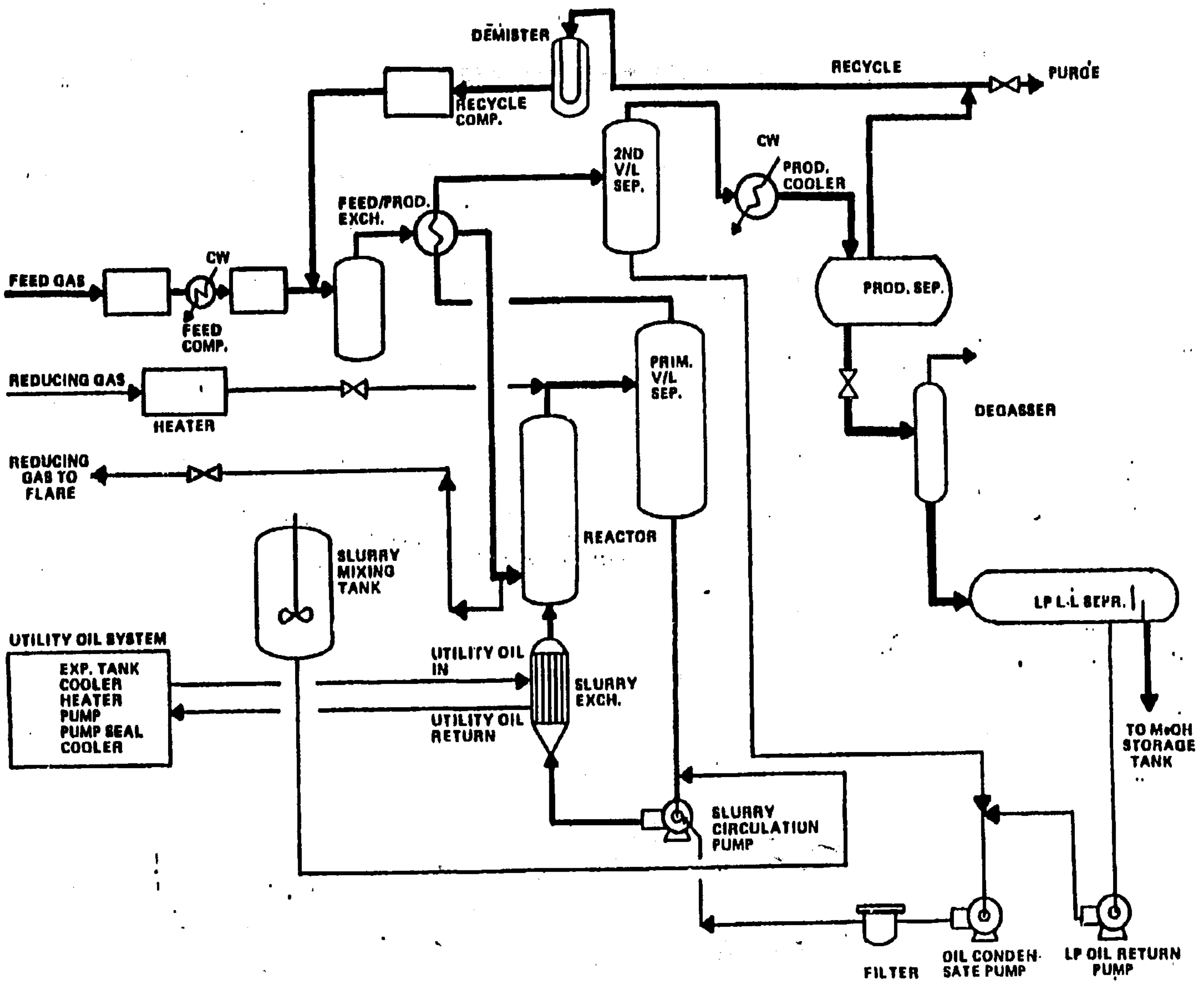


FIGURE 8
CATALYST ACTIVITY AND ATTRITION IN CSI LIQUID-FLUIDIZED LAB PDU WITH UNITED CATALYST

2/1 H_2/CO FEED GAS WITH 10% CO_2
250°C, 7000 kPa
3000 L/HR. - Kg CAT APPARENT SPACE VELOCITY
3.8 CM/SEC. SUPERFICIAL LIQUID VELOCITY