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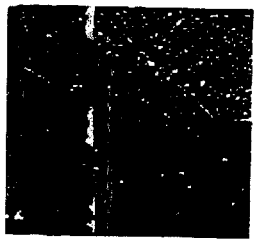

LaPorte Liquid-Phase Methanol Process Development Unit: Continued Operation in Liquid-Entrained Catalyst Mode

Prepared by
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REPORT SUMMARY

SUBJECTS: Coal-derived liquids / Gasification power plants

TOPICS: Methanol; Coproduction; Synthetic fuels; Gasification—combined cycles

AUDIENCE: Fuels and generation planners

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LaPorte Liquid-Phase Methanol Process Development Unit: Continued Operation in Liquid-Entrained Catalyst Mode

High reactor productivity is a key to improved methanol synthesis from coal gasification products. This effort to improve reactor volumetric productivity by increasing the catalyst concentration in the slurry showed that the LaPorte reactor has the mechanical ability to handle concentrated slurries. However, methanol productivity was below expectations.

BACKGROUND

Methanol synthesis in gasification–combined-cycle (GCC) power plants would give utilities greater flexibility in handling variable-load requirements. In September 1981, EPRI, DOE, and Air Products and Chemicals, Inc., jointly sponsored research to further develop liquid-phase methanol technology. Since then, the liquid-phase methanol process development unit (PDU) at Air Product's LaPorte, Texas, syngas facility has accumulated more than 2500 h of operating time. However, ineffective catalyst reduction hampered recent tests of the PDU's ability to operate at slurry concentrations above 40 wt%. Improvements in the catalyst reduction technique for concentrated slurries prompted the present experiments.

OBJECTIVES

To test the ability of the modified catalyst reduction procedure to produce 40-wt% activated catalyst slurry and to determine reactor performance at slurry concentrations above 40 wt%.

APPROACH

After preparing a batch of 41-wt% (oxide base) slurry using a commercial catalyst powder, researchers activated the slurry with the improved in situ catalyst reduction procedure. They then studied process performance and catalyst activity in response to a wide range of operating conditions. Parameters tested included carbon monoxide–rich and balanced reactor feed gases at 250°C and 5270 kPa; superficial gas and liquid velocities ranging from 12.2 to 15.6 cm/s and 1.8 to 6.5 cm/s, respectively; and slurry concentrations ranging from 33 to 47.4 wt%.

RESULTS

The modified in situ reduction technique successfully activated the 41-wt% slurry. The research showed that the PDU had the mechanical ability to handle catalyst slurries that were over 40-wt% solids. However, methanol

productivity was below that predicted by earlier laboratory work. Researchers concluded that gas-liquid mass transfer or inadequate gas and slurry mixing at slurry concentrations above 30-wt% solids limited methanol productivity. They suggested that improved reactor design and the use of alternative liquid media could enhance mass transfer.

EPRI PERSPECTIVE

Successful development of the liquid-phase methanol process would enhance the economic incentive for methanol synthesis in GCC plants. This research contributed to the development of the technology. The fact that the LaPorte PDU has the mechanical ability to operate at high-catalyst slurry concentrations indicates that it has the potential for improved volumetric efficiency. EPRI reports AP-4430 and AP-5049 describe earlier work under this project. EPRI report AP-3749 discusses the economic feasibility of the technology.

PROJECT

RP317-3
EPRI Project Manager: Norman Stewart
Advanced Power Systems Division
Contractor: Air Products and Chemicals, Inc.

Laporte Liquid-Phase Methanol Process Development Unit: Continued Operation in Liquid-Entrained Catalyst Mode

AP-5050
Research Project 317-3
DOE CONTRACT DE-AC22-85PC80007

Final Report, February 1987

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ABSTRACT

The LaPorte LPMEOH* Process Development Unit (PDU) was operated in July 1985 under Contract No. DE-AC22-85PC80007. This test (Run E-4) utilized catalyst powder F21/0E75-35 at an initial 41 wt% (oxide basis) solids concentration. This slurry was successfully activated using an improved in-situ reduction technique. Both CO-rich ($H_2/CO=0.69$) and balanced ($H_2/CO=2.89$) reactor feed gas were tested at 250°C (482°F) and 5,270 kPa (765 psia). Superficial gas and liquid velocities were varied from 12.2 to 15.6 cm/s (0.40 to 0.51 ft/s) and 1.8 to 6.5 cm/s (0.06 to 0.21 ft/s), respectively. Slurry concentration was also changed from 47.4 wt% to 33 wt%. The PDU achieved a 100% on-stream factor and was shut down after 231 hours of operation. Methanol productivity for all cases was less than the laboratory prediction. A mass transfer limitation and/or inadequate gas/slurry mixing are believed to exist in the present LPMEOH reactor system at elevated solids loadings (above about 30 wt%). Future work to identify other liquid media and reactor internals is planned within other tasks of this program.

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The LaPorte LPMEOH* Process Development Unit (PDU) was operated in July 1985 for the only test (Run E-4) of the Liquid Phase Methanol Process under Contract No. DE-AC22-35PC80007. A batch of 41 wt% (oxide basis) slurry using catalyst powder F21/0E75-35 was prepared. In-situ reduction was completed, and a CO-rich ($H_2/CO=0.69$) reactor feed gas was initially brought into the PDU. Methanol productivity at reactor conditions of 250°C (482°F), 5,270 kPa (765 psia), and 5,000 l/hr-kg space velocity was below the laboratory prediction. A solids density profile was also detected in the reactor.

Superficial gas and liquid velocities were varied from 12.2 to 15.6 cm/s (0.40 to 0.51 ft/s) and 1.8 to 6.5 cm/s (0.06 to 0.21 ft/s), respectively. Slurry concentration was also changed from 47.4 wt% to 33 wt%. A balanced gas ($H_2/CO=2.89$) was also tested. The PDU was shut down as planned after 231 hours of operation. An on-stream factor of 100% was achieved.

Methanol productivity for all cases in Run E-4 showed performance less than laboratory predictions; the approach to autoclave data varied from 58% to 83%. The relative improvement in performance and the disappearance of the solids density profile appeared to be directly related to the dilution steps. Liquid product analyses at the elevated solids levels indicated a higher distribution of C2+ alcohols and esters than in previous results. No poisons were detected on the catalyst Autoclave tests on slurry sample taken 33 hours into the operation and at the end of the run showed the expected activity, indicating that the catalyst had been properly activated.

Run E-4 demonstrated the mechanical ability of the LaPorte LPMEOH PDU to operate using concentrated slurries. The in-situ reduction technique was successfully applied to a 41 wt% slurry. It is concluded that a product methanol mass transfer limitation and/or inadequate gas/slurry mixing exist in the present LPMEOH reactor system at elevated solids loadings (above about 30 wt%). Future work under this contract will study alternate liquid media and reactor internals to improve the reactor performance.

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II. INTRODUCTION

Air Products and Chemicals, Inc., with the support of the U.S. Department of Energy (DOE), continues the research and development project initiated in September 1981 to further develop Liquid Phase Methanol (LPMEOH) technology. Chem Systems Inc., inventor of the technology, is performing as a key subcontractor in the program. Industrial participants are Air Products and the Electric Power Research Institute (EPRI).

LPMEOH technology has the potential to be a lower cost conversion route to methanol from coal than current gas phase processes. Laboratory work to date shows LPMEOH technology particularly suited to coal-derived synthesis gas rich in carbon monoxide. The LPMEOH process is capable of processing feed gas containing CO and H_2 in variable proportions, including those CO-rich proportions typical of modern, thermally efficient coal gasifiers without shift. The LPMEOH process can achieve high CO conversion per pass, because it readily accommodates the heat liberated by the exothermic methanol synthesis reactions.

A DOE-owned, skid-mounted process development unit (PDU) was relocated to Air Products' LaPorte, Texas syngas facility, refurbished, and expanded for service as the LPMEOH PDU. Operation and testing of the LaPorte LPMEOH PDU has included four runs conducted under contract No. DE-AC22-81PC30019 with operating time varying from 6 to 40 days. The unit has accumulated over 2,500 hours of operating time during which the process performed well with respect to catalyst productivity and activity maintenance.

The LaPorte PDU operation is supported by an extensive laboratory program principally conducted at Air Products' facilities in Allentown. The laboratory program includes catalyst screening, testing, development, preparation, and analysis of catalyst samples from the PDU during operation at LaPorte.

Table II-1 shows the range of operating variables for the LaPorte PDU. Two principal reactor feed compositions (Table II-2) used at LaPorte are:

A. Balanced Type--representative of synthesis gas from a Texaco gasifier with shift and CO_2 removal, suitable for total conversion to methanol via recycle of unreacted synthesis gas. This is the so-called "all-methanol" application.

B. CO-rich (Unbalanced) Type--representative of synthesis gas from a Texaco gasifier without shift and CO_2 removal, suitable for single-pass methanol production with a resulting CO-rich fuel gas. This is the "single-pass, co-product" application which is synergistic with the Integrated Gasification Combined Cycle (IGCC) process to make electric power.

These different reactor feed compositions are blended from hydrogen, carbon monoxide, nitrogen, and methane supplied by the adjacent Air Products synthesis gas facility. Carbon dioxide is trucked into the plant as liquid and stored on site.

Under the first contract with the DOE, four separate operating campaigns were made at the LaPorte LPMEOH PDU which utilized both the liquid-fluidized (ebullated-bed) and the liquid-entrained (slurry) modes of operation. Two separate campaigns (Runs E-1, April/May 1984 and E-3, May/June 1985) tested catalyst activity maintenance, while a six-day run (E-2) demonstrated the ability of the PDU to mechanically operate at slurry concentrations above 40 wt%. Results of these campaigns are documented in other reports (References 1, 2). The results of Run E-2 were below expectations from laboratory data, and subsequent research pinpointed improvements in the catalyst reduction technique for concentrated slurries. Based upon this information, a second PDU run at an elevated solids loading was made in July 1985. The results of this operation (Run E-4) are presented in this report.

TABLE II-1

LAPORTE LPMEOH PDU

RANGE OF OPERATING VARIABLES

	Minimum	"Normal"	Maximum
Reactor Pressure, kPa (psia)	3,550 (515)	5,270 (765)	6,310 (915)
Reactor Temperature, °C (°F)	220 (428)	250 (482)	270 (518)
Liquid-Entrained Space Velocity, l/hr-kg cat	2,000	6,000	15,000

TABLE II-2

LAPORTE LPMEOH PDU

FEED GAS COMPOSITIONS

(Based on Texaco Gasifier)

	Balanced	CO-rich
H_2	55%	35%
CO	19	51
CO_2	5	13
Inerts	21	1
	100%	100%
H_2/CO Ratio	2.89	0.69
Balance Ratio, $H_2/(CO + 1.5\ CO_2)$	2.08	0.50

III. LAPORTE LPMEOH PDU PROCESS DESCRIPTION

A simplified process flowsheet for the LaPorte LPMEOH PDU is shown in Figure III-1. The makeup synthesis gas is compressed from 1,030 kPa (150 psia) to the reactor pressure (between 3,500 and 6,310 kPa, 515-915 psia) by the 01.10 feed compressor. The compressed feed is mixed with recycle gas from the 01.20 recycle compressor and the combined flow is heated through the 21.10 feed/product exchanger.

The heated feed gas is introduced to the reactor bottom and mixed with the incoming catalyst/oil slurry in a distributor/plenum zone. The distributor system includes a bubble cap tray and gas and liquid spargers. A nuclear density gauge is mounted on a traversing mechanism outside the reactor; two- and three-phase hydrodynamics are determined from the output of this device. The slurry that circulates through the reactor is separated from the methanol product and unconverted synthesis gas in the 27.13 primary V/L separator. The slurry is recirculated to the bottom of the reactor via the 21.20 slurry heat exchanger by the 10.50 slurry circulation pump. The circulating slurry can be heated or cooled in the slurry heat exchanger to maintain a constant reactor temperature, depending on the current operating conditions. A utility oil system, which includes a utility oil expansion tank (28.53), utility oil circulation pumps (10.53), a utility oil cooler (21.40), and utility oil heaters (02.83, 15.40), is designed to provide indirect heating or cooling of the circulating slurry. The slurry circulation pump is a centrifugal pump driven by a variable-speed electric motor and equipped with a specially designed seal. The seal is provided with seal flush and a circulating barrier fluid to eliminate the possibility of leaks of the slurry to the atmosphere. A second nuclear density gauge is mounted on the discharge line from the slurry circulation pump. Readings from this instrument are used to calculate solids concentration in a gas-free environment.

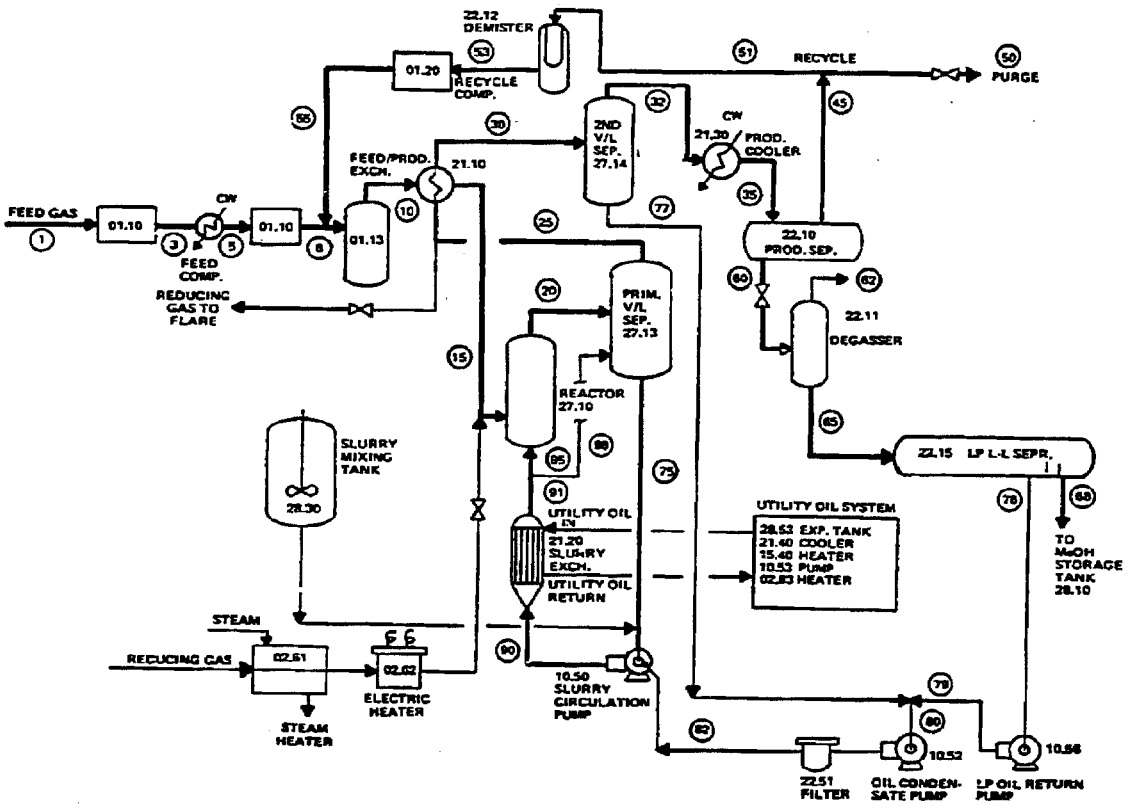

Figure III-1. Laporte Lpmeoh PDU, Simplified Process Flowsheet

The methanol product and unconverted synthesis gas exiting the top of the primary V/L separator are cooled against the incoming feed gas in the feed/product exchanger to 150°C (302°F), condensing most of the small amount of vaporized hydrocarbon liquid into the 27.14 intermediate V/L separator. The liquid is returned to the process as seal flush for the slurry circulation pump via the 10.52 oil condensate pumps. The uncondensed vapor is further cooled to about 40°C (104°F) by cooling water in the 21.30 product gas cooler. Condensed methanol product and a small quantity of inert hydrocarbons flow from the 22.10 product separator, are reduced in pressure, and the flashed gas vented at the top of the 22.11 degasser to the flare header. The methanol/hydrocarbon liquid passes through the 22.15 low-pressure liquid-liquid separator, where the hydrocarbon oil separates, and is returned to the process via the 10.56 oil return pump. The methanol product is sent to the 22.16 product day tank and batch-transferred to the 28.10 product storage tank.

The unconverted synthesis gas leaving the product separator is compressed and recycled to the front end of the PDU. A small purge stream is withdrawn to prevent the buildup of inerts in the reactor loop.

The oxide form of the catalyst is reduced (i.e., activated) with a mixture of hydrogen in nitrogen. This gas mixture is heated with the 02.61 reduction steam heater and the 02.62 reduction electric heater before its introduction to the reactor. The catalyst reduction actually takes place with the catalyst circulating in the reactor and slurry loop, but before the introduction of synthesis gas. This method is referred to as the liquid phase in-situ reduction.

IV. HIGH-SLURRY CONCENTRATION RUN (RUN E-4)

A. Objectives

A liquid-entrained operation (Run E-4) was conducted in the LaPorte LPMEOH PDU in July 1985. A commercially available catalyst powder (F21/0E75-35) was used; this was the second shipment of the same production batch of the catalyst that had been tested in previous LaPorte campaigns (Runs E-2, E-3). The objectives of Run E-4 were to demonstrate the revised in-situ reduction procedure for concentrated slurries and to obtain PDU performance data at a high solids loading.

B. In-Situ Reduction

A batch of 41 wt% (oxide basis) slurry using Freezene-100 oil and catalyst powder F21/0E75-35 was mixed in the 28.30 slurry prep tank. The slurry was pressure-transferred into the slurry loop, and the reducing gas was blended. Further details of the catalyst reduction for Run E-4 are presented in the Supplementary Volume of this report. No operational problems were encountered during reduction, and the nuclear density gauge located on the reactor indicated a flat solids density profile throughout the procedure. It was apparent from the analytical data (presented in the Results and Discussion section) that a successful in-situ reduction of a concentrated slurry had been completed.

C. Methanol Synthesis Operation

After the completion of catalyst reduction, the synthesis gas supplies were lined up, and the LaPorte LPMEOH PDU began operating under the first condition for Run E-4. The process parameters for this case (E-4A) are summarized in Table IV-1. During the initial 8 hours of operation, the reactor inlet gas composition was unsteady

during the change from reduction gas to synthesis gas. However, the observed methanol productivity was less than that expected from laboratory autoclave results. A plot of methanol concentration in the reactor effluent (mol%) as a function of time (Figure IV-1) illustrates that the reactor performance was declining rapidly throughout this interval. After 15 hours on synthesis gas, the presence of an axial solids density profile in the reactor was detected from the analysis of readings obtained from the nuclear density gauge (NDG). The NDG readings also indicated that regions of flow instability were present in the lower 1/3 of the reactor vessel.

As the run proceeded, the performance continued to deteriorate. As a result, process parameters were varied in an attempt to eliminate the solids density profile in the reactor and improve the catalyst performance. The list of all operating conditions is presented in Table IV-1; a run chronology is given in Table IV-2. The last parameter to be changed was the slurry concentration, since the ability to operate at high slurry loadings at the LaPorte LPMEOH PDU scale was an objective of Run E-4. Although a flat solids density profile was essentially restored at 40 wt% slurry concentration (Case E-4D), the slurry was further diluted to improve methanol productivity. However, at 34 wt% slurry concentration, the catalyst performance was still less than the autoclave prediction. Case E-4F was maintained for 104 hours in order to check for any loss of productivity over time. A balanced gas case (E-4G) was intended to test the effects of gas composition on reactor performance. The results will be presented and discussed in the next section.

TABLE IV-1

LAPORTE LPMEOH PDU

RUN E-4 OPERATING CONDITIONS

Case	Gas	P kPa (psia)	T °C (°F)	V_G cm/s (ft/s)	V_L cm/s (ft/s)	Slurry Conc. wt% ox	Hrs. at Condition
E-4A	CO-rich	5270 (765)	250 (482)	12.2 (0.40)	5.6 (0.18)	47	29
E-4B	CO-rich	5270 (765)	250 (482)	12.3 (0.40)	6.5 (0.21)	47	7
E-4C	CO-rich	5270 (765)	250 (482)	15.6 (0.51)	6.3 (0.21)	47	9
E-4D	CO-rich	5270 (765)	250 (482)	15.3 (0.50)	6.0 (0.20)	40	17
E-4E	CO-rich	5270 (765)	250 (482)	15.4 (0.51)	5.7 (0.19)	34	36
E-4F	CO-rich	5270 (765)	250 (482)	15.3 (0.50)	1.8 (0.06)	34	104
E-4G	Balanced	5270 (765)	250 (482)	15.4 (0.51)	1.9 (0.06)	34	29
							231

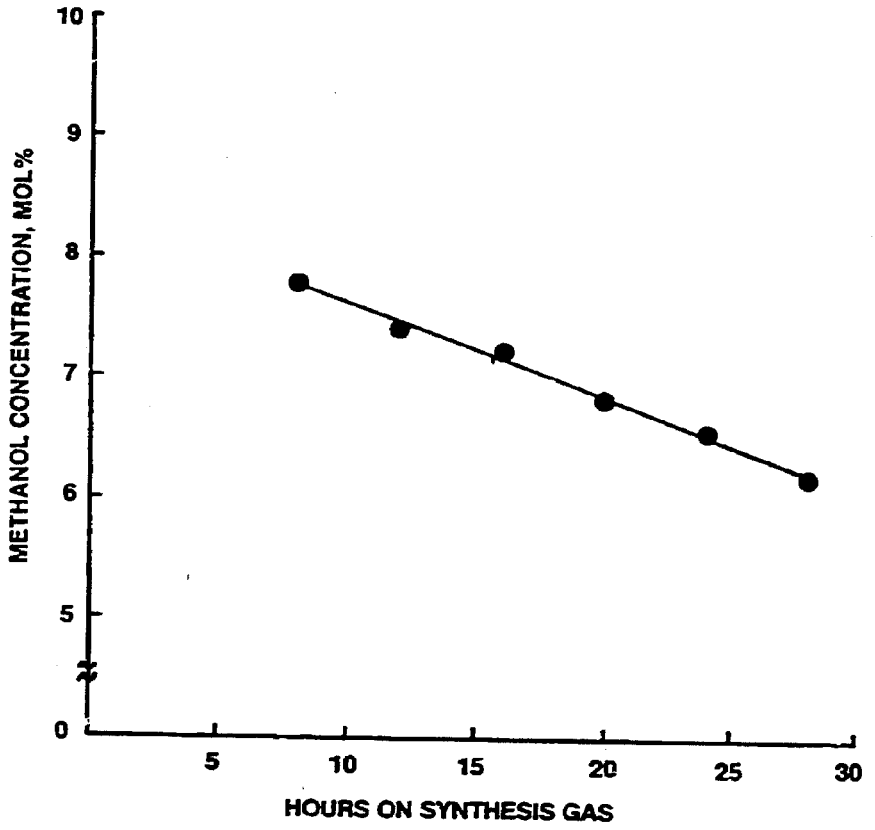

Figure IV-1. Laporte Lpmeoh PDU, Reactor Effluent Methanol Concentration-Case No. E-4A