DE00750387

LIQUID PHASE FLUID DYNAMIC (METHANOL) RUN IN THE LAPORTE ALTERNATIVE FUELS DEVELOPMENT UNIT

Topical Report

FINAL

Task 1: Engineering Modifications (Fluid Dynamic/Methanol Demonstration)

and

Task 2: AFDU Shakedown, Operations, Deactivation and Disposal (Fluid Dynamic/Methanol Demonstration)

Contractor:

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May 1997

Prepared for the United States Department of Energy
Under Contract No. DE-FC22-95PC93052
Contract Period January 1995 - December 1997

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ABSTRACT

A fluid dynamic study was successfully completed in a bubble column at DOE's Alternative Fuels Development Unit (AFDU) in LaPorte, Texas. Significant fluid dynamic information was gathered at pilot scale during three weeks of Liquid Phase Methanol (LPMEOH™) operations in June 1995. In addition to the usual nuclear density and temperature measurements, unique differential pressure data were collected using Sandia's high-speed data acquisition system to gain insight on flow regime characteristics and bubble size distribution. Statistical analysis of the fluctuations in the pressure data suggests that the column was being operated in the churn turbulent regime at most of the velocities considered. Dynamic gas disengagement experiments showed a different behavior than seen in low-pressure, cold-flow work. Operation with a superficial gas velocity of 1.2 ft/sec was achieved during this run, with stable fluid dynamics and catalyst performance. Improvements included for catalyst activation in the design of the Clean Coal III LPMEOH™ plant at Kingsport, Tennessee, were also confirmed. In addition, an alternate catalyst was demonstrated for LPMEOH™.

EXECUTIVE SUMMARY

A fluid dynamic study was successfully completed in a bubble column at pilot scale. Significant fluid dynamic information was gathered during three weeks of Liquid Phase Methanol (LPMEOH™) operations. In addition to the usual nuclear density gauge and temperature measurements, differential pressure (DP) measurements were made to better understand the hydrodynamics of the system. The DP measurements worked very well mechanically, without anticipated plugging problems, throughout the run. Gas holdup estimates based on DP measurements followed the same trends as those indicated by NDG readings. However, there appeared to be a systematic difference between gas holdup estimates from the two methods. The NDG-based gas holdups were 15-20% higher than the DP-based holdups. The difference can be explained if a radial profile for gas holdup exists in the bubble column with higher holdup in the center. Such a radial profile is expected to be prominent at the high velocities studied in this run.

Interesting differential pressure data were collected using Sandia's high-speed data acquisition system to gain insight on flow regime characteristics and bubble size distribution. Two types of statistical analyses of the fluctuations in the pressure data were performed, calculation of standard deviation and a Fourier spectrum analysis. The analysis suggests that the column was being operated in the churn turbulent regime at most of the velocities considered. High-speed differential pressure measurements were also used to perform dynamic gas disengagement (DGD) experiments. The DGD curves showed a single slope compared to two distinct slopes seen in low-pressure, cold-flow work corresponding to two classes of bubble sizes. A tracer study was conducted during the run to evaluate mixing in both gas and liquid phases at three different conditions. Results of the tracer study are included in a separate report (1).

High-velocity conditions were demonstrated during this run. Operation with a linear velocity of 1.2 ft/sec was achieved, with stable hydrodynamics and catalyst performance. Acceptable oil carry-over from the reactor was observed at this velocity. The magnitude of the velocity was limited only by the recycle gas compressor capacity, as the plant was designed for 1 ft/sec maximum velocity. Improvements for catalyst activation included in the design of the Clean Coal III LPMEOH™ plant at Kingsport, Tennessee, were also confirmed. Successful activations were achieved using dilute CO as reductant, a faster temperature ramp, and smaller gas flow, compared to previous "standard" activation procedures. An alternate catalyst was demonstrated for LPMEOH™. Expected catalyst activity, by-product formation, and stability were obtained with the alternate catalyst. Overall, the catalyst appeared very comparable to the baseline catalyst. Stable performance was obtained at both high and very low (turndown) velocity.

Dephlegmator testing was conducted at various conditions during the run. During the carbonyl burnout period, tests were performed with a two-phase system which eliminated catalyst fouling considerations. Further measurements were made with a three-phase system. The heat transfer performance of the dephlegmator continued to be lower than expected. In addition, the oil carry-over was significantly higher than expected at the operating temperatures. Although flooding was ruled out by calculations, variability in oil capture was still apparent. Further data analysis and additional tests are needed before a final decision can be made on inclusion of the dephlegmator in

commercial flow sheets. Approximately 64,300 gallons of methanol were produced during this demonstration, which will be useful for product testing.

INTRODUCTION

The Federal Energy Technology Center (FETC) at Pittsburgh sponsors an Indirect Liquefaction program as part of DOE's Coal Liquefaction program. The overall goal of the Coal Liquefaction program is to develop the scientific and engineering knowledge base with which industry can bring into the marketplace economically competitive and environmentally acceptable advanced technology for the manufacture of synthetic liquid fuels from coal. The specific area of interest for this project was to conduct a fluid dynamic study at pilot scale which would enhance the understanding of bubble column operation. This would improve design and trouble-shooting capabilities for commercial-scale bubble columns. Significant information exists in the literature for fluid dynamics of the bubble column in non-reactive, low-pressure, cold-flow systems. However, data for industrial scale reactive systems are lacking. The test run was conducted at DOE's Alternative Fuels Development Unit (AFDU) in LaPorte, Texas. The AFDU bubble column has been operated by Air Products and Chemicals in the past for slurry phase methanol, DME, water gas shift, Fischer-Tropsch, isobutylene and isobutanol synthesis. Slurry bubble columns provide improved performance for these reactions because they have significant heat effects.

OBJECTIVES

The main objective of this run was to perform a fluid dynamic study in a bubble column including:

(1) Differential pressure measurements along reactor height to estimate gas holdup, since nuclear density measurements for gas holdup are not feasible with large-diameter commercial reactors.

(2) Dynamic gas disengagement measurements during shutdown tests to understand flow regime and bubble size distribution.

(3) Radioactive tracer studies to evaluate mixing in both liquid and gas phases.

The study was conducted with liquid phase methanol (LPMEOH™) technology, for which the additional objectives described below were pursued:

(1) Demonstrate operation at high-velocity conditions (1.2 ft/sec) to improve commercial reactor design.

(2) Demonstrate improved reduction procedures developed for LPMEOH™ at Kingsport.

(3) Evaluate an alternate methanol catalyst.

(4) Produce methanol for end-use testing.

ENGINEERING AND MODIFICATIONS

Modifications were conducted in the AFDU to measure relevant fluid dynamic parameters during the operation:

(1) Two nozzles (N1 and N2) were added to the new high-pressure 27.20 reactor for differential pressure (DP) measurements, as well as liquid tracer injections. A schematic of the reactor is provided in Figure 1.

(2) Six new DP transmitters were added and connected to both the existing Distributed Control System (DCS) and a new high-speed data acquisition system from Sandia National Laboratories.

(3) A new stronger 8-curie Cs-137 source was installed for the reactor nuclear density gauge (NDG) to improve the resolution of the NDG reading by a factor of four, and the NDG was calibrated with N_2.

(4) The heater/cooler in the utility oil system were realigned to improve reactor temperature control by moving the heater downstream of the cooler. After a field inspection with Piping Design personnel, it was decided to install additional piping instead of physically moving the equipment. Installing the piping would be cheaper than moving the equipment, and the oil pump had enough capacity to handle the additional pressure drop caused by the piping. A process flow diagram for the utility system is provided in Figure 2.

(5) A sump and a pad were installed in the trailer area to enable better spill handling, and an overfill protection was installed for the trailers.

The data acquisition system was set up for methanol synthesis with the new measurements included.

Process Description

Changes were incorporated in the AFDU process flow diagrams to reflect the modifications; the new diagrams are shown in Figures 3 and 4. The operation of the plant is described as follows:

Hydrogen, carbon monoxide, carbon dioxide, and nitrogen are blended and compressed in the 01.10 feed gas compressor. This stream then mixes with recycle gas and additional hydrogen from a high-pressure pipeline to obtain the desired synthesis gas composition and flow. The reactor feed then passes through the 01.15 cooling water exchanger before compressing to approximately 1800 psig in the 01.30 booster compressor. The 01.34 aftercooler is used to control the inlet temperature to the 21.11 feed/product economizer, which preheats the feed against the reactor effluent. The mixed feed is further preheated against high-pressure steam in the 02.63 before the synthesis gas blend is introduced into the bottom of the new 27.20 high-pressure slurry reactor.

The synthesis gas flows upward through the slurry of catalyst and mineral oil as the reaction proceeds. The heat of reaction is absorbed by the slurry and removed through the internal heat exchanger, which also uses mineral oil as its heat transfer fluid. The product gas passes through the reactor freeboard with the unconverted synthesis gas, and the gross reactor effluent cools against the feed in the 21.11 economizer. Any traces of slurry oil entrained or vaporized in the effluent condense and are returned to the bottom of the reactor by the 10.52.02 pumps. The vapor leaving the 21.11 de-pressurizes across a valve to less than 1000 psig; chills against cooling water in the 21.30 hairpin exchangers; and passes into the 22.10 separator where liquid products (methanol, water, higher alcohols) collect. The liquids flash to near atmospheric pressure in the 22.11 degasser and collect in the 22.15 low-pressure separator before passing on to the 22.16 day tank and eventually a trailer for storage. To minimize the amount of gas sent to the flare, most of the synthesis gas leaving the 22.10 separator is recycled to the reactor. A small portion of this gas is purged to flare to prevent the buildup of inerts.

Bubble Column Reactor

The new 27.20 bubble column reactor for oxygenate synthesis measures 50 ft flange-to-flange and 18 in. inside diameter. Its design slurry level is 40 ft, with the remainder being vapor disengagement space. The reactor contains an internal heat exchanger consisting of twelve ¾-in. U-tubes occupying 8% of the reactor cross section. In addition, 13 thermocouples measure the longitudinal temperature profile at 4-ft intervals. A nuclear density gauge, mounted on an external hoist mechanism, spans the space occupied by the internal exchanger to measure slurry level and gas holdup. The design pressure of the reactor is 2000 psig at 700°F.

Analytical Setup

The analytical system was set up for methanol synthesis. Two GCs with Flame Ionization Detectors (FIDs) monitored hydrocarbon and alcohol concentrations in the reactor feed and effluent streams. Two other GCs with Thermal Conductivity Detectors (TCDs) measured H_2, N_2, CO, CO_2, H_2O, MeOH, and DME in feed, product, purge, and intermediate streams. A small amount of N_2 (approximately 1 mol %) was added to the reactor feed as an internal standard to verify flow measurements.

Hazards Review

A preliminary hazards review was conducted on 2 March 1995 for the modifications needed for this run. Facility Change Notice (FCN) forms were filled out and reviewed. A hazards review was conducted on 10 April 1995. FCNs on reactor differential pressure (DP) taps, flow totalizers, local HIC valves, trailer pad/sump and trailer overfill protection were approved.

Environmental Reviews

Radian Corporation was contracted to evaluate air permit requirements. Radian reviewed the proposed modifications and different operational options to determine whether we needed a new air permit exemption. No permit/exemption action was needed for the new reactor because its operation was covered by the 1994 exemption.

DEMONSTRATION RUN PLAN

Improvements in Catalyst Activation Procedure

Improvements applied for catalyst activation in the design of Clean Coal III LPMEOH™ plant at Kingsport, Tennessee, were included in the demonstration plan. The improvements were previously tested by R&D in an autoclave and found acceptable (see Appendix A for details). Activations for the two catalysts were conducted using dilute CO as reductant to minimize water formation and consequently avoid oil-water separation. Also a faster temperature ramp and smaller gas flow compared to previous "standard" activation procedures were used to reduce the cost of the reduction in commercial applications.

Alternate Catalyst Qualification

An alternate catalyst was first qualified by R&D in the laboratory. Activity, stability and slurry properties of this catalyst were evaluated and found equivalent to the baseline catalyst (see Appendix B for details).

Run Plan

Several meetings were held between Process Engineering, Operations and R&D to develop a run plan. It was decided to conduct two LPMEOH™ operations in the new reactor, a one-week run with the baseline catalyst and a two-week run with the alternate catalyst. The run conditions as adapted during the run are summarized in Table 1. Authorizations for the run are included in Appendix C.

RESULTS AND DISCUSSION

Preliminary results from this run were summarized earlier at the First Joint Power and Fuel Systems Contractors Conference in Pittsburgh (2).

Carbonyl Burnout

The reactor was loaded with oil and heated up on 30 May 1995 to start carbonyl burnout and two-phase dephlegmator testing. The carbonyl levels were extremely low during the entire burnout, i.e., 2-10 ppbv iron carbonyl and undetectable (<10 ppbv) nickel carbonyl. A summary of the carbonyl data is shown in Table 2.

During the burnout period, extensive testing of the 21.11 dephlegmator was also conducted. The dephlegmator had been added during the 1993 modifications of the plant as a possible replacement for the cyclone, the feed-product economizer and the vapor-liquid separator. During the 1994 isobutanol run, the dephlegmator did not perform as designed. Data were collected in the two-phase system during the current burnout period to rule out fouling. The dephlegmator continued to perform below expectation, indicating catalyst fouling was not the main reason for lack of adequate performance. The heat transfer performance of the dephlegmator was lower than expected. In addition, the oil carry-over was significantly higher than expected at the operating temperatures. The carbonyl burnout was completed at 19:00 on 2 June 1995. At the end of the burnout, the plant was cooled and drained in preparation for catalyst loading and reduction.

Slurry Preparation for Operations with Baseline Catalyst

A 40 wt % oxide catalyst slurry was mixed in the 28.30 Prep Tank. The Prep Tank was charged with 1767 lbs of Drakeol-10 oil at 09:00 on 2 June and 1179 lbs of standard baseline methanol catalyst at 08:00 on 3 June. Catalyst was taken from four drums of lot # 94/15730. The slurry was heated and agitated in the Prep Tank for two hours prior to transfer to the reactor. A detailed chronology for the entire run is given in Appendix D.

Baseline Catalyst Reduction

Catalyst reduction began at 14:30 on 3 June. The reduction gas (4% CO in N_2) was set at 12,500 SCFH with the reactor pressure at 67 psig (Run # A9). The heat up commenced at 15:45 and proceeded from 197 to 464°F at a rate of 15°F/hr, as shown in Figure 5. The temperature ramp was significantly faster than the previous "standard" ramp to save time in commercial applications.

The reduction under CO was quite rapid, as shown in Figure 6, and the total uptake peaked out very close to the theoretical maximum value of 2.82 SCF/lb oxide. This condition was obtained by about 360°F, or 12-13 hours on stream, which is an encouraging result for the Kingsport project. Reduction in the bubble column was faster compared to the autoclave. Despite the rapid uptake, the 27.20 internal heat exchanger was easily able to control temperature, and the ramp rate proceeded on schedule with no evidence of an exotherm. At 392°F, the reduction gas flow was reduced to 9,375 SCFH as planned to reduce oil loss from the reactor and conserve on nitrogen usage. Gas holdup during the reduction was close to expected, i.e., 27-30 vol % at

12,500 SCFH and 24 vol % at 9,375 SCFH. The catalyst concentration was in the 39-41 wt % range.

Process Variable/Fluid Dynamic Study with Baseline Catalyst

Reduction was completed at 10:00 hours on 4 June, and synthesis gas was brought into the reactor at 11:45. The initial data indicated typical hyperactivity of the catalyst. Problems were experienced with analytical communication boxes during the evening of 4 June. The problems were resolved and data were collected at the conditions of Run No. AF-R13.1 (Texaco gas, 7100 sl/hr-kg, 750 psig, 482°F, 0.85 ft/sec). A production rate of 12.1 T/D methanol was achieved, which was close to expected for fresh catalyst. Mass balance around the plant was excellent. Liquid analysis showed typical methanol product composition. Nuclear density gauge readings indicated a gas holdup of 50.5 vol %, higher than the expected holdup of 43 vol %. The catalyst concentration was estimated at 45.8 wt %. Data were taken for an additional mass balance period to examine initial catalyst aging. Steady operations continued, and conversion to methanol showed an expected drop from 16.5 to 15.5%. Nuclear density gauge readings indicated a gas holdup of 54.7 vol % and a catalyst concentration of 48.2 wt %. These results were very steady during this period, after both parameters showed measurable increases throughout the previous data period.

Conditions were changed to those of Run No. AF-R13.2 (Kingsport gas, 4000 sl/hr-kg, 735 psig, 482°F, 0.49 ft/sec) shortly after noon on 6 June. The plant operated very steadily for three days at expected performance. CO conversion of 49.6% and methanol production of 9.9 T/D were achieved. Liquid analysis showed stable methanol product composition comparable to that obtained in 1994 with Kingsport gas. Nuclear density gauge readings indicated a gas holdup of 42.7 vol % and a catalyst concentration of 41.9 wt %. During operation at these conditions, some methanol condensation was observed in the 27.14 oil separator. With almost 17 mol % methanol in the reactor effluent, the methanol dew point was 268°F. Hence, the temperature of the 27.14 was increased from 280 to 295°F to avoid methanol condensation.

A shutdown test was conducted at the end of Run AF-R13.2 to obtain a more accurate holdup estimate. Based on liquid level measurement using nuclear density gauge (NDG) with flow shutdown, gas holdup was calculated at 32.9 vol %. This compares with an estimate of 43.1 vol % based on NDG measurements and 36.5 vol % based on DP measurements. An attempt was made to measure the rate of drop of liquid level immediately after the gas was shut down using the NDG. However, this drop was too fast compared to the response of the NDG as well as the speed at which the NDG could be moved. DP data were collected during the shutdown test with the Sandia data acquisition system to help sort out the distribution of large bubbles vs. small bubbles.

After the shutdown test, the unit was brought on-stream with Texaco gas in an attempt to reach the conditions of Run AF-R13.3: 10,000 sl/hr-kg, 750 psig, 482°F, 1.2 ft/sec gas inlet velocity. With Texaco gas, the 01.20 recycle compressor reached its limit at 0.95 ft/sec. Operating at lower pressure helped little, since pressure drop through the plant increased. In order to achieve higher gas velocity, the feed composition was changed from Texaco gas to Kingsport gas. Higher methanol production was expected with Kingsport gas, which would lower the pressure drop in

the back end. A linear velocity of 1.13 ft/sec was achieved with this gas. The reactor performance was stable, with a production rate of about 18 T/D. The NDG readings showed higher fluctuations compared to those typically observed at lower velocities. A gas holdup of 55.8 vol % with a catalyst concentration of 48.7 wt % was estimated from the NDG readings. The DP measurements indicated a holdup of 44.9 vol % and a catalyst concentration of 39.2 wt %. Oil loss rate from the reactor was measured at this velocity. A modest loss rate of about 10 gph was estimated from level rises in vessels 21.11 and 27.14 downstream of the reactor.

At 00:45 hours on 11 June, the plant experienced a shutdown due to loss of compression. Belts on the motor for the two compressors broke, shutting down the plant six hours earlier than scheduled. Since we had enough data at this last condition with the baseline catalyst, it was decided to cool down the reactor in preparation for a turnaround to the alternate catalyst run. The slurry was drained directly from the reactor.

Slurry Preparation for Operations with Alternate Catalyst

A 40 wt % oxide catalyst slurry was mixed in the 28.30 Prep Tank. The Prep Tank was charged with 1766 lbs of Drakeol-10 oil at 08:00 on 10 June and 1178 lbs of the alternate methanol catalyst at 08:00 on 12 June. Catalyst was taken from 11 drums of lot # 022811. The slurry was heated and agitated in the Prep Tank for two hours prior to transfer to the reactor.

Alternate Catalyst Reduction

Catalyst reduction began at 14:30 on 12 June. The reduction gas (4% CO in N_2) was set at 12,500 SCFH, with the reactor pressure at 67 psig (Run # A10). The heat up commenced at 14:45 and proceeded from 193 to 464°F at a rate of 15°F/hr.

Initially, the reduction seemed a little slower than the previous baseline catalyst reduction. The rate increased later, and most of the uptake was completed by about 360°F (12-13 hours onstream, the same as the baseline catalyst). The total uptake peaked out close to the theoretical maximum value of 2.68 SCF/lb oxide (see Figure 7). Reduction in the bubble column was slightly slower compared to the autoclave. The 27.20 internal heat exchanger was easily able to control temperature, and the ramp rate proceeded on schedule with no evidence of an exotherm. At 392°F, the reduction gas flow was reduced to 9,375 SCFH as planned to reduce oil loss from the reactor and conserve on nitrogen usage. When the flow was reduced, the slow adjustment of CO concentration in the reduction gas caused the calculated uptake value to drift. Gas holdup during the reduction was slightly higher than expected, 29-34 vol % at 12,500 SCFH. The catalyst concentration was in the 41-42 wt % range.

Process Variable/Fluid Dynamic Study with Alternate Catalyst

Syngas flow to the reactor began at 11:00 on 13 June. The unit was fully lined out at the conditions of Run No. AF-R14.1 (Texaco gas, 7200 sl/hr-kg, 750 psig, 482°F, 0.84 ft/sec) by 18:00. The initial data indicated typical hyperactivity of the catalyst. The operational results were very similar to those seen previously during AF-R13.1 with the baseline catalyst. The production rate was 12.0 T/D of methanol, and the CO conversion rate was 16.4%. The mass balance around the plant was excellent. Liquid analysis showed typical methanol product composition with some very slight variations in the impurity mix. Nuclear density gauge readings indicated a

gas holdup of 49.6 vol %, and a catalyst concentration estimated at 45.4 wt %. Steady operations continued for another day at conditions of Run No. AF-R14.1. Compared to the baseline catalyst, the alternate catalyst showed even less decline in activity over its initial 24 hours of operation. The production rate decreased to 11.7 T/D of methanol, and the CO conversion rate dropped to 16.2%. Nuclear density gauge readings were identical to those of the previous data period. A shutdown test immediately following this run indicated 38.9 vol % gas holdup.

Conditions were changed to those of Run No. AF-R14.2 (Kingsport gas, 4000 sl/hr-kg, 735 psig, 482°F, 0.48 ft/sec) shortly after noon on 15 June. The plant ran smoothly at this condition for three days with stable catalyst performance. The alternate catalyst continued to perform very similarly to the baseline catalyst. The production rate was about 10 T/D methanol. Nuclear density gauge readings indicated a gas holdup of 37.8 vol %, and a catalyst concentration estimated at 39.6 wt %.

Due to lack of availability of adequate CO supply, the originally planned conditions of Run No. 14.3 (Kingsport gas, 10,000 sl/hr-kg, 735 psig, 482°F, 1.2 ft/sec inlet gas velocity) could not be achieved. Instead, it was decided to operate at another high-velocity condition which would consume less CO. Conditions were changed to 7,100 sl/hr-kg, 520 psig, 482°F and 1.18 ft/sec inlet gas velocity with Kingsport gas. The plant performed steadily at this condition. The catalyst performance was close to that expected. CO conversion was about 33% compared to a 2-CSTR expectation of 32.5%. Nuclear density readings had some fluctuations similar to those observed with the baseline catalyst at high velocity. A gas holdup of 50.4 vol % and a catalyst concentration of 45.6 wt % were estimated based on the nuclear density readings. DP measurements on the reactor indicated a holdup of 36.6 vol %. A shutdown test was conducted at the end of the mass balance period. Gas holdup of 36.6 vol % was measured during the shutdown test.

After the shutdown test, the unit was brought to the conditions of Run 14.4 (Texaco gas, 4,100 sl/hr-kg, 750 psig, 482°F, and 0.47 ft/sec inlet gas velocity). Catalyst activity was close to that expected. CO conversion was 17.5% compared to a 2-CSTR expectation of 17.7%. Increased levels of higher alcohols, methyl formate and methyl acetate were observed at this low space velocity condition. Nuclear density readings had no fluctuations, as the superficial velocity at this condition was low as well. A gas holdup of 42.9 vol % and catalyst concentration of 42.2 wt % were estimated based on the nuclear density readings. DP measurements on the reactor indicated a holdup of 33.3 vol %.

The operating conditions of the unit were changed to initial baseline conditions (Run No. AF-R14.5: Texaco gas, 7,200 sl/hr-kg, 750 psig, 482°F, and 0.83 ft/sec inlet gas velocity) on the morning of 21 June. Catalyst activity was very close to that observed initially at the same condition (Run No. AF-R14.1). The CO conversion dropped only slightly from 16.2 to 15.9%. Also, the by-product formation was down to the same level as that of Run 14.1 A gas holdup of 50.8 vol % and catalyst concentration of 46.5 wt % were estimated based on the nuclear density readings.

Further measurements were made on the 21.11 dephlegmator at the baseline condition. The heat transfer performance of the dephlegmator continued to be lower than expected. In addition, the oil carry-over was significantly higher than expected at the operating temperatures. Although flooding was ruled out by calculations, variability in oil capture was still apparent. Oil carry-over was higher at higher velocity. It is possible that oil was not coalescing and forming droplets efficiently. Further data analysis and additional tests are needed before a final decision can be made on inclusion of the dephlegmator in commercial flow sheets.

Tracer Study with Alternate Catalyst

ICI Tracerco personnel started setting up on 21 June for a 3-day tracer study. The study was started on 22 June at the baseline conditions (Run AF-R14.6: 0.83 ft/sec inlet velocity, 7200 sl/hr-kg, 750 psig, 482°F, Texaco gas). Detectors were set up at various locations outside the reactor, as shown in Figure 1. Sets of four detectors at 90° angles were set up at seven different heights. In addition, detectors were set up at the reactor inlet, the reactor outlet, the vapor space near the reactor top and the recycle feed line. During liquid injection, the detector at the reactor inlet was moved to the liquid injection nozzle.

A vapor residence time distribution study was initiated by injecting Argon-41 into the inlet gas line and monitoring its progress through the reactor. Excellent pulses were obtained at the inlet and sharp responses were observed at other locations. It appeared that the pulse moved through the reactor at a velocity that was equivalent to the superficial gas velocity. This was in contrast to the previous study during the 1993 isobutylene run, when the pulse appeared to move up more slowly.

Four injections of radioactive manganese oxide were made in the reactor slurry to study liquid phase mixing. Portions of radioactive Mn_2O_3 mixed in Drakeol-10 were injected at: (1) nozzle N2-4.5 in. from wall, (2) nozzle N2-wall, (3) nozzle N1-4.5 in. from wall, and (4) nozzle N1-wall. The data showed some of the tracer flowing in both an upward as well as downward direction. There appeared to be more downward movement at the wall.

Both gas and liquid injections were made at the two other conditions: low-velocity condition (Run AF-R14.7: 0.47 ft/sec, 4100 sl/hr-kg, 750 psig, 482°F, Texaco gas) and high-velocity condition (Run AF-R14.8: 1.18 ft/sec, 7100 sl/hr-kg, 520 psig, 482°F, Kingsport gas). A detailed analysis on data collected was conducted at Washington University in St. Louis. A topical report (1) and a paper (3) have been published on the results. Interpretation of the data based on an axial dispersion model (ADM), lumping different mixing mechanisms into a single dispersion coefficient, indicated an increase in both liquid and gas axial dispersion coefficients with superficial gas velocity. However, responses of detectors located at various column heights pointed to the inadequacy of the ADM to properly interpret the gas and liquid mixing. A two-dimensional model, which accounts for convective as well as turbulence effects, was proposed by the Washington University group. Initial results indicated that the model was able to predict both the radial and axial movement of the tracer in the column.

Following the tracer study, a very low-velocity condition (Run No. AF-R14.9: 0.15 ft/sec, 1270 sl/hr-kg, 750 psig, 482°F, Texaco gas) was operated briefly to evaluate the bed stability at the

expected minimum velocity. Hydrodynamic information was gathered at this condition to ensure the same turndown capability with this catalyst as we had with the baseline catalyst. All the fluid dynamic data such as nuclear density readings, differential pressure readings and reactor temperature appeared uniform and extremely stable, suggesting acceptable turndown capability. Following this test, the unit was shut down at 23:10 hours on 24 June. The plant was cooled overnight and liquid was drained on 25 June.

Catalyst Performance Comparison

Expected catalyst performance was obtained with both catalysts. The two catalysts are compared in Table 3 at two different conditions. Very similar CO conversion and methanol production rate are evident. Lower gas holdup was obtained with the alternate catalyst. CO conversions derived with both catalysts at different conditions are shown in Figure 8. In addition to the similarity of the two catalysts, the plot shows stable operation with the alternate catalyst, when conversion for R14.5 is compared with that for R14.1.

By-product data were analyzed more closely as increased levels of higher alcohols, methyl formate and methyl acetate were observed with the alternate catalyst at low space velocity conditions (Run No. AF-R14.4). The baseline catalyst was not operated at these conditions in the recent run; however, comparison of the two catalysts was available at two other sets of conditions: Run Nos. 13.1/14.1 and 13.2/14.2 (see Table 4). The by-product formation was very similar for the two catalysts at these conditions.

Operations at High Velocities

During both operations, attempts were made to operate at superficial gas velocities higher than the 1 ft/sec design velocity. Results obtained with the two catalysts at high velocity are presented in Table 5. A direct comparison cannot be made because the two conditions were different. However, some similarities are notable. During both runs, the NDG readings had high fluctuations compared to those typically observed at lower velocities, but average readings were stable. Also, the oil loss rate from the reactor was moderate. A superficial gas velocity of 1.13 ft/sec was achieved at 720 psig during the baseline run, limited by the capacity of the recycle compressor. The reactor performance was stable with a production rate of about 18 T/D. A modest loss rate of about 10 gph was estimated from level rises in vessels downstream of the reactor. During the run with the alternate catalyst, a superficial gas velocity of 1.18 ft/sec was achieved at a lower pressure (520 psig). The limitation for this case was CO supply. The plant performed steadily at this condition, with expected catalyst performance. CO conversion was about 33% compared to a 2-CSTR expectation of 32.5%. The two runs at high velocities demonstrated that we had not reached slurry reactor limitations at 1.2 ft/sec, and that operations at higher velocities were possible.

Mass Balance

Because some of the flow meters were not accurate, known chemistry was used along with measured gas concentrations to calculate correction factors for those flow rates. A run time table, which provides a cross-reference between run numbers, actual times and on-stream times, is given in Table 6. Mass balances for each data period are included in Appendix E. The elemental balance generally ranged from 98 to 102%, while the mass balance ranged from 99 to 101%. A

residual oil content of 0.2% for the methanol liquid was assumed initially, and this was later confirmed by analysis of various samples (see Appendix F).

Gas Holdup Estimates

The differential pressure (DP) measurements appeared to be working well mechanically throughout the run, without the anticipated plugging problems. The measurement locations on the reactor are shown in Figure 1. Gas holdup estimates based on DP measurements followed the same trends as those indicated by nuclear density gauge (NDG) readings. However, there appeared to be a systematic difference between the two estimates. To check the accuracy of the DP readings, the DP transmitters were calibrated at the end of the run by filling the reactor with water. The calibrations resulted in only minor corrections in the zero and the span. The NDG-based gas holdups remained 15-25% higher than the DP-based holdups (37-56 vol % vs. 28-48 vol %; see Figures 9-10 and Table 7). Holdups based on shutdown tests conducted at three different conditions compared well with the DP-based holdups. The holdups based on shutdown tests were estimated using liquid levels measured by NDG before and after the shutdown tests. The NDG is considered highly accurate in measuring liquid levels. The estimated holdups from correlations based on NDG data at low velocities also had a better match with holdups from DP data. The systematic error in the densitometry readings can be linked to the measurement technique, which relies on data obtained at a single chord (diameter). This method would be accurate if the gas holdup were uniform radially. However, a radial distribution of gas holdup is generally observed in two- and three-phase flows, such that gas holdup is highest at the centerline and decreases toward the wall (4, 5). For such a profile, the data averaged along the diameter would give too much weight to the area with highest gas holdup at the center, and therefore would overestimate the average gas holdup. This appears to be the case for the gamma densitometer measurements at the AFDU. The effect was more prominent during this run, since most of the operations were carried out at higher velocities.

Axial variations in gas holdup based on NDG are provided in Figures 11 and 12. The gas holdup showed an initial decrease and then an increase at the top, which is consistent with the profiles observed during the 1994 isobutanol run in the same reactor (6). The initially high gas holdup may have been a sparger effect, and the holdup decreased as the flow developed. There could also have been an effect of the gas encountering the heat exchanger tubes and their support. The holdup increase at the top is probably due to gas disengagement.

Statistical Analysis of Gas Holdups and Dynamic Gas Disengagement

The high-speed data acquisition system installed by Sandia National Laboratories personnel to monitor the DPs on the reactor column was operated throughout the run. Detailed analysis on data collected was conducted by Sandia personnel. A report written by Kim Shollenberger and Timothy O'Hern discussing the results is attached in Appendix G. Statistical analysis was performed on the gas holdup data to discern flow regime transitions. The standard deviation of the gas holdup increased with velocity as expected, possibly showing that the largest gas bubbles are increasing in size and/or number. A frequency spectrum obtained from Fourier transform analysis of the DP data at high velocity showed a wide band of frequencies, but also the existence of a discernible peak at about 0.05 Hz, suggesting that a large pocket of gas either enters or leaves the region between the pressure nozzles every 20 seconds. The strongest frequency was

found to increase with velocity, and there did not appear to be a dominant frequency for velocity less than 0.15 m/sec. The beginning of the appearance of a dominant frequency is an indication that large bubbles are present and that a transition to churn-turbulent flow has begun. Thus, the flow appears to be in the churn-turbulent regime for all conditions, except for the two low-velocity cases. A dynamic gas disengagement analysis was performed on DP data collected during the shutdown tests to determine bubble size distributions. High-speed differential pressure measurements were also used to perform dynamic gas disengagement (DGD) experiments. The DGD curves showed a single slope compared to two distinct slopes seen in low-pressure, cold-flow work, corresponding to two classes of bubble sizes. One explanation for the difference in the curves could be that the gas shutdown at the AFDU was too slow to measure bubble classes.

Reactor Temperature Control

The heater/cooler realignment in the utility oil system was tested during the run to check for any improvement in reactor temperature control. Valves were switched during Run 13.2B to shift the 15.40 and 02.83 heaters downstream of the 21.40 and 21.20 coolers (see Figure 2). Reactor control temperatures before and after the switch are shown in Figure 13. As expected for methanol synthesis, the temperature control was quite good with the old alignment, with a standard deviation of 0.27°F. The new alignment showed an improvement in control, with a standard deviation of 0.15°F. Significantly higher improvement is expected in Fischer-Tropsch operations, which involve higher heat effects and reactions that are not equilibrium limited.

CONCLUSIONS AND RECOMMENDATIONS

- A fluid dynamic study was successfully completed in a bubble column, gathering significant information at pilot scale. Differential pressure (DP) measurements made to better understand the dynamics of the system worked very well mechanically throughout the run, without the anticipated plugging problems.

- Gas holdup estimates based on DP measurements followed the same trends as those indicated by nuclear density gauge (NDG) readings. However, the NDG-based gas holdups were 15-20% higher than the DP-based holdups. The difference can be explained if a radial profile for gas holdup exists in the bubble column, with higher holdup in the center. Such a radial profile is expected to be prominent at the high velocities studied in this run.

- Differential pressure data collected using Sandia's high-speed data acquisition system provided insight on flow regime characteristics and bubble size distribution. Standard deviation and a Fourier spectrum analysis of the DP fluctuations suggested that the column was being operated in the churn turbulent regime at most of the velocities considered. Dynamic gas disengagement (DGD) experiments conducted during the run showed DGD curves with a single slope compared to two distinct slopes seen in low-pressure, cold-flow work corresponding to two classes of bubble sizes.

- Operation with a superficial gas velocity of 1.2 ft/sec was achieved with stable fluid dynamics and catalyst performance. Acceptable oil carry-over from the reactor was observed at this velocity.

- Improvements included for catalyst activation in the design of the Clean Coal III LPMEOH™ plant at Kingsport, Tennessee, were also confirmed. Successful activations were achieved using dilute CO as reductant, a faster temperature ramp, and smaller gas flow, compared to the previous "standard" activation procedure.

- An alternate catalyst was demonstrated for LPMEOH™. Expected catalyst activity, by-product formation, and stability were obtained with the alternate catalyst. Overall, the catalyst appeared very comparable to the baseline catalyst. Stable performances were obtained at both high and very low (turndown) velocities.

- Approximately 64,300 gallons of methanol were produced during this demonstration, which will be useful for end-use testing.

FUTURE PLANS

It is recommended that the fluid dynamic measurements be continued during subsequent AFDU operations. High-speed data, as well as tracer injections, will be particularly interesting in a Fischer-Tropsch system, where gas contraction is greater and there is a net liquid velocity if external filtration is used.

ACKNOWLEDGMENTS

The development work described here was supported in part under a contract (No. DE-FC22-95PC93052) from the United States Department of Energy. The author would like to thank Edward Heydorn, David Hanauer, and the Air Products operators for efficient operation of the pilot plant. Chris Chen, VanEric Stein, Elizabeth Schaub, and Mina Mazdai provided 24-hour process engineering coverage throughout the operation. We received laboratory data and valuable technical assistance from Bernard Toseland and X. D. Peng, while Dean Chin-Fatt and Robert Staskowski provided analytical support. Kim Shollenberger and Tim O'Hern from Sandia National Laboratory acquired and analyzed the high-speed data from the run.

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