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DEVELOPMENT OF ALTERNATIVE FUELS FROM COAL-DERIVED SYNTHESIS GAS

Draft Topical Report

Demonstration of a One-Step Slurry-Phase Process for the Co-Production of Methanol and Isobutanol

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DEMONSTRATION OF A ONE-STEP SLURRY-PHASE PROCESS FOR THE CO-PRODUCTION OF METHANOL AND ISOBUTANOL

Executive Summary

Liquid phase co-production of methanol and isobutanol (LPIBOH) was demonstrated at DOE's Alternative Fuels Development Unit (AFDU) in LaPorte, Texas. Methanol and isobutanol are key intermediates in a synthesis gas-based route to methyl t-butyl ether (MTBE). The technology was demonstrated in a new 18" slurry bubble-column reactor that was designed to demonstrate higher pressures and temperatures, higher gas superficial velocities, and lower gas hourly space velocities -- all of which are conducive to obtaining optimal isobutanol yield. The integration of the new reactor into the AFDU included the addition of a high-pressure synthesis gas compressor, a high-pressure hydrogen feed source, and a closed-loop methanol-solvent absorption system to remove CO_2 from the unconverted synthesis gas. These modifications were completed in January 1994.

Because this was the first demonstration for the new 2000 psig oxygenates reactor system, it was preceded by an extended checkout and characterization period, including six days of carbonyl burnout and two-phase gas holdup studies, and eight days of LPMEOH operations. The new reactor performed quite well during the LPMEOH shakedown trial, which ran with standard BASF S3-86 methanol catalyst at 40 wt%. Two feed gases were simulated: Texaco gasifier gas and the H_2-rich design feed composition for the Clean Coal III LPMEOH demonstration plant at Kingsport. Reactor productivity met expectations for both gases with a methanol yield of about 11 T/D.

After the close of the Kingsport data period, an additional day was dedicated to testing some of the new equipment. One of the test conditions set a new record for the liquid phase technology program with an inlet gas superficial velocity of 1.17 ft/sec. The new reactor seemed to operate stably during this brief test period.

The LPIBOH run followed after a short turnaround. It employed a cesium-promoted $Cu/ZnO/Al_2O_3$ catalyst developed in Air Products' laboratories and subsequently scaled up to a production-sized batch. Over a thirteen day campaign on simulated Shell gasifier gas, the catalyst and reactor system were tested at a matrix of pressures (750, 1300, 1735 psig) and space velocities (3000, 5000, 8200 sL/kg-hr), representing numerous first-of-a-kind run conditions for the AFDU. Inlet gas superficial velocities spanned an impressive 0.16 to 1.0 ft/sec. Stable reactor performance for a full twelve-hour data period at 1.0 ft/sec was another significant milestone for the liquid phase technology program.

Initial operation at baseline conditions showed slightly superior performance over the laboratory autoclave as measured by the yield of isobutanol and total higher alcohols. Subsequent data periods generally followed laboratory trends, but began to fall short of the laboratory performance results. The catalyst appeared to be deactivating at a faster rate than observed in the autoclave.

Gas holdup and catalyst concentration calculations from nuclear density gauge measurements were generally close to expectations and steady throughout the run.

The last few cases used alcohol injection into the reactor feed to simulate the effect of lower alcohol (methanol, ethanol, propanol) recycle on isobutanol synthesis. Initially alcohol injection caused a nearly threefold increase in isobutanol productivity, which agreed with laboratory observations and results from the chain growth mechanism for production of isobutanol from lower alcohols. However, during the last injection case before the run returned to baseline, the catalyst was poisoned by the inadvertent presence of 1,1,1-trichloroethane in the injected alcohol reactant. This unexpected outcome significantly hindered the investigation of the faster rate of catalyst deactivation observed at the AFDU.

Apart from the catalyst deactivation, the run successfully demonstrated mixed alcohol synthesis in a slurry bubble-column reactor, as well as all of the new equipment installed for the trial. Although the full capabilities of the new oxygenates system will not be tested until future runs, the design objectives for the modifications were met with respect to the LPIBOH run and show every indication of being applicable to other chemistries.

Introduction

The Pittsburgh Energy Technology Center (PETC) sponsors an Indirect Liquefaction program as part of DOE's Coal Liquefaction program. The overall goal of the Coal Liquefaction program is to develop a scientific and engineering knowledge base for the manufacture of synthetic liquid fuels from coal, with which U.S. industry can bring economically competitive and environmentally acceptable technology into the marketplace.

Since the 1990 Clean Air Act Ammendments, the market for oxygenated fuels has grown rapidly. MTBE (methyl t-butyl ether) has emerged as the most promising gasoline-blending oxygenate; its production has increased by a factor of 13 in the last 10 years. Currently, the reactants for MTBE production are derived from natural gas and petroleum feedstocks. For national energy security, the production of MTBE from non-petroleum sources is of current domestic interest.

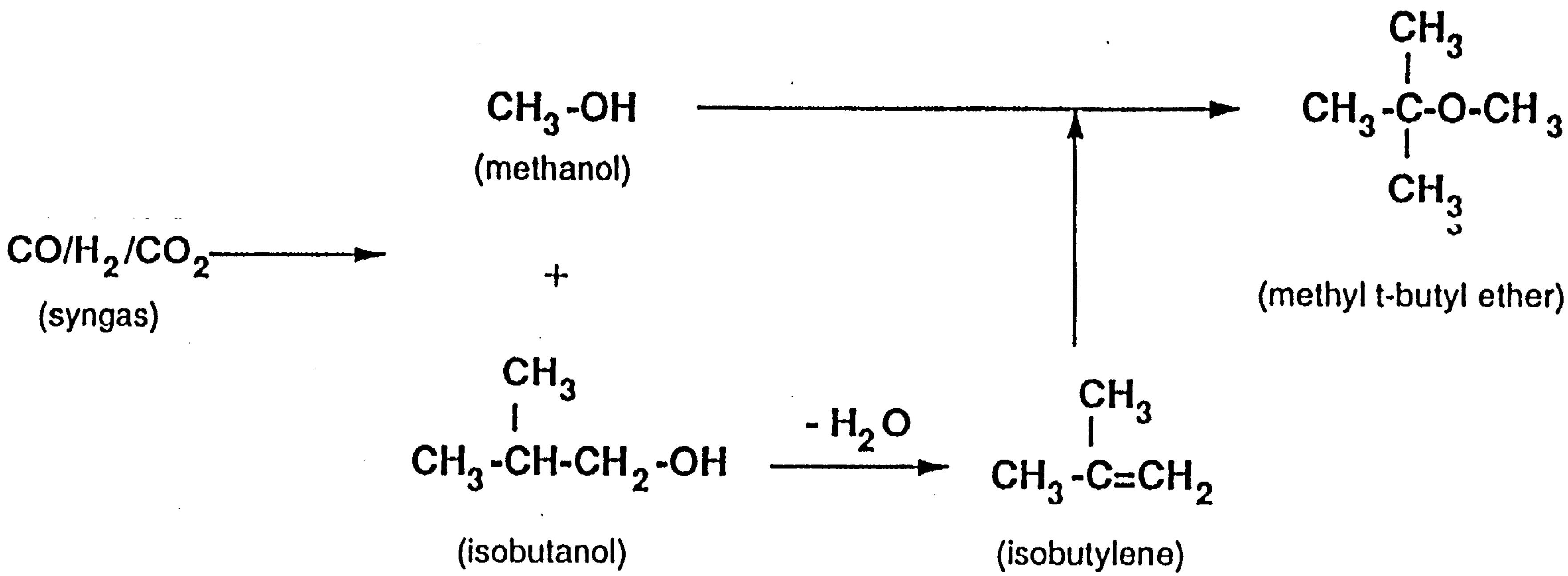
A major thrust of Air Products' ongoing DOE-sponsored Alternative Fuels contract has been the development of a new route to MTBE based on synthesis gas derived from domestic carbonaceous feedstocks, such as coal. The proposed route is shown schematically in Figure 1. Synthesis gas is converted by either a one- or two-stage process to methanol plus isobutanol. In the one-stage process, which is the subject of this work, methanol and isobutanol are co-produced in a single reactor. In the two-stage process, which is the subject of ongoing exploratory laboratory work, methanol is produced selectively from synthesis gas in the first reaction stage, and then part of the methanol is converted to isobutanol in a second reaction stage. The isobutanol produced by either of the two processes is then separated from the co-product methanol and dehydrated to isobutylene. Finally, the product isobutylene is reacted with methanol from the first step, and commercially established technology is used to produce MTBE.

Isobutanol synthesis and isobutanol dehydration are not currently practiced commercially, and thus represent the critical development issues. In previous work done by Air Products under the Alternative Fuels contract, isobutanol dehydration to isobutylene was successfully demonstrated at the pilot scale with high conversion (>90%) and excellent selectivity (>90%) compared with commercially available alumina catalyst (1). The most challenging aspect of the proposed route is the selective production of isobutanol from synthesis gas.

Because the synthesis of alcohols is highly exothermic and removal of this high reaction heat is problematic at high conversion, development has focused on the use of a slurry-phase reactor. This type of reactor has superior heat management capabilities, enabling high levels of catalyst productivity, and is amenable to on-line catalyst addition and withdrawal.

For this slurry-phase process, a cesium-promoted Cu/ZnO/Al_2O_3 catalyst was developed in Air Products' laboratories (2). This catalyst is effective at converting synthesis gas to branched primary alcohols, including isobutanol, at relatively low temperatures (540-600 °F) and, therefore, is compatible with slurry-phase operation using standard mineral oil as the liquid medium. Laboratory reaction studies, carried out using 50 ml and 300 ml continuous stirred autoclaves, revealed the best Cu/ZnO/Al_2O_3 substrate (BASF S3-86), the optimum cesium loading, and the calcination protocol. In the current study, production of this optimal catalyst was scaled up, and

Figure 1
Reaction Scheme



the conversion of synthesis gas to mixed alcohols was demonstrated at the pilot scale in a slurry bubble-column at DOE's Alternative Fuels Development Unit (AFDU) in LaPorte, Texas.

The AFDU was first commissioned in 1984 as a process development unit for the Liquid Phase Methanol (LPMEOH) process. It is located adjacent to Air Products' hydrogen and carbon monoxide production facility which allows for the demonstration of a wide range of simulated feedstocks. In addition to LPMEOH, the AFDU has been operated to demonstrate slurry-phase DME synthesis, water-gas shift reaction, Fischer-Tropsch synthesis, and isobutanol dehydration to isobutylene (1,3,4). All of these campaigns were carried out in a 22" diameter slurry bubble-column. As part of the current DOE program, the LaPorte AFDU was expanded to add a parallel reactor train, additional synthesis gas compression, and CO_2-removal equipment. The combined effect of these modifications is a more flexible facility to demonstrate and study the scaleup of oxygenated fuels technology.

Objectives

The main objective of this run was to demonstrate liquid phase co-production of methanol and isobutanol at the pilot scale, including scaleup of a proprietary catalyst. To accomplish this objective, the AFDU required significant modifications with the following design objectives:

- parallel reactor train dedicated to oxygenates technology development;
- demonstration at higher pressures and temperatures than existing reactor (2000 psig, 700°F design conditions vs. 1000 psig, 600°F);
- demonstration of higher gas superficial velocities and a wider range of space velocities;
- ability to remove CO_2 and DME from unconverted synthesis gas to maximize recycle and increase reactor throughput;
- ability to increase fresh feed capacity by tie-in to a new Air Products high-pressure hydrogen pipeline.

Engineering and Modifications

The main component of the AFDU expansion is an 18" diameter stainless steel reactor with a design pressure of 2,000 psig at 700°F. The design slurry height is 40 ft, which is twice that of the existing reactor. The internal heat exchanger in the new reactor has more than three times the heat removal capacity of the existing reactor in previous demonstration campaigns. This allows for more aggressive operating conditions with increased synthesis gas conversion. The reactor was designed to demonstrate higher pressures and temperatures, higher gas superficial velocities, and lower gas hourly space velocities--all of which are conducive to obtaining optimal isobutanol yield.

The integration of the new reactor with the existing 22.5" diameter reactor train included the addition of a high-pressure synthesis gas compressor, a high-pressure hydrogen feed source, and a closed-loop methanol-solvent absorption system to remove CO_2 from the unconverted synthesis gas. These modifications were completed in January 1994. The engineering effort is described in detail in another topical report (5).

Process Description
Process flow diagrams for the run are shown in Figures 2 and 3. 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 10.95 high-pressure injection pump may be used to simulate water or alcohol addition to the reactor feed. After injection, the mixed feed is further preheated against high-pressure steam in the 02.63 to ensure vaporization of any injected liquids 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 alcohol products pass 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 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 any 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. Since CO_2 is a by-product of much of the oxygenated fuels chemistry, it is often necessary to remove CO_2 from the 22.10 overheads before this stream is recycled. The new closed-loop CO_2-removal system uses methanol to preferentially absorb the CO_2 from the synthesis gas.

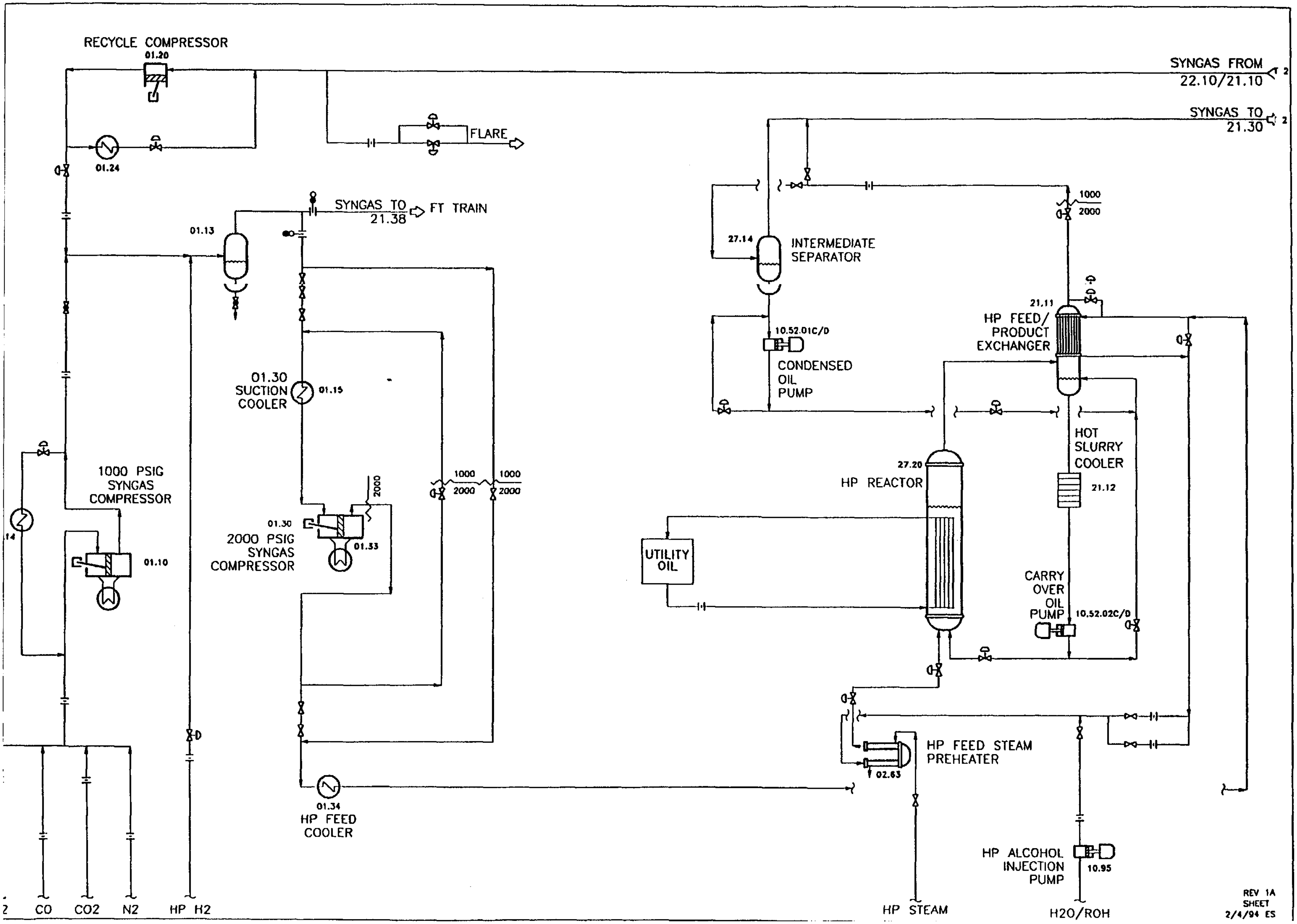
The vapor from the 22.10 cools against returning CO_2-lean synthesis gas in the 21.10 gas-gas economizer. It then feeds into the bottom of the 07.10 absorber and contacts against chilled methanol introduced at the top of the column. The CO_2-lean synthesis gas leaves the top of the absorber and rewarms to ambient temperatures in the 21.10 before being recompressed in the 01.20 recycle compressor. A small portion of this gas is purged to flare to prevent the buildup of inerts.

The CO_2-rich liquid collects in the bottom of the 07.10 absorber, de-pressurizes across a valve, and heats up against returning methanol in the 21.45 hairpin exchangers. This liquid then passes into the top of the 07.20 stripper, where it is reboiled to remove the dissolved gases such as CO_2 and DME. The overhead cooling water condenser reduces the amount of methanol solvent lost in the overhead stream, which goes to flare. The liquid from the bottom of the 07.20 cools in the

FIGURE 2

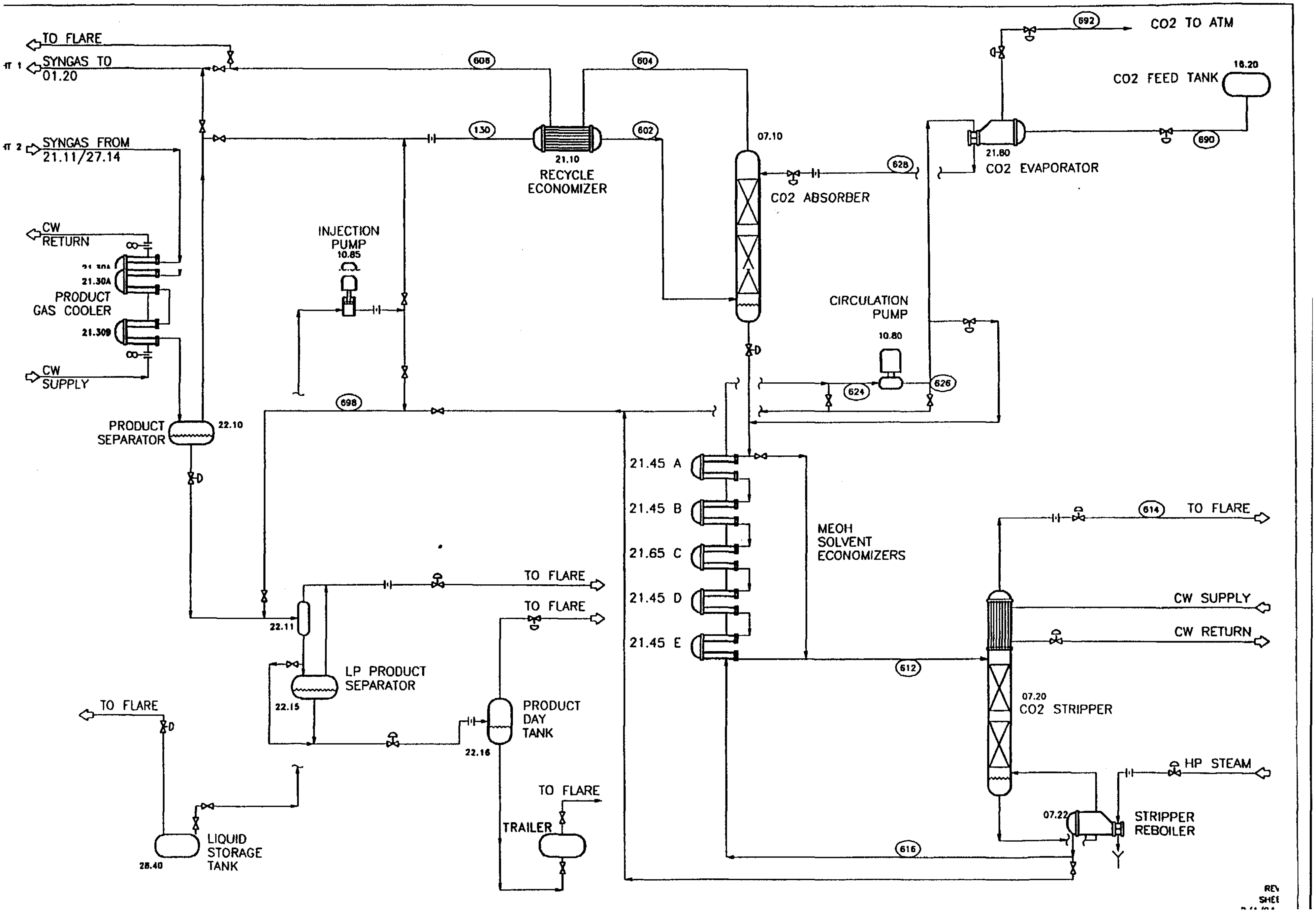
LAPORTE AFDU OXYGENATES MODIFICATIONS – FEED COMPRESSION AND SYNTHESIS

AIR PRODUCTS



AIR PRODUCTS

FIGURE 3
LAPORTE AFDU OXYGENATES MODIFICATIONS: PRODUCT COLLECTION & CO2 REMOVAL



21.45s prior to recompression in the 10.80 pump. The methanol then chills against liquid CO_2 in the 21.80 kettle evaporator before recycling to the top of the 07.10 absorber.

The synthesis gas from the 22.10 will include equilibrium amounts of methanol, water, and other hydrocarbons, which will build up in the methanol solvent. Methanol is also lost in the 07.20 overheads. As a result, the CO_2-removal system operates in an unsteady state as the composition of the solvent changes. Since this change affects the level of CO_2 removal, the system includes a solvent purge and fresh methanol makeup lines.

Bubble-Column Reactor

The new 27.20 bubble-column reactor for oxygenate synthesis measures 50 ft flange-to-flange and has an 18" 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 3/4" U-tubes occupying 8% of the reactor cross section. In addition, thirteen 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

Existing AFDU GCs were modified for on-line analysis of various process gas streams. Two GCs with Flame Ionization Detectors (FIDs) monitored hydrocarbon and alcohol concentrations in the reactor feed and effluent streams. Methods and standards for measuring concentrations of the numerous higher alcohol products were developed during the laboratory studies of this reaction (2). 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 mole%) was added to the reactor feed as an internal standard to verify flow measurements.

Environmental and Safety Issues

The engineering team conducted extensive hazard reviews to evaluate safety issues associated with the plant modifications and LLPIBOH operations. These sessions included a preliminary hazards review (PHR), a design hazards review (DHR), and a design verification review (DVR), all held at different stages of the project. In addition to the new sections of the plant, most of the existing sections required reviews because of new high-pressure and -temperature (2000 psig and 700 °F) tie-ins.

The hazard review team performed a "What If" analysis of the pilot plant to identify hazards. Existing safety relief devices were checked for new cases related to high-pressure tie-ins, and in some cases those devices or their piping circuits required modifications. Furthermore, relatively new regulations imposed by OSHA Process Safety Management (PSM) required complete documentation of cases and calculations for all of the existing relief devices, of which there were about 85 in total. In addition, approximately 30 new pressure relief devices were specified to cover new equipment. Subsequent work involved re-evaluating the vent lines and headers for all these devices, as well as checking the main flare header for all of the new flows. This effort led to a change in scope for the relief header from the new CO_2-removal system to include a new, local flare knockout pot.

Flare radiation effects were also evaluated, and calculations indicated that the existing flare would provide an acceptable radiation heat level to operators at grade or on any of the nearby platforms. Investigations also centered on the possibility of an unconfined vapor cloud explosion (UVCE) should the flare go out and flammables begin to accumulate. Even under this scenario, calculations showed that blast pressure and radiation effects would be acceptable. However, CO toxicity effects of this scenario warranted institution of new procedures for operator response to a flare malfunction condition. The CO_2 vent from the 21.80 evaporator underwent a similar analysis, and the hazard team recommended restricted access to the top platform in a nearby structure to reduce the potential for exposure to CO_2 releases.

The hazard team also conducted a plant Operational Readiness Inspection (ORI) in early February as a final review of the revisions and preparations for the upcoming run. Operator training was completed by process and plant personnel at this time per OSHA PSM standards.

The air emission operating permit exemption filed in 1993 for the LPIBOH run was initially deemed insufficient by the Texas Natural Resource Conservation Commission (TNRCC) in early February 1994. Air Products agreed with the TNRCC to place time limitations on each reaction chemistry demonstrated at the AAFDU to satisfy the new requirements of the EPA's Clean Air Act. Based on previous and current operating campaign durations, the accepted time restrictions should not restrict usage of the AAFDU so as to inhibit meeting the goals of the Alternative Fuels contract. Additional process calculations and all supporting information were compiled and forwarded to the TNRCC on February 18. Written approval of the exemption for LPIBOH followed on February 28, 1994, in time for start-up.

Catalyst Development

The catalyst used in this work was a commercially available $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst that had been promoted with cesium. Laboratory reaction studies, carried out using 50 ml and 300 ml continuous stirred autoclaves, revealed the best $Cu/ZnO/Al_2O_3$ substrate (BASF S3-86), the optimum cesium loading, and the calcination protocol. Production of this optimal catalyst was then scaled up to a pilot-scale quantity for use in the AFDU. The entire catalyst development effort is described in detail in another topical report (2).

AFDU Shakedown

Preliminary results from this demonstration were reported earlier at DOE's Liquefaction Contractors' Review Conference (6). Because this was the first demonstration for the new 2000 psig oxygenates reactor system, it was preceded by an extended checkout and characterization period, including six days of carbonyl burnout and two-phase gas holdup studies, and eight days of LPMEOH operations.

Two-Phase Gas Holdup Studies

The Nuclear Density Gauge (NDG) for the new 27.20 reactor was calibrated on March 8, 1994. Two-phase gas holdup studies were performed between March 11-16 to investigate the hydrodynamics of the new reactor. These tests were conducted concurrently with carbonyl burnout and equipment testing. The tests used both N_2 and a CO-rich synthesis gas (nominally 34% H_2, 65% CO, 1% N_2) at operating pressures and temperatures pertinent to the LPMEOH and LPIBOH demonstrations. The results are summarized in Figures 4 - 6.

Figure 4 shows all of the gas holdup data as a function of superficial gas velocity. The data concentrated on pressures of 750 psig and higher. At these pressures, little sensitivity to pressure or temperature was seen, and all the data collapsed toward one basic curve. The results appear to mimic the trends seen during the two-phase gas holdup studies from the LP-III E-5 methanol run (7). However, the current tests included much higher pressures (1750 psig vs. 900 psig) and superficial velocities (0.84 vs. 0.44 ft/sec) than the E-5 tests.

Notably, the gas holdup leveled off above about 0.4 ft/sec at a slightly higher level than in the previous studies (65-70% vs. 60-65%). This result may indicate errors introduced by NDG measurements that are more pronounced in the new reactor. Specifically, the smaller shell diameter and greater area blocked by heat exchanger tubes may contribute to more significant radial variations in the velocity profile. These variations, when weighted according to linear radiation path instead of cross-sectional area, may contribute to inaccuracies in the prediction of average gas holdup from NDG measurements.

In Figure 5, the two-phase gas holdup is plotted as a function of reactor height for various superficial velocities. The curves all exhibit the same general shape, including an interesting, yet repeatable, drop in gas holdup at 63", and again to a lesser degree at 135". The scale is expanded for the higher velocity curves in Figure 6 to magnify this phenomenon. These locations are 6"-8" below the bottom two U-tube supports within the reactor. The supports appear to provide enough of an obstruction to the flow to become manifest in the holdup profile. As the flow becomes more fully developed while moving up through the reactor, the effect decreases until it is no longer evident past the second support.

Carbonyl Burnout

The two-phase gas holdup studies were conducted concurrently with carbonyl "burnout." Because iron and nickel carbonyl, which are known catalyst poisons, can form on new stainless steel, synthesis gas is circulated through the plant to measure background carbonyl levels and passivate the steel if necessary. Initial conditions for carbonyl burnout were 482°F and 750 psig (LPMEOH conditions). Flows varied considerably during the burnout period from once-through to high recycle to accommodate the gas holdup studies. Early on March 14 the temperature was increased to 572°F to simulate conditions for isobutanol synthesis, and later that morning the new 02.63 steam preheater also came on-line. The new 01.30 high-pressure compressor then came on-line late that afternoon for holdup studies at 1300 and 1750 psig. During this period of widely varying operating conditions, $Fe(CO)_5$ readings peaked as high as 400 ppb at the reactor outlet. $Ni(CO)_4$ was never detected at any time.

Early on the morning of March 15, the pressure and temperature were returned to the baseline LPMEOH conditions with the 02.63 still on and the recycle compressor boosting total reactor flow to 78,000 SCFH. At this point, the baseline carbonyl values had leveled off at 62-65 ppb

FIGURE 4

Two-Phase Gas Holdup in 27.20 Reactor

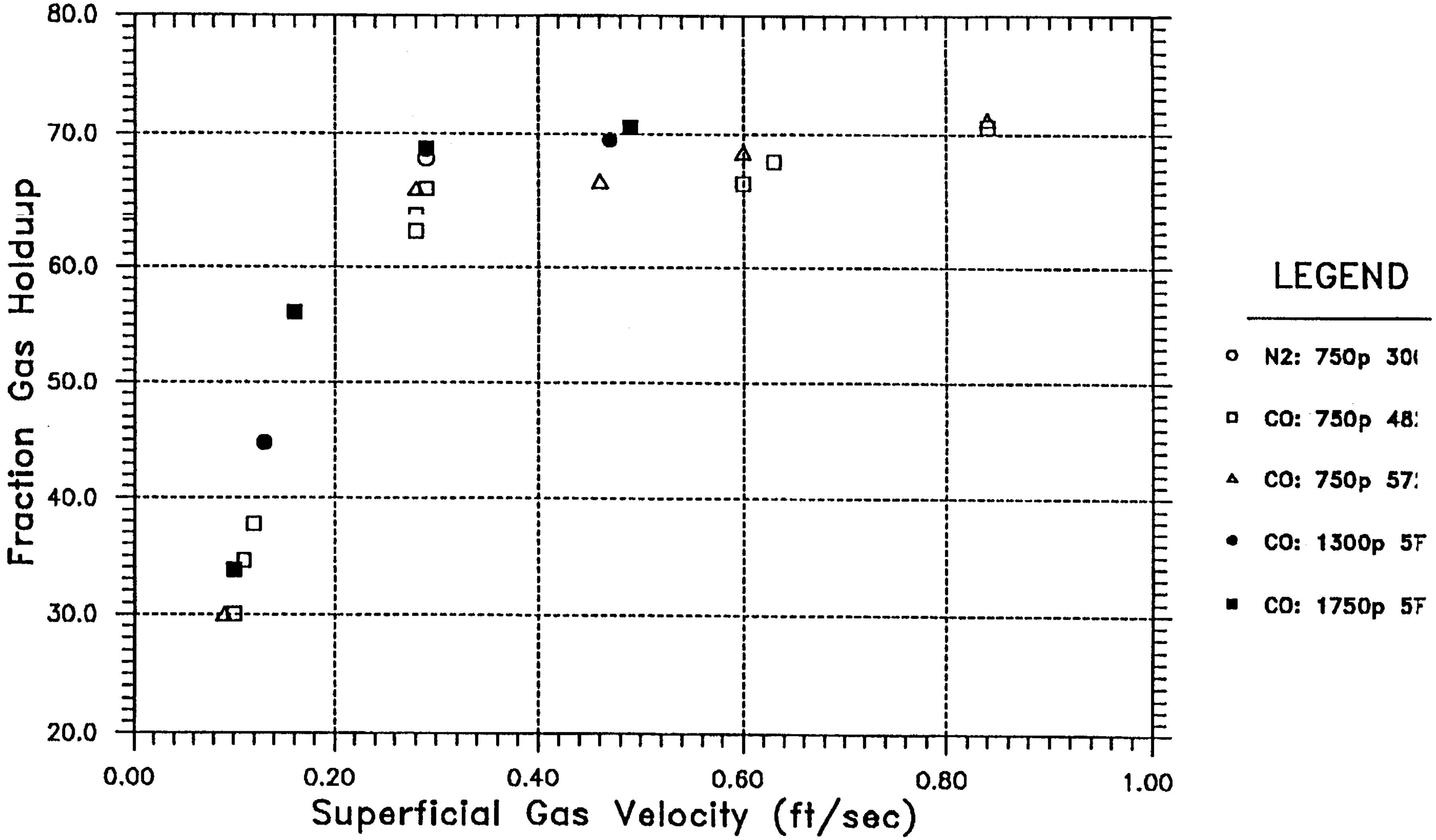
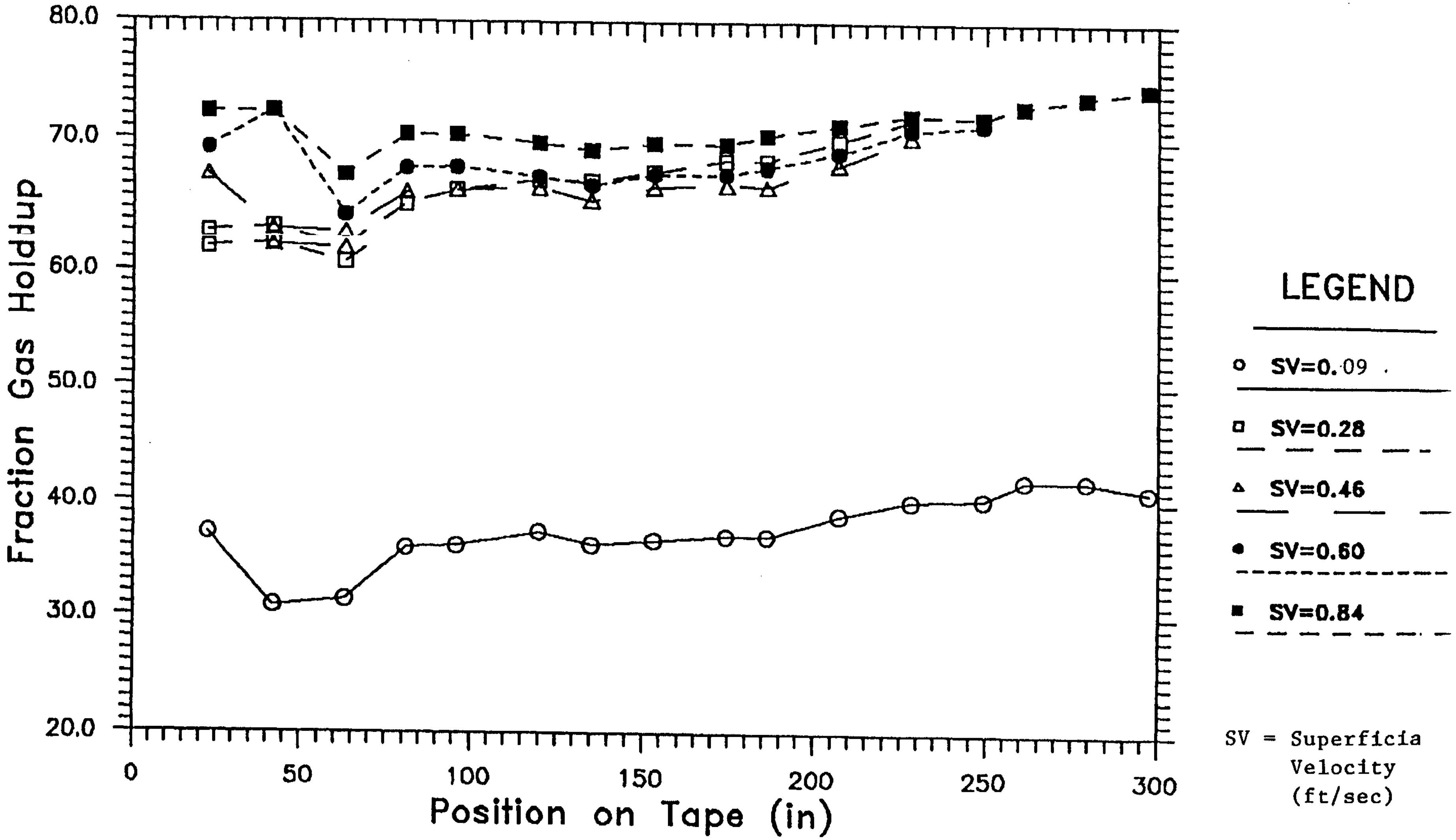


FIGURE 5



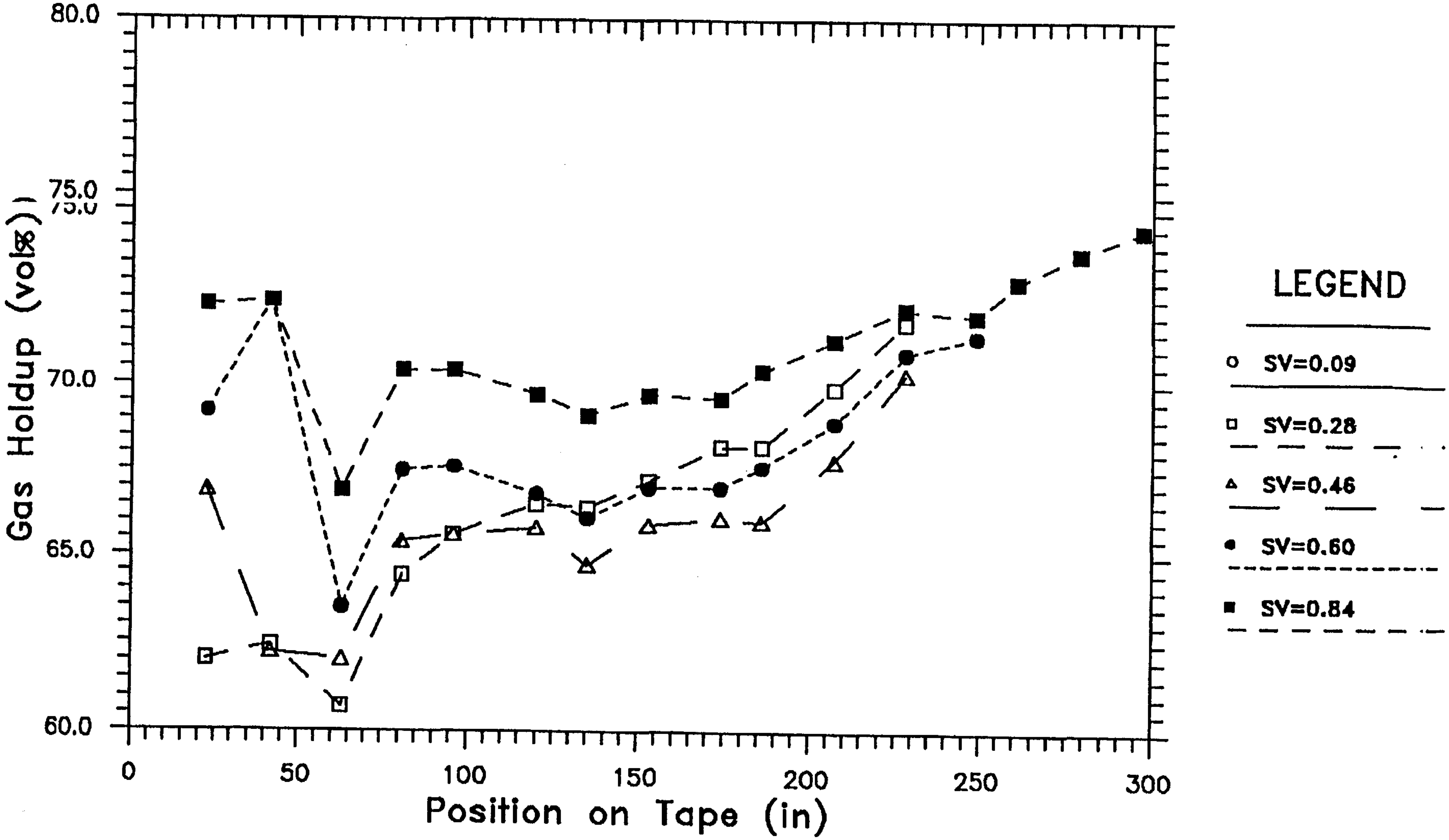
Two Phase Gas Holdup vs. Height in 27.20 Reactor

Syngas at 750 psig & 572 F

FIGURE 6

2–Phase Gas Holdup vs. Height in 27.20

Syngas at 750 psig & 572 F



$Fe(CO)_5$ at the reactor inlet and 68-71 ppb at the reactor outlet. The reactor loop was then cooled and drained. The oil removed from the system contained a visually significant quantity of metallic fines, which apparently contributed to the high level of carbonyl generation.

The system was recharged with fresh oil and brought back up to the baseline LPMEOH conditions, with once-through CO-rich synthesis gas at 20,000 SCFH. Iron carbonyl measurements quickly leveled out at much lower values: 2 ppb at sample point 4 (combined outlet of the 01.10 and 01.20 compressors); 7-9 ppb at sample point 15 (reactor inlet); and 16-17 ppb at sample point 3A (reactor/21.11 outlet). These results seemed to indicate that the particulates flushed out by the first charge of oil had indeed increased the production of iron carbonyls.

The reactor temperature and pressure were then raised to the most extreme conditions for isobutanol synthesis (572°F and 1750 psig) and held for approximately six hours in once-through mode at 20,000 SCFH. Again, no nickel carbonyls were detected, and iron carbonyls in the reactor outlet leveled off at approximately 80 ppb. This higher baseline was not unexpected at these conditions.

To determine if a higher flow rate would decrease the production of carbonyls, the plant was finally run in recycle mode at 58,000 SCFH for four hours. This condition simulated the minimum space velocity case planned for the isobutanol campaign. The $Fe(CO)_5$ measurements were steady at approximately 60 ppb at sample point 4 and 100 ppb at sample point 3A. These results indicate that indeed fewer carbonyls are formed as flow increases, with about 40 ppb $Fe(CO)_5$ produced at this condition, compared to about 80 ppb produced at 20,000 SCFH. Furthermore, it was surmised that additional time on-stream during methanol operations might reduce carbonyl levels even further before the start of isobutanol synthesis. Regardless of that speculation, however, these concentrations were deemed acceptable for the time scale of the operating campaign.

The carbonyl burnout period concluded at 23:55 on March 16, and the plant was cooled and drained in preparation for LPMEOH catalyst loading and reduction.

LPMEOH Catalyst Reduction

The LPMEOH shakedown run for the new reactor commenced on March 17, 1994. Test Authorizations are included in Appendix A, and the overall Run Chronology appears in Appendix B. A 40 wt% oxide catalyst slurry was prepared in the 28.30 catalyst prep tank by mixing 1875 lbs of Drakeol-10 oil with 1250 lbs of standard BASF S3-86 methanol catalyst. The slurry was heated and agitated in the prep tank prior to transfer to the reactor.

Catalyst reduction commenced at 22:00 on March 17. The procedure was carried out at 67 psig and 12,500 SCFH of dilute synthesis gas (nominally 1.4% H_2, 1.9% CO, 96.7% N_2). This flow rate was lower than specified in Test Authorization #37 because of some difficulties in keeping the flare lit with the high N_2 flow. The pressure was lowered accordingly to maintain the appropriate superficial velocity. In addition, the H_2 and CO concentrations were increased slightly from the target (1.2 and 11.8 mole%, respectively) to increase the flammability of the purge gas going to the flare.

The reduction temperature ramp is shown in Figure 7. It increased at 15°F/hr before entering a 12-hour hold period at 392°F. The temperature ramp then continued at 15°F/hr until the procedure concluded after a one hour hold at 464°F. The slight "stagger" in the curve near 310°F resulted from a temporary hold in the ramp rate to confirm the calculated uptake rates. Gas holdup measurements taken during the process with the NDG were steady at 26%.

Catalyst reduction concluded at 06:42 on March 19. Figures 8 and 9 show uptake vs. time and uptake vs. temperature for the entire reduction period. For these plots, the bottom curve represents H_2, the middle curve represents CO, and the top curve shows the total uptake. The final uptake was 2.34 SCF/lb of catalyst oxide, compared to a theoretical maximum value of 2.82 SCF/lb. This result is comparable to the 1991 LPDME activation, although the uptake rate was faster in that case.

LPMEOH Operations

A slightly H_2-rich synthesis gas blend was introduced to the plant once-through at 10:20 on March 19, 1994. The reactor reached 750 psig at 10:53, and recycle commenced at 11:12. Methanol first appeared in the reactor effluent at 11:22. During the first few hours of operation, significant oil carry-over contaminated the product. Subsequent discovery of an erroneous thermocouple reading controlling the 21.11 feed/product economizer outlet temperature, and operating optimization of its setpoint, markedly decreased the oil carry-over rate. During the balance of the first two days of operation, efforts were directed toward maintaining steady operation with the new equipment; reconciling flows, compositions, and liquid accumulation rates; and identifying other instrumentation (i.e., flowmeters, thermocouples, switches) that needed further calibration and adjustment. In addition, the new high-pressure H_2 tie-in to the fresh feed circuit, and its attendant safety systems, complicated the control of the reactor feed stream and caused several upsets due to swings in source pressure.

Operations were temporarily suspended at 11:52 on March 21, when CO feed flow was interrupted by a power loss at our supplier. An immediate slump test on the reactor slurry confirmed earlier predictions of 40 wt% catalyst concentration. The procedures for attaining the standby condition were executed next, principally cooling the reactor and purging with 1-2% H_2 in N_2. However, the power loss also knocked out cooling water pumps, which, in turn, eventually tripped the feed compressor. As a result, the plant was also depressurized, and the purge flows were re-established in reduction mode at 100 psig. During the outage, the high-pressure H_2 feed location was modified to improve controllability.

Synthesis gas was re-introduced to the plant at 17:51, and steady AF-R9.1 (Texaco gas) operating conditions were achieved by 01:25 on March 22. After restarting, operations remained stable through the balance of the Texaco data period. The addition of a new high-pressure H_2 tie-in at the suction of the 01.20 recycle compressor significantly stabilized the control of the reactor feed composition with respect to fluctuations in H_2 source pressure. The original tie-in point was left undisturbed, so that in future campaigns, for which very high recycle ratios are

FIGURE 7

Reduction Temperature Ramp

LPMEOH

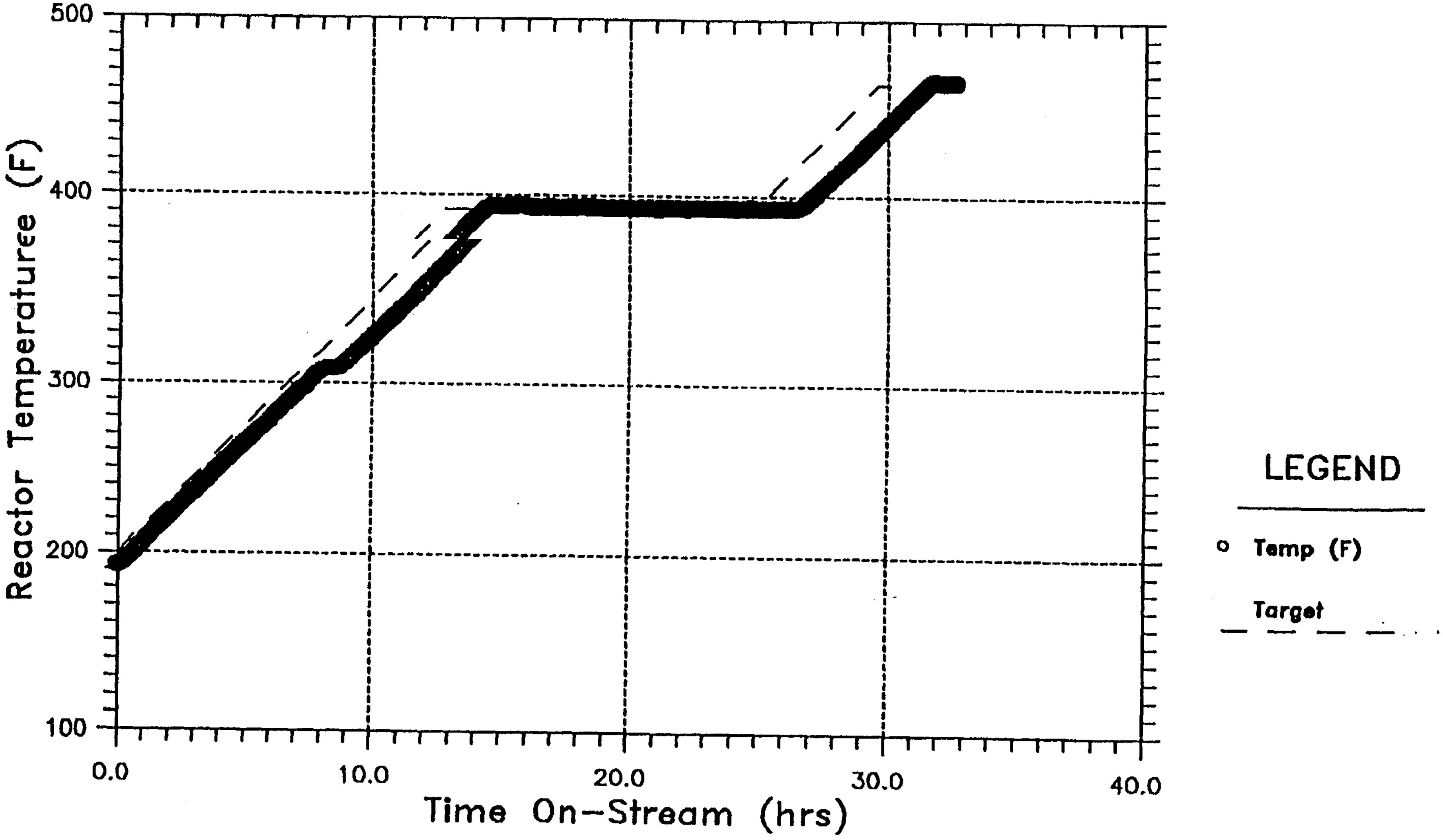


FIGURE 8

Reduction Gas Uptake vs. Time

LPMEOH