Section 2

LAPORTE PDU DESCRIPTION

PROCESS DESCRIPTION

The Liquid Phase Methanol (LPMEOH^{TM}) Process Development Unit (PDU) incorporates two modes of operation, namely: liquid-fluidized and liquid-entrained. In the liquid-fluidized operating mode, a methanol synthesis catalyst (extrudates of about 2-mm diameter and 6-mm length) is fluidized within the reactor by a circulating inert hydrocarbon liquid. This liquid controls the reaction temperature by absorbing heat released during the methanol reaction. In the liquid-entrained mode, the catalyst in powder form is suspended in the inert hydrocarbon liquid, forming a slurry that circulates through the reactor.

The process feed is formed by a mixture of hydrogen, carbon monoxide, carbon dioxide, and an inert gas (nitrogen and/or methane). To establish a broad and representative reactor feed composition for the LPMEOH process, two principal gas compositions were defined early in the program[1], including a "balanced-gas" containing a H_2/CO ratio of 2.9/1 and an "unbalanced-gas" with a H_2/CO ratio less than unity (see Table 2-1).

Table 2-1

PRINCIPAL REACTOR FEED GAS COMPOSITIONS AND GENERAL COMPOSITION RANGE OF INTEREST (Mole %)

	Unbalanced Type	Balanced Type	Broad General Range
H_2	35	55	25-75
CO	51	19	5-70
CO_2	13	5	0-35
CH_4	-	3	0-35
Inerts	1	18	0-25
	100	100	
H_2/CO	0.69	2.89	0.3-7.0
$H_2/(CO + 1.5\ CO_2)$	0.50	2.08	0.3-3.0
$(H_2-CO_2)/(CO + CO_2)$	0.34	2.08	0.2-3.0

A simplified process flowsheet for the LaPorte LPMEOH PDU is shown in Figure 2-1.

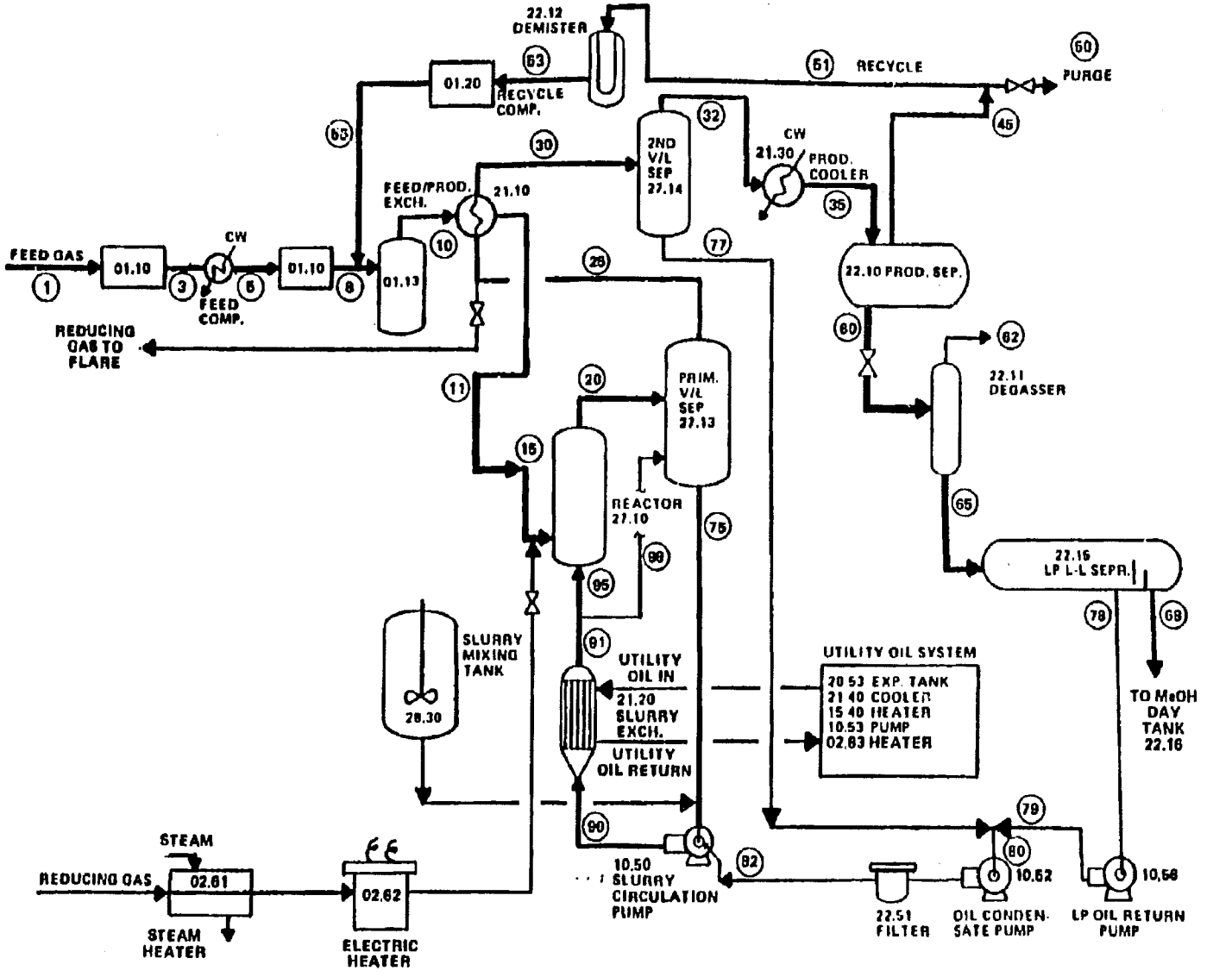

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Figure 2-1. Simplified Process ysheet for LaPorte LPMEOH PDU

The process feed is compressed from 1,000 kPa (150 psia) to the reactor pressure (between 3,500 and 6,400 kPa) by the 01.10 feed compressor. The compressor 01.10/01.20 is a two-throw, three-stage, balanced-opposed machine, which functions as two separate units sharing a common frame and lubrication system. The compressed feed with any recycle gas from the 01.20 compressor is heated by passing through the 21.10 feed/product exchanger and subsequently enters a two-stage guard bed system.

The initial process scheme included two alumina loaded iron carbonyl guard beds where the iron pentacarbonyl ($Fe(CO)_5$) formed in the piping and equipment under high CO partial pressure was to be removed. During the shakedown and 40-day runs the guard beds were not operational owing to modifications performed to eliminate an exotherm problem.[2] The heated gas from the feed/product exchanger flowed through the empty guard vessels and was introduced in the reactor bottom and mixed with the incoming inert oil or catalyst/oil slurry in a distributor. The 27.10 reactor is a cylindrical vessel constructed of low alloy steel (1/2 Mo) and lined internally with copper to prevent the formation of iron carbonyl (see Figure 2-2). The bubble cap tray distributor, intended for liquid-fluidized operation, operated satisfactorily during the entrained portion of the run.

The inert hydrocarbon liquid or slurry is separated from the methanol product and unconverted synthesis gas in primary separator 27.13. It is recirculated to the bottom of the reactor via the slurry heat exchanger 21.20 by the slurry pump. The circulating liquid can be heated or cooled in the slurry heat exchanger to maintain a constant reactor temperature, depending on the CO conversion in the reactor, heat loss of the system, and the rate of cold seal flush required by the 10.50 slurry circulation pump. A hot oil system, which includes hot oil expansion tank 28.53, hot oil circulation pump 10.53, oil cooler 21.40, and oil heater 15.40, is designed to provide indirect heating or cooling of the circulating liquid and to eliminate the possibility of overheating the catalyst. The slurry circulation pump is a centrifugal pump driven by a variable speed electric motor and provided with a specially designed double mechanical seal. The seal is provided with seal flush and a circulating barrier fluid to eliminate the possibility of leaks of catalyst slurry to the atmosphere.

The methanol product and unconverted synthesis gas exiting the top of the primary separator are cooled against the incoming feed gas in the feed/product exchanger, condensing the bulk of the vaporized hydrocarbon liquid. The uncondensed vapor is further cooled to about 40°C by cooling tower water in the 21.30 product gas

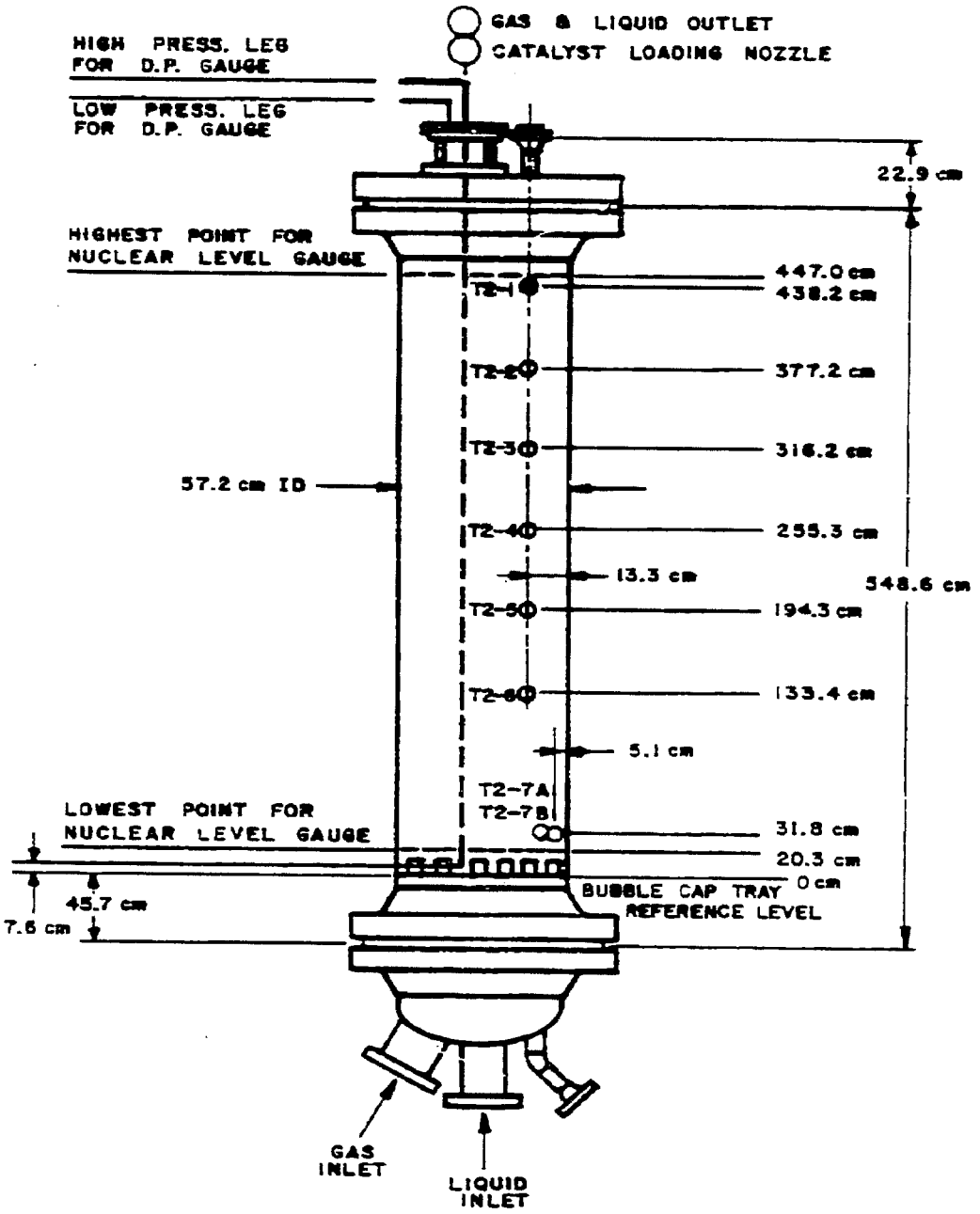

Figure 2-2. Location of Sensors LaPorte LPMEOH PDU Reactor

cooler. The condensed methanol product and a small quantity of inert hydrocarbon oil are reduced in pressure and the flashed gas is vented at the top of the 22.11 degasser to the plant flare header. The methanol-hydrocarbon stream passes through liquid-liquid separator 22.15, where the hydrocarbon oil separates and isreturned to the process via the 10.56 oil return pump. The methanol product is sent to the 28.10 product storage tank.

The unconverted synthesis gas leaving the 22.10 product separator is compressed and recycled to the reactor. A small purge stream prevents the buildup of inerts in the reactor loop.

The oxide form of the catalyst is initially activated with a mixture of hydrogen and nitrogen, which is heated with steam heater 02.61 and electrical heater 02.62 before to introduction to the reactor. In the liquid-fluidized operating mode, the catalyst reduction is done in the vapor state with a fixed bed in the 27.10 reactor before the injection of the synthesis gas and hot hydrocarbon liquid. In the liquid-entrained mode, the catalyst reduction takes place in-situ, in the liquid state, with slurry circulation in the slurry loop, also before the synthesis gas is introduced.

DATA ACQUISITION PROCESS DESCRIPTION

The primary objectives of the LaPorte program are to demonstrate the feasibility of the LPMEOH process at the PDU scale and to gather process design information. Therefore, the data pertinent for process design and the catalyst performance are the most important "products" from the LaPorte PDU operation. To achieve the objectives, a data acquisition system (DAS) was installed to collect, store, and report the process and the analytical data generated from the PDU.

The data acquisition system includes a Digital VT103 microcomputer with 128K bytes of memory. A process monitoring/process control software package (AIM), consisting mainly of a set of FORTRAN programs structured around an interactive data base, updates all the relevant process variables on a regular basis according to a preset scanning rate.

The current values of those variables are supplied to the data base in one of the following manners:

- Manually, through keyboard inputs.

- Directly, through the CPI gear terminal, which is hard wired to the plant monitoring points.

- Directly, through a port, which is hard-wired to a gas chromatograph microprocessor.

- Internally, through special calculation routines stored in memory.

For each of the 396 variables in the AIM data base, the following information is defined:

- Variable name and number.
- Signal name and CPI channel number.
- Averaging factor and scan rate.
- Engineering units and range.
- Instrument units and range.
- Type of sensor (in case of thermocouples).
- Type of calculation to be performed on the variable.

The AIM data base system interacts with the following programs so that the required data are received, manipulated, and stored:

- An analytical data program to read the on-line analytical reports supplied by the GC integrator (Spectra-Physics SP-4000) - the relevant component concentration data are sent to their proper variable locations in the AIM data base.

- CPI programs to reach the on-line signals coming through the CPI terminals - these signals are in the range of -40 to +40 MV for the thermocouple temperature measurements or 1 to 5 V for the flow or pressure sensor measurements. This program converts these analog signals to their proper units based on special calibration tables and user-defined engineering units. The calculated values are then sent to their proper variable locations in the AIM data base.

- User input program - to allow for manual input of process variables such as time and date.

From the information stored in the AIM data base, a set of 396 variables is retrieved every five minutes and stored in a historian file. The historian

sequentially stores the averaged values for all of the variables in the AIM data base every five minutes. A set of FORTRAN programs then interacts with these data and computes an hourly average of the 12 five-minute averages and creates a file to store 207 selected variables (HRDATA).

Non-routine process data that cannot be taken by the DAS automatically, such as catalyst bed density and bed heights, are recorded by the plant operators using a nuclear density gauge positioned at the LPMEOH reactor.

Analytical System

For the analytical portion of the system, gas analysis is performed using two on-line Carle Instruments gas chromatographs. The gas sampling system, which includes a multi-stream sample rotameter panel and automatic stream selector station, is provided with timers and automatic switches so that these analyses can proceed virtually unattended. Liquid samples of oil and product methanol are analyzed using two liquid sample chromatographs supplied by Schimadzu Scientific Instruments. A Spectra-Physics 4000 electronic integrator with three DIM (Data Interface Modules) is also provided to interface the chromatographic analyses with the microcomputer. An Epson MX-80 hardcopy printer is provided for GC analyses reporting. In addition, each DIM on the Spectra Physics 4000 has a separate strip chart recorder for GC analyses. Finally, a Karl Fisher apparatus and analytical balance are available for water determination and sample weighing.

The two gas chromatographs routinely analyze once every hour the following gas streams:

- Make-up feed
- Recycle and purge gas
- Guard bed feed
- Reactor feed
- V/L separator gas (reactor effluent)
- Flashed gas

Since the composition of the flashed gas is relatively uniform and the corresponding flow is not very significant in the overall plant balance, the flashed gas port is sometimes replaced by the reactor effluent stream. This substitution provides redundancy of analysis around the LPMEOH reactor.

Non-routine analytical data are obtained for:

- Methanol product and circulation oil (slurry)
- Impurities in the make-up gas and reactor feed gas
- Catalyst analyses

Figure 2-3 illustrates the structure of the analytical system.

Data Reduction

The process variable data file (HRDATA) is only a temporary file, and is rewritten hourly, each time a new set of variables is determined. Several programs written in BASIC language interact with this file and perform engineering calculations and material balances. A Process Hourly Report is printed every hour, and contains such information as process variables, conversions, and material balances. The information generated by the BASIC programs permits a thorough evaluation and assessment of the quality of the collected data.

In order to illustrate the usefulness of the data reduction programs, a sample printout of a Process Average Report is included as Table 2-2 (3 pages). The data correspond to the sixth day on unbalanced gas during the 40-day run. Catalyst weight related parameters have been updated with the most recent calculations of catalyst inventory. A description of each page of the Process Average Report follows:

Process Variables and Analytical Summary (Page 1)

This page of the report contains the main variables relevant to the plant and catalyst performance. Process variables that have been averaged from the individual hourly averaged data such as flows, temperatures, and pressures are included together with compositions of the different process streams.

Conversion-Selectivity-Productivity (Page 2)

Two sets of conversion data are available from GC#1 and GC#2. The chromatograph that gives better precision and closures is utilized as a basis for data reporting. The selectivities included on this page (percentage of carbon contained in CO and CO_2 that is converted to methanol) are useful to determine if the methanol concentrations in the reactor effluent or the product flow rates are correct.

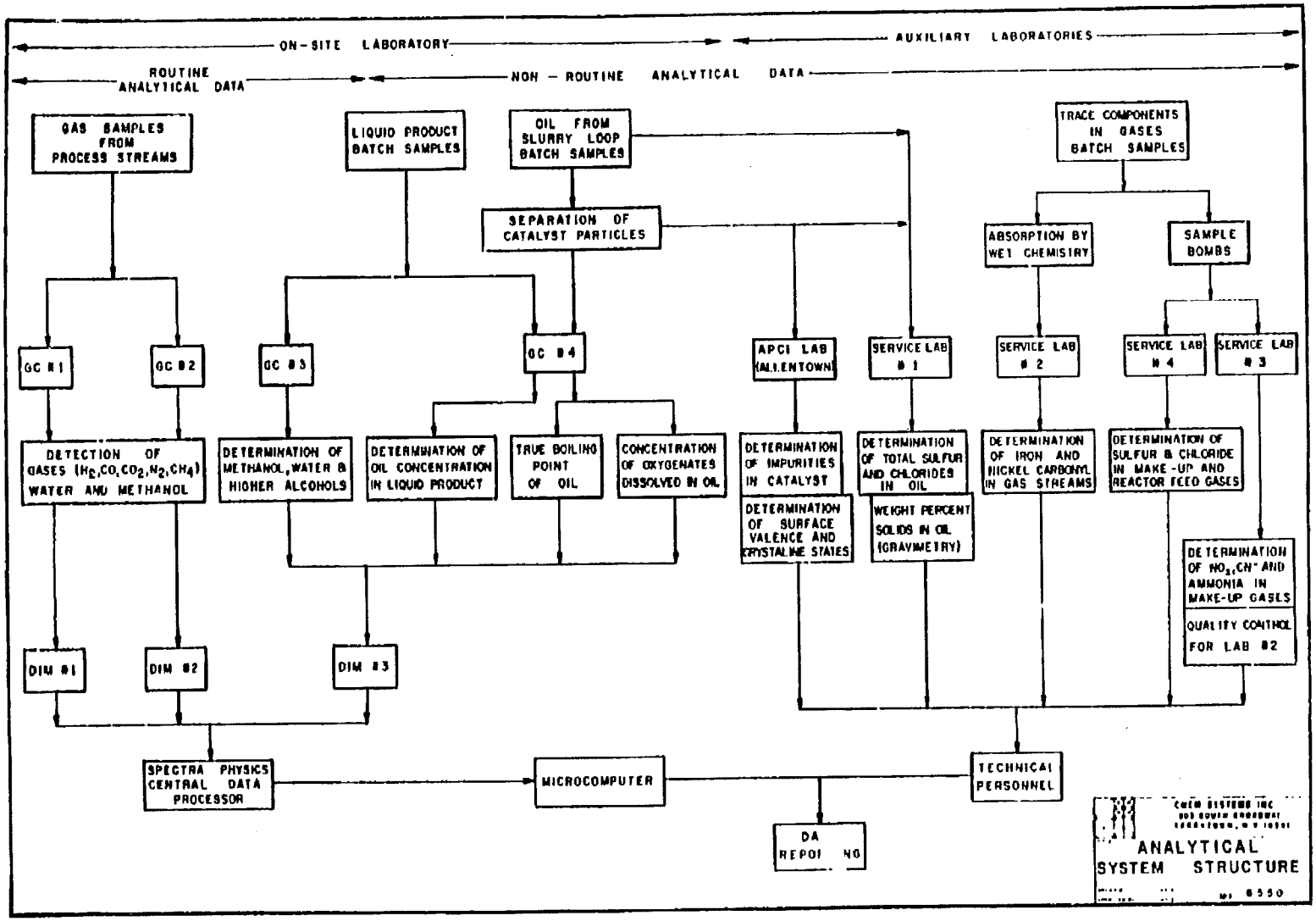

Figure 2-3. Analytical System Structure

Table 2-2

LAPORTE LP METHANOL PROCESS AVERAGE REPORT-ENTRAINED MODE-PROCESS VARIABLES AND ANALYTICAL SUMMARY

DATE :	22-Apr-84
TIME :	12:15 PM
TIME INTERVAL,	From: 0000 20 Apr
	To: 2400 20 Apr
NUMBER OF AVERAGED HOURS :	24
RUN ID NUMBER :	EU-X754
FEED GAS TYPE:	UNBALANCED GAS
REACTOR FEED GAS INLET TEMP. (deg.C) :	138.6
OIL/SLURRY INLET TEMP. (deg.C) :	251.0
AVE. REACTOR TEMPERATURE (deg.C) :	249.7
REACTOR OUTLET TEMP. (deg.C) :	251.0
GUARD BED FEED PRESSURE (kPa) :	5494
PRIMARY SEPARATOR GAS PRESSURE (kPa) :	5248
GAS SUPERFICIAL VELOCITY (cm/sec) :	10.7
LIQUID SUPERFICIAL VELOCITY (cm/sec) :	5.2
EXPANDED BED HEIGHT (cm) :	9
SLURRY CONCENTRATION (wt%) :	
CATALYST OXIDE WT IN REACTOR (%a oxide) :	
GAS HOLD-UP :	
SPACE VELOCITY (l/kg-hr) :	10,200
RECYCLE/FRESH FEED RATIO :	3.5856S
OIL/SLURRY CIRCULATION RATE (m3/hr) :	51.7
PROD.SEPARATOR GAS FLOWRATE (50) + (55) (kmol/hr) :	99.47
PURGE GAS FLOW RATE (50) (kmol/hr) :	2.13

STREAM #	1	55	10	15	25*	62	68	
STREAM NAME	FRESH FEED	RECYCLE GAS	GUARD-BED FEED	REACTOR FEED	V/L SEP GAS	FLASH GAS	MEOH PRODUCT	
COMPONENT								
	(MOLE)	(MOLE)	(MOLE)	(MOLE)	(MOLE)	(MOLE)	(MOLE)	(WT%)
H2	54.54	29.86	35.30	35.02	28.1e	10.09	———	———
CO	39.45	53.38	50.67	50.64	56.77	26.00	———	———
CO2	5.71	14.94	12.97	12.91	14.30	40.00	———	———
N2	0.13	0.38	0.35	0.33	0.33	0.00	———	———
CH4	0.15	0.53	0.44	0.42	0.55	0.00	———	———
H2O	0.00	0.00	0.01	0.00	0.15	0.00	2.74	1.54
CH3OH	0.00	0.39	0.40	0.29	0.04	23.00	96.75	96.58
DME	0.00	0.01	0.08	0.01	0.00	0.00	0.00	0.00
C3H5OH	———	———	———	———	———	———	0.25	0.33
C3OH'S	———	———	———	———	———	———	0.06	0.12
C4OH'S	———	———	———	———	———	———	0.04	0.10
C5OH'S	———	———	———	———	———	———	0.01	0.03
ALKANES	———	———	———	———	———	———	0.00	0.00
ESTERS	———	———	———	———	———	———	0.02	0.05
ALDEHYDES	———	———	———	———	———	———	0.00	0.00
OIL	———	———	———	———	———	———	0.11	1.21
TOTAL :	100.00	99.98	100.12	99.80	100.30	100.00	100.00	100.00
DENS,g/cc	0.004	0.047	0.033	0.034	0.028	0.075	———	0.795
AV.MOL.WT	14.72	22.59	20.88	20.91	23.16	32.89	32.10	———
Nm3/hr	579.7	2046.3	2613.5	2610.1	2356.0	5.5	———	———
kmol/hr	25.46	91.29	116.60	116.45	105.11	0.25	5.63	———
l/hr,prod	———	———	———	———	———	———	———	227.20

* Compositions correspond to STREAM#32

Table 2-2 (Continued)

22-Apr-94 / 12:06 PM

LaPORTE LPMETHANOL PROCESS AVERAGE REPORT
CONVERSION-SELECTIVITY-PRODUCTIVITY

CONVERSIONS ACROSS REACTOR :

		GC#1	GC#2
HYDROGEN CONVERSION	(%) :	26.4	27.4
CARBON MONOXIDE CONVERSION	(%) :	9.3	9.5
CARBON DIOXIDE CONVERSION	(%) :	-0.2	0.0

*** See next page for conversions as calc. by overall bal.

SELECTIVITIES :

	ACROSS REACTOR GC Average	OVERALL *
CO (+CO2) SELECTIVITY TO METHANOL (%) :	107.3	101.9
CO (+CO2) SELECTIVITY TO ETHANOL (%) :	----	0.3

* Methanol in flashed gas taken as zero
Ethanol only measured in product flow

METHANOL PRODUCTIVITIES & YIELDS

MEOH SOURCE	gmol/hr-kg cat	kg/1000 Nm3 fresh feed	kg/1000 Nm3 reactor feed
As calculated ACROSS REACTOR	23.59	337.8	73.9
As Net MeOH produced, OVERALL balance	21.8	307.6	67.3

REACTOR FEED (H2/(CO+1.5CO2)) :	0.50	
REACTOR FEED ((H2-CO2)/(CO+CO2)) :	0.35	
APPROACH TO METHANOL EQUILIBRIUM (deg.C) :	32.5	*
APPROACH TO WATER-GAS EQUILIBRIUM (deg.C) :	20.7	
METHANOL COLLECTED AS % OF CALCULATED :	90.5	
CALCULATED METHANOL PRODUCTION RATE (Kgmol/hr) :	6.02	

*35°C when MeOH concentration in reactor effluent is 5.79%.

Table 2-2 (Continued)

22-Apr-84 / 12:16 PM

LaPORTE LP METHANOL PROCESS AVERAGE REPORT
MATERIAL BALANCE SUMMARY

COMPONENT BALANCE (IN-OUT)/IN :

STREAMS # / STREAMS LOCATION / COMPONENT :	[PURE GASES - 1] FRESH FEED GAS	[(1+55)-15] REACTOR FEED	[25 - (50+51+62+68)] REACTOR EFFLUENT
	<% diff.>	<% diff.>	<% diff.>
H2	-6.88705	0.89538	-0.41968
CO	2.61536	0.44453	-0.52150
CO2	-34.00080	0.38905	0.49617
N2	-247.51600	2.11894	-0.56889
CH4	100.00000	7.51438	-0.35208
H2O	———	n.a.	-0.06282
CH3OH	———	4.01426	7.33587

OVERALL ELEMENTAL BALANCE (Kg-atoms/hr) :

	INPUTS	OUTPUTS					(IN-OUT)/IN
STREAM # / STREAM NAME	15 REACTOR FEED	55 RECYCLE	50 PURGE GAS	62 FLASH GAS	68 MeOH PRODUCT	TOTAL	%
CARBON:							
CO	58.9677	49.1862	4.4056	0.0494	———	53.6412	9.0329
CO2	15.0320	13.6359	1.2214	0.0988	———	14.9560	0.5052
CH3OH	0.3367	0.3507	0.0314	0.0716	5.4467	5.9005	-1652.6200
OTHERS	0.4879	0.4881	0.0437	0.0000	0.0561	0.5879	-20.4934
TOTAL C	74.8243	63.6619	5.7021	0.2198	5.5028	75.0857	-0.3494
HYDROGEN:							
H2	81.5488	54.5115	4.8826	0.0494	———	59.4435	27.1968
H2O	0.0000	0.0000	0.0000	0.0000	0.3089	0.3089	n.a.
OTHERS	3.2985	3.3556	0.3006	0.2864	21.9411	25.8837	-684.7160
TOTAL H	84.8472	57.8671	5.1831	0.3358	22.2500	85.6361	-0.9297
OXYGEN:							
TOTAL O	89.3683	76.8088	6.8797	0.3185	5.6246	89.6316	-0.2946
NITROGEN:							
TOTAL N	0.3749	0.3488	0.0312	0.0000	———	0.3801	-1.3868
TOTAL MASS FLOW (kg/hr)	2434.6000	2062.3900	184.7270	8.1190	180.7020	2435.9400	-0.0550

REACTOR GAS BALANCE (OUT/IN) :

	ACROSS REACTOR
MASS BALANCE, (%) :	100.000
ELEMENTAL BALANCE, (%) :	
CARBON	100.613
HYDROGEN	102.619
OXYGEN	100.642

In general, the methanol concentrations or production rates are less consistent and more difficult to measure than the relative amounts of CO and CO_2. The selectivity calculated across the reactor on page 2 of the report (107.3 percent) indicates that the concentration of methanol in the reactor effluent may be high. However, the value of selectivity calculated from the overall balance, which utilizes the product flow rate and liquid product concentrations, is closer to the expected selectivity, which should be between 98 and 99 percent (see Page 3 description).

In addition to catalyst and plant performance parameters such as productivities, yields, and approach to equilibrium, other useful data are included on the second page of the report. For example, the methanol collected in the liquid product as a percentage of the methanol production rate as calculated across the reactor (methanol collected as percent of calculated) also shows the relative values of the two modes to measure methanol make in the reactor.

Material Balance Summary (Page 3)

This page is a thorough material balance for both the individual components and the different atomic species. The "Component Balance" is helpful in assessing the correctness of the concentrations obtained by the different chromatographs. For the period included in Table 2-2, the major gases (H_2, CO, and CO_2) show less than 1 percent variations for the plant front-end and back-end component balances ("Reactor Feed" and "Reactor Effluent," respectively). The comparison between the "pure gases" flows (such as H_2, CO, and CO_2) and the calculated fresh feed flows could be a very useful check for the overall plant component balance. However, for the example included, only CO has an "acceptable" difference of 2.6 percent. In general, when two component balances show consistent and small variations, but a third such as the "fresh feed gas" in the example included shows diverging balances from the other two, it is reasonable to assume that some of the measuring pure gases flows are incorrect.

The third page of the report also provides CO, CO_2, and H_2 conversions in the seventh column of the "Overall Elemental Balance" (9.03, 0.51, and 27.1 percent, respectively). Methanol make could be obtained from this page by subtracting the methanol atomic carbon flow (kg-atoms/hr) of Stream #15 from the total output methanol carbon. Based on selectivity considerations, the resulting value of 5.56 kg atoms C/hr (kg mol MeOH/hr) is probably more accurate for obtaining the

corresponding catalyst methanol productivity:

$$\frac{5.56 \times 1{,}000}{255} = 21.8 \quad \frac{\text{g mol}}{\text{hr-kg cat}}$$

The closures included in the "Overall Elemental Balance" for the different atomic species (molecular for N_2) also aid in the evaluation of GC performance. For this plant balance, the closures are extremely good (less than one percent variation). The "Reactor Gas Balance" at the bottom of the third page also provides a check on concentrations. The hydrogen balance, for example, is not consistent with the carbon and oxygen balances (102.6 vs. 100.6 percent). This is, again, a consequence of high methanol concentrations coupled with the high hydrogen content of the methanol molecule (4 atoms/mol).

Thus, two parameters enable the accurate determination of methanol concentration: selectivities from the second page, and elemental balances from the third page. The use of two separate parameters is probably more accurate than relying on stoichiometric ratios across the reactor (i.e., $\Delta H_2/\Delta CO$).