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DOE/PC/90018--T13

LIQUID PHASE FISCHER-TROPSCH (II) DEMONSTRATION IN THE LAPORTE ALTERNATIVE FUELS DEVELOPMENT UNIT

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Topical Report

FINAL

(Volume VII: Appendix)

Task 1: Engineering Modifications (Fischer-Tropsch II Demonstration)

and

Task 2: AFDU Shakedown, Operations, Deactivation and Disposal (Fischer-Tropsch II Demonstration)

Contractor:

AIR PRODUCTS AND CHEMICALS
Allentown, PA 18195

Bharat L. Bhatt
September 1995

Prepared for the United States Department of Energy
Under Contract No. DE-AC22-91PC90018
Contract Period October 1990 - December 1995

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MASTER

LIQUID PHASE FISCHER-TROPSCH (II) DEMONSTRATION IN THE LAPORTE ALTERNATIVE FUELS DEVELOPMENT UNIT

Topical Report

FINAL

(Volume I/II: Appendix)

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APPENDIX A

Reactor Temperature Stability

MAR 22 1994

PROCESS ENGINEERING

To: Bharat Bhatt

From: V. Grant Fox
21 March 1994
V. Grant Fox

PROCESS DYNAMICS
LIQUID PHASE FISCHER-TROPSCH II

SUMMARY

The Laporte AFDU utility oil loop and reactor were simulated to determine how the reactor temperature will respond to external disturbances and changes in control action. The heat exchangers were modeled as lumped systems with the capacitance being the sum of the capacitance of the oil holdup and the metal mass associated with each exchanger. The Fischer-Tropsch reaction was simplified to first order and heat generation was modeled as the product of the extent of reaction and the heat that would be released at 100% conversion of the feed. Transportation lag between units determined from volumetric flow and piping volumes was also included in the model.

CONCLUSION

I. The system is open loop unstable. The combination of oil flow and the UA of the heat exchanger inside the reactor is insufficient to control reactor temperature. .The control action of the electric heater is definitely needed to achieve stability.

II. Process piping should be altered and the electric heater should be placed between the water cooled exchanger and the reactor in the AFDU. This placement accomplishes two things. First, stability is improved by eliminating the process lags associated with the exchangers and piping which. are presently between the heater and the reactor. Secondly, the control action will no longer be attenuated by the heat exchangers. Simulation shows that the process gain through the heat exchangers is about 0.5 (i.e. increasing the. temperature of the oil entering the fin/fan exchanger by one degree results in a 0.5 degree temperature rise in the oil exiting the water cooler). Thus in the present configuration about half of the control action of the heater is lost before it can be applied to the process.

MODELS

1. All models use steady state mass balances.
2. Dynamic energy balances describe the response of the oil in each process unit.
3. The dynamics of the process side of the reactor and the electric heater are modeled.
4. Steady state balances describe the response of the air and water temperatures in the fin/fan and water cooled exchangers respectively.

The expressions used to describe the process side of the reactor are shown below. As can be seen, the reaction was simplified to first order.

$$F\ (X_i - X_o) - R = 0.$$
$$R = K * X_o * EXP\ (-E/T)$$
$$EXTENT = (X_i - X_o)/X_i$$

HEAT GENERATION = EXTENT * HRXN
E = 23652 Deg Rankine

A first order expression is used to describe the dynamics of the oil temperature in the various heat exchangers. The time constant for the oil is shown below.

$$TAU = (M*Cp_{oil} + M*Cp_{metal})/(W*Cp_{oil} + UA)$$

RESULTS

The dynamics of three process configurations were studied and are labeled c1, c2, and c3 in the plots that follow. In configurations 1 and 2 the electrical heater is placed before the fin/fan cooler in the flow sheet. In configuration 1 there is no bypass around the fin/fan and the heater is firing at 90% of capacity. In configuration 2 30% of the oil bypasses the fin/fan and the heater fires at 50% of capacity. In configuration 3 the heater is placed between the water cooler and the reactor. A small amount of oil is bypassed around the fin/fan (3%) and the heater fires at 50%.

The first disturbance to the system was a 10000 btu/hr decrease in the reactor heat leak. A controller gain of twenty was used for the proportional controller which manipulated the firing of the heater to maintain the reactor temperature at an arbitrary set point. Figure 1 shows that all three process configurations did an acceptable job maintaining reactor temperature but that configuration 3 was clearly superior. Figure 2 show that much less control action, 5% of span vs. 10% of span, is needed for configuration 3.

The second disturbance studied was an abrupt 0.5 Deg F change in the reactor temperature set point. Figure 3 shows an overshoot of 80% of the intended change for configuration 1 and 2 and a 15% overshoot for configuration 3. Figure 4 shows again that much less control action after the initial jump is needed to control the reactor for configuration 3.

It should be kept in mind that the disturbances introduced in this study are small. It is highly likely that the control system in the AFDU will need to control much larger upsets than those studied here. Since control action is roughly proportional to the size of disturbance, I expect that in the present process configuration the control action will saturate and control could be lost. The combination of better control with less control action make configuration 3 (heater between water cooler and reactor) a much more robust process choice than configuration 1 or 2 (heater before fin/fan cooler).

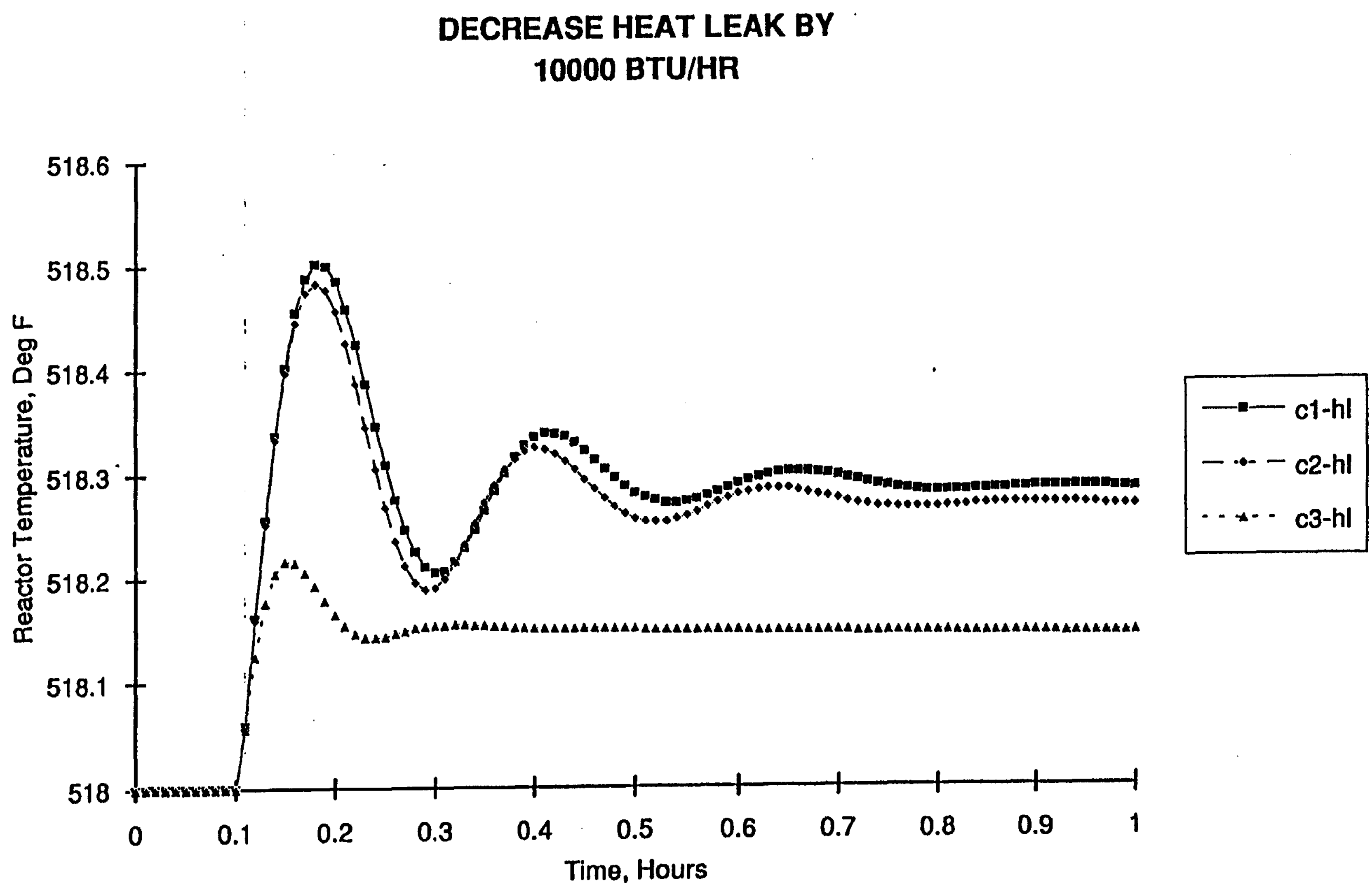
DECREASE HEAT LEAK BY
10000 BTU/HR
Reactor Temperature, Deg F
518.6
518.5
518.4
518.3
518.2
518.1
518
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Time, Hours
c1-hl
c2-hl
c3-hl

Fig 1

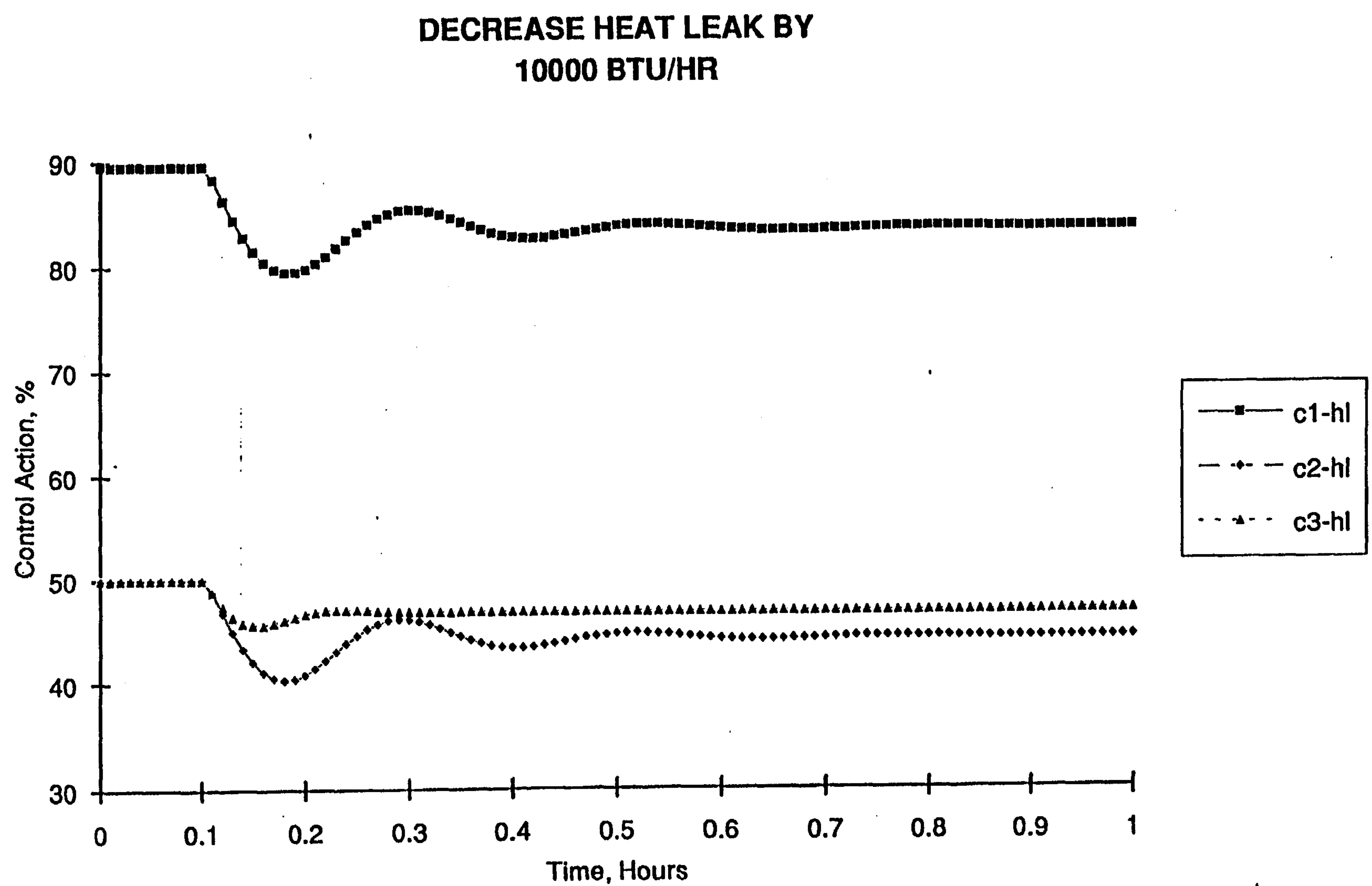
DECREASE HEAT LEAK BY
10000 BTU/HR
Control Action, %
90
80
70
60
50
40
30
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Time, Hours
c1-hl
c2-hl
c3-hl

Fig 2

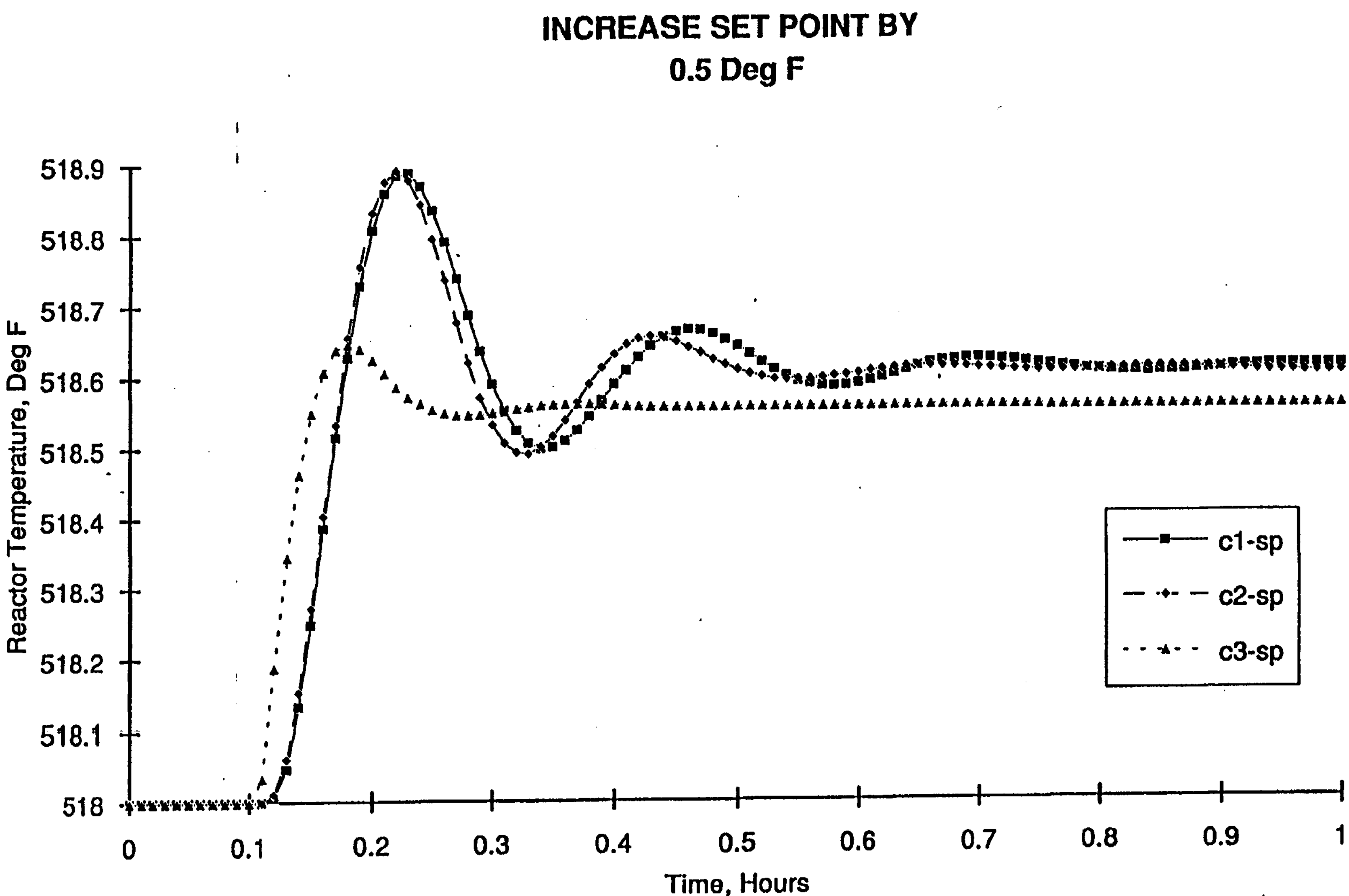
INCREASE SET POINT BY
0.5 Deg F
Reactor Temperature, Deg F
518.9
518.8
518.7
518.6
518.5
518.4
518.3
518.2
518.1
518
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Time, Hours
c1-sp
c2-sp
c3-sp

Fig 3

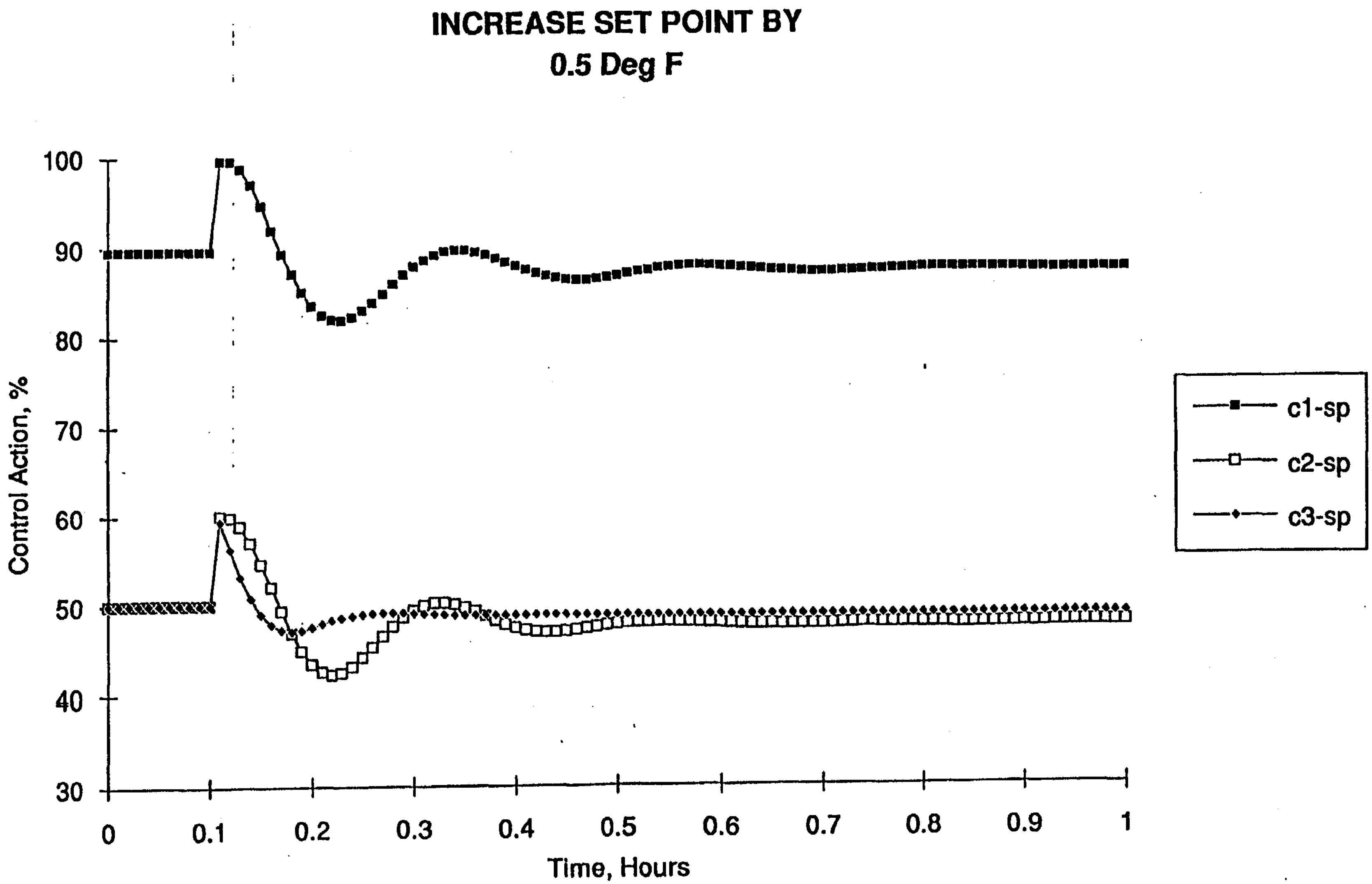
INCREASE SET POINT BY
0.5 Deg F
Control Action, %
100
90
80
70
60
50
40
30
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Time, Hours
c1-sp
c2-sp
c3-sp

Fig 4

APPENDIX B

Mott Cross-flow Filter Test for F-T II

mott MOTT METALLURGICAL CORPORATION
84 Spring Lane
Farmington Industrial Park
Farmington, CT 06032-3159
Fax: 203-674-1480 Phone: 203-677-7311

Controlled Porosity For Precision Products

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DEC 09 1993
PROCESS ENGINEERING

Laboratory Test Report

Tested **November 16-19, 1993**

Objective: Evaluate the flow stability of 0.2 micron porous filter media in the filtration of Fisher-Tropsch catalyst suspended in oil. Inertial filter tests were conducted using the Mott Bench Scale LSX Filter Model 7000-3/8-16". Barrier filtration tests were performed using the Mott 70 mm disc test filter and 0.2 micron media.

Customer: Air Products and Chemicals, Inc.
7201 Hamilton Ave.
Allentown, PA. 18195- 1501

Summary: Stable filtrate fluxes and filtrate clarity were obtained with 0.2 micron media with crossflow as well as barrier filtration.

Filtrate flux rates of about 0.02 gpm/ft2 remained stable over a period of 3 days of testing using the Mott Hypulse LSX Inertial (crossflow) filter. Feed slurry temperatures of 140-150°F were critical to maintain these rates. Mainstream velocity was about 6-7 ft/sec with the pressure drop across the element wall ranging from 12-14 PSI. Filtrate was visibly clear within 30 minutes. 1.0 micron media did not produce clear filtrate.

Barrier filtration testing using the Mott 70 mm disc test filter resulted with a filtrate fluxrate of .023 gpm/ft2 at 10 PSI. Filtrate was visibly clear. The resulting .093" thick cake was effectively backwashed using 30 PSI N2.

Further testing is recommended at the customers pilot plant to obtain more accurate sizing data for scale up design.

WO# 41042
Job# 1145-000
FN# 709-2
Sales: KJJ

By: Louise L Stange
Ms. Louise L. Stange

Approved: Klaus J. Julkowski
Mr. Klaus J. Julkowski

* Approval obtained on telephone from Dr. Klaus Julkowski(Mott) by Dr. Bhatt on 3/31/95 to release this report.

Information contained in this report is confidential to parties involved and should not be released without the consent of Air Products and Mott Metallurgical Corp.

Distribution: LHM, VJP, KJJ, LAB, REP# 004, Air Products

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Fax: 203-674-1460 Phone: 203-677-7311
Controlled Porosity For Precision Products

Laboratory Test Report

Customer: Air Products and Chemicals, Inc. **File #:709-2**
7201 Hamilton Ave.
Allentown, PA 18195-1501

Representative: Dr. Bharat L. Bhatt

MMC Sales Representative: Trist Co. Inc.

Material Tested: (3) 1 gallon samples of "unsupported" iron Fisher-Tropsch catalyst in oil supplied by the University of Kentucky. The catalyst had been deactivated and passivated for the testing .

Sample Disposition: All samples were returned to the University of Kentucky for analysis and disposal.

Summary of the Results: Inertial filter tests were performed using the Mott Hypulse LSX Inertial (cross-flow) filter with a 3/8" OD x 1/4" ID x 16" porous length element (.087 ft2 area). The feed was heated to 150 °F. A media life test was conducted by recirculating the filtrate back to the feed tank. The equipment arrangement and test procedure is described on pages 9 & 10.

Unsatisfactory filtrate quality was obtained using 1.0 micron porous media. Initial tests were conducted at a mainstream velocity of 7 ft/sec and a pressure drop across the element wall of 5-7 PSI. Filtrate was visibly cloudy. Filtrate turbidity was 20 NTU. Testing was discontinued after 125 minutes when the filtrate quality did not improve. Evaluation of the particle size range of the feed slurry using the Coulter Multisizer indicated a mean particle size of 3.4 microns.

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Laboratory Test Report

Clear filtrate was obtained using 0.2 micron porous media. Tests at a mainstream velocity of 6-7 FPS and a pressure drop across the element wall ranging from 12-14 PSI resulted with a filtrate flux of about .02 gpm/ft2 with slurry temperatures of 140-150°F. Filtrate was visibly clear within 30 minutes. Filtrate turbidity ranged from 0.45 - 20 NTU's.Refer to the graph of flowrate vs. cycle time in Figure 1.

At the conclusion of each day the feed slurry was removed from the tank and the system was flushed with clean oil. The filter was isolated once the oil was flushed thru the system. At start up the next morning the oil was removed and the feed slurry was added to the feed tank and temperatures were gradually increased from ambient to 150°F.

The inertial filter was backwashed once in the 3 days of testing. Backwashing did not significantly increase filtrate flux, which would indicate conditioning of the media.

Barrier filtration tests were conducted using the Mott 70 mm disc test filter and 0.2 micron media using the feed slurry sample isolated at the conclusion of Test 2. Average flux was .023 gpm/ft2 running at 10 PSI constant pressure. The resulting .093" thick cake was effectively backwashed using 30 PSI N2. Filtrate was visibly clear. Refer to Figure 5 for a schematic of equipment arrangement at test procedure.

<u>Conclusions and Recommendations:</u> 0.2 micron porous media is effective in both barrier and crossflow filtration in separating the unsupported iron catalyst from oil. In both cases average filtrate flux was .02 gpm/ft2.

Air Products "Unsupported Iron Catalyst" Mott Hypulse LSX Testing using 0.2 um Media (.087 ft2 area)

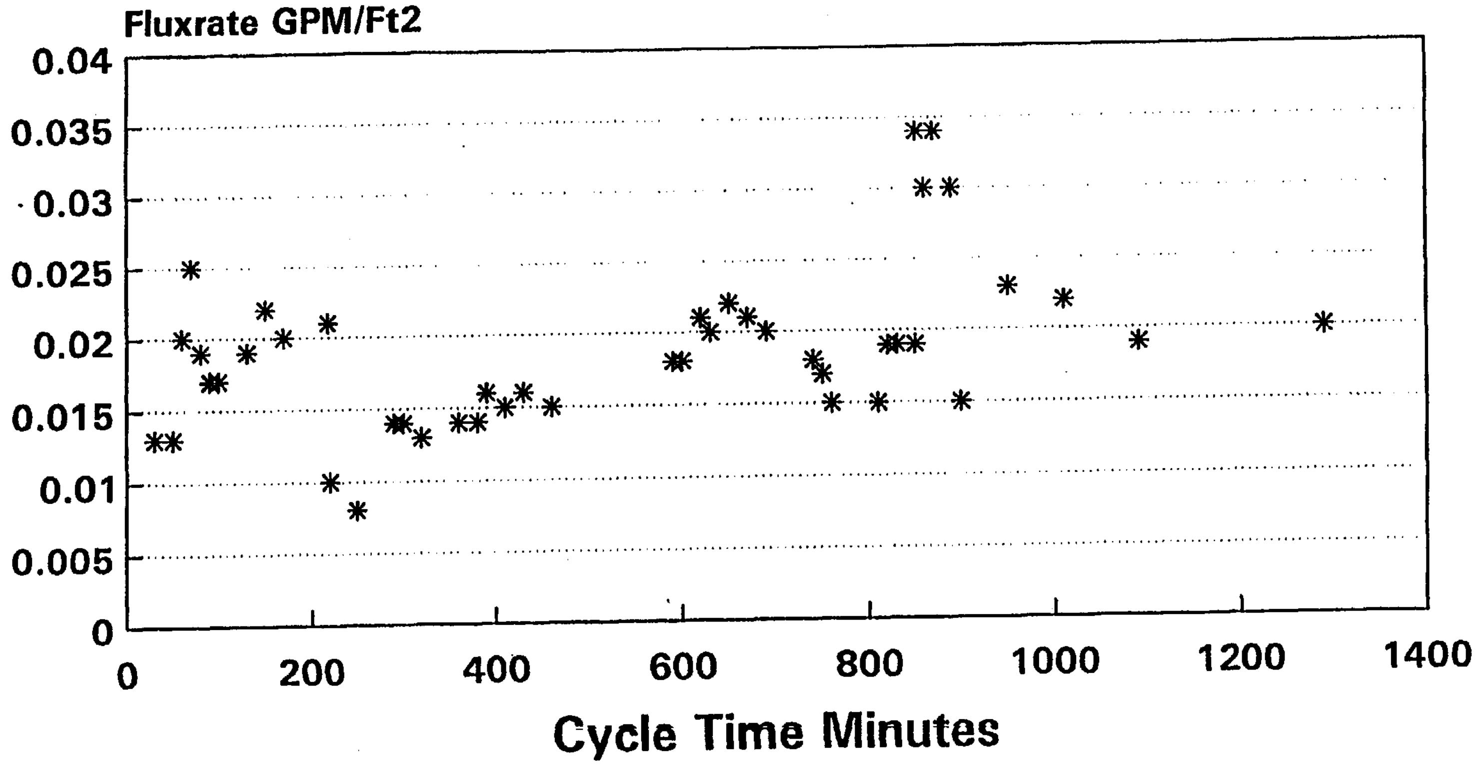

Figure 1

11/16/93

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Laboratory Test Report

Discussion of the Results:

Test #1 was run using 1.0 micron porous media. Unsatisfactory filtrate quality was obtained. Testing at a mainstream velocity of 7 ft/sec and a pressure drop across the element wall of 5-7 PSI resulted with filtrate fluxrates of .01 to .02 gpm/ft2. Filtrate was visibly cloudy. Filtrate turbidity was 20 NTU. Testing was discontinued after 125 minutes because filtrate quality did not improve.

Evaluation of the particle size range of the feed slurry using the Coulter Multisizer and the 100 micron aperature tube (having a range of 2.16 to 60 microns) indicated that the particle size of the feed ranged from 2.16 - 42 microns, with a mean particle size of 3-4 microns.

Test #2 was conducted using 0.2 micron porous media. Fluxrates of .02 gpm/ft2 were obtained within 1 hour of running time, with feed temperatures of 140°F. Pressure drop across the element wall was gradually increased from 6 to 15 PSI. The filter was run for a total of 218 minutes without backwashing. The system was shut down, the feed was drained from the system, and clean oil was used to flush the system. The next morning the oil was removed and the same feed slurry batch from the previous day was used.

The filter was restarted when feed slurry temperatures reached about 100°F. Mainstream velocity was about 6 ft/sec. Pressure drop across the element wall was gradually increased to about 12 PSI. Filtrate was visibly clear within 2 hours. We suspect that some residual solids from Test 1 were flushed from the lines. Fluxrates were about .015 gpm/ft2 with feed slurry temperatures of 100-130°F. Fluxrates of 0.2 gpm/ft2 were obtained once feed temperatures reached 138-140°F.

After 680 minutes the filter was backwashed (1/2 sec pulse, 60 PSI). After backwash filtrate flux returned to .02 gpm/ft2. Filtrate was slightly cloudy, but cleared up within 30 minutes.

A short cycle was run (46 minutes) to determine the effect of lowered velocity. Testing at a mainstream velocity of 5.6 ft/sec and a pressure drop across the element wall of 11-12 PSI resulted with an average flux of .0168 gpm/ft2. Feed slurry temperatures ranged from 135-140°F. The filter was shut down using the same procedure as the previous day.

The filter was restarted on 11/18 and within 1 hour fluxrate of .019 gpm/ft2 were obtained. After 90 minutes the pressure drop across the element wall was increased from 11.75 to 26 PSI. Mainstream velocity increased to 9 ft/sec. Filtrate flux increased

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Laboratory Test Report

to .03- .04 gpm/ft2. We could not maintain this pressure for extended testing because the pump seals were leaking. After 40 minutes he pressure was decreased to 13.5 PSI and the filter was run for about 5 hours with filtrate fluxrates holding at .018 - .02 gpm/ft2, with visibly clear filtrate.

At the conclusion of the inertial filter testing the feed slurry was removed from the feed tank. The particle size distribution of the feed was analyzed and compared to the feed at the start of the testing. The results are summarized in Figures 2 & 3. We suspect that the variation from start to finish is in the sampling technique.

<u>Barrier Filtration Testing:</u> Barrier filtration tests were conducted using the Mott 70 mm disc test filter and 0.2 micron media. Feed slurry collected at the conclusion of Test 2 was used in the evaluation . A one liter pressure vessel was used to feed the slurry to the filter at constant pressure. Average flux was .023 gpm/ft2. The resulting .093" thick cake was effectively backwashed using 30 PSI N2. Filtrate was visibly clear. Refer to the schematic and test procedure in Figure 5.

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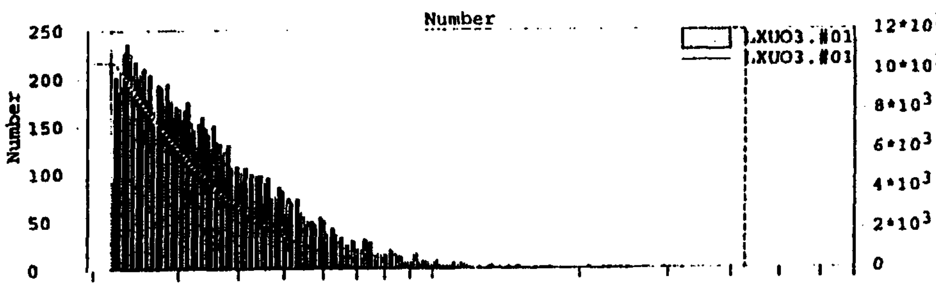
Controlled Porosity For Precision Products

COULTER(R) Multisizer AccuComp(R) Rev. 1.10 15:13 Tue Nov 16 1993

LXUO3.#01

Filename: LXUO3.#01 Sample Number: 1
Group ID: lxuo3
Sample ID: Feed at start
Comments: cake from gravimetric analysis acetone washed
Operator: LS
Electrolyte: Isoton II
Dispersant: 1A
Aperture Size: 100 um Aperture Current: 1600 uA
Channels 256 Kd: 991.49
Full Data Log Diameter Gain: 2
Control Method: Siphon 2000 ul
Raw Count: 10733
Coinc. Corr. Count: 10795 Variable 1: 0.000000
Variable 2: 0.000000
Acquired at: 10:49 Tue Nov 16 1993



Particle Diameter (um)
LC= 2.162 um UC= 42.58 um

Number Statistics (Geometric) LXUO3.#01

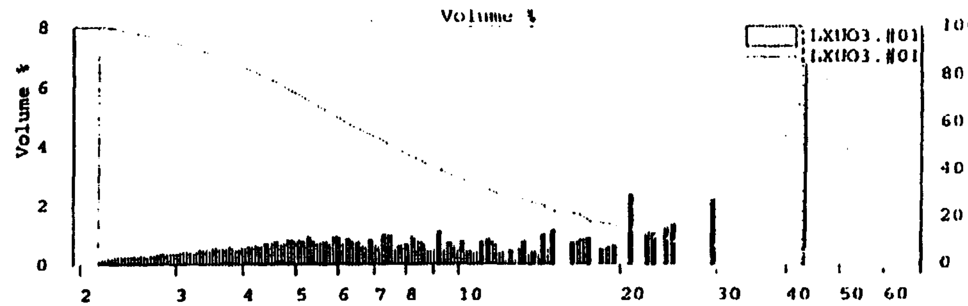
Calculations from	2.16 um to 42.58 um				
Number	10400		Coinc. Corrected:	10795	
Mean:	3.440	um	95% Conf. Limits:	3.417-3.464	um
Median:	3.174	um	Std. Dev.:	0.359	
Mean/Median Ratio:	1.084		Variance:	0.129	
Mode:	2.333	um	Coef. Var.:	29.09	%
			Skewness:	1.140e+000	Right skewed
			Kurtosis:	1.559e+000	Leptokurtic

% >	10.00	25.00	50.00	75.00	90.00
Size um	5.650	4.228	3.174	2.589	2.334

COULTER(R) Multisizer AccuComp(R) Rev. 1.10 15:14 Tue Nov 16 199

LXUO3.#01

Filename: LXUO3.#01 Sample Number: 1
Group ID: lxuo3
Sample ID: Feed at start
Comments: cake from gravimetric analysis acetone washed
Operator: LS
Electrolyte: Isoton II
Dispersant: 1A
Aperture Size: 100 um Aperture Current: 1600 uA
Channels 256 Kd: 991.49
Full Data Log Diameter Gain: 2
Control Method: Siphon 2000 ul
Raw Count: 10733
Coinc. Corr. Count: 10795 Variable 1: 0.000000
Variable 2: 0.000000
Acquired at: 10:49 Tue Nov 16 1993



Particle Diameter (um)
LC= 2.162 um UC= 42.58 um

Volume Statistics (Geometric) LXUO3.#01

Calculations from	2.16 um to 42.58 um				
Volume	$563.9*10^3$	um^3	Coinc. Corrected:	10795	
Mean:	7.463	um	95% Conf. Limits:	7.451-7.476	um
Median:	7.033	um	Std. Dev.:	0.646	
Mean/Median Ratio:	1.061		Variance:	0.417	
Mode:	20.85	um	Coef. Var.:	32.12	%
			Skewness:	2.765e-001	Right skewed
			Kurtosis:	-7.474e-001	Platykurtic

% >	10.00	25.00	50.00	75.00	90.00
Size um	19.53	11.61	7.033	4.584	3.277

Figure 2

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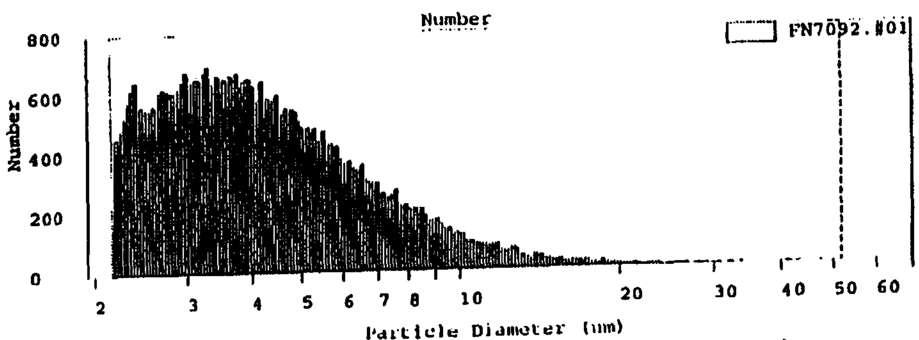
COULTER(R) Multisizer AccuComp(R) Rev. 1.10 09:57 Mon Nov 29 1993
FN7092.#01

Filename: FN7092.#01 Sample Number: 1
Group ID: fn7092
Sample ID: feed slurry end of testing
Comments: Air Products Catalyst after 1290 hrs
Operator: LS
Electrolyte: Isoton II
Dispersant: 1A
Aperture Size: 100 um Aperture Current: 1600 uA
Channels 256 Kd: 991.49
Full Data Log Diameter Gain: 2
Control Method: Siphon 2000 ul
Raw Count: 56855
Coinc. Corr. Count: 58672 Variable 1: 0.000000
Variable 2: 0.000000

Acquired at: 09:56 Mon Nov 29 1993



LC= 219.0 @ 2.162 um UC= 1.000 @ 51.70 um (52675)

Number Statistics (Geometric) FN7092.#01

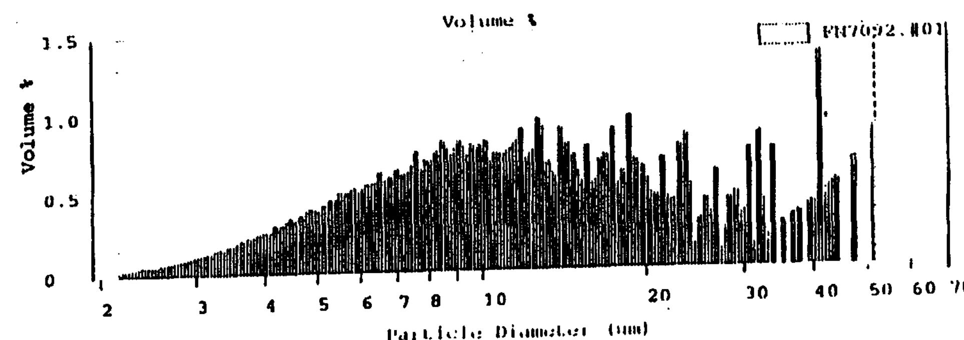
Calculations from 2.16 um to 51.70 um
Number 52675 Coinc. Corrected: 58672
Mean: 4.265 um 95% Conf. Limits: 4.249 4.282 um
Median: 3.975 um Std. Dev.: 0.452
Mean/Median Ratio: 1.073 Variance: 0.204
Mode: 3.299 um Coef. Var.: 31.14 %
Skewness: 8.298e-001 Right skewed
Kurtosis: 6.058e-001 Leptokurtic

% >	10.00	25.00	50.00	75.00	90.00
Size um	7.965	5.611	3.975	3.000	2.495

COULTER(R) Multisizer AccuComp(R) Rev. 1.10 09:58 Mon Nov 29 1993
FN7092.#01

Filename: FN7092.#01 Sample Number: 1
Group ID: fn7092
Sample ID: feed slurry end of testing
Comments: Air Products Catalyst after 1290 hrs
Operator: LS
Electrolyte: Isoton II
Dispersant: 1A
Aperture Size: 100 um Aperture Current: 1600 uA
Channels 256 Kd: 991.49
Full Data Log Diameter Gain: 2
Control Method: Siphon 2000 ul
Raw Count: 56855
Coinc. Corr. Count: 58672 Variable 1: 0.000000
Variable 2: 0.000000

Acquired at: 09:56 Mon Nov 29 1993



LC= 0.015% @ 2.162 um UC= 0.873% @ 51.70 um (100.00%)

Volume Statistics (Geometric) FN7092.#01

Calculations from 2.16 um to 51.70 um
Volume $0.120 \cdot 10^6$ um^3 Coinc. Corrected: 58672
Mean: 12.00 um 95% Conf. Limits: 11.99 12.01 um
Median: 11.70 um Std. Dev.: 0.687
Mean/Median Ratio: 1.025 Variance: 0.472
Mode: 41.13 um Coef. Var.: 27.63 %
Skewness: 6.812e-002 Right skewed
Kurtosis: -6.127e-001 Platykurtic

% >	10.00	25.00	50.00	75.00	90.00
Size um	31.96	19.26	11.70	7.318	4.916

Figure 3