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Interoffice Communication

To J. A. DeBernardi

From M. W. Cheesman

Date December 8, 1982

Subject Evaluation of Carbon Tetrachloride Injection System

An evaluation was made of the necessity of installing a Carbon Tetrachloride Injection System (preliminary cost estimate of $100M) before the VCM Plant begins operation with Oxygen-based Oxy. Carbon tetrachloride, CCl_4, acts as a cracking initiator (increases conversion and decreases energy consumption) in the pyrolysis of EDC to VCM. Presently, the Oxychlorination reaction system is the only identified source of CCl_4 in the plant. Following the conversion to Oxygen-based Oxy the production of CCl_4 is projected to drop considerably, thus, causing a drop in CCl_4 levels in the furnace feed. Therefore, the justification for direct injection of CCl_4 was evaluated as well as the use of recycle EDC bypass as ways to sustain high levels of CCl_4 in the furnace feed. The injection system only has an economic return if use of recycle EDC bypass to increase carbon tet levels in the furnace feed is unreliable. Based on current operations there is no reason not to expect reliable operation of recycle bypass at a 95% level (i.e., bypassing 95% of the recycle EDC stream to the Heavy Ends Column). This bypass level would provide a sufficient concentration of CCl_4 (1500 ppm) in the furnace feed without having to install the injection system. Therefore, it is recommended that the injection system not be installed before the Modernization startup. After the startup, data should be available to verify the need for an injection system.

The impact that CCl_4 has on conversion and in turn how conversion affects the energy input per pound of product was quantified using actual plant operating data. Correlations were generated (see Appendix A) and used to determine what effects lower levels of CCl_4 in the furnace feed would have on production and energy consumption. Operation of the VCM Plant at full production (2.1MM lbs. VCM/day) would be hampered by the reduced conversion due to the lower CCl_4 concentrations. Increasing the CCl_4 concentration in the furnace feed is possible without direct injection by increasing the percent of the recycle EDC stream that is bypassed to the Heavy Ends Column. For evaluating the injection system, the base CCl_4 concentration in the furnace feed was assumed to be 500 ppm which would be present due to bypassing 85% of the recycle stream. The bypass level of 85% was a conservative estimate while the actual level will probably be higher. The problems that might be encountered are the operational reliability of EDC recycle bypass, lower than anticipated CCl_4 make from Oxygen-based Oxy, controlling the CCl_4 concentrations at high (>85%) bypass levels, and controlling the concentrations of other impurities such as benzene and chloroform. Chloroform is a cracking inhibitor but its effects are much smaller than CCl_4. Present operation of recycle bypass has been extremely reliable since installation of the prefilters for the Recycle EDC Reactor, R-103 (eliminating the one problem in the system, plugging of R-103). In addition, there has not been any problems controlling the

Also minor chloroform which is inhibitor

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CCl_4 levels in the furnace feed. However, the effects of operations with Oxygen-based Oxy need to be evaluated based on actual CCl_4 production, and production and buildup of impurities.

Assuming that a CCl_4 concentration of only 500 ppm can be obtained with recycle bypass, the injection system for adding an additional 500 to 1500 ppm of CCl_4 to the furnace feed at full rates would have a DCF return of 123.3% to 308.3% (savings of $18.9M/month to $51.6M/month) for a sold-out VCM market (See Table I). At lower production rates (1.8MM lbs. VCM/day) the energy savings due to increased conversion that occurs because of an additional 500 to 1500 ppm of CCl_4 generates DCF returns (See Table IIA) of 51.3% to 130.6% (savings of $7.2M/month to $21.3M/month). Further details of the project economics can be found in the attached discussion.

If major problems are encountered with recycle EDC bypass and additional CCl_4 is necessary in the furnace feed to maintain production, the injection system would be installed. Howerver, if it were determined that such a system would be needed quicker than the 4-5 months required for installation of the system as designed, another alternative would be to use a metering pump and a small tank. A metering pump and 1000 gallon tank, preassembled on a skid, could be delivered 77 days after being ordered at a cost of $18,300. Installation of connecting piping could be completed by plant personnel one week following delivery (Maintenance Department estimate) which is one to two months less than the estimated installation time of the pressure injection system. This option needs to be investigated further, but is a viable alternative if a CCl_4 injection system were needed on an emergency basis.

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Therefore, it is recommended that the final design and engineering be completed on the Carbon Tetrachloride Injection System, but procurement of equipment be delayed until the need and timing can be assessed following startup of Oxygen-based Oxy. The necessary tie-ins will still be made during the 1983 modernization turnaround. Delaying installation will allow for confirmation of O_2-Oxy CCl_4 production and further deminstration of the reliability of recycle EDC bypass. Production losses will also be minimal since full rate operations during the summer months are limited due to cooling requirements, not the cracking furnaces.

If you have any questions please contact me at ETN 640-5060.

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DISCUSSION

The literature published concerning the pyrolysis of EDC to VCM and HCl indicates that CCl_4 in the EDC feed acts as a cracking initiator. The effect of the initiator is to increase the conversion of EDC to VCM while decreasing the energy input to the cracking furnaces per pound of product. Presently, the CCl_4 in the VCM Plant's furnace feed is generated in the Oxychlorination Unit (1000-3000 ppm in air-based Oxy EDC). The level of CCl_4 in the furnace feed (1000-2000 ppm) is set by the Light Ends Column C-102, split (percentage leaving with the bottoms EDC) of the CCl_4 entering with the Oxy and recycle EDC streams and the percent of the recycle EDC stream that is bypassed directly to the Heavy Ends Column, C-103. The Shell VCM Plant in Deer Park has indicated that following the conversion to O_2-based Oxy the production of CCl_4 drops considerably (0-800 ppm). With this drop Shell experienced a corresponding drop in CCl_4 in their cracking furnace feed which caused a decrease in conversion of EDC to VCM and also a higher energy requirement. The Conoco VCM Plant would also expect to encounter conversion problems and higher energy use in the cracking furnaces with such low levels of CCl_4.

An effort was made to quantify the impact that CCl_4 has on EDC conversion to VCM and in turn how conversion affects the natural gas energy input per pound of product. Actual plant operating data from June 11, 1982 to July 26, 1982 was used and the results are summarized in Appendix A. In general, every additional 100 ppm of CCl_4 in the furnace feed raises the conversion level 0.233% and each 1% rise in conversion decreased the furnace natural gas consumption by 21.41 BTU/lb. VCM. An increase in conversion also leads to decreased steam usage in the Heavy Ends Column, C-103, reboilers due to a smaller recycle EDC stream. The correlations also attempt to quantify the effects of furnace feed rate, maximum temperature, and the number of days since decoking on conversion and energy per pound of product.

There are two methods to increase the CCl_4 concentration in the EDC feed to the cracking furnaces:

1) Bypass a portion of the Recycle EDC stream around the wash system and C-102 directly to C-103.

2) Inject carbon tetrachloride directly into the furnace feed.

The first is to bypass a portion of the Recycle EDC stream directly to C-103. The CCl_4 concentration will increase as the percent bypassed increases. The CCl_4 level which can be maintained is dependent upon not just the percent bypassed but also the CCl_4 make in O_2-based Oxy and the carbon tet split from the Light Ends Column to the Heavy Ends Column. Figures IA & B, and II show the effects of varying any of these three parameters. Theoretically, any level of CCl_4 cna be obtained in the furnace feed with this method. However, there might be problems with controlling the CCl_4 concentration due to variations in the C-102 CCl_4 split, or the Oxy CCl_4 make. Also at high bypass levels (>85%), small changes in the percent bypass will cause significant changes in the CCl_4 furnace feed concentration. For example, if the assumed O_2-Oxy CCl_4 make is 400 ppm in the Oxy EDC, the C-102 CCl_4 split is 40% and the bypass level is 85%, the CCl_4 level in the furnace feed will be 500 ppm; increase the bypass to 90% and the CCl_4 concentration increases to 734 ppm. Operation of recycle bypass also increases the levels of other impurities such as benzene and chloroform ($CHCl_3$), a mild cracking inhibitor. Figures III A&B show the effects of recycle bypass on the $CHCl_3$ concentrations in the furnace feed at varying C-102 chloroform splits. Another concern is the reliability of operation of the Recycle Reactor, R-103, and thus recycle bypass itself. The major problem causing R-103 shutdowns was previously pluggage with coke fines, but this problem has been corrected with the installation of new prefilters. The original purpose of bypassing the recycle EDC stream was to save steam in the Light Ends Column reboilers. Therefore to maximize this savings the percent bypassed needs to be maximized. A conservative estimate of bypass level (85%) was used but current operation indicates that higher levels of recycle EDC bypass should be obtainable without any loss in reliability. This also creates the added bonus of increasing the carbon tet levels in the furnace feed without any additional capital investment.

The second method to increase the CCl_4 concentration in the EDC feed to the cracking furances is to inject carbon tet directly into the feed. The direct injection method allows for better control of the CCl_4 levels in the furnace feed. The injection rate would be set by the CCl_4 levels in the Pure EDC Tank, T-451. This method allows for an additional margin of reliability in the event that recycle EDC bypass is reduced or shutdown, or CCl_4 make from Oxy is drastically reduced. The estimated capital cost of the Carbon Tet Injection System is $100M. The economics associated with a sold-out VCM market are shown in Table I while Tables II A&B are for a market-limited VCM market. Both cases assume a base CCl_4 level of 500 ppm which corresponds to a recycle EDC bypass of 85%, 400 ppm CCl_4 in Oxy EDC, and a C-102 CCl_4 split of 40%. The DCF return varies from 123.3% to 308.3% for the sold-out VCM market (Table I) for CCl_4 levels of 1000 to 2000 ppm (injecting 500 to 1500 ppm). The largest impact here isthe additional production that could be claimed due to increased cracking furnace run time between decokings. Neglecting the additional production and considering just the energy savings, the DCF return varies from 40.7% to 70.8%. The market-limited VCM market cases (assumed VCM production of 1.8MM lbs./day) claim only savings in energy (natural gas and steam). The savings in Table IIA are due to increasing the conversion with higher CCl_4 levels in the furnace feed while assuming that the maximum temperature is constant. Increasing the conversion also decreases the furnace feed which is necessary to produce a set amount of VCM and also decreases the amount of recycle EDC. The DCF return varies from 51.3% to 130.6% for CCl_4 levels of 1000 to 2000 ppm (injecting 500 to 1500 ppm). The savings in Table IIB are due to decreasing the maximum cracking temperature with higher CCl_4 levels in the furnace feed while holding the conversion constant (as opposed to increasing conversion with higher temperatures in Table IIA). The savings due to the reduced temperature would not be sufficient to economically justify the injection system.

In general, higher levels of CCl_4 are necessary in order to maintain a production rate of 2.1MM lbs. VCM/day for a period longer than one week. Therefore, if the reliability and levels of recycle EDC bypass are questionable, an injection system, either by metering pump or by pressure is necessary. However, delaying installation of the system until three to six months following the Oxy modernization would allow for further insight to be gained into plant operations with O_2-based Oxy and therefore a more definitive justification for the system could be made.

TABLE I

ECONOMICS OF A CARBON TET INJECTION SYSTEM BASED ON A SOLD-OUT VCM MARKET

Carbon Tet Concentration in Feed Following Injection (ppm)	Additional Production M$/Yr	Decreased Natural Gas Usage in Furnaces M$/Yr.	Decreased Decoking Costs M$/Yr.	Decreased Steam Use in C-103 M$/Yr.	Cost of CCl_4 For Injection M$/Yr.	DCF Return %	DCF Return Without Additional Production %
1000	154.8	32.7	6.5	33.0	14.8	123.3	40.7
1500	309.8	49.8	12.9	58.4	29.6	220.3	61.0
2000	464.7	50.5	19.4	84.1	44.6	308.3	70.8

Basis:

1) Constant VCM production rate of 2.1MM lbs./day until reaching the assumed minimum conversion level of 50%. At this point a 1.5 day furnace decoking takes place.
2) Maximum temperature 515°C.
3) A turnaround length of 28 days.
4) Cost factors:
   a) Gross Margin of VCM in 1983 = 3.94 ¢/lb. (from JGD)
   b) Natural Gas cost of $4.0015/MSCF (1983 Variable Cost Budget)
   c) Steam cost of $6.4539/M lbs. (1983 Variable Cost Budget)
   d) Carbon Tetrachloride cost of $0.165/lb. (from JKM)
5) Capital Cost of Carbon Tet inject system is $100M.
6) All steam savings in C-103 can be claimed.
7) Recycle EDC bypass of 85% and a Light Ends Column CCl_4 split of 40% which amounts to a normal CCl_4 concentration in the Furnace Feed of 500 ppm.

TABLE IIA

ECONOMICS OF A CARBON TET INJECTION SYSTEM BASED ON A MARKET-LIMITED VCM MARKET WITH INCREASING CONVERSION

Carbon Tet Concentration in Feed Following Injection (ppm)	Decreased Natural Gas Usage in Furnaces M$/Yr.	Decreased Steam Use in C-103 M$/Yr.	Cost of CCl_4 for Injection M$/Yr.	DCF Return %
1000	55.3	31.2	12.2	51.3
1500	110.5	61.1	23.6	92.1
2000	165.8	90.3	34.7	130.6

Basis:

1) Constant VCM production rate of 1.8MM lbs./day for 7680 hours per year. The base case is for the furnace EDC feed to contain 500 ppm of CCl_4 which would be set by the level of recycle bypass (85%) and the CCl_4 split in the Light Ends Column (40%). The cracking depth for the 500 ppm case is 55% and will increase with increasing levels of CCl_4.
2) Cost factors:
   a) Gross Martin of VCM in 1983 = 3.94 ¢/lb. (from JGD).
   b) Natural Gas cost of $4.0015/MSCF (1983 Variable Cost Budget).
   c) Steam cost of $6.4539/M lbs. (1983 Variable Cost Budget).
   d) Carbon Tetrachloride cost of $0.165/lb. (from JKM).
3) Capital Cost of carbon tet injection system is $100M.
4) All steam savings in C-103 can be claimed.

TABLE IIB

ECONOMICS OF A CARBON TET INJECTION SYSTEM BASED ON A MARKET-LIMITED VCM MARKET WITH CONSTANT CONVERSION

Carbon Tet Concentration in Feed Following Injection (ppm)	Decreased Natural Gas Usage in Furnaces M$/Yr.	Decreased Steam Use in C-103 M$/Yr.	Cost of CCl_4 for Injection M$/Yr.	DCF Return %
1000	3.1	0	12.2	< 0
1500	6.2	0	23.6	<0
2000	9.4	0	34.7	<0

Basis:

1) Constant VCM production rate of 1.8MM lbs./day for 7680 hours per year. The base case is for the furnace EDC feed to contain 500 ppm of CCl_4 which would be set by the level of recycle bypass (85%) and the CCl_4 split in the Light Ends Column (40%). The cracking depth will be constant (55%) for all cases while the maximum temperature would decrease with increasing levels of CCl4.
2) Cost factors:
   a) Gross Margin of VCM in 1983 = 3.94 ¢/lb. (from JGD).
   b) Natural Gas cost of $4.0015/MSCF (1983 Variable Cost Budget).
   c) Steam cost of $6.4539/M lbs. (1983 Variable Cost Budget).
   d) Carbon Tetrachloride cost of $0.165/lb. (from JKM).
3) Capital cost of carbon tet injection system is $100M.
4) There would be no steam savings in C-103 due to constant conversion.

Figure IA

Furnace Feed CCl_4 Levels vs.

Recycle EDC Bypass from 0-90%

With Varying Light Ends Column Splits

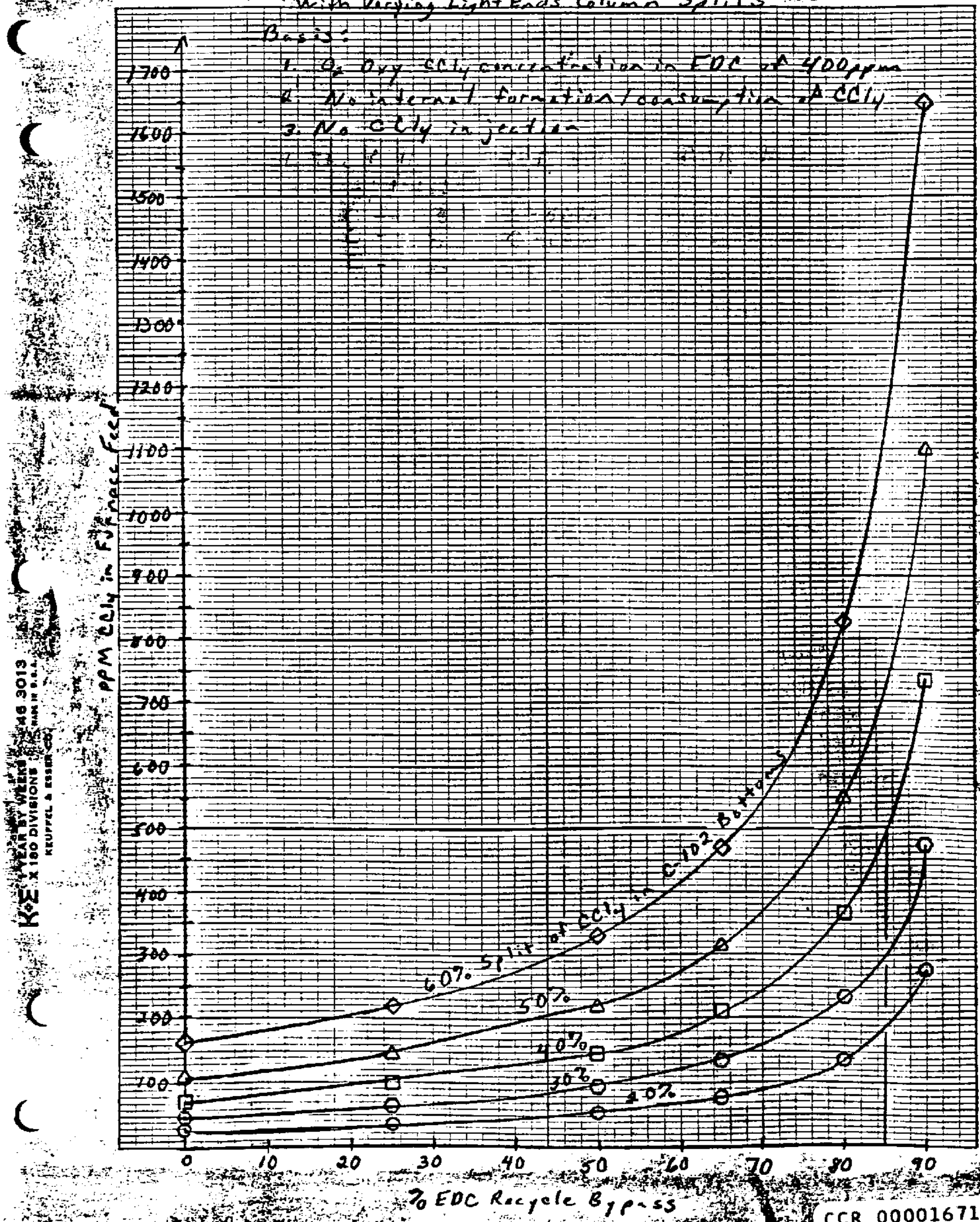

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Figure IB

Furnace Feed CCl_4 Levels vs.

Recycle EDC Bypass from 90%

With Varying Light Ends Column Splits

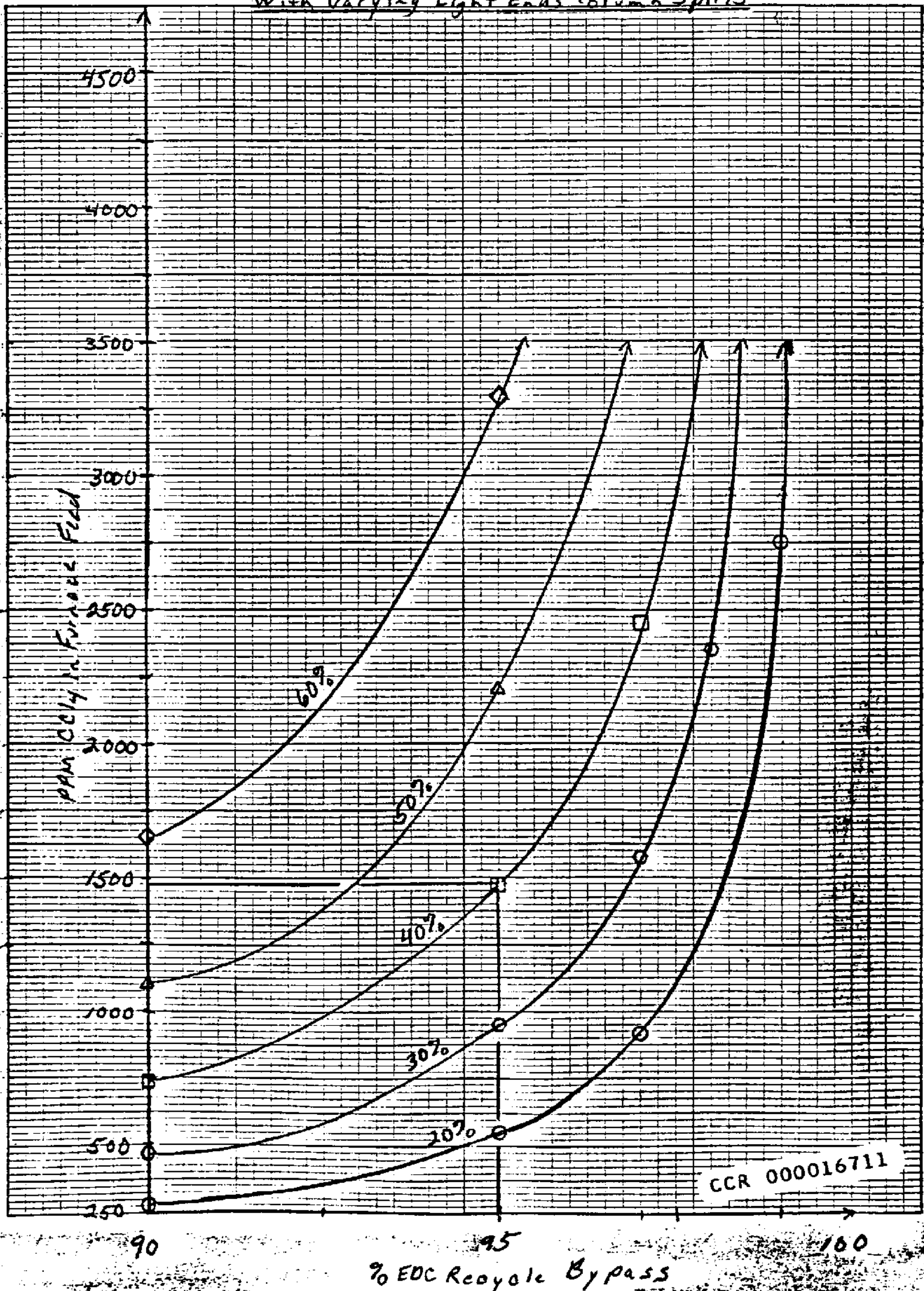


Figure II

Furnace Feed CCl_4 Levels vs.

Recycle EDC Bypass from 0-95%

with Varying Oxy CCl_4 Make

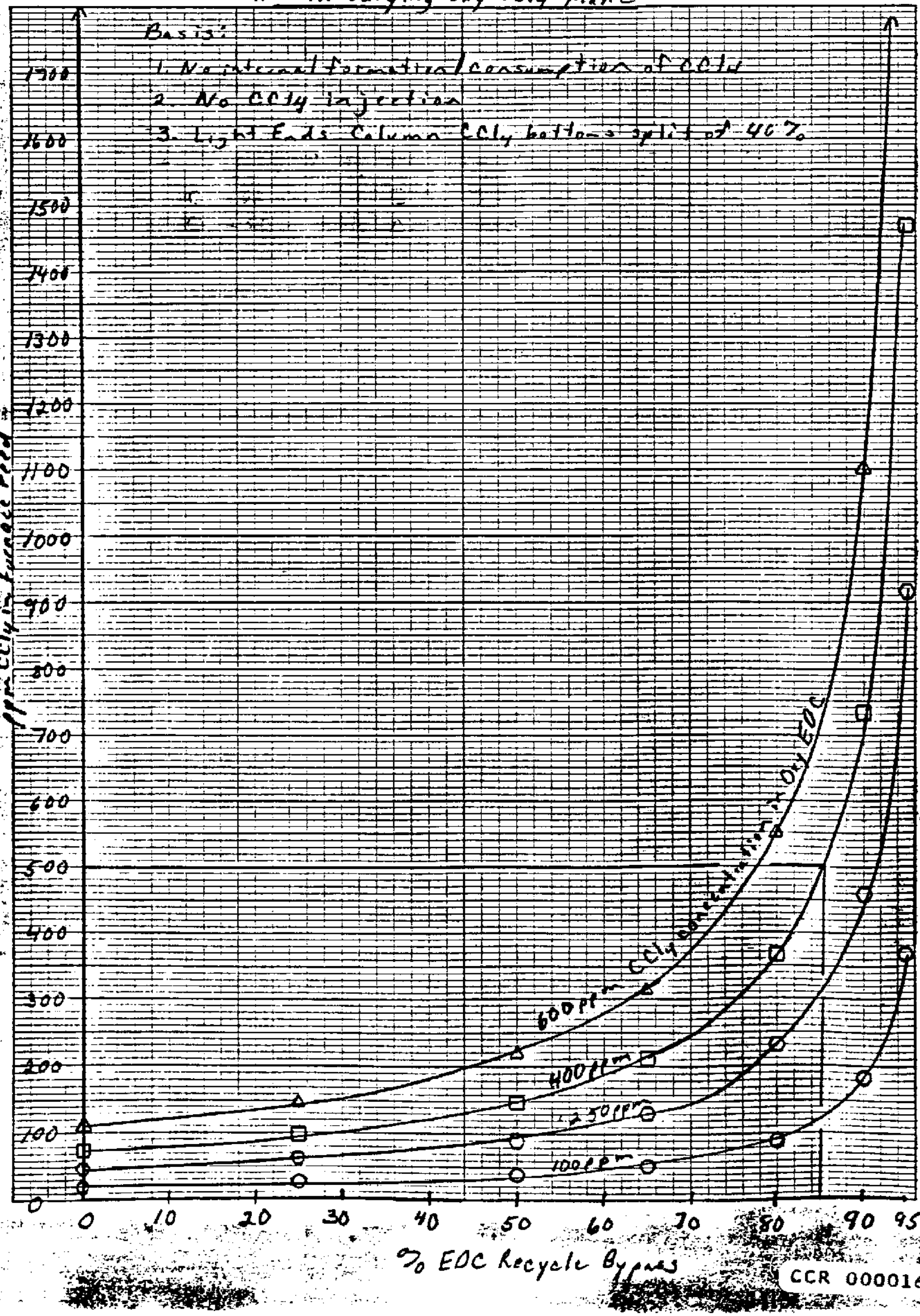


Figure IIIA
Furnace Feed $CHCl_3$ Levels vs.
Recycle EDC Bypass from 0-90%
With Varying Light Ends Column Splits

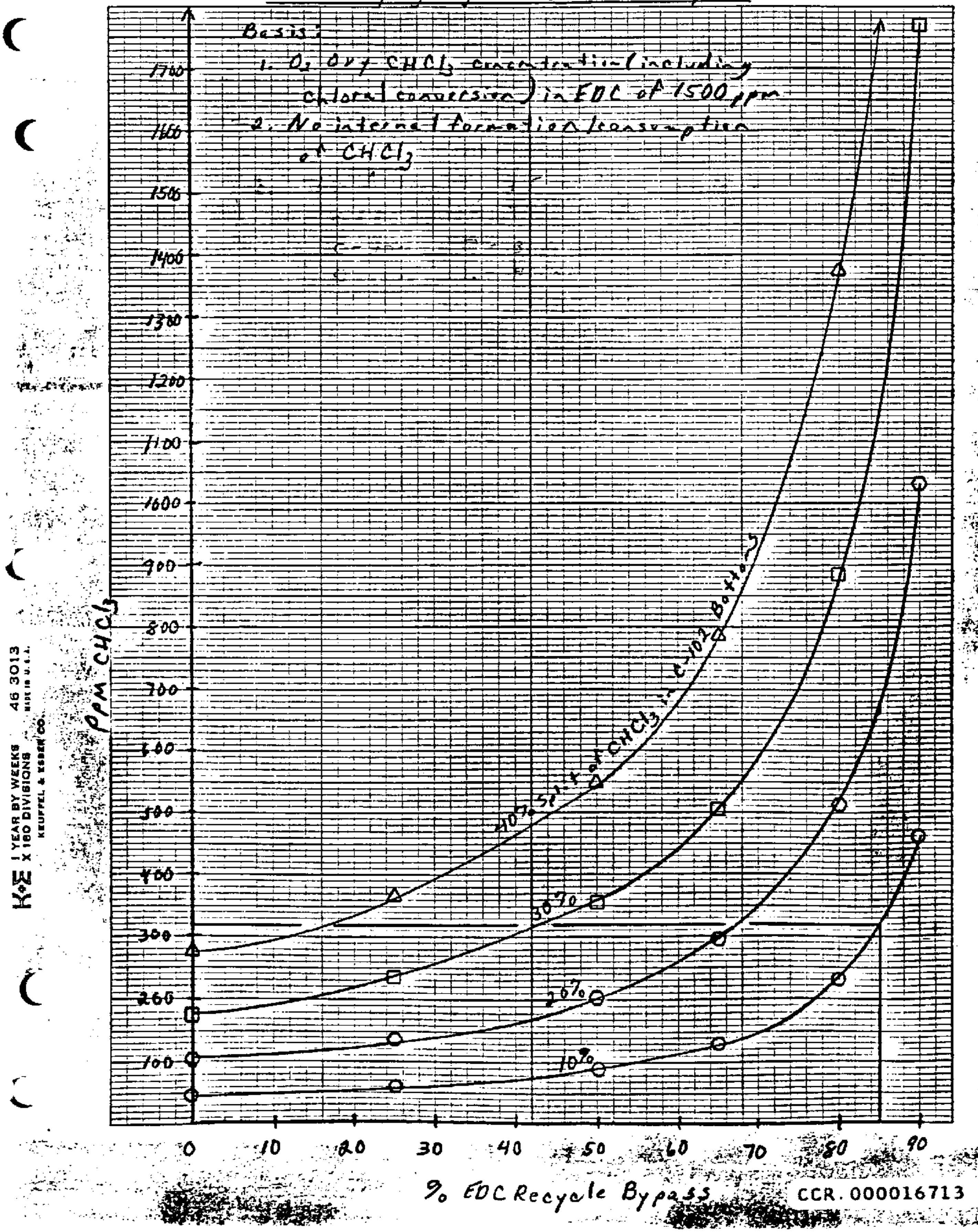
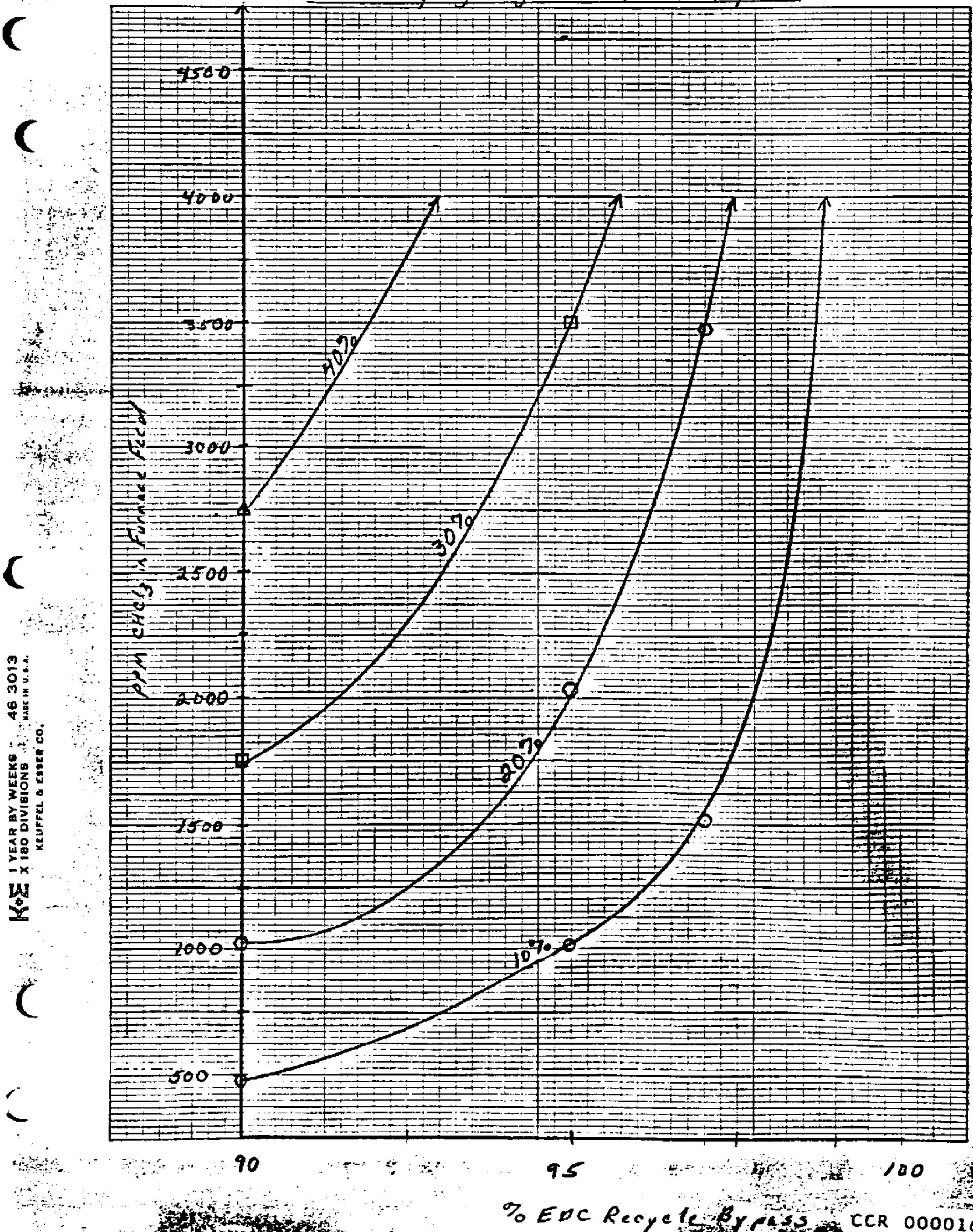


Figure III B
Furnace Feed $CHCl_3$ Levels vs.
Recycle EDC Bypass from 90%
With Varying Light Ends Column Splits



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Appendix A - CCl_4 Promoter Effect Correlations

Operating data from June 11, to July 26, 1982 (See Table III) were used to evaluate the affects of carbon tetrachloride, the number of days since decoking, the EDC feed rate to each furnace and the maximum coil temperature on the percent conversion of EDC to VCM on the cracking furnaces. The following linear model was the best fit of the data:

$$Y_1 = A_0 + A_1X_1 + A_2Y_2 + A_3X_3 + A_4X_4$$

Where: Y_1 = Conversion Levle, %

X_1 = The number of days since the decoking of the furnaces

X_2 = Furnace Feed Rate, MLbs/Hr./Furnace

X_3 = ppm CCl_4

X_4 = Maximum Coil Temperature - 490, ^oC

A_0, A_1, A_2, A_3, A_4 = Coefficients

	Coefficient	Standard Deviation of Coefficient	95% Confidence Interval of Coefficient
A_0	66.1356	-	-
A_1	-0.18201	0.07207	$\pm$0.02405
A_2	-0.13713	0.09233	$\pm$0.03081
A_3	0.00233	0.00115	$\pm$0.00038
A_4	0.27864	0.15846	$\pm$0.05288

Figure IV shows the deviations in the correlation by showing the Actual Conversion versus the Calculated Conversion.

The operating data was then used to determine the effects of conversion, the number of days since decoking, the EDC feed rate to each furnace and the maximum coil temperature on the energy (from natural gas) per pound of VCM product. The following model provided an excellent fit of the data:

$$Y_2 = A_5 + A_6Y_1 + A_7X_2X_5 + A_8 \text{ In } X_1$$

Where: Y_2 = BTU/Lb. of VCM make

X_1 = The number of days since the decoking of the furnaces

X_2 = Furnace Feed Rate, MLbs./Hr./Furnace

X_5 = Maximum Coil Temperature - 165., ^oC

Y_1 = Conversion Level, %

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A_5, A_6, A_7, A_8 = Coefficients

	Coefficient	Standard Deviation of Coefficient	95% Confidence Interval of Coefficient
A_5	2308.93726	-	-
A_6	-21.40793	2.08521	$\pm$.7055
A_7	0.00311	0.00240	$\pm$.00081
A_8	25.81595	8.16546	$\pm$2.7626

Figure V shows the deviations in the above correlation by showing the Actual BTU/lb. of VCM versus the calculated BTU/Lb. of VCM.

TABLE III

CORRELATION DATA

Date (1)	# Days Since Decoking	BTU's of Natural Gas Lb. of VCM (2)	Furnace Feed (MLbs/hr/ Furnace)	Conversion (%) (3)	Maximum Temp. (^{o}C)	CCl_4 in Furnace Feed (ppm)
6/11/82	1	1213.6	102.14	57.28	495	1190
6/13/82	3	1221.3	102.14	54.68	496	1660
6/14/82	4	1188.1	102.14	57.23	497	1390
6/15/82	5	1261.8	102.14	56.27	500	1710
6/16/82	6	1209.2	102.14	58.70	500	1670
6/17/82	7	1216.8	102.14	58.05	502	1370
6/18/82	8	1227.6	101.39	58.24	504	1520
6/19/82	9	1238.5	101.39	58.04	507	1280
6/20/82	10	1264.2	101.39	57.57	505	1310
6/21/82	11	1318.8	100.67	55.97	506	1180
6/22/82	12	1247.6	101.39	57.84	506	1100
6/23/82	13	1264.8	99.90	57.61	505	1050
6/24/82	14	1359.4	99.90	52.27	056	1010
6/25/82	15	1328.0	99.90	54.27	507	1270
6/26/82	16	1251.1	99.16	58.15	507	1140
6/27/82	17	1240.2	99.16	57.07	508	1090
6/28/82	18	1118.9	99.16	59.84	508	960
6/29/83	19	1265.1	96.18	58.10	504	1330
6/30/82	20	1268.0	95.43	57.55	507	1250
7/01/82	21	1298.4	94.43	55.73	500	1270
7/07/82	27	1307.2	114.81	57.35	514	970
7/08/82	28	1280.8	114.81	57.32	514	780
7/09/82	29	1466.7	114.81	51.49	516	280
7/10/82	30	1364.7	114.81	55.22	517	690
7/11/82	31	1375.3	114.81	54.22	514	760

TABLE III

CORRELATION DATA

Date (1)	# Days Since Decoking	BTU's of Natural Gas Lb. of VCM (2)	Furnace Feed (MLbs/hr/ Furnace)	Conversion (%) (3)	Maximum Temp. (°C)	CCl_4 in Furnace Feed (ppm)
7/12/82	32	1479.0	114.81	50.44	515	840
7/15/82	35	1526.3	114.81	48.31	515	830
7/16/82	36	1314.4	114.81	56.53	516	1110
7/17/82	37	1302.5	114.81	57.31	516	1690
7/18/82	38	1336.1	114.81	56.47	516	1560
7/19/82	39	1372.8	114.81	53.92	514	1360
7/20/82	40	1360.1	114.81	54.35	516	2350
7/21/82	41	1500.1	114.81	48.47	518	1250
7/22/82	42	1444.5	114.81	50.89	516	980
7/23/82	43	1312.5	114.81	53.86	515	1220
7/25/82	45	1301.7	114.81	52.85	518	1150
7/26/82	46	1370.1	114.81	50.18	515	1020

Notes:

1) Any days not included were due to the lack of at least one piece of data.
2) The natural gas useage was obtained for the given day and the gas used at the incinerator was subtracted from the total. The VCM production was obtained from the daily inventory sheets.
3) % Conversion =

$$\frac{(\text{VCM Production, Lbs./day})\left(1.584\ \frac{\text{Lbs. EDC}}{\text{Lb. VCM}}\right)}{\left(24\ \frac{\text{hrs}}{\text{day}}\right)(\text{Furnace Feed, Lbs./hr./Furnace})(\text{\#Furnaces in operation})}$$

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Figure IV

Actual vs. Calculated % Conversion

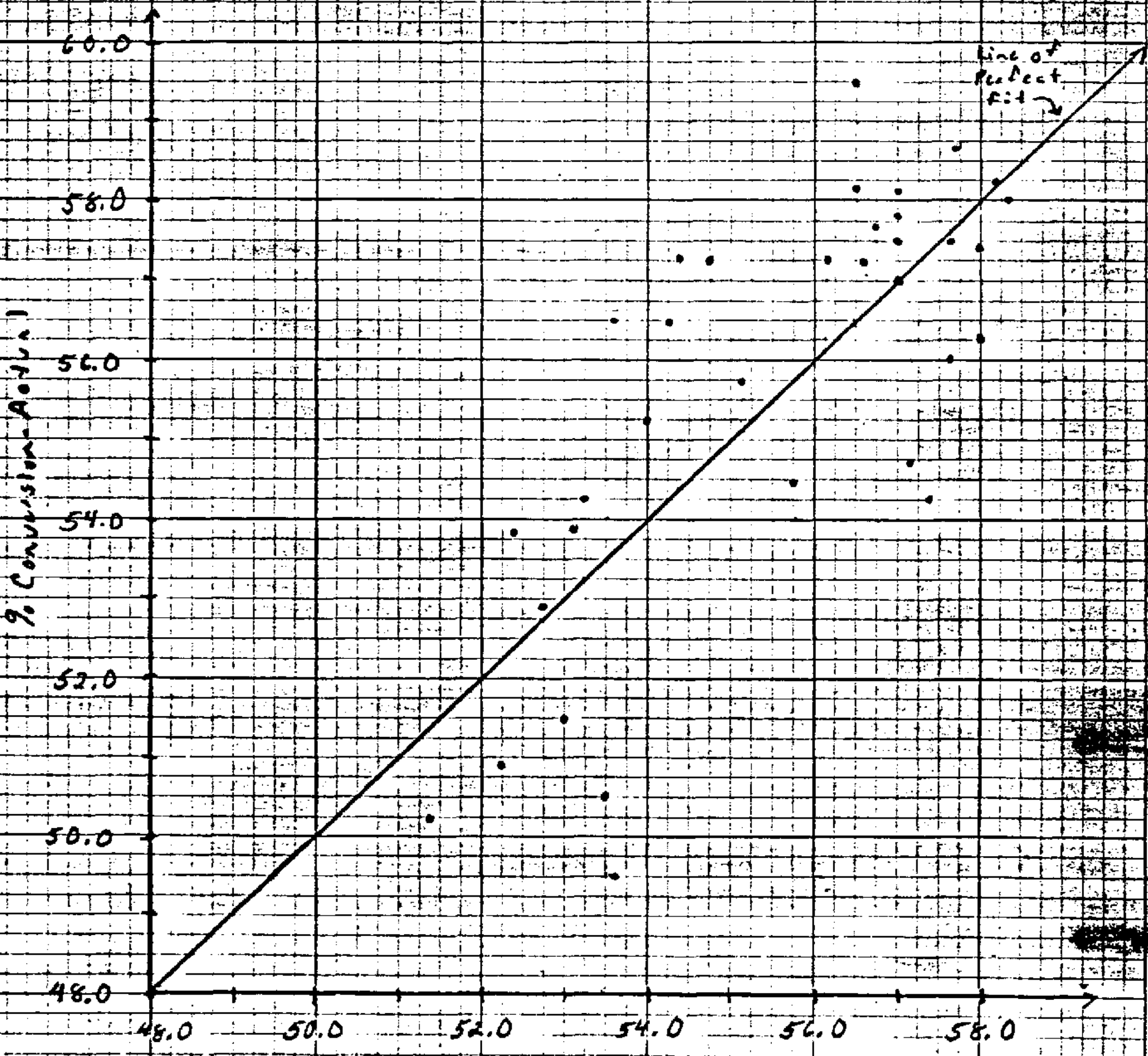

Figure V

Actual vs. Calculated BTU/Lb VCM