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Methyl Chloride Via Oxyhydrochlorination of Methane

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Contractor

Dow Corning Corporation
U.S. Hwy 42
Carrollton, KY 41008

Prepared for the

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Gas Research Institute

Contract No. 5091-222-2300

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Notices

This report contains information which is potentially patentable. U.S. patent applications covering these concepts will be filed with the U.S. Patent Office shortly. As per instructions from the Office of Patent Counsel, U.S. Department of Energy, Argonne, Illinois, the following notices are in effect:

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Contract Objective

The purpose of this contract is to develop a process for converting light alkane gases to methyl chloride via oxyhydrochlorination using highly selective, stable catalysts in fixed-bed reactors designed to remove the large amount of heat generated, so as to control the reaction temperature. Further, the objective is to obtain the engineering data base necessary for developing a commercially feasible process and to evaluate the economics of the process.

Task 1.0 Catalyst Definition and Separation Unit Operation Development

Task 2.0 Process Development Unit (PDU) Design Engineering

Task 3.0 PDU Construction and Procurement

Task 4.0 PDU Start-Up

Task 5.0 Evaluation of Packed Bed Technology

Task 6.0 Separation Optimization

Task 7.0 Process Optimization

Task 8.0 Economic Evaluation

Task 9.0 Preliminary Engineering Design Phase II

Task 10.0 Scale-Up Decision and Business Plan to Phase II

Abstract

Continuous progress is being made toward the contract objectives in our attempt to produce "Methyl Chloride via Oxyhydrochlorination of Methane." Specifically, gains have been achieved in Task 1.0 Catalyst Development and Separation Unit Operation Development and Task 4.0 PDU Startup.

Catalyst development continued forward to examine the copper, lanthanum, and lithium loadings as well as support surface area in four factor, two level, fully crossed design experiments carried out at five temperatures between 290°C and 310°C. Eight of the sixteen runs have been completed. Evaluation of these runs as a three factor, two level, fully crossed experiment has yielded some useful information. The choice of the Cu/La/Li metals system has been confirmed, and the high Cu, low La, low Li system hasn't proven itself to be the most active at this point.

Chemical feeds were brought on-line to the PDU. Small amounts of methyl chloride were made before the system was shut down due to equipment failure. Glass-lined equipment was found to be failing due to chemical etching. Replacement equipment with other materials of construction have been ordered. In addition, the FTIR windows clouded soon after chemical feeds were started. This materials problem is also being investigated.

Introduction

Methyl chloride (MeCl or CH_3Cl) is an important feedstock for the silicone industry. It is also used as an intermediate in the manufacture of other chlorocarbons, agrochemicals, methyl cellulose, quaternary ammonium salts, and as a solvent in the production of butyl rubber. MeCl consumption in the US was reported to be around 850 million lbs. in 1992 for these applications, although the actual consumption was probably much higher because of unreported, captive capacity. Currently, MeCl is derived from methanol. However, the demand for methanol in the U.S. is higher than the available domestic supply. As a result, methanol prices have recently exhibited a high degree of variance. Oxyhydrochlorination (OHC) technology utilizes domestic natural gas as a feedstock and thereby provides a reliable, low cost source of MeCl that is independent of the methanol market. Considerable savings are believed to be achievable via the application of this technology.

OHC is a key step in a potential gas-to-liquid fuels process. Currently, two approaches exist for converting natural gas to liquid hydrocarbon fuels, namely the Methanol-To-Gasoline (MTG) and the Fischer-Tropsch (FT) routes. Both of these processes begin with the production of synthesis gas from methane which is a high temperature, endothermic, and costly operation. The OHC process reacts methane, oxygen, and hydrogen chloride (HCl) in the presence of a special catalyst under controlled conditions to produce primarily MeCl and a byproduct, methylene chloride (CH_2Cl_2). These chlorohydrocarbons may then be fed to a fixed bed reactor where they are oligomerized to produce liquid hydrocarbon fuels. Data from the Department of Energy's Pittsburgh Energy Technology Center (PETC) show that a mixture of MeCl and CH_2Cl_2 can be converted over ZSM-5 zeolite without undue carbon deposition. Unconverted methane and other

light hydrocarbons may be recycled and the HCl recovered, thus improving the economics of the process. Despite the need for special materials of construction, OHC appears to be an attractive alternative to either MTG or the FT process.

Methyl chloride is a key raw material for the production of silicones. Currently, methanol and HCl are converted to MeCl which, in turn, reacts with silicon to produce dimethyldichlorosilane, $(\text{CH}_3)_2\text{SiCl}_2$, as the major product. Silicones are produced by hydrolysis of $(\text{CH}_3)_2\text{SiCl}_2$ which liberates HCl for recycle as shown in the equations below:

The overall reaction can be described by the equation below. However, the reaction sequence must go through CH_3Cl and the chlorosilane to manufacture silicones with the general formula: $[(\text{CH}_3)_2\text{SiO}]_x$.

The world's \$5.5 billion silicone market relies on the Direct Process to produce nearly all of its basic intermediates. U.S. producers supply almost 50% of the global market which has a healthy growth rate of 7-8% that is expected to continue into the future. Improved processes for manufacturing MeCl will enhance our domestic competitiveness in global markets. Dow Corning Corporation started working under contracts with DoE and GRI for the development of OHC in 1991.

Technical Strategy

The initial development of oxyhydrochlorination technology was accomplished in the laboratory. Years of studies developed a workable catalyst system including the choices of active OHC catalysis metal, activity promoter metal, stability promoter metal, and catalyst support. The absorber/stripper product recovery system was also initially developed in the laboratory. The absorbing oil was chemically and thermally tested for reactivity and decomposition. MeCl absorbance trials were then conducted both in batch and continuous modes.

Although an acceptable catalyst system has been developed, further laboratory studies continue. Dow Corning's Quality Policy states: Dow Corning will provide products and services that meet or exceed the expectation of our customers through our total commitment to continuous improvement in everything we do. The OHC catalyst system is continuously being examined and improved upon in an attempt to optimize the OHC system as a whole. Currently, a new avenue of research has begun. A designed experiment to optimize the support surface area and catalyst metal loadings is partially complete.

Final testing of developed catalysts is being accomplished on a larger scale in the PDU. More realistic conditions, including a shell and tube heat exchanging reactor, will more accurately test both the catalyst's activity and lifetime. The process as a whole is being piloted on this scale, including the product recovery system. Methane, oxygen, and HCl are being used to produce MeCl which is recovered as product. Data from the PDU is to be used both in an economic evaluation and for scale-up of the system to the next larger size demonstration unit. Currently, the PDU is in the startup stage where difficulties of the process are being identified and corrected. Evaluation and optimization of the reactor and product recovery unit will follow.

Experimental

Catalyst development is occurring on a laboratory scale. A CAMILE control system runs the system from reactant gas feeds to on-line GC analysis. Methane, oxygen, and HCl are fed through mass flow controllers to the reactor which is heated to approximately 300-320°C by a three zone furnace. The reactor, constructed of 1/4" Hastelloy C276 tubing, is a downfeed system containing approximately 12" of catalyst supported on 4" of inert packing. Catalyst compositions and syntheses are covered in detail in Appendix A. The product line exiting the reactor is heat traced to an on-line GC where continuous process monitoring takes place. The product then proceeds to a column where chlorocarbons, water, and HCl are absorbed to prevent corrosion of the valve that maintains the system pressure at 30 psig.

Final testing of the catalyst and process occurs in the PDU. This unit has been described in detail elsewhere, so only a brief overview follows. The PDU is similar to the laboratory unit, but has many improvements. The reactor contains 19 tubes in a shell and tube arrangement that allows control over the very exothermic OHC reactions. Product stream composition will be monitored using on-line FTIR allowing a quick analysis of the product stream as well as measurement of HCl, which is not possible with a GC. The PDU also regenerates its absorber oil by stripping out the chlorocarbons so that the oil can be recirculated and used continuously.

Results and Discussion

Task 1: Catalyst Development and Separation Unit Operation Development

Half of a four factor, two level, fully crossed designed experiment was completed in an attempt to optimize the catalyst support surface area and metal loadings. All sixteen catalysts have now been synthesized as detailed in Appendix A. The catalyst designed experiment criteria are outlined in Table 1.

Table 1. Catalyst Designed Experiment Criteria

	Support Surface Area (m ² /g)	Cu level (wt. %)	La level (wt.%)	Li level (wt.%)
high level	200	2.5	15	2.0
low level	30	1.0	10	0.5

The last three of the first half of the sixteen runs are now complete and are presented in Appendix B. The results from the first eight runs are detailed in Table 2.

Table 2. Designed Experiment Results to Date

Run #	Catalyst #	Factor Level	Con/Sel (%/%) @290°C	Con/Sel (%/%) @295°C	Con/Sel (%/%) @300°C	Con/Sel (%/%) @305°C	Con/Sel (%/%) @310°C
1206640	563	SA↑,Cu↑,La↑,Li↑	4/91	4/88	5/87	5/86	8/83
1206641	564	SA↑,Cu↑,La↑,Li↓	1/99	3/100	7/88	9/84	20/52
1206643	565	SA↑,Cu↑,La↓,Li↑	4/91	6/91	7/89	9/86	18/57
1206644	566	SA↑,Cu↑,La↓,Li↓	7/90	8/88	9/85	20/61	20/61
1206645	567	SA↑,Cu↓,La↑,Li↑	5/94	4/92	6/90	7/89	8/88
1206646	568	SA↑,Cu↓,La↑,Li↓	4/93	5/92	6/90	7/89	8/87
1206647	569	SA↑,Cu↓,La↓,Li↑	4/94	5/91	7/91	7/89	8/88
1206649	570	SA↑,Cu↓,La↓,Li↓	4/96	4/95	4/92	6/91	7/90

In Table 2, ↑ indicates the high level of the factor, and ↓ indicates the low level. Con/Sel (%/%) represents the % conversion of methane/% selectivity to MeCl @ a given temperature. The first half of the designed experiment (8 of 16 runs) will be analyzed as five three factor, two level, fully crossed designed experiments (surface area held constant ↑). Five designed experiments were, in fact, run because the catalysts were tested at five different temperatures.

The data was analyzed in terms of three responses: methane conversion, methyl chloride selectivity, and a function including a combination of the two. To this point conversion and selectivity have been shown to be mutually exclusive for this catalytic system. Therefore, a rough approximation combining the two has been created. A more rigorously correct function will be created at a later date once the economics of the PDU have been analyzed and proven. The combination function at this time consists of moles of waste subtracted from moles of product on a 10,000 mole methane feed scale. For example, the combination function calculations are shown for catalyst 563 at 290°C in Table 3 below.

Table 3. Combination Function Calculations for Catalyst 563 at 290°C.

%CH ₄ Conv.	%MeCl Sel.	Moles CH ₄ Unreacted	Moles MeCl Made	Moles Waste Made	Combination Value
4	91	9600	364	36	328

4% of CH₄ is converted to some product, leaving 9600 moles unreacted. Of the 400 moles that are reacted, 91% or 364 moles form MeCl, and 9% or 36 moles form some other waste. This yields a combination value = 364 - 36 = 328.

In order to analyze the designed experiments in terms of the responses conversion, selectivity, and the combination function, single degree of freedom ANOVA tables were generated to calculate

the estimated effects. The three factors (A - Copper, B - Lithium, and D - Lanthanum) were investigated and evaluated in terms of main effects (A, B, D) and interactions (-AB, -AD, -BD, and ABD). The following conclusions were drawn:

- 1) At 310°C, Cu is by far the largest indicator for all three responses. This is a case where the conclusion is obvious, but the reason must be noted. Cu is the largest indicator because three catalysts are burning at this temperature, and Cu was at a high level in each of these catalysts that burned. Data taken when the system is burning should not be compared to data taken when not burning.
- 2) The high Cu, low Li, low La catalyst had the highest CH₄ conversion at all five temperatures. Again, other factors may influence the results. This catalyst had the highest surface area of all eight catalysts as measured by BET. The high surface area of this catalyst could be more important than the actual metals levels for conversion.
- 3) The three factor ABD interaction was positive using the combination function at four out of five temperatures. This confirms the choice of the Cu/Li/La combination in the OHC catalyst.
- 4) All three main effects and all four interactions had negative responses for the combination function at 305°C. Future research will have to determine the meaning a reliability of this data. Note that one catalyst was burning, and this may skew the end results. As stated before, at this level of analysis, it is not advisable to compare runs that are burning versus runs that are not.

Analysis of the designed experiment data is both yielding insight into the optimum metals loadings and demonstrating the awareness necessary to draw sound conclusions from the data. Other factors than those being studied must be kept in mind such as the comparison of runs that are burning versus those that are not. At this point, it must also be remembered that even though targets for catalyst surface area and metals loading have been established, these targets have not always been exactly met. Further study into this topic promises rewarding results.

Task 4: PDU Startup

Chemical feeds were brought on-line in the PDU. This is a significant step toward completing Task 4: PDU Startup. The unit was started up at a conservative 30 PSIG and 260°C. Shortly after chemical feeds were initiated, the FTIR windows clouded over decreasing throughput and preventing FTIR data gathering. Instead bag samples were taken at 260°C, 265°C, and 275°C. GC analysis showed a small amount of methyl chloride being produced at these low temperatures.

After two day of operation, a release occurred when a 7" straight side glass lined spool on the stripper column developed a leak. An emergency shutdown was safely executed, and the stripper was isolated and vented down. Investigation revealed etching through the glass and a 1/4" orifice in the steel. Several pieces of equipment were then opened and spark tested in an attempt to

determine the cause of the equipment failure. The results of this investigation are shown in Table 4 below.

Table 4. Spark Test and Other Investigations of PDU Equipment

Equipment	Spark Test	Comments
Absorber Column	Passed	Glass looks new
Stripper Column	Failed	Chemical etching/overtorqued flanges
Stripper Knockout Pot	Failed	Chemical etching/pin hole failures
Stripper Bottom Phase Separator	Passed	Chemical etching (vaporspace)
Stripper Overhead Phase Separator	Passed	Glass looks new
Stripper Preheater	N/A	Significant corrosion
Stripper Overheads Condenser	N/A	Fouling/slight corrosion

The vendor of the glass-lined equipment thinks the etching was caused by steam condensation. Their theory is that the condensate droplets leach sodium from the glass. These droplets then become very basic and consequently etch the glass. This seems to match the observations made in the stripper bottom phase separator where the corrosion only occurred in the gas phase of the vessel (note that the glass covered by liquid looks new). New materials of construction were investigated and purchase orders issued for PFA-lined stripper column spools and tantalum stripper preheater and condenser replacements.

A significant amount of black sludge was found in a rag layer in the stripper bottom phase separator. Analysis showed approximately 8% titanium indicating that it came from the glass lining. This rag layer may have contributed to water being entrained in the solvent as it was returned to the solvent storage tank.

Furthermore, a gel-like rag layer was found in the absorber bottom phase separator. It is suspected that this material may have come from siloxane contaminants introduced when the solvent was loaded into the system. Analysis showed no solvent degradation. However, previously detected siloxane contaminants were no longer observed. This gel material may have contributed to poor phase separation in this unit leading to a larger than expected amount of acid being passed into the stripper preheater (see corrosion inspection results in Table 4 above).

Conclusions

Even though an adequate catalyst system has been developed, Dow Corning's commitment to continuous improvement has guided the catalyst development into a designed experiment to optimize the catalyst support surface area along with metal loadings. Optimization of the catalyst system could only improve the chances for success at completing the objectives of this project. Completion of the first half of the designed experiment has yielded some information while raising

other questions. The Cu/La/Li metals combination exhibits a positive three factor interaction confirming this choice for the OHC catalyst. The $SA\uparrow, Cu\uparrow, La\downarrow, Li\downarrow$ catalyst shows the highest activity at all five temperatures tested. However, the designed experiment results have been complicated by some catalysts burning when others aren't and catalyst surface areas and metals loadings not matching exactly to the targets that were set for their syntheses.

The PDU came close to completing Task 4: PDU startup. However, materials of construction problems have shut down the PDU. Replacement equipment in new materials of construction have been ordered. It is hoped that the new materials will increase PDU reliability and allow completion of Task 4. This will propel the project into the heart of proving this technology by evaluating and optimizing the packed bed shell and tube reactor and the product recovery system.

Appendix A - Catalyst Compositions and Syntheses

Eight catalysts numbered 563-570 were synthesized in the same general procedure as follows:

1. Appropriate amounts of the metal salts $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, and LiCl were weighed according to the metal loadings desired and dissolved in about 75 ml of distilled water.
2. To this solution was added 25 grams of CS 331-1 alumina ($200 \text{ m}^2/\text{g}$ - United Catalyst).
3. The solution was left overnight prior to the introduction of flowing nitrogen and allowing the solution to evaporate to dryness.

This technique yielded catalysts of the following compositions as determined by ICP and BET:

Catalyst #	Cu (wt. %)	La (wt. %)	Li (wt. %)	Surf. Area (m^2/g)
563	2.220	13.80	1.660	84.1
564	2.450	15.50	0.380	108.4
565	2.240	9.28	1.820	101.8
566	2.520	9.35	0.440	140.6
567	0.839	13.10	1.710	74.2
568	1.000	16.30	0.405	95.6
569	0.752	9.54	2.020	82.3
570	1.030	8.72	0.353	117.7
571	2.280	13.40	1.640	11.3
572	2.620	14.80	0.367	14.0
573	2.350	8.10	1.710	11.9
574	2.810	9.63	0.431	15.7
575	0.728	13.50	1.680	13.7
576	0.825	15.10	0.479	12.5
577	0.821	8.51	1.880	13.9
578	0.865	9.69	0.538	19.4

Appendix B - Catalyst Screening Data

Appendix B Definitions

CH₄ Conversion - % of methane converted.

M1 - % selectivity to CH₃Cl.

M2 - % selectivity to CH₂Cl₂.

M3 - % selectivity to CHCl₃

Cox - % selectivity to (CO + CO₂)

HOOD #7 RAMPING EXPERIMENT DEFINITION

OPERATOR NAME: Robin Cox DATE: 10-JUL-95
 LOG BOOK #: 12066 PAGE #: 103
 RUN #: 1206846 CATALYST #: 568
 CATALYST NAME: 568
 COMMENTS: DESIGNED EXPERIMENT

MASS OF CATALYST (g): 4.65
 REACTOR INSIDE DIAM (CM): 0.4
 CATALYST BED HEIGHT (CM): 30.5

TEMPERATURE RAMPING EXPERIMENT FOR HOOD #7

INITIAL FINAL ABSOLUTE
 TEMP TEMP RAMP RATE
 (DEG C) (DEG C) (DEG C / MIN)

BOTTOM: 300 290 1
 MIDDLE: 300 290 1
 TOP : 300 290 1

(INITIAL TEMPERATURE CAN BE GREATER THAN FINAL TEMPERATURE)

CH4 FLOW RATE (CC/MIN): 100 O2 FLOW RATE (CC/MIN): 22.8
 HCl FLOW RATE (CC/MIN): 29.8 AUX FLOW RATE (CC/MIN): 0

TIME TO MAINTAIN FINAL TEMPERATURES (HOURS): 8

Time (sec)	%CO	%CO ₂	%CO _x	%M1	%M2	%M3	%M4	ID	MASS BAL	CH ₄ CON	HCl CON	O ₂ CON	TEMP (C)
16740	0	0	0			0	0	1	65	4	25	3	290
21848	0	0	0	91	9	0	0	1	73	4	16	1	290
26948	0	0	0	93	7	0	0	1	72	3	11	-2	290
32049	0	0	0	94	6	0	0	1	72	4	18	1	290
37151	0	0	0	93	7	0	0	1	164		272	-1	290
42248	0	0	0	93	7	0	0	2	71	4	13	-3	291
48068	0	1	1	92	6	0	0	2	69	5	18	7	295
53168	0	2	2	91	7	0	0	2	69	3	10	5	295
58268	0	1	1	92	6	0	0	2	68	6	23	9	295
63368	0	1	1	92	7	0	0	2	68	5	17	5	295
68462	0	1	1	92	7	0	0	2	147		227	6	295
73567	0	1	1	92	7	0	0	3	66	5	18	10	298
78680	0	2	2	89	9	0	0	3	66	6	22	12	300
84488	0	2	2	90	8	0	0	3	68	6	23	13	300
89588	0	2	2	90	8	0	0	3	69	6	23	7	300
94680	0	2	2	89	9	0	0	3	70	7	24	8	300
99789	0	2	2	90	8	0	0	3	71	7	23	1	300
104889	0	2	2	91	7	0	0	4	71	5	19	3	302
110710	0	2	2	90	9	0	0	4	190		354	9	305
115807	0	2	2	88	10	0	0	4	192	8	360	8	305
120908	0	2	2	89	9	0	0	4	191	6	356	7	305
126000	0	2	2	90	8	0	0	4	191	7	360	9	305
131112	0	2	2	90	8	0	0	4	191	7	350	15	305
136201	0	3	2	89	9	0	0	5	191	8	355	8	308
141980	0	3	3	88	9	0	0	5	63	7	26	18	310
147087	0	3	3	87	10	0	0	5	64	9	34	19	310
152187	0	2	3	87	10	0	0	5	63	8	30	21	310
157270	0	3	2	87	10	0	0	5	63	10	35	21	310
162368	0	3	3	86	12	0	0	5	64	7	26	19	310
Avg@290													
AVG	0	0	0	93	7	0	0	1	86	4	59	0	290
STD	0	0	0	1	1	0	0	0	35	1	95	2	1
Avg@295													
AVG	0	1	1	92	7	0	0	2	81	5	52	7	295
STD	0	0	0	0	0	0	0	0	30	1	78	2	1
Avg@300													
AVG	0	2	2	90	8	0	0	3	69	6	22	7	300
STD	0	0	0	1	1	0	0	0	2	0	2	4	1
Avg@305													
AVG	0	2	2	89	9	0	0	4	191	7	356	9	305
STD	0	0	0	1	0	0	0	0	1	1	3	3	0
Avg@310													
AVG	0	3	3	87	10	0	0	5	63	8	30	19	310
STD	0	0	0	1	1	0	0	0	1	1	4	1	0

**computer error caused faulty data. CO2, M1, M2, M3, M4, CO, and CH4 were recalculated by GC trace.

RUN 1206646
CAT 568

RUN 1206646
CAT 568

RUN 1206646
CAT 568

RUN 1206646
CAT 568

HOOD #7 RAMPING EXPERIMENT DEFINITION

OPERATOR NAME: Robin Cox DATE: 12-JUL-95
 LOG BOOK #: 12066 PAGE #: 105
 RUN #: 1206647 CATALYST #: 569
 CATALYST NAME: 569
 COMMENTS: DESIGNED EXPERIMENT

MASS OF CATALYST (g): 4.81
 REACTOR INSIDE DIAM (CM): 0.4
 CATALYST BED HEIGHT (CM): 30.5

TEMPERATURE RAMPING EXPERIMENT FOR HOOD #7

INITIAL FINAL ABSOLUTE
 TEMP TEMP RAMP RATE
 (DEG C) (DEG C) (DEG C / MIN)

BOTTOM: 300 290 1
 MIDDLE: 300 290 1
 TOP : 300 290 1

(INITIAL TEMPERATURE CAN BE GREATER THAN FINAL TEMPERATURE)

CH4 FLOW RATE (CC/MIN): 100 O2 FLOW RATE (CC/MIN): 22.6
 HCl FLOW RATE (CC/MIN): 29.8 AUX FLOW RATE (CC/MIN): 0

TIME TO MAINTAIN FINAL TEMPERATURES (HOURS): 8

Time (sec)	%CO	%CO ₂	%CO _x	%M1	%M2	%M3	%M4	ID	MASS BAL	CH ₄ CON	HCl CON	O ₂ CON	TEMP (C)
17848	0	0	0	93	7	0	0	1	197	4	352	-3	290
22956	0	0	0	94	6	0	0	1	198	3	358	-3	290
28048	0	0	0	95	5	0	0	1	194		540	-6	290
33156	0	0	0	95	5	0	0	1	195	3	480	-3	290
38257	0	0	0	95	5	0	0	1	195	3	481	-2	290
43358	0	0	0	93	7	0	0	2	197	5	362	1	291
49176	0	2	2	91	7	0	0	2	195	4	357	12	295
54277	0	1	1	92	7	0	0	2	195	6	363	6	295
59369	0	2	2	92	7	0	0	2	195	4	358	2	295
64478	0	1	1	91	8	0	0	2	195	6	355	5	295
69575	0	1	1	92	7	0	0	2	194	6	348	8	295
74675	0	2	2	92	7	0	0	3	196	6	347	8	297
80495	0	2	2	90	8	0	0	3	193	7	363	11	300
85596	0	1	1	91	8	0	0	3	193	7	351	9	300
90696	0	2	2	91	7	0	0	3	193	7	356	7	300
95796	0	2	2	91	8	0	0	3	191	7	504	3	300
100896	0	2	2	91	8	0	0	3	193	7	351	3	300
105991	0	2	2	90	8	0	0	4	194	6	350	0	301
111750	0	2	2	90	8	0	0	4	190	7	360	5	305
116856	0	2	2	88	10	0	0	4	192	8	367	7	305
121956	0	2	2	89	9	0	0	4	192	8	361	5	305
127056	0	2	2	90	8	0	0	4	191	7	361	2	305
132156	0	2	2	89	9	0	0	4	191	5	353	8	305
137256	0	2	2	90	8	0	0	5	192	7	352	9	307
143078	0	2	2	88	10	0	0	5	189	8	356	14	310
148176	0	3	3	87	10	0	0	5	190	8	363	12	310
153269	0	2	2	88	10	0	0	5	189	8	354	13	310
158368	0	2	2	88	10	0	0	5	189	8	352	10	310
163475	0	2	2	89	9	0	0	5	189	8	354	15	311
Avg@290	%CO	%CO ₂	%CO _x	%M1	%M2	%M3	%M4	ID	MASS BAL	CH ₄ CON	HCl CON	O ₂ CON	TEMP (C)
AVG	0	0	0	94	6	0	0	1	195	4	422	-3	290
STD	0	0	0	1	1	0	0	0	1	1	70	2	0
Avg@295	%CO	%CO ₂	%CO _x	%M1	%M2	%M3	%M4	ID	MASS BAL	CH ₄ CON	HCl CON	O ₂ CON	TEMP (C)
AVG	0	1	1	91	7	0	0	2	195	5	354	7	295
STD	0	0	0	0	0	0	0	0	0	1	6	3	1
Avg@300	%CO	%CO ₂	%CO _x	%M1	%M2	%M3	%M4	ID	MASS BAL	CH ₄ CON	HCl CON	O ₂ CON	TEMP (C)
AVG	0	2	2	91	8	0	0	3	193	7	379	5	300
STD	0	0	0	0	0	0	0	0	1	0	56	4	1
Avg@305	%CO	%CO ₂	%CO _x	%M1	%M2	%M3	%M4	ID	MASS BAL	CH ₄ CON	HCl CON	O ₂ CON	TEMP (C)
AVG	0	2	2	89	9	0	0	4	191	7	359	6	305
STD	0	0	0	1	1	0	0	0	1	1	5	2	1
Avg@310	%CO	%CO ₂	%CO _x	%M1	%M2	%M3	%M4	ID	MASS BAL	CH ₄ CON	HCl CON	O ₂ CON	TEMP (C)
AVG	0	2	2	88	10	0	0	5	189	8	356	13	310
STD	0	0	0	0	0	0	0	0	0	0	4	2	0

** GC MISSED THE METHANE PEAKS. SO THE VALUES SHOWN FOR COX, M1, M2, M3, M4, AND CH4CON WERE RECALCULATED BY HAND

RUN 1206647
CAT 569

RUN 1206647
CAT 569

RUN 1206647
CAT 569

RUN 1206647
CAT 569

HOOD #7 RAMPING EXPERIMENT DEFINITION

OPERATOR NAME: Robin Cox DATE: 18-JUL-95
 LOG BOOK #: 12066 PAGE #: 108
 RUN #: 1206649 CATALYST #: 570
 CATALYST NAME: CATALYST #570
 COMMENTS: DESIGNED EXPERIMENT

MASS OF CATALYST (g): 4.18
 REACTOR INSIDE DIAM (CM): 0.4
 CATALYST BED HEIGHT (CM): 30.5

TEMPERATURE RAMPING EXPERIMENT FOR HOOD #7

INITIAL FINAL ABSOLUTE
 TEMP TEMP RAMP RATE
 (DEG C) (DEG C) (DEG C / MIN)

BOTTOM: 300 290 1
 MIDDLE: 300 290 1
 TOP : 300 290 1

(INITIAL TEMPERATURE CAN BE GREATER THAN FINAL TEMPERATURE)

CH4 FLOW RATE (CC/MIN): 100 O2 FLOW RATE (CC/MIN): 22.8
 HCl FLOW RATE (CC/MIN): 29.8 AUX FLOW RATE (CC/MIN): 0

TIME TO MAINTAIN FINAL TEMPERATURES (HOURS): 8

Time (sec)	%CO	%CO ₂	%CO _x	%M1	%M2	%M3	%M4	ID	MASS BAL	CH ₄ CON	HCl CON	O ₂ CON
22223	0	0	0	97	3	0	0	1	195	4	341	2
27323	0	0	0	96	4	0	0	1	193	4	707	0
32415	0	0	0	96	4	0	0	1	197	2	351	-2
37516	0	0	0	96	4	0	0	1	197	4	347	1
42622	0	0	0	95	5	0	0	1	196	3	440	3
47717	0	0	0	97	3	0	0	2	193	4	717	3
53477	0	0	0	94	6	0	0	2	196	4	353	6
58583	0	0	0	95	5	0	0	2	196	4	349	6
63683	0	0	0	94	6	0	0	2	196	4	346	2
68782	0	0	0	95	5	0	0	2	196	4	354	7
73882	0	0	0	95	5	0	0	2	196	4	354	2
78984	0	0	0	95	5	0	0	3	66	5	17	9
84803	0	1	1	92	6	0	0	3	67	5	17	8
89994	0	1	1	92	6	0	0	3	70	2	8	-2
95005	0	1	1	92	6	0	0	3	66	5	27	3
100096	0	1	1	93	6	0	0	3	67	6	33	3
105194	0	1	1	92	7	0	0	3	66	5	28	3
110297	0	1	1	93	6	0	0	4	67	3	20	1
116058	0	2	2	89	9	0	0	4	71	4	15	4
121164	0	2	2	90	8	0	0	4	70	3	12	3
126263	0	2	2	91	7	0	0	4	67	7	24	5
131363	0	1	1	92	7	0	0	4	66	6	22	9
136462	0	2	2	91	7	0	0	4	67	6	21	10
141555	0	2	2	91	7	0	0	5	65	5	17	7
147324	0	2	2	90	8	0	0	5	64	7	25	14
152424	0	2	2	90	8	0	0	5	64	7	26	15
157523	0	2	2	91	7	0	0	5	140		219	12
162616	0	2	2	91	7	0	0	5	65	5	17	10
167726	0	2	2	89	9	0	0	5	65	7	26	13
Avg@290												
AVG	0	0	0	96	4	0	0	1	195	4	484	1
STD	0	0	0	1	1	0	0	0	1	1	165	2
Avg@295												
AVG	0	0	0	95	5	0	0	2	174	4	296	5
STD	0	0	0	0	0	0	0	0	48	0	125	3
Avg@300												
AVG	0	1	1	92	7	0	0	3	66	4	22	2
STD	0	0	0	1	1	0	0	0	1	1	8	3
Avg@305												
AVG	0	2	2	91	7	0	0	4	66	6	19	6
STD	0	0	0	1	0	0	0	0	2	1	4	3
Avg@310												
AVG	0	2	2	90	8	0	0	5	80	7	63	13
STD	0	0	0	1	1	0	0	0	30	1	78	2

** %CO₂, %M1, %M2, %M3, %M4, AND %CH₄ CONV WERE CORRECTED FROM GC DATA. THE CH₄ POINTS IN BOLD WERE ASSUMED BASED ON SURROUNDING DATA BECAUSE THE GC TRACE WAS UNAVAILABLE.

RUN 1206649
CAT 570

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