DOW CHEMICAL U.S.A.

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OXYCHLORINATION OF ETHYLENE LOWER OXYGEN FLAMMABILITY LIMIT

The purpose of this work was to determine the LOFL (lower oxygen flammability limit) for reactors R-201 and R-202 at the Vinyl II Plant based on current operating parameters and to determine the change in LOFL assuming that a 2500 lb/hr POLY C ethylene vent stream is utilized as a source of feed to R-202.

BACKGROUND

Four (4) empirical models have been proposed in the Dow literature to generate LOFL values for the oxychlorination of ethylene process [1]:

(1) LOFL(%) =

(2) LOFL(%) =

(3) LOFL(%) =

(4) LOFL(%) =

[1] "Mathematical Analysis of Previously Published Ethylene Oxychlorination Flammability Studies", CK 88-41, Pamela Berg, 20-OCT-88.

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Equation 2 is referred to as the "Hill Equation" and is used in all of Dow's oxychlorination of ethylene processes. Equation 2 assumes that both CO and HCL do not effect the LOFL.

Equation 3 is a modified version of equation 2; the modification being that the data used in the development of equation 2 was transformed to separate the ethylene component into two parts: that which is coming into the reactor as recycle and that which is direct ethylene feed. Using SAS and outside literature sources, the author showed that both CO and HCL effect the lower oxygen flammable limit.

Equation 4 is referred to as the "Midland Equation" and was generated to account for non-turbulent flow conditions.

RESULTS

Given below is a listing of data ranges used in the development of the different LOFL equations. Also included are key operating parameters for R-201 and R-202 taken on the morning of July 10, 1991 at the Vinyl II Plant. The LOFL values have been calculated for both trains and for R-202 with the addition of the Poly C ethylene vent stream:

Component	Hill Eq's	Midland Eq.	R-201	R-202	R-202 (Poly C)
Ethylene					
Methane					
Ethane					
Carbon monoxide					
Carbon dioxide					
HCL					
Nitrogen					
Percent Oxygen in feed to reactor					
LOFL (1) ..... Heat Capacity Correlation					
LOFL (2) ..... Hill Equation					
LOFL (3) ..... Modified Hill Equation					
LOFL (4) ..... Midland Equation					

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The LOFL values calculated using equations 1, 2 and 3 show all three operating scenarios to be below the lower oxygen flammable limit. The Midland equation suggests that our current operation is in the flammable region. Past operating experience tells us that this is not the case.

The addition of the 2500 lb/hr Poly C ethylene vent stream to train R-202 will not adversely effect the lower oxygen flammability limit. Therefore, we will proceed with our research goals of determining the effects of this stream on ethylene dichloride cracking pattern (La.) and on oxychlorination catalyst activity (Texas, R&D).

Please contact me with any comments or concerns you may have.

Sincerely,

Bryan

Bryan Adams
C&PP Research

Attachments

CASE 1) R-201 OPERATION

COMPONENT	LBS/HR	LBMOL/HR	MOL %	C_p (BTU/LBMOL °F)

$\sum_i \eta_i C_{p_i} =$

LOFL (EQ A) =

LOFL (EQ B) =

LOFL (EQ C) =

LOFL (EQ D) =

ACTUAL O_2 IN FEED =

CASE 2) R-202 OPERATION

COMPONENT	LBS/HR	LBMOL/HR	MOL%	$\sum_i C_{Pi}$ (BTU/LBMOL°F)

LOFL (EQ A) =

LOFL (EQ B) =

LOFL (EQ C) =

LOFL (EQ D) =

ACTUAL O_2 IN FEED =

CASE 3) R-202 OPERATION W/ POLY C VENTS

COMPONENT	LBS/HR	LBMOL/HR	MOL%	$y_i C_{pi}$

LOFL (EQ A) =

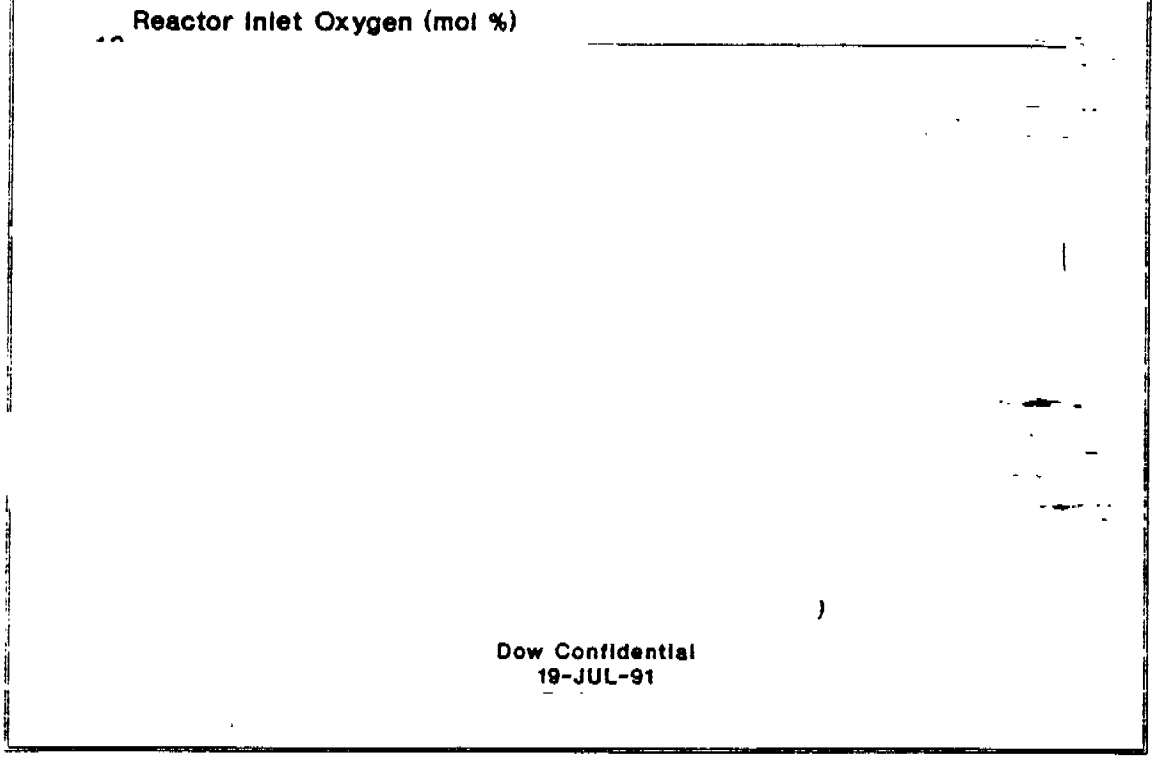
LOFL (EQ B) =

LOFL (EQ C) =

LOFL (EQ D) =

MINIMUM O_2 IN FEED =

Lower Oxygen Flammable Limit (LOFL)
Oxychlorination of Ethylene



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OXYCHLORINATION RECYCLE GAS ANALYSIS

TRAIN = R-201
DATE = 10-JUL-91
TIME = 08:00

Compound	Mole Wt.	MOL RRF	AREA CNT	MOL FRAC	WT FRAC	Elution (min)
TCD ANALYSIS						
FID ANALYSIS						

AVERAGE MOLECULAR WEIGHT =

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OXYCHLORINATION RECYCLE GAS ANALYSIS

TRAIN = R-202
DATE = 10-JUL-91
TIME = 08:05

Compound	Mole Wt.	MOL RRF	AREA CNT	MOL FRAC	WT FRAC	Elution (min)
TCD ANALYSIS						
FID ANALYSIS						

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GC FID/TCD Analysis of the Poly C Recycle
Ethylene Stream at LHC 3

INERTS ANALYSIS

GC ANALYSIS	Wt. % corrected analysis	GC analysis

R-201 SYSTEM (10-JUL-91)

OBS	DATE	TAG_1	TAG_2	TAG_3
1	10-JUL-1991 06:00			
2	10-JUL-1991 06:30			
3	10-JUL-1991 07:00			
4	10-JUL-1991 07:30			
5	10-JUL-1991 08:00			
6	10-JUL-1991 08:30			

OBS	TAG_4	TAG_5	TAG_6	TAG_7	TAG_8

Variable	Label	N	Mean	Std Dev	Minimum
TAG_1					
TAG_2					
TAG_3					
TAG_4					
TAG_5					
TAG_6					
TAG_7					
TAG_8					

Variable	Label	Maximum

R-202 SYSTEM (10-JUL-91)

OBS	DATE	TAG_1	TAG_2	TAG_3
1	10-JUL-1991 06:00			
2	10-JUL-1991 06:30			
3	10-JUL-1991 07:00			
4	10-JUL-1991 07:30			
5	10-JUL-1991 08:00			
6	10-JUL-1991 08:30			

OBS	TAG_4	TAG_5	TAG_6	TAG_7	TAG_8
1					
2					
3					
4					
5					
6					

Variable	Label	N	Mean	Std Dev	Minimum
TAG_1					
TAG_2					
TAG_3					
TAG_4					
TAG_5					
TAG_6					
TAG_7					
TAG_8					

Variable	Label	Maximum
TAG_1		
TAG_2		
TAG_3		
TAG_4		
TAG_5		
TAG_6		
TAG_7		
TAG_8		

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OXY-EDC Area Concerns

Concern: Oxygen system contamination

Improvements:

- Emphasis on field tag identification of O2 service equipment

Measures in place:

- Handling and identification procedures for O2 service
- Use of graphite free gaskets and Flurolube lubricant
- Cleaning procedures, bagging and labeling for O2 service
- Ultraviolet light inspection prior to installing item in O2 service

Opportunities:

- Update procedure for handling and identification of O2 service equipment

src:8/91

OXY-EDC Area Concerns

Concerns: Packing Deterioration- Organics and Temperature

Improvements:

- Approximately 800 ft3 kynar packing in C-211 EDC condensing column bottom replacing polypropylene

Opportunities:

- Inspect/repack C-212 in 9/91

src:8/91

OXY-EDC Area Concerns

Concern: VCM in acid to OXY

Measures in Place:

- Analysis of C-120 overhead for VCM with alarming
- Operating discipline on C-120
- Monitor & alarm C-120 tray temps

Opportunities:

- Mod5 control

src:8/91

OXY-EDC Area Concerns

Concern: Ethylene entering O2 header

Improvements: None since last review

Measures in Place:

- O2 header maintained 5 PSI above ethylene pressure
- Low flow trips on all reactor feeds

Opportunities:

- Mod5 control

src:8/91

Ecology Area

Concern: Polymerized chloroprene, moisture &/or iron in T-420 vent KO drum

Improvements:

- •O2 analyzer on C270

Measures in Place:

- Sampling and analysis procedures

Opportunities:

src:8/91

Ecology Area

Concern: Mixing Propylene with process in T-410

Improvements:

Measures in Place:

- T-410 is emptied and steamed out prior and after burning oil from K-320 C3H6 system
- Oil drummed to allow C3H6 to vent prior to putting in T-410

Opportunities:

src:8/91

BIF WASTE CHARACTERIZATION

WASTE STREAM NUMBER	T-410
WASTE NAME	WASTE OILS
PLANT NAME	VINYL II

PHYSICAL PROPERTIES

HEAT OF COMBUSTION	2000-7000 BTU/LB
VISCOSITY	1.1-1.6 CENTISTOKES
FLASH POINT	ND
HALOGENS	25-65 WT.%
SPECIFIC GRAVITY	1.1-1.35
ASH	0.05-.15 %

COMPONENT	CONCENTRATION RANGE	ANALYSIS	PROCESS KNOWLEDGE
METALS	**PPM**		
ARSENIC	BDL	X	
BARIUM	0.001-0.15	X	
CADMIUM	0.001-0.2	X	
CHROMIUM	0.01-10.0	X	X
LEAD	0.00-0.5	X	X
MERCURY	0.001-0.8	X	X
SILVER	0.001-20.0	X	X
ANTIMONY	0.001-0.4	X	X
BERYLLIUM	BDL	X	
THALLIUM	BDL	X	
ORGANIC ANALYTES	**WT. %**		
BENZENE	0.2-1.0	X	X
CARBON TETRACHLORIDE	2.0-10.0	X	X
CHLOROBENZENE	0.0-0.5	X	X
2-CHLOROETHYLVINYL ETHER	0.0-0.5	X	X
CHLOROFORM	2.0-10.0	X	X
1,1-DICHLOROETHANE	0.5-2.0	X	X
1,2-DICHLOROETHANE	1.0-30.0	X	X
TRANS 1,2-DICHLOROETHANE	0.1-1.0	X	X
TETRACHLOROETHANE	0.0-1.0	X	X
1,1,2-TRICHLOROETHANE	1.0-5.0	X	X
TRICHLOROETHANE	0.1-1.0	X	X
VINYL CHLORIDE	0.0-1.0	X	X
2-CHLORONAPHTHALENE	0.0-1.0	X	X
1,2-DICHLOROBENZENE	0.0-1.0	X	X
1,3-DICHLOROBENZENE	0.0-1.0	X	X
1,4-DICHLOROBENZENE	0.0-1.0	X	X
FLUORENE	0.0-1.0	X	X
HEXACHLOROETHANE	0.0-1.0	X	X
NAPHTHALENE	0.0-1.0	X	X
CHLORONATED PROPENES	0.0-15.0	X	X
CHLORONATED BUTENES	0.0-15.0	X	X
NVM & UNKNOWNS	1.0-25.0	X	X
PYRIDENE	0.0-10.0	X	X
WASTE OILS	0.0-100.0	X	X

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