



Interoffice Communication

To P. L. Fetzer
From H. L. Hackett
Date March 14, 1973
Subject Progress Report, February 1973

Summary

Tars Vacuum Flash Distillation--Flash distillation temperature-pressure-composition data were obtained for mixed plant tars containing 14.2 percent EDC and 35.4 percent 1,1,2 trichloroethane. A fifty-five weight percent overhead fraction was obtained with a combined EDC and 1,1,2 trichloroethane content of seventy-six percent. The bottoms were calculated to contain two percent EDC and sixteen percent 1,1,2 trichloroethane. Some decomposition and plugging occurred in the pre-heater at 170°C. It is planned to get the same type data for predominately EDC derived tars in March.

Reduction of Benzene and Trichloroethylene in the Vapor Feed EDC--Benzene and trichloroethylene removal by chlorination was investigated in a series of experiments with recycle EDC. This information was sought to help determine the feasibility of rerouting R-102 effluent (recycle chlorinator) into R-101 (direct chlorinator). Reductions of less than ten percent each were obtained at conditions close to those in R-101. High dissolved free chlorine and ferric chloride aid benzene removal but ferric chloride suppresses the reaction with trichloroethylene. There is some concurrent loss of EDC to 1,1,2 trichloroethane.

Oxygenates in EDC Streams--Chlorine treatment of R-102 effluent under conditions similar to those in R-101 gave only a moderate increase in the oxygenate level. The result of 2.8 is well below those found when the recycle EDC was sent directly to R-101.

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cc: LNV-RDG-RHG-GTH-JDM-RWC-DCS-JCL

Tars Vacuum Flash Distillation

The flash chamber was built from 12-inch by 3-inch diameter carbon steel schedule 40 pipe with pipe caps on top and bottom. The chamber was mounted with its axis in the vertical position. It was necessary to filter the tars to get consistent operation of the Milton Roy feed pump. Tars were pumped from a calibrated reservoir at 500-700 milliliters per hour into $\frac{1}{2}$ -inch stainless steel tubing 22-feet long coiled and immersed in an oil bath. The bath was usually maintained at 170°C. It was necessary to wrap the 3-foot section of tubing leading to the chamber and the chamber itself with heating tape to prevent excessive heat losses. Feed temperature was measured by a thermocouple placed in a well projecting into the central cavity of a pipe "T" at the chamber inlet. The chamber inlet was two thirds of the way up. The vapor takeoff was from the top cap. The overhead temperature was measured in a thermocouple well projecting into the cavity of a pipe "T". A concentric tube condenser, 3/8-inch inside diameter, sloped downward from the "T". The overhead product was collected in calibrated glassware. Unvaporized bottoms product was withdrawn through the bottom cap, through a valve, then into a calibrated glass receiver at system pressure. The valve was manually operated to maintain a 2-inch liquid level in the chamber as observed by a sight glass. The bottoms level was chosen to give sufficient thermocouple well (installed through the top cap) immersion for accurate temperature measurement. The bottoms drawoff rate was held as near constant as possible. Pressure was measured by a "U" tube manometer and controlled by a vacuum regulator.

The experimental data are summarized in Table I. Certain compromises were necessary in these experiments. These will be discussed as an aid to evaluation of the results. The general procedure was to line-out the distillation at the desired feed temperature and pressure with the overhead and bottoms products going to slop receivers. The products were then switched into the run receivers and collected for a period of 0.5 to 1.0 hour. If no significant changes occurred during this period the run and its products were accepted. The amount of overhead produced could be accurately measured but the amount of bottoms collected during a run was somewhat arbitrary because it depended on accurate liquid level judgements. The combined measurements of the two are considered more accurate than the feed entry since the feed reservoir calibration was only approximate. It is also important to note that the bottoms sample collected and analyzed is not necessarily representative of the non-volatilized material. In most cases the equipment was not operated long enough at run conditions to provide enough displacements of the retained bottoms. It is probably more accurate to calculate the bottoms composition from the feed stock and the overhead. This was done for part of the runs and entered in parentheses below the analyzed value.

Reduction of Benzene and Trichloroethylene in Vapor Feed EDC

Following the October 1972 installation of the separate recycle chlorinator, with its greatly reduced chlorine contact time, benzene and trichloroethylene levels gradually increased in the circulating EDC. The two compounds are not readily removed by the purification train because they boil so close to EDC. Some production time was lost in January and February due to problems in the HCl column and severe coking in the furnaces possibly related to higher levels of these impurities. A brief study was made of some of the factors involved in the chlorination of the two compounds and in the feasibility of routing R-102 effluent through R-101 instead of directly to T-101.

Chlorine diluted with some nitrogen sometimes accompanied with HCl and ethylene, was passed through either R-102 effluent or vinyl column bottoms. The EDC was maintained at 50°C. Samples were withdrawn periodically, usually every 10 minutes for dissolved free chlorine and for gas chromatography analyses. After an initial buildup period, an attempt was made to roughly maintain a desired

dissolved free chlorine for the rest of the run. The results are summarized in Table II. The first three runs were made in glassware where the ferric chloride level could be fixed instead of gradually increasing from near zero as in subsequent runs. Runs 4 through 7 were made in the apparatus previously described as the chamber for the flash distillations. Except for residence time and higher chlorine concentration, Runs 2 and 3 most closely approximate condition in R-101. The data shows benzene removal dependent on both chlorine and ferric chloride concentration. Increasing chlorobenzene was found in the product. The reaction of trichloroethylene is inhibited by ferric chloride. It was pointed out by Dr. Charles Starks, Research and Development, Ponca City, that trichloroethylene might react by alkylation instead of chlorine addition. The results of Runs 6A and 6B lend support to the suggested reaction pathway.

Oxygenates in EDC Streams

The effect of taking R-102 through R-101 on the oxygenate level was checked by comparison of the charge and reaction products from Run 7 above after distillation at standardized conditions. These results and some other checks on oxygenates in EDC streams are given in Table III. Comparison of Distillation Numbers 3 and 4 showed much higher oxygenate level in R-101 with no recycle EDC. There is no obvious explanation for this apparent discrepency. Comparison of Distillation Number 5 with Number 3 shows an oxygenate reduction of 67 percent across the wash system.

TABLE I VACUUM FLASH DISTILLATION OF MIXED TARS

CHARGE: VAC FILTERED TARS, T-405 2-21-73 EDC 14.2% 1,1,2 35.4% TOTAL 49.6%

DIST.	CUT	C ONDITIONS				QUANTITIES						COMPOSITION BY GAS CHROMATOGRAPHY									FLASH PT.
		FEED	VAP	BTM	PRESS. ADS. IN. Hg	MEASURED VOLUME			WEIGHT			OVERHEAD		OVER HEAD			BOTTOMS (2)			OF	
						FEED ⁽¹⁾ ML.	O.H. ML.	BTMS. ML.	O.H g.	BTMS g.	TOTAL g.	VOL %	WT. %	EDC WT%	1,1,2 WT%	TOTAL WT%	EDC WT%	1,1,2 WT%	TOTAL WT%		
2-28-73	3	122	82	85	14.92	425	30	370	38.42	498.9	537.1	7.5	7.2	52.5	47.5	100	13.0	39.3	52.3		
"	4	126	90	87	14.12	370	71	300	93.53	540.0	633.5	19.1	14.8	39.6	57.5	97	12.0	38.0	50.0		
3-1-73	2	129	102	101	12.92	190	82.5	105	111.0	N.A.		44.0		30.3	52.6	82.9	9.7	29.0	37.7		
"	3	129	104	102	10.92	-	90.0	78	120.49	98.08	218.6	53.6	35.1	24.4	51.6	76.0	6.9 (1.7)	34.7 (15.8)	41.6 (17.5)		
3-2-73	1	142	109	108	14.92	155	72	92	96.62	118.62	215.2	43.9	44.9	26.0	52.8	78.8	6.0 (4.7)	24.0 (21.5)	30.0 (26.2)	128	
"	3	143	102	100	15.92	115	33	75	42.67	95.50	138.2	30.6	30.9	31.3	55.4	86.7	10.4 (6.6)	37.4 (26.8)	47.8 (33.4)		
"	4	142	100	98	13.72	157			82.73	140.62	223.4		37.0	29.2	50.5	79.7	8.3 (5.4)	27.2 (26.6)	35.5 (32.0)	120	

COLLECTION SHEET

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(1) Not accurately measured

(2) Bottoms samples may not be representative. Some calculated compositions are shown below in parentheses.

TABLE II REMOVAL OF BENZENE AND TRICHLOROETHYLENE WITH CHLORINE

RUN	EDC	RUN TIME MIN.	AVERAGE FLOWS ⁽¹⁾				EXCESS Cl_2 ⁽²⁾ %	FeCl_3 ⁽³⁾ PPM	GC ANALYSES		REDUCTION %
			N_2	CO_2	HCl	C_2H_4			INITIAL%	FINAL%	
1	R-102 1-31-73	115	90	30	—	—	.1	1.0	Bz .389 TRI 1.646 1,1,2 .016	.389 1.17 .437	0 29 —
2	R-102 1-31-73	105	105	25	—	—	.13	50.0	Bz .389 TRI 1.646 1,1,2 .016	.340 1.39 .070	12.6 15.6 —
3	R-102 1-31-73	110	100	20	—	—	.12	50	Bz .389 TRI 1.646	.356 1.548	7.8 5.5
4	VC BTMS 1-31-73	125	80	30	—	—	.25	352	Bz .362 TRI 1.544 1,1,2 .009	.026 1.460 .078	92.8 5.0 —
5	VC OTMS 1-31-73	120	90	30	3	—	.23	840	Bz .362 TRI 1.544	.008 1.498	97.8 3.0
6A	VC BTMS 1-31-73	80	50	30 ⁺	4	30	.10		Bz .362 TRI 1.544	.341 1.540	5.8 0.3
6B	VC BTMS 1-31-73	50	50	30	—	40 ⁻	.08	158	Bz .341 TRI 1.540	.287 1.486	15.8 3.5
7	R-102 1-31-73		50	30	—	—	.32		Bz .389 TRI 1.646	.100 1.560	74.3 5.2

(1) Nitrogen and chlorine flows were varied to help control the excess chlorine level.

(2) This is only approximate since the levels varied considerably during a run.

(3) The first three runs were in Glass ware and FeCl_3 level was constant, but all other runs were in steel and level gradually built from near zero up to this value.

CCR 000034033

CONTINENTAL OIL COMPANY
CALCULATION SHEET

JOB NO.

TITLE

FIELD

STATE

TABLE III - OXYGENATES IN EDC STREAMS

(DISTILLED AT STANDARDIZED CONDITIONS TO CONCENTRATE OXYGENATES)

CONDITIONS:

400 ml EDC sample distilled at atmospheric pressure to 5 ml of Bottoms. Bottoms were diluted back to 10cc with a portion of the overhead and the carbonyl absorbance determined. The absorbance was divided by the cell path to obtain the oxygenate number.

<u>Distillation</u>	<u>EDC Samples</u>		<u>Remarks</u>	<u>Oxygenate No.</u>
1.	R-102	1-31-73	No treatment	1.4
2.	R-102	1-31-73	Chlorine Treated (R-7 TABLE II)	2.8
3.	R-101	2-20-73	With Recycle EDC (R-102 not in use)	2.9
4.	R-101	1-25-73	No Recycle EDC (R-102 in service)	6.5
5.	T-102	2-20-73	66% Oxygenate reduction in wash systems	1.0
6.	C-203 BTMS 2-20-73			nil