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AN IMPROVED COLUMN FOR DEPENTANIZER AND ISOPRENE FEED STREAM ANALYSIS

JAMES W. CARSON and GILBERT LEGÉ
Puerto Rico Olefins Co., Peñuelas, Puerto Rico (U.S.A.)
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SUMMARY

In the analysis of Depentanizer Overhead and Isoprene Feed streams within Ethylene Plants cracking naphtha and gas oil, one faces the necessity of analyzing a complex mixture of paraffins, olefins, diolefins, cycloparaffins, cycloolefins, and cyclodiolefins, all within the same carbon grouping (C_5) as well as the C_4 and C_5 acetylenes. To analyze such a complex mixture with its narrow boiling range generally has required several columns and/or separation of the sample into homologous groups by other analytical means prior to chromatographing. This paper describes an improved column which separates twenty-two of the C_5 and acetylene components normally found in the above noted streams. Three additional C_5 diolefins are eluted in combination with other C_5's.

INTRODUCTION

The total quantity of C_5 compounds in the effluent of naphtha and gas oil cracking furnaces is 2.0–5.0% for naphtha and 1.5–3.0% for gas oil, respectively, depending upon cracking severity[1]. These C_5's are concentrated within the process at the Depentanizer and removed in the overhead stream, usually as feed for specific fuels or as feed for an Isoprene Unit. Under normal operating conditions, the C_4 and lighter components, with the exception of the C_4 acetylenes, are removed prior to the Depentanizer, while the C_6 and heavier components are separated in the Depentanizer and removed through the bottom stream. This leaves a complex C_5 mixture with some acetylenes which must be analyzed in the Depentanizer Overhead. This mixture covers the full range of the C_5 hydrocarbons including paraffins, olefins, diolefins, cycloparaffins, cycloolefins, cyclodiolefins and acetylenes. Due to the complexity of the mixture and its narrow boiling range, this area of analysis readily becomes a problem for specific separation of the components.

Column technology inclines to follow the trend used in the analysis of gasoline, which uses capillary or multiple columns and/or separation of each homologous group by other analytical methods prior to chromatographing. These methods separate the C_5 paraffins, olefins, and cyclo-isomers with little or no separation of the diolefins, cyclodiolefins or the C_4 and higher acetylenes. Analytical times at best in these techniques are lengthy[2–6]. Ottmers *et al.*[7] determined a mixed pentene blend rapidly, using a single packed column but no attempt was made

to separate the other C_5's. Zakaib[8] used a packed coupled column for identification of the C_5 paraffins and olefins. Diolefins and the cyclo-isomers were not included and the author did not recommend the column for analysis of the higher acetylenes. The ASTM Standard Method D2427-67 (ref. 9) also separates the C_5 paraffins and olefins excluding the diolefins, cyclo-isomers and acetylenes.

Pop *et al.*[10], using three different phases to separate the C_5 paraffins, olefins and dienes in the hydrogenation of isopentane, obtained good resolution, particularly with the acetonitrile column. No endeavor was made to separate the cyclo-isomers of the different homologs or of the acetylenes. This also holds true for the investigation by Zhukhovitsky *et al.*[11]. Brodskii *et al.*[12] separated all of the C_5 homologs with the exception of the acetylenes. All three of these studies required exceptionally long chromatographic times.

Both Armitage[13] and ASTM[14] have presented column data for the analysis of high-purity isoprene. Armitage's manuscript contains excellent retention data for the separation of all the C_5 hydrocarbons and the acetylenes using a dimethylsulfolane column which is substantiated in part by Csicsery and Pines[15] and by Churchwell and Zlatkis[16]. Although sufficient for high-purity isoprene, the retention data do not indicate complete resolution of all components in the composition generally found in a Depentanizer Overhead or Isoprene Feed stream. The column data by ASTM for high-purity isoprene require multiple columns to effect the separation of all components.

The column described here consists of three sections connected in series. The first and shortest section has a liquid phase of di-*n*-propyl tetrachlorophthalate, the secondary section is *n*-methylformamide and the primary section contains bis[2-(2-methoxyethoxy)ethyl] ether (BMEE). BMEE has been used with considerable success in the determination of C_3 and C_4 hydrocarbons[17–19] and a combination of BMEE coupled with a secondary phase has proven its worth in the analysis of high-purity butadiene, cracked gas from ethylene naphtha cracking furnaces[20,21] and propylene concentrates[22]. BMEE alone will not resolve all of the acetylenes from the C_5's[23] and the dual-phase columns noted would require long analysis times and/or separation of the hydrocarbon mixture in a Depentanizer Overhead. However, if there is no need to separate 3-methylbutyne-1 from cyclopentene and 1,2-pentadiene from *trans*-1,3-pentadiene, the *n*-methylformamide section is not necessary as a dual-phase column of 4 ft. of di-*n*-propyl tetrachlorophthalate and 33 ft. of BMEE (using the coating weights noted herein) will make all of the other separations. Di-*n*-propyl tetrachlorophthalate is primarily used as a liquid phase for the separation of aromatics[15,24,25]. No reference could be found on the use of *n*-methylformamide in chromatograph columns.

EXPERIMENTAL

The column developed in this paper is composed of three sections connected in series. The first section is a 6 ft. × 3/16 in. length packed with 3.5% di-*n*-propyl tetrachlorophthalate on 60–80 mesh Chromosorb G-N-AW. The second section is a 10 ft. × 3/16 in. length with 7% *n*-methylformamide on 60–80 mesh Chromosorb P-N-AW, and the third section is a 34½ ft. × $\frac{1}{16}$ in. length with 10% BMEE on 60-80 mesh Chromosorb P-N-AW.

It is necessary that the di-*n*-propyl tetrachlorophthalate section comes first and the *n*-methylformamide second in order to elute all of the components as the retention time changes in a different position. We believe this is due to the difference in pressure drop across the columns as concluded by Keller and co-workers[26,27]. We have not tried preparing the column as a mixed solvent–mixed bed, although in our previous work on coupled BMEE columns[20], the mixed solvent column was prepared and a comparison made (though not noted in the article). It was found in that comparison that the mixed solvent column would not resolve all the peaks eluted by the coupled column. Several columns have been prepared in the above combination and used over a period of many months. All columns were made of 316 stainless steel and have performed satisfactorily.

The columns have been used successfully in both Varian 1800 (Varian, Palo Alto, Calif., U.S.A.) and Hewlett-Packard 5750 Series (Hewlett-Packard, Avondale, Pa., U.S.A.) Chromatographs having a thermal conductivity detector with WX filaments. Data reduction is accomplished through a Hewlett-Packard Model 7127-A recorder and an Infotronics Model CRS 101 digital integrator (Infotronics, Boulder, Colo., U.S.A.). The columns are used at ambient temperature (approximately 25°) and the carrier gas is helium at 230 ml/min. A Hamilton CR-700-20 automatic syringe (Hamilton, Reno, Nev., U.S.A.) is used for injecting the sample, which normally is 1.0 μl with the injector temperature at 180°. Samples are kept under refrigeration until ready for analysis to inhibit loss by evaporation. The column is connected to a Valco V-4-HP four-port back-flush valve (Valco, Houston, Texas, U.S.A.) to obtain heavier components that might be present when the Depentanizer is in an upset condition.

DISCUSSION

A chromatogram of a typical analysis from a Depentanizer Overhead stream in an Ethylene Plant cracking naphtha is shown in Fig. 1. The identification of the peaks and their concentration is shown in Table I. 1,4-Pentadiene and *cis*-pentene-2 elute in one peak except when present in low quantity. This also happens

TABLE I

TYPICAL ANALYSIS OF DEPENTANIZER OVERHEAD (ISOPRENE FEED) FROM A NAPHTHA FEEDSTOCK

Peak No.	*Component*	*Weight %*	*Peak No.*	*Component*	*Weight %*
1	Air	—	9	2-Methylbutene-2	3.90
2	Isopentane	7.33	10	Cyclopentane	1.99
3	3-Methylbutene-1	1.38	11	Isoprene	36.96
4	*n*-Pentane	7.90	12	Cyclopentene	0.91
5	Pentene-1	5.20	13	Butyne-2	2.13
6	2-Methylbutene-1	13.70	14	*trans*-1,3-Pentadiene	4.07
7	*trans*-Pentene-2	2.92	15	*cis*-1,3-Pentadiene	1.25
8	1,4-Pentadiene *cis*-Pentene-2	5.59	16	Cyclopentadiene	4.77
			17	2-Methyl-1-buten-3-yne	trace

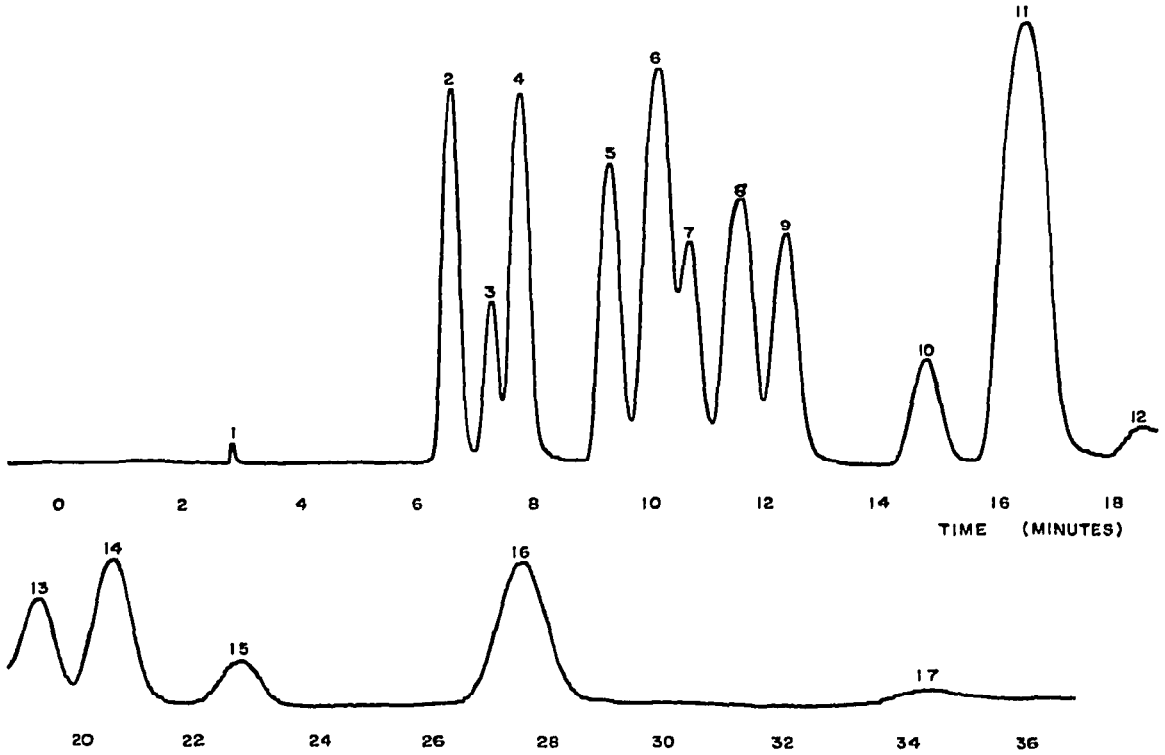

Fig. 1. Chromatogram of a typical Dependanizer Overhead Stream analysis in an Ethylene Plant cracking naphtha.

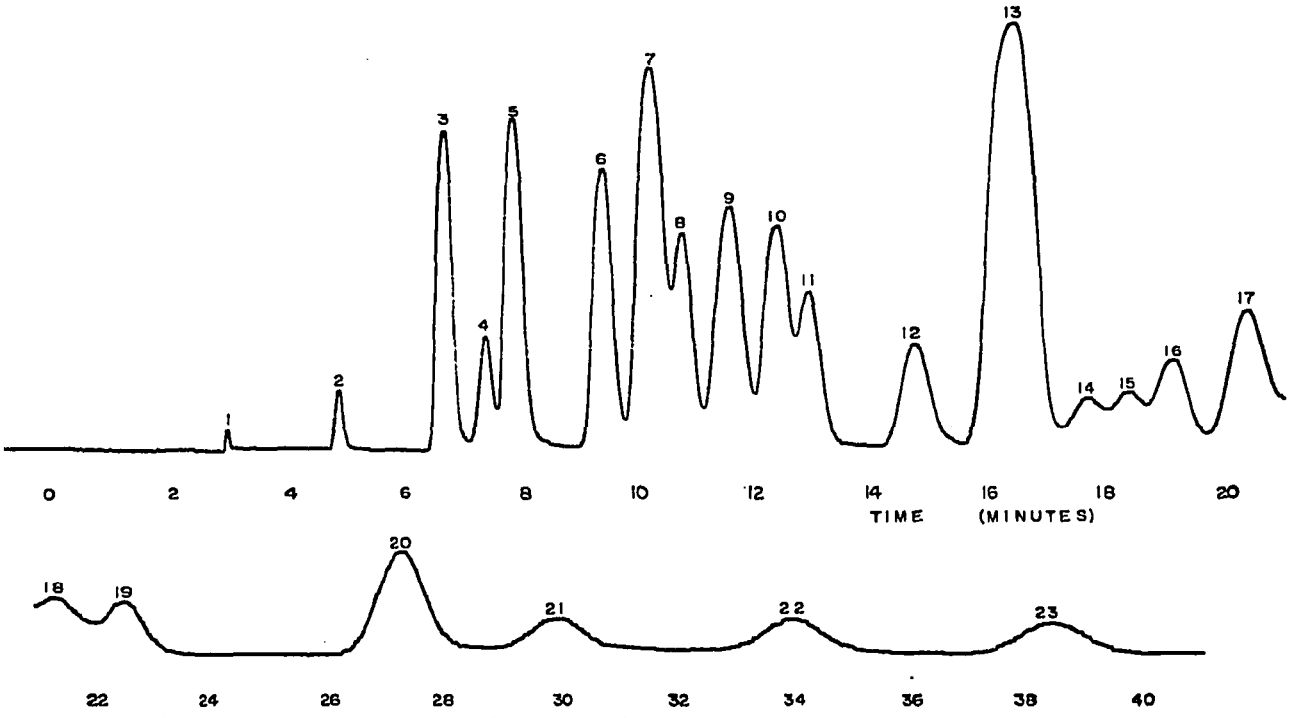

Fig. 2. Chromatogram of a synthetic blend of Dependanizer Overhead sample and other C_5 components which can be produced from the cracking of naphtha.

with 3-methylbutyne-1 and 3-methyl-1,2-butadiene. Quantitative calculation of the Dependanizer stream is determined from the molar response data by Carson and co-workers[28,29], which are based upon the original concept and applications of Rosie and co-workers[30,31] and the weight factor calculation proposed by Kaiser[32]. Fig. 2 is a typical Dependanizer stream analysis with the addition of neopentane, butyne-1, 3-methyl-1,2-butadiene, 3-methylbutyne-1, 1,2-pentadiene, 2,3-pentadiene, pentyne-1 and pentyne-2. These components are present depending upon cracking severity and are of particular importance when analyzing Isoprene Feed streams. Table II identifies the components along with their boiling points, molecular weights and relative retention.

TABLE II

COMPONENT IDENTIFICATION OF C_5 HYDROCARBON AND C_4 AND C_5 ACETYLENE BLEND

Peak No.	*Component*	*Relative retention**	*Boiling point (°C)*	*Molecular weight*
1	Air	—	—	—
2	Neopentane	0.140	9.503	72.146
3	Isopentane	0.277	27.852	72.146
4	3-Methylbutene-1	0.325	20.061	70.130
5	*n*-Pentane	0.365	36.074	72.146
6	Pentene-1	0.476	29.968	70.130
7	2-Methylbutene-1	0.539	31.163	70.130
8	*trans*-Pentene-2	0.576	36.353	70.130
9	1,4-Pentadiene	0.638	25.967	68.114
	cis-Pentene-2	0.638	36.942	70.130
10	2-Methylbutene-2	0.697	38.568	70.130
11	Butyne-1	0.738	8.07	54.088
12	Cyclopentane	0.871	49.262	70.130
13	Isoprene	1.000	34.067	68.114
14	3-Methylbutyne-1	1.085	29.35	68.13
	3-Methyl-1,2-butadiene	1.085	40.851	68.114
15	Cyclopentene	1.137	44.242	68.114
16	Butyne-2	1.192	26.99	54.088
17	*trans*-1,2-Pentadiene	1.288	42.032	68.114
18	1,2-Pentadiene	1.358	44.856	68.114
	2,3-Pentadiene	1.376	48.262	68.114
19	*cis*-1,3-Pentadiene	1.446	44.068	68.114
20	Cyclopentadiene	1.797	40.0	66.10
21	Pentyne-1	1.993	40.18	68.114
22	2-Methyl-1-buten-3-yne	2.292	34.0	66.10
23	Pentyne-2	2.620	56.07	68.114

* Relative to isoprene (=1.000).

Table III lists the volume molar factor (*VMF*), based on a 0.5-μl sample, relative molar response (*RMR*) (relative to benzene as 100) and weight factor for all hydrocarbons chromatographed in this work. Identification of all components

TABLE III

MOLAR RESPONSE DATA FOR ALL COMPONENTS NOTED IN THE FIG. 2 CHROMATOGRAM

Component	*VMF**	*RMR***	*Weight factor*
Neopentane	414	100	0.721
Isopentane	433	101	0.714
3-Methylbutene-1	451	98	0.716
n-Pentane	437	107	0.674
Pentene-1	460	103	0.681
2-Methylbutene-1	467	101	0.694
trans-Pentene-2	466	104	0.674
1,4-Pentadiene	489	98	0.695
cis-Pentene-2	471	102	0.688
2-Methylbutene-2	476	101	0.694
Butyne-1	601	83	0.652
Cyclopentane	535	97	0.723
Isoprene	504	93	0.732
3-Methylbutyne-1	493	97	0.702
3-Methyl-1,2-butadiene	508	100	0.681
Cyclopentene	571	91	0.749
Butyne-2	644	89	0.608
trans-1,3-Pentadiene	500	97	0.702
1,2-Pentadiene	512	103	0.661
2,3-Pentadiene	514	107	0.637
cis-1,3-Pentadiene	511	98	0.695
Cyclopentadiene	616	83	0.792
Pentyne-1	510	100	0.681
2-Methyl-1-buten-3-yne	511	101	0.655
Pentyne-2	526	106	0.643

* Based on a 0.5-μl sample.
** Relative to benzene (= 100).

was accomplished through prepared standards of C_5's and acetylenes in a Depentanizer Overhead stream, which were prepared in acetonitrile and injected into the column on an individual and overall component basis. Standards were of the highest purity available in the commercial market with the exception of cyclopentadiene, which was obtained from dicyclopentadiene by distillation cracking.

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