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Identification of Suitable Vacuum Gas Oils as Plasticizers Using HT-GC × GC-HRMS

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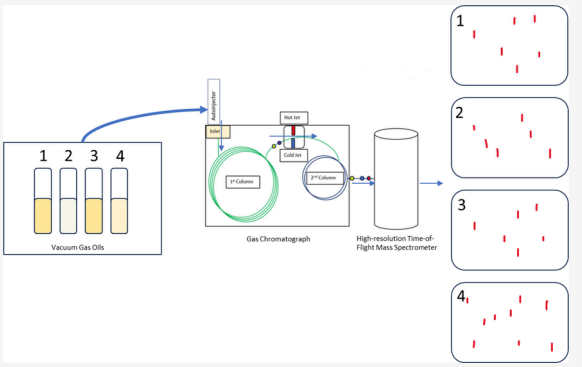
ABSTRACT: Vacuum gas oils (VGOs) have long been heralded as effective plasticizers due to their high boiling-points and lubricating properties. One of these VGOs, HyVac Oil 93050, is a paraffinic plasticizer that is currently utilized in polymer−plasticizer explosive formulations, while this oil effectively increases the elasticity and decreases the sensitivity for current formulations. We seek to identify alternative VGOs with similar density, viscosity, molecular composition, and impurities for future formulations. In this study, 18 VGOs, including HyVac Oil 93050, were initially evaluated for their density and viscosity. The oils were then ranked based on physical characteristics and analyzed for molecular composition using high-temperature comprehensive two-dimensional gas chromatography with high-resolution time-of-flight mass spectrometry (HT-GC × GC-HRMS). The HT-GC × GC-HRMS chromatograms of the top 10 most similar VGOs to HyVac Oil 93050, according to density, were compared utilizing the Pearson correlation coefficient. Three of the oils with densities similar to those of HyVac Oil 93050 had a Pearson correlation within the lot-to-lot variation of HyVac Oil 93050. For the top 3 candidates, Pearson correlation was then utilized as a feature selection technique to discover significant chemical differences. Positive chemical ionization (PCI) and negative chemical ionization (NCI) HT-GC × GC-HRMS chromatograms were also evaluated and aided in the discovery and identification of several key compounds including additives that acted as stabilizers for the VGOs. After this further chemical analysis, two of the original 17 potential VGOs were determined to be physically and chemically similar to HyVac Oil 93050.



1. INTRODUCTION

Plastic-bonded explosives (PBXs) are composite materials wherein the crystalline explosives are bound together in a matrix using a polymer and, occasionally, a plasticizer.[1] The polymer and plasticizer system, even at low weight percents (5−10%), can have a drastic impact on the sensitivity and mechanical properties of the PBX. However, it is desirable to utilize a chemically similar class of materials as PBX ingredients without specifically naming a brand or company to avoid potential supply chain issues. One plasticizer of importance is HyVac Oil 93050, a vacuum gas oil (VGO). While this VGO is readily available, it was determined that replacement VGOs with similar physical and chemical characteristics should be explored.

VGOs are manufactured through the hydrocracking, hydrodewaxing, and hydrotreating of vacuum distillation cuts produced from the residue of the atmospheric distillation process. These processes result in a medium to heavy distillate cut of oil with low sulfur and nitrogen content, low viscosity, and high stability through the saturation of aromatic compounds.[2−4] However, minor variations in these processes, along with variations in feedstocks, can produce different concentrations of linear, branched, cyclic, and aromatic compounds. Thus, variations between manufacturers and different feedstocks are expected to lead to variations within the chemical compositions of the VGOs. Because VGOs such as HyVac Oil are heavier distillate cuts of petroleum ranging from (nC_{13}−nC_{40}),[2−4] a form of gas chromatography that has the ability to analyze compounds with boiling points above 340 °C called high-temperature gas chromatography (HT-GC) must be employed.[5−7] The current industry standard for determining boiling point distribution in VGOs requires the use of HT-GC with a programmed temperature vaporizer (PTV) inlet.[8−10] Additionally, because VGOs contain a higher carbon range, the number of isomers is significantly higher compared to that of a lighter distillate cut such as diesel or gasoline. Therefore, in order to determine the molecular composition of VGOs, namely, the separation of the chemical groups such as alkanes, cycloalkanes, and aromatics, the ideal technique is high-temperature comprehensive two-dimensional

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Table 1. VGO Densities and Dynamic Viscosities As Compared to HyVac Oil at 20° C

Sample	Density (g/cm3)	Change (%)	Dynamic viscosity (mPa s)	Change (%)
HyVac Oil 93050	0.8782	Baseline	218.1	Baseline
Leybonol LVO 100	0.8762	0.23	179.8	17.5
Leybonol LVO 710	0.8892	1.26	179.4	17.7
Edwards Ultragrade 70	0.8667	1.31	179.3	17.8
Alfa 46	0.8666	1.31	172.5	20.8
KJLSS20	0.8660	1.39	264.3	21.1
Edwards Ultragrade Pure 20	0.8655	1.44	283.1	29.8
VWR 19	0.8644	1.57	283.4	29.9
Leybonol LVO 130	0.8631	1.72	284.9	30.6
Duratex Standard 68	0.8630	1.72	147.5	32.3
Vacuubrand	0.8625	1.78	335.9	33.3
KJLSS70	0.8625	1.79	142.5	34.6
VWR 20	0.8623	1.81	295.7	35.5
Pfieffer P3	0.8616	1.88	138.7	36.4
Tigol 48	0.8611	1.94	138.5	36.4
KJLSS19	0.8609	1.97	138.3	36.5
AVF Silver	0.8608	1.98	137.9	36.7
Edwards Ultragrade 19	0.8602	2.05	128.4	41.1

gas chromatography with high-resolution time-of-flight mass spectrometry (HT-GC × GC-HRMS). GC × GC utilizes a combination of two columns comprised of different stationary phases allowing for a higher separation of compounds that would typically coelute when a singular column is used.[11−16] This increased separation allows for the identification of three times more compounds within a complex mixture through a 10-fold increase in the overall peak capacity of a separation.[11−16] When GC × GC is further combined with HRMS, a higher degree in confidence of identification of unknown compounds is obtained.[11,17−20]

Due to the large data sets produced by HT-GC × GC-HRMS, application of chemometric techniques is required for comparison and classification of each of the VGO chromatograms. One chemometric technique that has previously been used for comparison of samples is the Pearson correlation coefficient which measures the linear correlation between two sets of data.[21] The comparison of these data sets is described in eq 1 which mathematically describes a normalized measure of covariance.

$$\rho_{X,Y} = \frac{\mathrm{cov}(X, Y)}{\sigma_X \sigma_y} \quad (1)$$

Herein, we perform a preliminary down selection of 17 VGOs based on density and dynamic viscosity followed by chemical composition analysis utilizing HT-GC × GC-HRMS. The Pearson correlation coefficient was then used to compare the top ten candidate VGOs to each other and to HyVac Oil 93050 to determine which were the most chemically similar. Finally, the Pearson correlation was then applied as a discovery-based technique to uncover the significant chemical differences between the samples.

2. EXPERIMENTAL SECTION

2.1. Density and Viscosity. The density and viscosity of HyVac oil and 17 high vacuum gas oil replacement candidates were measured using an Anton Paar SVM 3001 viscometer. Here, 1 mL of each oil was injected. Density and viscosity were measured at 20, 30, 40, 50, and 60 °C in triplicate.

2.2. Chemical Characterization Using HT-GC × GC-HRMS. Twenty VGOs, three lots of HyVac oil, and 17 replacement oils were analyzed in triplicate. Each sample was diluted by adding 2.6 mg to 6 mL *n*-heptane (Sigma-Aldrich, St. Louis, MO) and was spiked with 100 μL of hexachlorobenzene (Restek, Bellefonte, PA) as an internal standard. An *n*-alkane standard (nC_{10}−nC_{40}) (Restek, Bellefonte, PA), spiked with 1 mg of n-tetratetracontane (Sigma-Aldrich, St. Louis, MO), was analyzed in triplicate for determination of the carbon range of each of the oil samples.

Separation of the VGOs was performed on an 8890 GC instrument (Agilent Technologies, Palo Alto, CA) equipped with an MMI inlet and a dual stage thermal modulator coupled to a Pegasus HRT$^+$ high-resolution time-of-flight mass spectrometer (LECO, St. Joseph, MI). Helium (grade 5, 99.999%, Airgas, Radnor, PA) was used as a carrier gas at a constant flow rate of 2.0 mL/min. The MMI inlet was set to an initial temperature of 175 °C and was ramped to 400 °C at a rate of 360 °C/min. Then, 1 μL of the sample was injected with a split ratio of 20:1. The first dimension was a ZB-35HT 30 m × 0.25 mm × 0.25 μm (Phenomenex, Torrance, CA), and the second dimension was a ZB-1HT 4 m × 0.18 mm × 0.18 μm (Phenomenex, Torrance, CA). The oven was held at 175 °C for 1 min and then ramped at 1 °C/min to 340 °C. The temperature offset of the secondary oven was 12 °C relative to the primary oven temperature. The modulation period was 10 s with a hot jet duration of 3.33 s and a modulator block offset of 30 °C relative to the primary oven temperature. The transfer line was set to a temperature of 350 °C, and the ion source was set to 300 °C. Data were collected using electron impact ionization at −70 eV. For chemical ionization, methane gas was used as the reagent and was set to a flow rate of 1.26 mL/min. The electron energy for positive chemical ionization (PCI) was set to 140 and 130 eV for negative chemical ionization (NCI). Mass spectra 50−600 amu were collected at a rate of 100 Hz after a 140 s acquisition delay for each ionization method. The instrument was controlled via ChromaTOF (Version 5.53.70.0.113).

2.3. Statistical Analysis of Samples. For postrun data visualization and analysis, the data were exported as .csv files and was imported into MATLAB 2022a (Mathworks, Natick, MA). All samples were binned to unit resolution for this analysis to prevent the computer from running out of RAM when running the Pearson correlation. Each two-dimensional chromatogram was vectorized into one dimension and compared pairwise between each sample using the Pearson correlation coefficient.

The three samples (Leybonol LVO 100, Duratex 68, and VWR 19) that were found within the lot-to-lot variation of HyVac oil (see Results and Discussion) were then compared to HyVac oil using the chromatograms collected via PCI and NCI. As opposed to calculating a single Pearson correlation coefficient for the entire chromatogram, the covariance was calculated on a per pixel per m/z basis to facilitate

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discovery of chemical differences. Once the compounds were discovered using Pearson correlation, the compounds were identified using high-resolution mass spectral data in ChromaTOF (version 5.53.70.0.113).

3. RESULTS AND DISCUSSION

3.1. Density and Viscosity. We determined that the most important physical property to compare HyVac Oil 93050 to the other potential candidates was the density. Table 1 shows the densities and dynamic viscosities of each of the VGOs in comparison to those of HyVac oil. Looking at the data in Table 1, there are many VGOs available that have a density within 2% of that of HyVac oil. Unlike density, dynamic viscosity between all of VGOs is more varied ranging between 150 and 300 mPas. Dynamic vicosity of oils has also been shown to be affected by chemical composition and additives,[22,23] so rather than depending on viscosity for a second criterion for the oil specification, we turn to the chemical analysis of each oil using HT-GC × GC-HRMS as the second criterion.

3.2. Chemical Characterization Using HT-GC × GC-HRMS. Using HT-GC × GC-HRMS, it is possible to see just how complex HyVac oil is. Figure 1 shows the two-dimensional total ion current (TIC) chromatograms of HyVac oil (Figure 1A), Leybonol LVO 100 (Figure 1B), Leybonol LVO 710 (Figure 1C), and Duratex Standard 68 (Figure 1D). One example of how valuable the chemical characterization using a GC × GC method can be is the comparison of the chromatograms for HyVac oil and Leybonol LVO 710 (Figure 1A and C). Leybonol LVO 710 was originally considered the third highest ranked replacement oil for HyVac oil purely based on the density and dynamic viscosity values. However, after visually comparing the two chromatograms, it is clear that they are significantly different. This is most likely due to the fact that Leybonol LVO 710 is a synthetic oil, while HyVac oil is a conventional oil. All two-dimensional chromatograms can be found in the Suppoorting Information.

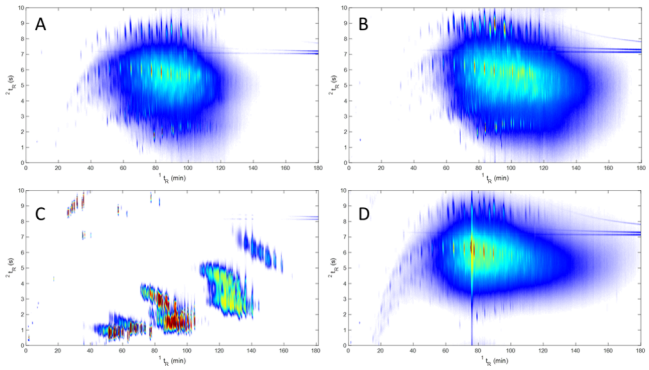

Figure 1. Two-dimensional chromatograms of (A) HyVac oil, (B) Leybonol LVO 100, (C) Leybonol LVO 710, and (D) Duratex Standard 68.

In an attempt to provide a single, simple metric to describe the chemical composition, the carbon ranges of each oil were evaluated. Because an *n*-alkane standard was evaluated, it is possible to convert the retention time to carbon number. While better than visual comparison, this crude comparison allowed for evaluation into which oils would make a good replacement for HyVac oil based on chemical composition. An example of the comparisons between the carbon distributions of each sample can be seen in Figure 2; HyVac oil has a carbon range between approximately n-C_{20} and n-C_{42} and appears to have a similar carbon distribution to Leybonol LVO 100 (Figure 2A) but has a much heavier distribution compared to Alfa 46 (n-C_{15} and n-C_{37}) and lighter distribution compared to Kurt J. Lesker grade 20 (n-C_{25} and n-C_{50}) (Figure 2C).

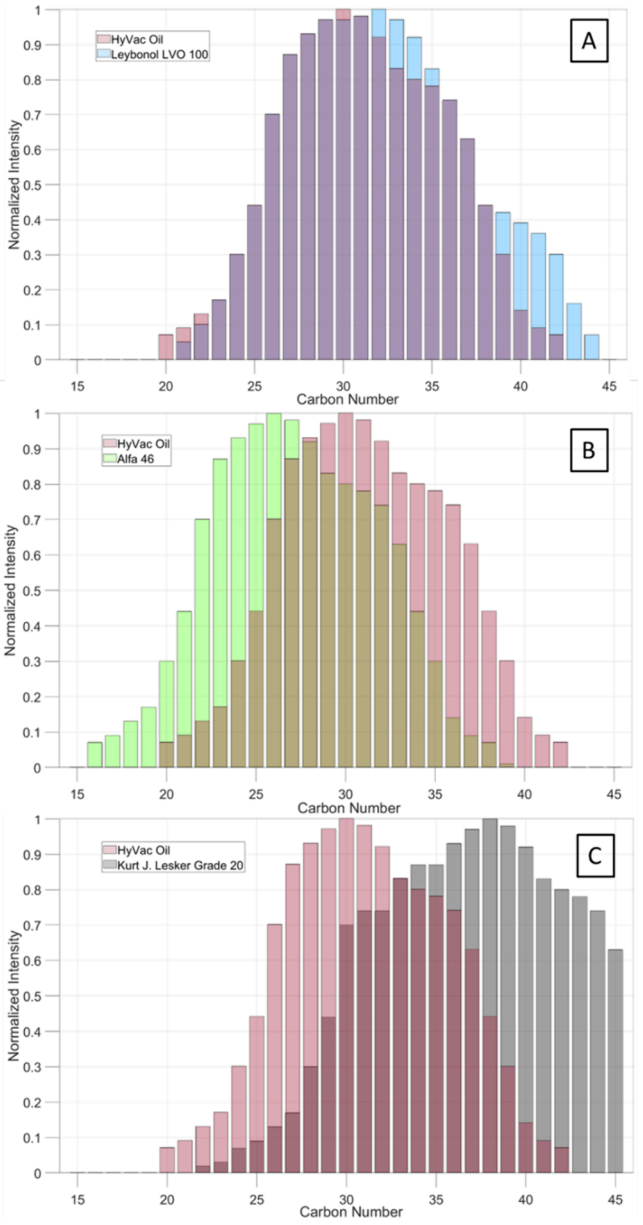

Figure 2. Carbon range distribution for HyVac oil and (A) Leybonol LVO 100, (B) Alfa 46, and (C) Kurt J. Lesker grade 20.

A second method that utilized the high-resolution capabilities of the mass spectrometer was a comparison of the ring double bond equivalent (RDBE) and the carbon number of the total ion spectrum for each sample. These plots have previously been used for petroleomics research to determine families of different compounds found within a mixture analyzed with high-resolution multidimensional GC data.[24] In Figure 3, the RDBE versus carbon number for HyVac oil (A), Leybonol LVO 100 (B), Alfa 46 (C), and Kurt J. Lesker grade 20 (D) were compared. While more information was gained utilizing this method, the amount of

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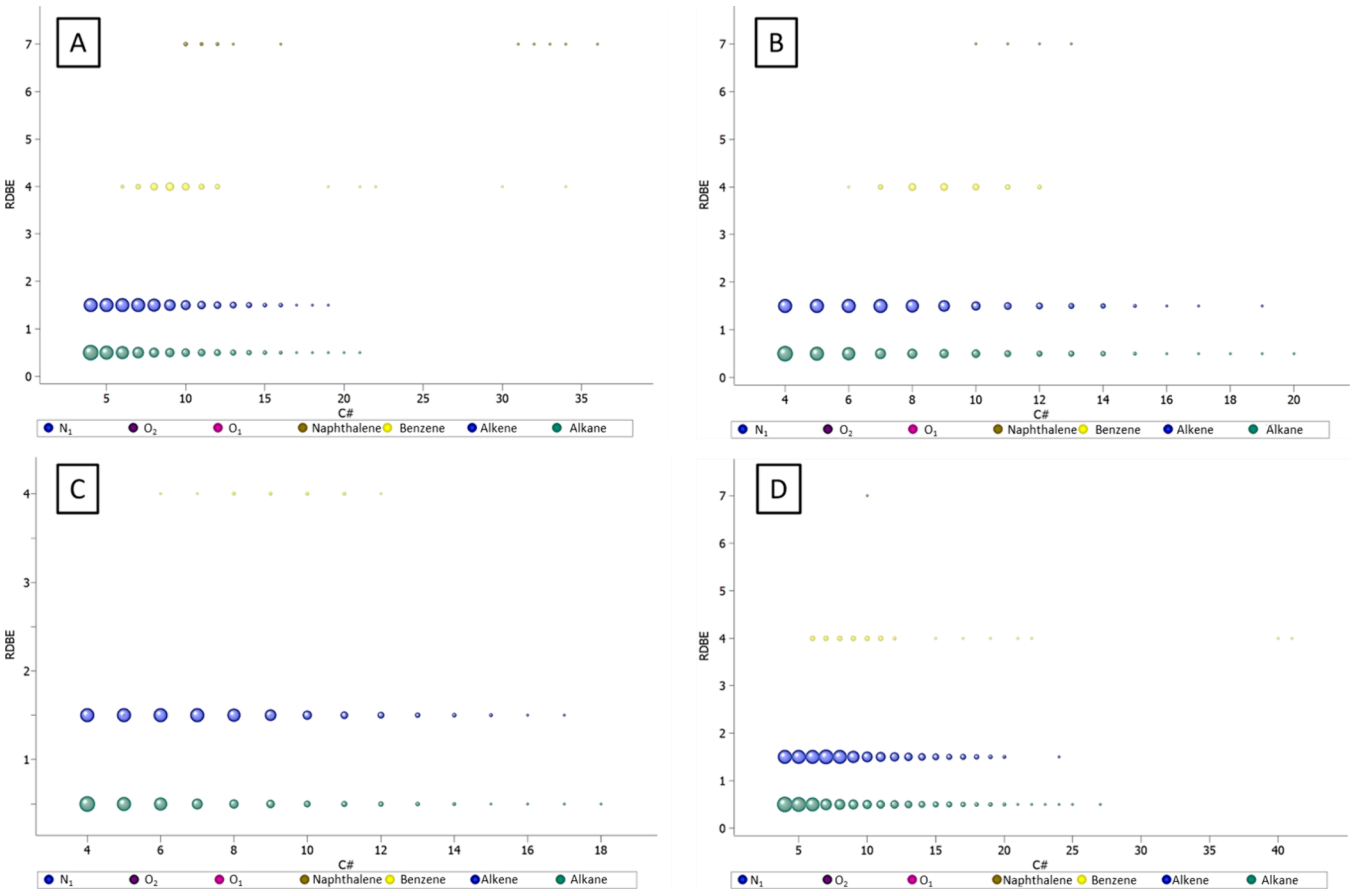

Figure 3. RDBE compared vs carbon number for (A) HyVac oil, (B) Leybonol LVO 100, (C) Alfa 46, and (D). Kurt J. Lesker grade 20.

data lost by summing away the chromatographic dimensions severely decreased the ability to classify and compare these oils to one another. Also, because the samples were analyzed via a nontargeted method, it was difficult to identify all the defect species that could be found within each of the samples. Therefore, while interesting, the loss of chromatographic information overly reduced the amount of data necessary to make correlations between samples. All RDBE versus carbon number plots can be found in the Supporting Information.

Out of the 17 replacement oils tested using the HT-GC × GC-HRMS method, 10 of them had a carbon range between n-C_{20} and n-C_{42} and a similar RDBE versus carbon number plot. These oils were then further characterized and compared using the Pearson correlation coefficient as it was determined that the carbon range, while useful, did not provide enough discrimination between the oils.

3.3. Statistical Analysis of Samples. For oils with similar carbon ranges (e.g., HyVac oil (Figure 1A), Leybonol LVO 100 (Figure 1B), and Duratex Standard 68 (Figure 1D)), a statistical comparison of the two-dimensional chromatograms was necessary. Furthermore, because the data sets for the chromatograms being analyzed were large and complex (approximately 10 million data points in vector form), a simple metric was preferred when determining the similarities and differences between samples. This single metric concept led to the application of the Pearson correlation coefficient. The Pearson correlation coefficient was performed on three lots of HyVac oil, where the values between all three lots of HyVac oil were determined to be the lot-to-lot variation of the VGO itself. The three lots of HyVac oil had Pearson correlation coefficient values between 0.93 and 0.99 (Figure 4). This was somewhat expected because different lots of material could be made at different times, utilizing different refining methods, and are typically from different crude oils. In the case of the three lots of HyVac oil in Figure 4, Lot 2 had higher cycloalkane and isoparaffinic contents as compared to lots 1 and 3, and lot 3 had a larger aromatic content as compared to lots 1 and 2.

Figure 5 shows the Pearson correlation coefficients of the HT-GC × GC-HRMS using electron impact ionization between HyVac oil and the top ten candidates as ranked by density. Green represents a high correlation between the two samples, while red indicates a low correlation. Three oils, Leybonol LVO 100, Duratex 68, and VWR 19, were found to have correlation coefficients above 0.93. Because these three oils were within the lot-to-lot variation of HyVac oil, they were considered good replacement oil candidates due to their chemical composition similarities.

Interestingly, while some VGOs did not have Pearson correlations within the lot-to-lot variation of HyVac oil, they were found to be chemically similar to one another. The first set of oils within the top 10 candidates that had highly similar characteristics (0.98 Pearson correlation coefficient or above) to one another were Edwards 70 (no. 2), Leybonol LVO 130 (no. 6), and VWR 19 (#10). While VWR 19 (#10) was within the lot-to-lot Pearson correlation coefficient variation of HyVac oil, Edwards 70 (#2) and Leybonol LVO 130 (#6) were not. This is because the numbers of aromatics and hopanes between Edwards 70 (no. 2), Leybonol LVO 130 (no. 6), and VWR 19 (no. 10) are slightly different (fewer aromatics in

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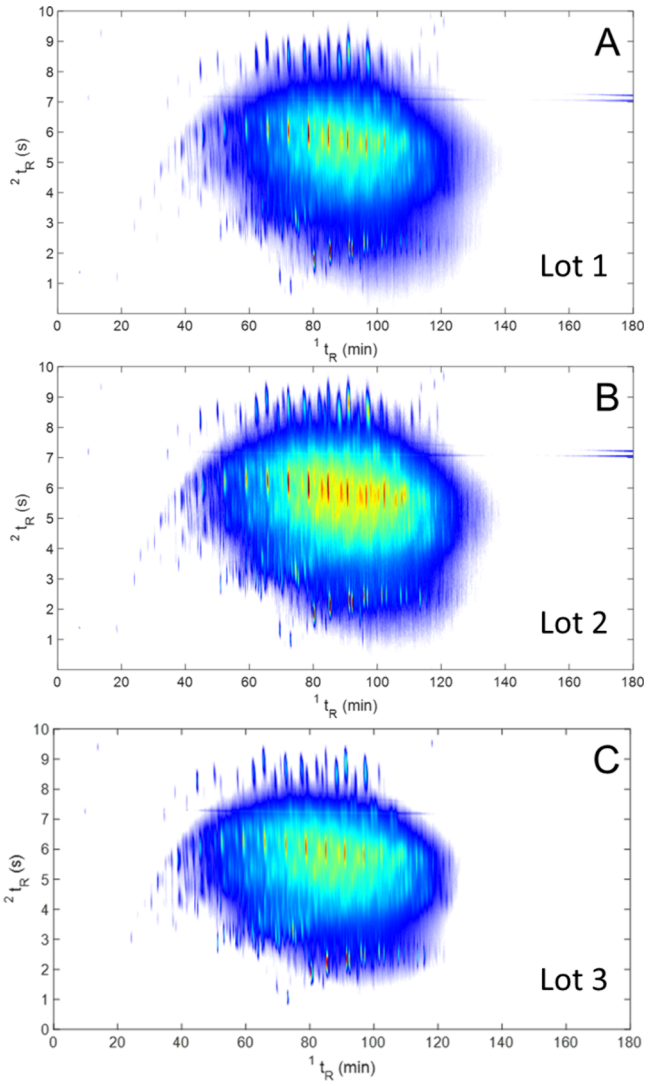

Figure 4. Lot-to-lot comparison of HyVac oil using Pearson correlation coefficient where the Pearson correlation coefficient between A and B is 0.95, B and C is 0.93, and A and C is 0.99.

	1	2	3	4	5	6	7	8	9	10	11
1	1.00										
2	0.91	1.00									
3	0.86	0.92	1.00								
4	0.14	0.13	0.14	1.00							
5	0.94	0.92	0.88	0.14	1.00						
6	0.91	0.99	0.92	0.14	0.91	1.00					
7	0.93	0.90	0.85	0.11	0.91	0.90	1.00				
8	0.88	0.90	0.96	0.13	0.83	0.92	0.85	1.00			
9	0.87	0.90	0.96	0.13	0.83	0.91	0.85	0.99	1.00		
10	0.93	0.98	0.91	0.13	0.90	0.98	0.91	0.93	0.93	1.00	
11	0.70	0.84	0.87	0.13	0.83	0.82	0.71	0.74	0.74	0.75	1.00

1. HyVac® Oil
2. Edwards 70
3. Kurt J. Lesker 70
4. Leybonol LVO 710
5. Leybonol LVO 100
6. Leybonol LVO 130
7. Duratex 68
8. Edwards 19
9. Kurt J. Lesker 19
10. VWR 19
11. Edwards 20

Figure 5. Pearson correlation coefficients of HyVac oil and potential replacement oils as compared with one another with electron ionization.

Edwards 70 (no. 2) and Leybonol LVO 130 (#6)). However, it is highly interesting to note that both Leybonol and Edwards are owned by the same parent company (Atlas Copco) which could account for why these two oils are so similar to one another. Another set of oils with high chemical similarity to one another are Edwards 19 (no. 8) and Kurt J. Lesker 19 (no. 9) with a Pearson correlation coefficient of 0.99. These oils are made to the same grade, have similar carbon ranges and similar concentrations of normal alkanes, cycloalkanes, and aromatics, and have similar additives. Therefore, it is highly possible that these two oils are also from the same source.

3.4. Chemical Ionization and Identification. The three oils (Leybonol LVO 100, Duratex 68, and VWR 19) determined to be chemically similar based on the Pearson correlation coefficients of the electron impact ionization chromatograms were further analyzed by comparing the PCI and NCI data sets to one another. The Pearson correlation coefficient for lot-to-lot variation between the three lots of HyVac oil for PCI was 0.94 to 1.00 while for the NCI the lot-to-lot variation decreased to a range of 0.93 to 0.97.

All values for these Pearson correlation coefficients were within the lot-to-lot variation of HyVac oil except for Duratex 68 for the NCI comparison, where a Pearson correlation of 0.92 between the two oils was obtained which falls outside the lot-to-lot variation of HyVac oil (Figure 6). This result showed the value in performing chemical ionization on the samples that were deemed to be statistically similar to HyVac oil when only analyzing the samples with electron ionization.

An impurity analysis was deemed necessary for Duratex 68 due to its lower Pearson correlation coefficient when analyzing the sample in NCI mode and also because the oil began to turn brown after being exposed to air for 1 week. Identifying the compound causing the color change in this oil was extremely important in determining whether the oil could be listed as a replacement for HyVac oil. In order to accomplish this, the Pearson correlation coefficient was utilized, but instead of calculating a single value for the entire chromatogram as performed in Figures 5 and 6, it was calculated on a per pixel per m/z basis. The m/z dimension was then summed away and normalized to the number of m/z channels to give the visual of a two-dimensional chromatogram. A measurement of the covariances across the chromatogram utilizing the Pearson correlation coefficient equation was utilized. Because the Pearson correlation coefficient is a metric of the linear correlation between two sets of data (eq 1), a linear regression of the Pearson's correlation can be calculated. The equation for this regression line can then be compared to each data point along the linear correlation. Data points with the largest distance from the equation of the regression line were determined to be chemical differences between each pair of two-dimensional chromatograms. An example of this can be seen in Figure 7 with a comparison of the two-dimensional chromatograms of HyVac oil and Duratex 68. The major difference between the two samples was an unknown compound with a high intensity found in Duratex 68 at approximately 75 min. Utilizing the high-resolution data, the mass spectrum for the unknown compound was compared to a high-resolution mass spectral library and was identified as 4,4′′-diamino-p-terphenyl with a similarity of 917 and a probability of 78.2. 4,4′′-Diamino-p-terphenyl undergoes aniline oxidation to form multiple different products that are reddish-brown in color when mixed (typically composed of yellow and red azobenzene-based oxidation products). Because

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PCI	1	2	3	4
1	1.00			
2	0.98	1.00		
3	0.97	0.95	1.00	
4	0.95	0.93	0.90	1.00

1. HyVac® Oil
2. Leybonol LVO 100
3. Duratex 68
4. VWR 19

NCI	1	2	3	4
1	1.00			
2	0.96	1.00		
3	0.92	0.89	1.00	
4	0.95	0.92	0.88	1.00

1. HyVac® Oil
2. Leybonol LVO 100
3. Duratex 68
4. VWR 19

Figure 6. Pearson correlation coefficients of HyVac oil and potential replacement oils as compared with one another with positive chemical ionization (PCI) and negative chemical ionization (NCI).

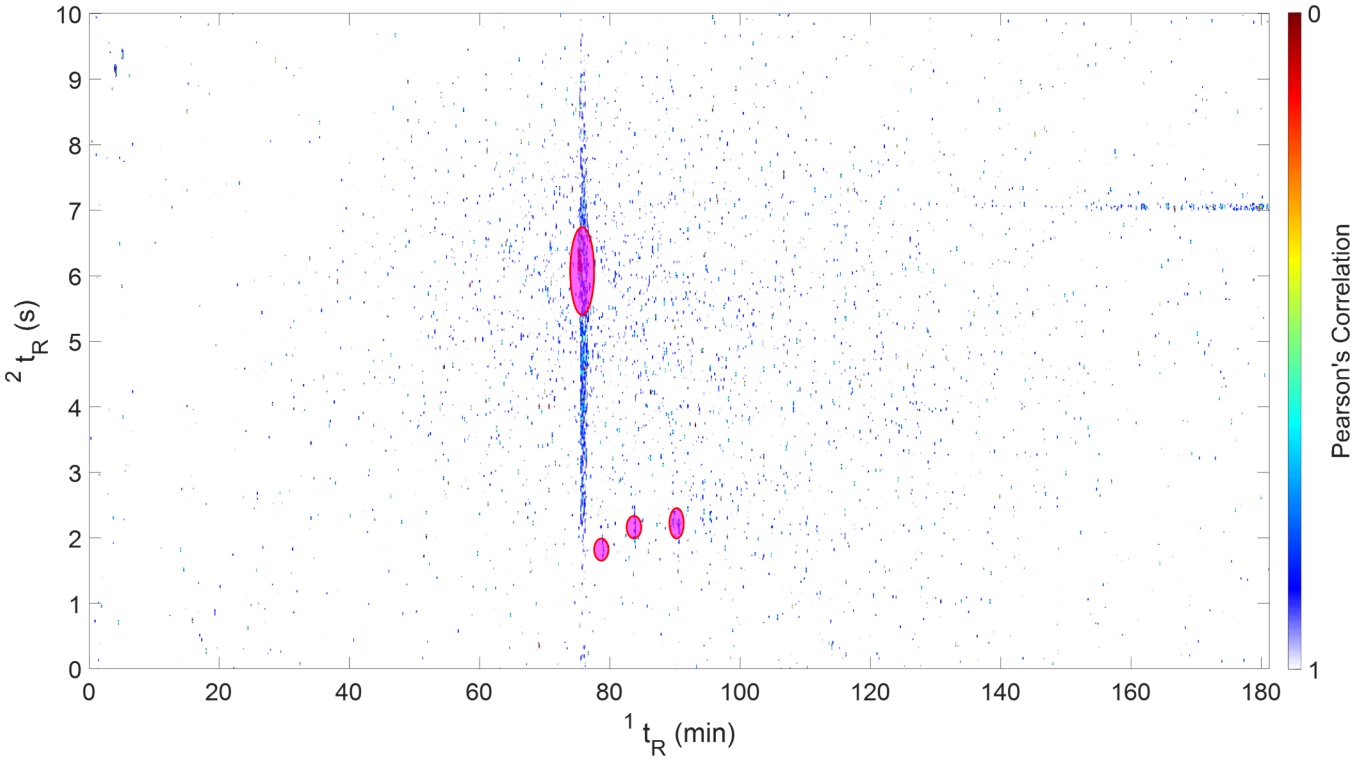

Figure 7. Pearson correlations between the two-dimensional chromatograms of HyVac oil and Duratex 68 with negative chemical ionization. Red circles mark the four compounds with a Pearson correlation of 0.75 or less between Duratex 68 and HyVac oil.

of the identification of this impurity, Duratex 68 was determined to not be chemically similar to HyVac oil.

The other three impurities determined to have major differences between the negative chemical ionization two-dimensional chromatograms were identified utilizing the same high-resolution mass spectral library as the impurity identified at 75 min. All three compounds were identified as hopanes, with the compound at 78 min being 28-nor-17α(H)-hopane (similarity 907), the compound at 82 min being 17α(H), 21β(H)-hopane (similarity 887), and the compound at 90 min being 17α(H), 21β(H)-homohopane (similarity 929).

The identification of all four compounds was made easier by using both electron and chemical ionization. First, the use of electron ionization with the Pearson correlation allowed for a preliminary pairing down of VGOs that could replace HyVac oil. This reduced the analysis time for the remaining studies as only three replacement VGOs and three lots of HyVac oil needed to be analyzed via chemical ionization. Furthermore, impurities in Duratex 68 that were at a lower intensity in the chromatogram obtained using electron ionization were more prominent in the chromatograms utilizing chemical ionization. Finally, the high-resolution mass spectra acquired with chemical ionization allowed for more accurate identification of the compounds within Duratex 68 that were found to be the most chemically different from HyVac oil.

This discovery-based method was also used for the comparison of HyVac Oil to Leybonol LVO 100 and VWR 19. In general, it was found that the majority of the chemical differences between Leybonol LVO 100 and HyVac oil were due to Leybonol LVO 100 having a slightly higher molecular weight range. Similarly, VWR 19 had a higher molecular weight range than both Leybonol LVO 100 and HyVac oil, explaining why VWR 19 had a lower Pearson correlation coefficient with HyVac oil. Using this method, it was determined that Leybonol LVO 100 and VWR 19 are considered sufficient replacements, both physically and chemically, for HyVac oil.

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4. CONCLUSION

Through the use of density, carbon range, and HT-GC × GC-HRMS in tandem with chemometrics, a new set of VGOs similar to HyVac oil has been identified. Impurities found within the potential replacement oils utilizing high-resolution mass spectrometry have given great insight into the different additives that companies add to VGOs along with impurities from different sources of crude oil. While these chemical differences and impurities were noted in this study, further analysis into their effects on formulations are ongoing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.4c03906.

Two-dimensional chromatograms, RDBE versus carbon number plots for all VGOs, and high-resolution mass spectra for impurities of Duratex 68 (PDF)

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Notes

The authors declare no competing financial interest.

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