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Research Article

Size-exclusion chromatography for the determination of the boiling point distribution of high-boiling petroleum fractions

The paper describes a new procedure for the determination of boiling point distribution of high-boiling petroleum fractions using size-exclusion chromatography with refractive index detection. Thus far, the determination of boiling range distribution by chromatography has been accomplished using simulated distillation with gas chromatography with flame ionization detection. This study revealed that in spite of substantial differences in the separation mechanism and the detection mode, the size-exclusion chromatography technique yields similar results for the determination of boiling point distribution compared with simulated distillation and novel empty column gas chromatography. The developed procedure using size-exclusion chromatography has a substantial applicability, especially for the determination of exact final boiling point values for high-boiling mixtures, for which a standard high-temperature simulated distillation would have to be used. In this case, the precision of final boiling point determination is low due to the high final temperatures of the gas chromatograph oven and an insufficient thermal stability of both the gas chromatography stationary phase and the sample. Additionally, the use of high-performance liquid chromatography detectors more sensitive than refractive index detection allows a lower detection limit for high-molar-mass aromatic compounds, and thus increases the sensitivity of final boiling point determination.

Keywords: Distillation curves / Fuels / Liquid chromatography / Simulated distillation / Size-exclusion chromatography
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1 Introduction

The boiling point distribution (BPD) is one of the fundamental parameters determined for numerous petroleum products. The boiling range is a characteristic quality parameter of motor fuels. In process streams, knowledge of BPD enables optimization of operations and processes used to obtain fractions with a specific range of boiling points. For some feed-

stock streams in refinery and petrochemical processes there are limits of boiling range. This is associated primarily with the maximum allowed distillation temperature of the feedstock, characteristic of the types of catalyst used. Catalytic hydrocracking is an example of such processes, in which an excessively high final boiling point (FBP) results in the carbonization of the feedstock on the surface of the catalyst and its premature deactivation. This is caused mostly by precursors of coking (asphaltene-like molecules) occurring in the feedstock [1, 2], as well as the precursors formed during hydrocracking as a result of condensation reactions (polycyclic aromatic compounds) [3, 4].

The determination of boiling point distribution is carried out using standardized procedures involving classical atmospheric and vacuum distillation [5–7] or simulated distillation based on GC [8–17]. Standardized distillation apparatus is used in the classical method. The procedure is time consuming and requires a large sample volume. At present, additional limitations of the classical distillation are safety issues resulting from the possibility of ignition of samples and burning the lab technician carrying out the determina-

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Abbreviations: BPD, boiling point distribution; EC-GC, empty column gas chromatography; ELSD, evaporative light scattering detector; FBP, final boiling point; FID, flame ionization detection; GPC, gel permeation chromatography; HT, high temperature; IBP, initial boiling point; RID, refractive index detector; SIMDIS, simulated distillation; VGO, vacuum gas oil

tion and/or the risk associated with vacuum distillation of high-boiling petroleum products. For this reason, the classical procedures have been replaced by simulated distillation (SIMDIS), which makes use of the elution of hydrocarbon components from a column packed with the stationary phase of low polarity in order of increasing boiling point [18]. To determine the dependence of retention time on boiling point, *n*-alkanes are used as standards. Recently, the procedures performing simulated distillation in an empty capillary column with deactivated internal surface but without any stationary phase have been developed. Such separation conditions are called empty column gas chromatography (EC-GC) [19, 20].

The SIMDIS method does not cause serious problems for samples with FBP not exceeding 400°C. Problems arise for samples with higher FBP values—for crude oil and the vacuum distillation residue fractions these values reach 750°C. These types of materials requires high-temperature (HT) SIMDIS. The final separation temperature can reach 450°C, which results in a number of problems, including insufficient stability of the stationary phase and a large increase in the detector signal. Disadvantages of the SIMDIS method have been discussed in a number of papers [21–25]. Some of these problems have been eliminated by EC-GC conditions, in which the elution temperature is considerably lower compared to SIMDIS. In addition to being used in the analytics of petroleum products, SIMDIS has been recently applied to the characterization of volatile fraction released from industrial effluents and bitumens [26, 27]. In some cases, the fumes contain microdrops of low-boiling organic fraction, which requires conditions of HT-SIMDIS or EC-GC.

Correlation of physicochemical properties of compounds with their retention in selected chromatographic systems has been discussed in a large number of papers for both gas and LC. A special role in correlation methods for LC is played by gel permeation chromatography (GPC)/SEC, wherein for selected groups of chemical compounds there is a linear relationship between the elution volume and the logarithm of molar mass or, more specifically the logarithm of hydrodynamic radius of a molecule. This special feature of separation conditions in GPC/SEC is used in applications dealing with the determination of molar mass distribution and average molar mass of various types of polymers [28–30]. There is a number of simple applications making use of LC as well as microflow devices for the determination of physicochemical properties of complex mixtures of low-boiling chemical compounds [31, 32]

For chemical compounds belonging to the same homologous series, there is a strong correlation between the molar mass and the boiling point. In contrast, such a relationship does not exist for chemical compounds with much different structures, such as, for example, benzene (C₆H₆, B.p. 80.1°C, M 78.11 g/mol) and hexafluorobenzene (C₆F₆, B.p. 80.1°C, M 186.05 g/mol) [33]. No unambiguous relationships were found for complex mixtures of chemical compounds with similar physicochemical properties.

For mixtures consisting mostly of hydrocarbons, i.e. petroleum and its individual fractions, it seems possible to

correlate boiling point and molar mass with chromatographic retention by using a series of suitable standards. This paper discusses the attempt to correlate distillation temperature with retention of heavy fractions of crude oil under SEC conditions. Similarly to the SIMDIS and EC-GC method, *n*-alkanes were used as standards.

2 Material and methods

2.1 Materials

Please refer to Appendix A. Supporting Information–Section S.1.1.

2.2 Instrumentation

2.2.1 SEC–RID

SEC was carried out using a Merck-Hitachi L-6200 pump, a Rheodyne Rh-7161 sampling valve with a 20 µL sample loop, a thermostat, and a Merck–Hitachi model 1037A refractive index detector (RID). Data acquisition was performed using a Perkin Elmer Nelson 900 interface and a Perkin Elmer Totalchrom v. 6.3 software.

2.2.2 SIMDIS Investigations carried out in the Lotos Lab (Lotos S.A. Group)

Please refer to Appendix A. Supporting Information–Section S.1.2.1.

2.2.3 EC-GC

Please refer to Appendix A. Supporting Information–Section S.1.2.2 and Refs. [19, 20].

2.3 Methods

2.3.1 Preparation of solutions

For the SIMDIS and EC-GC procedure, 0.1% w/w solutions of the examined materials were prepared in carbon disulfide. Solutions of the investigated samples for the SEC–RID analysis were prepared by dissolving *ca.* 250 mg of sample in 5 mL of tetrahydrofuran (0.05 g/mL). The TLC with flame ionization detection (FID) determinations were performed on solutions containing 50 mg of the sample in 5 mL of dichloromethane.

2.3.2 Chromatographic conditions

2.3.2.1 SEC–RID

Separation in the SEC–RID procedure was carried out using two columns connected in series –Phenogel 5u 50 Å

and Phenogel 5u 100 Å having dimensions 300 × 7.8 mm (Phenomenex) with tetrahydrofuran as the eluent at a constant flow rate of 1.0 mL/min. Sample volume: 50 µL was introduced into the injection port, which constituted 2.5-fold volume of the sample loop. Separation temperature was 30.0 ± 0.1°C. The dead time determined from the acetone peak was 24.1 min.

2.3.2.2 Simulated distillation

Please refer to Appendix A. Supporting Information–Section S.1.3.1.

2.3.2.3 EC-GC

Please refer to Appendix A. Supporting Information–Section S.1.3.2.

2.3.3 Determination of boiling point distribution

In both cases, i.e. for SIMDIS–EC-GC and SEC–RID, the algorithm for the determination of boiling point distribution was identical to the procedure described in ASTM D2887 standard [11]. Before the analysis of petroleum products, a blank chromatogram was obtained for pure sample solvent. Next, chromatographic analysis of the investigated materials was carried out. Chromatograms of individual samples were corrected by subtracting the chromatogram for the blank. Based on the corrected chromatogram, the entire peak was sliced into sections corresponding to 5% of the total peak area. The boiling point range distribution is then plotted against temperature from the initial boiling point (IBP; 0.5%) to the FBP (99.5%).

2.3.4 Quality assurance/QC

Retention times of *n*-paraffin standards were calculated as the average values from three successive chromatograms of separation of standard mixtures. It was assumed that the difference between a retention time and the average value must be less than 3 s.

Three determinations were carried out for each of the petroleum products investigated. The calculated points of the boiling point distribution curve were averaged.

3 Results and discussion

The use of SEC for the determination of distillation characteristics of petroleum products is more difficult than the use of GC. In the case of using GC, the key requirement is to provide the same retention characteristics for compounds with various polarities relative to *n*-alkanes. Using a stationary phase of low polarity (polydimethylsiloxane) should ensure elution of mixture components according to their boiling point. However, the SIMDIS investigations carried out thus far reveal significant deviations of the determined boiling point relative to the expected value [11, 19, 20]. It was demonstrated that

by using the EC-GC conditions the distillation temperature determined by the chromatographic method was in agreement with the true value [20]. The dependence of retention time on boiling point is used for calibration of the SIMDIS procedure. The use of the FID, universal for hydrocarbons, allows calculation of percentage of individual fractions directly from the chromatogram. In SEC, separation conditions should ensure elimination of sorptive interactions, and the observed elution order should depend on the hydrodynamic radius of a molecule. For compounds with a similar spatial structure, the dependence of the common logarithm of molar mass on retention volume is almost linear. Mixtures of compounds of petroleum origin, especially mixtures of high-boiling compounds, contain a wide variety of chemicals belonging to several classes: saturated hydrocarbons (paraffins and naphthenes), olefins and aromatic compounds as well as resins and asphaltenes. A combination of aliphatic, alicyclic, and aromatic moieties results in a complex mixture with the resultant physicochemical properties. Universal and linear response is an important problem in SEC analyses. In SEC, the detector best meeting SIMDIS requirements is the differential RID. The measurement of the refractive index of the eluate relative to the eluent ensures universal detection, although for chemical compounds having much different refractive index values the detector response for the same concentration will be different. Refractive index values for selected hydrocarbons are listed in Supporting Information Table S1. Getting a chromatogram in which only positive peaks are observed thus depends on the eluent used. In case of comparing the “critical” RI value of *n*-alkanes relative to the eluent, the initial boiling point of a sample that can be analyzed under specific SEC–RID conditions can be estimated. For example, using tetrahydrofuran (THF; RI = 1.407) as the eluent should enable the determination of boiling point distribution for samples with a boiling point above 151°C (RI value of *n*-nonane = 1.405), while with dichloromethane (DCM; RI = 1.424) as the eluent the initial boiling point of samples must be greater than 234°C (*n*-tridecane, RI = 1.425). Consequently, THF was used as the mobile phase in this work, because it allows the analysis of samples of petroleum products with a wider range of boiling points. As a result of the above limitations, further investigations should include the use of evaporative light scattering detector (ELSD) and a CORONA detector. In both cases, optimization should include the problem of “universal” response for groups of compounds present in high-boiling petroleum fractions. The manufacturer of the CORONA detector claims independence of detector response on the structure of chemical compounds. In the case of using ELSD detector for SIMDIS under SEC conditions, it is important to examine the “recovery” for the most volatile sample components—a low response is expected for hydrocarbons below C13 due to partial evaporation of the analytes in the detector—this phenomenon can be minimized by a proper selection of nebulization conditions and the drift tube [34, 35]. However, a comparison of RID versus ELSD for lipids revealed that in this case RID had a much more universal response than ELSD [36].

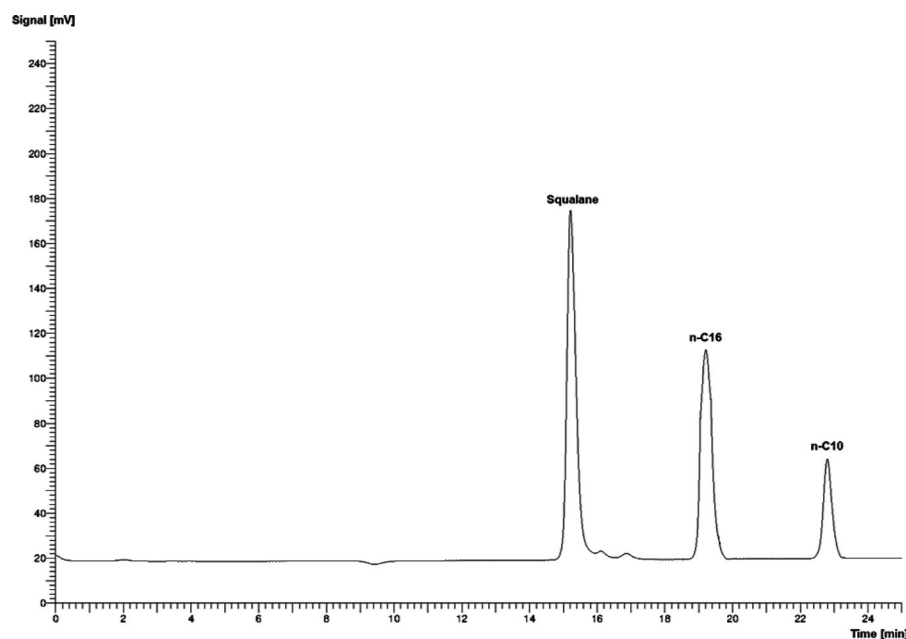


Figure 1. SEC-RID chromatogram of squalane (Sq), *n*-C16 and *n*-C10 separation.

3.1 Determination of boiling point distribution using SEC-RID

In SIMDIS and EC-GC procedure, successive fractions of the distillate were added together from the initial retention time to the final retention time—according to the principle of elution of sample components in order of increasing boiling points. In SEC-RID, the addition of peak segments was carried out in reverse order, i.e. from the final retention time to initial retention time.

Calibration of the SEC-RID procedure was carried out by analyzing a mixture of *n*-alkane standards in *n*C₅–*n*C₆₀ range. Due to incomplete separation of the mixture of standards, additional standards (squalane, hexadecane, and *n*-decane) were also used. The set of columns used in SEC-RID ensures effective separation of relatively low-molar-mass (for SEC) compounds. When using SIMDIS, it is not necessary to accomplish complete separation of all sample components. Similarly, it is unnecessary to separate all *n*-alkanes standards in the sample boiling point range. It is required, however, that the calibration includes standards containing IBP and FBP values of the examined materials. SEC-RID chromatograms of mixtures of standards are shown in Fig. 1 and Supporting Information Fig. S1 while an SEC-RID calibration curve is depicted in Fig. 2. The obtained results reveal that the retention times of *n*-alkanes can be correlated with their boiling points under conditions of SEC.

An important advantage of the SEC-RID procedure for the determination of boiling point distribution compared to the “classical” SIMDIS procedure is that in the former method the highest boiling components are eluted from the column first. When using GC, the most serious problems are encountered for high-boiling mixtures of petroleum origin, since to ensure complete elution of all sample components very high oven temperatures, reaching 450°C, have to be used.

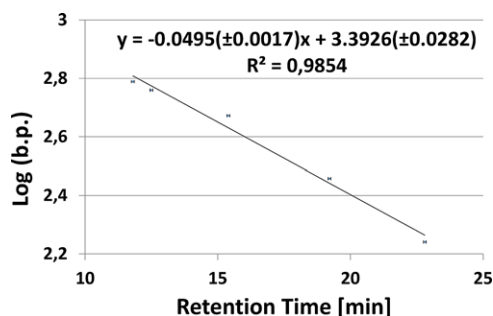


Figure 2. Calibration curve for SEC-RID procedure.

The increase in baseline associated with it and resulting from the bleed of stationary phase lowers detection sensitivity for the heaviest sample components. The use of sample solvent and the eluent from the same manufacturer and, preferably, from the same batch is essential in SEC-RID. The occurrence of differences in composition can cause the presence of extra chromatographic peaks, i.e. a negative water peak, in the dead time value if the water content in the eluent and the sample is different. In addition, before the determination of boiling point distribution sample chromatograms should be corrected by subtracting a blank chromatogram recorded for the analysis of pure solvent.

Boiling point distributions determined by SIMDIS, EC-GC, and SEC and the differences between the procedures are compiled in Tables 1 and 2 for the vacuum gas oil (VGO) and for fractions A–D and the hydrocracking feedstock R1 and R2, respectively. An overlay of SEC-RID chromatograms for four of the examined materials, VGO, Fractions B and D and feedstock R1, is depicted in Supporting Information Fig. S2.

The differences between boiling point distributions for SEC-RID relative to EC-GC and SIMDIS can result primarily from two phenomena: a lack of correlation between

Table 1. Comparison of boiling point distribution determined by SIMDIS, EC-GC and SEC for the light vacuum gas oil and fractions from vacuum distillation

% mass	VGO	FRA						FRB						FRC						FRD					
		Temp. [°C]			Difference (Δ°C)			Temp. [°C]			Difference (Δ°C)			Temp. [°C]			Difference (Δ°C)			Temp. [°C]			Difference (Δ°C)		
		SIMDIS	EC-GC	SEC	SIMDIS vs SEC	ECGC vs SEC		SIMDIS	EC-GC	SEC	SIMDIS vs SEC	ECGC vs SEC		SIMDIS	EC-GC	SEC	SIMDIS vs SEC	ECGC vs SEC		SIMDIS	EC-GC	SEC	SIMDIS vs SEC	ECGC vs SEC	
IBP	198.5	195.0	193.5	5.0	1.5			316.0	311.5	309.0	7.0	2.5		323.0	325.5	323.0	6.5	2.5		374.5	369.5	367.5	7.0	2.0	
5	262.5	260.0	258.0	4.5	2.0			342.5	338.0	335.0	7.5	3.0		353.0	357	353.0	10.5	4.0		417.0	411.5	409.5	7.5	2.0	
10	285.5	282.5	281.0	4.5	1.5			352.5	348.5	344.0	8.5	4.5		363.5	368.5	363.5	11.5	5.0		430.0	424.5	422.5	7.5	2.0	
15	298.0	292.5	291.0	8.0	1.5			359.5	353.0	351.0	8.5	2.0		374.5	376	374.5	8.0	1.5		438.0	432	429.5	8.5	2.5	
20	309.0	304.0	303.0	6.0	1.0			365.0	361.5	358.0	7.0	3.5		381.0	383	381.0	7.0	2.0		444.0	439.5	436.5	7.5	3.0	
25	317.0	311.5	309.0	8.0	2.5			370.0	366.0	363.5	6.5	2.5		384.0	387.5	384.0	9.0	3.5		449.0	443.5	441.0	8.0	2.5	
30	324.5	319.0	316.0	8.5	3.0			374.0	370.0	368.0	6.0	2.0		393	393	393.0	8.0	4.0		453.5	448	444.0	9.5	4.0	
35	331.5	324.5	322.0	9.5	2.5			378.0	375.0	372.5	5.5	2.5		396.5	396.5	396.5	8.0	4.0		458.0	452.5	449.0	9.0	3.5	
40	337.0	332.0	329.0	8.0	3.0			381.5	379.0	376.0	5.5	3.0		397.0	400.5	397.0	7.0	3.5		462.0	456	452.5	9.5	3.5	
45	343.0	337.5	332.0	11.0	5.5			384.5	382.0	377.0	7.5	5.0		400.5	404	400.5	7.0	3.5		465.5	460	456.0	9.5	4.0	
50	348.0	343.0	338.0	10.0	5.0			388.0	385.0	380.0	8.0	5.0		404.5	407	404.5	6.0	2.5		469.5	463.5	461.5	8.0	2.0	
55	352.5	348.0	343.0	9.5	5.0			391.0	387.0	382.0	9.0	5.0		407.5	410	407.5	6.0	2.5		473.0	467.5	464.0	9.0	3.5	
60	357.0	351.5	347.0	10.0	4.5			394.0	391.5	388.0	6.0	3.5		409.0	412	409.0	7.0	3.0		477.0	471	467.0	10.0	4.0	
65	361.5	356.0	351.0	10.5	5.0			397.0	394.0	390.5	6.5	3.5		411.0	415	411.0	8.0	4.0		481.0	475.5	469.0	12.0	6.5	
70	365.5	360.5	357.5	8.0	3.0			400.5	395.5	391.5	9.0	4.0		410.5	417	410.5	11.5	6.5		485.0	480.5	476.0	9.0	4.5	
75	370.5	366.0	365.5	5.0	0.5			403.5	396.5	392.0	11.5	4.5		412.5	419	412.5	12.5	6.5		489.5	484.5	481.5	8.0	3.0	
80	374.5	370.5	370.0	4.5	0.5			407.0	399.5	395.5	11.5	4.0		416.0	422	416.0	12.0	6.0		494.5	491	488.0	6.5	3.0	
85	380.0	375.0	372.5	7.5	2.5			411.5	403.5	399.0	12.5	4.5		421.0	425.5	421.0	10.0	4.5		500.0	495.5	492.5	7.5	3.0	
90	385.5	381.5	379.0	6.5	2.5			416.0	410.0	408.0	8.0	2.0		425.5	430	425.5	9.0	4.5		506.0	502	498.5	7.5	3.5	
95	393.0	389.5	386.5	6.5	3.0			423.0	419.0	417.0	6.0	2.0		430.5	434.5	430.5	9.0	4.0		515.0	510	506.5	8.5	3.5	
FBP	411.5	409.0	408.0	3.5	1.0			437.5	435.5	431.5	6.0	4.0		445.5	449.5	445.5	7.5	4.0		534.0	531	527.5	6.5	3.5	

Table 2. Comparison of boiling point distribution determined by SIMDIS, EC-GC and SEC for the hydrocracking feedstocks

% mass	R1					R2				
	Temp. [°C]			Difference ($\Delta^\circ\text{C}$)		Temp. [°C]			Difference ($\Delta^\circ\text{C}$)	
	SIMDIS	EC-GC	SEC	SIMDIS vs SEC	EC-GC vs SEC	SIMDIS	EC-GC	SEC	SIMDIS vs SEC	ECGC vs SEC
IBP	246.5	240.0	236.0	10.5	4.0	266.0	261.0	258.0	8.0	3.0
5	317.5	312.0	308.0	9.5	4.0	336.0	331.0	327.0	9.0	4.0
10	342.0	336.0	331.0	11.0	5.0	355.0	346.5	343.0	12.0	3.5
15	357.5	353.0	351.0	6.5	2.0	365.5	359.0	355.0	10.5	4.0
20	368.0	364.0	361.0	7.0	3.0	372.5	367.0	362.0	10.5	5.0
25	377.0	372.5	369.5	7.5	3.0	378.5	368.5	364.0	14.5	4.5
30	384.5	380.0	377.0	7.5	3.0	384.0	374.5	370.5	13.5	4.0
35	391.5	388.0	385.0	6.5	3.0	388.5	378.0	374.5	14.0	3.5
40	398.0	393.0	389.5	8.5	3.5	393.0	381.5	377.0	16.0	4.5
45	404.0	400.0	397.0	7.0	3.0	397.5	387.5	383.0	14.5	4.5
50	410.0	404.5	401.0	9.0	3.5	401.5	392.0	387.0	14.5	5.0
55	416.0	411.0	408.0	8.0	3.0	406.5	399.5	395.0	11.5	4.5
60	422.0	416.5	412.5	9.5	4.0	411.0	403.0	398.5	12.5	4.5
65	428.0	423.0	418.0	10.0	5.0	416.5	411.0	406.0	10.5	5.0
70	434.5	429.5	425.0	9.5	4.5	422.5	414.5	410.0	12.5	4.5
75	442.0	436.5	433.0	9.0	3.5	429.0	421.0	416.5	12.5	4.5
80	452.0	446.5	442.0	10.0	4.5	437.5	430.0	426.0	11.5	4.0
85	467.0	459.0	454.5	12.5	4.5	449.5	440.5	437.5	12.0	3.0
90	487.0	480.5	475.0	12.0	5.5	466.5	461.5	458.0	8.5	3.5
95	513.0	506.5	502.5	10.5	4.0	491.0	487.0	483.5	7.5	3.5
FBP	567.0	558.5	553.5	13.5	5.0	537.5	531.5	527.0	10.5	4.5

elution and boiling point of individual groups of compounds compared to *n*-alkanes and the nonlinearity of the RID detector. Inspection of the experimental data reveals that despite substantial differences in the separation mechanism and detection method, SIMDIS, EC-GC, and SEC–RID can provide similar boiling point distributions for fractions from vacuum distillation of crude oil. The differences in IBP and FBP values for vacuum distillates were within 5.0–7.0 and 3.5–9.0°C, respectively, when comparing SEC–RID and SIMDIS. Analogous comparison of the SEC–RID and EC-GC procedures revealed the difference between IBP and FBP of 1.5–3.0 and 1.0–4.5°C, respectively. The smallest differences were observed for the distillate with the lowest IBP and FBP values while the largest differences were found for the heaviest of the analyzed fractions, fraction D. For hydrocracking feedstocks R1 and R2 the differences in IBP and FBP values were larger: 8.0–10.5 and 9.0–13.5°C for SEC–RID versus SIMDIS, respectively, and 3.0–4.0 and 4.5–5.0°C for SEC–RID versus EC-GC, respectively. The differences for the remaining points of the distribution ranged from 4.5 to 12.5°C for vacuum distillates and from 6.5 to 16.0°C for hydrocracking feedstocks for comparison of SEC–RID versus SIMDIS. Comparison of the results for SEC–RID and EC-GC revealed differences of 0.5–6.5°C for vacuum distillates and 2.0–5.5°C for hydrocracking feedstocks. An overlay of distillation curves is depicted in Fig. 3 and Supporting Information Fig. S3.

It was demonstrated in a previous work [20] that EC-GC provided a better agreement of distillation temperatures with the true values than SIMDIS for number of chemical compounds with varying polarities. Consequently, the results of the newly developed SEC–RID procedure should be compared with those determined by EC-GC. On this basis it can be concluded that for the examined high-boiling petroleum products the results of distillation temperature distribution are in a good agreement with the expected value. The fact that SIMDIS, EC-GC and SEC–RID yielded consistent results demonstrates wide applicability of the new SEC procedure not only for analytical but also for preparative purposes. Preparative work is much simpler with LC than with GC. The possibility of collection of fractions with a specific range of boiling points of crude oil as well as distillates or other feedstocks is an undisputed advantage of the developed procedure. The developed procedure supplements of the existing LC x GC methodologies used for a detailed characteristic of petroleum products and determination of selected components [37, 38].

4 Concluding remarks

The paper describes a novel application of SEC for the determination of the boiling point distribution of high-boiling petroleum products. The use of an analogous approach as in classical SIMDIS, involving the determination of dependence

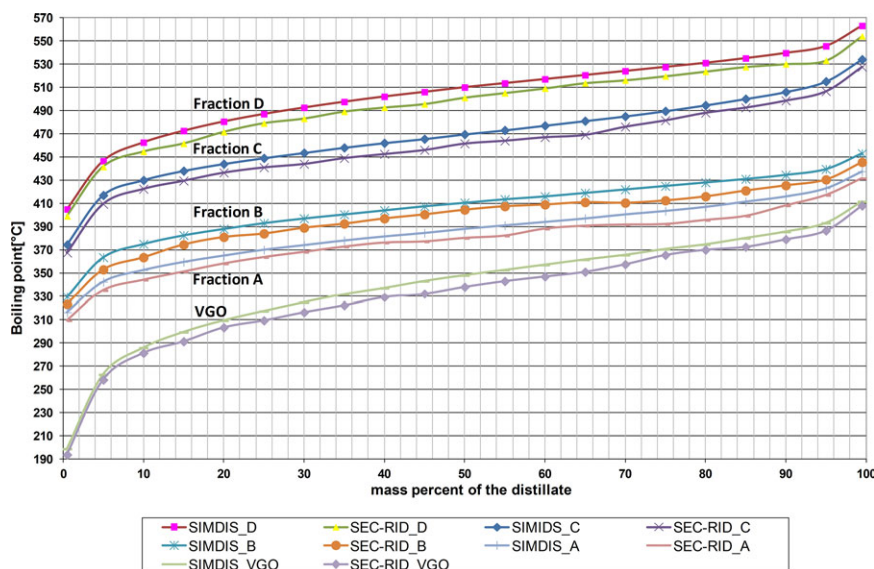


Figure 3. Overlay of distillation curves for fractions from vacuum distillation for SIMDIS/GC-FID and SEC-RID.

between retention time and boiling point relative to *n*-alkanes and the application of a universal detector, allows obtaining similar results of determinations. Despite a greater number of phenomena affecting retention time and RID signal under SEC conditions compared to GC-FID, it was possible to determine distillation characteristics of complex mixtures of hydrocarbons using SEC.

The applicability of the developed SEC-RID procedure is limited due to the simplicity and availability of GC equipment, which can be used for SIMDIS. The main application of the SEC-RID procedure would be for the determination of FBP value for high-boiling mixtures, for which HT-SIMDIS would otherwise be used. Very high final oven temperatures lower sensitivity of FBP determination by the HT-SIMDIS procedure and can compromise thermal stability of samples. Moreover, if the material analyzed by SIMDIS contains non-volatile components, the determination has to be carried out by the internal standard method due to incomplete elution of sample components under HT-SIMDIS conditions. In the SEC procedure, the heaviest sample components are eluted first. Among numerous applications of SIMDIS, an important one is control of boiling point range of feedstocks for catalytic processes. In particular, the FBP value of the feedstock is limited to ensure safety of a catalyst. An example of such a process is hydrocracking in which the presence of high-boiling compounds with the b.p. above the maximum allowed value results in coking of the feedstock on the catalyst surface analytical a premature decrease in its activity. Application of SEC to control FBP is also convenient due to the possibility of using alternative to RID detection methods by connecting LC detectors in series. The addition of a UV or a UV-DAD detector allows a significant improvement in sensitivity for UV-absorbing compounds, which in case of petroleum products are mostly aromatic compounds. Polycyclic aromatic compounds are known to cause problems due to coking of the feedstock on the surface of a catalyst. The

use of the UV-DAD detector allows acquisition of UV spectra, which can then be used for additional characterization of chemical compounds causing the increase in FBP of a feedstock [39]. The fluorometric detector, which enables selective detection of selected groups of chemical compounds with a very high sensitivity, is another possibility. These options will be discussed in future papers. The developed procedure is advantageous in case of scaling up the separation process for preparative purposes. The possibility of collection of fractions having a particular range of boiling points enables more sophisticated sample characterization by advanced techniques, such as NMR spectroscopy or MS.

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