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INVESTIGATION ON FEASIBILITY TO SIMULATE CRUDE OIL TRUE BOILING POINT DISTILLATION BY APPLICATION OF ASTM D-7169 SIMULATED DISTILLATION AND COMBINATION OF ASTM D-86 AND ASTM D-1160 PHYSICAL DISTILLATION METHODS

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Abstract

13 different crude oils around the world pertaining to the low and high gravity, low and high sulphur grades were distilled by the use of four methods: TBP – a combination from ASTM D-2982 and ASTM D-5236, high temperature simulated distillation (HTSD, ASTM D-7169), a combination from ASTM D-86 and ASTM D-1160, and a calculated TBP by the use of procedures described in references [1] and [4] and a combination from ASTM D-86 and ASTM D-1160 methods. It was found that the HTSD (ASTM D-7169) best simulated the crude oil TBP. During crude oil distillation by a combination of ASTM D-2892 (TBP) and ASTM D-5236 a gap in the fraction following the cut point between ASTM D-2892 and ASTM D-5236 appears. This gap does not reflect the true distillation curve and can be overcome by application of Riazi's boiling point distribution model to both ASTM D-2892 and ASTM D-5236 crude oil distillation data. Riazi's boiling point distribution model is not capable of providing a reliable rating of the true VGO and VR yields only on the basis of crude oil distillation data boiling up to 360^0C according to the ASTM D-2892 method. Further investigations with more data are needed to improve the accuracy of prediction of the crude oil TBP from the surrogate faster distillation methods, especially in the diesel area.

Keywords: crude oil; TBP; HTSD; ASTM D86; ASTM D1160; ASTM D5236; physical distillation; simulated distillation.

1. Introduction

Quality of crude oil processed in a refinery crude distillation unit (CDU) and the crude oil cost are among the most important determinants for the profitability of an oil company. The quality and value of a crude oil depends on its TBP curve that is the content of light fractions (boiling up to 360°C), 360 – 540°C (vacuum gas oil) fraction, and the bottom of the crude oil barrel (540°C+; vacuum residue), and the level of impurities like sulphur, nitrogen, metals, etc. The light oil fractions are generally used for production of transportation fuels. The vacuum gas oil (360 – 540°C) fraction can be used as a feedstock for catalytic cracking or hydrocracking units which produce motor fuels, or for production of base lubricating oils. The crude oil bottom (black-oil fraction) is generally used for production of fuel oil. Depending on the quality of the crude oil bottom fraction (Conradson carbon, metals, asphalthenes, *etc.*) it could be converted in high value transportation fuels by thermal conversion or hydrocracking processes. Unfortunately, the TBP analyses are costly and time consuming, and a TBP analysis typically requires about three working days to accomplish it. That is why it is impractical to use it as a tool for daily monitoring of the crude distillation unit operation. For refineries, which often switch the crude oils, the lack of information about the crude oil quality could negatively impact the optimum operation and in this way the profitability of the crude distillation unit.

Considering the importance of the crude oil TBP analysis and reduction of the time to deliver the crude oil TBP analysis data to the process engineers in the refinery, the chief process engineer department in LUKOIL Neftohim Burgas (LNB) has been working for several years to find a quick and reliable surrogate of the crude oil TBP analysis [1-2]. Simulated distillation of light fractions according to ASTM D-2887 was found to be the best surrogate of TBP of oil fractions boiling between 55 and 360°C [3]. This finding encourages the LNB Research laboratory to acquire a gas-chromatographic simulated distillation equipment that was supposed to simulate the crude oil TBP by employing the ASTM D-7169 method. Another possibility to simulate crude oil TBP was to combine the physical distillation methods ASTM D-86 that distills the crude oil fractions boiling at atmospheric pressure up to 300°C and the atmospheric residue, boiling above 300°C to be analyzed for its distillation characteristics under vacuum according to the ASTM D-1160 method. Moreover, there were methods already established to convert crude oil ASTM D-86 into TBP for the atmospheric part of the crude oil distillation and ASTM D-1160 into ASTM D-5236 for the vacuum part of the distillation of the crude oil atmospheric residue [1, 4].

The aim of this study is to investigate how accurate are both methods ASTM D-7169 simulated distillation and the combination of ASTM D-86 and ASTM D-1160 distillation methods in their approximation of TBP distillation of 13 crude oils pertaining to the four main groups of crude oils: around the world (I group – light, low sulfur one (30 - 40^0 API; S ≤ 0.5 % mass); II group – light, sulfur one (30-40^{0}API; S= 0, 5 -1.5 % mass); III group – heavy, high sulfur one (15-30^{0}API; S=1.5 ÷ 3.1% mass); IV group –extra-heavy, high sulfur one (15^{0}API, S ≥3 % mass).

2. Experimental

Density and sulphur content of the investigated 13 crude oils are given in Table 1.

Table 1 Density and sulphur content of the investigated crude oils in this work

Crude oil	CPC Blend 11.2011	El Bouri 05.2015	Rhas Gharib	Kirkuk 04.2015	Kumkol 04.2013	Oryx,04.2 015	Oryx 04.15 + Cheleken 1:2
d_4^{20}	0.8015	0.8878	0.9222	0.8498	0.8173	0.9122	0.8588
Sulfur content, %	0.63	1.72	3.44	2.24	0.22	4.21	1.77
Crude oil	REBCO 03.2015	REBCO 04.2015	Caspian + REBCO 03.2015	Kazakh + REBCO 03.2015	Caspian 03.2015	Kazakh 03.2015	
d_4^{20}	0.8636	0.8647	0.9031	0.8693	0.9269	0.8738	
Sulfur content, %	1.28	1.24	1.57	0,84	1.86	0.41	

2.1. Crude oil physical distillation according to True Boiling Point (TBP) - ASTM D-2892 and vacuum distillation according to ASTM D-5236 of the atmospheric residue left from the TBP analysis

The crude oils under study were analyzed for their TBP distillation characteristics in TBP Euro Dist System from ROFA Deutschland GmbH. The apparatus performs fractionation according to ASTM D-2892 using a column of 15 theoretical plates with a reflux ratio of 5:1 and pressure drop from 760 to 2 mm Hg. Having finished the crude oil TBP analysis up to

360^{0}C, the atmospheric residue, boiling above 360^{o}C, was transferred from the TBP Euro Dist System in the Potstill Euro Dist System and was distilled under vacuum from 1 to 0.2 mm Hg according to ASTM D-5236 requirements. The combined TBP (ASTM D-2892) and ASTM D-5236 distillation characteristics of the investigated crude oils are summarized in Table 2.

Table 2 TBP distillation (ASTM D-2892 and ASTM D-5236) data

Crude oils	CPC Blend 11.2011	El Bouri 05.2015	Rhas Gharib	Kirkuk 04.2015	Kumkol 04.2013	Oryx,04.2015	Oryx 04.15 + Cheleken 1:2	REBCO 03.2015	REBCO 04.2015	Caspian + REBCO 03.2015	Kazakh + REBCO 03.2015	Caspian 03.2015	Kazakh 03.2015
Distillation boiling point, ^{0}C	Evaporate from atmospheric part (ASTM D-2892), cumulative wt.%												
70	9.9	3.0	2.7	6.2	5.3	2.2	4.1	3.9	3.9	4.2	3.8	4.4	3.8
110	19.3	6.4	5.0	12.5	12.0	5.6	9.2	8.3	8.3	6.3	7.5	4.4	6.7
130	24.8	8.5	6.5	16.0	16.2	8.1	12.3	10.7	11.1	7.6	9.6	4.7	8.4
150	30.4	11.1	8.4	19.7	19.6	10.5	15.6	13.4	13.5	8.9	11.9	4.7	10.5
170	35.4	13.8	10.5	23.5	23.1	13.1	19.1	16.2	16.3	10.5	14.3	4.9	12.3
180	38.3	15.3	11.5	25.4	24.9	14.4	21.0	17.7	17.8	12.2	15.5	6.9	13.3
200	40.7	17.9	13.6	29.0	28.2	16.9	24.1	20.6	20.6	14.4	18.2	8.4	15.9
220	45.3	20.4	16.1	32.2	31.5	19.4	27.4	23.4	24.0	16.4	20.5	9.6	17.6
240	49.9	23.5	18.7	35.6	35.1	21.9	31.1	26.9	27.4	19.4	24.0	12.2	21.2
260	53.3	26.6	20.8	39.1	39.0	24.5	34.8	30.4	30.9	22.9	27.9	15.6	25.3
280	56.8	29.8	23.6	42.7	42.9	27.5	38.4	34.1	34.3	26.3	31.4	18.8	28.8
300	61.1	32.9	26.2	46.1	46.9	30.1	42.1	37.8	37.9	29.8	35.1	22.1	32.5
320	65.2	36.1	28.4	49.7	50.4	33.1	45.6	40.9	41.3	33.3	39.0	26.0	37.1
340	68.5	39.1	30.7	52.3	53.9	35.6	48.9	44.1	44.8	36.4	42.9	28.8	41.6
360	71.7	42.3	33.1	55.3	57.8	38.1	52.1	47.3	48.1	39.6	46.8	32.0	46.3
	Evaporate from vacuum part (ASTM D-5236), cumulative wt.%												
380	71.7	42.8	33.7	55.4	58.8	38.2	52.4	47.7	48.7	40.0	47.1	32.5	46.4
390	74.0	44.4	35.2	56.1	60.7	40.6	54.2	49.4	50.6	41.7	48.7	34.3	48.0
430	82.1	53.6	41.6	62.4	71.5	47.4	62.3	59.1	59.9	49.7	55.9	40.5	52.7
470	86.1	61.1	48.2	68.8	77.2	53.1	68.3	65.7	66.8	57.8	67.0	50.1	68.3
490	88.3	65.7	52.4	71.7	80.7	56.2	72.0	69.7	70.0	61.6	70.9	53.7	72.1
540	92.0	73.3	59.8	76.5	86.4	62.6	77.4	76.3	76.8	69.4	77.3	62.6	78.4
550	93.0	74.6	61.4	77.4	87.4	63.8	78.5	77.6	78.0	71.4	78.7	65.4	79.8
550+	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Wide fractions	Yields, wt.%												
IBP- 110°C	16.6	5.38	3.98	11.5	11	5.55	8.24	7.27	7.26	5.27	6.47	3.7	5.67
110-180°C	18.9	8.88	6.48	13	12.9	8.85	11.7	9.47	9.58	5.95	8.07	2.47	6.67
180-240°C	11.7	8.23	7.27	10.1	10.2	7.51	10.1	9.12	9.56	7.21	8.47	5.3	7.82
240-360°C	21.7	18.8	14.41	19.8	22.7	16.2	21.0	20.5	20.7	20.2	22.8	19.8	25.1
IBP-360°C	68.9	41.3	32.14	54.3	56.8	38.1	51.1	46.3	47.1	38.6	45.8	31.3	45.3
360-540°C	20.4	31	26.65	21.1	28.6	24.5	25.3	29	28.8	29.8	30.6	30.6	32.1
> 540°C	8.0	26.7	40.21	23.5	13.6	37.4	22.6	23.7	23.2	30.7	22.7	37.6	21.6

2.2. Crude oil high temperature simulation distillation

The 13 investigated crude oils were analyzed for their distillation characteristics according to the gas-chromatographic high temperature simulation distillation method ASTM D-7169. Carbon disulfide (99.99%) was used as a solvent. The analyses were carried out with the Agilent Technologies GC System 7890B, which was equipped with FID (flame ionization detector). Liquid nitrogen was used as a coolant. The carrier gas was helium with 99.99% purity (14 mL/min), the inlet pressure was 1.2 psi with the total flow equal to 87 mL/min. Hydrogen was used as a fuel gas (40 mL/min) and nitrogen was a makeup flow (15 mL/min). The installed column was 5 m long, 530 μm in diameter and the film thickness was 0.15 μm. The oven operated under the program from -20°C to 430°C, at a ramp rate of 15°C/min and a 4 min hold time at the maximum temperature. Injected sample volume was 4 μl.

Before the simulation distillation analysis of the studied crude oils, all crude oil samples were stirred preliminary, accurately weighted (0.02 g), dissolved in 1.5 ml CS_2 and mixed by shaking. All prepared samples were stored at a temperature around 4°C prior to analyses.

The simulation distillation characteristics were automatically calculated by the SIMDIS software and the distillation curve boiling point in °C versus evaporate in wt.% was obtained. Minor intervention of the operator took place during the chromatograms processing. The HTSD GC was calibrated with a blend of normal paraffins having carbon number between C_5 and C_{120}. The software (GC OpenLab CDS with Simdis program for ASTM D-7169) used in this application of HTSD allows estimating final boiling point of the residual oils higher than 750°C. Simulated distillation results in accordance with ASTM D-7169 obtained for the crude oils under study are presented in Table 3.

2.3. Crude oil physical distillation according to ASTM D-86 and ASTM D-1160

The 13 crude oils were also analyzed for their distillation characteristics according to ASTM D-86 at atmospheric pressure up to 300°C and the residual oil boiling above 300°C was analyzed for the distillation characteristics at reduced pressure according to ASTM D-1160 requirements. The crude oil samples were distilled up to the temperature of 300°C. The residues, collected from the ASTM D-86 distillation, were transferred from the ASTM D-86 apparatus to Euro Dist MPS (ROFA) operating under the ASTM D-1160 requirements. The pressure in the Euro Dist MPS (ROFA) apparatus during the whole analysis was 0.5 mm Hg. To achieve similar distillation intervals convenient for comparison between TBP and D-86 and D-1160 Riazi's distribution model was applied to approximate the full distillation curve as described in [1]. The results from the combined ASTM D-86 and ASTM D-1160 crude distillations are presented in Table 4.

2.4. Crude oil physical distillations according to ASTM D-86 and ASTM D-1160 and their conversions in ASTM D-2892 and ASTM D-5236

The 13 studied crude oils were distilled up to 300°C at atmospheric pressure according to ASTM D-86 and the ASTM D-86 distillation was converted in ASTM D-2892 according to the procedure described in [1]. The vacuum distillation of the residual fraction boiling above 300°C performed according to ASTM D-1160 was converted in ASTM D-5236 according to the procedure described in [4] (LNB method). The results of application of the procedure described above for the 13 studied crude oils are summarized in Table 5.

Riazi [5] developed a simple and versatile distribution model for various properties of a hydrocarbon plus fraction in the following form:

$$\frac{Pi - Po}{Po} = \left[\frac{A}{B} Ln\left(\frac{1}{1-xi}\right)\right]^{\frac{1}{B}} \qquad (1)$$

where: *Pi* is property of the hydrocarbon fraction such as absolute boiling point (Tb), and molecular weight (Mw); *xi* is the cumulative weight, mole, or volume fraction; *Po* is property of the hydrocarbon fraction at *x*i = 0.

Riazi's distribution model was applied to all distillation data generated in this work and the parameters A_T, B_T, and T_0 for the four studied distillation methods are summarized in Table 6. Table 6 also contains data of squared correlation coefficient (R^2) of Riazi's distribution model and the average absolute deviation (AAD) from the measured percent of evaporates at certain boiling points. These parameters serve as criteria of the precision of the experimental boiling point distribution approximation by Riazi's distribution model.

Table 3 High temperature simulated distillation (ASTM D-7169) data

Crude oils	CPC Blend 11.2011	El Bouri 05.2015	Rhas Gharib	Kirkuk 04.2015	Kumkol 04.2013	Oryx,04.2015	Oryx 04.15 + Cheleken 1:2	REBCO 03.2015	REBCO 04.2015	Caspian + REBCO 03.2015	Kazakh + REBCO 03.2015	Caspian 03.2015	Kazakh 03.2015
Distillation boiling point, ^{0}C	Evaporate, cumulative wt.%												
70	0.4	1.7	1.6	1.9	2.3	2.2	1.2	2.1	1.8	0.1	1.8	0.0	2.0
110	5.3	4.1	3.3	6.6	6.0	4.7	4.9	4.8	4.8	1.2	4.1	0.0	3.9
130	8.9	5.7	4.4	9.7	8.5	6.4	7.4	6.6	6.9	2.3	5.6	0.0	5.2
150	13.2	7.7	5.8	13.1	11.4	8.3	10.4	8.8	9.2	3.7	7.5	0.3	6.7
170	17.9	9.9	7.3	16.7	14.6	10.4	13.6	11.2	11.9	5.6	9.6	1.2	8.6
180	20.4	11.2	8.2	18.6	16.4	11.5	15.4	12.5	13.4	6.6	10.8	1.8	9.6
200	25.5	13.8	10.1	22.6	20.0	14.0	19.0	15.4	16.5	9.0	13.4	3.4	11.9
220	30.8	16.8	12.2	26.6	23.9	16.7	22.8	18.5	19.8	11.7	16.3	5.6	14.5
240	36.1	20.0	14.5	30.7	28.1	19.5	26.7	21.9	23.4	14.7	19.5	8.1	17.4
260	41.4	23.4	17.0	34.8	32.3	22.5	30.7	25.4	27.1	18.0	22.9	11.1	20.6
280	46.5	27.0	19.8	38.9	36.6	25.6	34.8	29.1	31.0	21.6	26.6	14.5	24.1
300	51.5	30.8	22.7	42.9	41.0	28.9	38.9	33.0	35.0	25.4	30.4	18.2	27.8
320	56.3	34.7	25.8	46.8	45.4	32.3	42.9	36.9	39.0	29.4	34.4	22.2	31.8
340	60.8	38.7	29.0	50.7	49.8	35.7	46.8	40.9	43.0	33.5	38.6	26.5	35.9
360	65.1	42.8	32.4	54.4	54.0	39.1	50.7	44.9	47.0	37.7	42.8	30.9	40.3
380	69.0	46.9	35.9	57.9	58.1	42.6	54.5	48.9	51.0	41.9	47.0	35.4	44.7
390	70.9	48.9	37.7	59.6	60.1	44.3	56.3	50.9	53.0	44.1	49.1	37.6	47.0
430	77.6	56.9	44.9	66.1	67.7	51.2	63.2	58.7	60.5	52.5	57.5	46.8	56.0
470	83.1	64.4	52.2	71.9	74.4	57.9	69.5	66.0	67.5	60.6	65.5	55.6	64.8
490	85.4	67.9	55.8	74.5	77.4	61.1	72.4	69.4	70.7	64.4	69.2	59.8	68.9
540	90.1	76.0	64.5	80.3	83.9	68.6	78.7	77.0	78.0	73.1	77.6	69.4	78.3
550	90.9	77.4	66.2	81.3	85.0	70.0	79.8	78.4	79.3	74.7	79.1	71.2	79.9
550+	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Wide fractions	Yields, wt.%												
IBP- 110°C	5.3	4.1	3.3	6.6	6.0	4.7	4.9	4.8	4.8	1.2	4.1	0.0	3.9
110-180°C	15.1	7.1	4.9	12.0	10.3	6.8	10.5	7.7	8.5	5.4	6.7	1.8	5.7
180-240°C	15.7	8.8	6.3	12.0	11.7	8.0	11.4	9.3	10.0	8.1	8.7	6.3	7.8
240-360°C	29.0	22.8	17.9	23.7	26.0	19.6	24.0	23.1	23.6	23.0	23.3	22.7	22.9
IBP-360°C	65.1	42.8	32.4	54.4	54.0	39.1	50.7	44.9	47.0	37.7	42.8	30.9	40.3
360-540°C	25.0	33.2	32.1	25.9	29.9	29.5	28.0	32.1	30.9	35.4	34.8	38.6	38.0
> 540°C	9.9	24.0	35.5	19.7	16.1	31.4	21.3	23.0	22.0	26.9	22.4	30.6	21.7

Table 4 Distillation data according to ASTM D-86 and ASTM D-1160

Crude oils	CPC Blend 11.2011	El Bouri 05.2015	Rhas Gharib	Kirkuk 04.2015	Kumkol 04.2013	Oryx,04.2015	Oryx 04.15 + Cheleken 1:2	REBCO 03.2015	REBCO 04.2015	Caspian + REBCO 03.2015	Kazakh + REBCO 03.2015	Caspian 03.2015	Kazakh 03.2015
Distillation boiling point, ^{0}C	Evaporate from the atmospheric part (ASTM D-86), cumulative vol.%												
70	0.0	0.0	0.0	2.3	1.4	0.2	0.0	3.7	0.2	1.1	2.4	0.8	0.0
110	6.0	2.5	2.5	11.0	9.4	5.8	5.5	9.1	5.7	2.9	7.7	1.5	2.2
130	11.3	5.3	4.9	15.6	13.9	9.1	10.1	12.3	9.2	4.3	10.7	2.0	4.3
150	17.2	8.4	7.6	20.3	18.5	12.5	14.6	15.6	12.9	6.1	13.8	2.6	6.7
170	23.3	11.7	10.5	24.9	23.0	16.0	19.0	19.2	16.7	8.2	17.0	3.4	9.4
180	26.4	13.4	12.0	27.2	25.3	17.7	21.2	21.0	18.6	9.4	18.7	3.9	10.8
200	32.6	16.9	15.1	31.6	29.7	21.1	25.4	24.7	22.5	12.1	21.9	4.9	13.8
220	38.7	20.3	18.3	35.9	34.0	24.5	29.5	28.4	26.3	15.2	25.2	6.1	16.8
240	44.5	23.8	21.5	40.1	38.2	27.8	33.5	32.2	30.1	18.7	28.4	7.4	20.0
260	50.1	27.2	24.8	44.0	42.2	31.1	37.2	35.9	33.8	22.5	31.7	9.0	23.2
280	55.3	30.6	28.1	47.8	46.0	34.2	40.8	39.6	37.4	26.7	34.8	10.8	26.4
300	60.2	33.9	31.3	51.4	49.6	37.3	44.2	43.3	40.9	31.1	37.9	12.9	29.6
	Evaporate from the vacuum part (ASTM D-1160), cumulative vol.%												
320	60.9	38.2	32.2	53.2	52.0	38.7	47.2	45.7	42.8	32.3	35.7	22.0	30.8
340	65.0	41.8	33.1	55.0	56.0	40.0	50.6	49.2	46.4	33.5	39.4	26.0	35.4
360	69.0	45.5	36.1	58.2	59.9	42.7	54.0	52.7	50.0	37.6	43.1	30.2	40.2
380	72.8	49.2	39.2	61.3	63.8	45.4	57.4	56.1	53.6	41.8	46.9	34.7	45.2
390	74.6	51.1	40.8	62.9	65.7	46.8	59.1	57.8	55.4	43.9	48.8	36.9	47.7
430	81.2	58.5	47.3	68.8	72.9	52.2	65.6	64.4	62.4	52.2	56.4	46.1	57.8
470	86.7	65.7	53.8	74.3	79.3	57.5	71.7	70.7	69.1	60.3	63.8	55.3	67.4
490	89.0	69.1	57.1	76.8	82.1	60.1	74.5	73.6	72.2	64.2	67.3	59.7	71.9
540	93.5	77.1	65.0	82.5	88.2	66.4	80.9	80.1	79.4	73.1	75.5	70.0	81.7
550	94.2	78.5	66.5	83.5	89.2	67.6	82.1	81.3	80.7	74.7	77.0	71.9	83.4
550+	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Wide fractions	Yields, vol.%												
IBP- 110°C	6.0	2.5	2.5	11.0	9.4	5.8	5.5	9.1	5.7	2.9	7.7	1.5	2.2
110-180°C	20.4	11.0	9.4	16.2	15.8	11.8	15.7	11.9	12.9	6.4	11.0	2.4	8.7
180-240°C	18.1	10.4	9.6	12.9	12.9	10.1	12.3	11.2	11.5	9.3	9.8	3.6	9.2
240-360°C	24.5	21.7	14.6	18.1	21.8	14.9	20.6	20.5	19.9	19.0	14.7	22.8	20.2
IBP-360°C	69.0	45.5	36.1	58.2	59.9	42.7	54.0	52.7	50.0	37.6	43.1	30.2	40.2
360-540°C	24.5	31.6	28.9	24.3	28.2	23.7	26.9	27.4	29.4	35.4	32.3	39.8	41.5
> 540°C	6.5	22.9	35.0	17.5	11.8	33.6	19.1	19.9	20.6	26.9	24.5	30.0	18.3

Table 5 TBP and D-5236 distillation data calculated from ASTM D-86 and ASTM D-1160 according to the procedures described in [1] and [4] (LNB method)

Crude oils	CPC Blend 11.2011	El Bouri 05.2015	Rhas Gharib	Kirkuk 04.2015	Kumkol 04.2013	Oryx,04.2015	Oryx 04.15 + Cheleken 1:2	REBCO 03.2015	REBCO 04.2015	Caspian+ REBCO 03.2015	Kazakh + REBCO 03.2015	Caspian 03.2015	Kazakh 03.2015
Distillation boiling point, ^{0}C	Evaporate, cumulative wt.%												
70	1.9	1.2	1.5	3.6	3.3	2.0	1.4	3.8	2.1	1.7	3.3	1.3	1.7
110	10.2	4.2	3.6	9.5	10.2	5.2	6.6	8.1	6.3	3.7	7.2	2.2	4.3
130	15.1	6.1	5.1	12.8	14.0	7.1	9.6	10.7	8.9	5.1	9.5	2.8	6.0
150	20.1	8.4	6.7	16.3	18.0	9.2	12.9	13.5	11.8	6.7	12.1	3.6	8.1
170	25.2	10.8	8.5	19.9	22.1	11.4	16.4	16.4	14.9	8.6	14.8	4.5	10.4
180	27.8	12.1	9.5	21.8	24.1	12.6	18.1	17.9	16.5	9.6	16.2	5.0	11.6
200	32.8	14.8	11.6	25.5	28.2	15.1	21.7	21.1	19.7	11.9	19.2	6.1	14.3
220	37.7	17.7	13.8	29.1	32.2	17.6	25.2	24.4	23.1	14.4	22.3	7.3	17.3
240	42.4	20.7	16.2	32.8	36.2	20.2	28.8	27.7	26.6	17.2	25.4	8.8	20.4
260	46.9	23.8	18.7	36.4	40.0	22.9	32.4	31.1	30.0	20.2	28.6	10.5	23.7
280	51.2	27.0	21.3	39.9	43.7	25.6	35.9	34.5	33.5	23.5	31.9	12.4	27.1
300	55.2	30.2	24.0	43.4	47.4	28.4	39.3	37.9	37.0	26.9	35.2	14.5	30.7
	D-5236 Evaporate, cumulative wt.%												
320	59.1	33.4	26.8	46.7	50.8	31.1	42.6	41.2	40.4	30.5	38.4	16.9	34.3
340	62.7	39.3	29.6	50.0	54.1	33.9	45.9	45.2	43.8	34.3	41.7	21.7	38.3
360	66.3	44.3	32.7	53.1	58.0	36.9	50.0	49.4	47.9	38.3	46.1	26.6	43.0
380	69.8	48.6	36.1	56.3	61.8	40.0	53.7	53.4	51.8	42.6	50.5	31.4	47.9
390	71.4	50.7	37.8	58.0	63.7	41.5	55.5	55.3	53.7	44.7	52.7	33.8	50.4
430	77.5	57.8	44.7	64.3	70.6	47.6	61.7	62.4	60.5	52.9	60.8	42.9	60.1
470	82.3	63.6	51.2	70.1	76.5	53.4	67.0	68.6	66.4	60.3	67.8	51.0	68.6
490	84.3	66.2	54.3	72.7	79.0	56.1	69.3	71.3	69.0	63.6	70.8	54.7	72.4
540	88.3	71.7	61.5	78.4	84.1	62.3	74.3	77.2	74.6	71.0	77.3	62.9	80.3
550	88.9	72.7	62.8	79.4	85.0	63.5	75.2	78.3	75.6	72.3	78.4	64.4	81.6
550+	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Wide fractions	Yields, wt.%												
IBP- 110°C	10.2	4.2	3.6	9.5	10.2	5.2	6.6	8.1	6.3	3.7	7.2	2.2	4.3
110-180°C	17.5	7.9	5.9	12.3	13.9	7.4	11.6	9.8	10.1	5.9	9.0	2.7	7.4
180-240°C	14.6	8.6	6.7	11.0	12.0	7.6	10.7	9.8	10.1	7.6	9.2	3.9	8.8
240-360°C	24.3	23.6	16.5	20.3	21.8	16.7	21.2	21.7	21.3	21.1	20.7	17.8	22.6
IBP-360°C	66.5	44.3	32.7	53.1	58.0	36.9	50.0	49.4	47.9	38.3	46.1	26.6	43.0
360-540°C	24.2	27.5	28.8	25.4	26.1	25.5	24.3	27.8	26.7	32.6	31.2	36.3	37.3
> 540°C	9.2	28.3	38.5	21.6	15.9	37.7	25.7	22.8	25.4	29.0	22.7	37.1	19.7

3. Results and discussion

The crude oils investigated in this work were selected in such a way to differentiate widely in their TBP distillation characteristics. As evident from Table 2 the TBP content of the wide fractions for the selected data set of crude oils varies as follows:

wide crude oil fractions	fraction content variation in the studied crude oils, wt.%
IBP- 110°C (Light naphtha)	3.7 – 16.6
110-180°C (Heavy naphtha)	2.5 – 18.9
180-240°C (Kerosene)	5.3 – 11.7
240-360°C (Diesel)	14.4 – 22.8
360-540°C (Vacuum gas oil)	20.4 – 32.1
> 540°C (Vacuum residue)	8.0 – 40.2

As can be seen from the data in Table 6 all squared correlation coefficient (R^2) of Riazi's distribution model for the four studied distillation methods are higher than 0.99 which could be considered as a criterion for correctly performed distillations [3]. If a comparison between the TBP wide fraction yields and the other three distillation methods yields is made, the following total AAD from the TBP wide fraction yields would be obtained:

AAD (ASTM D-2892+ASTM D-5236)-(ASTM D-7169) = 2.54 wt.%

AAD (ASTM D-2892+ASTM D-5236)-(Calculated from D-86 and D-1160) = 1.54 wt.%

AAD (ASTM D-2892+ASTM D-5236)-(ASTM D-86 and ASTM D-1160) = 2.60 wt.%

Table 6 Riazi's distribution model variables for the four methods under investigation

Crude oils		CPC Blend 11.2011	El Bouri 05.2015	Rhas Gharib	Kirkuk 04.2015	Kumkol 04.2013	Oryx,04.2015	Oryx 04.15 + Cheleken 1:2	REBCO 03.2015	REBCO 04.2015	Caspian + REBCO 03.2015	Kazakh + REBCO 03.2015	Caspian 03.2015	Kazakh 03.2015
Application of the method of Riazi for the TBP distillation data	**AAD, wt.%**	1.22	0.53	0.40	0.54	0.67	0.40	0.17	0.50	0.43	0.50	0.60	0.62	0.98
	T_o, °C	24	-49	-41	24	-30	9	26	-45	-30	-140	-60	123	-146
	A_t	1.38	18.85	20.01	2.05	6.00	5.02	2.57	12.80	8.93	388.82	21.81	2.07	434.45
	B_t	1.38	2.41	2.27	1.34	2.02	1.69	1.54	2.24	2.11	3.08	2.46	1.98	3.17
	R^2	0.9977	0.9908	0.9937	0.9990	0.9928	0.9967	0.9991	0.9943	0.9960	0.9978	0.9973	0.9971	0.9975
Application of the method of Riazi for the SIMDIS distillation data	**AAD, wt.%**	0.15	0.07	0.06	0.16	0.12	0.08	0.12	0.09	0.10	0.06	0.07	0.19	0.06
	T_o, °C	58	-20	-63	36	2	-23	39	-20	3	50	-40	125	-103
	A_t	1.37	11.56	48.11	2.27	4.71	11.35	2.61	10.03	5.74	4.28	19.91	1.86	176.13
	B_t	1.69	2.42	2.75	1.65	2.10	2.20	1.76	2.33	2.12	2.22	2.65	2.11	3.31
	R^2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.9995	1.0000
Application of the method of Riazi for the calculated from D-86 and D-1160	**AAD, wt.%**	0.41	0.60	0.18	0.37	0.53	0.19	0.34	0.34	0.32	0.23	0.45	0.80	0.35
	T_o, °C	53	21	-13	20	29	8	48	-20	24	-28	-31	-273	-47
	A_t	1.16	4.60	11.64	2.53	1.95	5.61	2.00	6.36	3.20	15.85	9.16	1E+20	23.69
	B_t	1.40	1.96	2.17	1.56	1.54	1.77	1.46	1.97	1.71	2.47	2.13	5.18	2.76
	R^2	0.9998	0.9988	0.9996	0.9994	0.9988	0.9997	0.9998	0.9996	0.9997	0.9995	0.9989	0.9968	0.9987
Application of the method of Riazi for the original distillation data of D-86 and D-	**AAD, wt.%**	0.63	0.41	0.75	0.76	0.88	0.51	0.63	0.42	0.65	0.57	1.15	1.08	0.97
	T_o, °C	77	45	79	56	50	67	72	0	64	3	34	-264	34
	A_t	0.83	2.91	2.00	1.17	1.40	1.71	1.25	3.75	1.60	8.32	2.49	2E+12	4.22
	B_t	1.41	1.88	1.34	1.20	1.49	1.23	1.30	1.78	1.47	2.31	1.47	5.98	2.16
	R^2	0.9979	0.9944	0.9967	0.9986	0.9951	0.9985	0.9977	0.9983	0.9962	0.9982	0.9924	0.9941	0.9931

**AAD = Average absolute deviation;*

$AAD = \frac{\sum \left| X_{i\ narrow\ cut}^{measured} - X_{i\ narrow\ cut}^{calculated} \right|}{N_{cuts}}$, where: $X_{i\ narrow\ cut}^{measured}$ – experimentally determined narrow cut yield, wt. %; $X_{i\ narrow\ cut}^{calculated}$ – calculated by Riazi's distribution model narrow cut yield, wt. %; N_{cuts}– number of narrow cuts.

Based on this comparison one may conclude that the LNB method, calculated from ASTM D-86 and ASTM D-1160 best approximates the crude oil TBP. Having regressed the data from Tables 2-5 the following equations predicting the TBP wide fraction yields from the simulation distillation ASTM D-7169; the LNB method that uses the combination of ASTM D-86 and D-1160 and the calculation procedures described in [1] and [4]; and the combination of ASTM D-86 and D-1160 were obtained:

1. Prediction of TBP wide fraction yields from data of the wide fraction yields from the high temperature simulated distillation (HTSD) ASTM D-7169:

$$X_{IBP-180^oC}^{TBP} = 0.008746 * X_{IBP-180^oC}^{HTSD\ 3} - 0.24719 * X_{IBP-180^oC}^{HTSD\ 2} + 3.21291 * X_{IBP-180^oC}^{HTSD} - 2.80591, \quad (2)$$

$R^2 = 0.9718$

$$X_{110-180^oC}^{TBP} = 0.005618 * X_{110-180^oC}^{HTSD\ 3} - 0.13086 * X_{110-180^oC}^{HTSD\ 2} + 2.009387 * X_{110-180^oC}^{HTSD} - 1.14657, \quad (3)$$

$R^2 = 0.9817$

$$X_{IBP-110^oC}^{TBP} = X_{IBP-180^oC}^{TBP} - X_{110-180^oC}^{TBP} \quad (4)$$

$$X_{180-240^oC}^{TBP} = -0.0402 * X_{180-240^oC}^{HTSD\ 2} + 1.456 * X_{180-240^oC}^{HTSD} - 1.3176, \quad (5)$$

$R^2 = 0.9229$

$$X_{>360^oC}^{TBP} = 0.000725 * X_{>360^oC}^{HTSD\ 3} - 0.1186 * X_{>360^oC}^{HTSD\ 2} + 7.426 * X_{>360^oC}^{HTSD} - 117.3, \quad (6)$$

$R^2 = 0.9712$

$$X_{240-360^oC}^{TBP} = 100 - X_{>360^oC}^{TBP} - X_{IBP-180^oC}^{TBP} - X_{180-240^oC}^{TBP} \quad (7)$$

$$X_{>540^oC}^{TBP} = -0.00123 * X_{>540^oC}^{HTSD\ 3} + 0.0832 * X_{>540^oC}^{HTSD\ 2} - 0.3963 * X_{>540^oC}^{HTSD} + 4.8694, \quad (8)$$

$R^2 = 0.9779$

$$X_{360-540^oC}^{TBP} = X_{>360^oC}^{TBP} - X_{>540^oC}^{TBP} \quad (9)$$

2. Prediction of TBP wide fraction yields from data of the wide fraction yields from the LNB method, calculated from ASTM D-86 and ASTM D-1160

$$X_{IBP-180^oC}^{TBP} = 0.00537 * X_{IBP-180^oC}^{LNB\ 3} - 0.24787 * X_{IBP-180^oC}^{LNB\ 2} + 4.54268 * X_{IBP-180^oC\ I}^{LNB} - 14.744, \quad (10)$$

$R^2 = 0.9735$

$$X_{110-180^oC}^{TBP} = 0.005013 * X_{110-180^oC}^{LNB\ 3} - 0.142 * X_{110-180^oC}^{LNB\ 2} + 2.1785 * X_{110-180^oC}^{LNB} - 2.7014, \quad (11)$$

$R^2 = 0.9696$

$$X_{IBP-110^oC}^{TBP} = X_{IBP-180^oC}^{TBP} - X_{110-180^oC}^{TBP} \quad (12)$$

$$X_{180-240^oC}^{TBP} = -0.00554 * X_{180-240^oC}^{LNB\ 3} + 0.149 * X_{180-240^oC}^{LNB\ 2} - 0.599 * X_{180-240^oC}^{LNB} + 5.8601, \quad (13)$$

$R^2 = 0.9718$

$$X_{>360^oC}^{TBP} = -0.0109 * X_{>360^oC}^{LNB\ 2} + 2.1828 * X_{>360^oC}^{LNB} - 32.244, \quad (14)$$

$R^2 = 0.9767$

$$X^{TBP}_{240-360^oC} = 100 - X^{TBP}_{>360^oC} - X^{TBP}_{IBP-180^oC} - X^{TBP}_{180-240^oC} \quad (15)$$

$$X^{TBP}_{>540^oC} = -0.002566 * X^{LNB}_{>540^oC}{}^{3} - 0.20203 * X^{LNB}_{>540^oC}{}^{2} - 6.005454 * X^{LNB}_{>540^oC} - 39.2985, \quad (16)$$

$R^2 = 0.9646$

$$X^{TBP}_{360-540^oC} = X^{TBP}_{>360^oC} - X^{TBP}_{>540^oC} \quad (17)$$

3. Prediction of TBP wide fraction yields from data of the wide fraction yields from the combination of ASTM D-86 and D-1160

$$X^{TBP}_{IBP-180^oC} = 0.0049 * X^{D86+D11603}_{IBP-180^oC} - 0.21193 * X^{D86+D11602}_{IBP-180^oC} + 3.549985 * X^{D86+D1160}_{IBP-180^oC} - 8.28002, \quad (18)$$

$R^2 = 0.8675$

$$X^{TBP}_{110-180^oC} = 0.002669 * X^{D86+D11603}_{110-180^oC} - 0.06641 * X^{D86+D11602}_{110-180^oC} + 1.17635 * X^{D86+D1160}_{110-180^oC} - 0.1175, \quad (19)$$

$R^2 = 0.9891$

$$X^{TBP}_{IBP-110^oC} = X^{TBP}_{IBP-180^oC} - X^{TBP}_{110-180^oC} \quad (20)$$

$$X^{TBP}_{180-240^oC} = -0.00729 * X^{D86+D11603}_{180-240^oC} + 0.2336 * X^{D86+D11602}_{180-240^oC} - 1.6785 * X^{D86+D1160}_{180-240^oC} + 8.75699, \quad (21)$$

$R^2 = 0.9569$

$$X^{TBP}_{>360^oC} = 0.000868 * X^{D86+D11603}_{>360^oC} - 0.14152 * X^{D86+D11602}_{>360^oC} + 8.3877 * X^{D86+D1160}_{>360^oC} - 121.73, \quad (22)$$

$R^2 = 0.9311$

$$X^{TBP}_{240-360^oC} = 100 - X^{TBP}_{>360^oC} - X^{TBP}_{IBP-180^oC} - X^{TBP}_{180-240^oC} \quad (23)$$

$$X^{TBP}_{>540^oC} = 0.001454 * X^{D86+D11603}_{>540^oC} - 0.09016 * X^{D86+D11602}_{>540^oC} + 2.714819 * X^{D86+D1160}_{>540^oC} - 6.65255, \quad (24)$$

$R^2 = 0.9636$

$$X^{TBP}_{>360-540^oC} = X^{TBP}_{>360^oC} - X^{TBP}_{>540^oC} \quad (25)$$

Detailed data of the AAD of the predicted TBP yields of the wide fractions from the measured ones for all 13 studied crude oils employing the three distillation methods and the regressed equations are summarized in Tables 7-9. These data indicate that among the three investigated distillation methods the HTSD ASTM D-7169 and equations 2-9 best predict the crude oil TBP wide fractions with a total AAD of 0.93 wt.%. The LNB method, calculated from ASTM D-86 and ASTM D-1160 and equations 10-17 was the second in accuracy of prediction the TBP wide fraction yields with a total AAD of 1.10 wt.%. The poorest prediction of the crude oil TBP wide fraction yields is obtained by the use of the combination of ASTM D-86 and D-1160 and equations 18-25 with a total AAD of 1.50 wt.%.

It can be noted from the data in Tables 7-9 that the three surrogate distillation methods predict the TBP diesel fraction and the VGO fraction yields with the least accuracy among all other predicted TBP crude oil fractions. A possible poor separation between diesel and VGO could be the explanation of this observation. Indeed, if one looks at the separation between the diesel and the VGO in the TBP distillation data (cut point of 360°C) from Table, 2 he will see that there is a gap in the fraction 360-380°C. For all 13 studied crude oils the yield of the fraction 360-380°C varies between 0 and 1.0 wt.%, while that of the nearest fraction 340-360°C varies between 2.4 and 4.8%. The application of Riazi's boiling point distribution model to the combined ASTM D-2892 (TBP) and ASTM D-5236 distillation data indicates the same yields of the fractions 340-360^{0}C and 360-380°C for all 13 investigated crude oils and this is logical because these fractions have the same temperature interval width of 20^{0}C and they

are far away from the 10% and 90% of the distillation curve, which are the thresholds for changing the slope of boiling point temperature of the evaporate versus the evaporate yield. The reason for the 360-380°C yield gap could be the transition from the ASTM D-2892 (atmospheric TBP distillation) to the ASTM D-5236 vacuum pot still distillation of the atmospheric residue from the ASTM D-2892. Obviously, both distillations differentiate in their fractionation efficiency. A cut point of 360°C for the ASTM D-2892 distillation equals to 375 – 380°C cut point for the ASTM D-5236 distillation.

Table 7 Absolute average deviation of the regression lines of the relationships (Equations 2-9) TBP = f (ASTM D-7169 – HTSD) from the TBP yields

Crude oils	CPC Blend 11.2011	El Bouri 05.2015	Rhas Gharib	Kirkuk 04.2015	Kumkol 04.2013	Oryx,04.2015	Oryx 04.15 + Cheleken 1:2	REBCO 03.2015	REBCO 04.2015	Caspian + REBCO 03.2015	Kazakh + REBCO 03.2015	Caspian 03.2015	Kazakh 03.2015	
Δ (TBP- predicted) yields, wt.%														AAD
IBP- 110°C	1.33	0.53	1.53	2.56	0.91	0.98	0.34	0.58	0.36	1.87	0.57	0.16	0.20	**0.92**
110-180°C	0.18	0.38	0.26	0.85	1.08	0.59	0.30	0.29	0.39	0.80	0.11	0.13	0.47	**0.45**
180-240°C	0.03	0.18	0.99	0.26	0.06	0.22	0.06	0.36	0.32	0.62	0.18	0.86	0.25	**0.34**
240-360°C	4.31	3.23	0.88	1.55	1.19	2.42	1.59	1.81	2.15	1.47	0.34	1.06	3.36	**1.95**
360-540°C	0.07	2.11	0.37	2.45	0.48	1.84	0.11	0.59	0.99	0.28	0.75	0.70	2.69	**1.03**
>540°C	0.10	0.46	0.21	3.57	1.26	1.20	0.36	1.01	0.14	0.29	1.23	0.88	1.25	**0.92**
AAD	**1.00**	**1.15**	**0.71**	**1.87**	**0.83**	**1.21**	**0.46**	**0.77**	**0.73**	**0.89**	**0.53**	**0.63**	**1.37**	***0.93***

Table 8 Absolute average deviation of the regression lines of the relationships (Equations 10-17) TBP = f(Calculated from D-86 and D-1160 - the LNB method) from the TBP yields

Crude oils	CPC Blend 11.2011	El Bouri 05.2015	Rhas Gharib	Kirkuk 04.2015	Kumkol 04.2013	Oryx,04.2015	Oryx 04.15 + Cheleken 1:2	REBCO 03.2015	REBCO 04.2015	Caspian + REBCO 03.2015	Kazakh + REBCO 03.2015	Caspian 03.2015	Kazakh 03.2015	
Δ (TBP- predicted) yields, wt.%														AAD
IBP- 110°C	0.3	0.1	0.5	1.3	1.3	0.6	1.4	1.0	0.5	0.7	1.1	0.1	0.3	**0.70**
110-180°C	0.1	0.7	0.3	1.1	0.7	1.1	0.5	0.3	0.4	0.3	1.0	0.0	1.0	**0.58**
180-240°C	0.0	0.0	0.4	0.2	0.4	0.0	0.4	0.1	0.3	0.3	0.2	0.0	0.5	**0.21**
240-360°C	2.5	4.1	2.9	2.1	0.6	0.4	1.5	2.2	1.4	0.7	1.7	0.6	3.2	**1.83**
360-540°C	1.1	2.5	0.3	3.0	3.8	0.2	0.8	1.7	1.8	3.5	0.2	1.5	1.1	**1.92**
> 540°C	0.5	0.3	1.4	1.6	1.8	0.0	2.6	0.7	1.7	3.1	0.3	2.0	0.5	**1.34**
AAD	**0.75**	**1.28**	**0.95**	**1.54**	**1.45**	**0.40**	**1.19**	**0.99**	**1.01**	**1.43**	**0.75**	**0.72**	**1.79**	***1.10***

Table 9 Absolute average deviation of the regression lines of the relationships (Equations 18-25) TBP = f(D-86 and D-1160) from the TBP yields

Crude oils	CPC Blend 11.2011	El Bouri 05.2015	Rhas Gharib	Kirkuk 04.2015	Kumkol 04.2013	Oryx,04.2015	Oryx 04.15 + Cheleken 1:2	REBCO 03.2015	REBCO 04.2015	Caspian + REBCO 03.2015	Kazakh + REBCO 03.2015	Caspian 03.2015	Kazakh 03.2015	
Δ (TBP- predicted) yields, wt.%														AAD
IBP- 110°C	7.6	0.6	1.0	5.7	1.7	0.8	2.1	1.9	1.0	0.3	1.2	0.2	1.0	**1.94**
110-180°C	0.0	0.6	0.8	0.1	0.5	0.1	0.6	0.5	0.1	0.5	0.2	0.1	0.1	**0.33**
180-240°C	0.0	0.1	0.4	0.2	0.2	0.6	0.2	0.1	0.3	0.3	0.6	0.0	0.4	**0.27**
240-360°C	10.5	4.4	2.9	5.1	1.2	2.9	1.7	2.1	1.8	0.6	3.8	0.8	3.3	**3.16**
360-540°C	0.2	1.3	4.2	2.8	0.9	4.9	1.3	1.9	0.2	2.2	0.6	2.0	5.4	**2.14**
> 540°C	0.4	1.0	0.0	2.5	1.6	0.5	0.2	0.6	0.5	1.2	4.5	1.5	0.1	**1.13**
AAD	**3.12**	**1.32**	**1.56**	**2.75**	**1.01**	**1.64**	**1.02**	**1.19**	**0.67**	**0.83**	**1.82**	**0.78**	**1.73**	***1.50***

In order to verify that the cut points are different for the ASTM D-2892 and the ASTM D-5236 a sample of REBCO was distilled twice with a cut point of the atmospheric part of 300^{0}C and 360^{o}C respectively. The results of these two performed distillations are presented in Table 10. These data show that after the atmospheric part distillation of REBCO (ASTM D-2892) the next fraction 360-380^{o}C or 300-320^{o}C (obtained from the ASTM D-5236) is undervalued. The cuts 280-300^{0}C and 300-320^{o}C in the REBCO distillation with a cut point between ASTM D-2892 and ASTM D-5236 of 360^{o}C have the same yields of 3.6 wt.%, while in the REBCO distillation with a cut point between ASTM D-2892 and ASTM D-5236 of 300^{o}C the yield of 280-300^{o}C cut is 2.5 wt.% and the 300-320^{0}C cut has an yield of 0.9 wt.%, that is these cuts have different yields when the cut point is 300^{0}C. The yield of the cut 360-380^{o}C in the REBCO distillation at the cut point between ASTM D-2892 and ASTM D-5236 of 300^{o}C is 4.8% while the yield of the cut 360-380^{o}C in the REBCO distillation at the cut point between ASTM D-2892 and ASTM D-5236 of 360^{o}C is 0.4 wt.%. These data clearly indicate that the value of the cut point between the ASTM D-2892 and the ASTM D-5236 distillation has impact on the yields of the wide fractions diesel and VGO. For example, the yield of the diesel at the cut point between ASTM D-2892 and ASTM D-5236 of 300^{0}C is 17.7 wt.% while at cut point of 360^{o}C the diesel fraction has a yield of 21.2 wt.%. The VGO yield at cut point of 300^{0}C is 31.6 wt. %, while at cut point of 360^{o}C the VGO yield is 27.9 wt.%. There is also a difference in the VR yields at the two REBCO distillation having different cut points between ASTM D-2892 and ASTM D-5236. However, this difference is about 1% which is within uncertainty of the measurement of evaporate yield according to the standard method ASTM D-5236.

The difference in the yields of diesel and VGO at the different cut points between ASTM D-2892 and ASTM D-5236 are indeed significant and are beyond the reproducibility of both ASTM D-2892 and ASTM D-5236. If a comparison between wide fraction yields obtained from both distillations of REBCO at the two different cut points between ASTM D-2892 and ASTM D-5236 300 and 360^{o}C respectively and approximated by Riazi's distribution model one can see that no significant difference between simulated yields of the wide fractions exists. Therefore, a conclusion could be made that Riazi's boiling point distribution model is capable of smoothing the difference in the efficiency of separation between the ASTM D-2892 and the ASTM D-5236 and removes the observed gap in the yield of the fraction following the cut point between ASTM D-2892 and ASTM D-5236.

Considering the good results obtained with the application of Riazi's boiling point distribution model, we decided to employ it to the ASTM D-2892 distillation data (up to 360^{o}C) and extrapolate beyond 360^{o}C and thus obtain the VGO and the VR fraction yields. Then we

compared the extrapolated VGO and VR fraction yields with those measured by ASTM D-5236 and also tried to correlate them with the three investigated distillation methods: HTSD (ASTM D-7169); the LNB method; and the combination of ASTM D-86 and ASTM D-1160. Figure 1 present graphs of relation between the yields of VGO and VR of the three investigated distillation methods and the yields of VGO and VR measured by ASTM D-5236 and the ones extrapolated by application of Riazi's boiling point distribution model to the ASTM D-2892 distillation data boiling to 360°C.

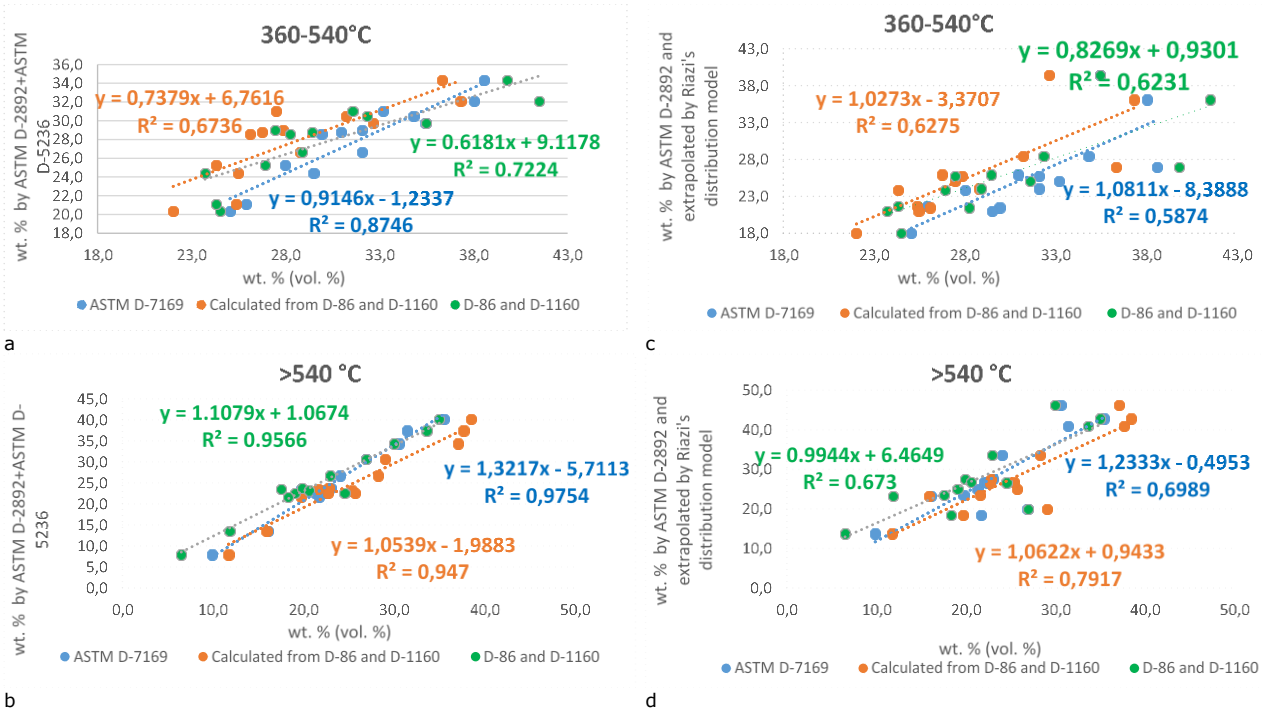

Figure 1 Relation between measured VGO and VR TBP yields (a) and (b) (based on the ASTM D-5236 distillation data of the atmospheric residue from ASTM D-2892) and the extrapolated by Riazi's distribution model (c) and (d) (based on ASTM D-2892 only) and the VGO and VR yields from the three investigated distillation methods

These data indicate that the yields of VGO and VR obtained by extrapolation from the ASTM D-2892 distillation data boiling to 360°C by the use of Riazi's boiling point distribution model have a weaker correlation with the VGO and VR of the three investigated distillation methods than the measured by ASTM D-5235 VGO and VR yields. The correlation between extrapolated by application of Riazi's boiling point distribution model to the ASTM D-2892 distillation data boiling to 360°C VGO and VR yields and the measured by ASTM D-5235 VGO and VR yields is also weak (squared correlation coefficient R^2=0.4073 for VGO yield and R^2=0.6801 for the VR yield). Regardless of the excellent fit of the distillation data to the Riazi's boiling point distribution model the predicted by the model VGO and VR yields extrapolated on the base of the atmospheric TBP distillation boiling up to 360°C do not coincide well with the measured ones by the ASTM D-5236 method. Therefore, the extrapolated VGO and VR yields by the use of Riazi's boiling point distribution model are not a reliable rating of the true VGO and VR yields.

Riazi's boiling point distribution model is capable of filling the gap in the fraction following the cut point between the ASTM D-2892 and the ASTM D-5236. However, Riazi's boiling point distribution model is not capable of providing a reliable rating of the true VGO and VR yields.

All these results and speculations cannot explain why the three surrogate distillation methods predict the TBP diesel fraction and the VGO fraction yields with the least accuracy among

all other predicted TBP crude oil fractions. Further investigation with more data is needed to improve the accuracy of prediction of the crude oil TBP especially in the diesel area.

Table 10 Two distillations ASTM D-2892 and ASTM D-5236 of a sample of crude oil - REBCO at two different cut points between ASTM D-2892 and ASTM D-5236 – 300°C and 360°C

		Cut point between ASTM D-2892 and ASTM D-5236 of 300°C			Cut point between ASTM D-2892 and ASTM D-5236 of 360°C	
Distillation	ASTM-D 2892	%	∑ %	ASTM-D 2892	%	∑ %
Gas C3-C4		1.00	1.00		1.00	1.00
IBP- 70°C		3.36	4.36		2.85	3.85
70-110°C		4.41	8.77		4.34	8.19
110-130°C		2.56	11.33		2.53	10.72
130-150°C		2.49	13.82		2.53	13.25
150-170°C		2.57	16.39		2.74	15.99
170-180°C		1.42	17.82		1.49	17.48
180-200°C		5.47	23.28		2.74	20.22
200-220°C		1.92	25.20		3.26	23.48
220-240°C		2.30	27.51		3.28	26.76
240-260°C		5.67	33.18		3.67	30.43
260-280°C		2.13	35.31		3.54	33.97
280-300°C		2.49	37.80		3.59	37.56
300-320°C	ASTM-D 5236	0.94	38.74		3.61	41.17
320-340°C		2.76	41.50		3.40	44.57
340-360°C		3.67	45.18		3.39	47.96
> 360°C		45.18		ASTM-D 5236	52.04	
360-380°C		4.82	50.00		0.40	48.36
380-390°C		2.67	52.67		2.27	50.63
390-430°C		6.46	59.12		8.05	58.68
430-470°C		8.39	67.51		6.33	65.01
470-490°C		3.81	71.32		3.50	68.51
490-540°C		5.50	76.82		7.39	75.90
540-550°C			76.82		1.62	77.52
> 550°C		23.18	100.00		22.48	100.00
Wide fractions yieds, wt.%		Simulated by Riazi's distribution model	Measured		Simulated by Riazi's distribution model	Measured
IBP- 110°C		7.51	7.77		6.92	7.19
110-180°C		9.36	9.04		9.04	9.29
180-240°C		9.74	9.69		9.63	9.28
240-360°C		21.00	17.67		21.25	21.20
IBP-360°C		47.61	44.18		46.85	46.96
360-540°C		26.80	31.64		27.60	27.94
> 540°C		24.59	23.18		24.55	24.10

4. Conclusions

Based on distillation data of four methods: TBP – a combination from ASTM D-2982 and ASTM D-5236, high temperature simulated distillation (ASTM D-7169), a combination from

ASTM D-86 and ASTM D-1160, and a calculated TBP by the use of procedures described in references [1] and [4] and a combination from ASTM D-86 and ASTM D-1160 methods of 13 widely different crude oils the following conclusions could be made:

1. The HTSD (ASTM D-7169) best approximates the crude oil TBP.
2. During crude oil distillation by a combination of ASTM D-2892 (TBP) and ASTM D-5236 a gap in the fraction following the cut point between ASTM D-2892 and ASTM D-5236 appears. This gap does not reflect the true distillation curve and can be overcome by application of Riazi's boiling point distribution model to both ASTM D-2892 and ASTM D-5236 crude oil distillation data.
3. Riazi's boiling point distribution model is not capable of providing of reliable rating of the true VGO and VR yields only on the bases of crude oil distillation data boiling up to 360^0C according to the ASTM D-2892 method.
4. Further investigations with more data are needed to improve the accuracy of prediction of the crude oil TBP from the surrogate faster distillation methods, especially in the diesel area.

Reference

[1] Stratiev D, Nedelchev A, Dinkov R, Batchvarov A. It's possible to derive TBP from partial distillation data, Oil & Gas Journal, Oct. 3, 2011, 114 – 122.

[2] Nedelchev A, Stratiev D, Ivanov A, Stoilov G. Boiling point distribution of crude oils based on TBP and ASTM D-86 distillation data. Pet. Coal 53 (4) 275-290.

[3] Stratiev DS, Marinov I, Nedelchev A, Velkov I, Stratiev DD, Veli A, Mitkova M, Stanulov K. Evaluation of approaches for conversion of ASTM into TBP distillation data of oil fractions, OGEM, December, 4/2014, 216-221.

[4] Nikolaychuk E, Stratiev D, Velkov I, Veli A, Sotirov S, Mitkova M Conversion of heavy oil distillation data from ASTM D-1160 to ASTM D-5236, Pet Coal 57(3) 266-279, 2015.

[5] Riazi MR. Distribution Model for Properties of Hydrocarbon-Plus Fractions. Industrial Engineering Chemistry Research, 1989, 28:1831–1835.

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