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CONVERSION OF HEAVY OIL DISTILLATION DATA FROM ASTM D-1160 TO ASTM D-5236

Ekaterina Nikolaychuk[1], Dicho Stratiev[1], Ilian Velkov[1], Anife Veli[2], Sotir Sotirov[2], Magdalena Mitkova[2]

[1]Chief Process Engineer Department, Lukoil Neftochim Bourgas, 8104 Bourgas, Bulgaria, e-mail: stratiev.dicho@neftochim.bg; [2]University "Prof. Dr. Assen Zlatarov", 9010 Bourgas, Bulgaria

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Abstract

The ASTM D-5236 method was proven to be the closest to true boiling point (TBP) of heavy oil distillation data. That is why 60 heavy oils have been characterized for their distillation charactersistics by ASTM D-5236 and ASTM D-1160 in the Research laboratory of LUKOIL Neftochim Burgas and an attempt was made to find an accurate method to convert ASTM D-1160 to ASTM D-5236. Six approaches were investigated to convert the heavy oil distillation data from ASTM D-1160 to ASTM D-5236, such as the simple comparison of ASTM D-1160 and ASTM D-5236, the method of Edmister-Okamoto with original coefficients, as well as the one with modified coefficients, Daubert, artificial neural networks and LNB methods. It was found that the LNB method converts the heavy oil distillation data ASTM D-1160 to ASTM D-5236 with the least error. The methods of Edmister-Okamoto with modified coefficients and of Daubert convert the heavy oil distillation data ASTM D-1160 to ASTM D-5236 with slightly higher AAD and SD than the LNB method. Other methods such as Edmister-Okamoto with original coefficients, ANN and simple comparison of D1160 and D5236 were proven to be the least accurate methods and thereby the least appropriate ways for petroleum fraction distillation interconversion. The use of the three methods: LNB, Daubert's, and Edmister-Okamoto with modified coefficients improve the conversion of heavy oil distillation data ASTM D-1160 to ASTM D-5236 and can be applied in the refinery practice for quick characterization of heavy oil distillation data which are closest to the TBP method.

Key words: Heavy oil distillation; ASTM D-5236; ASTM D-1160; TBP; distillation interconversion.

1. Introduction

Oil characterization is an essential step in the design, simulation, and optimization of refining facilities. Crude oils, heavy oils and their fractions are undefined mixtures with compositions that are not well known (volume, weight, and molar fractions of all the present components). For that reason in refinery applications, the oil is typically characterized based on a distillation assay. This procedure is reasonably well-defined and is based on the representation of the mixture of actual components that boil within a boiling point interval by hypothetical components that boil at the average boiling temperature of the interval [1-2]. The crude oil assay typically includes TBP distillation according to ASTM D-2892, which can characterize this part of oil that boils up to 400^{0}C atmospheric equivalent boiling point [3], and vacuum distillation according to ASTM D-5236 [4] which characterizes the heavy oil obtained as a residue from the ASTM D-2892 distillation [5-7]. ASTM D-1160 vacuum distillation is also used to characterize the distillation curve of high boiling materials [8-11]. However, it was determined that the ASTM D1160 vacuum distillation did not provide well established saturated bubble temperatures. On the other hand the ASTM D5236 methodology was found to provide well-defined saturated bubble temperatures that correspond to actual thermodynamic state points [12]. The developed by Satyro and Yarranton methodology allows the use of ASTM D-5236 distillation data to convert them into TBP and estimate the entire distillation curves for heavy hydrocarbons. Unfortunately the performance of high boiling oil fraction ASTM D-5236 vacuum distillation analysis requires more time than the faster ASTM D-1160. For example the ASTM D-5236 can characterize one sample of heavy oil per working day, while the ASTM D-1160 can perform three analyses of heavy oils for the same time. This was an incentive for the LUKOIL Neftochim Burgas process department to develop procedure for conversion of heavy oil ASTM D-1160 distillation data into ASTM D-5236 for the purposes of technological analysis of the heavy oil processing refinery units. The aim of this study is to test capabilities of several mathematical approaches to accurately convert of ASTM D-1160 distillation data into ASTM D-5236 by analyzing 60 heavy oils.

2. Experimental

60 heavy oils were analyzed for their distillation characteristics in the LUKOIL Neftochim Burgas (LNB) Research laboratory in accordance with the methods ASTM D-5236 and ASTM D-1160. The analyses were carried out in Potstill Euro Dist System from ROFA Deutschland GmbH according to ASTM D-5236 requirements and in Euro Dist MPS (ROFA) according to ASTM D-1160 requirements. The pressure profile in the ASTM D-5236 Potstill apparatus was following: the fraction boiling up to 430°C was separated from the atmospheric residue at pressure 1 mm Hg, and the other narrow cuts (up to 540°C) – at pressure of 0.2 mm Hg. The pressure in the Euro Dist MPS ASTM D-1160 apparatus during the whole analysis was 0.5 mm Hg. Densities of some of the heavy oils were measured at 20°C according to ASTM D-4052. The heavy oil atmospheric equivalent boiling point (AEBP) distillation data of ASTM D-5236 and ASTM D-1160 are summarized in Tables 1 and 2. Having in mind that the distillations finished at 560°C for ASTM D-5236 and at 550°C for ASTM D-1160 and the per cent of evaporate was between 46 and 95 % to obtain the full distillation curve Riazi's distribution model was applied [13]. In an earlier study it was found out that this distribution model best extrapolates boiling points of heavy oils [13]. The values in red in Tables 1 and 2 indicate extrapolated by Riazi's distribution model AEBP. The last right hand columns in Tables 1 and 2 show the squared correlation coefficient (R^2) of applied Riazi's distribution model. The average R^2 for ASTM D-5236 was 0.9969, while for ASTM D-1160 it was 0.9975.

3. Results and Discussions

3.1 Application of Edmister-Okamoto method to convert ASTM D-1160 to ASTM D-5236

The only method widely used under subatmospheric pressure condition for conversion of distillation curves is the one developed by Edmister-Okamoto [14], which is used to convert ASTM D 1160 to TBP, both at 10 mmHg. This method is graphical and it is also recommended by the API-DTB [15]. In this method it is assumed that at 50% and higher points ASTM D 1160 and TBP temperatures are equal. Table 3 presents data of differences between ASTM D-1160 and ASTM D-5236 at 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 95 %.

AAD = average absolute deviation; $AAD = \frac{1}{n}\sum_{i=1}^{n}\left|\Delta T_i\right|$, where n= number of observation

It is evident from these data the average temperature difference is not equal to zero at any per cent. The average absolute deviation varies between 5 and 8°C for the evaporate between 5 and 60%. With increasing of evaporate per cent the difference in temperatures between ASTM D-1160 and ASTM D-5236 becomes higher (from 11 to 38°C for evaporates between 70 and 95%). It should be noted here that the difference between initial boiling points of both methods is also high (average absolute difference = 23°C). The direct application of the method of Edmister-Okamoto gave average absolute deviation (AAD) of 7.5°C between measured and converted boiling points (Figure 1) for the data presented in Tables 1 and 2.

Table 1 The AEBP distillation data of ASTM D-1160 method of the 60 heavy oils under study

		ASTM D1160 (vol.%)												
№	**Samples**	**IBP**	**5%**	**10%**	**20%**	**30%**	**40%**	**50%**	**60%**	**70%**	**80%**	**90%**	**95%**	***R^2***
1	AR from AD-5 (22.05.09)	287	383	398	424	451	477	506	547	584	637	721	799	0,9995
2	AR t. „Rirol 5"(03.12.10)	307	376	397	422	443	473	501	531	562	603	666	721	0,9978
3	AR t. "King E" (04.12.10)	289	336	371	406	439	465	498	533	558	596	648	691	0,9974
4	t. „Caspian Mariner" (22.05.13)	300	361	390	425	465	512	554	604	664	741	862	972	0,9967
5	t. „Vera Cruz" (16.05.13)	297	359	388	420	444	467	492	523	547	579	625	663	0,9975
6	t. „NS Parade" (07.05.13)	311	361	387	418	441	467	494	525	554	592	647	694	0,9981
7	AR Novorossiysk (06.14)	277	342	365	405	433	459	486	516	545	582	634	678	0,9994
8	AR Kerch (06.14)	249	341	372	415	446	476	507	535	567	605	659	703	0,9998
9	AR average sample (06.14)	306	366	400	425	458	488	520	539	567	599	645	682	0,9916
10	AR Kavkaz (02.13)	336	370	394	427	451	475	499	522	554	589	639	683	0,9984
11	AR Novorossiysk (02.13)	304	359	387	417	436	458	487	517	542	576	624	665	0,9938
12	AR Tuapse (02.13)	331	377	398	421	441	465	493	521	546	581	633	678	0,9965
13	AR Temruk (01.13)	335	374	395	418	437	459	489	527	549	588	647	700	0,9951
14	AR Tuapse (01.13)	310	377	398	428	443	468	492	520	545	580	629	673	0,9970
15	AR Kerch (01.13)	328	360	383	412	434	456	480	510	541	579	634	682	0,9963
16	VGO/AGO	341	377	396	416	428	443	456	468	481	499	521	539	0,9979
17	VGO/AGO	327	374	388	405	417	427	438	448	459	472	489	502	0,9994
18	VGO/AGO	334	374	386	399	410	419	427	435	444	454	467	478	0,9994
19	VGO/AGO	332	375	388	404	416	423	437	449	464	481	504	524	0,9975
20	VGO/AGO	342	375	386	401	413	422	433	445	457	475	502	520	0,9983
21	AGO-100	329	371	382	394	402	410	418	428	436	444	456	466	0,9987
22	VGO-100	345	387	400	416	430	441	457	472	490	510	527	555	0,9983
23	AGO-100	327	369	380	394	403	408	412	418	425	433	443	450	0,9906
24	VGO mix sample -11.12-01.13	339	373	396	418	431	446	457	470	482	497	515	526	0,9984
25	AR t. "Ray G" (06.09.13)	265	350	386	426	460	493	527	556	590	630	688	735	0,9982
26	H-Oil (AR) France	309	357	378	409	435	464	498	523	557	601	666	723	0,9990
27	AR Kerch (09.13)	252	344	371	405	432	462	495	536	564	609	674	731	0,9974
28	AR (17.10.13)	241	367	391	422	446	469	495	526	550	584	631	672	0,9984
29	AR (11.10.13)	310	362	389	421	445	468	495	526	550	584	633	673	0,9978
30	AR (01.10.13)	324	381	398	422	442	463	487	516	537	567	611	649	0,9962
31	AR (17.11.13)	301	366	388	419	442	463	489	518	545	579	629	671	0,9987

		ASTM D1160 (vol.%)												
№	**Samples**	**IBP**	**5%**	**10%**	**20%**	**30%**	**40%**	**50%**	**60%**	**70%**	**80%**	**90%**	**95%**	R^2
32	AR (15.11.13)	326	379	403	433	457	481	507	537	564	600	651	695	0,9990
33	AR (06.11.13)	312	363	386	419	445	469	496	526	556	594	650	697	0,9992
34	AR Tuapse (19.12.13)	321	368	391	419	442	465	491	522	547	582	633	676	0,9982
35	AR Kavkaz (22.12.13)	328	376	394	421	444	467	493	523	546	580	629	671	0,9975
36	AR from AD-4 (6.12.12)	349	391	405	442	470	503	536	569	607	655	725	787	0,9957
37	AR from VDM-2 (28.01.14)	313	362	390	425	454	482	514	543	576	616	673	722	0,9987
38	AR RMP (28.01.14)	317	360	386	419	446	470	497	528	555	591	642	686	0,9986
39	AR Kavkaz (01.14)	310	367	390	420	442	466	493	524	547	582	632	676	0,9958
40	AR Novorossiysk (01.14)	320	371	393	424	447	469	497	530	553	588	638	681	0,9976
41	AR Tuapse mix (01.14)	327	372	395	423	445	469	494	525	552	588	641	686	0,9984
42	AR Tuapse (3.01.14)	331	379	396	421	443	466	493	523	548	585	640	689	0,9990
43	AR Tuapse (13.01.14)	320	374	392	420	443	464	490	521	547	583	635	681	0,9983
44	AR Tuapse (18.01.14)	322	380	399	425	448	471	497	528	554	592	648	698	0,9960
45	AR VDM (13.02.14)	328	383	401	426	445	472	501	534	558	597	655	706	0,9978
46	AR AVD-1 (14.02.14)	363	404	426	458	486	518	540	570	604	646	708	763	0,9975
47	AR Novorossiysk	308	357	385	418	445	470	499	531	556	591	641	683	0,9981
48	AR Novorossiysk (07.14)	272	346	383	431	477	514	554	596	644	702	787	859	0,9990
49	AR from CO El Bouri (07.14)	394	418	429	451	472	492	521	551	589	638	719	796	0,9990
50	AR Kavkaz (08.14)	314	377	395	424	448	474	500	532	560	598	655	705	0,9991
51	AR Taman (08.14)	293	374	403	444	479	513	543	575	611	654	715	766	0,9996
52	AR from Azeri crude oil (08.14)	388	408	421	437	448	463	484	515	538	574	631	684	0,9879
53	AR from LSCO (08.14)	383	404	411	426	443	468	496	530	566	623	721	819	0,9975
54	AR Kavkaz (01.15)	335	379	399	427	451	476	503	534	570	614	682	742	0,9990
55	AR Novorossiysk (01.15)	313	359	387	420	447	471	496	530	552	585	631	670	0,9983
56	AR Offshore Kavkaz (01.15)	337	372	396	431	458	485	515	544	576	615	671	718	0,9988
57	AR Kavkaz (12.14)	325	370	394	425	449	428	501	537	563	602	659	708	0,9976
58	AR Novorossiysk (12.14)	299	351	381	419	446	472	498	532	555	589	636	676	0,9963
59	AR Tuapse (12.14)	334	377	398	434	461	488	518	564	611	673	770	859	0,9966
60	AR Offshore Cherno More (12.14)	333	368	391	423	448	472	497	534	558	595	648	694	0,9977

Table 2 The AEBP distillation data of ASTM D-5236 method of the 60 heavy oils under study

		ASTM D5236 (wt.%)												
№	Samples	IBP	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	R^2
1	AR from AD-5 (22.05.09)	338	364	382	415	447	479	515	555	603	666	764	855	0,9986
2	AR t. „Rirol 5"(03.12.10)	328	370	392	428	460	491	523	558	598	648	723	789	0,9982
3	AR t. "King E" (04.12.10)	312	349	371	408	442	476	512	552	598	657	748	829	0,9994
4	t. „Caspian Mariner" (22.05.13)	332	361	384	425	467	510	559	614	682	772	914	1048	0,9990
5	t. „Vera Cruz" (16.05.13)	305	357	379	412	440	466	493	520	551	589	644	691	0,9983
6	t. „NS Parade" (07.05.13)	310	357	378	411	439	465	492	521	553	593	651	701	0,9965
7	AR Novorossiysk (06.14)	285	345	370	407	438	466	495	525	559	600	659	709	0,9989
8	AR Kerch (06.14)	254	342	373	416	451	483	514	546	581	623	682	732	0,9987
9	AR average sample (06.14)	328	366	387	422	454	486	518	555	596	649	730	801	0,9999
10	AR Kavkaz (02.13)	331	372	392	423	451	476	503	531	563	603	662	714	0,9994
11	AR Novorossiysk (02.13)	310	355	376	409	437	464	492	521	554	595	655	707	0,9974
12	AR Tuapse (02.13)	337	376	395	424	449	473	498	524	554	592	646	694	0,9979
13	AR Temruk (01.13)	327	357	376	406	435	463	493	526	565	615	690	758	0,9967
14	AR Tuapse (01.13)	310	369	391	423	449	473	497	522	549	582	630	670	0,9977
15	AR Kerch (01.13)	331	356	371	398	422	447	474	503	537	582	649	711	0,9983
16	VGO/AGO	332	371	385	404	420	434	447	462	477	496	522	544	0,9986
17	VGO/AGO	351	373	384	401	415	428	442	457	473	494	524	550	0,9969
18	VGO/AGO	259	356	376	401	419	434	449	463	478	495	517	535	0,9855
19	VGO/AGO	334	366	378	395	410	423	436	449	464	482	508	530	0,9946
20	VGO/AGO	336	367	379	397	412	426	440	454	470	490	517	541	0,9930
21	AGO-100	100	347	364	384	397	407	416	425	433	443	455	464	0,9708
22	VGO-100	329	374	389	409	425	439	453	467	482	500	526	546	0,9972
23	AGO-100	200	345	361	378	391	400	409	418	426	435	448	457	0,9705
24	VGO mix sample -11.12-01.13	222	346	368	394	414	430	445	459	474	491	514	531	0,9990
25	AR t. "Ray G" (06.09.13)	296	351	378	418	453	486	520	556	597	647	721	786	0,9993
26	H-Oil (AR) France	300	344	366	401	432	461	492	524	561	608	676	736	0,9995
27	AR Kerch (09.13)	314	344	364	397	428	460	494	532	576	634	722	802	0,9984
28	AR (17.10.13)	326	367	387	417	444	469	495	523	554	593	651	701	0,9983
29	AR (11.10.13)	329	368	387	416	441	466	490	517	547	584	639	687	0,9962
30	AR (01.10.13)	343	371	387	414	438	462	488	516	549	591	654	710	0,9925
31	AR (17.11.13)	322	362	382	412	439	465	491	519	551	591	650	701	0,9966

		ASTM D5236 (wt.%)												
№	Samples	IBP	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	R^2
32	AR (15.11.13)	313	372	394	428	455	481	506	532	561	597	648	690	0,9985
33	AR (06.11.13)	324	360	379	410	439	467	496	527	564	610	679	741	0,9994
34	AR Tuapse (19.12.13)	327	364	383	413	440	465	491	520	552	593	653	705	0,9978
35	AR Kavkaz (22.12.13)	309	363	385	417	445	470	496	523	553	589	641	686	0,9969
36	AR from AD-4 (6.12.12)	346	376	395	428	459	490	523	560	604	660	747	826	0,9991
37	AR from VDM-2 (28.01.14)	324	365	387	423	456	488	521	558	600	654	734	806	0,9992
38	AR RMP (28.01.14)	311	361	384	418	447	475	502	532	565	606	666	717	0,9989
39	AR Kavkaz (01.14)	331	368	387	418	446	473	500	530	565	608	673	730	0,9982
40	AR Novorossiysk (01.14)	339	364	380	410	438	467	498	533	574	628	713	790	0,9905
41	AR Tuapse mix (01.14)	338	369	387	417	444	471	500	531	567	613	682	744	0,9993
42	AR Tuapse (3.01.14)	328	373	394	425	451	477	502	529	560	597	652	699	0,9991
43	AR Tuapse (13.01.14)	331	366	385	415	442	468	495	524	558	600	663	718	0,9993
44	AR Tuapse (18.01.14)	328	369	389	420	447	473	499	528	560	600	658	710	0,9993
45	AR VDM (13.02.14)	328	367	388	420	449	477	506	537	572	617	683	741	0,9995
46	AR AVD-1 (14.02.14)	356	394	416	452	484	517	551	589	632	688	771	846	0,9990
47	AR Novorossiysk (01.14)	310	360	383	418	448	476	505	536	570	613	675	729	0,9993
48	AR Novorossiysk (07.14)	282	349	380	430	472	513	555	599	650	712	805	885	0,9993
49	AR from CO El Bouri (07.14)	376	399	415	442	468	495	523	556	594	644	722	794	0,9978
50	AR Kavkaz (08.14)	325	365	385	417	445	473	501	531	565	608	672	728	0,9986
51	AR Taman (08.14)	290	365	395	439	476	511	545	581	621	670	740	799	0,9994
52	AR from Azeri crude oil (08.14)	379	392	402	422	441	462	486	513	545	589	660	726	0,9987
53	AR from LSCO (08.14)	375	389	400	422	444	468	495	526	565	617	701	782	0,9982
54	AR Kavkaz (01.15)	329	370	391	423	450	477	505	534	568	609	671	725	0,9977
55	AR Novorossiysk (01.15)	321	358	378	411	440	469	499	532	569	617	688	751	0,9989
56	AR Offshore Kavkaz (01.15)	299	365	391	429	461	491	520	550	584	626	685	735	0,9979
57	AR Kavkaz (12.14)	321	367	388	421	450	477	505	534	567	609	669	721	0,9971
58	AR Novorossiysk (12.14)	309	356	378	413	444	473	502	534	570	615	681	738	0,9993
59	AR Tuapse (12.14)	301	339	363	403	441	478	518	562	614	680	782	873	0,9884
60	AR Offshore Cherno More (12.14)	309	366	390	426	456	484	512	542	575	616	674	724	0,9993

Table 3 Difference between AEBP measured by ASTM D-1160 and ASTM D-5236 methods

		ΔT, °C											
№	**Samples**	Δ_{IBP}	ΔT_5	ΔT_{10}	ΔT_{20}	ΔT_{30}	ΔT_{40}	ΔT_{50}	ΔT_{60}	ΔT_{70}	ΔT_{80}	ΔT_{90}	ΔT_{95}
1	AR from AD-5 (22.05.09)	51	19	16	9	4	2	9	8	19	28	43	56
2	AR t. „Rirol 5"(03.12.10)	21	6	5	6	17	18	22	27	36	45	58	68
3	AR t. "King E" (04.12.10)	23	13	0	2	3	11	14	18	40	62	100	138
4	t. „Caspian Mariner" (22.05.13)	32	1	6	0	1	2	5	10	18	30	53	76
5	t. „Vera Cruz" (16.05.13)	9	2	9	8	4	0	0	3	5	10	19	28
6	t. „NS Parade" (07.05.13)	1	4	8	7	2	1	2	4	1	1	4	8
7	AR Novorossiysk (06.14)	8	3	5	2	5	7	9	9	14	18	25	31
8	AR Kerch (06.14)	5	1	1	1	5	7	7	10	13	17	23	29
9	AR average sample (06.14)	22	0	13	3	4	2	2	16	30	50	85	119
10	AR Kavkaz (02.13)	5	2	2	4	0	1	4	9	10	15	23	31
11	AR Novorossiysk (02.13)	6	4	11	8	1	6	5	4	12	19	31	42
12	AR Tuapse (02.13)	6	1	3	3	8	8	5	3	8	10	14	16
13	AR Temruk (01.13)	8	17	19	12	2	4	4	1	16	26	43	59
14	AR Tuapse (01.13)	0	8	7	5	6	5	5	2	4	3	0	3
15	AR Kerch (01.13)	3	4	12	14	12	9	6	7	4	3	16	29
16	VGO/AGO	8	6	11	12	9	9	8	7	4	3	2	6
17	VGO/AGO	23	1	4	4	2	1	4	8	14	22	35	48
18	VGO/AGO	74	18	10	2	9	16	22	28	34	41	50	58
19	VGO/AGO	2	9	10	8	7	1	1	0	0	1	4	6
20	VGO/AGO	7	8	7	4	1	4	7	9	13	15	16	21
21	AGO-100	229	24	17	10	5	2	2	3	3	1	1	2
22	VGO-100	17	13	11	7	5	2	4	5	8	9	1	9
23	AGO-100	127	24	19	16	12	7	2	0	1	2	5	7
24	VGO mix sample -11.12-01.13	117	27	28	23	17	16	12	11	8	6	1	5
25	AR t. "Ray G" (06.09.13)	31	2	8	8	8	7	7	0	7	17	34	50
26	H-Oil (AR) France	9	13	12	8	3	2	6	1	4	7	10	13
27	AR Kerch (09.13)	62	0	8	8	4	2	1	5	12	24	48	71
28	AR (17.10.13)	85	0	4	5	2	1	0	3	4	10	20	29
29	AR (11.10.13)	19	7	2	4	3	2	4	9	3	0	7	14
30	AR (01.10.13)	19	11	11	8	4	0	1	1	12	23	42	61
31	AR (17.11.13)	21	4	6	6	3	2	2	1	7	12	21	30

		ΔT, °C											
№	**Samples**	**Δ_{IBP}**	**ΔT_5**	**ΔT_{10}**	**ΔT_{20}**	**ΔT_{30}**	**ΔT_{40}**	**ΔT_{50}**	**ΔT_{60}**	**ΔT_{70}**	**ΔT_{80}**	**ΔT_{90}**	**ΔT_{95}**
32	AR (15.11.13)	13	7	8	6	2	1	1	5	3	3	4	4
33	AR (06.11.13)	12	3	7	8	6	2	0	1	8	16	30	44
34	AR Tuapse (19.12.13)	5	4	8	6	3	0	0	2	5	10	20	29
35	AR Kavkaz (22.12.13)	19	14	10	4	1	4	3	0	7	9	13	15
36	AR from AD-4 (6.12.12)	3	15	10	14	11	13	13	9	3	6	22	39
37	AR from VDM-2 (28.01.14)	11	3	4	2	2	6	8	15	24	38	61	84
38	AR RMP (28.01.14)	6	1	2	1	1	5	6	4	10	15	24	32
39	AR Kavkaz (01.14)	21	1	3	1	4	7	8	6	18	26	40	54
40	AR Novorossiysk (01.14)	19	8	13	15	9	2	0	2	22	41	75	109
41	AR Tuapse mix (01.14)	11	3	7	6	1	2	5	5	15	25	42	58
42	AR Tuapse (3.01.14)	4	6	2	4	8	11	9	7	12	12	12	10
43	AR Tuapse (13.01.14)	10	7	6	5	1	4	5	3	11	17	27	37
44	AR Tuapse (18.01.14)	6	11	10	5	1	2	2	0	6	8	10	12
45	AR VDM (13.02.14)	0	16	14	6	4	5	5	3	14	20	28	36
46	AR AVD-1 (14.02.14)	7	11	10	6	2	0	11	19	28	42	63	84
47	AR Novorossiysk (01.14)	2	3	2	0	3	6	6	4	15	22	34	47
48	AR Novorossiysk (07.14)	10	2	3	2	5	1	1	3	6	11	18	25
49	AR from CO El Bouri (07.14)	17	18	14	9	4	3	2	4	6	6	3	2
50	AR Kavkaz (08.14)	11	12	10	6	3	1	0	1	5	10	16	22
51	AR Taman (08.14)	3	9	8	4	2	2	2	6	10	16	25	33
52	AR from Azeri crude oil (08.14)	9	16	19	15	6	1	2	3	8	16	29	42
53	AR from LSCO (08.14)	8	15	11	4	1	0	2	4	1	6	20	38
54	AR Kavkaz (01.15)	6	8	9	5	1	1	2	0	2	5	11	17
55	AR Novorossiysk (01.15)	8	1	9	9	7	2	3	2	17	32	57	81
56	AR Offshore Kavkaz (01.15)	38	7	5	1	3	5	5	7	9	11	14	17
57	AR Kavkaz (12.14)	5	3	6	3	1	49	4	3	4	6	10	13
58	AR Novorossiysk (12.14)	10	5	3	6	2	1	4	2	15	26	45	62
59	AR Tuapse (12.14)	33	37	35	31	21	10	0	2	2	7	12	14
60	AR Offshore Cherno More (12.14)	24	1	1	3	9	12	15	9	17	20	26	30
AAD		**23.0**	**8.3**	**8.9**	**6.8**	**4.8**	**5.3**	**5.2**	**5.9**	**11.1**	**16.9**	**27.0**	**37.6**
AAD (5-80%)		**8.1**											

In order to improve the accuracy of conversion of ASTM D-1160 into ASTM D-5236 we modified the method of Edmister-Okamoto in the following form:

$$D5236(100\%) = \text{ASTM D1160}(80\%) + F_{10} \quad (1)$$
$$D5236(90\%) = \text{ASTM D1160}(70\%) + F_{9} \quad (2)$$
$$D5236(80\%) = \text{ASTM D1160}(60\%) + F_{8} \quad (3)$$
$$\text{D5236}(70\%) = \text{ASTM D1160}(50\%) + F_{7} \quad (4)$$
$$D5236(60\%) = \text{ASTM D1160}(40\%) + F_{6} \quad (5)$$
$$\text{D5236}(40\%) = \text{ASTM D1160}(60\%) - F_{4} \quad (6)$$
$$\text{D5236}(30\%) = \text{ASTM D1160}(50\%) - F_{3} \quad (7)$$
$$\text{D5236}(20\%) = \text{ASTM D1160}(40\%) - F_{2} \quad (8)$$
$$\text{D5236}(10\%) = \text{ASTM D1160}(30\%) - F_{1} \quad (9)$$
$$\text{D5236}(0\%) = \text{ASTM D1160}(10\%) - F_{0} \quad (10)$$
$$\text{D5236}(50\%) = \text{ASTM D1160}(50\%), \quad (11)$$

where functions F are given in terms of temperature difference in the ASTM D 1160

$$F_{<50\%;>50\%}=A+B(\Delta T_i)-C(\Delta T_i)^2+D(\Delta T_i)^3 \quad (12)$$
$$F_{0\%}=A(\Delta T_i)-B(\Delta T_0)^2+C(\Delta T_0)^3 \quad (13)$$

where ΔT_i is calculated for each per cent as follows

$$\Delta T_{0\%} = \text{ASTM D1160}(10\%) - \text{ASTM D1160}(0\%) \quad (14)$$
$$\Delta T_{10\%} = \text{ASTM D1160}(30\%) - \text{ASTM D1160}(10\%) \quad (15)$$
$$\Delta T_{20\%} = \text{ASTM D1160}(40\%) - \text{ASTM D1160}(20\%) \quad (16)$$
$$\Delta T_{30\%} = \text{ASTM D1160}(50\%) - \text{ASTM D1160}(30\%) \quad (17)$$
$$\Delta T_{40\%} = \text{ASTM D1160}(60\%) - \text{ASTM D1160}(40\%) \quad (18)$$
$$\Delta T_{60\%} = \text{ASTM D1160}(60\%) - \text{ASTM D1160}(40\%) \quad (19)$$
$$\Delta T_{70\%} = \text{ASTM D1160}(70\%) - \text{ASTM D1160}(50\%) \quad (20)$$
$$\Delta T_{80\%} = \text{ASTM D1160}(80\%) - \text{ASTM D1160}(60\%) \quad (21)$$

After regression following values for the coefficients A, B, C, and D of equations 12 and 13 were obtained (Table 4)

Table 4 New coefficients of the equations 12 and 13 for the Edmister-Okamoto method

Coefficients in eqs 12 and 13	>50%	<50%	0%
A	0.290277	0.562367	2.898921
B	1.108612	1.476152	0.049172
C	0.000000	0.013280	0.000267
D	0.000006	0.000093	

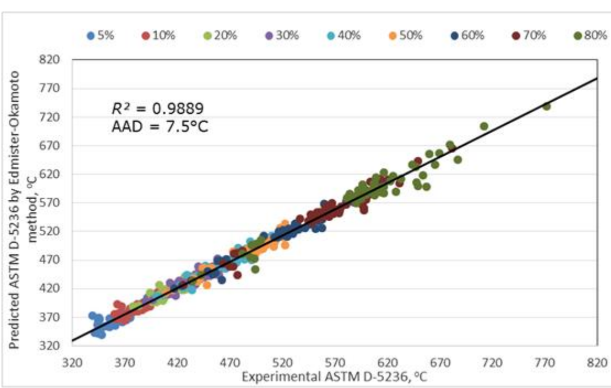

Figure 1 Comparison of experimental (ASTM-D5236) and predicted by Edmister-Okamoto method (with original coefficients) boiling point distribution using ASTM D-1160 data

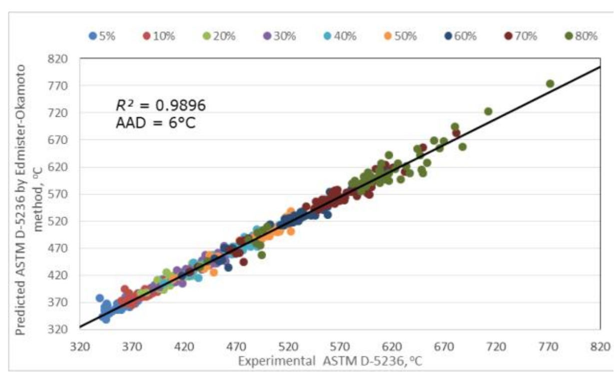

Figure 2 Comparison of experimental (ASTM-D5236) and predicted by Edmister-Okamoto method (with new coefficients) boiling point distribution distribution using ASTM D-1160 data

Figure 2 presents the agreement between measured and converted by the modified method of Edmister-Okamoto. The average absolute deviation (AAD) of this method is 6°C, which is better than the AAD of the original method of Edmister-Okamoto.

3.2 Application of Daubert methodology to convert ASTM D-1160 to ASTM D-5236

Methodology of Daubert [15-16] is widely known scheme for distillation interconversions. What is more, his methodology was proven to be the second most precise method to convert ASTM D-86 into TBP for oil fractions [17]. That is why we applied Daubert's methodology to convert ASTM D-1160 heavy oil distillation data to ASTM D-5236 using the following calculations:

$$D5236(50\%) = A_{50\%}(D1160(50\%))^{B50\%} \quad (24)$$

where D5236 (50%) - distillation temperature at 50 wt% distilled,°C; D1160 (50%) - observed distillation temperature at 50 vol%,°C.

$$(\Delta D5236)_i = A_i(\Delta D1160)^{Bi} \quad (25)$$

$(\Delta D5236)_i$ - difference in D5236 distillation temperatures between two cut points, °C
$(\Delta D1160)_i$ - observed difference in ASTM D1160 distillation temperatures between two cut points, °C.

For the data set in Tables 1 and 2 following coefficients of equations 24 and 25 were obtained (Table 5).

Table 5 A and B coefficients of equations 24 and 25 for the Daubert method

№	cut-point range	A	B
1	95%-90%	1.59568	0.93285
2	90%-80%	1.64044	0.92373
3	80%-70%	1.63540	0.91102
4	70%-60%	1.65568	0.89681
5	60%-50%	1.70185	0.87931
6	50%-40%	1.78677	0.85608
7	40%-30%	1.94537	0.82255
8	30%-20%	2.29439	0.76730
9	20%-10%	3.30692	0.65983
10	10%-00%	21.82135	0.25643
11	50%	0.92607	1.01308

D-5236 temperatures were calculated using following equations:

$$D5236(0\%) = D5236(50\%) - (\Delta D5236)_6 - (\Delta D5236)_7 - (\Delta D5236)_8 - (\Delta D5236)_9 - (\Delta D5236)_{10} \quad (26)$$
$$D5236(10\%) = D5236(50\%) - (\Delta D5236)_6 - (\Delta D5236)_7 - (\Delta D5236)_8 - (\Delta D5236)_9 \quad (27)$$
$$D5236(20\%) = D5236(50\%) - (\Delta D5236)_6 - (\Delta D5236)_7 - (\Delta D5236)_8 \quad (28)$$
$$D5236(30\%) = D5236(50\%) - (\Delta D5236)_6 - (\Delta D5236)_7 \quad (29)$$
$$D5236(40\%) = D5236(50\%) - (\Delta D5236)_6 \quad (30)$$
$$D5236(60\%) = D5236(50\%) + (\Delta D5236)_5 \quad (31)$$
$$D5236(70\%) = D5236(50\%) + (\Delta D5236)_5 + (\Delta D5236)_4 \quad (32)$$
$$D5236(80\%) = D5236(50\%) + (\Delta D5236)_5 + (\Delta D5236)_4 + (\Delta D5236)_3 \quad (33)$$
$$D5236(90\%) = D5236(50\%) + (\Delta D5236)_5 + (\Delta D5236)_4 + (\Delta D5236)_3 + (\Delta D5236)_2 \quad (34)$$
$$D5236(95\%) = D5236(50\%) + (\Delta D5236)_5 + (\Delta D5236)_4 + (\Delta D5236)_3 + (\Delta D5236)_2 + (\Delta D5236)_1 \quad (35)$$

Agreement between estimated and experimental data is depicted in Figure 3.

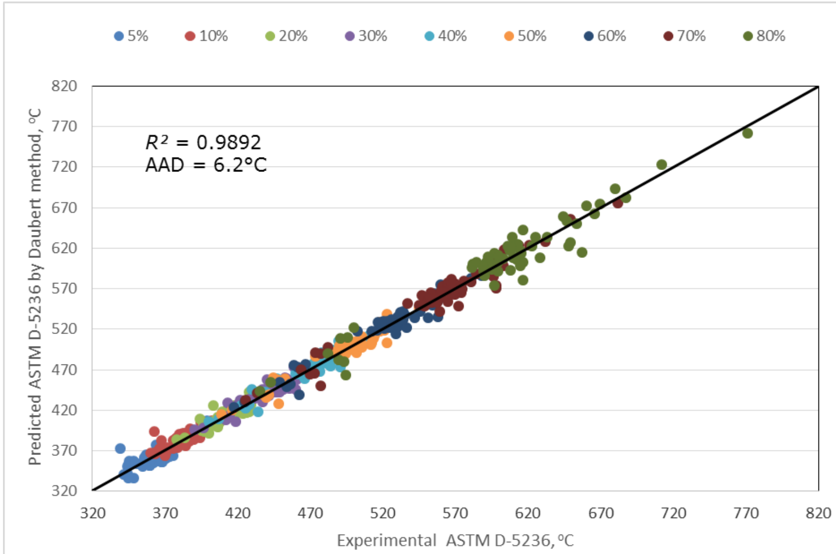

Figure 3 Comparison of experimental and predicted (by Daubert method) temperatures for ASTM D-5236 using ASTM D-1160 data

The average absolute deviation of this method is 6.2°C, which is better than the original method of Edmister-Okamoto and slightly worse than the AAD of the modified method of Edmister-Okamoto.

3.3 Application of artificial neural networks (ANN) to convert ASTM D-1160 to ASTM D-5236

Taking into account our earlier positive results achieved by application of artificial neural networks (ANN) to simulate and model oil properties [18], we decided to apply ANN for conversion of ASTM D-1160 to ASTM D-5236. The way of processing data by the ANN method is described in [18]. Agreement between predicted by ANN method and measured ASTM D-5236 distillation data is given in Figure 4. These data indicate a relatively high dispersion of the predicted values and this method turned out to be the least accurate (the lowest R^2) among all studied in this work procedures for conversions of heavy oil distillation data from ASTM D-1160 into ASTM D-5236.

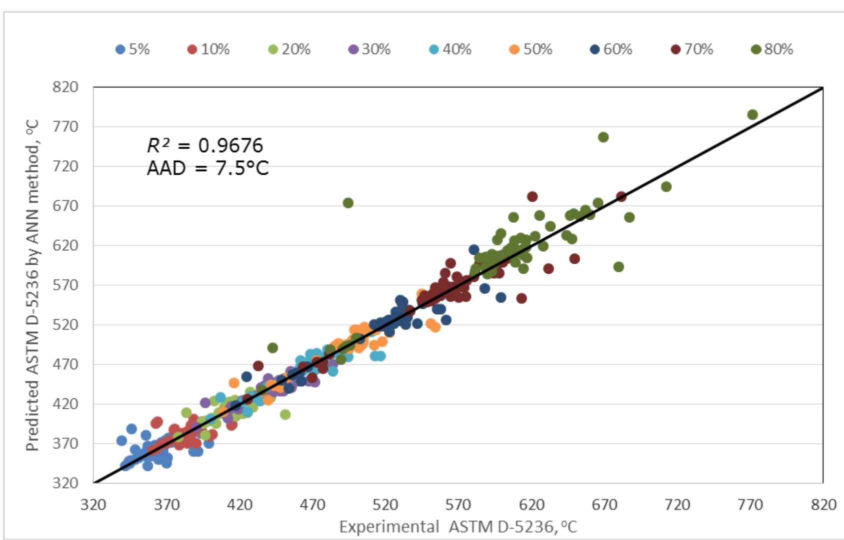

Figure 4 Comparison of experimental and predicted (by ANN) temperatures for ASTM D-5236 using ASTM D-1160 data.

3.4 Application of a method developed at Lukoil Neftochim Bourgas to convert ASTM D-1160 to ASTM D-5236

Based on the data in Tables 1 and 2 and application of linear regression in the LNB Research laboratory, following equations were established:

$$D5236(5\%) = 123{,}819 + 0{,}6472 * (D1160(5\%)) \quad (36)$$
$$D5236(10\%) = 76{,}292 + 0{,}7834 * (D1160(10\%)) \quad (37)$$
$$D5236(20\%) = 14{,}751 + 0{,}9507 * (D1160(20\%)) \quad (38)$$
$$D5236(30\%) = -0{,}2459 + 0{,}9966 * (D1160(30\%)) \quad (39)$$
$$D5236(40\%) = 35{,}959 + 0{,}9272 * (D1160(40\%)) \quad (40)$$
$$D5236(50\%) = -0{,}2302 + 1{,}0059 * (D1160(50\%)) \quad (41)$$
$$D5236(60\%) = -5{,}17605 + 1{,}01565 * \left(D1160(60\%)\right) \quad (42)$$
$$D5236(70\%) = -11{,}0791 + 1{,}03811 * (D1160(70\%)) \quad (43)$$
$$D5236(80\%) = -13{,}9023 + 1{,}05086 * (D1160(80\%)) \quad (44)$$

Agreement between measured and estimated by equations 36-44 is depicted in Figure 5. It is evident from these data that the LNB method achieves the lowest AAD (5.9°C) and almost the highest squared correlation coefficient (R^2 = 0.9893) among all studied in this work methods.

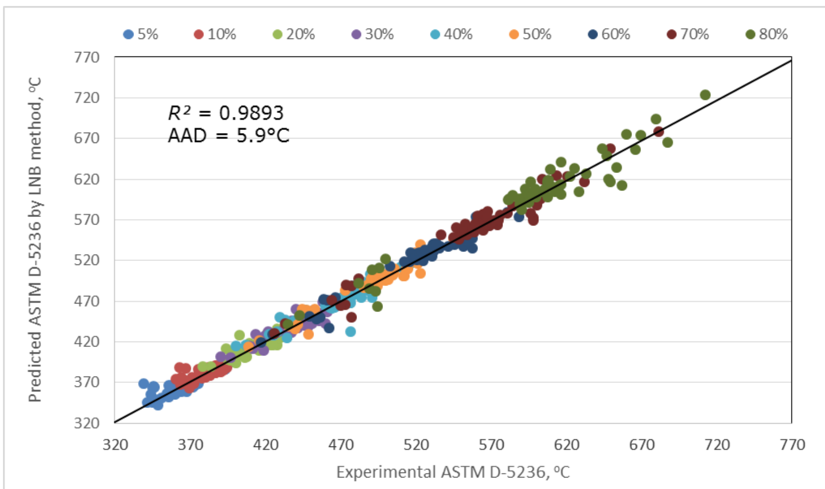

Figure 5 Comparison of experimental and predicted (by LNB) temperatures for ASTM D-5236 using ASTM D-1160 data.

3.5 Evaluation of the precision of the methods for conversion of ASTM D-1160 to ASTM D-5236

The predictive capabilities of the studied in this research methods to convert heavy oil ASTM D-1160 to ASTM D-5236 distillation data were classified as proposed by Sanchez *et al.* [10] according to their statistical indicators and the results are shown in Table 6. Standard deviation (SD) values, which are calculated by eq. 45 and AAD (eq. 47) both are considered the main criteria for establishing the ranking. The correlation coefficient (R^2), slope and intercept were also considered.

$$\mathrm{SD} = \sqrt{\frac{\mathrm{RSS}}{\mathrm{n}-2}} \quad \text{Eq. 45}$$

where n is the number of observations and RSS is the residual sum of squares, defined in eq. 46

$$RSS = \sum_{i=1}^{540} \left(D5236measured_i - D5236calculated_i\right)^2 \quad \text{Eq. 46}$$

where D5236 $measured_i$ is the boiling point determined according to ASTM D-5236 and D5236 $calculated_i$ is the boiling point, calculated by one of the studied five models. Direct comparison of boiling point of evaporate at the same per cent between ASTM D-1160 and ASTM D-5236 is also given in Table 6. Standard deviation values for all models range from 8.5 to 15.1

$$AAD = \frac{1}{n}\sum_{i=1}^{n}\left|D5236measured_i - D5236calculated_i\right| \quad \text{Eq. 47}$$

where n= number of observation.

Table 6 Comparison of the accuracy of the investigated methods to convert ASTM D-1160 distillation data to ASTM D-5236

Model	R^2	Slope	Intercept	AAD	AAD based ranking	SD	2SD	SD based ranking	Obser-vations
D1160→D5236	0.9869	1.090	-42.0	8.14	6	11.7	23.4	5	540
Edmister-Okamoto with original coefficients	0.9889	0.9190	34.8	7.51	5	11.0	22	4	540
Edmister-Okamoto with modified coefficients	0.9896	0.9600	18.3	5.97	2	8.8	17.6	3	540
Daubert method	0.9892	0.9970	1.9	6.18	3	8.6	17.2	2	540
ANN	0.9676	0.9999	-0.7	7.49	4	15.1	30.2	6	540
LNB	0.9893	0.9893	5.0	5.86	1	8.5	17.0	1	540
Repeatability of D-5236 method	5.14								
Reproducibility of D-5236 method	11.69								

As can be seen from Table 6, the LNB method converts the heavy oil distillation data ASTM D-1160 to ASTM D-5236 with the least error exemplified by the lowest absolute average deviation (AAD) and the lowest standard deviation (SD). The methods of Edmister-Okamoto with modified coefficients and of Daubert convert the heavy oil distillation data ASTM D-1160 to ASTM D-5236 with slightly higher AAD and SD and comparatively lower coefficients of correlation (0.9896 and 0.9892 respectively) than the LNB method. Other methods such as Edmister-Okamoto with original coefficients, ANN and simple comparison of D1160 and D5236 were proven to be the least accurate methods and thereby the least appropriate ways for petroleum fraction distillation interconversion. Assuming that the error of prediction of distillation data of ASTMD-1160 to ASTM D-5236 is equivalent to 2 times the standard deviation [19] one can see that all methods of conversion of the heavy oil distillation data are less accurate than the measurement according to ASTM D-5236 (2SD is bigger than reproducibility of ASTM D-5236 method). Nevertheless the use of the three methods: LNB, Daubert's, and Edmister-Okamoto with modified coefficients improve the conversion of heavy oil distillation data ASTM D-1160 to ASTM D-5236 and are better from the direct comparison of D-1160 with D-5236 distillation data. Therefore they can be employed in the refinery practice for quick characterization of heavy oil distillation data which are the closest to the TBP method.

4. Conclusions

60 heavy oils have been characterized for their distillation charactersistics by ASTM D-5236 and ASTM D-1160 methods for 80 working days in the Research laboratory of LUKOIL Neftochim Burgas. Six approaches were investigated to convert the heavy oil distillation data from ASTM D-1160 to ASTM D-5236, such as the simple comparison of ASTM D-1160 and ASTM D-5236, the method of Edmister-Okamoto with original coefficients, as well as the one with modified coefficients, Daubert, artificial neural networks and LNB methods. All of them may be classified according to standard deviation in the following order: the most precise method

of conversion is the LNB method. It provides the lowest SD and the highest correlation coefficient, followed by the Daubert method. The method of Edmister-Okamoto with modified coefficients and the one with original coefficients were found to be on the third and the forth places respectively in relation to their reliability. Simple comparison of ASTM D-1160 and ASTM D-5236 and the ANN method were proved to have the highest standard deviations and the lowest correlation coefficients.

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