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Estimation of the Full-Range Distillation Curve of Libyan Crude Oils Based on ASTM D–86 and TBP Distillation Data

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ABSTRACT
TBP (True Boiling Point) analysis is considered a reliable method for characterizing crude oil and its fractions. It determines boiling point distribution using the ASTM (American Society for Testing and Materials) D–2892 standard instrument. This method is expensive and time–consuming, making it unsuitable for quick estimations of crude oil distillation characteristics. An alternative, ASTM D–86, is a faster and easier method for analyzing crude oil and converting its data to TBP data. In this paper, fourteen samples of Libyan crude oil were characterized by using ASTM D–86 and TBP distillation. The study tested the Riazi–Dabuert method for converting ASTM D–86 to TBP distillation data across the entire distillation curve. The Riazi distribution model accurately predicted the full–range distillation curve, with an R^2 value greater than 0.99.

KEYWORDS: *Crude oil, characterization, distillation, true boiling point, ASTM D–2892, ASTM D–86*

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1. INTRODUCTION

Crude oil contains a mixture of hydrocarbons as well as other compounds such as sulfur, nitrogen and oxygen compounds, with a volatility varying widely depending on the components of the crude oil. The price of a barrel of oil is highly dependent on its quality. The quality and value of crude oil depend significantly on its distillation curves. Distillation curves provide a wide range of information about crude oil and its fractions [1]. The distillation (or boiling) curve is one of the useful parameters used to measure a crude oil mixture. The distillation curve is a graphical depiction of the boiling temperature of crude oil plotted against the volume fraction distilled, which is usually expressed as a cumulative percent of the total volume [2]. True Boiling Point (TBP) distillation curve is one of the most common experimental procedures used to verify and test the properties of crude oil, usually for marketing and refining purposes [3]. The results obtained from TBP distillation are very close to the results obtained via real distillation or industrial distillation. The experimental determination of TBP distillation curve is expensive and time consuming, however, requiring use of expensive laboratory equipment. A single TBP distillation can take up to 48 hour, which makes it impractical for daily monitoring of refinery crude quality [1,4].

Therefore, it is necessary to have other alternative methods that are less expensive and faster to convert ASTM data into TBP information. Some of these methods have been developed to convert American Society for Testing and Materials (ASTM) methods into TBP used for crude oil and its fractions [5]. ASTM D 86 is a fast and a low cost method for distillation of crude oil and its fractions at atmospheric pressure. This determines the boiling range characteristics of crude oil and its fractions with a boiling point between 20 and 400ºC. When the ASTM D 86 is used to analyze crude oil samples, the recommended final boiling point of the distillate is not higher than 300ºC. Thus one needs knowledge of a boiling point distribution model that would be able to describe the full distillation curve for crude oil. A full–range distillation curve is created from an incomplete distillation data set. Specifically, the full–range true boiling point distillation curve for the crude oil is created from only the atmospheric distillation part of the crude oil distillation analysis [1].

Distribution characteristics of crude oil and its fractions, that is measured by ASTM D 2892 and ASTM D 86, can be accurately described by Riazi's boiling point distribution model. With this approach, the crude oil curve TBP can be created in 45 min instead of the 48 hr typically necessary of crude oil TBP analysis [6]. The Riazi's model proposed in this study can be used in refineries that frequently run on different crudes creating the full crude oil TBP curve from the simple and quick ASTM D-86 analysis of the distillation characteristics of the crude fraction boiling up to 300ºC.

This study examines the validity of using the Riazi model to distribute boiling point data of distillation of fourteen types of Libyan crude oil. The aim is to study the conversion of ASTM D–86 data into TBP distillation data and, based on this investigate, to propose other methods that is capable of creating the full–range crude TBP from ASTM D-86 data.

2. Materials and methods:

This assay is a part of a series of crude oil reports have been prepared for crude oil marketing department of Libyan National Oil Corporation. A total of 60 Liters of crude oil samples were collected from different sources in Libya according to standard method ASTM D4057. The samples were analyzed using well–recognized standard procedures given in ASTM, IP and UOP methods. The crude oil was distilled using a batch fractionation unit made according to ASTM D-2892 method and ASTM D-86 methods. The crude oil was distilled under atmospheric pressure and further distilled to obtain distillate fractions. Distillate fractions corresponding to true boiling points up to 550^{+0}C were collected. The results of TBP distillation of the studied crude oil samples are presented in table 2, which shows ASTM D–2892 distillation of fourteen Libya crude oil samples. The distillation of the fourteen crude oil samples up to 300ºC was performed in accordance with ASTM D-86. The results of the distillation are given in table 3, which shows ASTM D–86 distillation of fourteen Libya crude oil samples.

3. Calculation

3.1. Prediction of complete distillation curves:

The distribution function for the boiling point of crude oil was proposed by Riazi, it is presented by the following equation:

$$\frac{T - T_0}{T_0} = \left[\frac{A}{B}\ln\left(\frac{1}{1-x}\right)\right]^{\frac{1}{B}} \quad (1)$$

Where;

T is the temperature on the distillation curve in Kelvin.

T_0 is the initial boiling point in Kelvin, which is determined experimentally.

x is the volume or weight fraction of the mixture distilled.

A and B are constants and can be determined by using the following linear form:

$$Y = C_1 + C_2 X \quad (2)$$

Where,

$$Y = \ln\left[\frac{(T - T_0)}{T_0}\right] \quad \text{and} \quad X = \ln\ln\left[\frac{1}{(1-x)}\right]$$

C_1 and C_2 are determined from linear regression of Y versus X.

Then, A and B are determined from C_1 and C_2 as,

$$B = \frac{1}{C_2} \text{ and } A = B\exp(C_1 B)$$

For explanation, data for atmospheric distillation Brega crude oil are presented in table 1. Due to known limitation of the equipment, the distillation was performed at temperature not higher than 550ºC.

Table 1: Distillation characteristics of Brega crude oil.

Cut Temperature (ºC)	Yield		Cumulative Yield		Specific Gravity @ 60/60ºF
	wt.%	vol.%	wt.%	vol.%	0.5556
Condensate	1.84	2.69	1.84	2.69	0.6432
C5 - 70	6.13	7.74	7.97	10.43	0.6861
70 - 90	3.42	3.85	11.39	14.28	0.7215
90 - 110	3.54	3.90	14.93	18.18	0.7375
110 - 130	4.42	4.87	19.35	23.05	0.7462
130 - 150	4.35	4.73	23.70	27.78	0.7628
150 - 175	5.22	5.56	28.92	33.34	0.7837
175 - 195	4.80	4.97	33.72	38.31	0.7912
195 - 215	3.82	3.92	37.54	42.24	0.7997

215 - 235	3.60	3.66	41.14	45.89	0.8089
235 - 255	3.94	3.96	45.08	49.85	0.8175
255 - 275	3.82	3.80	48.90	53.64	0.8233
275 - 295	4.00	3.95	52.90	57.59	0.8304
295 - 315	3.36	3.29	56.26	60.88	0.8392
315 - 335	3.58	3.46	59.84	64.34	0.8456
335 - 350	2.55	2.45	62.39	66.79	0.8612
350 - 370	3.35	3.16	65.74	69.95	0.8787
370 - 400	3.62	3.35	69.36	73.30	0.8857
400 - 440	4.87	4.47	74.23	77.76	0.9007
440 - 460	3.14	2.83	77.37	80.59	0.9096
460 - 480	3.35	2.99	80.72	83.58	0.9149
480 - 500	2.42	2.15	83.14	85.73	0.9215
500 - 520	1.92	1.69	85.06	87.42	0.9334
520 - 550	2.80	2.44	87.86	89.86	0.9775
550+	12.14	10.09	100.00	100.00	0.5556

Figure 1 presents graph of equation 1 applied to the data of table 1. From this, data it is clear that equation 1 completely descries the boiling point distribution of Brega crude oil ($R^2 = 0.9998$). Considering the validity of equation 1 for the full–range, the TBP distillation curve can be created (figure 2) based on the data of A and B extracted from figure 1.

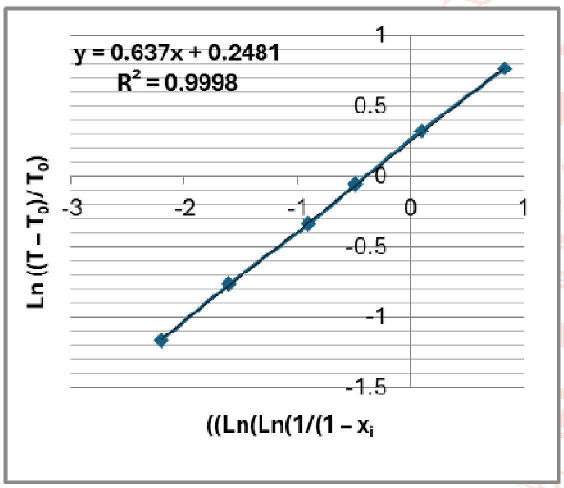

Figure 1: application of the Riazi's model (equation 1) for approximation of TBP distillation curve of Brega crude oil.

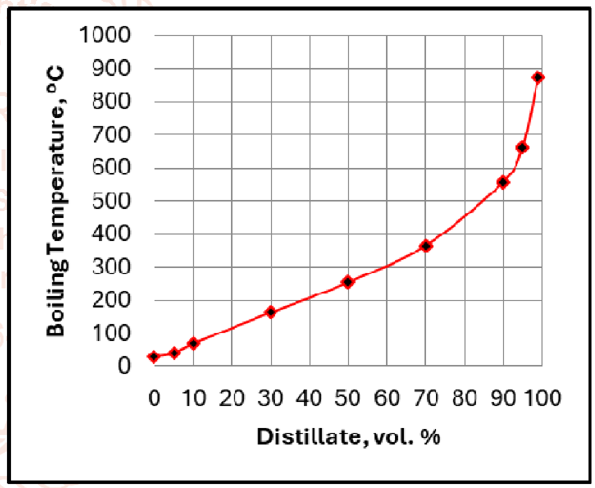

Figure 2: Full–range TBP distillation curve of Brega crude oil obtained by the use of the Riazi's model (equation 1).

3.2. Interconversion distillation data

When ASTM D–86 distillation is available and the desired distillation is TBP, Riazi–Dauberts method can be used for interconversion of ASTM D–86 into TBP distillation is given by the following equation [7]:

$$TBP = a\,(ASTM\ D\text{–}86)^{b} \qquad (3)$$

Where TBP and ASTM temperatures are for the same vol.% distilled and are in Kelvin. Constants a and b are given in table 1.

Table 1: Equation constants for equation 3.

Vol.%	a	b	ASTM D–86 range, °C
0	0.9177	1.0019	20 – 320
10	0.5564	1.0900	35 – 305
30	0.7617	1.0425	50 – 315
50	0.9013	1.0176	55 – 320
70	0.8821	1.0226	65 – 330
90	0.9552	1.0110	75 – 345
95	0.8177	1.0355	75 – 400

Table 2: TBP (ASTM D–2892) distillation of fourteen crude oil samples.

Crude Oil Sample	ASTM D–2892, vol. %						
	IBP–70	70 – 110	110 –175	175 –235	235 –350	350 –550	550+
Amna	6.10	5.90	10.7	9.90	20.3	25.8	21.3
Brega	10.4	7.80	15.2	12.6	20.9	23.1	10.1
Bouri	2.80	5.10	7.00	7.70	15.3	38.2	23.8
El Feel	6.80	7.40	16.9	14.0	23.7	26.6	4.80
El Mabrouk	6.20	6.90	14.0	13.0	24.0	27.3	8.60
El Wafa	21.4	14.2	18.9	10.0	11.8	19.1	4.60
Hamada	5.90	8.00	15.5	12.7	22.2	25.3	10.4
Mellitah Blend	10.7	9.10	17.1	13.4	18.6	24.3	4.50
Messla	8.00	6.70	11.2	9.30	20.1	34.4	10.2
Sarir–Massla Blend	8.70	6.80	11.1	9.80	20.0	29.4	14.3
Sarir	7.40	6.40	11.4	9.00	20.3	28.7	16.3
Sedra	7.50	6.00	11.7	10.5	21.4	30.2	12.7
Sertica	5.00	5.40	10.3	9.00	22.0	28.4	20.0
Zuetina	8.10	9.50	16.6	12.1	20.6	22.8	10.3

Table 3: ASTM D–86 distillation of fourteen crude oil samples.

Crude Oil Sample	ASTM D–86, vol.%						
	IBP, ºC	5 vol.% $T_{5\%}$, ºC	10 vol.% $T_{10\%}$, ºC	30 vol.% $T_{30\%}$, ºC	50 vol.% $T_{50\%}$, ºC	70 vol.% $T_{70\%}$, ºC	EB
Amna	50	108	133	246	344	368	371
Brega	40	80	99	165	255	315	317
El Bouri	65	110	150	280	352	-	360
El Feel	50	94	111	174	260	-	315
El Mabrouk	55	99	120	196	283	332	340
El Wafa	38	48	55	89	131	218	327
Hamada	54	98	120	190	283	-	331
Mellitah Blend	47	76	94	152	240	333	335
Messla	52	79	109	215	312	-	336
Sarir-Messla Blend	49	89	115	175	313	335	337
Sarir	51	91	113	172	314	-	337
Sedra	42	84	110	201	29	-	339
Sertica	52	79	98	169	268	321	324
Zuetina	55	104	125	198	283	338	341

Table 4: TBP (ASTM D–2892) distillation data of crude oils under study.

Crude Oil Sample	Volume Percent, (%)								R^2	A	B
	5	10	30	50	70	90	95	99			
Amna	59	98	218	332	469	700	823	1071	0.9997	3.7368	1.6493
Brega	39	68	162	254	365	558	662	874	0.9998	2.3175	1.5699
El Bouri	103	151	281	392	515	708	806	994	0.9904	7.3462	2.0717
El Feel	58	89	177	252	342	438	555	696	0.9988	2.8843	1.9339
El Mabrouk	60	94	190	276	375	535	618	780	0.9997	3.2437	1.8737
El Wafa	12	29	96	169	268	454	561	791	0.9907	1.1494	1.2710
Hamada	59	92	189	275	375	536	620	785	0.9963	3.1747	1.8529
Mellitah	40	68	152	231	326	485	570	739	0.9953	2.1461	1.6790
Messla	52	86	192	291	410	610	716	829	0.9897	3.0833	1.6703
Sarir-Messla Blend	43	76	185	294	428	662	790	1053	0.9983	3.2405	1.6121
Sarir	52	88	201	309	440	564	784	1027	0.9960	2.7675	1.5160
Sedra	54	89	197	298	418	620	726	941	0.9972	3.2275	1.6835
Sertica	69	109	229	339	467	679	789	1009	0.9993	4.2919	1.7702
Zuetina	46	76	169	256	360	535	627	812	0.9956	2.5419	1.6872

Table 5: ASTM D–86 distillation data of crude oils under study.

Crude Oil Sample	Volume Percent, (%)								R^2	A	B
	5	10	30	50	70	90	95	99			
Amna	100	138	237	316	400	527	589	707	0.9726	6.0064	2.4125
Brega	65	95	174	240	312	423	478	584	0.9903	2.9252	2.2007
El Bouri	108	152	268	362	464	620	697	843	0.9921	7.4946	2.2889
El Feel	45	75	171	263	372	558	657	857	0.9995	2.5665	1.6431
El Mabrouk	86	119	203	269	339	445	496	592	0.9929	4.2583	2.4716
El Wafa	74	111	210	295	391	540	616	763	0.9523	4.1115	2.0475
Hamada	84	117	203	272	345	456	510	613	0.9819	4.1839	2.3929
Mellitah	63	91	166	227	294	397	449	546	0.9735	2.6371	2.2321
Messla	71	109	216	311	419	593	682	857	0.9999	4.1292	1.9128
Sarir-Messla Blend	80	109	180	234	292	376	416	492	0.9117	3.2561	2.6455
Sarir	76	109	198	271	351	474	536	653	0.9435	3.7975	2.2143
Sedra	73	109	207	291	385	534	609	754	0.9971	3.9880	2.0425
Sertica	65	96	180	250	328	449	510	627	0.9886	3.0872	2.1272
Zuetina	90	123	207	272	341	444	494	587	0.9936	4.5157	2.5381

Table 6: ASTM D–86 conversion to TBP distillation data of crude oils under study.

Crude Oil Sample	Volume Percent, (%)								R^2	A	B
	5	10	30	50	70	90	95	99			
Amna	82	122	229	320	421	581	662	818	0.9711	4.8655	2.0653
Brega	50	80	166	244	334	481	558	709	0.9949	2.5268	1.8265
El Bouri	91	136	262	372	496	693	794	990	0.9896	6.0692	1.9736
El Feel	58	90	178	255	342	480	551	689	0.9907	2.9311	1.9584
El Mabrouk	69	102	193	271	358	494	563	696	0.9941	3.5030	2.0648
El Wafa	16	32	87	141	208	326	390	523	0.9903	0.9657	1.5108
Hamada	65	99	195	278	372	523	599	749	0.9926	3.4606	1.9611
Mellitah	43	71	158	240	336	498	583	754	0.9935	2.2912	1.6990
Messla	54	91	208	321	458	692	818	1074	0.9995	3.3862	1.5995
Sarir-Messla Blend	61	94	189	273	370	525	605	761	0.9617	3.2277	1.8986
Sarir	59	92	187	272	370	529	611	772	0.9593	3.1424	1.8660
Sedra	53	90	206	319	457	692	819	1077	0.9954	3.3313	1.5891
Sertica	49	79	169	251	347	506	589	753	0.9917	2.5817	1.7724
Zuetina	73	107	198	274	359	490	555	681	0.9959	3.7408	2.1380

Summary of results for predicted distillation curves versus experimental data are showing in figure 3. As can be seen from the results presented in both tables 4, 5, 6 and figure 3, a good prediction of the entire distillation curve is possible through use of only three distillation data points.

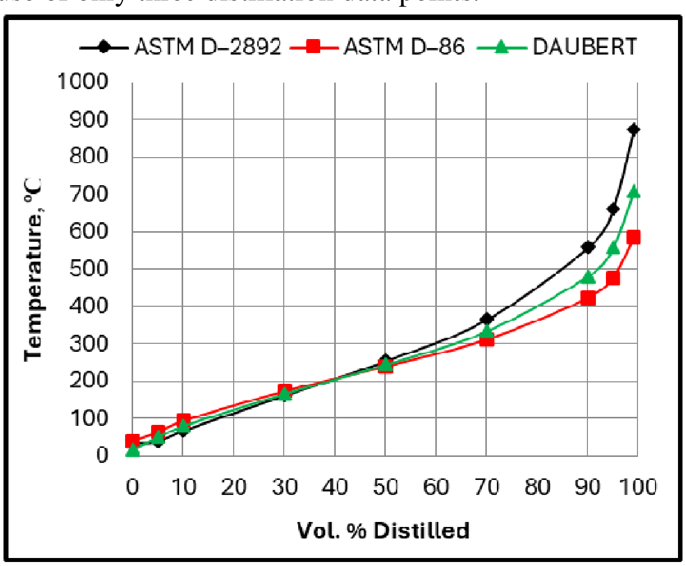

Figure 3: Prediction of full–range distillation curves for the Brega crude oil.

Results and Discussions

Table 4 shows TBP distillation data for fourteen Libyan crude oil samples, estimated on the base of the parameters A and B computed by equation 1. Assuming that T_0 is the initial boiling point of isobutane ($T_0 = -11.7^0C$), which is supposed to be the lightest compound in a crude oil [7]. The squared correlation coefficient R^2 for all Libyan crude oil samples except that of the Messla crude oil is above 0.99. For the Messla crude the $R^2 = 0.9897$ which is also high enough. This explains that the Riazi model describes very well the full–range TBP distillation curve for Libyan crude oils.

Table 5 shows ASTM D-86 distillation data of the fourteen Libyan crude oil samples estimated on the base of the parameters A and B computed by equation 1. The squared correlation coefficient R^2 was high enough, ranging from 0.9117 for Sarir–Messla crude oil to 0.9999 for Messla crude oil. This indicates that the Riazi model also describes well the full–range ASTM D-86 distillation curve of crude oil. It may be concluded that by the use of calculated A and B and the initial boiling point the distillation curve could be safely extrapolated to 99 vol.%. In other words by applying the Riazi model from ASTM D-86 distillation data of a crude oil boiling up to 300ºC it can be estimated the amount of compounds boiling above this temperature and build the full range distillation curve.

To examine the correlations available in previous studies for converting of ASTM D-86 into TBP distillation. There is number of empirical approaches for converting ASTM D–86 distillations to true boiling point (TBP) distillations. In this study, Riazi–Daubert correlation was used. Table 5 shows data of TBP distillation of the fourteen crude oil samples in volume percent. The squared correlation coefficient R^2 for this data set is above 0.9617, its high enough.

Conclusion

In this, study it was found that the boiling point distribution of fourteen samples of Libyan crude oil measured by ASTM D–86 and TBP distillation is approximated by Riazi model.

The Riazi model allows the prediction of a full–range distillation curve from incomplete distillation data, regardless of the method used to measure distillation characteristics. On this base the entire distillation curve can be created by the ASTM D–86 method for measuring of the boiling point up to 300ºC. An attempt to apply the Riazi–Dauberts method for converting ASTM D–86 into TBP of the investigated crude oils was found to be unsuccessful.

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