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METHOD TO PREDICT COMPLETE PRODUCT FRACTION TBP DISTRIBUTIONS FROM THAT OF THE WHOLE CRUDE USING REGRESSION TECHNIQUES: APPLIED TO SHALE OIL

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Abstract

The aim of this work is to develop and validate a calculation method to predict the complete True Boiling Pont (TBP) temperature distributions of a set of oil product fractions, given only its whole oil TBP curve. This potentially reduces cost and time in conducting multiple TBP experiments for fractions. An operations research based regression approach is followed. For fractions from five crudes, it is verified that the TBP temperatures of the middle sections of the curves, from 20% to 80% fraction volume% range is in common with that of the corresponding whole crude, with average error of only 3%. This data is then fit to Riazi model, and predictions for the light and heavy curved ends of the fraction TBP curves are made by applying two methods: linear regressions and non-linear regression. The results show accurate predictions at light ends using linear regression, whereas heavy ends in comparison show lesser fit with Riazi model. At heavy ends non-linear regression performs significantly better than linear regression. The procedure is extended to a shale oil to demonstrate its utility for heavier oils where TBP experimentation is cumbersome.

Keywords: *True boiling point; Oil fractions; Riazi model; Shale oil; Regression; Operations research.*

1. Introduction

True Boiling Point (TBP) experiment (ASTM- D2892) provides the TBP temperature distribution for whole crudes and its product fractions, which is the single most important data for crude characterization and refinery design. TBP analysis is a laboratory batch distillation process which gives fractions of sufficient volume to be used to determine weight average boiling point, specific gravity, molecular weight and other properties of crude oil and its product fractions [1]. The utility of the resulting TBP data cannot be over emphasized. In general, it provides the physical and chemical properties of the crude oil and helps to determine the anticipated product yield and the quality of product fractions. It provides an estimate of the maximum separation between the consecutive product fractions that constitute the oil. It helps to determine the pricing of different crude oils based on the impurities present or other undesirable properties of the crude [2-3].

Riazi modeled the TBP temperature distribution for whole crudes and product fractions by the following highly non-linear equation [4]:

$$\frac{T_i-T_o}{T_o} = [\frac{A_T}{B_T} ln(\frac{1}{1-x_i})]^{1/B_T} \quad (1)$$

So, $$T_i = T_o[\frac{A_T}{B_T} ln(\frac{1}{1-x_i})]^{1/B_T} + T_o \quad (2)$$

More recently the Riazi model was used in the following linearized form to predict the TBP temperature distribution at the heavy end of the TBP curve when it was difficult to obtain the complete 100 volume % distillation data for the whole crude [5].

$$Y = C_1 + C_2 X \quad (3)$$

where: $X = ln\left[ln(\frac{1}{1-x_i})\right]$; (4)

$$Y = ln(\frac{T_i - T_o}{T_o}); \quad (5)$$

$$B_T = {}^{1}/_{C_2}; \quad A_T = B_T.exp(C_1.B_T) \quad (6)$$

where: T_o is the initial TBP temperature in K; T_i is the TBP temperature in K after *i* volume% distillation; x_i is the volume% distilled/100.

In this work, the applicability of Riazi model to product fractions was assumed. A data driven regression approach from operations research was adopted to develop and validate the proposed calculation method [6]. Regression was applied to model the relationship between independent variable (fraction volume % distilled) and dependent variable (TBP temperature). With the only input as the TBP curve of whole oil, a calculation method is developed to predict the individual fraction TBP curves which constitute the oil.

2. Method and validation

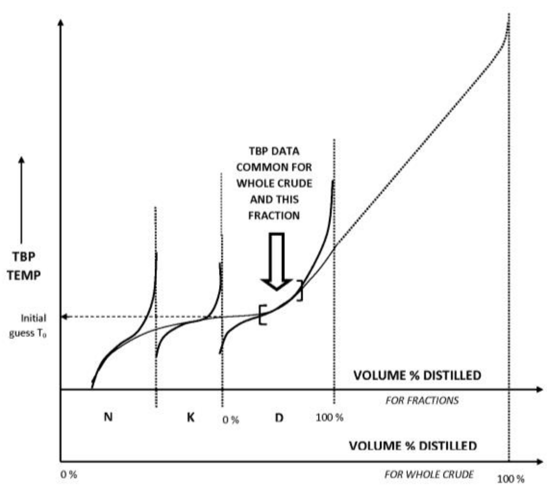

Figure 1. Nature of TBP curves for whole crude its product fractions

From theory, the middle sections of the TBP curves for individual product fractions superimpose on the whole crude TBP curve [2] as shown in Figure1. Deviations are only observed at the light end and heavy end of the fraction TBP curves. To observe this, consider the *y*-axis (volume % distilled) for fraction TBP curves, which differs in scale from that of the whole crude, as shown for example for diesel (D) fraction in Figure 1. The fractions TBP data in common with that of the whole crude is pointed out in Figure 1, for fraction D.

To determine the extent of commonality, the plots of TBP experimental data (ASTM D-2892) of each whole crude with corresponding fractions, as reported by Dicho Stratiev *et al.* [5], were superimposed and examined.

Specifically, the more valued fractions of heavy naphtha, 110-180°C (N); kerosene, 180-240 °C (K); and diesel 240-360 °C (D), were chosen for all the reported crudes, namely CPC, Kirkuk, Oil Blend, REBCO, and SLCO (only data from K and D known). From all the plots it was observed that at least 20% to 80% (fraction volume % range) had their TBP temperatures in common with the whole crude, with a maximum absolute error of 8.3%, and an average absolute error of approximately 3%. This implies that *at the very least*, the middle 60% of the fraction TBP curves are reasonably well approximated by the whole crude TBP curve. Hence this common middle section of the fraction TBP curve can be assumed from whole crude TBP curve, and the remainder of the fraction TBP curves on the light and heavy ends, i.e. 0 to 20% and 80% to 99% respectively, can be constructed by assuming the Riazi distribution model for the fraction TBP curve as a whole. Thereby the set of TBP curves for all the fractions of an oil sample can be predicted, as long as the TBP curve for the whole oil is known. This reduces expensive or time consuming experimental runs (the number of which equals the number of fractions) or at least provides a useful approximation.

The calculation method is formalized as follows:

1. Experimental TBP curve of the given oil is plotted (If required, the TBP data for the entire range may be extrapolated using Riazi model for the whole oil [7]).
2. The cut temperatures are used to demarcate the required fractions on the whole crude TBP curve. A second *x*-axis for fractions volume%, with a scale from 0 to 100% for *each* fraction, is set up (The dual *x*-axis is shown in Figure 1)

3. The TBP temperatures in the range 20% to 80% (fraction volume %) are tabulated for each fraction in the form (x_i ,T_i).
4. The fraction TBP curve in the range 0 to 20% and 80% to 99%, are predicted using linearized Riazi model (Equation 3) or alternatively non-linear regression of Riazi model directly (Equation 1).

For the purpose of a more thorough validation, predictions using both liner regression (LR) and non-linear regression (NLR) were made by employing MS Office Excel 16.

Method for LR: seven fraction data points (xi ,T_i) were input for (i=20, 30, 40 to 80 vol%). The corresponding (X,Y) were calculated using Equations 4 and 5 respectively, and were fit to a straight line equation, which was subsequently used to extrapolate T_i at light end (vol%=10e-3, 5, 10) and heavy end (vol%=90, 95, 99) by using Equations 4 and 5 in reverse. Note that the nature of Equation 3 does not allow T_i to be extrapolated at exactly 0 and 100 vol%.

Method for NLR: Excel add-in solver (under Data tab, Analysis section) was used. The input (xi ,T_i) was the same as for LR. Three decision variables: T_o, A_T and B_T were considered for optimization, so their Initial guess values were input. Initial guess T_o was always taken to be the beginning temperature of the whole crude TBP cut for the given fraction, since this temperature was in the vicinity of fraction T_o and clearly defined (guess T_o is shown for fraction D in Figure 1). Initial guesses for A_T and B_T were always simply taken to be 1. Equation 2 was implemented using the initial guess data to calculate values of T_i (for i=20, 30, 40 to 80 vol%). These predicted values of T_i were compared to the input values of T_i, and for each pair the squared error were calculated. Their sum was then minimized as the objective by the iterative solver, which did so by optimizing the decision variables T_o, A_T and B_T. Given constraints: $A_T>0$ and $B_T>0$, to avoid 0 or ∞ results for LHS of Equation 1 during iteration. The solver was run several times, and it was ensured that no further change in decision variables was observed. For the same inputs and initial guesses, solver repeatability was verified. It was verified that the dependence of T_o, A_T and B_T on initial guess values was not significant, as long as the guess values were reasonably near those suggested. The resulting optimized T_o, A_T and B_T values were then used in Equation 2 to predict T_i, for vol% = 5, 10, 90, 95, 99.

3. Results and discussion

Method validation: For the seven input points (xi,T_i), the R^2 values for the linearized Riazi model, were found on average to be 0.9911 for all 14 fractions, with worst and best of 0.9211 and 0.9999 respectively. This high goodness of fit formed the basis to predict remaining values using linear Riazi model. The term 'linear regression results' might be misleading, since parameters of the non-linear Riazi equation are still ultimately determined, only that a linearized *form* of Riazi equation is used. Only for validation calculations, since the experimental TBP curve for fractions was known, the required input points were taken from the same, instead of from whole crude (as outlined in method, point No. (3)). In the latter case, R^2 would be expected to reduce slightly, due to the 3% approximation error previously mentioned.

Same input was given for NLR. Here R^2 has no significance, so the goodness of fit was indicated by the value of the minimum sum of squared errors (MSSE) after solver optimization, which was at best 0.8654 and at worst 8.5261. The average was 4.2129. The lack of upper bound makes MSSE difficult to evaluate, but values reasonably near zero, as is the case here, are usually taken to indicate a good fit. Both LR and NLR predictions represent the same Riazi model, the main difference being in the optimization techniques used to carry out the regression, which were the Sum of Squared Errors (for LR) and Generalized Reduced Gradient (for NLR). Appendix Table A1 reports A_T and B_T values for both LR and NLR. After establishing a good fit of the LR and NLR results to Riazi model, their comparison with experimental data was made, as shown in Figures 2 to 6. Appendix Tables A2.1-A2.5 and Tables A3.1-A3.5 provide the predicted values, and errors with respect to experimental data respectively.

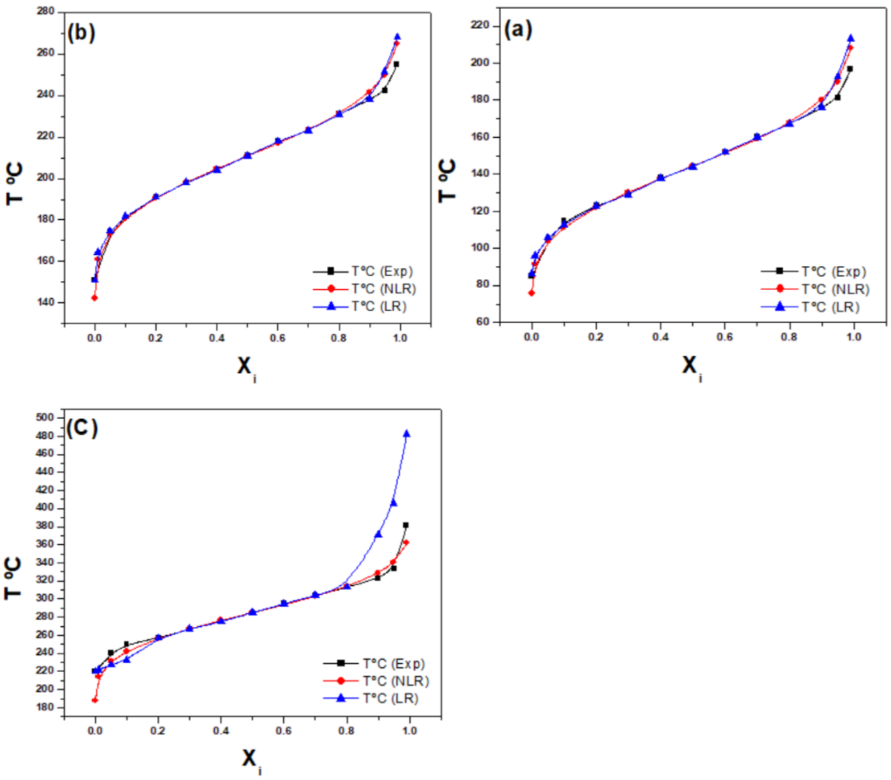

Figure 2. Comparison of experimental TBP curve with Riazi model linear and non-linear regression predictions at light and heavy ends, for CPC crude fractions of (a) Naphtha (b) Kerosene and (c) Diesel

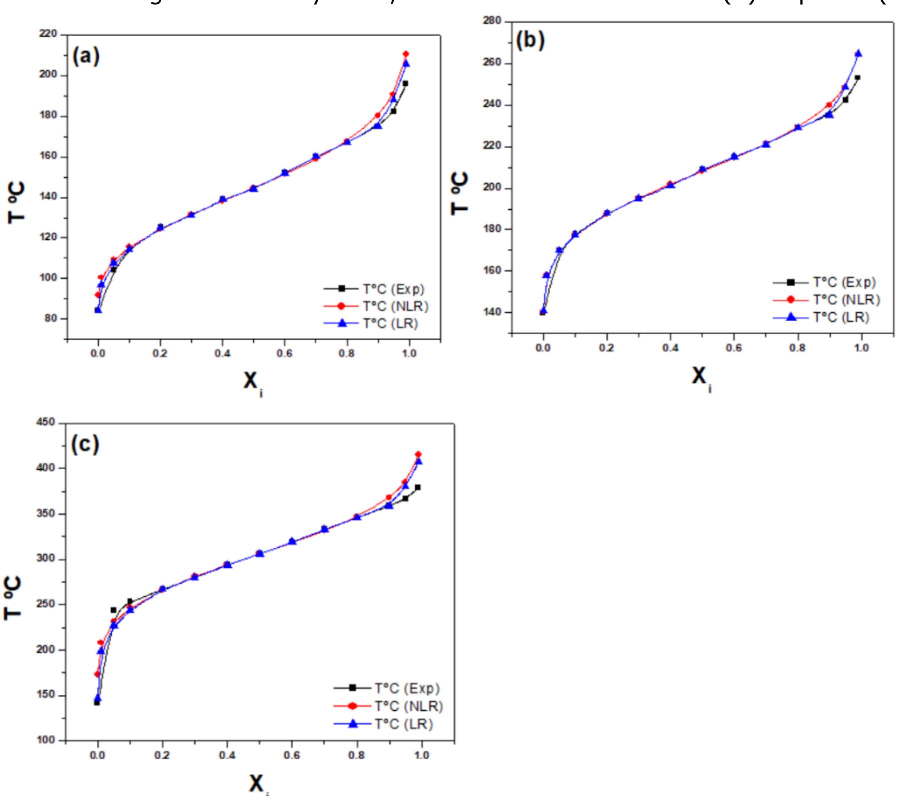

Figure 3. Comparison of experimental TBP curve with Riazi model linear and non-linear regression predictions at the light and heavy ends, for Kirkuk crude fractions of (a) Naphtha (b) Kerosene and (c) Diesel

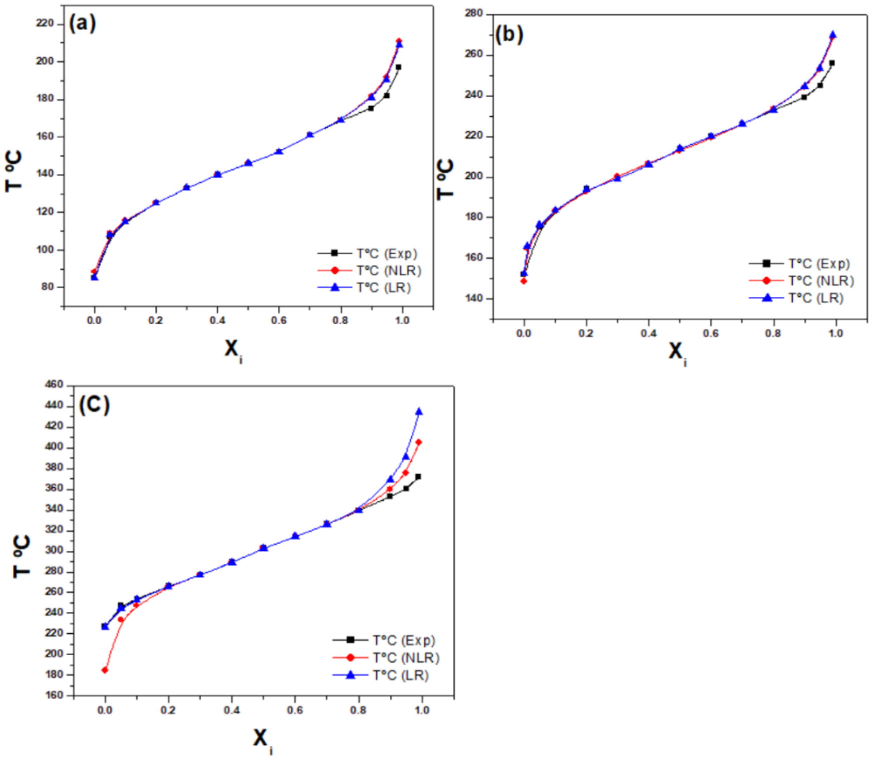

Figure 4. Comparison of experimental TBP curve with Riazi model linear and non-linear regression predictions at light and heavy ends, for Oil Blend crude fractions of (a) Naphtha (b) Kerosene and (c) Diesel

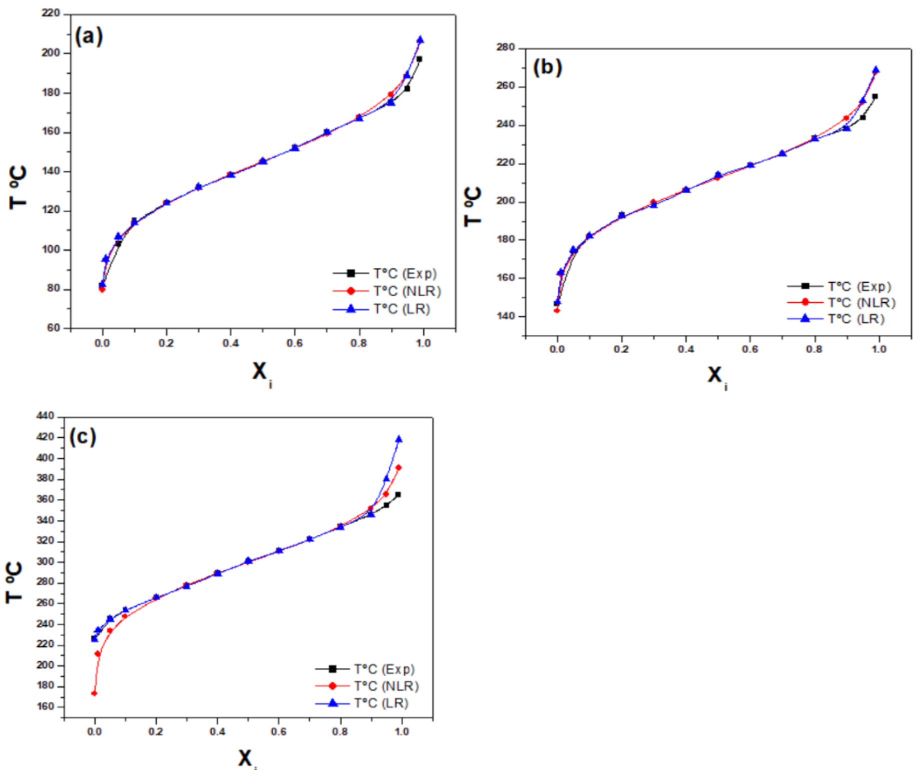

Figure 5. Comparison of experimental TBP curve with Riazi model linear and non-linear regression predictions at the light and heavy ends, for REBCO crude fractions of (a) Naphtha (b) Kerosene and (c) Diesel

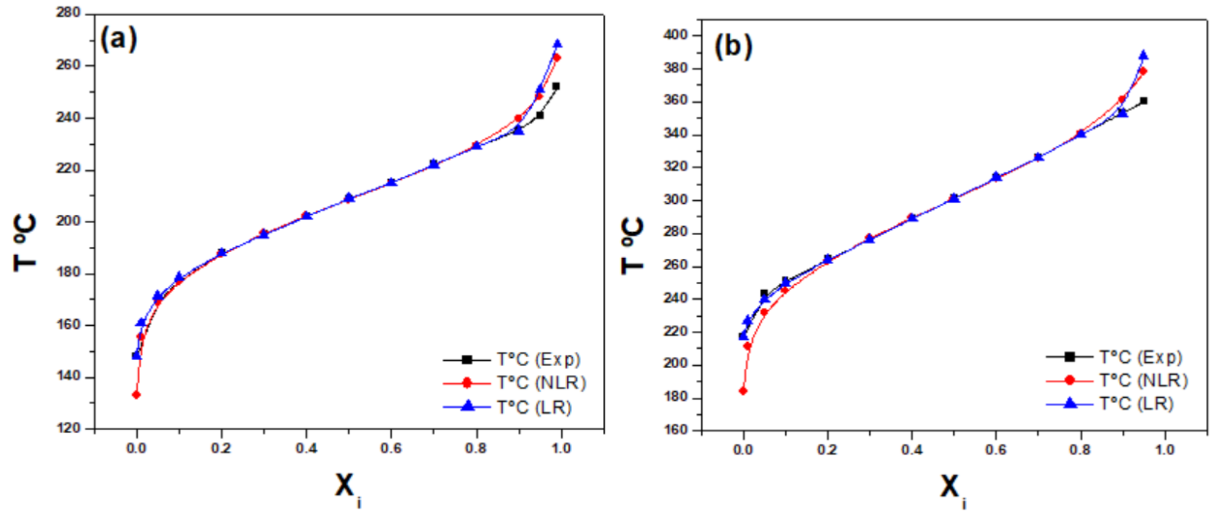

Figure 6. Comparison of experimental TBP curve with Riazi model linear and non-linear regression predictions at the light and heavy ends, for SLCO crude fractions of (a) Kerosene (b) Diesel

For the light ends: comparison of LR and NLR predictions with the experimental data shows that LR predicts very well as seen by the low average error in Table 3. In general, NLR under predicts, though sometimes it performs the same as LR, as in the case of Kirkuk fractions. Further LR also predicts T_o very well as seen by the <1% error for most of the fractions in Appendix TA4, and the small average error magnitude % in Table 1. NLR almost always under predicts T_o with under prediction error % of -5.0962, and absolute error % given in Table 1.

For the heavy ends: comparison of LR and NLR predictions with the experimental data shows that both always over predict, though NLR over predicts to a comparatively lesser extent as seen by the average absolute error % (Table 1). The poorer performance of both LR and NLR at heavy ends suggests that in general, Riazi model fits experimental curves better at the lighter ends than at heavier ends. The reason for this is simply the asymptotic nature of the Riazi equation towards 100 volume%, which incidentally does not allow calculation of discrete TBP temperature at this point. Hence in the plots, 99% was taken instead of 100% for both LR and NLR. Experimental data simply does not reflect this asymptotic behavior because even the last drop of material in the TBP flask does manifest a finite TBP temperature. Experimental TBP curves at the ends are comparatively flatter when compared to predictions, as seen for all fractions in Figures 2 to 6.

Table 1. Comparison of Linear Regression and Non-Linear Regression errors with respect to experimental at both light and heavy ends.

Average absolute error % at	Linear regression	Non-Linear regression
Light ends	1.2717	4.6614
Heavy ends	6.4076	4.0907
T_o	0.6700	10.0796
$T_{99\%}$	9.4153	6.2513

Method application to shale oil: Since TBP curves of heavier oils differ from conventional oils only in having steeper slopes for the middle section, it would be reasonable to extend the method to the heavier oils such as shale oil. This would be very beneficial since TBP experiments of heavier oils are difficult to carry out due to high TBP temperatures which cause cracking problems. Also heavy residual oils were reported to obey Riazi model [5], and since TBP curves for fractions are small-scale prototypes to their whole crude TBP distribution, Riazi model may hence be reasonably extended to heavy or unconventional oil fractions as well. Figure 7 demonstrates the results of extracting fractions data from that of a whole oil TBP which in this case was selected to be shale oil produced by indirect Paraho Process from Tipton Member Green River Formation shale, Wyoming (Mol. wt =290, API=26) [8].

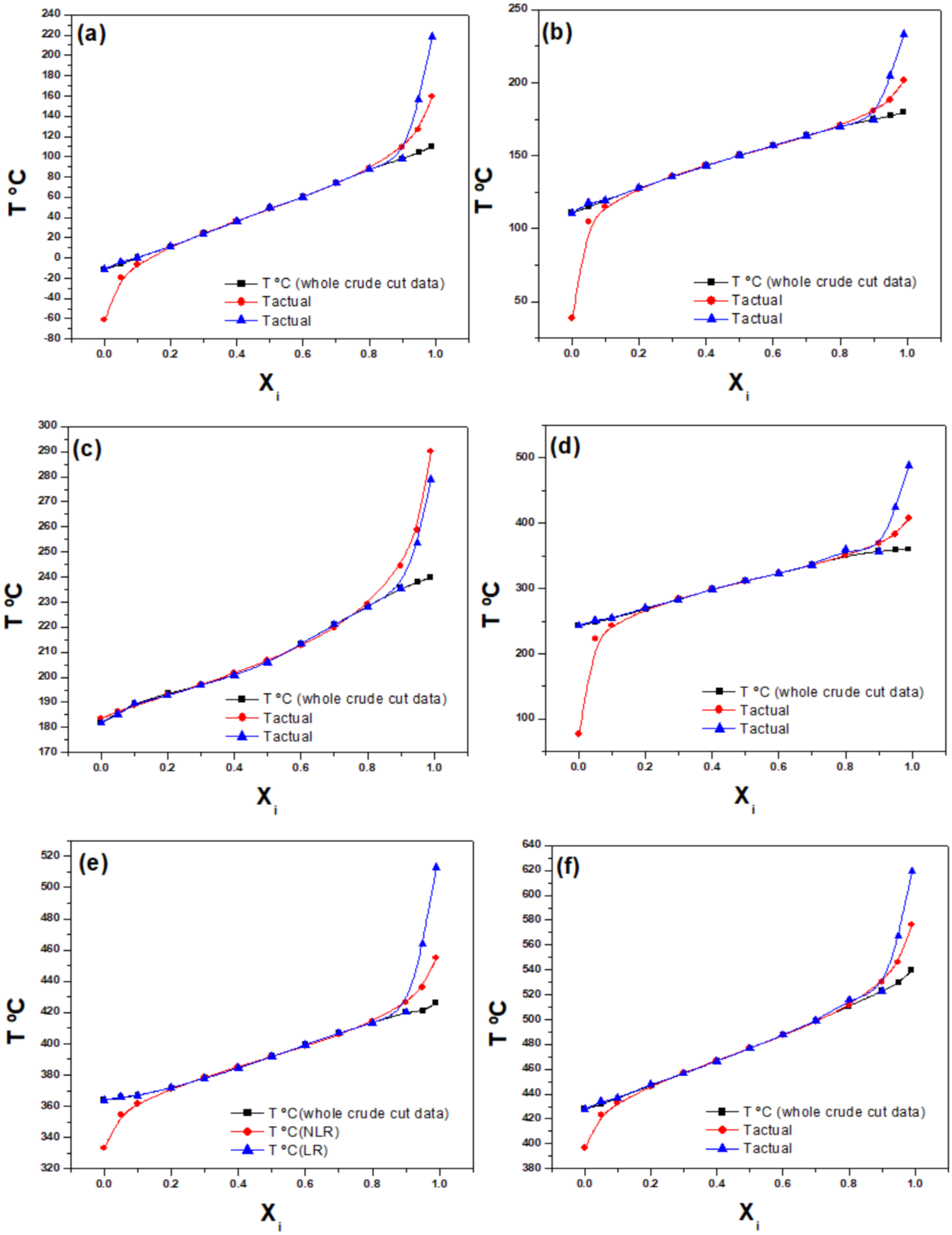

Figure 7. Riazi model linear and non-linear regression predictions for shale oil fractions of (a) Light Naphtha (b) Naphtha (c) Kerosene (d) Diesel (e) Gas oil (f) Vacuum Gas Oil.

This shale was designated a western reference shale oil by the Department of Energy. The cut temperatures were the same as mentioned previously with the addition of gas oil, 360-540°C; and vacuum gas oil, 540°C+. Similar results were obtained as before, with NLR over predicting with respect to LR at the lighter ends and LR over predicting with respect to NLR at the heavier ends. These observations seem to again confirm that LR gives better results at light ends, and NLR gives better results at heavier ends

4. Conclusion

A calculation procedure assuming Riazi model was developed to predict the complete TBP curves of oil fractions, including end points, given only the whole crude TBP curve. Predictions for fourteen fractions belonging to five different crude oils; showed that Riazi model fit the experimental data better at the light ends than at the heavy ends. Accurate predictions were obtained at light ends when LR was used. At heavy ends, the error was on average 5.25% for both LR and NLR, with NLR performing better. Hence LR is recommended at light end and NLR at heavy end for the fraction TBP predictions using Riazi model. The procedure was also applied to a reference shale oil to demonstrate the utility of reducing TBP experiments for heavy oil fractions.

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Appendix

Table A1. Riazi model parameters for product fractions obtained from linear and non-linear regression

Crude oil	Fractions	A_T		B_T	
		NLR	LR	NLR	LR
CPC	Naphtha	0.0381	0.0425	2.8933	2.428953
	Kerosene	0.0132	0.0162	3.2552	2.82167
	Diesel	0.0298	0.1234	3.2646	1.2530
REBCO	Naphtha	0.0327	0.0333	2.8692	2.7716
	Kerosene	0.0139	0.0151	3.2490	3.0525
	Diesel	0.0608	0.0656	3.5156	1.9581
SLCO	Kerosene	0.0143	0.0190	3.4861	2.7518
	Diesel	0.0806	0.0800	2.8962	2.0247
Oil Blend	Naphtha	0.0358	0.0340	2.5164	2.6824
	Kerosene	0.0143	0.0156	3.0471	2.8752
	Diesel	0.0728	0.0797	2.9930	1.8228
Kirkuk	Naphtha	0.0366	0.03172	2.3460	2.7285
	Kerosene	0.0155	0.01552	3.1419	3.1575
	Diesel	0.0997	0.1464	3.1775	3.9604

Table A2.1. Error with respect to experimental for predicted TBP Temperatures of CPC crude fractions

Vol %	NLR (error %)			LR (error %)		
	Naphtha	Kerosene	Diesel	Naphtha	Kerosene	Diesel
0%	-10.9246	-5.7065	-14.7998	1.8744	0	0
5%	-0.2980	-0.4895	-3.5664	1.9072	0.4483	-5.3140
10%	-2.9630	-0.1313	-3.0818	-1.8462	0.3815	-6.8515
90%	2.2166	1.4179	1.7170	3.2328	1.9188	14.8314
95%	4.8739	3.1858	2.2196	6.4305	3.9328	21.9740
99%	5.6371	3.8689	-5.0067	8.2698	5.1231	26.6132

Table A2.2. Error with respect to experimental for predicted TBP Temperatures of Kirkuk crude fractions

Vol %	NLR (error %)			LR (error %)		
	Naphtha	Kerosene	Diesel	Naphtha	Kerosene	Diesel
0%	9.1792	0.2333	21.6073	0.5235	0.6898	3.8843
5%	4.9680	-0.0168	-5.0890	3.2837	-0.0237	-6.8480
10%	0.3785	-0.2223	-2.5462	-0.4488	-0.2074	-3.4422
90%	2.8889	2.0507	2.4222	1.9476	2.1054	1.6378
95%	4.6936	2.6905	4.7776	3.2786	2.7415	3.5947
99%	7.3587	4.4972	9.556	4.9557	4.5387	7.5224

Table A2.3. Error with respect to experimental for predicted TBP Temperatures of Oil Blend crude fractions

Vol %	NLR (error %)			LR (error %)		
	Naphtha	Kerosene	Diesel	Naphtha	Kerosene	Diesel
0%	4.0527	-2.2133	-18.6171	0.4789	0.3734	0.0202
5%	1.8213	0.5944	-5.3556	1.1260	0.9532	-0.9684
10%	0.6427	0.1872	-2.7155	0.3021	0.3747	-0.3407
90%	3.6725	2.1507	1.8452	3.3316	2.3558	4.5137
95%	5.3172	3.1652	4.3266	4.7848	3.4729	8.6047
99%	7.06307	4.8963	8.8868	6.1356	5.4232	16.8283

Table A2.4. Error with respect to experimental for predicted TBP Temperatures of REBCO crude fractions

Vol %	NLR (error %)			LR (error %)		
	Naphtha	Kerosene	Diesel	Naphtha	Kerosene	Diesel
0%	-2.5731	-2.6216	-23.3156	0.6012	0.5441	0.0336
5%	3.1614	0.1665	-4.9664	3.5680	0.5309	-0.2710
10%	-1.0653	0.0076	-2.5496	-0.8759	0.1922	-0.0304
90%	2.3848	2.3448	1.6647	2.4883	2.5630	4.3108
95%	3.6869	3.3009	2.9945	3.8742	3.6239	7.1329
99%	4.7229	4.8883	7.0279	5.0846	5.4326	14.5806

Table A2.5. Error with respect to experimental for predicted TBP Temperatures of SLCO crude fractions

Vol %	NLR (error %)			LR (error %)		
	Naphtha	Kerosene	Diesel	Naphtha	Kerosene	Diesel
0%	-	-10.1198	-15.1506	-	0.3081	0.0498
5%	-	-0.6748	-4.6384	-	0.8674	-1.2673
10%	-	0.0398	-2.3264	-	0.8437	-0.5156
90%	-	2.0110	2.3169	-	2.7825	3.9789
95%	-	2.9429	5.0055	-	4.1185	7.7421
99%	-	4.4437	9.6659	-	6.4815	14.8261

Table A3.1. Riazi model predicted TBP temperatures of CPC crude fractions

Vol%	Naphtha			Kerosene			Diesel		
	Exp.	NLR	LR	Exp.	NLR	LR	Exp.	NLR	LR
0%	85	75.71	86.59	151	142.38	151	220	187.44	220
5%	104	103.69	105.98	174	173.14	174.78	240	231.44	227.24
10%	115	111.59	112.87	181	180.76	181.69	250	242.29	232.87
90%	176	179.90	181.68	238	241.37	242.56	323	328.54	370.90
95%	181	189.82	192.63	242	249.70	251.51	333	340.39	406.17
99%	197	208.10	213.29	255	264.86	268.06	381	361.92	482.39

Table A3.2. Riazi model predicted TBP temperatures of Kirkuk crude fractions

Vol%	Naphtha			Kerosene			Diesel		
	Exp.	NLR	LR	Exp.	NLR	LR	Exp.	NLR	LR
0%	84	91.71	84.43	140	140.32	140.96	142	172.68	147.51
5%	104	109.16	107.41	170	169.97	169.95	244	231.58	227.29
10%	115	115.43	114.48	178	177.60	177.63	253	246.55	244.29
90%	175	180.05	178.40	235	239.81	239.94	359	367.69	364.87
95%	182	190.54	187.96	242	248.51	248.63	367	384.53	380.19
99%	196	210.42	205.71	253	264.37	264.48	379	415.23	407.51

Table A3.3 Riazi model predicted TBP Temperatures of Oil Blend crude fractions

Vol%	Naphtha			Kerosene			Diesel		
	Exp.	NLR	LR	Exp.	NLR	LR	Exp.	NLR	LR
0%	85	88.44	85.40	152	148.63	152.56	227	184.73	227.04
5%	107	108.94	108.20	175	176.04	176.66	247	233.77	244.60
10%	115	115.73	115.34	183	183.34	183.68	254	247.10	253.13
90%	175	181.42	180.83	239	244.14	244.63	353	359.51	368.93
95%	182	191.67	190.70	245	252.75	253.50	360	375.57	390.97
99%	197	210.91	209.08	256	268.53	269.88	372	405.05	434.60

Table A3.4 Riazi model predicted TBP Temperatures of REBCO crude fractions

Vol%	Naphtha			Kerosene			Diesel		
	Exp.	NLR	LR	Exp.	NLR	LR	Exp.	NLR	LR
0%	82	79.89	82.49	147	143.14	147.79	226	173.30	226.0
5%	103	106.25	106.67	174	174.28	174.92	246	233.78	245.33
10%	115	113.77	113.99	182	182.01	182.34	254	247.52	253.92
90%	175	179.17	179.35	238	243.58	244.09	346	351.76	360.91
95%	182	188.71	189.05	244	252.05	252.84	355	365.63	380.32
99%	197	206.30	207.01	255	267.46	268.85	365	390.65	418.21

Table A3.5 Riazi model predicted TBP Temperatures of SLCO crude fractions

Vol%	Kerosene			Diesel		
	Exp.	NLR	LR	Exp.	NLR	LR
0%	148	133.02	148.45	217	184.12	217.10
5%	170	168.85	171.47	243	231.72	239.92
10%	177	177.07	178.49	251	245.16	249.70
90%	235	239.72	241.53	353	361.17	367.04
95%	241	248.09	250.92	360	378.01	387.87
99%	252	263.19	268.33	373	409.05	428.30

Table A4. Initial and end point temperatures for product fractions obtained from linear and non-linear regression

Crude Oil	Fractions	T_0 (error%)		T_{99} (error%)	
		NLR	LR	NLR	LR
CPC	Naphtha	-10.9246	1.8744	5.6371	8.2698
	Kerosene	-5.7065	0	3.8689	5.1231
	Diesel	-14.7998	0	-5.0067	26.6132
REBCO	Naphtha	-2.5731	0.6012	4.7229	5.0846
	Kerosene	-2.6216	0.5441	4.8883	5.4326
	Diesel	-23.3156	0.0336	7.0279	14.5806
SLCO	Kerosene	-10.1198	0.3081	4.4437	6.4815
	Diesel	-15.1506	0.0498	9.6659	14.8261
Oil Blend	Naphtha	4.0527	0.4789	7.06307	6.1356
	Kerosene	-2.2133	0.3734	4.8963	5.4232
	Diesel	-18.6171	0.0202	8.8868	16.8283
KIRKUK	Naphtha	9.1792	0.5235	7.3587	4.9557
	Kerosene	0.2333	0.6898	4.4972	4.5387
	Diesel	21.6073	3.8843	9.5560	7.5224

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