

Simulation of Molecular Distillation Process. 1. Formulation of Generalized Correlation for Predicting Heavy Liquid Petroleum Fractions Properties of Brazilian Oil Petroleum

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In this work, the generalized correlation to predict the molecular weight of heavy liquid petroleum fractions had been developed. The heavy petroleum fractions have been obtained from conventional distillation processes: ASTM D-2892 and ASTM D-5236. The correlation was developed using the generalized method of Fang and Lei (1999). The equation needs only specific gravity at 15.6°C and 50% boiling point as input parameters. Better results are given by the generalized correlation generated with a good correspondence between the predicted and experimental values for 127 fractions derived from 14 Brazilian heavy oils petroleum with a total of 777 points. The formulated correlation will be used to define the mathematical modeling of the molecular distillation process of heavy petroleum fractions (AET 400°C+) (part 2.).

Keywords: Molecular distillation, Heavy petroleum fractions, Specific gravity, 50% boiling point, Molecular weight correlation.

1. Introduction

Molecular distillation belongs to the class of process that use separation under high vacuum, operation at reduced temperatures and low exposition of the material at the operating temperature. A typical mathematical modeling of falling film distillator includes: the velocity profile, the film thickness, the temperature profile in the liquid layer, the concentration profile in the liquid layer, the distillate local composition, the local separation factor and the surface evaporating rate under vacuum \dot{G}_i , which is represented by equation (1) (Batistella and Maciel, 1996):

$$\dot{G}_i = C_{is} P_i^{sat} \left(\frac{MW_i}{2\pi R g T} \right)^{\frac{1}{2}} \left[1 - (1 - F) \left(1 - e^{-\frac{h}{k\beta}} \right)^d \right] \quad (1)$$

The majority of the properties in equation (1) are formulated for binary systems, as well as the molecular weight, where practically there not exit a unique standard expression to predict it for mixtures containing heavy hydrocarbon fractions. Lack of experimental data for these mixtures and the necessity for representing the highly complex heavy

fractions by means of relatively parameters make the solution of this problem difficult. The heavy fraction is normally split in boiling point fractions, each of which may comprise many different components. So it is necessary to estimate the parameters from the properties which have been measured in each fraction. Specific gravity, viscosity and molecular weight can easily be measured and the boiling range is known from the distillation process. A number of correlations for predict the molecular weight have been published; several these are summarized in Pedersen et al. (1984). The API technical data book correlation was used by Fang and Lei (1999) to predict the molecular weight of 47 fractions of 15 world crude oils, with only two input properties, 50% boiling point and the density at 15.6 °C. The fraction boiling range of fractions considered for Fang and Lei was 93°C – 454°C. For the calculation of these properties, the authors split the whole fraction in four minor fractions for each crude oil, considering the boiling point for this. The aim of this work was to formulate a generalized correlation to predict the molecular weight of heavy liquid petroleum fractions of 127 fractions of 14 Brazilian crude oils using the generalized method of Fang and Lei. Heavy boiling fractions in the range of 403 – 1000°C were considered with a total of 777 points.

2. Development of molecular weight correlation

The first stage to develop the expression to predict the molecular weight of heavy liquid petroleum fractions was the computing of this property using the correlation of Fang – Lei (Fang and Lei, 1999), equation (2).

$$MW = 219.05 \exp(0.003924(t_b + 273.15)) \exp(-3.07SG)(t_b + 273.15)^{0.118} SG^{1.88} \quad (2)$$

The objective of this was to explore the possibility of using equation (2) to predict the molecular weight of heavy fractions which are being studied in this work. For that, was calculated of specific gravity at 15.6 °C (SG) of heavy petroleum fractions, what have been obtained of the ASTM D-2892 and ASTM D-5236 (feeding of molecular distillator). The total heavy fractions were split in boiling point fractions (subfractions), each of which with many different components. The boiling point range was 403°C – 1000 °C. For each subfraction were estimated of SG, and 50% boiling point (t_b). The molecular weigh were calculated through software specially developed for that, in Fortran 6. The analyses of the initial results allowed to conclude that equation (2) was not suitable to predict the molecular weight of heavy liquid petroleum fractions studied here, for this, adjustment of equation was necessary. The Microcal Origin 6.0 was used for that.

3. Results and discussion

3.1 Calculation of average specific gravity SG_{av} at 15.6°C/15.6°C

The estimation of SG was carried out considering the components present in each subfractions generated by partitioning of the total boiling point range (403°C to 1000°C). Also, the average 50% boiling point (t_{bav}), was calculated using the equation (3). The values of SG_{av} for each fraction are presented in Table 1.

$$t_{bav} = (t_{bl} + t_{bf})/2 \quad (3)$$

Table 1. SG_{av} values for each fraction of crude oils studied.

Fractions	F 1	F 2	F 3	F 4	F 5	F 6	F 7	F 8	F 9	F 10	F 11	F 12	F 13	F 14	F 15	F 16	SG _{av}
th _{av} (°C)	425.46	480.89	537.36	587.68	631.68	668.96	702.73	735.50	762.33	779.08	858.25	876.67	891.00	917.25	931.13	962.67	
Crude oil																	
CB-M	0.9295	0.9449	0.9591	0.9830	1.0077	1.0253	1.0379			1.1517							1.0049
CB	0.9426	0.9544	0.9760	1.0027	1.0155	1.0241	1.0347			1.0488		1.0637					1.0069
BA	0.9259	0.9411	0.9590	0.9810	1.0088	1.0287		1.0518					1.0933				0.9987
MS-P38	0.9415	0.9501	0.9637	0.9866	1.0070	1.0233	1.0345		1.0501					1.1043			1.0068
BI	0.9351	0.9492	0.9634	0.9845	1.0060	1.0212	1.0327		1.0499					1.1715			1.0126
VO	0.9303	0.9509	0.9627	0.9785	1.0023	1.0210	1.0343			1.0576		1.0542				1.0655	1.0057
M-P35	0.9449	0.9552	0.9708	1.0003	1.0274	1.0444	1.0594		1.0743					1.2331			1.0344
M-P19	0.9398	0.9537	0.9698	0.9920	1.0119	1.0256	1.0352		1.0505		1.1186					1.1285	1.0226
ML	0.9538	0.9655	0.9805	1.0039	1.0251	1.0406	1.0526			1.0848		1.1570					1.0293
RO-42	0.9447	0.9535	0.9613	0.9768	0.9937	1.0061	1.0163		1.0339		1.1336					1.1660	1.0022
JE-110	0.9499	0.9590	0.9697	0.9858	1.0006	1.0113	1.0199			1.0493				1.1467			1.0103
MS-3B	0.9528	0.9667	0.9872	1.0155	1.0387	1.0561	1.0681		1.0811				1.0858				1.0280
FA	0.9443	0.9511	0.9604	0.9893	1.0167	1.0352	1.0497			1.0889					1.2007		1.0262
BC	0.9550	0.9719	0.9852	1.0051	1.0259	1.0421	1.0536			1.1045				1.2266			1.0411
															SG _{av} overall		1.0164

3.2 Molecular weight estimate

With the SG_{av} and the t_{bav} the molecular weight was calculated using equation (2). A software in Fortran 6 was developed for that. The comparison between experimental molecular weight and the molecular weight estimated by equation (2) is given in Table 2, including t_{bav} , the number of fractions and the total number of components present in each fraction of the crude oils studied. The average absolute deviation, AAD was calculated using the following equation:

$$AAD\% = (1/n) \sum_{i=1}^n \frac{|MW_{i,cal} - MW_{i,exp}|}{MW_{i,exp}} * 100 \quad (4)$$

In Table 4, the randomized distribution of error ($e = MW_{exp} - MW_{cal}$) is observed for the molecular weight predicted, however, the equation lead molecular weights which are above the experimental values for overall of crude oils investigated. Of another side, the correlation (2) predicts the molecular weight with an average absolute deviation range of 3.51%-9.20%. This correlation is not quite reasonable for the characterization of the heavy petroleum fractions, because, the parameters were set for fractions with boiling point range from 93°C to 454°C. The fractions investigated in this project are in the boiling point range from 400°C to 1000°C, for that reasons, the adjustment of equation (2) was necessary.

Table 2. Comparison of the experimental molecular weight with the Fang-Lei correlation.

Crude oil	50% boiling point range (°C)	No. of fractions	Points (components)	MW_{exp}	MW_{cal}	e ($MW_{exp} - MW_{cal}$)	AAD
CB-M	425.46 - 858.67	8	45	728.54	795.56	-67.02	9.20
CB	425.46 - 891.00	9	51	842.43	904.78	-62.35	7.40
BA	425.46 - 917.25	8	49	827.99	886.83	-58.84	7.11
MS-P38	425.46 - 931.13	9	48	854.66	924.49	-69.82	8.17
BI	425.46 - 917.25	9	49	835.11	889.56	-54.44	6.52
VO	425.46 - 962.67	10	55	1000.80	1085.67	-84.87	8.48
M-P35	425.46 - 1767.84	9	50	816.75	854.06	-37.31	4.57
M-P19	425.46 - 962.67	10	58	961.07	1035.42	-74.35	7.74
ML	425.46 - 1603.60	9	57	814.84	851.52	-36.68	4.50
RO-42	425.46 - 2119.95	10	57	927.33	1016.02	-88.68	9.56
JE-110	425.46 - 1926.16	9	63	852.71	922.59	-69.88	8.20
MS-3B	425.46 - 1877.49	9	58	845.28	893.42	-48.15	5.70
FA	425.46 - 1881.28	9	70	846.15	888.72	-42.57	5.03
BC	425.46 - 1856.82	9	67	840.44	869.97	-29.52	3.51
Overall	425.46 - 2119.95	127	777				

3.3 Adjusting of parameter of Fang-Lei correlation

The Microcal Origin 6.0 was used to define the new parameter of equation (2). The correlation has 5 parameter described in Table 3. For the calculation, it was allowed a maximum variation of initial parameter values of -30% (lower bound) and +30% (upper bound). The values of final parameter are presented in Table 3. With this adjustment, the parameters of Fang-Lei correlation were corrected and equation (2) can be rewritten:

$$M = 284.752 \exp(0.00322(t_b + 273.15)) \exp(-2.517SG)(t_b + 273.15)^{0.0826} SG^{2.44} \quad (5)$$

A graphical representation of the results generated of corrected correlation (5) is observed in Figure 1. An excellent correspondence is observed between the experimental and estimated values. In Table 4, the values of experimental and estimated molecular weight are compared for each crude oil studied, and Figure 2 illustrates the behavior of the error ($e = MW_{\text{experimental}} - MW_{\text{calculated}}$). The distribution of the error is at randomized and in addition it oscillates around of zero for overall of crude oils investigated. The corrected correlation makes better representation of experimental values and an important reduction of average absolute deviation range is obtained (0.03% - 4.35%).

Table 3. Initial and final parameter values for adjusting Fang-Lei correlation.

Parameter	Initial value	Lower bound (-30%)	Upper bound (-30%)	Final value
P1	219.05	153.335	284.77	284.752
P2	0.003924	0.002747	0.005101	0.00322
P3	-3.07	-3.991	-2.149	-2.517
P4	0.118	0.0826	0.1534	0.00826
P5	1.88	1.216	2.444	2.44

Table 4. Experimental and estimated molecular weight comparison

No.	Crude oil	MW _{exp}	MW _{cal corrected}	e	AAD
1	CB-M	728.54	754.83	-26.29	3.61
2	CB	842.43	828.77	13.66	1.62
3	BA	827.99	812.92	15.07	1.82
4	MS-P38	854.66	846.51	8.16	0.95
5	BI	835.11	831.76	3.36	0.40
6	VO	1000.80	957.29	43.51	4.35
7	M-P35	816.75	824.06	-7.31	0.90
8	M-P19	961.07	944.06	17.01	1.77
9	ML	814.84	812.83	2.02	0.25
10	RO-42	927.33	931.49	-4.16	0.45
11	JE-110	852.71	850.96	1.75	0.20
12	MS-3B	845.28	835.38	9.89	1.17
13	FA	846.15	843.79	2.36	0.28
14	BC	840.44	840.15	0.29	0.03

4. Conclusion

A generalized correlation, with 50% boiling point temperature and specific gravity as input parameters has been developed to predict the molecular weight of heavy liquid petroleum fractions for the range of average boiling point of 403°C – 1000°C. Good agreement between predicted and experimental values has been observed with a maximum average absolute deviation of 4.35% for 127 fractions derived from 14 Brazilian crude oils with a total of 777 points. Better results for heavy petroleum fractions are given by the corrected correlation than the Fang-Lei correlation. The correlation generated

constitutes a better alternative for predict the evaporating rate in the mathematical modeling of molecular distillation.

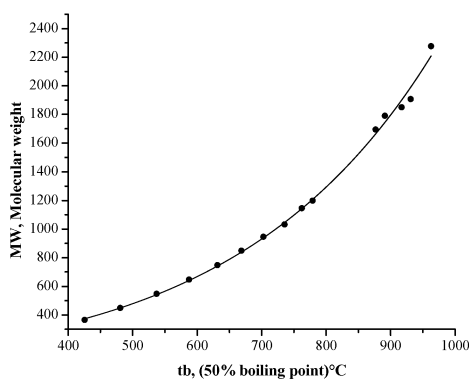


Figure 1. Molecular weight estimated by corrected correlation (● MW_{exp}; — MW_{Corrected model})

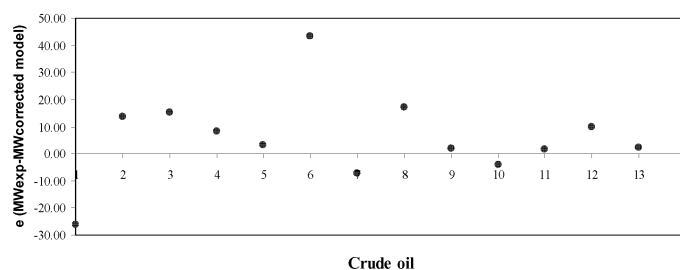


Figure 2. Error distribution for the molecular weight estimated by corrected correlation

5. References

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Nomenclature

AAD: Average absolute deviation; C_{is} : Composition, mole fraction of the liquid phase in liquid film surface; C_N : Carbon number; d : Constant; F : Surface ratio; \dot{G} : Evaporating rate in $\text{kg/m}^2\cdot\text{s}$; SG: Specific gravity at $15.6^\circ\text{C}/15.6^\circ\text{C}$; SG_{av} : Average specific gravity; h : Distance between evaporator and condenser surfaces in m; k : Anisotropy of vapour; MW: Molecular weight; MW_{av} : Average molecular weight; P^{sat} : Vapour pressure in Pa; R_g : Universal gas constant in $\text{J/kgmol}\cdot\text{K}$; T : Temperature in K; t_b : 50% boiling point; t_{bav} : Average 50% boiling point; T_B : Boiling point in K; z_N : Mole fraction of carbon number fraction C_N ; β : Mean path of vapour molecule in m; t_{bi} : initial boiling point fraction; t_{bf} : final boiling point fraction