Prediction of Molecular-Type Analysis of Petroleum Fractions and Coal Liquids

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Different sets of correlations for prediction of composition of petroleum fractions and coal liquids in terms of readily available parameters are proposed. Paraffinic, naphthenic, and aromatic portions of olefin-free fractions can be predicted from the knowledge of either specific gravity, refractive index, and viscosity or molecular weight, refractive index, and carbon to hydrogen weight ratio. The proposed correlations may be used for fractions with molecular weights of 70–600. For coal liquids or highly aromatic fractions, correlations in terms of molecular weight, refractive index, and density are proposed to predict monoaromatic and polyaromatic portions of the fraction. These correlations are applicable to fractions with molecular weights up to 250.

Petroleum fractions are mixtures of different hydrocarbons from different homologous groups. When the pseudocompound method is used for prediction of thermophysical properties of undefined petroleum fractions (Huang and Daubert 1974; Riazi, 1979), knowledge of the paraffin, olefin, naphthene, and aromatic content of the fraction is necessary. However, most petroleum fractions for which data on their composition are available are free from olefins, and most coal liquids are highly aromatic (80–90% aromatic).

The n–d–M method of Van Nes and Van Westen (1951) for estimating the percentage carbon as an aromatic, naphthenic, or paraffinic structure from measured values of density, refractive index, and molecular weight is based on limited and mainly saturated data. Riazi (1979) has shown that the method gives high errors in the prediction of the composition of petroleum fractions. Riazi and Daubert (1980) developed a set of correlations for molecular-type analysis which required viscosity, specific gravity, density, and refractive index as input parameters. The fractions were divided into light ($M < 200$) and heavy ($M > 200$) molecular weight ranges, and the correlations were in terms of the refractivity intercept (RI) and viscosity gravity relation (VG). These two characterizing parameters were defined as

$$\mathrm{RI} = n - d/2 \qquad (1)$$

$$\mathrm{VG} = \mathrm{VGF} \quad \text{when} \quad M < 200$$

$$\mathrm{VG} = \mathrm{VGC} \quad \text{when} \quad M > 200$$

$$\mathrm{VGF} = -1.816 + 3.484S - 0.1156 \ln \nu_1 \qquad (2)$$

$$\mathrm{VGF} = -1.948 + 3.535S - 0.1613 \ln \nu_2 \qquad (3)$$

$$\mathrm{VGC} = \frac{10S - 1.0752 \log (V_1 - 38)}{10 - \log (V_1 - 38)} \qquad (4)$$

$$\mathrm{VGC} = \frac{S - 0.24 - 0.022 \log (V_2 - 35.5)}{0.755} \qquad (5)$$

where V_1 and V_2 are Saybolt universal viscosities at 100 and 210 °F, respectively.

In 1980 when new correlations for composition prediction in terms of RI and VG were developed, only 42 light and 16 heavy petroleum fractions with complete information on the composition and related properties were available. An extensive bank of characterization data has now been compiled, making more data available on the composition of petroleum fractions and coal liquids. Since for many fractions, especially light fractions, viscosity data may not be available, alternative correlations for predicting the composition using properties other than viscosity are required. The main purpose of this work was to develop new correlations for the composition prediction of petroleum fractions and coal liquids in terms of readily available parameters. For coal liquids which are highly aromatic, correlations for prediction of different types of aromatics are needed.

Development of Correlations

An attempt was made to determine the best set of characterization parameters for the purpose of composition predictions. Although RI and VG are excellent parameters for determination of PNA, alternative parameters are required for the cases where viscosity is not known and therefore VG cannot be estimated. In addition to RI and VG two other parameters were found to be suitable for the purpose of PNA estimation. These two other parameters are CH and m, where CH is the carbon to hydrogen weight ratio and m is a parameter defined as in eq 6 where M is the molecular weight.

$$m = M(n - 1.4750) \qquad (6)$$

Fryback (1981) shows how the ratio of hydrogen to carbon characterizes different types of oils and petroleum products. The CH ratio for paraffins varies from 5.1 to 5.8, for naphthenes from 6 to 7, and for aromatics from 7 to 12. Therefore, average values of CH for paraffins, naphthenes, and aromatics are 5.5, 6.5, and 9.5, respectively. The basis for the definition of parameter m can be shown by a graph of the refractive index (n) vs. $1/M$ which

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Table I. Experimental Data on the Composition of Light Petroleum Fractions

no.	ID no.	M	T_b	S	RI	VGF	m	composition P%	N%	A%
1	370	78.0	130.0	0.6580	1.0427	0.5721	−8.24	82.0	15.5	2.5
2	293	79.0	127.4	0.6620	1.0423	0.5901	−8.22	89.0	9.0	2.0
3	890	80.0	130.1	0.6570	1.0428	0.5748	−8.48	92.7	6.0	1.3
4	681	81.0	136.4	0.6700	1.0422	0.6138	−8.11	82.0	16.0	2.0
5	371	82.0	145.4	0.6715	1.0425	0.6159	−8.12	77.5	19.5	3.0
6	891	82.0	136.4	0.6647	1.0425	0.5993	−8.40	89.5	9.1	1.4
7	1213	83.0	143.6	0.6750	1.0422	0.6312	−8.10	84.0	13.0	3.0
8	1320	88.0	174.2	0.6935	1.0426	0.6840	−7.74	68.0	30.0	2.0
9	372	92.0	195.8	0.7025	1.0431	0.7098	−7.63	71.5	17.0	11.5
10	790	93.0	199.4	0.7110	1.0430	0.7397	−7.32	80.0	15.0	5.0
11	892	93.0	197.6	0.6963	1.0434	0.6889	−7.97	78.6	16.0	5.4
12	682	94.0	201.2	0.7090	1.0431	0.7291	−7.49	65.0	25.5	9.5
13	1321	94.0	201.2	0.7080	1.0432	0.7250	−7.53	63.7	32.8	3.5
14	297	96.0	206.6	0.7130	1.0432	0.7424	−7.44	71.0	18.0	11.0
15	683	97.0	212.0	0.7160	1.0434	0.7493	−7.36	63.5	26.0	10.5
16	1002	100.0	228.0	0.7140	1.0438	0.7360	−7.64	68.5	23.0	8.5
17	792	101.0	230.0	0.7270	1.0438	0.7790	−7.07	56.5	32.5	11.0
18	374	102.0	236.3	0.7235	1.0440	0.7661	−7.30	67.5	16.0	16.5
19	1324	102.0	230.0	0.7230	1.0438	0.7648	−7.34	60.0	35.0	5.0
20	1003	103.0	237.2	0.7205	1.0440	0.7541	−7.52	66.0	24.0	10.0
21	684	104.0	237.2	0.7300	1.0440	0.7868	−7.10	59.5	27.5	13.0
22	1004	106.0	249.8	0.7270	1.0443	0.7703	−7.36	63.5	25.5	11.0
23	379	107.0	233.6	0.7390	1.0439	0.8213	−6.83	64.0	16.5	19.5
24	901	108.0	242.6	0.7348	1.0441	0.8017	−7.10	66.9	21.1	12.0
25	903	114.0	271.4	0.7463	1.0448	0.8269	−6.75	66.4	19.6	14.0
26	380	115.0	255.2	0.7470	1.0445	0.8353	−6.81	51.9	41.7	6.4
27	250	120.9	260.0	0.7395	1.0445	0.8078	−7.55	61.9	30.6	7.5
28	1853	122.0	327.2	0.8679	1.0565	1.2243	1.62	22.0	21.0	57.0
29	247	131.0	282.0	0.7774	1.0461	0.9285	−5.56	39.7	39.6	20.7
30	251	142.4	322.0	0.7624	1.0460	0.8524	−7.12	59.3	30.8	9.9
31	1891	154.0	475.3	0.9709	1.0752	1.4984	12.89	3.3	3.3	93.4
32	1830	155.0	434.3	0.9606	1.0748	1.4870	12.10	10.4	5.0	84.6
33	1794	156.0	509.0	0.9802	1.0756	1.5085	13.85	4.6	4.0	91.4
34	1866	156.0	473.2	0.9693	1.0748	1.4944	12.88	3.8	2.0	94.2
35	1908	156.0	497.3	0.9807	1.0766	1.5183	14.05	3.9	3.0	93.1
36	1843	158.0	472.3	0.9733	1.0761	1.5082	13.57	5.3	4.0	90.7
37	1899	161.0	474.3	0.9732	1.0760	1.5069	13.79	3.0	4.0	93.0
38	1856	167.0	472.3	0.9553	1.0708	1.4449	11.95	5.8	6.0	88.2
39	1617	171.0	456.0	0.9360	1.0667	1.3869	9.86	3.0	12.3	84.7
40	1631	186.0	509.0	0.9652	1.0712	1.4548	14.30	4.7	9.6	85.7
41	1613	187.0	504.0	0.9715	1.0733	1.4790	15.37	2.2	15.1	82.7
42	254	214.0	535.0	0.8475	1.0497	1.0148	−0.75	38.8	41.5	19.7
43	1213	82.0	143.6	0.6630	1.0430	0.5914	−8.43	87.5	11.0	1.5
44	1215	92.0	194.0	0.6940	1.0433	0.6826	−8.00	80.0	15.0	5.0
45	1216	95.0	206.6	0.7000	1.0435	0.6980	−7.95	77.5	15.5	7.0
46	1217	97.0	219.2	0.7060	1.0438	0.7133	−7.81	76.5	15.5	8.0
47	1218	100.0	228.2	0.7110	1.0439	0.7264	−7.78	75.5	16.0	8.5
48	686	101.0	212.0	0.7280	1.0433	0.7900	−7.07	56.5	31.5	12.0
49	1005	101.0	213.8	0.7195	1.0434	0.7607	−7.49	67.0	29.0	4.0
50	1223	102.0	219.0	0.7210	1.0435	0.7650	−7.47	72.0	19.0	9.0
[illegible]	1006	104.0	224.6	0.7260	1.0436	0.7786	−7.34	64.5	28.5	7.0
[illegible]	798	106.0	233.6	0.7440	1.0440	0.8356	−6.49	48.0	40.0	12.0
53	897	107.0	235.4	0.7380	1.0440	0.8163	−6.88	63.0	22.0	15.0
54	1008	107.0	239.0	0.7420	1.0441	0.8271	−6.65	52.5	33.0	14.5
55	1007	108.8	240.8	0.7355	1.0441	0.8041	−7.07	61.5	28.0	10.5
56	800	109.0	240.8	0.7480	1.0443	0.8463	−6.43	47.5	40.0	12.5
57	1228	110.0	242.6	0.7360	1.0441	0.8061	−7.16	68.5	19.5	12.0
58	690	114.0	260.0	0.7525	1.0447	0.8536	−6.41	51.0	32.5	16.5
59	799	114.0	260.6	0.7550	1.0448	0.8611	−6.26	45.5	40.5	14.0
60	1009	115.0	266.0	0.7470	1.0447	0.8312	−6.78	56.5	30.5	13.0
61	1227	115.0	262.4	0.7430	1.0446	0.8202	−7.03	68.5	19.0	12.5
62	1011	117.0	271.4	0.7500	1.0449	0.8389	−6.70	56.0	30.0	14.0
63	303	118.0	273.2	0.7550	1.0450	0.8566	−6.45	62.0	20.0	18.0
64	383	126.0	296.6	0.7555	1.0454	0.8466	−6.80	60.5	13.5	26.0
66	905	126.0	307.4	0.7666	1.0459	0.8779	−6.04	63.7	17.4	18.9
67	693	127.0	296.6	0.7720	1.0460	0.9018	−5.74	51.0	31.0	18.0
68	802	127.0	298.4	0.7725	1.0460	0.9021	−5.70	42.0	39.0	19.0
69	1012	127.0	296.6	0.7675	1.0458	0.8871	−6.05	50.0	27.0	23.0
70	694	129.0	305.6	0.7740	1.0462	0.9038	−5.68	49.0	31.5	19.5
71	803	130.0	307.4	0.7755	1.0462	0.9071	−5.61	42.0	40.0	18.0
72	907	130.0	311.9	0.7667	1.0460	0.8754	−6.22	65.6	17.1	17.3
73	1013	130.0	307.4	0.7710	1.0461	0.8926	−5.93	50.0	29.0	21.0
74	385	133.0	317.3	0.7690	1.0461	0.8814	−6.19	60.0	15.0	25.0
75	695	133.0	316.4	0.7760	1.0464	0.9045	−5.69	47.5	32.0	20.5
76	804	133.0	318.2	0.7785	1.0465	0.9113	−5.51	40.5	41.0	18.5

Table I (Continued)

no.	ID no.	M	T_b	S	RI	VGF	m	composition P%	N%	A%
77	696	137.0	329.0	0.7800	1.0467	0.9106	−5.55	45.5	35.0	19.5
78	910	153.0	384.8	0.7896	1.0474	0.9124	−5.34	53.8	18.1	28.1
79	1234	154.0	374.0	0.7890	1.0473	0.9155	−5.43	60.0	21.0	19.0
80	1017	157.0	384.8	0.7955	1.0477	0.9300	−4.97	43.5	38.5	18.0
81	1016	160.0	392.0	0.7970	1.0478	0.9307	−4.93	42.5	39.5	18.0
82	697	161.0	384.8	0.8030	1.0481	0.9558	−4.42	37.5	44.0	18.5
83	1018	165.0	404.6	0.8000	1.0479	0.9331	−4.81	42.0	40.5	17.5
84	699	166.0	404.6	0.8060	1.0483	0.9537	−4.28	36.5	45.5	18.0
85	1019	170.0	417.0	0.8025	1.0480	0.9339	−4.72	42.0	41.0	17.0

is linear for all different types of homologous hydrocarbon groups. This graph is shown by Hersh et al. (1950) where m is the slope of the refractive index lines with the intercept of 1.4750 for different groups (eq 7).

$$n = 1.4750 + \frac{m}{M} \tag{7}$$

Rearrangement of eq 7 gives eq 6 for the determination of parameter m. Some values of m for different types of hydrocarbons are given below:

hydrocarbon type	m
paraffins	−8.79
monocyclopentanes	−5.41
monocyclohexanes	−4.43
benzenes	2.64
naphthalenes	19.5
condensed tricyclics	43.6

From the above table, it is clear that the factor m separates different types of hydrocarbons, most notably different types of aromatics.

On the basis of the new data bank on composition of petroleum fractions and coal liquids, the following sets of correlations are proposed for estimation of molecular-type analysis of undefined fractions.

For light fractions, $M < 200$

$$\text{P\%} = -1335.9 + 1445.91\text{RI} - 141.344\text{VGF} \tag{8}$$

$$\text{N\%} = 2398.25 - 2333.304\text{RI} + 81.517\text{VGF} \tag{9}$$

$$\text{A\%} = 100 - (\text{P\%} + \text{N\%}) \tag{10}$$

For heavy fractions, $M > 200$

$$\text{P\%} = 257.37 + 101.33\text{RI} - 357.3\text{VGC} \tag{11}$$

$$\text{N\%} = 246.4 - 367.01\text{RI} + 196.312\text{VGC} \tag{12}$$

$$\text{A\%} = 100 - (\text{P\%} + \text{N\%}) \tag{10}$$

RI, VGF, and VGC are defined through eq 1–5. Since in many cases viscosity is not available especially for light fractions, VGF cannot be estimated and correlations are needed in terms of other parameters. The best sets of alternative correlations which have been derived are as follows.

For light fractions, $M < 200$

$$\text{P\%} = 257 - 287.7S + 2.876\text{CH} \tag{13}$$

$$\text{N\%} = 52.641 - 0.7494(\text{P\%}) - 2.1811m \tag{14}$$

$$\text{A\%} = 100 - (\text{P\%} + \text{N\%}) \tag{10}$$

or

$$\text{P\%} = 373.87 - 408.29S + 1.4772m \tag{15}$$

$$\text{N\%} = -150.27 + 210.152S - 2.388m \tag{16}$$

$$\text{A\%} = 100 - (\text{P\%} + \text{N\%}) \tag{10}$$

For heavy fractions, $M > 200$

$$\text{P\%} = 198.42 - 27.722\text{RI} - 15.643\text{CH} \tag{17}$$

$$\text{N\%} = 59.77 - 76.1745\text{RI} + 6.8048\text{CH} \tag{18}$$

$$\text{A\%} = 100 - (\text{P\%} + \text{N\%}) \tag{10}$$

or

$$\text{P\%} = 193.82 + 0.74855m - 19.966\text{CH} \tag{19}$$

$$\text{N\%} = -42.260 - 0.777m + 10.7625\text{CH} \tag{20}$$

$$\text{A\%} = 100 - (\text{P\%} + \text{N\%}) \tag{10}$$

In all of the above correlations, the total aromatic content of the fraction can be estimated. For coal liquids, which are highly aromatic, a more detailed composition of the aromatic portion is required. The aromatic portion of fractions was divided into two parts: MA% (monoaromatic percent) and PA% (di- and polyaromatic percent). The only two parameters capable of characterizing different types of aromatics were determined to be RI and m. The appropriate correlations for MA% and PA% are as follows.

For fractions, $M < 250$

$$\text{MA\%} = -6282.45 + 5990.816\text{RI} - 2.48335m \tag{21}$$

$$\text{PA\%} = 1188.175 - 1122.13\text{RI} + 2.3745m \tag{22}$$

$$\text{A\%} = \text{MA\%} + \text{PA\%} \tag{23}$$

For heavier fractions ($M > 250$), detailed composition data for aromatics were not available. Thus, at this time correlations similar to (21) and (22) have not been developed for heavier fractions. Note that in all these correlations if data on M, CH, n, or d for a given fraction are not available, they may be predicted from the following correlations developed by Riazi and Daubert (1985).

Table II. Experimental Data on the Composition of Heavy Petroleum Fractions[a]

						composition		
no.	ID no.	*M*	RI	VGC	*m*	P%	N%	A%
1	1967	263.0	1.0590	0.8740	5.73	43.0	45.0	12.0
2	1986	265.0	1.0600	0.8735	7.79	57.0	28.0	15.0
3	2007	266.0	1.0610	0.8890	9.31	42.0	37.0	21.0
4	2024	268.0	1.0620	0.8979	10.40	40.0	41.0	19.0
5	1968	277.0	1.0590	0.8771	6.73	43.0	43.0	14.0
6	2025	283.0	1.0610	0.8933	10.75	43.0	39.0	18.0
7	2009	284.0	1.0610	0.8920	11.53	45.0	33.0	22.0
8	2009	284.0	1.0610	0.8920	11.53	45.0	33.0	22.0
9	2026	296.0	1.0600	0.8871	10.95	48.0	34.0	18.0
10	1970	306.0	1.0570	0.8657	7.77	51.0	36.0	13.0
11	2011	300.0	1.0600	0.8918	13.20	47.0	30.0	23.0
12	2012	307.0	1.0600	0.8924	14.03	46.0	31.0	23.0
13	2027	307.0	1.0590	0.8817	10.99	48.0	35.0	17.0
14	1988	311.0	1.0570	0.8570	7.84	61.0	25.0	14.0
15	2013	313.0	1.0600	0.8913	14.65	47.0	29.0	24.0
16	2014	319.0	1.0600	0.8897	14.99	46.0	31.0	23.0
17	1971	321.0	1.0560	0.8610	8.02	55.0	32.0	13.0
18	2002	330.0	1.0580	0.8838	13.93	48.0	32.0	20.0
19	2031	341.0	1.0570	0.8699	11.42	53.0	32.0	15.0
20	1928	343.0	1.0530	0.8281	2.95	72.0	16.0	12.0
21	1991	348.0	1.0550	0.8467	8.00	65.0	21.0	14.0
22	1930	353.0	1.0520	0.8197	2.47	75.0	16.0	9.0
23	2052	354.0	1.0570	0.8817	14.94	46.0	28.0	26.0
24	1992	357.0	1.0540	0.8453	8.00	64.0	23.0	13.0
25	1932	363.0	1.0520	0.8175	2.58	75.0	17.0	8.0
26	2055	364.0	1.0520	0.8331	4.08	60.0	34.0	6.0
27	1993	366.0	1.0540	0.8443	8.38	66.0	21.0	13.0
28	2036	372.0	1.0550	0.8658	13.32	52.0	34.0	14.0
29	2058	374.0	1.0500	0.8149	0.60	68.0	31.0	1.0
30	1975	378.0	1.0540	0.8548	10.55	58.0	29.0	13.0
31	1936	383.0	1.0510	0.8124	2.68	76.0	17.0	7.0
32	1995	387.0	1.0530	0.8531	8.90	65.0	23.0	12.0
33	1937	388.0	1.0510	0.8128	3.10	77.0	16.0	7.0
34	1956	392.0	1.0510	0.8228	4.12	71.0	21.0	8.0
35	1938	393.0	1.0500	0.8130	3.26	76.0	17.0	7.0
36	1949	397.0	1.0510	0.8238	4.76	71.0	20.0	9.0
37	1996	398.0	1.0520	0.8387	9.15	64.0	25.0	11.0
38	1958	400.0	1.0510	0.8218	4.40	72.0	20.0	8.0
39	1959	405.0	1.0500	0.8214	4.58	72.0	20.0	8.0
40	1960	412.0	1.0500	0.8209	4.74	73.0	20.0	7.0
41	2064	415.0	1.0480	0.8016	−1.25	74.0	26.0	0.0
42	1943	422.0	1.0490	0.8104	4.30	78.0	15.0	7.0
43	1962	426.0	1.0500	0.8197	5.20	73.0	19.0	8.0
44	2117	428.0	1.0480	0.8051	0.60	74.0	24.0	2.0
45	1944	430.0	1.0490	0.8098	4.56	78.0	16.0	6.0
46	2115	435.0	1.0480	0.8117	2.31	70.0	26.0	4.0
47	1968	438.0	1.0490	0.8185	5.43	73.0	19.0	8.0
48	1945	440.0	1.0490	0.8113	4.80	79.0	15.0	6.0
49	1964	442.0	1.0490	0.8191	5.66	73.0	20.0	7.0
50	2067	446.0	1.0470	0.7906	−2.50	81.0	19.0	0.0
51	1947	482.0	1.0470	0.8080	5.74	78.0	15.0	7.0
52	1982	483.0	1.0500	0.8412	16.37	66.0	24.0	10.0
53	2002	494.0	1.0490	0.8290	14.33	79.0	13.0	8.0
54	1983	497.0	1.0500	0.8391	16.90	66.0	24.0	10.0
55	1948	521.0	1.0460	0.8074	7.29	75.0	20.0	5.0
56	1984	571.0	1.0470	0.8322	19.41	68.0	22.0	10.0
57		233.0	1.0480	0.8940	6.20	34.1	45.9	20.0
58		248.0	1.0530	0.9170	11.46	30.4	43.0	26.6
59		267.0	1.0580	0.9340	16.45	30.9	37.0	32.1
60		281.0	1.0620	0.9410	19.73	31.8	34.0	34.2
61		305.0	1.0620	0.9420	22.63	32.9	32.2	34.9
62		245.0	1.0470	0.8360	−0.76	58.4	31.8	9.8
63		282.0	1.0490	0.8440	2.59	56.5	30.7	12.8
64		325.0	1.0500	0.8460	5.49	58.4	28.9	12.7
65		403.0	1.0500	0.8480	10.16	59.0	28.0	13.0
66		265.0	1.0480	0.8130	−2.99	70.0	22.7	7.3
67		297.0	1.0480	0.8110	−1.66	69.4	22.4	8.2
68		523.0	1.0500	0.8050	6.01	78.4	13.3	8.3
69		250.0	1.0440	0.9310	3.65	10.5	63.9	25.6
70		394.0	1.0440	0.8010	0.79	72.0	25.0	3.0
71		253.0	1.0450	0.8500	2.23	58.0	34.0	8.0
72		364.0	1.0610	0.9770	14.27	10.2	45.5	44.3

[a] References for fractions 57–72: 57–67, Van Nes and Van Western (1951); 68–72, private communications.

Table III. Prediction of PNA Analysis of Light Petroleum Fractions

		range				abs dev,[a] vol %					
						P%		N%		A%	
methods	no. of data pts.	M	P%	N%	A%	av	max	av	max	av	max
eq 8–10	85	78–214	2–93	2–46	1–93	4.1	18.2	5.9	15.2	3.8	9.8
eq 13, 14, 10						5.1	12.1	8.1	18.3	6.8	20.2
eq 15, 16, 10						5.3	16.3	8.6	20.7	5.5	14.0
API TDB						11.2	32.0	12.2	20.2	7.1	12.0

[a] Absolute deviation = predicted value − experimental value. av = ($\sum$|abs dev|)/no. of data pts.

Table IV. Prediction of PNA Analysis of Heavy Petroleum Fractions

		range				abs dev,[a] vol %					
						P%		N%		A%	
methods	no. of data pts.	M	P%	N%	A%	av	max	av	max	av	max
eq 11, 12, 10	72	233–571	10–81	13–64	0–31	3.1	20.0	4.0	17.9	2.0	8.9
eq 17, 18, 10						6.5	32.0	5.9	28.0	2.2	25.7
eq 19, 20, 10						6.1	28.0	5.7	25.0	2.2	22.0
API–TDB						4.3	15.1	5.9	26.6	4.1	12.2
n–d–M method[b]	70		30–81			6.4	23.8	8.6	33.5	5.9	27.9

[a] Defined in Table III. [b] Described by Van Nes and Van Westen (1951).

For M = 70–300 and T_b = 80–650 °F

$$M = 981.62 \exp(-1.135 \times 10^{-3}T_b - 11.869S + 2.509 \times 10^{-3}T_bS)\, T_b^{1.2732}\, S^{7.4615} \quad (24)$$

$$\mathrm{CH} = 17.220 \exp(8.25 \times 10^{-3}T_b + 16.94S - 6.94 \times 10^{-3}T_bS)\, T_b^{-2.725}\, S^{-6.798} \quad (25)$$

$$n = \left(\frac{1 + 2I}{1 - I}\right)^{1/2} \quad (26)$$

where

$$I = 0.02266 \exp(3.905 \times 10^{-4}T_b + 2.468S - 5.704 \times 10^{-4}T_bS)\, T_b^{5.721 \times 10^{-2}}\, S^{-0.72} \quad (27)$$

$$d = 0.98255T_b^{0.002016}S^{1.0055} \quad (28)$$

For M = 300–600 and T_b = 650–1000 °F

$$M = 9.35 \times 10^{12} \exp(0.00522T_b - 7.262S - 3.476 \times 10^{-4}T_bS)\, T_b^{-3.21}\, S^{6.03} \quad (29)$$

$$\mathrm{CH} = 3.408 \times 10^{-22} \exp(4.684 \times 10^{-3}T_b + 103.12I - 0.0152T_bI)\, T_b^{-0.786}\, I^{-21.567} \quad (30)$$

$$I = 2.341 \times 10^{-2} \exp(6.464 \times 10^{-4}T_b + 5.144S - 3.289 \times 10^{-4}T_bS)\, T_b^{-0.407}\, S^{-3.333} \quad (31)$$

n can be determined by eq 24

$$d = 2.83086M^{0.03975}I^{1.13543} \quad (32)$$

For heavy (M > 300) fractions, the boiling point may not be available; in such cases, properties can be estimated by using M and S as input parameters. Details of such correlations are given by Riazi and Daubert (1985). All these equations are based on properties of pure hydrocarbon as well as petroleum fractions.

Evaluation of the Proposed Methods

Experimental data on PNA analysis of 85 light (M < 200) fractions and 72 heavy (M > 200) fractions are given in Tables I and II. It should be noted that in Table II for heavy fractions, values of the density, d, were predicted from eq 32 using M and n. Data in Tables I and II have been taken from the bank of data collected at Penn State from private, open literature, and government sources. Summaries of the results for evaluation of the different proposed correlations for PNA prediction of light and heavy fractions are shown in Tables III and IV. Procedure 2B4.1 in API *Technical Data Book—Petroleum Refining* (1982) as well as the *n–d–M* method were also used for the purpose of comparisons. Note that the *n–d–M* method is applied only to fractions with molecular weights greater than 200 and P% greater than 25%, the range for which the method is valid.

It is clear from Tables III and IV that proposed correlations in terms of RI and VG for both light and heavy fractions are superior to the other proposed correlations for prediction of PNA analysis. Therefore, if data on viscosity are available, eq 8–12 are recommended to be used for PNA analysis of olefin-free petroleum fractions. If data on the density or refractive index are not available, they can be predicted by using appropriate equations as described earlier. At this time a simple and accurate correlation for prediction of viscosity at 100 or 210 °F similar to eq 24–32 has not yet been developed. Therefore, if viscosity of the fraction is not known, eq 13–16 for light fractions and eq 17–20 for heavy fractions should be used for PNA prediction. In these correlations the input parameters of CH, n, M, S, and d are usually available or they may be predicted from any two available parameters, as given by Riazi and Daubert (1985).

For highly aromatic fractions or coal liquids, determination of different types of aromatics using the pseudocompound method is necessary for better prediction of thermodynamic properties. Equations 21 and 22 can be

Table V. Experimental Data on Aromatic Composition of Petroleum Fractions and Coal Liquids

						exptl			predicted		
no.	ID no.	M	S	RI	m	MA%	PA%	A%	MA%	PA%	A%
1	1786	85	0.7234	1.0468	−5.9	6.2	0.0	6.2	3.5	0.0	3.5
2	1850	86	0.7489	1.0484	−4.7	5.7	0.3	6.0	9.7	0.7	10.4
3	1851	93	0.7701	1.0502	−3.9	15.2	0.5	15.7	18.5	0.5	19.0
4	1886	93	0.7672	1.0499	−4.1	16.6	0.0	16.6	17.2	0.4	17.6
5	1787	95	0.7701	1.0500	−4.0	15.6	0.0	15.6	18.1	0.4	18.5
6	246	102.4	0.7366	1.0464	−6.4	5.5	0.1	5.6	2.2	0.0	2.2
7	1887	106	0.8043	1.0529	−2.4	32.8	0.3	33.1	30.9	1.1	32.0
8	1852	107	0.8111	1.0535	−1.9	29.1	0.0	29.1	33.5	1.4	34.9
9	1788	108	0.7696	1.0494	−4.7	13.5	0.1	13.6	15.7	0.0	15.7
10	1862	108	0.7996	1.0523	−2.7	30.2	0.0	30.2	28.3	0.9	29.2
11	1789	114	0.8125	1.0532	−2.0	33.0	0.0	33.0	32.1	1.5	33.6
12	250	120.1	0.7393	1.0460	−7.4	7.6	0.0	7.6	2.4	0.0	2.4
13	1853	122	0.8679	1.0580	1.8	50.8	0.2	51.0	51.4	5.3	56.6
14	1791	126	0.9538	1.0658	8.3	80.4	1.1	81.5	82.2	11.8	94.0
15	1888	127	0.8787	1.0587	2.7	57.2	0.7	57.9	53.2	6.5	59.7
16	1863	128	0.8847	1.0592	3.1	56.9	0.2	57.1	55.0	7.1	62.1
17	1874	128	0.8866	1.0593	3.3	60.9	0.3	61.2	55.7	7.2	62.9
18	247	131	0.7774	1.0491	−5.2	20.4	0.1	20.5	15.4	0.0	15.4
19	1790	131	0.8956	1.0599	4.0	55.9	0.1	56.0	57.4	8.3	65.8
20	1841	134	0.9586	1.0655	9.1	77.2	1.3	78.5	78.0	14.1	92.2
21	1864	138	0.9572	1.0649	9.2	83.2	1.5	84.7	74.6	15.0	89.6
22	1854	139	0.9382	1.0631	7.7	70.9	3.5	74.4	67.5	13.4	81.0
23	1897	139	0.9424	1.0635	8.0	79.6	3.6	83.2	68.9	13.8	82.8
24	1792	140	0.9622	1.0652	9.7	72.7	9.4	82.1	74.8	15.9	90.7
25	1889	141	0.9406	1.0632	8.0	77.5	3.9	81.4	67.0	14.1	81.1
26	1842	142	0.9729	1.0659	10.7	80.4	7.7	88.1	76.8	17.5	94.2
27	1907	142	0.9786	1.0664	11.2	80.6	9.5	90.1	78.1	18.1	96.7
28	251	142.4	0.7620	1.0473	−7.0	9.9	0.0	9.9	9.1	0.0	9.1
29	1898	143	0.9700	1.0656	10.5	83.8	9.0	92.8	75.1	17.5	92.5
30	248	144	0.8044	1.540	−3.4	10.6	0.0	10.6	22.2	0.7	22.9
31	1875	145	0.9603	1.0645	9.8	79.3	12.0	91.3	70.5	17.0	87.5
32	1855	147	0.9531	1.0637	9.3	72.9	14.4	87.6	66.9	16.7	83.5
33	1865	150	0.9610	1.0641	10.1	77.4	12.2	89.6	67.1	18.2	85.4
34	1793	154	0.9761	1.0650	11.7	51.4	29.4	80.8	68.5	21.0	89.5
35	1891	154	0.9709	1.0645	11.2	76.8	15.9	92.7	67.0	19.3	87.4
36	1830	155	0.9606	1.0636	10.4	63.7	9.2	72.9	63.5	19.3	82.8
37	1908	156	0.9807	1.0651	12.3	63.6	3.9	67.5	68.2	22.1	90.2
38	1843	158	0.9733	1.0643	11.7	68.7	21.5	90.2	64.7	21.6	86.4
39	252	162.3	0.8086	1.0505	−3.6	4.8	0.0	4.8	20.0	0.8	20.8
40	1611	164	0.9540	1.0622	10.2	37.5	39.5	77.0	55.6	20.5	76.1
41	1856	167	0.9553	1.0620	10.5	60.9	25.3	86.2	54.0	21.3	75.3
42	1614	169	0.9645	1.0626	11.5	51.7	28.5	80.2	54.7	23.1	77.8
43	1867	169	0.9812	1.0639	13.1	59.5	34.3	93.8	58.4	25.5	83.9
44	1831	170	0.9693	1.0628	12.0	70.2	19.3	89.5	55.0	24.0	79.0
45	1892	171	0.9884	1.0642	13.9	55.9	39.7	95.6	58.4	27.1	85.5
46	1844	172	0.9879	1.0641	14.0	56.0	37.7	93.7	57.5	27.3	84.8
47	1857	173	0.9593	1.0618	11.2	45.8	42.0	87.8	50.9	23.2	74.1
48	1877	174	0.9888	1.0639	14.2	64.1	31.9	96.0	56.2	28.0	84.1
49	1616	175	0.9594	1.0616	11.3	32.1	45.3	77.4	49.6	23.7	73.2
50	1832	175	0.9848	1.0635	13.8	56.7	34.6	91.3	54.6	27.6	82.2
51	1900	175	0.9860	1.0636	14.0	67.4	28.2	95.6	54.8	27.8	82.6
52	1613	187	0.9715	1.0614	13.1	51.4	31.3	82.7	43.6	28.4	72.0
53	1901	188	1.0010	1.0634	16.4	39.0	58.0	97.0	47.3	33.8	81.1
54	1845	190	0.9972	1.0629	16.1	54.6	42.6	97.2	45.2	33.7	78.8
55	1868	190	0.9955	1.0628	15.9	42.2	53.5	95.7	44.9	33.4	78.3
56	1833	200	1.0050	1.0624	17.6	39.0	55.5	94.5	38.3	37.9	76.2
57	1893	200	1.0180	1.0632	19.1	28.2	35.1	63.3	39.5	40.4	80.0
58	1878	201	1.0090	1.0625	18.1	50.4	45.6	96.0	37.9	39.0	76.8
59	1902	202	1.0190	1.0630	19.3	26.3	45.3	71.6	38.0	41.2	79.2
60	254	214	0.8483	1.0512	−0.3	11.6	5.6	17.2	15.9	7.8	23.7
61	1834	215	1.0310	1.0623	21.7	16.4	55.7	72.1	27.6	47.7	75.4
62	1879	222	1.0500	1.0625	24.6	21.7	52.9	74.6	21.7	54.3	76.0
63	1903	222	1.0470	1.0623	24.2	18.8	50.7	69.5	21.7	53.6	75.3
64	1913	224	1.0880	1.0641	29.5	18.1	58.8	76.9	19.4	64.0	83.4
65	1880	225	1.0590	1.0626	26.0	11.5	57.7	69.2	18.8	57.5	76.3
66	253	227.5	0.8602	1.0513	1.0	16.4	6.0	22.4	13.3	10.9	24.2
67	1914	228.0	1.1000	1.0641	31.4	7.1	64.5	71.6	14.6	68.5	83.2
68	1796	230	1.0392	1.0610	23.9	11.1	65.8	76.9	14.6	54.3	68.9
69	1912	231	1.0580	1.0618	26.4	12.8	59.6	72.4	13.2	59.3	72.4
70	1904	233	1.0680	1.0620	27.8	11.2	60.1	71.3	10.8	62.5	73.3
71	1835	235	1.0510	1.0610	25.8	12.8	60.7	73.5	9.7	58.9	68.6
72	1882	241	1.0750	1.0613	29.4	8.5	57.9	66.4	2.5	67.2	69.7
73	1798	243	1.0918	1.0617	31.8	4.0	62.2	66.2	0.0	72.4	72.4
74	1797	246	1.0793	1.0608	30.5	7.6	65.9	73.5	0.0	70.1	70.1
75	1918	246	1.0950	1.0614	32.5	8.2	59.6	67.8	0.0	74.4	74.4

Table VI. Prediction of Different Types of Aromatics in Petroleum Fractions and Coal Liquids

		range				abs dev,[a] vol %					
						MA%		PA%		A%	
eq	no. of data pts.	M	MA%	PA%	A%	av	max	av	max	av	max
21–23	75	85–246	5–84	0–66	5–96	5.6	18.1	6.5	24.2	6.3	22.7

[a] Defined in Table III.

used to estimate monoaromatic (MA%) and di- and polyaromatic (PA%) portions of the mixture.

For evaluation of eq 21–23 for prediction of different types of aromatics in petroleum fractions and coal liquids, data on the aromatic content of 75 fractions are shown in Table V. Predicted values of MA%, PA%, and A% from eq 21–23 are also shown in Table V. A summary of results is given in Table VI.

When using all of the correlations developed, if the calculated value for P%, N%, A%, MA%, or PA% is less than zero, the calculated value should be changed to zero since a negative value for composition has no meaning. Such cases occur when the actual values are close or equal to zero. It also should be noted that for prediction of the aromatic portion (A%), eq 10 is more accurate than eq 23 provided the fraction is free from olefins. If it is known that the sample is coal liquid or it is highly aromatics, it is recommended that A% be calculated by eq 23 and P% and N% by eq 8 and 9 or 11 and 12.

In summary, based on the new bank of data on petroleum fractions and coal liquids, correlations in terms of readily available or predictable parameters for predictions of the paraffin, naphthene, and aromatic content of petroleum fractions are proposed. For highly aromatic fractions or coal liquids, a method is developed to predict the percentage of monoaromatics and polyaromatics. Accuracy of the proposed correlations is within 5%, an error which does not significantly affect estimated properties by the pseudocompound approach as shown by Riazi and Daubert (1980).

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Nomenclature

CH = carbon to hydrogen weight ratio
d = liquid density at 20 °C, g/cm^3
I = Huang characterization factor, $(n^2 - 1)/(n^2 + 2)$
M = molecular weight
m = parameter defined in eq 6
MA% = percent of monoaromatics in a fraction
N% = percent of naphthenes in a fraction
n = sodium D-line refractive index at 20 °C and 1 atm
RI = refractivity intercept defined in eq 1
P% = percent of paraffins in a fraction
PA% = percent of di- and polyaromatics in a fraction
PNA = paraffin, naphthene, and aromatic contents
S = specific gravity at 60/60 °F
T_b = normal boiling point, °R
VG = viscosity gravity (=VGF or VGC)
VGF = viscosity gravity function defined in eq 2 and 3
VGC = viscosity gravity constant defined in eq 4 and 5

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