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Prediction of Critical Properties of Normal Alkanes Using Pakmakar−Ivan Topological Index

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ABSTRACT: For the first time Pakmakar−Ivan (PI) topological index has been applied for prediction of various critical properties of normal alkanes from methane to eicosane. A general fifth-order polynomial as a function of just a single variable of PI index has been proposed for this prediction. Predicted critical properties of normal alkanes based on this method were compared with the other well-known predictive methods as well as the experimental data, and excellent agreement was obtained.

INTRODUCTION

Many efforts have been carried out during the past 6 decades toward the understanding of the relationships between the chemical structures of organic compounds and their various physio-chemical properties. These activities belong to a well-known class of research called as the quantitative structure−property/activity relationship (QSPR/QSAR) studies.[1] The structure of a chemical compound is modeled by the molecular graph of this compound.[2] In fact, there are several ways to represent the structure of a molecule, but the required information for determination of the chemical constitution of a molecule is conventionally provided by a molecular graph, which is characterized by two sets:[3]

1. vertex set $v = \{1, 2, ..., N\}$
2. edge set $\varepsilon = \{(i,j)|$vertices i and j are connected by an edge$\}$

In particular, a molecular graph is the graph representation of a molecule where atoms and bonds correspond to vertices and edges, respectively. Graph theory provided the chemists with a variety of very useful tools of topological indices.[4] Topological indices are numerical quantities derived from a graph theoretical representation of the molecular structure through mathematical invariants.[5] Although more than 100 indices have been introduced in the literature, but the most well-known topological indices are Wiener W index, Zagreb M_1 and M_2 indices, Balaban J index, Harary H number, Randic χ index, and Pakmakar−Ivan (PI) index.[1,4,5] The PI index is a graph invariant defined as the summation of the sums of $n_{eu}(e|G)$ and $n_{ev}(e|G)$ over all the edges $e = uv$ of a connected graph G, i.e., PI = $\sum_{e\in E(G)}[n_{eu}(e|G) + n_{ev}(e|G)]$, where $n_{eu}(e|G)$ is the number of edges of G lying closer to u than v and $n_{ev}(e|G)$ is the number of edges of G lying closer to v than to u.[4] Topological indices can be used for predicting the physical properties of substances. For example the Wiener index was the first one which was used to predict some physical properties such as boiling point, heat of vaporization, and molar refraction of alkanes.[6−10] According to our best knowledge PI index has not been used for prediction of physical properties of normal alkanes. In the present work PI index will be calculated and used as the only parameter required for prediction of critical properties of normal alkanes.

PI APPROACH FOR PREDICTION OF CRITICAL PROPERTIES

Critical properties including critical temperature, critical pressure, and critical volume of a substance have vital rule in thermophysical properties estimation of fluids through equations of state or corresponding states models.[11] Besides their significance in phase equilibrium calculations, critical properties are necessary for predicting saturation properties such as vapor pressure and phase density as well as thermal and transport properties including enthalpy of vaporization, viscosity or interfacial tension.[12] Although experimental determination of the critical properties is preferred, such measurements include many obstacles including time and cost consuming and inapplicability for heavy molecules, and these are the main reasons of the importance of the models for predicting critical properties of substances.[12] Among the many correlations for the critical properties, here the most well-known correlations are summarized in Table 1, because they are the basis of comparison between their predictions with the new method presented in the present work.

Based on the general mathematical definition of PI, a detailed computer program was written for calculation of the PI index of normal alkanes from methane to eicosane. Details of this program are given in Appendix A. The results for the calculated PI indices are shown in Table 2. The resultant general equation

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Table 1. Correlations for Prediction of Critical Properties

correlation	critical temperature (T_c/K), critical pressure (P_c/MPa)
Tsonopolous and Tan[13]	$T_C = 959.98 - \exp(6.81536 - 0.21145 N_C^{2/3})$ $P_C = \exp(2.01718 - 0.27428 N_C^{2/3})$
Magoulas and Tassios[14]	$T_C = 959.98 - \exp(6.81536 - 0.21145 N_C^{2/3})$ $P_C = 0.1 \exp(4.3398 - 0.3155 N_C^{0.6032})$
Teja et al.[15]	$T_C = 1143.8 - \exp(7.15908 - 0.303158 N_C^{0.469609})$ $P_C = 0.1 \cdot 10^{[0.84203 + \exp(1.75059 - 0.3155 N_C^{0.890006})]}$
Morgan and Kobayashi[16]	$T_C = 981.38 - 10^{(2.95993 - 0.0960146 N_C^{0.0007})}$ $P_C = 10^{(0.84888 - 0.0112727 N_C^{0.0007})}$
Hu et al.[17]	$T_C = \dfrac{0.38106 + N_C}{0.0038432 + 0.0017607 N_C^{0.5} + 0.00073827 N_C}$ $P_C = \dfrac{10}{0.19694 - 0.059777 N_C^{0.5} + 0.46718 N_C}$
Elhassan et al.[18]	$T_C = \exp[5.3919 + 1.15819 \ln(14.027 N_C + 3.79662) - 0.9221 \ln(14.02 N_C + 27.3698)] P_C$ $P_C = 0.1 \exp[9.09361 - 2.30525 \ln(14.027 N_C + 27.3698) + 1.15819 \ln(14.02 N_C + 3.79662)]$
Constantinou and Gani[19]	$T_C = 186.481 \ln[2 \times 1.3788 + (N_C - 2) \times 3.1136] P_C$ $P_C = \dfrac{0.1}{[0.1068 + 2 \times 0.018377 + (N_C - 2) \times 0.00903]^2}$

for all critical properties (CP) including critical temperature (T_c), critical pressure (P_c), and critical volume (V_c) of normal alkanes (methane to eicosane) and some light naphthenic hydrocarbons can be expressed by a fifth order logarithmic function of PI

$$\mathrm{CP} = a + bx + cx^2 + dx^3 + ex^4 + fx^5 \quad (1)$$

where

$$x = \ln(\mathrm{PI}) \quad (2)$$

The coefficients a to f of eq 1 are given in Table 3 for different critical properties for normal alkanes.

RESULTS AND DISCUSSION

To examine the precision of the proposed method for calculation of critical properties of normal alkanes, we have compared the predicted results of this method with the previous methods as well as the existing experimental data. These comparisons are given in Tables 4 and 5 for critical temperature and pressure, respectively. As shown in these tables, the new proposed method has a good accuracy among the other existing methods for prediction of critical properties of normal alkanes. It is worthwhile to mention that this method can be easily used for calculation of the critical properties of heavier hydrocarbons where the experimental data for these heavy molecules are not available. The only parameter needed for these calculations if PI index which is ready to calculate by the computer codes introduced in the present work.

Table 2. Calculated PI Index of Normal Alkanes from Methane to Eicosane

hydrocarbon	PI index	hydrocarbon	PI index
methane	144	undecane	57024
ethane	1296	dodecane	68256
propane	3456	tridecane	80496
butane	6624	tetradecane	93744
pentane	10800	pentadecane	108000
hexane	15984	hexadecane	123264
heptane	22176	heptadecane	139536
octane	29376	octadecane	156816
nonane	37584	nonadecane	175104
decane	46800	eicosane	194400

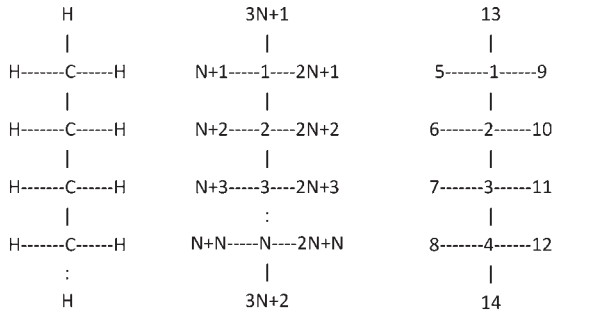

Figure A.1. Indexing method.

APPENDIX A: PI INDICES OF NORMAL ALKANES

A computer program was written to generate PI index of normal alkanes. This work is divided into two main parts. Generating graph of a normal alkane molecule and calculating of PI index which are explained in the following sections, respectively.

a. Generating Graph of a Normal Alkane. In order to generate a graph, a unique index is assigned for each atom first. Secondly, a data structure is created to represent the molecule structure. Using this data structure, graph adjacency matrix is created and passed to second part of the program. Figure A.1 shows indexing method. Figure A.1a shows molecular generic structure of normal alkanes, Figure A.1b illustrates general indexing method with N carbon atoms, while Figure A.1c shows a sample with 4 carbon atoms.

By this way all indices between 1 and N are corresponded with carbon atom and the others are corresponded to Hydrogen atoms. Each Carbon atom has 4 neighbors which are cited in a row of $4 \times N$ matrix. Each element of this matrix represents a C−H joint that will be an edge in resultant graph. Table A1 shows data structure for a sample normal alkane with $N = 4$.

Generating graph of normal alkanes is briefly expressed below in two consecutive flow-charts given by Figures A.2 and A.3. The first one (Figure A.2) gets number of carbon atoms (N) as an input argument and generates a 4-column matrix (GM) which is the molecule structure of corresponding normal alkane. The second flow-chart makes adjacency matrix (AM) of graph representation using GM matrix which is shown in Figure A.3.

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Table 3. Coefficients of eq 1 for Different Critical Properties of Normal Alkanes

critical property	*a*	*b*	*c*	*d*	*e*	*f*
T_c/K	−3025.1680	1859.2700	−421.6220	46.7502	−2.4596	0.04981
P_c/MPa	−5.4388	2.25985	0.3249	−0.1143	0.0090	−0.00023
V_c/cm^3·mol^{-1}	−2309.989	1685.488	−469.131	64.9251	−4.4853	0.1272

Table 4. Comparison Between the Predicted Critical Temperatures of the Proposed Method and Other Methods

component	T_c K (exp.[a])	Tsonopolous and Tan	Magoulas and Tassios	Teja et al.	Morgan and Kobayashi	Hu et al.	Elhassan et al.	Constantinou and Gani	this work
methane	190.564 ± 0.015	222.01	222.01	194.31	233.36	217.76	199.32	N/A	190.63
ethane	305.32 ± 0.04	308.20	308.20	298.84	315.51	304.88	298.34	189.16	304.70
propane	369.83 ± 0.1	372.69	372.69	370.06	377.42	371.23	369.75	330.08	371.52
butane	425.12 ± 0.1	424.83	424.83	424.86	427.80	424.62	425.04	409.43	424.61
pentane	469.7 ± 0.2	468.67	468.67	469.58	470.39	469.08	469.95	464.91	468.91
hexane	507.6 ± 0.2	506.40	506.40	507.38	507.25	507.01	507.70	507.62	506.81
heptane	540.2 ± 0.3	539.41	539.41	540.11	539.65	539.97	540.25	542.34	539.83
octane	568.7 ± 0.3	568.65	568.65	568.94	568.48	569.00	568.86	571.61	568.96
nonane	594.6 ± 0.6	594.77	594.77	594.66	594.35	594.88	594.39	596.89	594.93
decane	617.7 ± 0.6	618.29	618.29	617.85	617.75	618.15	617.45	619.16	618.29
undecane	639 ± 1	639.60	639.60	638.94	639.04	639.25	638.49	639.05	639.44
dodecane	658 ± 1	659.00	659.00	658.24	658.49	658.51	657.85	657.01	658.71
tridecane	675 ± 1	676.74	676.74	676.02	676.36	676.19	675.79	673.40	676.35
tetradecane	693 ± 2	693.02	693.02	692.47	692.81	692.50	692.51	688.47	692.57
pentadecane	708 ± 2	708.02	708.02	707.77	708.03	707.62	708.18	702.41	707.54
hexadecane	723 ± 2	721.87	721.87	722.04	722.13	721.69	722.93	715.37	721.41
heptadecane	736 ± 2	734.70	734.70	735.40	735.23	734.82	736.87	727.50	734.30
octadecane	747 ± 3	746.60	746.60	747.94	747.44	747.13	750.08	738.88	746.30
nonadecane	758 ± 8	757.68	757.68	759.76	758.84	758.70	762.65	749.61	757.50
eicosane	768 ± 8	768.00	768.00	770.90	769.49	769.60	774.64	759.76	767.99
AAD%		0.88	0.88	0.29	1.28	0.74	0.47	4.6	0.13

[a] Taken from *J. Chem. Eng. Data* **1995**, *40*, 531−546 [ref 20].

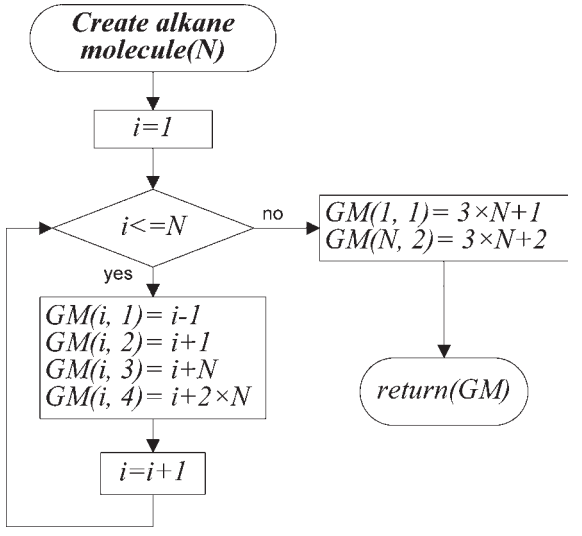

Figure A.2. Generation of a 4-column matrix (GM).

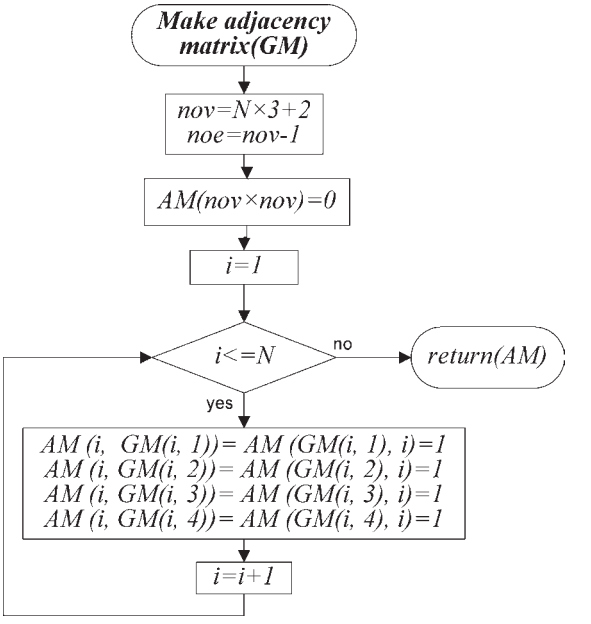

Figure A.3. Adjacency matrix (AM) of graph representation using GM matrix.

b. PI Index Calculation. As metioned in the Introduction, PI index is defined as the summation of the sums of $n_{eu}(e|G)$ and

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$n_{ev}(e|G)$ over all the edges e = uv of the connected graph G, where $n_{eu}(e|G)$ is the number of edges of graph lying closer to u than v and $n_{ev}(e|G)$ is the number of edges of G lying closer to v than to u. Instead of calculating sums $n_{eu}(e|G)$ and $n_{ev}(e|G)$ for each e = uv, here we have calculated the difference of $n_e(e|G) - n_{uev}(e|G)$, where $n_e(e|G)$ is the total number of edges of graph G and $n_{uev}(e|G)$ is the number of edges of G with equal distance to u and v named parallel edges. The following flow-charts (shown in Figures A.4 to A.6) express methods for making distance matrix (DM), counting parallel edges of an edge, and calculating PI index, respectively.

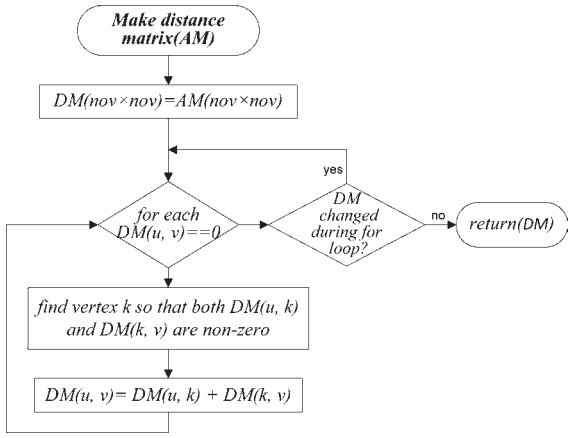

Figure A.4. Method of making distance matrix (DM).

Table A1. Molecule Data Structure of a Normal Alkane with 4 Carbon Atoms

carbon index	up	down	left	right
1	13	2	5	9
2	1	3	6	10
3	2	4	7	11

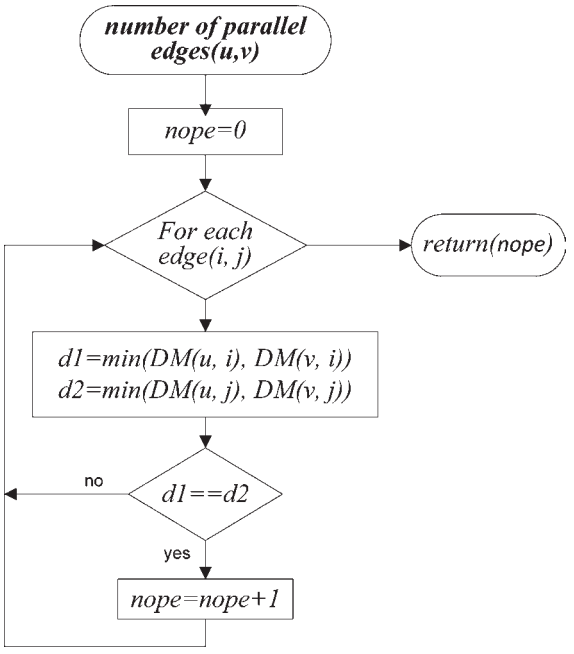

Figure A.5. Method of counting parallel edges of an edge.

Table 5. Comparison Between the Predicted Critical Pressures of the Proposed Method and Other Methods

component	P_c MPa (exp.[a])	Tsonopolous and Tan	Magoulas and Tassios	Teja et al.	Morgan and Kobayashi	Hu et al.	Elhassan et al.	Constantinou and Gani	this work
methane	4.599 ± 0.003	5.714	5.594	5.042	6.88	16.547	4.685	5.526	4.598
ethane	4.872 ± 0.01	4.864	4.749	4.051	6.78	9.553	4.683	4.853	4.876
propane	4.248 ± 0.01	4.249	4.158	3.331	6.69	6.689	4.248	4.295	4.270
butane	3.796 ± 0.01	3.766	3.703	2.791	6.61	5.138	3.787	3.829	3.762
pentane	3.37 ± 0.02	3.371	3.334	2.378	6.55	4.168	3.377	3.434	3.353
hexane	3.025 ± 0.02	3.039	3.027	2.059	6.48	3.504	3.030	3.098	3.020
heptane	2.74 ± 0.03	2.755	2.764	1.810	6.42	3.022	2.737	2.808	2.742
octane	2.49 ± 0.03	2.509	2.538	1.615	6.36	2.656	2.489	2.558	2.506
nonane	2.29 ± 0.05	2.294	2.339	1.461	6.31	2.368	2.278	2.339	2.302
decane	2.11 ± 0.05	2.105	2.164	1.339	6.26	2.137	2.097	2.147	2.125
undecane	1.95 ± 0.1	1.936	2.008	1.242	6.21	1.946	1.940	1.978	1.968
dodecane	1.82 ± 0.1	1.785	1.868	1.165	6.16	1.787	1.804	1.829	1.829
tridecane	1.68 ± 0.1	1.650	1.742	1.103	6.12	1.652	1.684	1.695	1.705
tetradecane	1.57 ± 0.2	1.528	1.628	1.054	6.07	1.535	1.578	1.576	1.592
pentadecane	1.48 ± 0.2	1.418	1.524	1.014	6.03	1.434	1.483	1.469	1.490
hexadecane	1.4 ± 0.2	1.317	1.429	0.981	5.99	1.345	1.399	1.372	1.397
heptadecane	1.34 ± 0.2	1.226	1.343	0.955	5.95	1.267	1.323	1.285	1.312
octadecane	1.29 ± 0.2	1.143	1.263	0.934	5.91	1.197	1.254	1.205	1.234
nonadecane	1.16 ± 0.2	1.066	1.190	0.917	5.87	1.135	1.192	1.133	1.162
eicosane	1.07 ± 0.2	0.996	1.122	0.904	5.83	1.078	1.135	1.067	1.095
AAD%		4.46	2.84	42.03	278.13	13.81	0.83	3.17	0.86

[a] Taken from *J. Chem. Eng. Data* **1995**, *40*, 531−546 [ref 20].

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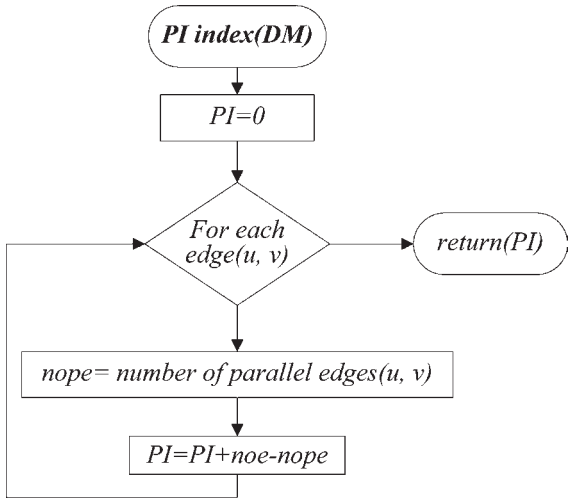

Figure A.6. Method of calculating PI index.

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