

Prediction of Pure Component Properties of Alkenes and Dienes by Group Contributions

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The pure component properties of many alkenes and dienes required for the design of process plants are not common in the open literature. Estimation methods are veritable tools for bridging this information gap. In this study, three Group Contribution Methods were employed to predict critical properties of twenty three alkenes and ten dienes. The capabilities of the three methods were compared and contrasted within obtainable experimental data. Generally, there was a good agreement between predicted and experimental properties.

1. Introduction

Alkenes have a wide range of applications in the industry. They are used as precursors in the syntheses of detergents, plastics, alcohols, lacquers, and fuels. In particular they serve as feedstock for the petrochemical industry since they can take part in numerous reactions, especially polymerization and alkylation reactions. Pure component and thermodynamic property data of these compounds are crucial for the fabrication of process plants (Cunico et al., 2013). Quite a lot of industrially important compounds lack experimental data (Kolská et al., 2012), hence, different estimation methods have been developed over the years to provide data that cannot be sourced readily in the open literature (Constantinou and Gani, 1994). Such models are validated by comparing available experimental data with predicted values (Patrasciou and Doicin, 2015).

Group Contribution Methods (GCMs) have been found to be very suitable and easy to employ for the prediction of a large number of pure component properties (Monago and Otoberise, 2010), as well as thermodynamic and physico-chemical properties of thousands of compounds (Marrero and Gani, 2001). GCMs have been developed to predict properties of hazardous compounds (Mondejar et al., 2017) and compounds that pose serious environmental challenges (Moosavi et al., 2014). He et al., (2016) evolved a Group Contribution Method (GCM) for the prediction of certain thermodynamic characteristics of hydrocarbon compounds with bulky carbon-carbon chain. The group interaction within a molecule was obtained by using an exponential decay function of the distance between atom groups in series. Overall, the GCM provided satisfactory results for alkanes and alkenes.

Many GCMs have a limitation of being capable to predict properties of pure compounds, this is because information on the features of the disparate relations between groups of atoms and molecules or between atom groups alone is not easily extracted from pure component data, that are fundamental in determining the contributions of functional groups (Papaioannou et al., 2014). Three pure component properties are extensively used, namely: critical temperature (T_c), critical pressure (P_c) and critical volume (V_c) (Verevkin et al., 2006; Otoberise et al., 2018). The objective of this study is to predict with acceptable accuracy the critical properties of some alkenes and dienes, by means of GCMs. Experimental critical property data are mostly only obtainable for molecules of sufficient thermal stability. Molecules that are thermally labile often require estimation or prediction techniques to determine their pure component properties.

2. Estimation Methods

Three GCMs were tested for critical property prediction, namely; the methods of Lydersen (1955), Constantinou and Gani (1994) and Marrero and Gani (2001).

2.1. The Method of Lydersen

The method utilizes contributions from atoms, groups of atoms or functional groups to estimate T_c , P_c and V_c . Equations 1, 2 and 3 gives the relationship for the prediction of critical properties.

$$T_c = T_b \left[0.567 + \Sigma \Delta_T - (\Sigma \Delta_T)^2 \right]^{-1} \quad (1)$$

$$P_c = M (0.34 + \Sigma \Delta_p)^{-2} \quad (2)$$

$$V_c = 40 + \Sigma \Delta_v \quad (3)$$

In equation (1) T_c is in units of Kelvin; in equation (2) P_c is in units of atmospheres, however the final predictions were converted to bar units in tandem with the unit of the same parameter for other GCMs in this study. In equation (3) V_c is in units of cubic centimeters per mole. The summation of contributions for various atoms or groups of atoms yields the Δ quantities. Lydersen's critical property values for various atoms or groups can be easily sourced (Reid *et.al.*, 1977). The required experimental input parameters for this GCM are the normal boiling point (T_b) and the molar mass (M). The average relative deviations (ARD) associated with these relations varies.

2.2 The Method of Constantinou and Gani (C & G).

This GCM finds application in the estimation of a number of thermodynamic properties. The prescriptions for T_c , P_c and V_c are as follows:

$$\exp(T_c / t_{co}) = \sum_i N_i C_i + W \sum_j M_j D_j \quad (4)$$

$$(P_c - P_{c1})^{-0.5} - P_{c2} = \sum_j N_j C_j + W \sum_j M_j D_j \quad (5)$$

$$V_c - V_{co} = \sum_i N_i C_i + W \sum_j M_j D_j \quad (6)$$

The parameters and summation quantities represented by the various symbols in equations (4) – (6) and contributions for various atoms or groups have been described elsewhere (Constantinou and Gani, 1994; Otobrise *et al.*, 2018).

2.3 The Method of Marrero and Gani (M & G).

This GCM estimates the properties of pure organic compounds in three steps. The prescriptions for T_c , P_c and V_c are as follows:

$$\exp(T_c / t_{co}) = \sum_i N_i C_i + W \sum_j M_j D_j + Z \sum_k O_k E_k \quad (7)$$

$$(P_c - P_{c1})^{-0.5} - P_{c2} = \sum_j N_j C_j + W \sum_j M_j D_j + Z \sum_k O_k E_k \quad (8)$$

$$V_c - V_{co} = \sum_i N_i C_i + W \sum_j M_j D_j + Z \sum_k O_k E_k \quad (9)$$

The summation quantities and other parameters, represented by the various symbols in equations (7) – (9) and contributions for various atoms or groups have been described elsewhere (Marrero and Gani, 2001; Otobrise *et al.*, 2018).

3. Results and discussions

In table 1 the predicted values of T_c , P_c and V_c for the alkenes and dienes by the GCMs are presented. The method of Constantinou and Gani under-predicted V_c unlike the other GCMs. The negative value of the adjustable parameter V_{co} in equation (9) makes this GCM particularly unsuitable for the prediction of critical volumes of alkenes and dienes. The prediction of the properties of isomers improved with GCMs that had second and third order contributions, especially the method of Marrero and Gani. Distinguishing the properties of isomers was particularly difficult with the method of Lydersen.

In tables 2 and 3 the deviations of predicted properties from available experimental data of some alkenes and dienes are presented.

Table 1: Critical Properties of Alkenes and Dienes Predicted by the GCMs

Alkenes	N_c	Predicted T_c/K			Predicted P_c/bar			Predicted $V_c/cm^3 mol^{-1}$		
		Lydersen	C & G	M & G	Lydersen	C & G	M & G	Lydersen	C & G	M & G
Ethene	2	280.65	292.04	271.08	48.56	65.99	61.87	140.00	112.13	106.38
1-Propene	3	363.15	344.32	371.24	43.32	49.48	49.14	195.00	187.17	162.66
1-butene	4	417.66	420.37	426.07	38.26	43.18	42.43	250.00	242.93	244.01
(E)-2-Butene	4	433.47	429.74	435.49	39.35	42.03	41.44	246.00	241.14	243.08
(Z)-2-Butene	4	439.64	430.03	436.42	39.35	71.81	68.37	246.00	69.71	243.58
2-methyl-1-propene	4	432.99	414.58	424.61	57.38	39.83	42.19	241.00	237.56	236.05
2-methyl-1-butene	5	475.02	469.48	469.15	33.98	35.28	36.98	296.00	293.32	292.33
2-methyl-2-butene	5	474.45	477.91	475.53	34.79	35.43	35.84	291.00	294.04	296.89
3-methyl-1-butene	5	451.99	456.08	460.34	34.79	38.00	37.60	301.00	293.74	312.36
1-Pentene	5	461.36	473.77	470.36	33.98	38.04	37.18	305.00	298.69	300.29
(E)-2-Pentene	5	476.96	480.79	478.17	34.79	37.09	41.44	301.00	296.9	299.36
(Z)-2-Pentene	5	477.87	481.01	478.94	34.79	71.81	56.98	301.00	125.47	299.86
2,3-Dimethyl-2-butene	6	540.82	524.41	524.00	31.09	32.01	32.01	337.00	371.99	372.01
3,3-Dimethyl-1-butene	6	479.78	489.67	495.19	31.09	34.64	33.60	346.00	336.91	340.44
1-Hexene	6	506.30	514.96	507.52	30.46	33.79	32.98	360.00	354.45	356.57
1-Heptene	7	490.92	548.49	539.52	31.49	30.25	29.58	415.00	410.21	412.85
1-Octene	8	563.32	576.78	567.63	25.13	27.25	26.79	470.00	465.97	469.13
2,4,4-Trimethyl-1-Pentene	8	559.02	556.50	557.35	25.53	26.14	27.10	447.00	443.06	445.04
2,4,4-Trimethyl-2-Pentene	8	561.78	561.76	561.73	32.65	26.23	26.45	442.00	443.78	389.25
1-decene	10	611.25	622.78	615.30	21.33	22.50	22.51	580.00	577.49	581.69
1-undecene	11	631.88	642.04	635.89	19.82	20.60	20.85	635.00	633.25	637.97
1-dodecene	12	650.49	659.44	654.80	18.51	18.95	19.43	690.00	689.01	694.25
1-hexadecene	16	711.84	715.98	717.95	14.62	14.09	15.40	910.00	912.05	919.37
Dienes										
1,2-Butadiene	4	456.85	444.10	455.95	38.70	45.59	44.15	231.00	219.00	219.87
1,3-Butadiene	4	426.25	417.59	431.37	39.83	46.27	45.40	236.00	228.61	230.81
2-methyl-1,3-Butadiene	5	482.09	445.61	473.56	35.21	37.52	39.30	281.00	279.00	279.13
3-methyl-1,2-Butadiene	5	535.28	468.55	506.38	34.37	35.91	36.74	277.00	294.04	291.01
1,2-Pentadiene	5	497.71	491.73	495.30	34.37	40.02	38.53	286.00	274.76	276.15
(E)-1,3-Pentadiene	5	486.93	478.80	482.40	35.21	39.52	71.11	291.00	282.58	286.16
(Z)-1,3-Pentadiene	5	490.09	479.02	481.92	35.21	66.18	61.95	291.00	281.60	286.66
1,4-Pentadiene	5	462.10	471.70	451.60	35.21	40.57	39.51	291.00	284.37	287.09
2,3-Pentadiene	5	508.46	506.08	438.40	35.21	44.15	39.87	282.00	292.27	284.82
1,5-hexadiene	6	512.55	513.31	511.25	31.44	35.89	34.86	346.00	340.13	343.37

The deviations of estimated properties were calculated using the relationship in equation (10). The deviations in the predicted properties from experimental data are clearly related to the number of carbon atoms in each molecule.

$$D = \frac{\text{Experimental}_{(data)} - \text{Predicted}_{(data)}}{\text{Experimental}_{(data)}} \times 100 \quad (10)$$

Table2: Deviations of Predicted T_c from Available Experimental T_c .

Alkenes	N_c	Predicted T_c/K			Experimental T_c/K	Deviation (%)		
		Lydersen	C & G	M & G		Lydersen	C & G	M & G
Ethene	2	280.65	292.04	271.08	282.30 ^a	0.58	-3.45	3.97
1-Propene	3	363.15	344.32	371.24	365.60 ^a	0.67	5.82	-1.54
1-butene	4	417.66	420.37	426.07	419.60 ^a	0.46	-0.19	-1.54
(E)-2-Butene	4	433.47	429.74	435.49	428.60 ^a	-1.14	-0.27	-1.61
1-Pentene	5	461.37	473.77	470.36	464.80 ^b	0.74	-1.93	-1.20
1-Hexene	6	506.30	514.96	507.52	504.00 ^b	-0.46	-2.18	-0.70
1-Heptene	7	490.92	548.49	539.52	537.40 ^b	8.65	-2.07	-0.40
1-Octene	8	563.32	576.78	567.63	567.00 ^b	0.65	-1.73	-0.11
1-decene	10	611.26	622.78	615.30	616.00 ^b	0.77	-1.10	0.11
1-dodecene	12	650.49	659.44	654.80	658.00 ^b	1.14	-0.22	0.49
1-hexadecene	16	711.84	715.99	717.95	718.00 ^b	0.86	0.28	0.01

Source: ^a(Wick et al., 2000) ^b(Brauner et al., 2008).

Table3: Deviations of Predicted V_c from Available Experimental V_c .

Alkenes	N_c	Predicted V_c/cm^3mol^{-1}			Experimental V_c/cm^3mol^{-1}	Deviation (%)		
		Lydersen	C & G	M & G		Lydersen	C & G	M & G
1-butene	4	250.00	242.93	244.01	239.00*	-4.60	-1.64	-2.10
2-methyl-1-propene	4	241.00	237.56	236.05	238.00*	-1.26	0.18	0.82
2-methyl-1-butene	5	296.00	293.32	292.33	292.00*	-1.37	-0.45	-0.11
3-methyl-1-butene	5	301.00	293.74	293.58	302.10*	0.36	2.77	2.82
1-Pentene	5	305.00	298.69	300.29	296.00*	-3.04	-0.91	-1.45
1-Hexene	6	360.00	354.45	356.57	350.00*	-2.86	-1.27	-1.88
1-Heptene	7	415.00	410.21	412.85	413.00*	-0.48	0.68	0.04
1-Octene	8	470.00	465.97	469.13	472.00*	0.42	1.28	0.61
1-decene	10	580.00	577.49	581.69	585.00*	0.85	1.28	0.57
1-undecene	12	635.00	633.25	637.97	642.00*	1.09	1.36	0.63
1-dodecene	12	690.00	689.01	694.25	700.00*	1.43	1.57	0.82
Dienes								
1,2-Butadiene	4	231.00	219.00	219.87	219.00*	-5.48	0.00	-0.40
1,3-Butadiene	4	236.00	228.61	230.81	220.80*	-6.88	-3.54	-4.53
3-methyl-1,2-Butadiene	5	277.00	294.04	291.01	291.00*	4.81	-1.04	0.00
1,2-Pentadiene	5	286.00	274.76	276.15	276.00*	-3.62	0.45	-0.05
1,4-Pentadiene	5	291.00	284.37	287.09	276.00*	-5.43	-3.03	-4.02
2,3-Pentadiene	5	282.00	292.27	284.82	295.00*	4.41	0.93	3.45
1,5-hexadiene	6	346.00	340.13	343.37	328.00*	-5.49	-3.70	-4.69

Source: *(Zuas and Styarini, 2009).

Generally, the GCMs of C&G and M&G had a tendency to under predict T_c and V_c . Also their predictive capability improved with increase in the number of carbon atoms of each compound. The GCM of Lydersen could only differentiate between isomers in the prediction of T_c due to the variation in their boiling temperature (T_b). This however, was not the case in the prediction of P_c and V_c where the experimental boiling temperature (T_b) was not an input parameter. In such cases the same critical values of P_c and V_c were obtained for isomers. In order to validate the predicted values for T_c , experimental data available from other studies were used to appraise the average relative deviation (ARD) according to the relationship:

$$ARD\% = \frac{\sum Deviation}{N} \quad (11)$$

The ARD for predicted T_c by the GCMs is 1.17 %, -0.64 % and -0.23 % for the methods of Lydersen, C &G and M&G respectively. The ARD for Predicted V_c is -1.51 %, -0.28 % and -0.53 % respectively for the three GCMs. In terms of ARD, the GCMs of C & G and M & G are comparable and both elicited good predictions of T_c and V_c .

For the other critical property considered in this work, i.e. P_c , experimental data could not be sourced in the open literature. Analysis among the selected GCMs can only be carried out in such a case in relation to the observed trends of their predicted values. Figures 1 and 2 shows the estimated values for the critical pressures for alkenes and dienes as a function of their carbon chain length.

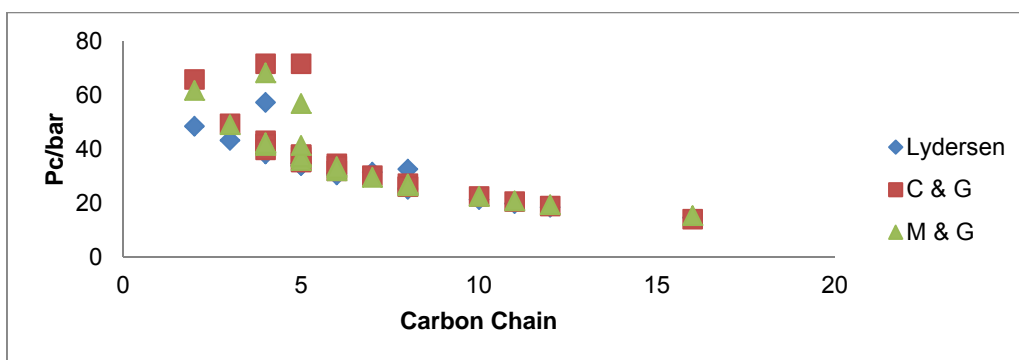


Figure 1: Critical Pressures of Alkenes Estimated by different GCMs.

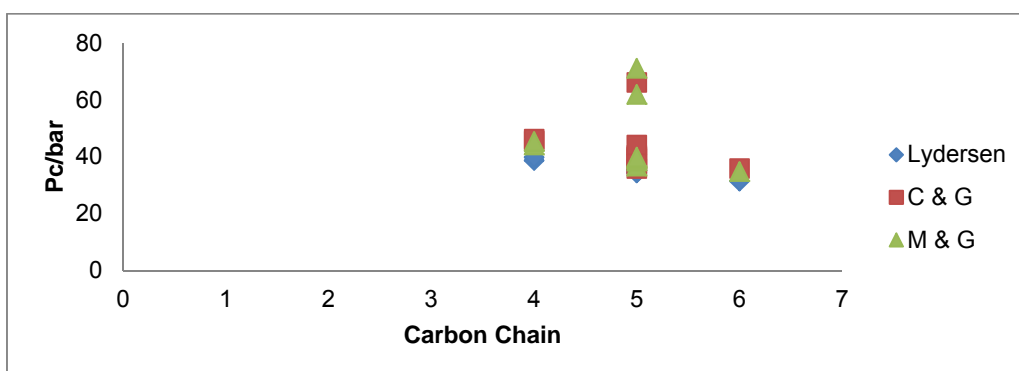


Figure 2: Critical Pressures of Dienes Estimated by different GCMs.

It can be observed from figures 1 and 2 that the three methods predicted similar P_c s for alkenes and dienes. As the carbon chain increased values predicted by the methods of C & G and M & G become closer. The inability of the method of Lydersen to distinguish between isomers, gave rise to noticeable variations in the curve.

4. Conclusions

A data bank was generated using three GCMs to estimate critical properties such as T_c , P_c and V_c for important alkenes and dienes in the chemical industry. Experimental data that are available for such

properties are very few. In the course of this work only T_c for a few alkenes were found in the open literature. The method of M & G had comparable predictive advantage for the critical properties considered over the methods of Lydersen and C & G. In the largest part, good agreement between experimental data and predicted values was attained.

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