Estimation of Critical and Thermophysical Properties of Saturated Cyclic Alkanes by Group Contributions

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Abstract

Group Contribution Methods (GCMs) of Marrero & Gani (M & G), Constantinou & Gani (C & G) and Lydersen (LYD) were employed in the prediction of some critical and thermophysical properties(TPPs), namely; critical temperature (T_c), critical pressure (P_c), critical volume (V_c), boiling temperature (T_b) and melting temperature (T_m), for various cycloalkanes. The predicted properties were compared with available experimental data. Experimental data for T_m were unfortunately very scanty in the open literature; no comparison was done to appraise any of the methods. For T_c, LYD, C & G and M & G gave average relative deviation (ARD) values of 0.02%, 1.57% and 14.64%, respectively. In the case of V_c, ARD values for LYD, C & G and M & G are 2.6 %, 23.97 %, -4.53 %, respectively. Predicted P_c values using the methods gave ARD of -31.55 %, -1.49 %, -277.98 %, respectively. C & G and M & G recorded ARD values of 0.63 % and 10.30 % for T_b, respectively.

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1. Introduction

Cycloalkanes have numerous applications. They are widely used in the pharmaceutical industry as organic solvent for the production of drugs. They are largely employed in the petroleum industry for the production of fuels. In modern chemical processes hundreds of thousands of components are used. Chemical processing units are designed on the basis of a set of physical and thermodynamic properties of compounds [1]. It is not feasible to measure them as the need arises due thermal instability in most cases, estimation/prediction methods are generally employed in such situations. Different esti-

mation methods have been developed over the years to provide data that cannot be sourced readily in open literature [2]. Such models are validated by comparing available experimental data with predicted values [3]. Predictive methods can replace measurements/experiments if they provide sufficiently good estimations. More chemists now employ computational models to elucidate details of compounds observed in the laboratory [4]. The estimated properties cannot be as precise as experimental measurements, but for many purposes the quality of the estimated properties is sufficient [5].

Estimation methods depending on the required input data have been divided into Quantity-property-property-relationship (QPPR) or Quantity-structure-property-relationship (QSPR) [6]. QPPR methods are input data intensive. QSPR methods

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need only knowledge of the chemical structure of a compound to predict the estimated property [6, 7]. GCMs are presented as empirical QSPR approaches. They have been found to be very suitable and easy to employ for the prediction of a large number of pure components properties [8], as well as physicochemical properties of thousands of compounds [1]. A lot of GCMs have been designed already with varying predictive capabilities. They have been used to predict critical properties [9, 10], state equation parameters [11, 12], acentric factor [2, 9], activity coefficients [13], normal boiling temperature [1, 14], liquid density [10, 15, 16], and flash temperatures [17]. The purpose of this work is to predict with good accuracy, some critical and TPPs of saturated cyclic hydrocarbons. Such data are significant in the design of process plants.

2. Numerical Methods

The GCMs of LYD, C & G and M & G were employed in the determination of T_c, P_c, V_c, T_b and T_m, for $C_3 - C_{13}$ cycloalkanes. This range of cycloalkanes with or without side chains are 49 common and experimental data can be readily sourced for a good number of them. The rest are large, thermally labile compounds with paucity of experimental data to compare with the results of predictive models.

2.1. The Method of Lydersen

The LYD estimates T_c, P_c, and V_c. The method is the prototype for many new models. It employs structural combinations and the relations are shown in equations (1), (2), (3) below:

$$T_c = \frac{T_b}{0.567 + \Sigma\Delta_T - (\Sigma\Delta_T)^2} \tag{1}$$

$$P_c = \frac{M}{(0.34 + \Sigma\Delta_P)^2} \tag{2}$$

$$V_c = 40 + \Sigma\Delta_V \tag{3}$$

M represents the molar mass of the compound, Δ_T, Δ_P, Δ_V are the group contributions for different groups of atoms in the molecule. T_c and T_c are in kelvin (K), P_c is measured in atmospheres (atm), and V_c is in Cubic centimeters per gram mole (cm³/gm). Contributions of atoms and molecules as stipulated by LYD are accessible [18].

2.2. The Method of Constantinou & Gani

This method makes use of first and second order level group contributions. The second level involves groups that permit a better description of proximity effects and differentiation among isomers. Property estimation in this model takes the form of equation (4) below:

$$f(x) = \Sigma_i N_i C_i + W\Sigma_j M_j D_j \tag{4}$$

C_i in equation (4) is the contribution of the first order group type-i which occurs N_i times and D_j is the contribution of the

second order group type-j with M_j occurrence in a compound. For T_c, $f(x) = \exp(T_c/t_{c0})$. Hence, for T_c equation (4) becomes

$$\exp(T_c/t_{c0}) = \left(\Sigma_i N_i t_{c1i} + \Sigma_j M_j t_{c2j}\right) \tag{5}$$

This can also be expressed as:

$$T_c = t_{c0} \ln\left(\Sigma_i N_i t_{c1i} + \Sigma_j M_j t_{c2j}\right) \tag{6}$$

t_{c0} is a constant (universal adjustable parameter) with the value 181.128 K, t_{c1i} represents group contribution of the first order group of type-i, t_{c2j} represents group contribution of the second order group of type-j.

For P_c $f(x) = (P_c - P_{ci})^{-0.5} - P_c 2$. Hence, P_c takes the form

$$(P_c - P_{ci})^{-0.5} - P_c 2 = \Sigma_i N_i p_{c1i} + \Sigma_j M_j p_{c2j} \tag{7}$$

P_{c1} and P_{c2} are universal constants (adjustable parameters) with values 1.3705 bar and 0.100220 82 bar$^{-0.5}$, respectively, P_{c1i} represents group contribution of the first order of type-i, P_{c2j} represents group contribution of the second order of type-j.

For V_c, $f(x) = V_c - V_{c0}$. Therefore, we can write:

$$V_c - V_{c0} = \Sigma_i N_i V_{c1i} + \Sigma_j M_j V_{c2j} \tag{8}$$

V_{c0} is a universal constant (adjustable parameter) with a value of -0.004350 m³/Kmol, V_{c1i} represents group contribution of the first order of type-i, V_{c2j} represents group contribution of the second order of type-j.

For T_m, $f(x) = \exp(T_m/t_{m0})$. Equation (4) will take the form of equation (9) for T_m

$$\exp(T_m/t_{m0}) = \Sigma_i N_i t_{c1i} + \Sigma_j M_j t_{c2j} \tag{9}$$

This can be written as:

$$T_m = t_{m0} \ln\left(\Sigma_i N_i t_{m1i} + \Sigma_j M_j t_{m2j}\right) \tag{10}$$

t_{m0} is a constant (adjustable parameter) with value 102.425 k. t_{m1i} represents group contribution of first order of type-i, t_{m2j} represents group contribution of the second order of type-j.

For T_b, $f(x) = \exp(T_b/t_{b0})$. This can be expressed as:

$$\exp(T_b/t_{b0}) = \Sigma_i N_i t_{b1i} + \Sigma_j M_j t_{b2j} \tag{11}$$

$$T_b = t_{b0} \ln\left(\Sigma_i N_i t_{b1i} + \Sigma_j M_j b_{m2j}\right) \tag{12}$$

t_{b0} is a constant (adjustable parameter) with value 204.359 k. t_{b1i} represents group contribution of first order of type-i, t_{b2j} represents group contribution of the second order of type-j. A table of the contributions for various atoms or groups as proposed by C & G can be readily sourced [2].

2.3. The Method of Marrero & Gani

The above method considers the molecular structure of a compound to be collection of three types of groups. The property estimation method takes the form of equation (13).

$$f(x) = \Sigma_i N_i C_i + \omega\Sigma_j M_j D_j + z\Sigma_k O_k E_k \tag{13}$$

Table 1: Critical properties predicted by the GCMs

Cycloalkanes	N_c	T_c/K			P_c/bar			$V_c/cm^3/gmol$		
		LYD	C & G	M & G	LYD	C & G	M & G	LYD	C & G	M & G
Cyclopropane	3	397.04	379.91	320.46	66.14	55.75	611.42	173.5	162.92	176.79
Cyclobutane	4	463.25	459.93	386.98	64.48	49.85	346.54	218	217.82	233.07
Methylene cyclobutane	5	499.7	498.61	442.24	59.65	42.78	268	254.5	171.26	268.19
Spiropentane	5	511.81	480.44	388.3	60.97	58.35	331.72	249	217.79	249.08
Cyclopentane	5	514.52	510.83	438.58	59.89	43.85	223.94	262.5	273.58	289.35
Cyclohexane	6	553.59	558.22	480.74	54.71	37.74	157.34	307	331.85	345.63
Methyl cyclopentane	6	535.76	533.33	469.91	50.94	38.51	160.16	319	228.48	340.64
Cycloheptane	7	602.57	578.95	516.38	49.77	38.4	117.19	351.5	378.92	401.91
1,1-dimethyl cyclopentane	7	559.89	555.95	504.53	46.35	35.06	122.51	359	232.8	385.8
Cis-1,2 dimethyl cyclopentane	7	565.19	553.33	512.09	43.78	34.89	113.27	375.5	182.98	388.18
Trans-1,2 dimethyl cyclopentane	7	553.57	562.24	512.09	43.78	34.82	113.27	375.5	182.98	388.18
Trans-1,3 dimethyl cyclopentane	7	553.36	553.33	497.49	43.78	34.11	120.77	375.5	183.38	391.93
Ethyl cyclopentane	7	569.54	563.89	508.34	44.22	34.15	120.1	374	284.24	395.21
Methyl cyclohexane	7	571.35	575.78	507.13	46.64	33.48	118.96	363.5	286.74	396.92
Cyclooctane	8	642.25	603.14	547.26	45.36	30.69	91.12	396	441.73	458.19
1,1-dimethyl cyclohexane	8	598.11	593.9	536.92	42.51	30.69	94.67	403.5	291.06	442.08
Cis-1,2-dimethyl cyclohexane	8	601.16	599.02	543.51	40.35	30.5	88.49	420	241.24	444.46
Trans-1,2-dimethyl cyclohexane	8	592.19	599.02	543.51	40.35	30.5	88.49	420	241.24	444.46
Cis-1,3-dimethyl cyclohexane	8	586.97	591.78	530.82	40.35	29.92	93.52	420	241.64	448.21
Trans-1,3 dimethyl- cyclohexane	8	592.94	591.78	530.82	40.35	29.92	93.52	420	241.64	448.21
Cis-1,4-dimethyl cyclohexane	8	593.69	591.78	530.82	40.35	29.92	93.52	420	241.64	448.21
Trans-1,4-dimethyl cyclohexane	8	585.47	591.78	530.82	40.35	29.92	93.52	420	241.64	448.21
Ethyl cyclohexane	8	602.71	600.36	540.24	40.72	29.95	93.07	418.5	342.5	451.49
Propyl cyclopentane	8	0.00	590.03	540.24	38.82	30.52	93.07	429	340	451.49
Cis-octahydro-1h-indene	9	688.01	640.73	517.9	43.59	42.46	89.62	413.5	386.67	433.93
Trans-octahydro-1h-indene	9	677.04	640.73	517.9	43.59	42.46	89.62	413.5	386.67	433.93
Butyl cyclopentane	9	0.00	612.86	568.27	34.47	27.46	74.62	484	395.76	507.77
Propyl cyclohexane	9	624.61	622.01	568.27	35.98	26.98	74.62	473.5	398.26	507.77

Table 2: Predicted critical properties continued

Cycloalkanes	N_c	T_c/K			P_c/bar			$V_c/cm^3/gmol$		
		LYD	C & G	M & G	LYD	C & G	M & G	LYD	C & G	M & G
1,1-bicyclopentyl	10	0.00	642.13	571.77	37.01	29.62	72.19	488	446.3	533.19
Cis- decahydronaphthalene	10	718.14	650.8	548.59	39.93	36.64	87.42	458	444.93	490.21
Trans- decahydronaphthalene	10	705.81	650.8	548.59	39.93	36.64	87.42	458	444.93	490.21
Butyl cyclohexane	10	646.31	641.34	593.26	32.15	24.96	61.47	482.5	454.02	564.05
1,4-diethyl cyclohexane	10	0.00	634.53	587.52	31.92	24.43	62.49	530	353.16	557.35
1,1-dimethylethyl cyclohexane	10	642.12	629.19	581.52	39.98	24.64	63.03	514.5	296.3	346
Decahydro-1-methylnaphthalene	11	0.00	667.78	567.33	32.74	25.76	60.29	544.5	406.2	584.48
Decahydro-2- methylnaphthalene	11	0.00	667.78	567.33	32.74	25.76	60.29	544.5	406.2	584.48
Ethyl octahydro-1h- indene	11	0.00	660.72	590.75	31.53	26.21	60.67	555	697.39	582.77
Decahydro dimethyl naphthalene	12	0.00	677.58	615.92	29.3	23.38	49.44	601	361.1	632.02
Ethyl decahydronaphthalene	12	0.00	682.97	613.54	29.49	23.4	51.17	599.5	461.97	639.05
1, ethyl decahydronaphthalene	12	0.00	682.97	613.54	29.49	23.4	51.17	599.5	461.97	639.05
2, ethyl decahydronaphthalene	12	0.00	682.97	613.54	29.49	23.4	51.17	599.5	461.96	639.05
Octahydro (1- methylethyl)-1h- indene	12	0.00	670.9	608.29	34.43	23.76	51.92	606	358.6	632.35
Decahydro (1- methylethyl) naphthalene	13	0.00	692	629.48	31.92	21.35	44.52	650.5	416.86	688.63
Decahydro-1-(1- methylethyl) naphthalene	13	0.00	692	629.48	31.92	21.35	44.52	650.5	416.86	688.63
Decahydro-1-propyl naphthalene	13	0.00	682.97	634.28	26.75	21.37	43.94	654.5	517.73	695.33
2 methyl-1,1- bicyclohexyl	13	0.00	696.99	633.58	28.56	21.37	43.72	633.5	517.73	697.04
1,1-methylene biscyclohexane	13	0.00	701.84	638.98	28.73	19.61	43.37	632	618.59	702.03
Heptyl cyclohexane	13	701.58	689.38	655.24	24.2	26.98	38.68	647.5	621.3	732.89

In equation (13), C_i is the contribution of the first order group of type-i that occurs N_i times, D_j is the contribution of the second order group of type-j that occurs M_j times, the E_k is the contribution of the third order group of type-k that has O_k occurrence in a compound. In the first level of estimation, the constants ω and z are assigned zero values because only first order groups are employed. In the second order level, the constants ω and z are assigned unit and zero values, respectively, because only

Table 3: Thermophysical properties predicted by the GCMs

Cycloalkanes	N_c	T_m/K		T_b/K	
		C & G	M & G	C & G	M & G
Cyclopropane	3	145.79	-41.54	240.37	169.55
Cyclobutane	4	133.96	0.88	285.65	233.57
methylene cyclobutane	5	155.49	61.81	322.07	279.07
Spiropentane	5	184.01	4.59	291.06	228.28
Cyclopentane	5	170.92	33.78	320.75	283.23
Cyclohexane	6	200.95	60.67	356.78	323.81
methyl cyclopentane	6	168.87	54.36	343.67	308.2
Cycloheptane	7	218.76	83.4	391.93	358.11
1,1-dimethyl cyclopentane	7	198.67	130.45	363.88	334.1
cis-1,2 dimethyl cyclopentane	7	175.27	92.54	378.87	346.04
trans-1,2 dimethyl cyclopentane	7	175.27	92.54	378.87	346.04
trans-1,3 dimethyl cyclopentane	7	166.79	72.41	364.27	330.65
ethyl cyclopentane	7	185.63	67.43	376.04	344.97
methyl cyclohexane	7	199.43	78.01	376.16	344.81
Cyclooctane	8	204.96	103.09	408.47	387.83
1,1-dimethyl cyclohexane	8	222.33	145.01	393.53	366.97
cis-1,2-dimethyl cyclohexane	8	204.22	111.12	406.55	377.3
trans-1,2-dimethyl cyclohexane	8	204.22	111.12	406.55	377.3
cis-1,3-dimethyl cyclohexane	8	197.89	93.52	393.87	363.99
trans-1,3 dimethyl-cyclohexane	8	197.89	93.52	393.87	363.99
cis-1,4-dimethyl cyclohexane	8	197.89	93.52	393.87	363.99
trans-1,4-dimethyl cyclohexane	8	197.89	93.52	393.87	363.99
ethyl cyclohexane	8	212.12	89.21	404.08	376.37
propyl cyclopentane	8	190.05	89.21	403.98	376.37
cis-octahydro-1H-indene	9	254.65	87.62	408.76	352.06
trans-octahydro-1H-indene	9	254.65	87.62	408.76	352.06
butyl cyclopentane	9	212.66	108.19	428.55	403.89
propyl cyclohexane	9	223.42	108.19	428.65	403.89

Table 4: Predicted thermophysical properties continued

Cycloalkanes	N_c	T_m/K		T_b/K	
		C & G	M & G	C & G	M & G
1,1-bicyclopentyl	10	230.3	34.78	448.35	409.52
cis-decahydronaphthalene	10	269.01	106.79	432.89	382.54
trans-decahydronaphthalene	10	269.01	106.79	432.89	382.54
butyl cyclohexane	10	233.59	125	450.57	428.37
1,4-diethyl cyclohexane	10	222.2	113.11	442.47	418.87
1,1-dimethylethyl cyclohexane	10	210.17	155.69	433.76	411.37
decahydro-1-methylnaphthalene	11	246.85	55.22	461.11	424.02
decahydro-2-methylnaphthalene	11	246.85	55.22	461.11	424.02
ethyl octahydro-1H-indene	11	238.38	42.8	461.02	424.14
decahydro dimethyl naphthalene	12	245.88	93.21	468.97	447.27
ethyl decahydronaphthalene	12	255.02	68.22	479.95	446.6
1, ethyl decahydronaphthalene	12	255.02	68.22	479.95	446.6
2, ethyl decahydronaphthalene	12	255.02	68.22	479.95	446.6
octahydro (1-methylethyl)-1H-indene	12	237.33	50.41	472.88	437.85
decahydro (1-methylethyl) naphthalene	13	254.12	74.65	490.79	459.03
decahydro-1-(1-methylethyl) naphthalene	13	254.12	74.65	490.79	459.03
decahydro-1-propyl naphthalene	13	262.59	89.89	497.21	466.99
2 methyl-1,1-bicyclohexyl	13	262.59	99.02	497.21	466.9
1,1-methylene biscyclohexane	13	270.4	103.71	503.43	474.68
heptyl cyclohexane	13	259.15	166.29	505	488.9

Table 5: Experimental data for the various properties used in the comparison [19].

Cycloalkanes	N_c	T_c/K	P_c/bar	$V_c/cm^3/gmol$	T_b/K	(M) g/mol
Cyclopropane	3	397.91	55.77	162.8	240.37	42.081
Cyclobutane	4	459.93	49.85	210	285.66	56.107
methylene cyclobutane	5	NA	NA	NA	NA	68.118
Spiropentane	5	499.74	52.13	236.5	312.19	68.118
Cyclopentane	5	511.76	45.02	258.3	322.4	70.134
Cyclohexane	6	553.54	40.75	307.9	353.87	84.161
methyl cyclopentane	6	532.79	37.85	318.9	344.96	84.162
Cycloheptane	7	604.32	38.4	359	391.94	98.188
1,1-dimethyl cyclopentane	7	547	34.45	360	361	98.188
cis-1,2 dimethyl cyclopentane	7	565.15	34.45	370	372.68	98.188
trans-1,2 dimethyl cyclopentane	7	553.15	34.45	360	365.02	98.188
trans-1,3 dimethyl cyclopentane	7	553	34.45	360	364.88	98.188
ethyl cyclopentane	7	569.52	33.98	374.5	376.62	98.189
methyl cyclohexane	7	572.19	34.71	368	374.08	98.186
Cyclooctane	8	647.2	35.5	410	424.3	112.21
1,1-dimethyl cyclohexane	8	591.15	29.38	450	392.7	112.22
cis-1,2-dimethyl cyclohexane	8	606.15	29.38	460	402.94	112.21
trans-1,2-dimethyl cyclohexane	8	596.15	29.38	460	396.58	112.21
cis-1,3-dimethyl cyclohexane	8	591.15	29.38	450	393.24	112.21
trans-1,3 dimethyl-cyclohexane	8	598	29.38	460	397.61	112.21
cis-1,4-dimethyl cyclohexane	8	598.15	29.38	460	397.47	112.21
trans-1,4-dimethyl cyclohexane	8	590.15	29.38	450	392.51	112.21
ethyl cyclohexane	8	609.15	30.4	450	404.95	112.21
propyl cyclopentane	8	NA	NA	NA	NA	112.21
cis-octahydro-1H-indene	9	NA	NA	NA	NA	124.22

NA = Not available.

the first and the second order groups are involved while the third level both ω and z are set to unity values. The left hand side of equation (13) is a simple function $f(x)$ of the target property "x".

For T_c, $f(x) = \exp(T_C/T_{C0})$. Hence,

$$\exp(T_C/T_{C0}) = \left(\Sigma_i N_i t_{c1i} + \Sigma_j M_j T_{c2j} + \Sigma_k O_k T_{c3k}\right) \quad (14)$$

$$T_C = T_{C0} \ln\left(\Sigma_i N_i T_{c1i} + \Sigma_j M_j T_{c2j} + \Sigma_k O_k T_{c3k}\right). \quad (15)$$

T_{c0} is a constant (adjustable parameter) with value 231.239 k. T_{c1i} represents group contribution of first order of type-i, T_{c2j} represents group contribution of the second order of type-j, T_{c3k} represents group contribution of third order of type-k.

For P_c, $f(x) = (P_c - P_{c1})^{-0.5} - P_{c2}$. Therefore

$$(P_c - P_{c1})^{-0.5} - P_{c2} = \left(\Sigma_i N_i P_{c1i} + \Sigma_j M_j P_{c2j} + \Sigma_k O_k P_{c3k}\right)(16)$$

$$P_c = 1/\left(\Sigma_i N_i P_{c1i} + \Sigma_j M_j P_{c2j} + \Sigma_k O_k P_{c3k} + P_{c2}\right) + P_{c1}(17)$$
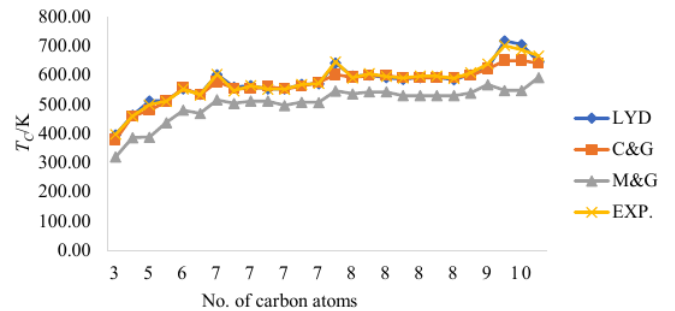

Figure 1: Plot of experimental T_c versus T_cs obtained from the GCMs.

P_{c1} and P_{c2} are both universal constants (adjustable parameters) with values 5.9827 bar and 0.108998 bar-0.5, respectively. P_{c1i} represents group contribution of first order of type-i, P_{c2j} represents group contribution of second order of type-j and P_{c3k}

Table 6: Experimental properties used in the comparison continued [19].

Cycloalkanes	N_c	T_c/K	P_c/bar	$V_c/cm^3/gmol$	T_b/K	(M) g/mol
trans-octahydro-1H-indene	9	NA	NA	NA	NA	124.22
butyl cyclopentane	9	625.05	27.64	480.5	429.76	126.24
propyl cyclohexane	9	639.15	28.87	477	429.9	126.24
1,1-bicyclopentyl	10	NA	NA	NA	NA	138.25
cis-decahydronaphthalene	10	702.25	32.42	480	468.97	138.25
trans-decahydronaphthalene	10	687.05	28.37	480	460.46	138.25
butyl cyclohexane	10	667	25.7	574	454.13	140.27
1,4-diethyl cyclohexane	10	NA	NA	NA	NA	140.27
1,1-dimethylethyl cyclo-hexane	10	NA	NA	NA	NA	152.28
decahydro-1-methylnaphthalene	11	NA	NA	NA	NA	152.28
decahydro-2-methylnaphthalene	11	NA	NA	NA	NA	152.28
ethyl octahydro-1H-indene	11	NA	NA	NA	NA	152.28
decahydro dimethyl naphthalene	12	NA	NA	NA	NA	166.3
ethyl decahydronaphtha-lene	12	NA	NA	NA	NA	166.3
1, ethyl decahydronaph-thalene	12	NA	NA	NA	NA	166.3
2, ethyl decahydronaph-thalene	12	NA	NA	NA	NA	166.3
octahydro (1-methylethyl)-1H-indene decahydro (1-methylethyl)	12	NA	NA	NA	NA	204.35
naphthalene decahydro-1-(1-methylethyl) naphthalene	13	NA	NA	NA	NA	208.38
decahydro-1-propyl naphthalene	13	NA	NA	NA	NA	208.38
2 methyl-1,1-bicyclohexyl	13	NA	NA	NA	NA	180.33
1,1-methylene biscyclo-hexane	13	NA	NA	NA	NA	180.33
heptyl cyclohexane	13	NA	NA	NA	NA	182.35

NA = Not available.
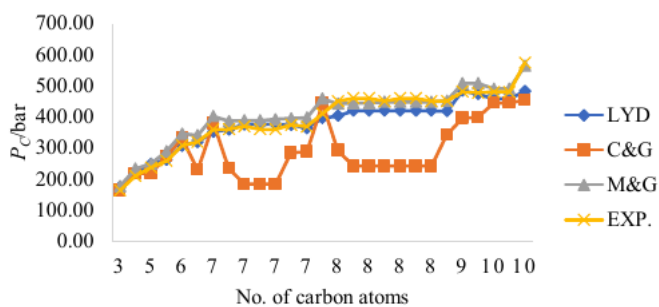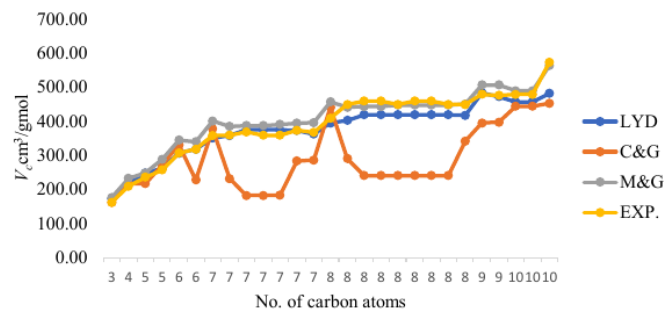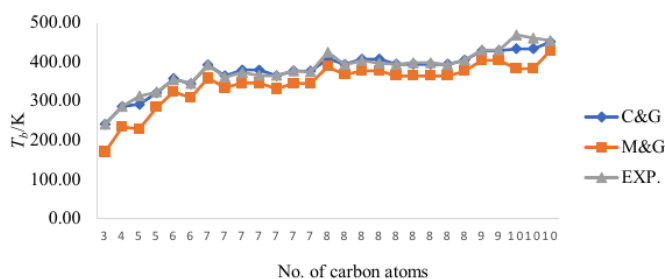

Figure 2: Plot of experimental P_c versus P_cs obtained from the GCMs.

Figure 3: Plot of experimental V_c versus V_cs obtained from the GCMs.

Table 7: Deviations of predicted properties from experimental data

Cycloalkanes	N_c	T_c (% Dev.)			P_c (% Dev.)			V_c (% Dev.)			T_b (% Dev.)	
		LYD	C & G	M & G	LYD	C & G	M & G	LYD	C & G	M & G	C & G	M & G
Cyclopropane	3	0.22	4.52	24.17	-	0.04	-	-6.57	-0.07	-8.59	0.00	29.4
Cyclobutane	4	-	0.00	18.85	-18.59	0.00	-996	3 -3.81	-3.72	-	0.00	6 18.2
methylene cyclobutane	5	-0.72	-	-	-29.35	-	3 - 595.	-1	-	-10.99	-	-3
Spiropentane	5	-	3.86	28.7	-	-	-7	-5.29	7.91	-5.32	6.77	26.8
Cyclopentane	5	-2.41	0.18	16.69	-16.96	11.93 2.6	-536	3 -1.63	-5.92	-	0.51	12.1 8
Cyclohexane	6	-0.54	-0.85	15.14	-33.03	7.39	-397.4	4 0.29	-7.78	-12.02	-0.82	5 8.50
methyl cyclopentane	6	-0.01	-0.1	13.38	-34.58	-1.74	286. - 3	1 -0.03	28.35	-6.82 12.25	0.37	10.6
Cycloheptane	7	0.56 0.29	4.2	17.03	-34.58	0.00	323. - 2	1 2.09	-5.55	-	0.00	8.63 6
1,1-dimethyl cyclopentane	7	-	-1.64	8.42	-29.61	-1.77	5 205. -	1 0.28	35.33	-7.17 11.95	-0.88	7.45
cis-1,2 dimethyl	7	-2.36	2.09	10.36	-34.54	-1.28	255. - 7	6 -1.49	50.55	-4.91	-1.66	7.15
cyclopentane trans-1,2 dimethyl	7	-0.01	-1.64	8.02	-27.08	-1.07	-228.2	8 -4.31	49.17	-7.83	-3.79	5.2
trans-1,3 cyclopentane dimethyl	7	-0.08	-0.06	11.16	-27.08	0.99	1 - 228.	8 -4.31	49.06	-8.87	0.17	9.38
cyclopentane ethyl cyclopentane	7	0.06 0.00	0.99	12.03	-27.08	-0.5	- 1 250.	5 0.13	24.1	-5.53	0.15	8.4
methyl cyclohexane	7	0.15	-0.63	12.83	-30.14	3.54	253. - 8	4 1.22	22.08	-7.86	-0.56	7.83
Cyclooctane	8	0.77	6.88	18.26	-34.37	13.55	5 242. -	7 3.41	-7.74	-	3.73	8.6
1,1-dimethyl cyclohexane	8	-	-0.47	10.1	-27.77	-4.46	156. - 2	6 10.33	35.32	11.75 1.76	-0.21	6.55
cis-1,2-dimethyl	8	0.18 0.82	1.18	11.53	-44.69	-3.81	222. - 8	2 8.70	47.56	3.38	-0.9	6.36
cyclohexane trans-1,2-dimethyl	8	0.66	-0.48	9.69	-37.34	-3.81	201. - 4	2 8.70	47.56	3.38	-2.51	4.86
cyclohexane cis-1,3-dimethyl	8	0.71	-0.11	11.37	-37.34	-1.84	-201	2 6.67	46.3	0.4	-0.16	7.44
cyclohexane trans-1,3 dimethyl-	8	0.85	1.04	12.66	-37.34	-1.84	-218	3 8.70	47.47	2.56	0.94	8.45
cyclohexane cis-1,4-dimethyl	8	0.75	1.06	12.68	-37.34	-1.84	-218.1	3 8.70	47.47	2.56	0.91	8.42
cyclohexane trans-1,4-dimethyl	8	0.79	-0.28	11.18	-37.34	-1.84	-218.1	3 6.67	46.3	0.4	-0.35	7.27
cyclohexane ethyl cyclohexane	8	1.06	1.44	12.76	-37.34	1.48	1 - 218.	3 7.00	23.89	-0.33	0.21	7.06
propyl cyclopentane	8	-	-	-	-39.95	-	206. - 1	-1	-	-	-	-
cis-octahydro-1H-indene	9	-	-	-	-	-	-6	-	-	-	-	-
trans-octahydro-1H-indene	9	-	-	-	-	-	-	-	-	-	-	-
butyl cyclopentane	9	-	1.95	9.99	-	0.65	-	-0.73	17.64	-5.68	0.28	6.02
propyl cyclohexane	9	2.28	2.68	12.47	-24.71	6.55	-169	6 0.73	16.51	-6.45	0.29	6.05
1,1-bicyclopentyl	10	-	-	-	-24.63	-	4 158. -	-4	-	-	-	-
cis-decahydronaphthalene	10	-	7.33	28.01	-	-	-7	4.58	7.31	-2.13	7.69	18.4
trans-decahydronaphthalene	10	-2.26	5.28	25.24	-23.16	-13.02	-169	6 4.58	7.31	-2.13	5.99	16.9 3
butyl cyclohexane	10	2.73 3.10	3.85	12.43	-25.1 40.75	2.88 29.15	208. - 4	1 15.94	20.9	1.73	0.78	5.67 2

Figure 4: Plot of experimental T_b versus T_bs obtained from the GCMs.

represents group contribution of third order of type-k. For V_c, $f(x) = V_C - V_{c0}$. Consequently,

$$V_C - V_{c0} = \left(\Sigma_i N_i V_{c1i} + \Sigma_j M_j V_{c2j} + \Sigma_k O_k V_{c3k}\right) \quad (18)$$

$$V_C = 1/\left(\Sigma_i N_i V_{c1i} + \Sigma_j M_j V_{c2j} + \Sigma_k O_k V_{c3k}\right) + V_{c0} \quad (19)$$

V_{c0} is a universal constant (adjustable parameter) with a value 7.95 cm^3/mol, V_{c1i} represents group contribution of first order of type-i, V_{c2j} represents group contribution of second order of type-j and V_{c3k} represents group contribution of third order of type-k.

For T_m, $f(x) = \exp(T_m/T_{m0})$. Therefore,

$$\exp(T_m/T_{m0}) = \left(\Sigma_i N_i T_{m1i} + \Sigma_j M_j T_{m2j} + \Sigma_k O_k T_{m3k}\right) \quad (20)$$

$$T_m = T_{m0} \ln\left(\Sigma_i N_i T_{m1i} + \Sigma_j M_j T_{m2j} + \Sigma_k O_k T_{m3k}\right). \quad (21)$$

T_{m0} is a constant (adjustable parameter) with value 147.450 k. T_{m1i} represents group contribution of first order of type-i, T_{m2j} represents group contribution of the second order of type-j, T_{m3k} represents group contribution of third order of type-k.

For T_b, $f(x) = \exp(T_b/T_{b0})$. Hence,

$$\exp(T_b/T_{b0}) = \left(\Sigma_i N_i T_{b1i} + \Sigma_j M_j T_{b2j} + \Sigma_k O_k T_{b3k}\right) \quad (22)$$

$$T_b = T_{b0} \ln\left(\Sigma_i N_i T_{b1i} + \Sigma_j M_j T_{b2j} + \Sigma_k O_k T_{b3k}\right). \quad (23)$$

T_{b0} is a constant (adjustable parameter) with value 222.543 k. T_{b1i} represents group contribution of first order of type-i, T_{b2j} represents group contribution of the second order of type-j, T_{b3k} represents group contribution of third order of type-k. A table of the contributions for various atoms or groups as proposed by M & G is readily available [1].

3. Results and Discussion

Three GCMs were employed in the prediction of the critical properties. TPPs were estimated by C & G and M & G. Tables 1 and 2 show the predicted T_c, P_c and V_c values. Tables 3 and 4 contain predicted T_b and T_m for the cycloalkanes. Experimental data for the various TPPs used in the comparison are presented on tables 5 and 6. LYD required molecular weight (M) and

T b as input parameters, they are also shown on tables 5 and 6 Where experimental T_b was not found in the literature for a particular cycloalkane, T_b predicted by the method of C & G was utilized. Deviations of the predicted properties from available experimental data were calculated using the equations below:

$$\text{Deviation}\% = \frac{\text{Exp (data)} - \text{Pred (data)}}{\text{Exp (data)}} \times 100.$$

$$\text{Average Relative Deviation} = \frac{\Sigma \text{Deviation}}{N}$$

Table 7 shows the deviations of predicted critical properties and TPPs from available experimental data. The experimental data were obtained from the Handbook of Chemical Compound Data for Process Safety [19].

LYD provided better results for T_c prediction with Average Relative Deviation of 0.02 %. M & G with ARD of 14.64 % under predicted T_c for all the compounds. C & G with ARD of 1.57 %, like Lydersen's method, gave results comparable with experimental data. Figure 1 is a comparative plot of experimental T_c and the T_cs obtained from the GCMs.

As the number of carbon atoms increased, the predicted P_c decreased for the three methods. This trend is typical of organic compounds. LYD and M & G predicted Pc values that were similar. The latter with ARD of -1.49 % gave a better prediction of P_c. C & G with an ARD of -31.55 % under predicted P_c as shown on figure 2.

C & G under predicted V_c for most of the compounds as can be seen on figure 3. As the number of carbon atoms increased the accuracy of the predicted Vc by LYD declined. LYD and M & G proved more efficient in this particular critical property as they gave values close to available experimental data with ARD of 2.6 % and -4.35 %, respectively. ARD for C & G was 23.97 %.

The method of C & G with ARD of 0.63 % proved a more reliable method for the prediction of T_b. It was able to differentiate between structural isomers having different boiling points in most cases. The method of M & G slightly under predicted Tb with ARD of 10.30 % as shown on figure 4.

4. Conclusion

Three GCMs were employed in the prediction of some critical and TPPs, namely; T_c, P_c, V_c, T_b and T_m, for cycloalkanes. The predicted properties were compared with available experimental data. LYD provided better results for T_c prediction with Average Relative Deviation of 0.02 %. C & G predicted P_c values that were similar to values obtained experimentally. With ARD of -1.49 %, it gave a better prediction of P_c. LYD proved more efficient in the prediction of V_c with ARD of 2.6 %. C &

G with ARD of 0.63 % proved a more reliable method for the prediction of T_b.

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