International Journal of Engineering and Technical Research (IJETR)
ISSN: 2321-0869, Volume-2, Issue-2, February 2014

Application of non parametric regression to ideal gas specific heat

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Abstract— **The specific heat of ideal gas is generally available as a function of temperature and type of gas. The common form is $Cp = \sum_{0}^{n} a_i T^i$ where a_i's are type of gas dependent coefficients; hence a correlation for each gas.**

This paper is aimed to apply non parametric regression to existing ideal gas specific heat correlation to: (1) identify inconsistent in the coefficients of the existing correlation and smoothen them and (2) generalize the existing correlation. The well established data on physical parameters of molecular weight (M), normal boiling point (T_b), critical temperature (T_c) and pressure (P_c) and accentric factor (ω) are used to define the gas; $a_i = f_i(M, Tb, Tc, Pc; \omega)$. The specific heat correlation is tested for four groups of gases n-Alkane, Alkene (Olefin), Naphthene (Cycloalkane) and Alcohol. It is found that the coefficients assume clear trend with physical parameters, however, the coefficient a_i for some compounds within the same group lay off the curve, unfolding inconsistency. The physical parameters are correlated to specific heat and the inconsistent is smoothened and a generalized correlation for n-Alkane is produced using non parametric regression. The developed generalized correlation reproduced the coefficients of the existing correlation for n-Alkane with absolute average percent deviation (AAPD) of less than 3%. It also reproduced the specific heats at the maximum and minimum temperatures with AAPD of about 1.0%.

Index Terms— **GRACE Algorithm, n-Alkane, Physical parameter, Specific heat.**

I. INTRODUCTION

Figure 1 shows the dependency of specific heats on temperature and type of gas. It can be seen that at low temperature, where only the translation and rotational kinetic energy are active, the specific heat is constant. At higher temperature it increases due to the presence of vibration energy in addition to translation and rotational energy. The increase continues until all the three degrees of freedoms are fully excited. Beyond full excitation of all modes of kinetic energy the curve asymptotes [1]. This is valid for all gases with exception of the monatomic gases ***Ar, He, Kr, Ne, Rn*** and ***Xe*** where their specific heat is constant and approach the value of kinetic theory $Cp/R = 5/2$ [2]. For monatomic gas, the molecules move by translation kinetic energy only; no excitation to rotational or vibration energy. The vibration part of the curve is generally available as functions of temperature in various forms such as graphs, tables and equations. Equations (1 to 3) are the common types of specific heats correlation for molecule vibration part. Equation (1) is more accurate and applicable for wide temperature range of up to 1500 K, however, it is not widely used. Equations (2 and 3) are simple polynomials however, are widely used [3], [4].

$$Cp = A + B\left(\frac{C/T}{\sinh(C/T)}\right)^2 + D\left(\frac{E/T}{\cosh(E/T)}\right)^2 \qquad (1)$$

$$Cp = \sum_{0}^{n} a_i T^i \qquad (0 \le n \le 3) \qquad (2)$$

$$Cp = \sum_{0}^{n} \alpha_i T^i \qquad (-2 \le n \le 3) \qquad (3)$$

In (1) to (3) the specific heat is in J/mole. K and the temperature (T) is in K, ***R*** is the universal gas constant and ***A; B; C; D; a*** and ***α*** are coefficients which are type of fluid dependent. These coefficients are obtained by fitting experimental data using parametric regression; fitting a prescribed model to data [5]. Parametric regression is good in representing data, however, "it provides little insight into the interrelation of the independent variables, nor does it provide a 'global' minimum expected error of the dependent and independent variables. On the contrary non parametric regression such as **GRACE** Algorithm of Breiman and Friedman [6] provides exactly such a 'non-biased' mechanism for the purpose of establishing the minimum error relationship between the dependent - and independent variables" [5].

The objectives of this work are to apply non parametric regression to: (1) identify the inconsistence in the coefficients of specific heat correlation and (2) generalize the ideal gas specific heat correlation (2).Thecoefficients a's are correlated to gas physical parameters of molecular weight (***M***),normal boiling point temperature (***Tb***),critical temperature (***Tc***), critical pressure (***Pc***) and accentric factor (***ω***).

Four groups of chemical compounds are selected to test the first objective, namely n-Alkane, Olefin, Naphthene and Alcohol. The second objective is applied to the group of n-Alkane.

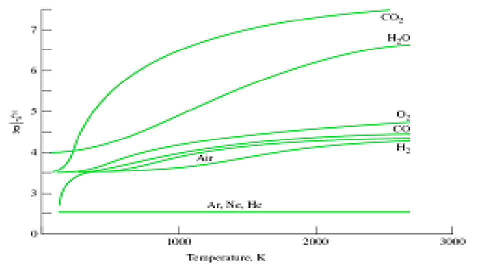

Figure 1: Variation of *Cp/R* with temperature for a number of gases modeled as ideal gases [2]

II. DATA BANK

Four groups of chemical compounds are used in this work, namely n-Alkane, Olefin, Naphthene and Alcohol. The compounds of each group are listed in the appendix [7]. The

Manuscript received Feb. 18, 2014.

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coefficients of (2) and their range of application ***Tmin*** and ***Tmax*** as well as the physical parameters (***M, Tb, Tc, Pc,*** **ω**) for the groups under consideration are obtained from Reid et al. [7]. The data on physical parameter is cross-checked with that available in Danesh [8] and VDI [1]. As an example, table (1) shows the physical parameters and coefficients of (2) for n-Alkane (**C1 to nC20**).

III. COEFFICIENTS OF SPECIFIC HEATS

As mentioned earlier the specific heat is a function of temperature and type of gas as

$$Cp = f(T, a_i) \tag{4}$$

where the coefficients *ai* are type of gas dependent. If the gas is defined with its physical
parameters of ***M; Tb; Tc; Pc*** and ***ω***; the coefficient of (4) becomes

$$a_i = f(M, T_b, T_c, P_c, \omega_i) \tag{5}$$

Hence *Cp* is a function of six independent variables rather two independent variables [cf. (4)]. To test the consistency of the coefficients *ai*'s, four groups of hydrocarbons, namely n-Alkane, Alkene (Olefin), Naphthene and Alcohol, are selected for demonstration. For the group of Naphthene there exist two or more compound with same molecular weight. Under such conditions the molecular weight is excluded from the independent variables. Figures (2a to 2d) show the dependency of *ai*'s on the physical parameters of the compound of the selected groups. Again, to be remembered, the plots are arbitrary samples from total plots of 20 plots (four groups each with 5 independent variables). For illustration the case of n-Alkane will be discussed in details. It can be seen that there is a clear trend of dependency between the coefficients and the independent variables (*M; Tb; Tc; Pc,* ***ω***) [cf. Fig. (2a]. However, it is clear that the coefficients of some components are inconsistent with the general trend, i.e. lay off the curve. In particular all coefficients (**a_o to a_3**) of C1 to C4 lay significantly off the curve. The coefficient a_0 of nC9 and nC20 are also lay off the curve. Similar trend can be clearly observed among the compounds of Alkene, Naphethe and Alcohol [Figs. (2a to 2d)]. The inconsistency of the coefficients does mean that the correlation is incorrect or yield high error for the identified compounds. It is rather an overlook of the independent variables that characterize the gas, when the correlation is initially developed. This approach of non parametric analysis will bring in more insight to the interrelation between dependent and independent variables. This is consistent with the wisdom that says "*The mountain looks smooth from far, when you come close you will find the large and small rocks, clifs, etc...*".

Equation (2) is generalized by writing the coefficients *a*'s as a function of gas physical parameters as given by (5). To find the relation between *ai* and the independent variables, non parametric regression of GRACE algorithm is used

IV. GENERALIZATION OF SPECIFIC HEAT CORRELATION

[5]. GRACE algorithm is explained in the following three steps:

1. Transformation: Fit the independent variables ***M, Tb, Tc, Pc,*** **ω** to each of the coefficients of (2) as

$$a_i(M) = f(M); a_i(T_b) = f(T_b); a_i(T_c) = f(T_c); a_i(P_c) = f(P_c); a_i(\omega) = f(\omega) \tag{6}$$

Where

$$f_i(x) = \sum_i^n \beta_k x^k \tag{7}$$

where *x* stands for either *M*, *Tb*,*Tc*, *Pc* or *ω*.

2. Sum of Transformation

$$z_i = \sum_i^n a_i(x) = f(M) + f(T_b) + f(T_c) + f(P_c) + f(\omega) \tag{8}$$

3. InverseTransformation:

$$a_i = a_i(M, T_b, T_c, P_c, \omega_i) = \sum_0^n \beta_i z^i \tag{9}$$

Figure (3) shows, as an example, the regression of the coefficients *a*'s to the physical parameters (*M; Tb; Tc; Pc; ω*). It should be noted that the coefficients of C1 to C4 are excluded against the background that they are off curve [cf. Fig.(2)]. Table (2) gives the values of the constants a_i's and correlation coefficient *r* of Eqs. (7 and 9) obtained using regression analysis [cf. Fig. (3)]. The correlation coefficient for each a_i's is $r > 0.99$.

V VALIDATION OF GENERALIZED CORRELATION

The following statistical parameters are considered to validate the data [9], [10].

$$PD_i = \frac{X_{ex,i} - X_{cal,i}}{X_{ex,i}} 100\% \tag{10}$$

$$AAPF = \frac{1}{N} \sum |PD_i| \tag{11}$$

where **PD** is the percent deviation, **AAPD** is the average absolute percent deviation, **X$_{ex}$** is the existing value, **X$_{cal}$** is the calculated or predicted value, ***N*** is the number of the data points and *i* is a dummy index. In addition, the minimum absolute percent deviation (**APD$_{min}$**),the maximum absolute percent deviation (**APD$_{max}$**) and the grand average **AAPD** were considered.

To validate the procedure, the data of n-Alkane is considered. Two levels of validation are made. Firstly the predicted coefficients are compared with the existing one. Secondly the specific heat calculated with existing correlation as in (2) is compared with that calculated with the predicted coefficients. Table (3) shows the result of comparison between the existing and predicted coefficients. All the existing coefficients, with exception of that of nC9 and nC20, are predicted with satisfactory **AAPD**; it is generally below 1.5% and with **APD$_{max}$** of less than 3.0%. For nC9 and nC20 the predicted values of the coefficients *ai*'s are incomparable. This is not because the predicted value is incorrect but the existing value is off curve; inconsistent with the rest of the coefficients. To verify that, the predicted coefficients of nC9 and nC20 are correct and consistent with rest of the coefficients the value of the specific heats at the minimum and maximum temperature range are calculated. Table (4) shows comparison between the values of *Cp* predicted using, as in. (2), and this work at the minimum and maximum temperature range. For specific heats, the $\mathbf{APD_{max}}$ for all n-Alkane (C5 to C20) including nC9 and C20 is about 1% with **AAPD** of less than 0.5 %. Hence the new values of *ai*'s of nC9 and nC20 can be used instead of the existing values. The use of non parametric regression is not only a vital tool of regression but it can be effectively used to find errors caused by parametric regression. Instead of equation for each gas the current work provides one correlation for all n-Alkane.

VI CONCLUSION

None parametric regression is an effective tool to correct inconsistent in the coefficients of specific heats within the group of chemical compounds. It can also be used to generalize the existing correlation and provide more insight to the relation between dependent and independent variables.

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BIOGRAPHY

Dr. Rabah is an associate Professor of Chemical Engineering at University of Khartoum. He received his BSc in Chemical Engineering from the University of Khartoum in 1989 and PhD (Dr.-Ing.) from the Institute of Thermodynamics at Hannover University in 2003. He was an Alexander von Humboldt fellow at the University of Helmut-Schmidt in Hamburg in 2008. He authored about 32 research papers. He supervised over 23 MSc students and more than 8 PhD students. He is a reviewer to a number of local and international journals.

Table 1: n-Alkane physical parameters and coefficients of (2) [7], [8]

Chemical	M	T_b	T_c	P_c	w	a_o	a_1	$a_2\times10^4$	$a_3\times10^8$
		K	K	bar					
Methane	16.04	111.66	190.56	46.99	0.0115	19.251	0.0521	0.1197	-1.1320
Ethane	30.07	184.55	305.32	48.72	0.0995	5.409	0.1781	-0.6938	0.8713
Propane	44.10	231.11	369.83	42.48	0.1523	4.224	0.3063	-1.5860	3.2146
n-Butane	58.12	272.65	425.12	37.96	0.2002	9.487	0.3313	-1.1080	-0.2822
n-Pentane	72.15	309.22	469.70	33.70	0.2515	-3.626	0.4873	-2.5800	5.3047
n-Hexane	86.18	341.88	507.60	30.25	0.3013	-4.413	0.5820	-3.1190	6.4937
n-heptane	100.20	371.58	540.20	27.40	0.3495	-5.146	0.6762	-3.6510	7.6577
n-Octane	114.23	398.83	568.70	24.90	0.3996	-6.096	0.7712	-4.1950	8.8551
n-Nonane	128.26	423.97	594.60	22.90	0.4435	3.144	0.6774	-1.9280	-2.9810
n-Decane	142.29	447.30	617.70	21.10	0.4923	-7.913	0.9609	-5.2880	11.3090
n-Undecane	156.31	469.08	639.00	19.49	0.5303	-8.395	1.0538	-5.7990	12.3680
n-Dodecae	170.34	489.47	658.00	18.20	0.5764	-9.33	1.1489	-6.3470	13.5900
n-Tridecane	184.37	508.62	675.00	16.80	0.6174	-10.463	1.2452	-6.9120	14.8970
n-Tetradecane	198.39	526.73	693.00	15.70	0.6430	-10.982	1.3377	-7.4230	15.9810
n-Pentadecane	212.42	543.83	708.00	14.80	0.6863	-11.916	1.4327	-7.9720	17.1990
n-Hexadecane	226.45	560.01	723.00	14.00	0.7174	-13.017	1.5290	-8.5370	18.4970
n-heptadecane	240.48	575.30	736.00	13.40	0.7697	-13.967	1.6241	-9.0810	19.7200
n-Octadecane	254.50	589.86	747.00	12.70	0.8114	-14.470	1.7170	-9.5920	20.7830
n-Nonadecane	268.53	603.05	758.00	12.10	0.8522	-15.491	1.8125	-10.1500	22.0520
n-Eicosane	282.56	616.93	768.00	11.60	0.9069	-22.383	1.9393	-11.1700	25.2840

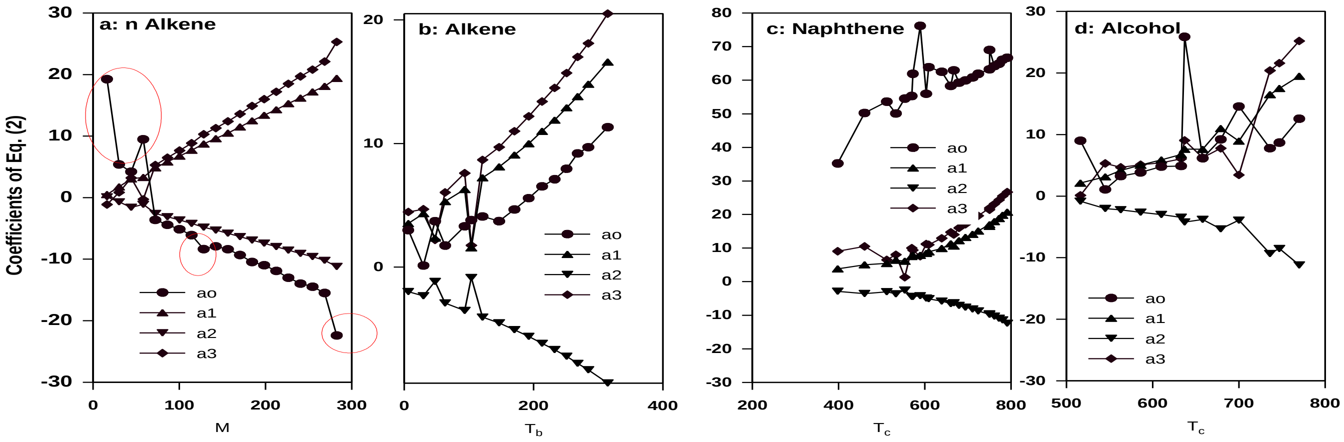

Figure 2: Dependency of the coefficient *a*'s on Carbon physical parameters. For convenient the coefficients are written in scientific format at $a1 = a1 \times 10;\ a2 = a2 \times 10^4;\ a3 = a3 \times 10^8$

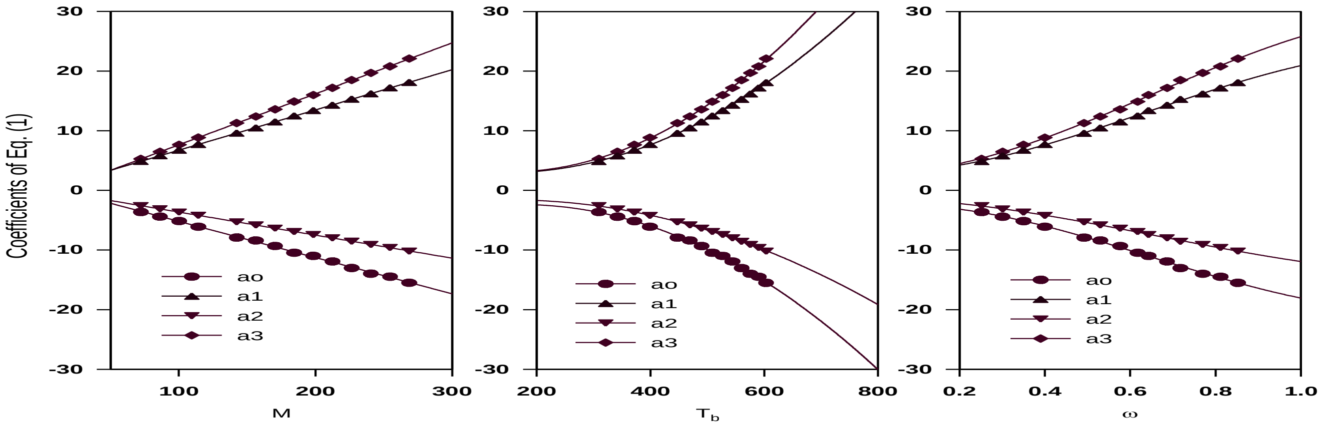

Figure 3: Regression of the coefficients *a*'s to physical parameters. For convenient the coefficients are written in scientific format at $a1 = a1 \times 10$; $a2 = a2 \times 10^4$; $a3 = a3 \times 10^8$

β	M	Tb	Tc	Pc	w	z
			a_0			
1	8.62E-01	-4.46E+00	-1.93E+01	-4.27E+01	-2.62E+00	9.99E-02
2	-6.07E-02	2.42E-02	7.83E-02	3.37E+00	4.70E+00	2.01E-01
3		-7.02E-05	-9.64E-05	-1.06E-01	-4.12E+01	
4				1.20E-03	2.11E+01	
r	**-0.9993**	**0.9993**	**0.9991**	**0.9988**	**0.9992**	**0.9993**
			a_1			
1	3.70E-04	4.40E-01	1.95E+00	4.72E+00	3.00E-01	1.36E-02
2	6.75E-03	-2.01E-03	-7.77E-03	-3.59E-01	-7.43E-02	1.98E-01
3		7.07E-06	9.96E-06	1.12E-02	3.91E+00	
4				-1.30E-04	-2.04E+00	
r	**1**	**0.9999**	**0.9996**	**0.9995**	**0.9997**	**0.9999**
			a_2			
1	2.19E-05	-2.55E-04	-1.14E-03	-2.72E-03	-1.37E-04	-2.31E-05
2	-3.86E-06	1.26E-06	4.60E-06	2.11E-04	-5.95E-05	1.95E-01
3		-4.17E-09	-5.82E-09	-6.68E-06	-2.00E-03	
4				8.00E-08	1.01E-03	
r	**-1**	**0.9998**	**0.9995**	**0.9994**	**0.9996**	**0.9998**
			a_3			
1	-8.94E-09	5.22E-08	2.48E-07	5.95E-07	2.91E-08	6.65E-08
2	8.54E-10	-2.79E-10	-1.02E-09	-4.64E-08	-5.83E-09	2.25E-01
3		9.22E-13	1.00E-12	1.46E-09	4.80E-07	
4				-1.70E-11	-2.46E-07	
r	**1**	**0.9999**	**0.9996**	**0.9995**	**0.9996**	**0.9999**

Table 3: Values of *a*'s of (2) and new model

	a_0			**$a_1 \times 10$**			**$a_2 \times 10^4$**			**$a_3 \times 10^8$**		
	Ref[7]	**New**	**APD**	**Ref[7]**	**New**	**APD**	**Ref[7]**	**New**	**APD**	**Ref[7]**	**New**	**APD**
C1	19.251	-1.510		0.521	1.567		0.120	-0.362		-1.132	1.936	
C2	5.409	-0.423		1.781	0.575		-0.694	0.282		0.871	0.033	
C3	4.224	-1.979		3.063	2.611		-1.586	-1.074		3.215	2.737	
nC4	9.487	-2.882		3.313	3.825		-1.108	-1.864		-0.282	4.207	
nC5	-3.626	-3.676	1.39	4.873	4.871	0.05	-2.580	-2.527	2.07	5.305	5.449	2.72
nC6	-4.413	-4.416	0.07	5.820	5.804	0.26	-3.119	-3.095	0.76	6.494	6.541	0.73
nC7	-5.146	-5.172	0.50	6.762	6.718	0.65	-3.651	-3.636	0.41	7.658	7.622	0.46
nC8	-6.096	-5.980	1.90	7.712	7.664	0.62	-4.195	-4.186	0.21	8.855	8.769	0.98
nC9	-8.374	-6.801	18.78	8.730	8.602	1.47	-4.820	-4.725	1.97	10.300	9.914	3.75
nC10	-7.913	-7.678	2.97	9.609	9.587	0.23	-5.288	-5.288	0.01	11.309	11.145	1.45
nC11	-8.395	-8.542	1.75	10.538	10.547	0.08	-5.799	-5.834	0.61	12.368	12.349	0.15
nC12	-9.328	-9.434	1.14	11.489	11.528	0.34	-6.347	-6.392	0.71	13.590	13.601	0.08
nC13	-10.463	-10.346	1.11	12.452	12.526	0.60	-6.912	-6.959	0.68	14.897	14.892	0.03
nC14	-10.982	-11.194	1.93	13.377	13.448	0.53	-7.423	-7.483	0.81	15.981	16.063	0.51
nC15	-11.916	-12.079	1.37	14.327	14.408	0.56	-7.972	-8.028	0.70	17.199	17.312	0.66
nC16	-13.017	-12.911	0.81	15.290	15.307	0.11	-8.537	-8.538	0.02	18.497	18.473	0.13
nC17	-13.967	-13.780	1.34	16.241	16.244	0.02	-9.081	-9.071	0.11	19.720	19.706	0.07
nC18	-14.470	-14.609	0.96	17.170	17.137	0.19	-9.592	-9.580	0.13	20.783	20.895	0.54
nC19	-15.491	-15.407	0.54	18.125	17.995	0.72	-10.150	-10.070	0.79	22.052	22.033	0.09
nC20	-22.383	-16.232	27.48	19.393	18.882		-11.170	-10.580	5.28	25.284	23.227	
APD_{max}			**18.78**			**1.47**			**2.07**			**3.75**
APD_{min}			**0.07**			**0.02**			**0.01**			**0.03**
AAPD			**4.00**			**0.43**			**0.95**			**0.82**

Table 4: Values of *Cp* at *Tmin* and *Tmax*

			$Cp(T_{min})$			$Cp(T_{max})$		
	T_{min}	T_{max}	Eq (2)	This Work	APD	Eq (2)	This Work	APD
C1	-180	-153	24.20	12.79		25.67	16.82	
C2	-143	-74	27.43	7.54		38.20	12.15	
C3	-109	-24	50.37	38.11		71.18	56.83	
nC4	-78	17	69.90	64.97		96.22	93.43	
nC5	-53	57	91.72	91.89	0.18	131.06	131.55	0.38
nC6	-28	97	120.47	120.24	0.19	171.56	171.34	0.13
nC7	-3	127	152.39	151.28	0.72	211.87	210.31	0.74
nC8	19	152	185.62	184.39	0.66	252.76	250.94	0.72
nC9	39	179	220.30	218.68	0.74	297.33	294.69	0.89
nC10	57	203	255.75	255.21	0.21	341.92	340.95	0.29
nC11	75	225	293.42	293.13	0.10	387.94	387.32	0.16
nC12	91	247	331.44	332.18	0.22	435.68	436.41	0.17
nC13	107	267	371.20	373.45	0.61	483.94	486.69	0.57
nC14	121	287	410.74	412.46	0.42	533.51	535.56	0.38
nC15	135	304	451.73	454.01	0.51	582.48	585.35	0.49
nC16	150	321	495.13	495.92	0.16	632.87	633.88	0.16
nC17	161	337	536.11	536.60	0.09	683.70	684.40	0.10
nC18	172	352	578.11	576.82	0.22	734.82	733.34	0.20
nC19	183	366	621.02	616.80	0.68	785.91	780.87	0.64
nC20	198	379	669.81	662.85	1.04	837.40	829.65	0.93
APD_{max}					**0.09**			**0.10**
APD_{min}					**1.04**			**0.93**
AAPD					**0.42**			**0.43**

Table 5: Compounds of chemical groups

Chemical Name	Formula	Chemical Name	Formula
n-Alkane		**Naphthene (Cycloalkanes)**	
METHANE	CH4	CYCLOPROPANE	C3H6
ETHANE	C2H6	CYCLOBUTANE	C4H8
PROPANE	C3H8	CYCLOPENTANE	C5H10
N-BUTANE	C4H10	CYCLOHEXANE	C6H12
N-PENTANE	C5H12	METHYLCYCLOPENTANE	C6H12
N-HEXANE	C6H14	CYCLOHEPTANE	C7H14
N-HEPTANE	C7H16	ETHYLCYCLOPENTANE	C7H14
N-OCTANE	C8H18	METHYLCYCLOHEXANE	C7H14
N-NONANE	C9H20	ETHYLCYCLOHEXANE	C8H16
N-DECANE	C10H22	N-PROPYLCYCLOPENTANE	C8H16
N-UNDECANE	C11H24	N-PROPYLCYCLOHEXANE	C9H18
N-DODECANE	C12H26	N-BUTYLCYCLOHEXANE	C10H20
N-TRIDECANE	C13H28	N-HEXYLCYCLOPENTANE	C11H22
N-TETRADECANE	C14H30	N-HEPTYLCYCLOPENTANE	C12H24
N-PENTADECANE	C15H32	N-OCTYLCYCLOPENTANE	C13H26
N-HEXADECANE	C16H34	N-NONYLCYCLOPENTANE	C14H28
N-HEPTADECANE	C17H36	N-DECYLCYCLOPENTANE	C15H30
N-OCTADECANE	C18H38	N-DECYLCYCLOHEXANE	C16H32
N-NONADECANE	C19H40	N-DODECYLCYCLOPENTANE	C17H34
N-EICOSANE	C20H42	N-TRIDECYLCYCLOPENTANE	C18H36
Alkene (olefin)		N-TETRADECYLCYCLOPENTANE	C19H38
ETHYLENE	C2H4	N-PENTADECYLCYCLOPENTANE	C20H40
PROPYLENE	C3H6	N-HEXADECYLCYCLOPENTANE	C21H42
1-BUTENE	C4H8	**Alcohol**	
1-PENTENE	C5H10	ETHANOL	C2H6O
1-HEXENE	C6H12	ALLYL ALCOHOL	C3H6O
1-HEPTENE	C7H14	N-BUTANOL	C4H10O
1-OCTENE	C8H16	1-PENTANOL	C5H12O
1-NONENE	C9H18	1-HEXANOL	C6H14O
1-DECENE	C10H20	1-HEPTANOL	C7H16O
1-UNDECENE	C11H22	1-OCTANOL	C8H18O
1-DODECENE	C12H24	2-OCTANOL	C8H18O
1-TRIDECENE	C13H26	1-DECANOL	C10H22O
1-TETRADECENE	C14H28	DODECANOL	C12H26O
1-PENTADECENE	C15H30	HEPTADECANOL	C17H36O
1-HEXADECENE	C16H32	1-OCTADECANOL	C18H38O
1-OCTADECENE	C18H36	1-EICOSANOL	C20H42O