

A STUDY OF REGULARITIES ASSOCIATED WITH
BIOCHEMICAL PROCESSES AND RENEWABLE ENERGY RESOURCES

by

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B.Tech., Indian Institute of Technology, Kharagpur, India, 1979

A MASTER'S THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

CHEMICAL ENGINEERING

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1981

Approved by:



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ACKNOWLEDGMENTS

I wish to express my gratitude to Dr. Larry E. Erickson for his valuable guidance and helpful criticism throughout the course of this work.

I would also like to thank Dr. L. T. Fan and Dr. S. J. Clark for their comments and suggestions.

I also appreciate the statistical advice of Dr. Dallas E. Johnson and the assistance of Dr. J. L. Copeland in heat of combustion measurements.

I wish to thank my parents, Mr. and Mrs. Ambubhai Patel and my friends for support and encouragement during my graduate work at Kansas State University.

This work was partially supported by the U. S. Department of Energy through Grant No. DE-FG02-79ET00079.

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CHAPTER I

INTRODUCTION AND SUMMARY

INTRODUCTION:

Material and energy balances are used widely in the analysis of processes associated with solar energy. It is necessary to know moisture content, chemical composition, and heating value (enthalpy) of the products in order to make exact balances. Also required is the free energy of combustion of the product in order to calculate the second law efficiency of the process. In biochemical engineering, the carbon weight fraction in dry microbial biomass, the number of equivalents of available electrons per g atom carbon in biomass, and heat of reaction per equivalent of available electrons transferred to oxygen are nearly constant [1].

This research is concerned with the extension of these regularities to new applications such as combustion processes and their second law efficiencies, and characterization of renewable energy resources such as crop residues, cereal products, forest products, wood wastes and municipal/domestic wastes. This work is divided into three self contained chapters. References, tables, and figures are located at the end of that chapter.

OVERVIEW OF CHAPTERS:

Chapter II compares the method of Thornton and Dulong's formula for estimating heats of combustion. Heats of combustion predicted by Thornton's method for renewable resources such as wood, straw and municipal solid wastes are considerably closer to experimentally measured values compared to values predicted by Dulong's formula. Thornton's method states that the heat of combustion is directly proportional to the quantity of oxygen consumed in the combustion process [2]. Chapter II also presents a method which utilizes the

weight fraction carbon on a dry basis and the reductance degree to predict the heat of combustion of renewable resources.

Chapter III reviews prior work with regularities in living systems. Work on the utilization of these concepts in the analysis of process efficiency in living systems is presented.

Chapter IV presents a comprehensive review of literature with respect to the elemental composition, and the experimental enthalpy and free energy of combustion values for various organic compounds. Also presented is the elemental composition and enthalpy data for wastes, woods, agricultural residues and other renewable energy resources. Statistical analysis of the above data has been carried out and the results are reported. An attempt has been made to characterize renewable energy resources with respect to moisture content, density and enthalpy.

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1. Minkevich, I.G. and V.K. Eroshin, *Folia Microbiologica*, 18, 376 (1973).
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CHAPTER II

ESTIMATION OF HEATS OF COMBUSTION OF BIOMASS
FROM ELEMENTAL ANALYSIS USING AVAILABLE ELECTRON CONCEPTS

INTRODUCTION:

Material and energy balances are widely used in the analysis of processes associated with solar energy. In the utilization of agricultural and forest products such balances are frequently required for engineering analysis and design. One of the most important properties which has to be known, for such products, in order to make exact material and energy balances is the heating value. In biochemical engineering, the carbon weight fraction in dry microbial biomass, the number of equivalents of available electrons per gram atom carbon in biomass, and the heat of reaction per equivalent of available electrons transferred to oxygen are relatively constant [1]. The average values of these regularities have been used with considerable success by Erickson, Minkevich and Eroshin in the analysis of microbial growth and product formation [2]. In this chapter these concepts have been extended to cover combustion processes. This work is based on the earlier work of Thornton [5] after whom this method is being named.

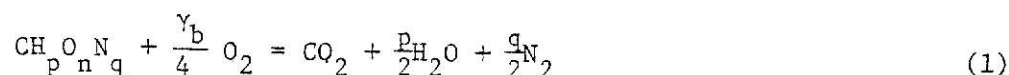
Dulong's formula has been the most widely used method for estimating the heats of combustion of organic substances whose elemental composition is known. Though it gives fairly accurate results when used for coals, it has its shortcomings when used for other organic substances. The group contribution method has been very successful in estimating the heats of combustion of organic substances but it calls for a more rigorous analysis of the sample, in the sense that its constituent groups are to be known.

The objective of this work is to provide a simple but fairly accurate relationship between the elemental composition and the heat of combustion of renewable energy resources such as crop residues, cereal products, forest products and wood wastes. This can be done by finding average values of the weight fraction carbon on a dry basis, the number of equivalents of available electrons per gram atom carbon and the heat of combustion per equivalent of available electrons transferred to oxygen for each substance of interest.

This chapter also makes a comparison between the values of the heats of combustion calculated using Dulong's formula and those calculated using the available electron concept.

THEORY:

Available Electron Concept: The balance equation for oxidation of dry biomass can be expressed



where, $\text{CH}_p\text{O}_n\text{N}_q$ denotes the elemental composition of the biomass calculated per atom of carbon, and

$$\gamma_b = 4 + p - 2n \quad (2)$$

is the reductance degree of the biomass; that is, γ_b is the number of equivalents of oxygen required per quantity of biomass containing one gram atom carbon for oxidation of biomass to CO_2 , H_2O and N_2 . In Equation (2), the values of reductance degree, $\text{C} = 4$, $\text{H} = 1$, $\text{O} = -2$ and $\text{N} = 0$ are used; thus, CO_2 , H_2O and N_2 have reductance degrees of zero.

γ_b may also be defined as the number of equivalents of available electrons per quantity of the biomass containing 1 gram atom carbon. Then, an available electron balance for Equation (1) would result in Equation (2). Thus, γ_b also gives the number of equivalents of available electrons in the

biomass which are transferred to oxygen. Since the heat of reaction per equivalent of available electrons transferred to oxygen, Q_o , is relatively constant, the heat of combustion for the biomass can be calculated; that is,

$$\Delta H = Q_o \gamma_b \quad (3)$$

Equations (1) and (3) are for a quantity of biomass containing 1 gram atom of carbon. In order to obtain the heat of combustion per gram mole of biomass, the result in Equation (3) should be multiplied by the number of carbon atoms per molecule. The heat of combustion per unit mass of biomass, $\Delta H'$, is obtained by multiplying Equation (3) by $C/12$ gram atoms carbon/gram to obtain

$$\Delta H' = Q_o C \gamma_b / 12 \quad (4)$$

or

$$\Delta H' = Q_o \left(\frac{4C}{12} + H - \frac{O}{8} \right) \quad (5)$$

where C, H, and O represent the weight fractions of carbon, hydrogen and oxygen in the biomass. Equation (5) is obtained from Equation (4) by substituting

$$\gamma_b = \frac{\frac{4C}{12} + H - \frac{O}{8}}{\frac{C}{12}} \quad (6)$$

Equation (6) is the defining equation for γ_b when weight fractions are used.

Dulong's formula is an empirical expression for determining the approximate calorific value of a fuel by computation from the ultimate analysis of the fuel. This formula gives reasonably accurate results for

most coals. In British Thermal Units per pound it is [3] :

$$\Delta H' = 14,450C + 61,500\left(H - \frac{O}{8}\right) + 4000S, \text{ Btu/lb.}$$

or in kcal/g

$$\Delta H' = 8.028C + 34.167\left(H - \frac{O}{8}\right) + 2.222S, \text{ kcal/g} \quad (7)$$

The symbols represent the proportional parts by weight of the constituents of the fuel (carbon, hydrogen, oxygen and sulphur); the coefficients represent the approximate calorific values of the constituents.

The term $O/8$ is a correction applied to the hydrogen in the fuel to allow for the hydrogen already combined with oxygen in the form of moisture. There are certain sources of possible error in the use of this formula which offer the explanation as to why it is not applicable to all fuels [4].

When carbon and hydrogen are combined as hydrocarbons, the heating value of such a combination will involve the heat of dissociation, apart from the heating value of the individual constituents. This factor has not been represented in the above formula. Neither does the formula take into consideration the oxygen which might exist in a free state or in combination with nitrogen or carbon in the form of nitrates or carbonates [4].

The contribution of sulfur in biomass to the heat of combustion can often be neglected. When the last term in Equation (7) is omitted, Equations (6) and (7) may be combined to obtain

$$Q_D = 34.167 - \frac{40.333}{\gamma_b} \quad (8)$$

where Q_D has units of kcal/g equivalent of available electrons.

Equation (7) modified to give the heating value in terms of kcal/gram mole, would be :

$$\text{kcal/gram mole} = 96.335c + 34.167(h - 2o) + 71.112s \quad (9)$$

The symbols in this equation represent the number of gram atoms of the constituents per gram mole of the fuel.

RESULTS AND DISCUSSION:

To evaluate the heat evolved per equivalent of available electrons transferred to oxygen during combustion, the graph, as shown in Figure 1, was drawn. The ordinate of the plot is the heat of combustion, and the abscissa is the number of available electrons in one molecule of the substance. The data for this figure was taken from the papers published by Kharasch [7,8].

The figure shows a very close crowding of data points along a straight line of slope 26.5 which passes through the origin. Thus 26.5 kcals of heat is evolved per equivalent of available electrons transferred to oxygen during combustion. This value is in agreement with those obtained by Thornton [5] and by Erickson, Selga and Viesturs [6].

Heats of combustion for various groups of hydrocarbons were calculated using the value of 26.5 and compared with the actual values available in literature [7,8]. A very close match was observed between the two. Table 1 summarises the calculations for thirty groups of hydrocarbons which total 488 compounds. The standard deviation in the case of values calculated using Thornton's method is significantly less than in the case of values calculated using the conventional Dulong's formula. Also tabulated are the mean values of heat evolved per electron transferred to oxygen during combustion, and these vary around 26.5 with an overall mean of 26.62 kcals per equivalent of available electrons transferred.

Tables 2 and 3 give details of individual compounds for two groups of hydrocarbons which form a large portion of naturally occurring organic

substances. These two groups are, primary alcohols and carbohydrates. The individual compounds are arranged in the order of increasing molecular weights. In the case of primary alcohols the average value of heat evolved per equivalent of electrons transferred is around 26.78 while in the case of carbohydrates it is much higher at 27.70. In each case results obtained using Thornton's method are closer to the actual value than those obtained using Dulong's formula. Another important feature of Thornton's method is its consistency. In each of the two cases shown in tables 2 and 3 the value of absolute error decreases with an increase in molecular weight which means the value obtained using Thornton's method converges toward the actual value at high molecular weights. There is no such regularity observed in the case of Dulong's formula. Figures 2 and 3 illustrate this point for alcohols and carbohydrates. Most of the naturally occurring organic substances consist of long chain compounds, having very high molecular weights. For these, Thornton's method appears to be most appropriate.

Another comparison between Dulong's formula and Thornton's method has been made in Figure 4. This is a plot with heat evolved per equivalent of electrons transferred, Q , on the ordinate and the reductance degree, γ_b , on the abscissa. The plot of Thornton's method is represented by the horizontal line at 26.5 kcals/equiv. a.e. The curved line represents Dulong's formula, Equation (8). The close proximity of the experimental values of heats of combustion for various organic compounds to Thornton's plot is evident in this figure. The experimental points with the largest deviations from Thornton's predicted value are for small molecules. Table 4 lists some compounds whose reductance degrees lie over the range of the above plot. Oxalic acid, whose reductance degree is 1.0 has a negative value for its heat of combustion when calculated using Dulong's formula.

Thornton's method may be used to estimate the heats of combustion of

naturally occurring organic substances with complex molecular structures. Some data for softwoods, hardwoods, chars, coals, straws, and municipal solid wastes is available in the literature [9, 10, 11, 12]. In Tables 5 - 9, estimates from Dulong's formula and Thornton's method are compared with experimentally observed values. Table 5 gives the results for coals; values obtained using Dulong's formula are about as good as estimates from Thornton's method. In Tables 6 and 7, Thornton's method gives better estimates than Dulong's formula for all of the softwoods and hardwoods in these tables. The results are similar to those for carbohydrates. In Table 9, the estimated values from Thornton's method are also closer to the observed values for straw and M.S.W. than the estimates from Dulong's formula. In Tables 5 and 8, where considerable free carbon is present, some of the estimates from Dulong's formula are superior to those obtained using Thornton's method. The results in Tables 5 - 9 show that Thornton's method is superior to Dulong's formula for biomass with little or no free carbon, but that Dulong's formula is appropriate and reasonably accurate for coal and chars where considerable free carbon is present.

Thornton's equation for obtaining the heat of combustion of biomass, knowing its elemental composition, can now be derived. The heat obtained on combusting biomass containing one gram equivalent of carbon would be obtained by using $Q_o = 26.5$ kcal/equiv. a.e. in Equations (4) and (5). For wood and other materials with a high carbohydrate fraction larger values of Q_o may be used. For example $Q_o = 27.29$ and 27.23 for the softwoods and hardwoods in Tables 6 and 7, respectively.

All of the values in Tables 5-9 are on a dry basis. The values of γ_b and Q_o are independent of moisture content; however, the weight fraction carbon, C , depends on moisture and ash content. The values of γ_b in Tables 5-9 are relatively constant. They range from 4.0 to 4.7. Similarly, the

values of weight fraction carbon on a dry basis are relatively constant for softwoods, hardwoods, and municipal solid wastes. Thus, a reasonable estimate of the heat of combustion may be made using Thornton's method together with available data on similar or related substances and measured values of moisture content.

CONCLUSIONS:

Thornton's method provides a simple but effective way of estimating the heats of combustion of biomass. The agreement between values estimated by Thornton's method and experimental values is better for large molecules than for small molecules. Thornton's method is better than Dulong's formula for most natural organic substances having little or no free carbon. Further experimental analysis of various groups of natural organic substances would be useful to refine Thornton's method. Average values of weight fraction carbon on a dry basis, reductance degree, and heat of combustion per equivalent of available electrons may be used with Thornton's method.

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Table 1. Summary of Properties of Various Groups of Organic Substances

GROUP NAME	STD. DEV.		Q, kcal/eq.a.e.	MEAN γ_b	NO. OF COMP
	DULONGS	THORNTONS			
Saturated hydrocarbons	6.3	2.1	25.980	6.11	18
Unsaturated hydrocarbons (type I)	3.6	2.9	26.154	5.33	32
Unsaturated hydrocarbons (type II)	3.5	0.9	26.335	5.78	6
Primary alcohols	3.2	2.6	26.779	5.67	10
Tertiary alcohols and phenols	3.7	1.9	26.043	5.03	21
Polyhydroxy alcohols	11.8	6.0	28.038	4.42	6
Aromatic ethers	2.5	0.8	26.538	4.98	15
Esters	4.6	1.7	26.480	4.74	24
Ketones	2.5	1.3	26.295	5.48	19
Acids	13.0	2.5	26.364	4.42	46
Amino acids	2.4	2.5	25.962	4.65	4
Amino acids (aliphatic)	5.7	1.9	26.146	4.65	27
Primary amines (aliphatic)	5.7	2.8	26.676	6.66	15
Primary amines (aromatic)	2.0	2.0	26.073	5.12	14
Secondary amines (aliphatic)	4.2	2.5	26.692	6.24	6
Secondary amines (aromatic)	1.3	1.9	26.080	5.04	5
Tertiary amines (aliphatic)	4.6	2.1	26.649	6.19	5
Tertiary amines (aromatic)	1.4	1.2	26.345	5.24	3
Carbylamines	5.1	6.0	27.878	5.52	7
Aliphatic nitriles	9.7	6.3	27.763	4.90	26
Aromatic nitriles	4.5	1.7	26.425	4.65	8
Isocyanates	17.6	13.1	29.117	4.75	2
Imides	8.5	1.7	26.510	4.15	12
Amides	7.0	2.4	25.936	4.73	37
Acid amides (aromatic)	2.9	2.1	26.011	4.62	23
Amides (aliphatic)	9.3	2.4	26.237	4.83	30
Carbohydrates	13.2	4.8	27.697	4.06	13
Alkaloids	5.1	1.5	26.600	5.00	7
Cyclic ureides	11.5	6.7	26.530	4.17	24
Ring nitrogen compounds	4.5	2.3	26.449	4.94	23
OVERALL MEANS (488 compounds)	5.9	3.0	26.616	5.13	

Table 2. Heats of Combustion Calculations for Primary Alcohols

COMPOUND	FORMULA	MOL. WT	AVAIL. ELECT.	γ_b	Q, kcal/ eq. a. e.	ACTUAL kcal/mol	DULONG'S kcal/mol	%Error	THORNTON'S kcal/mol	%Error
Methyl alcohol	C_1H_4O	32	6	6.00	28.435	170.6	164.7	-3.5	159.0	-6.8
Ethyl alcohol	C_2H_6O	46	12	6.00	27.253	327.0	329.3	0.7	318.0	-2.8
Propyl alcohol	C_3H_8O	60	18	6.00	26.989	485.8	494.0	1.7	477.0	-1.8
Butyl alcohol	$C_4H_{10}O$	74	24	6.00	26.596	638.3	658.7	3.2	636.0	-0.4
Isobutyl alcohol	$C_4H_{10}O$	74	24	6.00	26.546	637.1	658.7	3.4	636.0	-0.2
Cyclobutyl carbinol	$C_5H_{10}O$	86	28	5.60	26.707	747.8	755.0	1.0	742.0	-0.8
Benzyl alcohol	C_7H_8O	108	34	4.86	26.347	895.8	879.3	-1.8	901.0	0.6
Cyclohexyl carbinol	$C_7H_{14}O$	114	40	5.71	26.180	1047.2	1084.4	3.5	1060.0	1.2
Heptyl alcohol	$C_7H_{16}O$	116	42	6.00	26.286	1104.0	1152.7	4.4	1113.0	0.8
Saligenin	$C_7H_8O_2$	124	32	4.57	26.450	846.4	811.0	-4.2	848.0	0.2

SUMMARY (for 10 compounds)

	DULONG'S	THORNTON'S
Mean error	0.8	-1.0
Standard deviation	3.2	2.6
Variance	10.1	6.7
Mean Q	= 26.779	
Mean γ_b	= 5.67	

Table 3. Heats of Combustion Calculations for Carbohydrates

COMPOUND	FORMULA	MOL. WT	AVAIL ELECT	γ_b	Q, kcal/ eq. a. e.	ACTUAL kcal/mol	DULONG'S kcal/mol %Error	THORNTON'S kcal/mol %Error
Arabinose	C ₅ H ₁₀ O ₅	150	20	4.00	27.900	558.0	481.7 -13.7	530.0 -5.0
Xylose	C ₅ H ₁₀ O ₅	150	20	4.00	28.075	561.5	481.7 -14.2	530.0 -5.6
Levogluconan	C ₆ H ₁₀ O ₅	162	24	4.00	28.237	677.7	578.0 -14.7	636.0 -6.2
Rhamnose	C ₆ H ₁₂ O ₅	164	26	4.33	27.612	717.9	646.3 -10.0	689.0 -4.0
Fucose	C ₆ H ₁₂ O ₅	164	26	4.33	27.381	711.9	646.3 -9.2	689.0 -3.2
D-Glucose	C ₆ H ₁₂ O ₆	180	24	4.00	28.042	673.0	578.0 -14.1	636.0 -5.5
L-Fructose	C ₆ H ₁₂ O ₆	180	24	4.00	28.150	675.6	578.0 -14.4	636.0 -5.9
Sorbinose	C ₆ H ₁₂ O ₆	180	24	4.00	27.846	668.3	578.0 -13.5	636.0 -4.8
Galactose	C ₆ H ₁₂ O ₆	180	24	4.00	27.896	669.5	578.0 -13.7	636.0 -5.0
Glucoheptose	C ₇ H ₁₄ O ₇	210	28	4.00	27.982	783.5	674.3 -13.9	742.0 -5.2
Rhamnose triacetate	C ₁₂ H ₁₈ O ₈	290	50	4.17	27.010	1350.5	1224.4 -9.3	1325.0 -1.9
Pentaacetylglucose	C ₁₆ H ₂₂ O ₁₁	390	64	4.00	26.973	1726.3	1541.4 -10.7	1696.0 -1.8
Pentaacetylgalactose	C ₁₆ H ₂₂ O ₁₁	390	64	4.00	26.961	1725.5	1541.4 -10.7	1696.0 -1.7

SUMMARY (for 13 compounds)

DULONG'S

-12.5

Mean error

Standard deviation

Variance

Mean Q = 27.697

Mean γ_b = 4.06

THORNTON'S

-4.3

4.8

22.6

Table 4. Variation of Q with Reductance Degree

COMPOUND	FORMULA	γ_b	Q: kcal/g. equiv. a. e.		
			ACTUAL	DULONG'S	THORNTON'S
Oxalic acid	$C_2H_2O_4$	1.00	30.100	-6.165	26.5
Mesoxalic acid	$C_3H_4O_6$	1.33	32.050	3.916	26.5
Formic acid	CH_2O_2	2.00	31.400	14.001	26.5
Oxaminic acid	$C_2H_3O_3N$	2.50	26.540	18.034	26.5
Glycollic acid	$C_2H_4O_3$	3.00	27.800	20.723	26.5
Acetic acid	$C_2H_4O_2$	4.00	26.175	24.084	26.5
Glycocoll	$C_2H_5O_2N$	4.50	25.933	25.204	26.5
Formamide	CH_3ON	5.00	26.980	26.101	26.5
Urea	CH_4ON_2	6.00	25.383	27.445	26.5
Ethane	C_2H_6	7.00	26.314	28.405	26.5
Methane	CH_4	8.00	26.350	29.126	26.5
Methyl amine	CH_5N	9.00	28.600	29.686	26.5

Table 5. Heats of Combustion Calculations for Coals*

TYPE	% C	γ_b	Q kcal/eq. a.e.	OBSERVED		DULONG'S		THORNTON'S	
				kcal/kg	% Error	kcal/kg	% Error	kcal/kg	% Error
Charcoal	84.62	4.25	26.208	7827	-5.8	7371	-5.8	7915	1.1
Bituminous coal	89.53	4.36	25.461	8738	-0.1	8728	-0.1	9094	4.1
Anthracite	93.09	4.20	25.452	8577	-2.1	8397	-2.1	8930	4.1
West Kentucky coal	80.26	4.66	25.967	8067	-0.6	8018	-0.6	8233	2.1
Pittsburgh seam coal	84.17	4.70	25.761	8454	0.2	8472	0.2	8696	2.9
Utah coal	81.23	4.73	25.720	8209	-0.1	8199	-0.1	8458	3.0
Wyoming elkcol coal	74.63	4.53	26.236	7370	-3.4	7120	-3.4	7445	1.0
Lignite	71.43	4.34	25.828	6642	-3.2	6428	-3.2	6815	2.6
Mean	82.37	4.47	25.829	7986	-1.9	7842	-1.9	8198	2.6

* all values are on dry ash-free basis.

Summary (for 8 coals)

Standard deviation

Variance

3.0

9.2

Table 6. Heats of Combustion Calculations for Softwoods

TYPE	% C	γ_b	Q		OBSERVED	DULONG'S		THORNTON'S	
			kcal/eq.	a.e.		kcal/kg	% Error	kcal/kg	% Error
Cedar, white	48.80	4.20	27.433		4667	4178	-10.5	4508	-3.4
Cypress	54.98	4.39	27.380		5483	5002	-8.8	5307	-3.2
Fir, Douglas	52.30	4.28	27.036		5028	4603	-8.4	4928	-2.0
Hemlock, western	50.40	4.18	27.415		4789	4245	-11.4	4600	-4.0
Pine, pitch	59.00	4.63	27.727		6289	5775	-8.2	6011	-4.4
Pine, white	52.55	4.21	26.920		4945	4516	-8.7	4867	-1.6
Pine, yellow	52.60	4.46	27.425		5339	4891	-8.4	5159	-3.4
Redwood	53.50	4.19	26.970		5022	4572	-9.0	4935	-1.7
Mean	53.02	4.32	27.288		5183	4723	-9.1	5039	-2.9

Summary (for 8 softwoods)

Standard deviation

Variance

3.3

11.1

Table 7. Heats of Combustion Calculations for Hardwoods

TYPE	% C	γ_b	Q kcal/eq. a.e.	OBSERVED		DULONG'S		THORNTON'S	
				kcal/kg	% Error	kcal/kg	% Error	kcal/kg	% Error
Ash, white	49.73	4.37	27.447	4956	-9.1	4504	-9.1	4785	-3.5
Beech	51.64	4.25	26.711	4867	-7.6	4496	-7.6	4828	-0.8
Birch, white	49.77	4.26	27.337	4806	-9.7	4340	-9.7	4658	-3.1
Elm	50.35	4.30	27.208	4895	-8.9	4461	-8.9	4767	-2.6
Hickory	49.67	4.27	27.386	4817	-9.8	4347	-9.8	4661	-3.2
Oak, black	48.78	4.12	27.276	4545	-10.7	4060	-10.7	4415	-2.8
Oak, red	49.49	4.28	27.463	4828	-9.9	4350	-9.9	4658	-3.5
Oak, white	50.44	4.30	27.206	4895	-8.9	4458	-8.9	4767	-2.6
Poplar	51.64	4.25	27.199	4956	-9.3	4496	-9.3	4828	-2.6
Maple	50.64	4.19	27.064	4767	-9.2	4328	-9.2	4667	-2.1
Mean	50.22	4.26	27.230	4833	-9.3	4384	-9.3	4703	-2.7

Summary (for 10 hardwoods)

Standard deviation

2.9

Variance

8.6

Table 8. Heats of Combustion Calculations for Chars *

TYPE	% C	γ_b	Q kcal/eq. a.e.	OBSERVED kcal/kg	DULONG'S		THORNTON'S	
					kcal/kg	% Error	kcal/kg	% Error
Fir bark char	63.49	4.23	26.221	5839	5485	-6.0	5901	1.1
Rice hull char	70.87	4.38	25.989	6672	6433	-3.6	6827	2.3
Grass straw char	67.37	4.29	25.384	6091	5967	-2.0	6359	4.4
Animal waste char	72.78	4.42	23.912	6387	6732	5.4	7079	10.8
M.S.W. char	93.37	4.13	23.700	7578	7806	3.0	8474	11.8
Redwood char	77.38	4.16	26.398	7051	6541	-7.2	7079	0.4
Oak char	79.55	4.11	25.665	6959	6606	-5.1	7185	3.3
Mean	74.97	4.25	25.310	6654	6510	-2.2	6986	4.9

* All values are on dry ash-free basis

Summary (for 7 chars)

Standard deviation

Variance

7.0

48.7

Table 9. Heats of Combustion Calculations for Miscellaneous Organic Substances

TYPE	%C	γ_b	Q kcal/eq.a.e.	OBSERVED kcal/kg	DULONG'S kcal/kg % Error	THORNTON'S kcal/kg % Error
Straw [10]	46.90	4.28	26.686	4445	4120 - 7.3	4413 - 0.7
Rice hulls	38.50	4.23	27.193	3672	3325 - 9.4	3579 - 2.5
Rice Straw	39.20	4.19	26.643	3633	3350 - 7.8	3614 - 0.5
MEAN	41.53	4.23	26.841	3917	3598 - 8.2	3869 - 1.2
M.S.W. [11]*	52.83	4.40	27.135	5241	4836 - 7.7	5119 - 2.3
M.S.W. [12]*	47.74	4.00	30.658	4859	3818 -21.4	4200 -13.6
M.S.W. [10]*	54.09	4.48	26.848	5457	5121 - 6.2	5386 - 1.3
MEAN	51.55	4.29	28.214	5186	4592 -11.8	4902 - 5.7

*all values are on dry ash-free basis

SUMMARY

Standard deviation

straws

10.1

2.6

M.S.W.

16.7

9.8

Variance

straws

101.2

7.0

M.S.W.

277.8

96.0

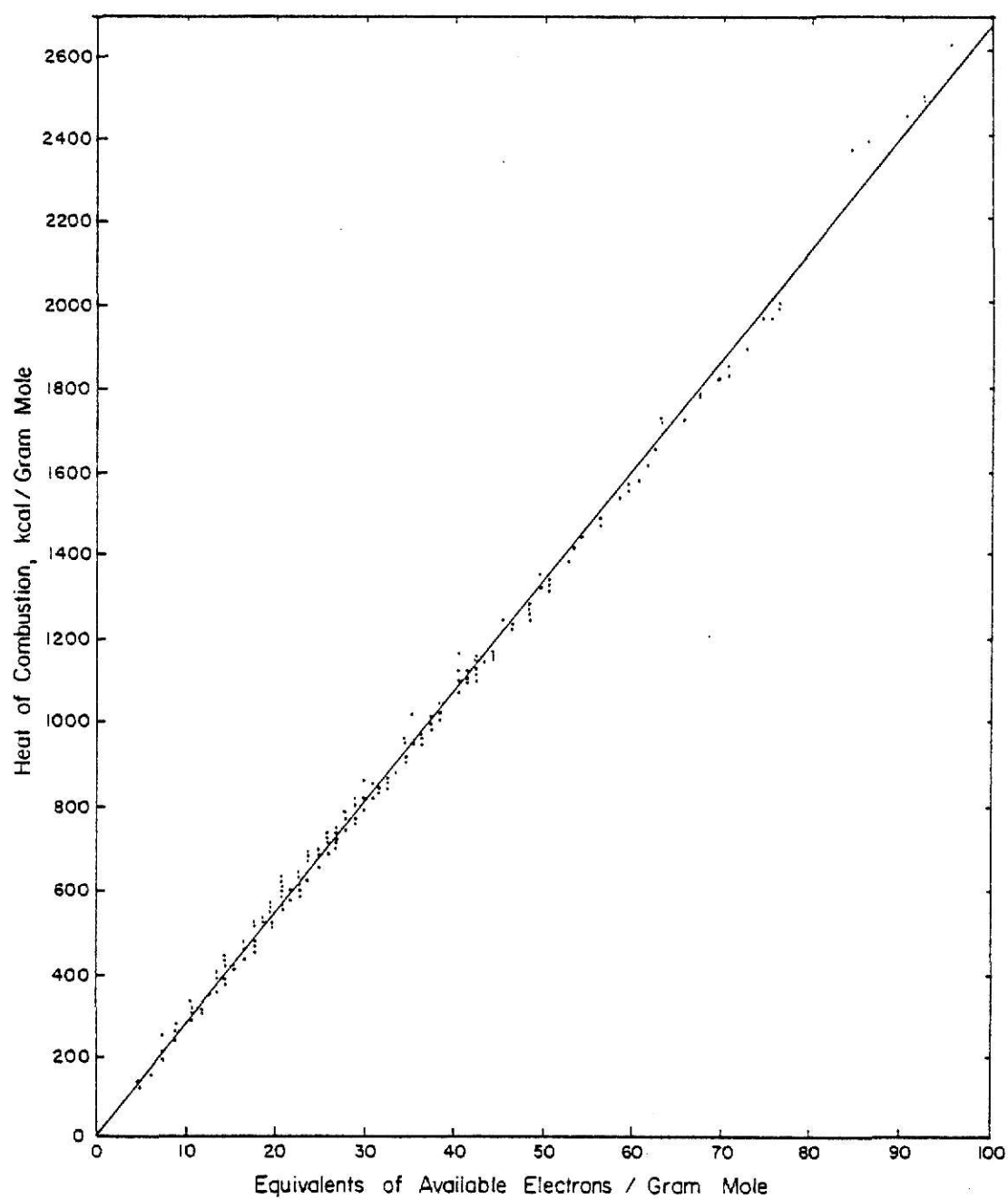


Figure 1. Linear variation of heat of combustion with number of equivalents of available electrons.

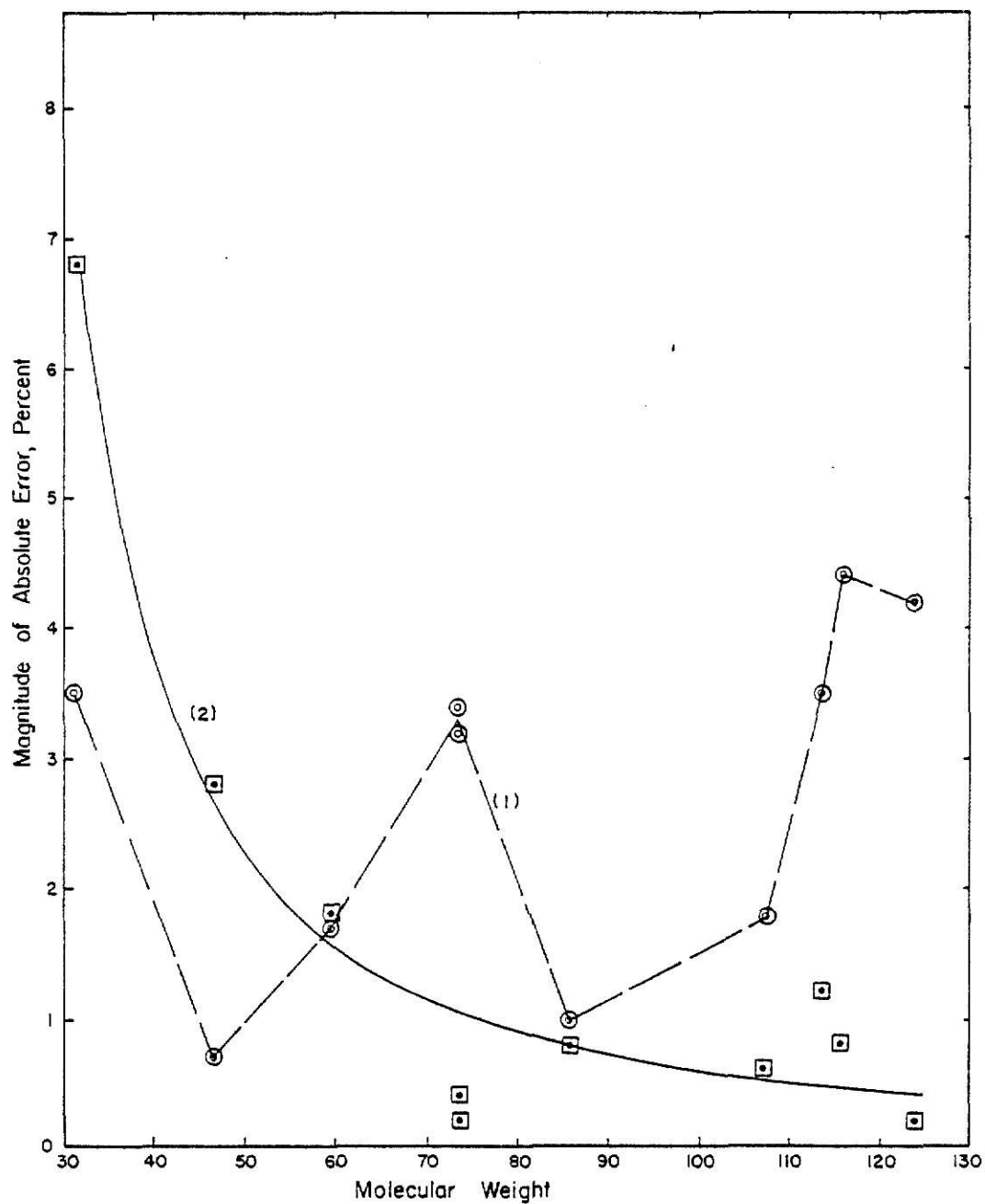


Figure 2. Magnitude of absolute error vs molecular weight for primary alcohols for Dulong's formula (⊙,1) and Thornton's method (□,2).

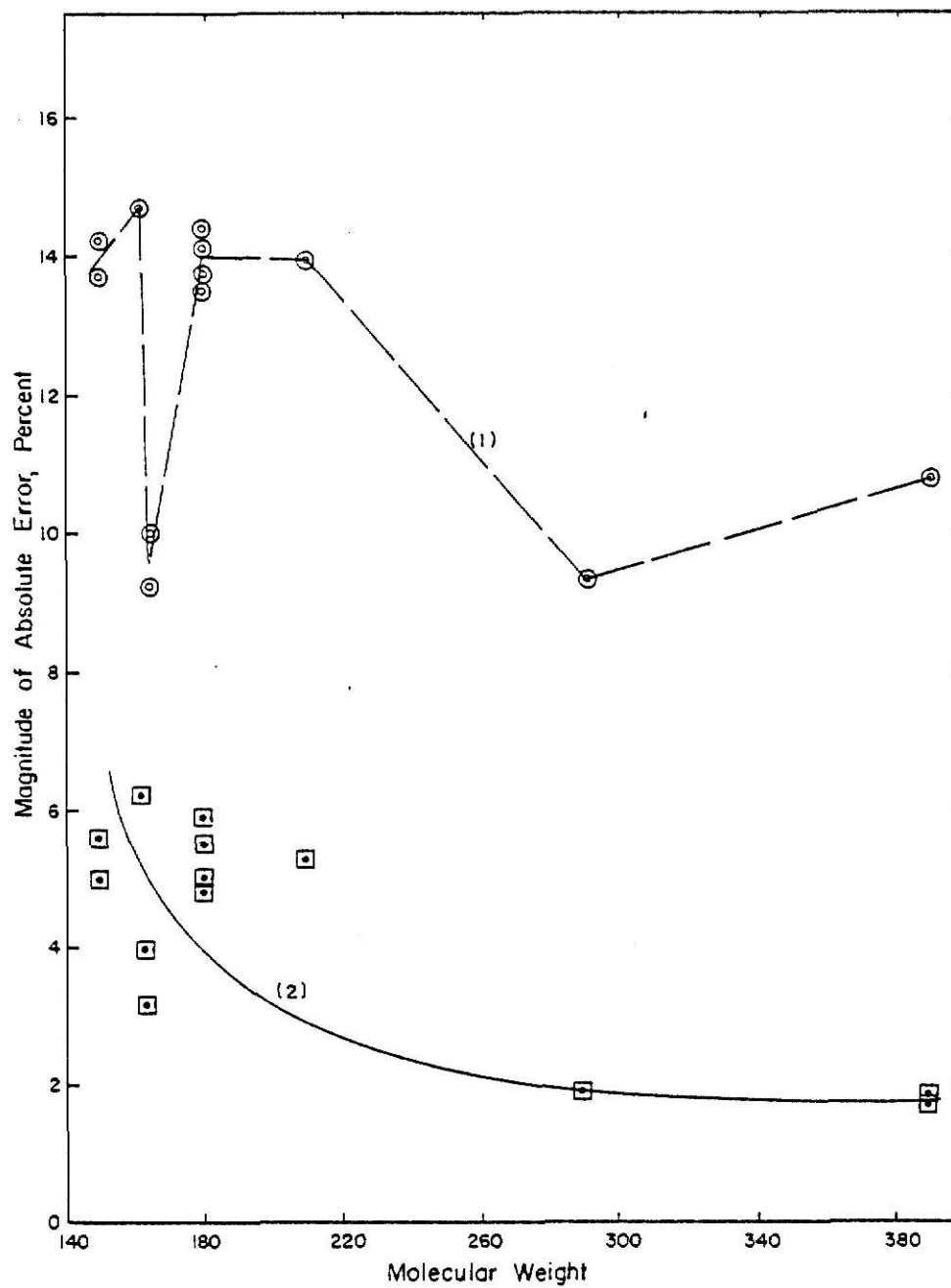


Figure 3. Magnitude of absolute error vs molecular weight for carbohydrates for Dulong's formula (\odot ,1) and Thornton's method (\square ,2).

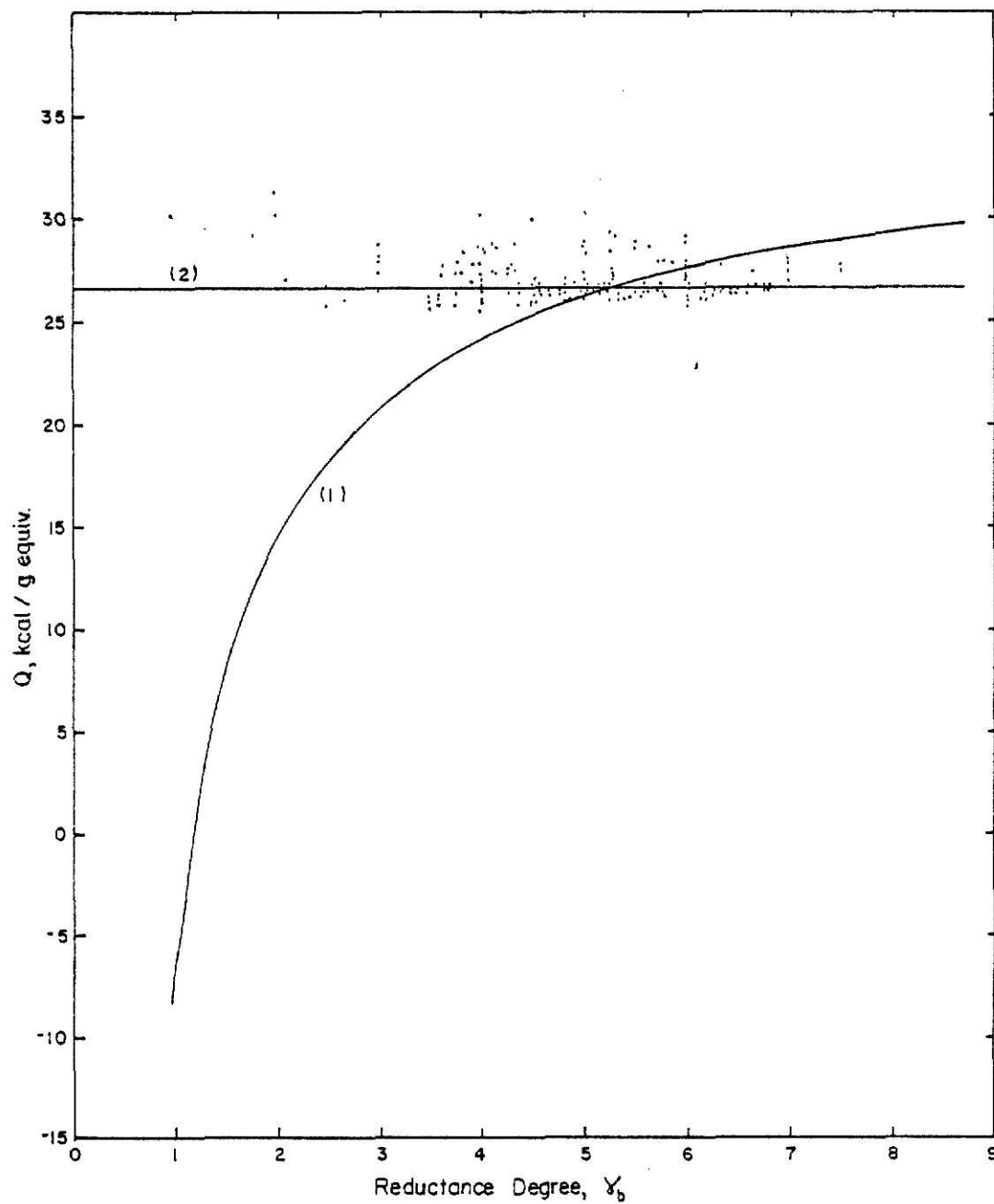


Figure 4. Heat of combustion in kcal per equivalent of available electrons as a function of reductance degree for Dulong's formula (1) and Thornton's method (2).

CHAPTER III

ANALYSIS OF REGULARITIES AND PROCESS
EFFICIENCIES IN LIVING SYSTEMS

INTRODUCTION:

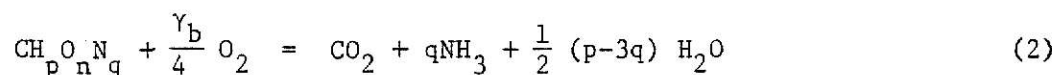
Several regularities have been identified and used in the analysis of biological processes. The most widely used regularity is that associated with the energy given up when biochemical compounds are oxidized [1 - 10]. Kleiber [8] refers to Thornton's rule as

$$\Delta H = -53 n \text{ (kcal)} = -222 n \text{ (kJ)} \quad (1)$$

where n is the number of g atoms of oxygen consumed in the oxidation process. For fats, proteins, and carbohydrates, Kleiber reports values of 105, 101, and 112 kcal/mole of oxygen consumed respectively, for the heats of combustion (in kJ/mole these values are 439, 423, and 469). Rabinowitch [7] reports a value of 110 kcal/g mole of oxygen (460 kJ/mole). For microbial biomass, an average value of 108 kcal/g mole (452 kJ/mole) has been reported [4 - 6]. This regularity has been extensively used. Oxygen consumption measurements have been used to estimate metabolic heat production [6, 8, 9, 11]. Oxygen consumption and metabolic heat production are tied together by this regularity. Measuring one and using the regularity gives an estimate of the other [4, 6, 8]. Measuring both allows one to calculate a value for the regularity. This can provide an approximate check on the accuracy of the experimental measurements.

Two other regularities have been used in the analysis of microbial processes of growth and product formation [4, 5, 6, 12, 13, 14, 15, 16, 17]. The first of these is that the average weight fraction carbon in dry microbial biomass is 0.462 and the second is that the average reductance degree of

microbial biomass is 4.291. The concept of reductance degree, γ , or equivalents of available electrons per g atom carbon is illustrated by the balance equation for oxidation of microbial biomass



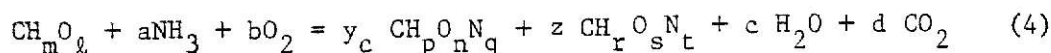
where

$$\gamma_b = 4 + p - 2n - 3q \quad (3)$$

is the reductance degree of the biomass of elemental composition

$\text{CH}_p\text{O}_n\text{N}_q$. That is, γ_b is the number of equivalents of oxygen required per quantity of biomass containing one g atom carbon for oxidation of the biomass to CO_2 , H_2O , and NH_3 . Ammonia is selected rather than N_2 because nitrogen in biomass and in the feed frequently has the reductance degree of ammonia ($N = -3$). In Equation (3), the values of reductance degree $C = 4$, $H = 1$, $O = -2$, and $N = -3$ are used; thus, CO_2 , H_2O , and NH_3 have reductance degrees of zero.

For microbial processes, these two regularities have been used with a carbon balance and an available electron balance to analyze growth and product yields. Consider the balance equation of microbial growth



where CH_mO_ℓ denotes the elemental composition of the organic substrate, $\text{CH}_p\text{O}_n\text{N}_q$ is the elemental composition of the biomass, and $\text{CH}_r\text{O}_s\text{N}_t$ gives the elemental composition of the extracellular product. The coefficients y_c , z , and d give the fraction of organic substrate carbon converted to biomass, products, and CO_2 , respectively.

The reductance degree, γ_s , of the organic substrate is

$$\gamma_s = 4 + m - 2\ell \quad (5)$$

For the products, the reductance degree, γ_p , is

$$\gamma_p = 4 + r - 2s - 3t \quad (6)$$

Note that γ_s and γ_p are also defined as the equivalents of available electrons per quantity of substrate and product, respectively, containing one g atom carbon.

Equation (4) may be used as the basis for a total mass balance, a carbon balance, a hydrogen balance, an oxygen balance, a nitrogen balance, an energy balance, and an available electron balance; however, only five independent balances may be written. The carbon balance is

$$y_c + z + d = 1.0 \quad (7)$$

The available electron balance is

$$\gamma_s - 4b = y_c \gamma_b + z \gamma_p \quad (8)$$

The nitrogen balance is

$$a = y_c q + zt \quad (9)$$

A total mass balance and an energy balance may be written to complete the set of five independent balances.

Equations (7), (8), (9) are exact as written; however, if average values are used to estimate the weight fraction carbon, σ_b , and the reductance degree, γ_b , for the dried biomass, then the balances will no longer be satisfied exactly. If the heat of reaction per electron transferred to oxygen is assumed to be constant, the energy balance for Equation (4) is

$$Q_o \gamma_s - 4Q_o b = y_c Q_o \gamma_b + z Q_o \gamma_p \quad (10)$$

where Q_o is the heat evolved per equivalent of available electrons transferred to oxygen. This equation is not independent of Equation (8) when Q_o is assumed to be constant. Thus, when this regularity is used, only four independent equations may be written.

One of the purposes of this work is to extend some of the methods and regularities used in the analysis of microbial processes to other biological processes. Regularities similar to those used for microbial processes may be identified for proteins, fats, and carbohydrates in other biological materials. Another purpose of this work is to use the regularities to examine thermodynamic efficiency in living systems. In living systems, the maximum thermodynamic efficiency which is possible, the maximum efficiency based on the biochemical pathways which are available, and the actual efficiency are all of interest.

BIOLOGICAL REGULARITIES:

The three regularities, σ , γ , and Q_O may be defined in several useful forms. The weight fraction carbon, σ , may be on a wet or dry basis; a dry basis is most useful because mean values have smaller standard deviations on this basis. The most useful reference state should be considered in selecting the form of the reductance degree, γ , and the energy evolved per equivalent of available electrons, Q_O . Minkevich [4, 18] has shown that proper choice of reference state or "dead" state can simplify calculations. For combustion processes, the normal end point of combustion ($\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, $\text{N}_2(\text{g})$, and $\text{SO}_2(\text{g})$ at 1 atmosphere and 25°C) is the most useful dead state. For physiological processes, a physiological end point or dead state may be defined to be $\text{CO}_2(\text{g})$, urea (l), $\text{H}_2\text{O}(\text{l})$ and $\text{H}_2\text{S}(\text{g})$ at 1 atmosphere and 25°C . Substances in the reference state have a zero energy level as well as zero available electrons. Using this concept, the available electrons associated with elements are $\text{C} = 4$, $\text{H} = 1$, $\text{O} = -2$, $\text{N} = 0$, $\text{S} = 4$ for the normal combustion end point and $\text{C} = 4$, $\text{H} = 1$, $\text{O} = -2$, $\text{N} = -3$, $\text{S} = -2$ for the physiological base. Table 1 lists the formulas associated with the computation of Q_O , σ , γ for compounds reduced to these two dead states. It should be noted that when q and r are zero, that is, for all CHO compounds such as fats and carbohydrates, the value of σ , γ , and Q_O are the same for these two dead states. However for proteins these values are dependent on the dead state being considered.

Statistical analysis [19]: The three regularities Q_O , σ , γ , are the means of the population distributions for the respective variables. The object of this study is to estimate values for Q_O , σ , γ , using available samples. The populations are assumed to be normally distributed. The

sample mean will then be an estimate of the population mean (or the respective regularity). The standard error of the sample mean supplies information about the error in this mean when used to estimate the population mean. The relationship determining the standard error is given as:

$$\text{standard error of sample mean} = \frac{\text{sample standard deviation}}{\sqrt{\text{sample size}}}$$

The "student's" t-distribution can now be used to compute confidence limits for the population mean, μ , knowing the sample mean, \bar{X} , and standard deviation, s . The quantity t is given by the equation,

$$t = \frac{\bar{X} - \mu}{s/\sqrt{n}}$$

where n is the sample size. For large samples ($n > 30$) the t-distribution is practically normal. Thus the 95% confidence interval for the population becomes

$$\bar{X} - t_{0.05, n-1} s/\sqrt{n} \leq \mu \leq \bar{X} + t_{0.05, n-1} s/\sqrt{n}$$

The SAS package, available on most computers, was used to calculate the sample mean \bar{X} and its standard error s/\sqrt{n} .

Carbohydrates: Carbohydrates are a major component of the diet of man and livestock and, as such, are primary sources of heat and energy for mammals. They constitute a major source for several of the alcohols used in industrial and consumer products (particularly beverage alcohols derived from fermentation). The mono-, di- and trisaccharides, commonly termed sugars, possess properties that make them attractive for incorporation into a wide variety of food products. Polysaccharides such as starch and cellulose are the basis for numerous products, including adhesives, paper and rayon. [20]

In the study on carbohydrates average values for the three regularities were calculated for a few mono-, di-, tri and tetrasaccharides. These values could be extended to cover polysaccharides such as starch, glycogen, and cellulose with very little error. Table 2 gives the values of regularities for carbohydrates. The narrow confidence intervals give an idea of the consistency among regularities for various carbohydrates.

The weight fraction, σ , varies with the degree of polymerization. For glucose, $\sigma = 0.4$ while for starch, $\sigma = 0.44$. The largest variation in the regularities is due to the effect of the degree of polymerization on the value of σ .

Proteins: Proteins, which are peptides of high molecular weight, are indispensable components of all biological systems as they are intimately concerned with virtually all physiological events [20]. Since proteins essentially are polymers of α -amino acids joined in an α -peptide linkage, the properties of proteins are determined in part by their amino acid compositions.

The values of the regularities for proteins in various foods have been calculated based on their essential and nonessential amino acid compositions [22]. The amino acids considered in Tables 3a and 3b constitute the major ingredients of all proteins found in foods. Values of the chemical formula and weight fraction carbon, σ , are for the amino acid as it appears in the protein polymer. The values of σ , γ and Q_o have been calculated for the amino acids for each of the two dead states using relationships described in Table 1. The heat of combustion values required for the calculation of Q_o were obtained from the literature [23, 24, 25]. The Q_o value is

marginally higher for estimates on the physiological base which could be attributed to lower heat of combustion to reductance degree ratios for urea and H_2S .

In the second part the values of σ , γ and Q_o were estimated for proteins in foods of plant and animal origin. The amino acid compositions of these proteins were used in the analysis [22]. The weight distribution (W_i) of amino acids is given for protein containing 1 g nitrogen. The equations used to calculate the values of σ , γ , and Q_o for the food protein are given below. (The summation is over the 18 amino acids).

$$\sigma_{pr} = \frac{\text{weight of carbon in protein}}{\text{total weight of protein}} = \frac{\sum_{i=1}^{18} W_i \cdot \sigma_i}{\sum_{i=1}^{18} W_i}$$

$$\gamma_{pr} = \frac{\text{total equivalents of available electrons in protein}}{\text{g atoms carbon in protein}}$$

$$= \frac{\sum_{i=1}^{18} W_i \cdot \sigma_i \cdot \gamma_i / 12}{\sum_{i=1}^{18} W_i \cdot \sigma_i / 12}$$

$$Q_o = \frac{\text{total energy contribution from amino acids}}{\text{total equivalents of available electrons in protein}}$$

$$= \frac{\sum_{i=1}^{18} Q_{oi} \cdot \sigma_i \cdot \gamma_i \cdot W_i / 12}{\sum_{i=1}^{18} \sigma_i \cdot \gamma_i \cdot W_i / 12}$$

Also calculated was the energy evolved per gram of protein (EGE), the equation for which is

$$\text{EGE} = \frac{\text{total energy contribution from amino acids}}{\text{total weight of protein}}$$

$$= \frac{\sum_{i=1}^{18} Q_{oi} \cdot \sigma_i \cdot \gamma_i \cdot W_i / 12}{\sum_{i=1}^{18} W_i}$$

Table 4 lists the values of σ , γ , Q_o and EGE for beef protein for both the dead states. Table 5 summarizes results for 33 animal proteins and 51 plant proteins for the respective dead states together with the confidence intervals. The results show the consistency of the regularities. A commonly used regularity has been the calorific value of protein per unit weight defined as EGE (kJ/gram) in this work. Looking at the results we see that the confidence interval for the regularity Q_o is very narrow ($\pm 0.04\%$) while the confidence interval for the quantity EGE is comparatively wider ($\pm 1.8\%$). Thus, using the regularity Q_o the energy contents of proteins may be predicted accurately.

Fats: Fats are the storehouses of energy in the animal body. The animal and plant fats contain three fatty acids esterified to glycerol and are called triglycerides. Fatty acids are long hydrocarbon chains with a terminal carboxyl group. The properties of animal and plant fats are essentially determined by their fatty acid components.

The regularities for food fats have been calculated based on the γ , σ and Q_o values of constituent fatty acids. The saturated fatty acids are lauric, myristic, palmitic and stearic, the unsaturated acids are oleic, palmitoleic, linoleic and linolenic. Table 6 gives the values of γ , σ , Q_o for each of these fatty acids.

Table 7 gives a summary of the values of γ , σ , Q_o and EGE estimated for plant and animal fats. The equations used to estimate these parameters are similar to those used for proteins. Note the very narrow confidence interval for Q_o ; the confidence interval for EGE is also relatively narrow for fats. The fatty acid analysis of foods was taken from reference [22] and the heat of combustion values required for the calculation of Q_o were obtained from [2, 24].

One of the differences between studies with animals and those with microorganisms has to do with the fat or lipid fraction. In animal nutrition, energy storage in the form of fat is frequently considered; however, in microbial process analysis, average values for the entire organism are used for weight fraction carbon and reductance degree. Kleiber [8] has used the following regularities for physiological processes: fat, 9.5 kcal/g (40 kJ/g); protein, 5.7 kcal/g (24 kJ/g) (heat of combustion) and 4.8 kcal/g (20 kJ/g) (physiological fuel equivalent); and carbohydrates, 4.0 kcal/g (17 kJ/g). These values are in relatively good agreement with the values reported in Tables 5 and 7.

Water: In nutrition experiments and other physiological studies, total body weight is relatively easy to measure. However, in order to effectively use this information, the water content of the body is required. Mitchell [26] has reviewed some of the data on water content of the adult body on a fat free basis. For a variety of animals, the average value is $72.3\% \pm 0.98\%$ [26]. For adult humans, the average value is $72.1\% \pm 2.68\%$ water on a fat-free basis. Pearson [27] has also reviewed data on the water content on a fat free basis. The average value of his data for mammals is $73.74\% \pm 2.00\%$.

Pawan and Clode [28] point out that the water content of adipose tissue varies with fatness. Obese subjects average 18.8% water while lean subjects averaged 28.6% water in the adipose tissue [28]. However, this variation has little effect on the water content on a fat free basis.

Panaretto [29] states that the water content on a fat free basis decreases from the time of conception and reaches a relatively constant level at an age which is characteristic for each species. For young pigs, for example, the water content in per cent is larger at two weeks, than at eight weeks. The data of Filer and Churella [30] show that the per cent water (on a fat free basis) decreases from 79.6 to 75.9 and from 79.2 to 76.3 for two groups of pigs as their age increases from two to eight weeks. The average water content of these young pigs is $78.1\% \pm 1.3\%$; this is considerably larger than the values for older pigs (Pearson [27] reports 74.4%, 75.3%, and 74.6% and Mitchell [26] 73.5%).

Since the water content on a fat free basis is relatively constant, this regularity may be used when experimental values are not available; however, care should be used in doing so because of the variability in water content.

Ash: On a fat free, dry basis, the composition of the bodies of sheep and cattle were found to be relatively constant by Reid et al. [31]. For 65 observations with sheep, they found $80.5\% \pm 2.4\%$ protein and $19.5\% \pm 2.4\%$ ash. For 251 observations with cattle, they found $80.3\% \pm 1.7\%$ protein and $19.7\% \pm 1.7\%$ ash [31]. Filer and Churella [30] measured water, fat, protein, and ash contents of young pigs. On a fat free dry basis, they found $81.9\% \pm 2.4\%$ protein and $18.1\% \pm 2.4\%$ ash. Mitchell et al. [32]

measured the water, fat, protein, ash, and heat of combustion of an adult human body. On a dry, fat free basis the body was 74.8% protein and 25.2% ash. Later studies by Widdowson et al. [33] and Forbes et al. [34] contain similar data. From Widdowson's data, the dry, fat free composition is 70.6% protein and 29.4% ash and from Forbes data 77.4% protein and 22.6% ash. The average is $74.3\% \pm 3.4\%$ protein.

Energy: Reid et al. [31] has attempted to estimate the energy content of sheep based on information on body composition of the sheep. Because of the great variation in fat content and since fat has a large energy content per unit mass, any attempt to estimate the energy content must be based on a fairly accurate estimate of fat content. The per cent water on a fat free basis also needs to be known with relatively good accuracy; however, this value is much more regular than the per cent fat. Pearson [27] has reviewed a number of methods for estimating the water and fat content of the body.

The regularities which exist and which may be used to estimate the energy content of the body include the regularities associated with the energy content per equivalent of available electrons and the reductance degree of protein and fat, the weight fraction carbon in protein and fat, the fraction of protein and ash in the body on a fat free, dry basis, and the water content of the body on a fat free basis. If all of these regularities are used, the fat content of the body is the only additional value required (besides the values of the regularities) to estimate the energy content of the body.

Heat and free energy of combustion: In the section on carbohydrates, proteins and fats values of the regularities were estimated from the properties of foods. This section provides a simple but fairly accurate relationship between the elemental composition and the heat and free energies of combustion of organic substances.

The procedure used for estimating the heats of combustion is based on Thornton's method [1, 10]. The conventional method used to estimate this value has been Dulong's formula which was primarily intended for coals. Heats of combustion for various groups of organic compounds were calculated using a Q_o value of 26.5 kcal/eq.a.e. (110.90 kJ/eq.a.e.) and compared with the actual values available in literature. A very close match was observed between the two. Calculations for thirty groups of organic compounds consisting of a total of 488 compounds gave a mean value for Q_o equal to 26.62 kcal/eq.a.e. (111.405 kJ/eq.a.e.). The error involved in estimating the heats of combustion using Thornton's method was 3% while that using Dulong's formula was 6% [10]. The accuracy of Thornton's method improves with long chain compounds thus making it very useful for naturally occurring organic substances which in fact have high molecular weights. Details about this method of calculating the heat of combustion have been presented in Chapter II.

The Gibbs free energy of combustion is another important property of biological substances. Its importance is realized while calculating the second law thermodynamic efficiency of processes and the lost work involved.

The free energy of combustion, with reactants and products at 25°C, is very close to the heat of combustion for most organic substances. Thus the concept of regularities can be extended to predict the Gibbs free energy of combustion for such substances. Values of Q_G , the free energy evolved

per equivalent of available electrons, were calculated for twenty two groups of organic compounds with a total of 253 compounds. Table 8 summarizes the calculations for these compounds. Free energy of combustion was calculated using free energy of formation data available in literature [35, 36, 37, 38]. The free energy of biological important fatty acids is not shown in Table 8 because palmitic acid with $Q_G = 108.67$ kJ/eq.a.e. was the only value found in the literature. The values of free energy evolved on combustion for the various compounds are plotted against the number of equivalents of available electrons, on a g mole basis, in Figure 1. Also drawn is the regression line, for the same data, when forced through the origin. The slope of the regression line is 107.065 kJ/eq.a.e. with a 95% confidence interval from 106.810 to 107.319. The value of the coefficient of determination is $r^2 = 0.99633$. Statistical analysis of the 253 Q_G values gives an overall mean of 108.735 kJ/eq.a.e. with 95% of the values expected to fall within $\pm 0.47\%$ of the mean. This value is 2.4% smaller than the mean value of 111.405 kJ/eq.a.e. for the heat evolved on combustion. Thus, values of heat of combustion and free energy of combustion are similar for large biological molecules. The regularities $Q_O = 111.405$ kJ/eq.a.e. and $Q_G = 108.735$ kJ/eq.a.e. may be used to estimate the heat of combustion and free energy of combustion of biological substances from knowledge of the elemental composition.

EFFICIENCY OF GROWTH AND PRODUCT FORMATION :

There is currently considerable interest in the thermodynamic efficiency of processes. For many biological processes, an approximate analysis of thermodynamic efficiency may be obtained by utilizing the regularities. The availability function which was first introduced by Gibbs is defined as the maximum amount of useful work that could be performed when a substance in a given state passes to the "dead" state [39]. For flow systems at constant temperature and pressure, the change in availability is the same as the change in free energy. Since many biological processes are flow processes with nearly constant temperature and pressure, an analysis of the Gibbs free energy changes in the process may be used to obtain the approximate thermodynamic efficiency [70].

The definition of the "dead" state is frequently taken as the condition of the surroundings. In biological processes, several states can be considered which may be useful in thermodynamic analysis. The end point of normal combustion processes (CO_2 (g), H_2O (l), and N_2 (g) at 1 atmosphere and 25°C) allows free energies of combustion to be used with the "dead" state having zero free energy of combustion. Another "dead" state which can be considered is the physiological state defined recently by Minkevich [18]. It consists of oxygen, carbon dioxide, and ammonia in aqueous solution, orthophosphoric acid, hydrogen sulfide, ions of metals and halogens. These substances are taken at the normal conditions of physiological systems. That is, the surroundings may be taken to be the physiological condition of the host in which the process of interest is carried out. For both of these dead states, oxidation processes may be analyzed using regularities to

estimate the free energy change associated with each equivalent of oxygen which is consumed in the oxidation process. Using the end point of normal combustion processes $Q_G = 108.7$ kJ/eq. a. e. and $Q_O = 111.4$ kJ/eq. a. e. as pointed out in the previous section. Using the physiological state as "dead" state, Minkevich [18] found $Q_G = 27.898$ kcal/eq. (116.7 kJ/eq.) and $Q_O = 27.580$ kcal/eq. (115.4 kJ/eq.) when an aqueous standard state was used for the 65 substances examined. For 84 pure substances, Minkevich found $Q_G = 27.407$ kcal/eq. (114.7 kJ/eq.) and $Q_O = 26.901$ kcal/eq. (112.6 kJ/eq.). The coefficient of variation was between 5 and 6% for each of these values.

From these results it is easy to see that free energy changes and enthalpy changes are relatively similar for many biological oxidation processes in which oxygen is consumed.

Thus, many of the efficiencies which appear in the published literature based on enthalpy measurements are useful estimates of thermodynamic efficiency.

Many of the efficiencies of interest in biological processes are related to growth and product formation. When the efficiency of nutrient utilization is considered, the available electron balance [4, 14] may often be used to estimate the thermodynamic efficiency. When the regularities of constant enthalpy and free energy per equivalent of oxygen consumed are used, the thermodynamic efficiency can be found from the allocation of available electrons to growth, maintenance and product formation. Table 9 shows the biomass energetic yield, fraction of energy evolved as heat, and product energetic yield of polysaccharide for Rhizobium trifolii cultured

on mannitol, asparagine, and NH_4Cl [40]. The biomass energetic yield may be considered to be the thermodynamic efficiency with which the substrates are converted to biomass in this process; however, since we are also interested in product formation, $\eta + \xi_p$ is a measure of the thermodynamic efficiency of the process. Since energy is used for maintenance, growth, and product formation in this process, it is also of interest to try to identify the separate thermodynamic efficiencies of growth and product formation based on the fraction of energy allocated to each process. The true growth yield, $\eta_{\text{max}} = 0.59$, and the true product yield $\xi_p^{\text{max}} = 0.89$. The thermodynamic maximum efficiency is one for each of these processes. However, one may also examine the biochemical pathways by which growth and product formation occur. For example, for this process the maximum product formation efficiency is 93% [40] based on the pathway operating at maximum efficiency. For aerobic growth of microbial cells on glucose, the maximum thermodynamic efficiency appears to be 88% [17].

Thus, the actual thermodynamic efficiencies and the maximum thermodynamic efficiencies based on the biochemical pathways which have evolved are less than those for a reversible process.

In human and animal nutrition, an available electron or energy balance may also be used to determine the efficiencies of growth and product formation. The available electrons in the nutrients which are consumed are used for growth, maintenance, and product formation. Let η be the fraction of available electrons incorporated into biomass for growth. Let ξ_p be the portion of available electrons incorporated into products such as milk and eggs.

Fat production may be included with the biomass for growth or it may be considered as a product. Let ϵ be the fraction of available electrons transferred to oxygen and evolved as heat. The available electron balance is given by the equation

$$\epsilon + \eta + \xi_p = 1 \quad (11)$$

Brody [41] refers to ξ_p as the gross efficiency. For milk production, he finds ξ_p ranges from 0.28 to 0.35. For egg production, the gross efficiency ranges from 0.07 to 0.20.

The energetic yield associated with growth of microorganisms and various embryos is compared in Table 10. The results indicate that the yields are similar. The value for microbial growth is the average for aerobic growth on carbohydrates [42]. These values are expected to differ from those for postnatal growth where energy expenditures for assimilation of food into the body and maintenance energy for temperature control are important.

The thermodynamic efficiencies of growth and product formation may be investigated by dividing the energy input into three fractions in a manner similar to that employed in microbial nutrition [14, 40, 43]. The thermodynamic efficiency of growth is then

$$\eta_{\max} = \frac{\text{energy incorporated into biomass}}{\text{energy allocated for biomass production}}$$

Similarly, the thermodynamic efficiency for product formation is

$$\xi_p^{\max} = \frac{\text{energy incorporated into products}}{\text{energy allocated for product formation}}$$

The available electron or energy balance may be written

$$\begin{aligned} \text{Energy Input} &= \text{Energy allocated for biomass production} + \text{Maintenance energy} \\ &+ \text{Energy allocated for product formation} \end{aligned} \quad (12)$$

For an energy input of one equivalent of available electrons, equation (12) becomes

$$1 = \frac{\eta}{\eta_{\max}} + \epsilon_m + \frac{\xi_p}{\xi_p^{\max}} \quad (13)$$

where ϵ_m is the fraction of available electrons transferred to oxygen because of maintenance. It is related to the total fraction of available electrons transferred to oxygen by the relationship [14]

$$\epsilon = \epsilon_g + \epsilon_m + \epsilon_p \quad (14)$$

where ϵ_g is the fraction of available electrons in the energy input which are transferred to oxygen because of the inefficiency of the growth process and ϵ_p is the fraction associated with the inefficiency of the product formation process.

Brody [41] has reported that the energy required for basal metabolism is

$$Q_b = 295M^{0.73} \quad (15)$$

where M is the mass of the animal in kg and Q_b is heat evolved in kJ/day. This equation is approximately correct for a wide variety of animals ranging from mice to horses.

Brody [41] refers to ξ_p^{\max} as the net efficiency of product formation. For milk, he finds an average value of 0.61. For egg production he reports

0.77 [41]. Demchenko [44] has investigated energy metabolism in two groups of heifers up to and including the first lactation period. Analysis of their data for Group I prior to lactation gives a true growth yield, $\eta_{\max} = 0.73$ and a maintenance coefficient of $608.8 \text{ kJ/kg}^{0.75} \text{ (day)}$. For the entire set of data for Group I, $\eta_{\max} = 0.71$, $\xi_p^{\max} = 0.74$ and the maintenance coefficient, $M_e = 598.3 \text{ kJ/kg}^{0.75} \text{ (day)}$. For Group II, $\eta_{\max} = 0.77$ and $M_e = 604.3 \text{ kJ/kg}^{0.75} \text{ (day)}$ prior to lactation and $\eta_{\max} = 0.78$, $M_e = 608.2 \text{ kJ/kg}^{0.75} \text{ (day)}$, and $\xi_p^{\max} = 0.76$ when the lactation data is also considered. The product energetic yields of 0.74 and 0.76 may be compared to Brody's average value of 0.61.

Patle and Mudgal [45] have obtained similar values in their investigation of crossbred cows. They found $\eta_{\max} = 0.65$, $\xi_p^{\max} = 0.66$ and $M_e = 547.4 \text{ kJ/kg}^{0.75} \text{ (day)}$. In all cases the metabolizable energy intake is used in finding these parameter values.

Experimental work has also been carried out to find growth efficiencies for a variety of animals. Walker and Jagusch [46] have investigated energy utilization in lambs on cow's milk. Their data may be analyzed to obtain $\eta_{\max} = 0.69$ and $M_e = 419.7 \text{ kJ/kg}^{0.75} \text{ (day)}$. Close and Mount [47,48] have conducted nutrition experiments with pigs. Analysis of their data gives $\eta_{\max} = 0.72$ and $M_e = 534.2 \text{ kJ/kg}^{0.75} \text{ (day)}$. McCracken and coworkers [49,50] found $\eta_{\max} = 0.72$ and $M_e = 644 \text{ kJ/kg}^{0.75} \text{ (day)}$ in their analysis of pigs on milk based diets.

Pullar and Webster [51] have studied the energy metabolism in fat and lean rats. For all rats together, $\eta_{\max} = 0.80$ and $M_e = 435.9 \text{ kJ/kg}^{0.75} \text{ (day)}$.

For the fat rats, $\eta_{\max} = 0.63$ and $M_e = 238.8 \text{ kJ/kg}^{0.75} \text{ (day)}$, while for the lean rats, $\eta_{\max} = 0.59$ and $M_e = 428.3 \text{ kJ/kg}^{0.75} \text{ (day)}$. The value of M_e of $238.8 \text{ kJ/kg}^{0.75} \text{ (day)}$ is less than the value of $295 \text{ kJ/kg}^{0.75} \text{ (day)}$, reported for basal metabolism by Brody [41].

These results are summarized in Table 11. True growth yields are relatively similar for all of these biological growth processes. There is greater variation in product yields because of the differences in the extent of transformation which is required to convert the food to products. For example, glucose is easily converted to ethanol and ATP is produced in the process while energy is required for milk production.

An important aspect of our recent work with microbial yields has involved the utilization of balance equations and regularities to examine data consistency [12, 13, 14, 40]. These relationships have also been used with statistics to develop improved methods of parameter estimation [52, 53]. The design of experiments to obtain appropriate data for parameter estimation is also important. In research on animal nutrition and energy metabolism, data consistency should also be examined. Further work on experimental design and statistical analysis of data is also needed.

PHOTOSYNTHETIC EFFICIENCY :

Photosynthesis is one of the most important processes through which solar energy is converted to chemical energy. The maximum thermodynamic efficiency with which solar energy may be converted to chemical energy has been considered by Ross [54, 55, 56]. Radiant energy is thermal energy which is received by an absorber. Part of the energy received is reradiated, part is lost by convective heat transfer and part is transferred into chemical energy. The maximum efficiency with which radiant energy can be converted to chemical energy is limited by the Carnot efficiency factor $1 - T_L/T_R$ where T_L is the ambient temperature and T_R is the effective radiation temperature. Figure 2 shows the maximum effective radiation temperature for a source temperature of 6000°K and a reduction of intensity of 10^5 ; this approximately corresponds to the effective radiation temperature of the sun as seen by a nondirectional absorber on earth. No correction is made in Figure 2 for atmospheric absorption. As pointed out by Ross [54], the effective radiation temperature significantly influences the maximum efficiency of the absorber. Figure 3 which is also from Ross [54] shows the efficiency of solar radiation as a function of wavelength for full black-body intensity, intensity reduced by 10^5 and intensity reduced by 10^{10} .

An absorber which transfers part of the absorbed energy to free energy storage will have a temperature T_H , which is less than the effective radiation temperature. The efficiency will depend on the fraction of absorbed energy which is stored; that is,

$$\eta = \left(1 - \frac{T_L}{T_H}\right) \left(1 - \frac{I_{out}}{I_{in}}\right) \quad (16)$$

where I_{in} is the input intensity and I_{out} is the loss intensity which is primarily reradiation [54]. Ross [54] has shown that there is an optimum value for T_H . Neglecting convective heat transfer, Ross found the maximum efficiency as a function of wavelength for free energy storage as shown in Figure 4. The decrease in carnot efficiency which occurs when the optimum absorber temperature is used instead of T_R is represented by the difference between the highest and middle curves. The loss due to actual reradiation is shown by the difference between the middle and lowest curves.

The above results are for the wavelengths shown. In photosynthesis, radiant energy with wavelength shorter than some cutoff wavelength may be collected and used. Photon energies greater than the band-gap energy are dissipated as heat. Photons with wavelengths longer than the cutoff are not used by the system. By also taking these factors into consideration, Ross and Hsiao [57] showed that the maximum efficiency of converting sunlight to chemical free energy is about 29% if one assumes the sunlight is not attenuated by the atmosphere. If recombination is considered the maximum efficiency is about 33% [58]. This compares with 31% by Henry [59].

The above analysis of second law thermodynamic efficiency does not consider how the photosynthetic system functions. Govindjee [60] and others [61, 62, 63] in their studies have concluded that eight photons are required to evolve one O_2 and reduce one CO_2 molecule. However, values ranging from 4 to 12 have been found by various workers [64]. Using the value of eight photons to evolve one O_2 molecule and reduce one CO_2 molecule, Bassham [61] showed that the efficiency with which the photons are converted to free energy is 29%. Since according to Bassham [61] only about 43% of the solar

radiation is photosynthetically active, the maximum efficiency of a plant for which eight photons per O_2 are required is $(0.43)(0.286) = 0.123$ or 12% [61]. Bassham [61] has also pointed out that because of the inability of the leaf canopy to absorb all of the radiation and because of plant respiration, the maximum expected efficiency is only about 6.6%. Measured maximum yields in selected plants show efficiencies ranging from 0.7 to 3.2% [61].

If the more recent value for chlorophyll a of 24% of Ross and Collins [58] is used in place of the 43% of Bassham, the maximum value is $(0.24)(0.29) = 0.0696$ or a maximum efficiency of 7% for conversion of solar energy to chemical energy using photosynthesis. Consideration of canopy efficiency and respiration would further reduce this value.

Recently, Pirt and coworkers [64] investigated photosynthetic efficiencies with algal cultures of Chlorella and mixed cultures of an algal species with heterotrophic bacteria. A fluorescent lamp light source with 97% of the light in the 400-750 nm range was used. The gas supply was 5% CO_2 in the air. For the Chlorella, the maximum photosynthetic efficiency was 34.7% while 46.8% was reported for the mixed culture. Both of these values are considerably larger than the 29% based on eight photons per O_2 . In earlier work Goedheer and Hammans [65] reported an efficiency of 30% for the conversion of light energy into chemical energy using Anacystis nidulans and 5% CO_2 in air. Bassham [61] has reviewed work with plants in which photosynthetic rates and yields are much larger when enhanced CO_2 concentrations are present. From thermodynamic analysis, it is clear that $W = RT \ln p_2/p_1 = 3.0 \text{ kcal/g mole (12.5 kJ/g mole)}$ is the minimum requirement to increase the partial pressure of the CO_2 from that in the air (0.0314%)

to that in the air with 5% CO_2 . This energy requirement is of the order of 3% of the energy change in converting one g mole CO_2 to carbohydrate. It is not clear if the gaseous CO_2 concentration affects the minimum number of photons required to produce one mole of oxygen.

When one reviews the results of Pirt and coworkers [64], it appears that their computation of the chemical energy in the biomass includes that in the urea. The value of 22.7 kJ/g dry weight which they reported is considerably higher than the value of 18.7 kJ/g which is obtained using the average values of the regularities for biomass with NH_3 and urea taken as having no available electrons and zero energy. Using the data supplied in Table 2 of Pirt et al. [64], one obtains $\sigma_b = 0.486$ and $\gamma_b = 4.51$. For these values and $Q_o = 112.8$ kJ/eq. a. e., one obtains 20.6 kJ/g dry weight. The reported value of 46.8% for photosynthetic efficiency is reduced to 38.5% when the average values of the regularities are used. This value is still larger than the maximum efficiency of 29% of Bassham [61].

EFFICIENCY OF WORK :

Mechanical work can be performed by man and animals. Chemical energy in foods and feeds is processed by the digestive system to obtain chemical energy in the form of glucose and other biochemicals which may be carried by the blood to muscle cells where they can be processed to provide energy for work. Glucose, glycogen, and fatty acids, for example, may be used as energy sources in muscle cells. The energy in these substances is converted to high energy phosphate bonds in the form of ATP prior to conversion to mechanical forces by muscle cells. Small quantities of readily available energy in the form of ATP and phosphocreatine can be stored in muscle cells. Phosphocreatine and ADP react reversibly to produce ATP and creatine.

The thermodynamic efficiency with which free energy in food is converted to work has been studied by several investigators. Several definitions of efficiency have been presented [8, 41, 66]. Ricci [66] defines the gross efficiency as

$$\text{Gross Efficiency} = \frac{\text{Work Performed}}{\text{Energy Input}} \quad (17)$$

where the energy input is the total energy consumed during the work period and the recovery period. Net efficiency is defined as [66]

$$\text{Net Efficiency} = \frac{\text{Work Performed}}{\text{Net Energy Input}} \quad (18)$$

where the net energy input is the energy input beyond that required for maintenance (at rest). Brody [41] and Kleiber [8] have presented similar definitions of work efficiency.

By making use of the energy regularity, the energy input because of work may be measured for short periods of activity by measuring the oxygen uptake. Energy stored in high energy bonds of phosphocreatine and ATP may be used anaerobically without oxygen consumption. Similarly glucose and glycogen may be anaerobically fermented to lactic acid, to obtain ATP. During the recovery period, creatine is converted to phosphocreatine, ADP to ATP, and lactic acid is converted to glycogen if the recovery is under resting conditions [67]. The oxygen which is consumed during this recovery process provides a measure of the energy input which is required for the anaerobic inputs to the work process. When oxygen is used to measure the energy input, the recovery period should be included whenever a substantial fraction of the energy supplied during the work period comes from anaerobic processes.

The maximum thermodynamic efficiency with which chemical free energy may be converted to work is 100%. In man and animals, the maximum thermodynamic efficiency is considerably less. Of the biochemical processes involved in converting food to mechanical work, the process efficiency of ATP formation from glucose is understood best [17, 67]. Since, at most, 38 moles of ATP are produced by oxidizing glucose to CO_2 and H_2O , the efficiency of this process is about 68% if the physiological conditions are such that the free energy change in going from ATP to ADP is about -12 kcal/mole. Under standard state conditions, where the free energy change in going from ATP to ADP is about -7.4 kcal/mole, the maximum efficiency is about 42%. Another way to view the conversion is in terms of moles of ATP produced per equivalent of available electrons. For glucose, $38/24 = 1.58$ moles ATP/eq.; for stearic acid, the corresponding value is 1.41 moles ATP/eq. and for palmitic acid it is 1.40 moles ATP/eq.

The maximum efficiency with which fats are converted to ATP is lower (64% compared to 68%).

Brody [4] has reported the following efficiencies based on his studies with horses: 25% for gross efficiency, 28% for net efficiency and 35% for absolute efficiency. Brody defines the absolute efficiency as work performed/energy expended above that of walking without the load. Brown and Brengelmann [68] point out that under optimal conditions the net efficiency of the body as a machine is about 25%. Kleiber [8] has reviewed some other early studies on the efficiency of man as a machine.

The maximum thermodynamic efficiency with which ATP can be converted to work by muscle fibers needs to be investigated further. Astrand [67] reports that only part of the cross-bridges are effectively linked and gives an efficiency value of 50%. If the ATP formation efficiency is 60%, the product of these two efficiencies is 30% which is close to the reported net efficiency of Brody of 28%.

DISCUSSION:

In this work, the thermodynamic efficiency of biological processes is examined and some of the available data is reviewed. Regularities associated with biological processes are also reviewed. Biological processes may be viewed as consisting of the rearrangement of available electrons with similar energy levels except for the processes by which available electrons are transferred to and from oxygen.

Further investigation of the thermodynamic efficiency of biological processes is needed. Some of the information which was not found in this review includes the maximum biochemical efficiency of conversion of solar energy to chemical energy in plants, the effect of gaseous CO_2 concentration on the above efficiency, and the maximum biochemical efficiency of animal growth, milk production, egg production, fat production, wool production, etc. The maximum and nominal biochemical efficiency with which ATP can be converted to work in muscles should also be investigated further.

Thermodynamic efficiencies of individual processes should also be investigated further. For example, the efficiency of assimilation of food into the form it is used by the cells of the body has been investigated. The specific dynamic action of a food is the obligatory energy expenditure that occurs during assimilation of the food into the body. Based on assimilation of an amount of protein sufficient to provide 100kJ, an increase of 30kJ is required in the metabolic energy; for 100kJ of carbohydrate, 6 kJ is required; for a similar amount of fat, 4 kJ is needed [69].

NOMENCLATURE:

b	moles O_2 /quantity organic substrate containing 1 g atom carbon; see Equation (4)
d	moles CO_2 /quantity organic substrate containing 1 g atom carbon; see Equation (4)
EGE	energy evolved per gram
G	free energy
H	enthalpy
Q_G	free energy evolved per equivalent of available electrons
Q_O	heat evolved per equivalent of available electrons
W_i	weight fraction of component i
y_c	biomass carbon yield
z	product carbon yield
γ	equivalents of available electrons per g atom carbon
ϵ	fraction of energy in organic substrate that is evolved as heat
η	biomass energetic yield
ξ_p	product energetic yield
σ	weight fraction carbon

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Table 1. Formulas used to compute Q_o , σ and γ for compounds* reduced to the two dead states.

	Combustion end point	Physiological base
σ	$12/(12 + p + 16n + 14q + 32r)$	$12/(12 + p + 16n + 14q + 32r)$
γ	$4 + p - 2n + 4r$	$4 + p - 2n - 3q - 2r$
Q_o^{**}	$-\Delta H_c/\gamma$	$-(\Delta H_c - \frac{q}{2} \cdot \Delta H_u - r \cdot \Delta H_s)/\gamma$

* the molecular formula of the compound is $CH_pO_nN_qS_r$

** ΔH_c , ΔH_u and ΔH_s are heats of combustion of one mole of the compound, urea and hydrogen sulphide, respectively.

Table 2. Values of γ , σ and Q_o for carbohydrates*

TYPE	γ_b	σ^{**}	Q_o kJ/eq.a.e.	No. of samples
Short chain				
Monosaccharides	4.000	0.4000	117.09 (116.66, 117.51)	7
Disaccharides	4.000	0.4211	117.41 (117.08, 117.73)	8
Tri- and Tetra- saccharides	4.000	0.4295 (0.4264, 0.4326)	117.94 (117.04, 118.84)	4
Overall	4.000	0.4151 (0.4092, 0.4210)	117.40 (117.14, 117.66)	19
Long chain				
Starch	4.000	0.4444	117.98	1
Cellulose	4.000	0.4444	118.03	1

* data taken from references [2] and [21].

** values within parenthesis give the 95% confidence intervals.

Table 3a. Values of σ , γ and Q_o for individual amino acids in proteins on the basis of complete combustion.

Amino acid	Formula	** σ	γ	Q_o (kJ/eq.a.e.)
Histidine	$C_6H_7ON_3$	0.526	4.883	117.95
Isoleucine	$C_6H_{11}ON$	0.637	5.500	108.60
Leucine	$C_6H_{11}ON$	0.637	5.500	108.48
Lysine	$C_6H_{12}ON_2$	0.563	5.667	108.33
Methionine	C_5H_9ONS	0.458	6.200	99.40
Phenylalanine	C_9H_9ON	0.735	4.778	108.13
Threonine	$C_4H_7O_2N$	0.475	4.750	110.60
Tryptophan	$C_{11}H_{10}ON_2$	0.710	4.727	108.19
Valine	C_5H_9ON	0.606	5.400	108.60
Alanine	C_3H_5ON	0.507	5.000	108.14
Arginine	$C_6H_{12}ON_4$	0.462	5.667	106.09
Aspartic acid	$C_4H_5O_3N$	0.417	3.750	107.36
Cystine	$C_6H_{10}O_3N_2S_2$	0.324	6.000	115.51
Glutamic acid	$C_5H_7O_3N$	0.465	4.200	108.07
Glycine	C_2H_3ON	0.421	4.500	109.02
Proline	C_5H_7ON	0.619	5.000	109.12
Serine	$C_3H_5O_2N$	0.414	4.333	110.62
Tyrosine	$C_9H_9O_2N$	0.663	4.556	109.21

**The chemical formulas and values of σ are for the amino acids in polymeric form with one molecule of water removed.

Table 3b. Values of σ , γ and Q_o for individual amino acids in proteins for the physiological base.

Amino acid	Formula ^{**}	σ ^{**}	γ	Q_o (kJ/eq.a.e.)
Histidine	C_6H_7ON	0.526	3.333	123.45
Isoleucine	$C_6H_{11}ON$	0.637	5.000	108.89
Leucine	$C_6H_{11}ON$	0.637	5.000	108.75
Lysine	$C_6H_{12}ON_2$	0.563	4.667	108.89
Methionine	C_5H_9ONS	0.458	4.400	100.08
Phenylalanine	C_9H_9ON	0.735	4.444	108.31
Threonine	$C_4H_7O_2N$	0.475	4.000	111.52
Tryptophan	$C_{11}H_{10}ON_2$	0.710	4.182	108.52
Valine	C_5H_9ON	0.606	4.800	108.96
Alanine	C_3H_5ON	0.507	4.000	108.75
Arginine	$C_6H_{12}ON_4$	0.462	3.667	106.30
Aspartic acid	$C_4H_5O_3N$	0.417	3.000	107.77
Cystine	$C_6H_{10}O_3N_2S_2$	0.324	3.000	133.28
Glutamic acid	$C_5H_7O_3N$	0.465	3.600	108.46
Glycine	C_2H_3ON	0.421	3.000	110.67
Proline	C_5H_7ON	0.619	4.400	109.58
Serine	$C_3H_5O_2N$	0.414	3.333	112.09
Tyrosine	$C_9H_9O_2N$	0.663	4.222	109.49

^{**}The chemical formulas and values of σ are for the amino acids in polymeric form with one molecule of water removed.

Table 4. Values of σ , γ , Q_o and EGE for the illustrative case of beef protein for both dead states.

	σ	γ	Q_o (kJ/eq.a.e.)	EGE(kJ/g)
Complete combustion base	0.5262	4.942	108.55	23.52
Physiological base	0.5262	4.097	109.26	19.63

Table 5. Values of σ , γ , Q_o and EGE for proteins for both dead states.*

<u>Complete combustion</u> <u>base</u>	σ	γ	Q_o (kJ/eq.a.e.)	EGE(kJ/g)	No. of Samples
animal proteins	0.5349 (0.5280, 0.5418)	4.9835 (4.9419, 5.0251)	108.50 (108.45, 108.54)	24.119 (23.609, 24.629)	33
plant proteins	0.5468 (0.5388, 0.5548)	5.0380 (4.9791, 5.0969)	108.50 (108.46, 108.55)	24.956 (24.312, 25.600)	51
all proteins	0.5421 (0.5365, 0.5477)	5.0166 (4.9776, 5.0556)	108.50 (108.47, 108.53)	24.627 (24.186, 25.068)	84
<u>Physiological base</u>					
animal proteins	0.5349 (0.5280, 0.5418)	4.1641 (4.1142, 4.2140)	109.18 (109.12, 109.23)	20.288 (19.776, 20.800)	33
plant proteins	0.5468 (0.5388, 0.5548)	4.2204 (4.1658, 4.2750)	109.17 (109.12, 109.22)	21.043 (20.464, 21.622)	51
all proteins	0.5421 (0.5365, 0.5477)	4.1983 (4.1601, 4.2365)	109.17 (109.14, 109.21)	20.746 (20.340, 21.152)	84

* values within parenthesis give the 95% confidence intervals.

Table 6. Values of σ , γ and Q_o for individual fatty acids.

Fatty acids	Formula	σ	γ	Q_o (kJ/eq.a.e.)
Lauric	$C_{13}H_{24.667}O_2$	0.7335	5.590	109.01
Myristic	$C_{15}H_{28.667}O_2$	0.7479	5.644	109.08
Palmitic	$C_{17}H_{32.667}O_2$	0.7593	5.686	108.81
Stearic	$C_{19}H_{36.667}O_2$	0.7685	5.719	109.10
Oleic	$C_{19}H_{34.667}O_2$	0.7738	5.614	108.99
Palmitoleic	$C_{17}H_{30.667}O_2$	0.7650	5.569	109.08
Linoleic	$C_{19}H_{32.667}O_2$	0.7790	5.509	108.99
Linolenic	$C_{19}H_{30.663}O_2$	0.7844	5.403	108.99

Table 7. Values of σ , γ , Q_o and EGE for fat content in foods.*

	σ	γ	Q_o (kJ/eq.a.e.)	EGE(kJ/g)	No. of Samples
animal fats	0.7685 (0.7677, 0.7693)	5.6301 (5.6238, 5.6364)	109.03 (109.03, 109.04)	39.311 (39.275, 39.347)	42
plant fats	0.7726 (0.7710, 0.7742)	5.5762 (5.5665, 5.5857)	109.01 (109.01, 109.02)	39.139 (39.075, 39.203)	42
all fats	0.7706 (0.7696, 0.7716)	5.6032 (5.5950, 5.6114)	109.02 (109.02, 109.03)	39.225 (39.184, 39.266)	84

* values within parenthesis give the 95% confidence intervals.

Table 8. Summary of Free Energy Properties of Various Groups of Organic Substances.

Group Name	Mean γ	Mean Q_G (kJ/eg.a.e.)	95% C.I. for Q_G^*	No. of compounds
Alcohols	5.4162	113.20	109.03, 117.37	8
Aldehydes	4.8333	115.66	94.69, 136.62	3
Ketones	5.3300	108.34	—	1
Carbohydrates	4.0000	120.47	119.95, 120.98	11
Amino acids	4.8418	109.88	108.46, 111.29	17
Aromatics	4.5020	108.91	107.77, 110.04	15
Monocarboxylic acids	4.4345	112.15	108.92, 115.38	11
Dicarboxylic acids	3.3350	113.62	69.98, 157.26	2
Purines	4.1500	114.72	112.89, 116.55	4
Misc. Nitrogen compounds	5.0800	112.69	110.17, 115.22	5
Normal alkanes	6.3600	105.91	105.46, 106.36	20
Normal alkyl cyclopentanes	6.0000	106.47	106.42, 106.51	17
Normal alkyl cyclohexanes	6.0000	106.29	106.21, 106.37	17
Normal monolefins	6.0000	107.58	107.12, 108.03	19
Normal alkylbenzenes	5.5029	106.54	106.48, 106.59	17
Branched alkylbenzenes	5.3060	105.93	105.84, 106.03	10
Styrenes	5.0917	107.61	107.43, 107.79	6
Cyclopentanes	6.0000	106.08	106.01, 106.16	5
Cyclohexanes	6.0000	105.81	105.74, 105.87	7
Branched alkanes	6.2803	105.87	105.82, 105.91	31
Diolefins	5.5857	111.07	109.88, 112.26	7
Branched alkynes	5.6965	110.68	108.95, 112.42	20
All compounds	5.5199	108.74	108.22, 109.25	253

* C.I. = confidence interval

Table 9. Evaluation of the consistency of experimental measurements using the available electron balance, Equation (11).

specific growth rate, hr^{-1}	biomass energetic yield, η	fraction of energy evolved as heat, ε	product energetic yield, ξ_p	$\varepsilon + \eta + \xi_p$
0.0446	0.427	0.349	0.133	0.909
0.0521	0.570	0.385	0.076	1.031
0.0559	0.405	0.368	0.141	0.914
0.0600	0.416	0.344	0.173	0.930
0.101	0.343	0.313	0.244	0.900
0.107	0.442	0.368	0.192	1.002
0.111	0.399	0.330	0.192	0.921
0.112	0.419	0.299	0.242	0.960
0.114	0.394	0.292	0.249	0.935
0.131	0.396	0.342	0.242	0.980
0.135	0.331	0.274	0.202	0.807

Table 10. Values of biomass energetic yield for microbial and prenatal growth [41, 42].

	η
Aerobic microbial growth	0.59
Silk worm embryo	0.65
Chick embryo	0.63
Frog embryo	0.51
Sea urchin embryo	0.59

Table 11. Comparison of true growth yields and true product energetic yields.

	True growth energetic yield, η_{\max}	True product energetic yield, ξ_p^{\max}	Maintenance coefficient	Ref.
Cattle	0.71	0.74 (milk)	598.3 kJ/kg ^{0.75} (day)	44
Cattle	0.78	0.76 (milk)	608.2 kJ/kg ^{0.75} (day)	44
Cattle	0.65	0.66 (milk)	547.4 kJ/kg ^{0.75} (day)	45
Lambs	0.69		419.7 kJ/kg ^{0.73} (day)	46
Pigs	0.72		534.2 kJ/kg ^{0.75} (day)	47
Pigs	0.72		644. kJ/kg ^{0.75} (day)	49
Rats	0.63		238.8 kJ/kg ^{0.75} (day)	51
Rats	0.59		428.3 kJ/kg ^{0.75} (day)	51
Bacteria	0.59	0.89 (polysaccharide)		40
Yeast	0.80	1.02 (ethanol)		43

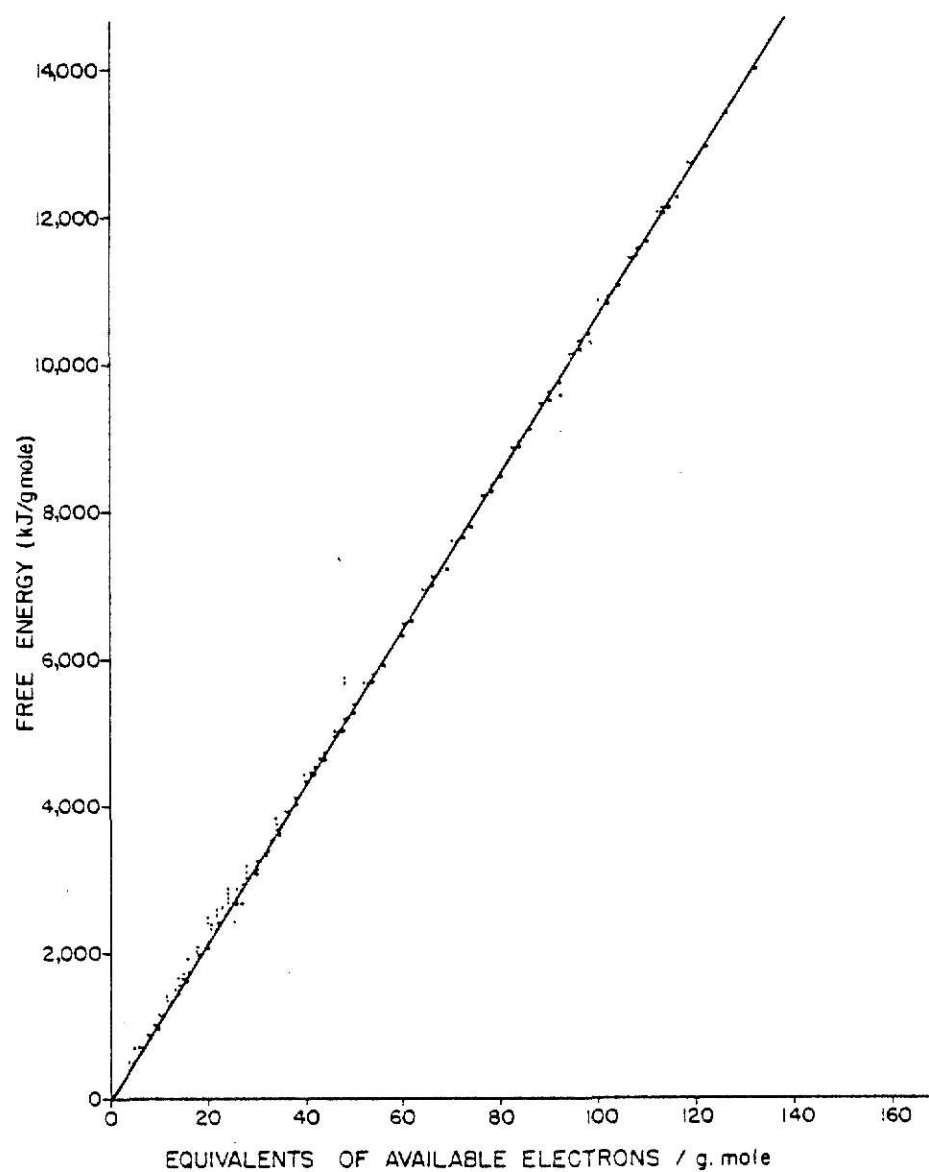


Figure 1. Linear variation of free energy evolved on combustion with number of equivalents of available electrons for organic molecules.

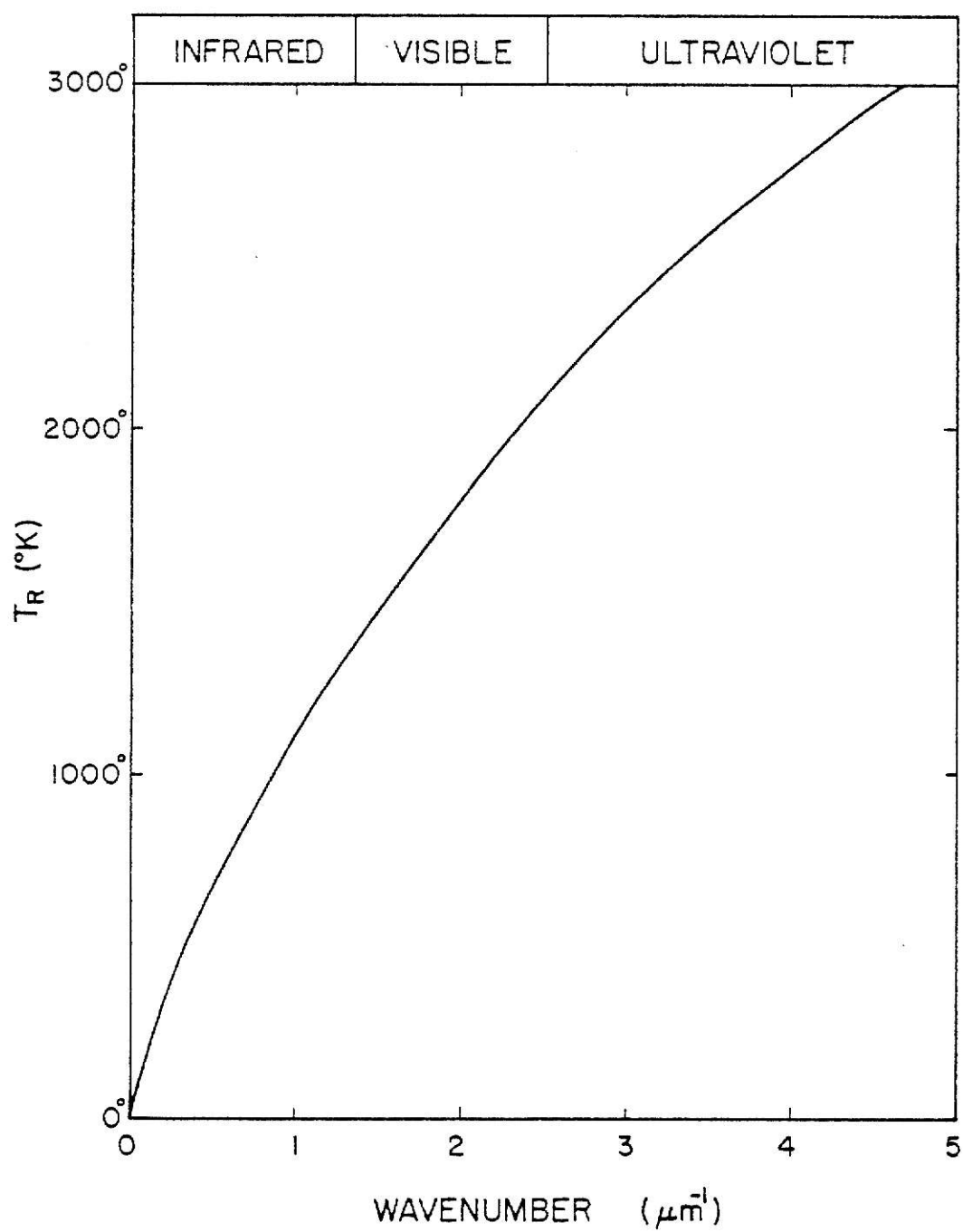


Figure 2. Maximum effective radiation temperature for a nondirectional narrow-band absorber on Earth, illuminated by a 6000°K blackbody sun [54].

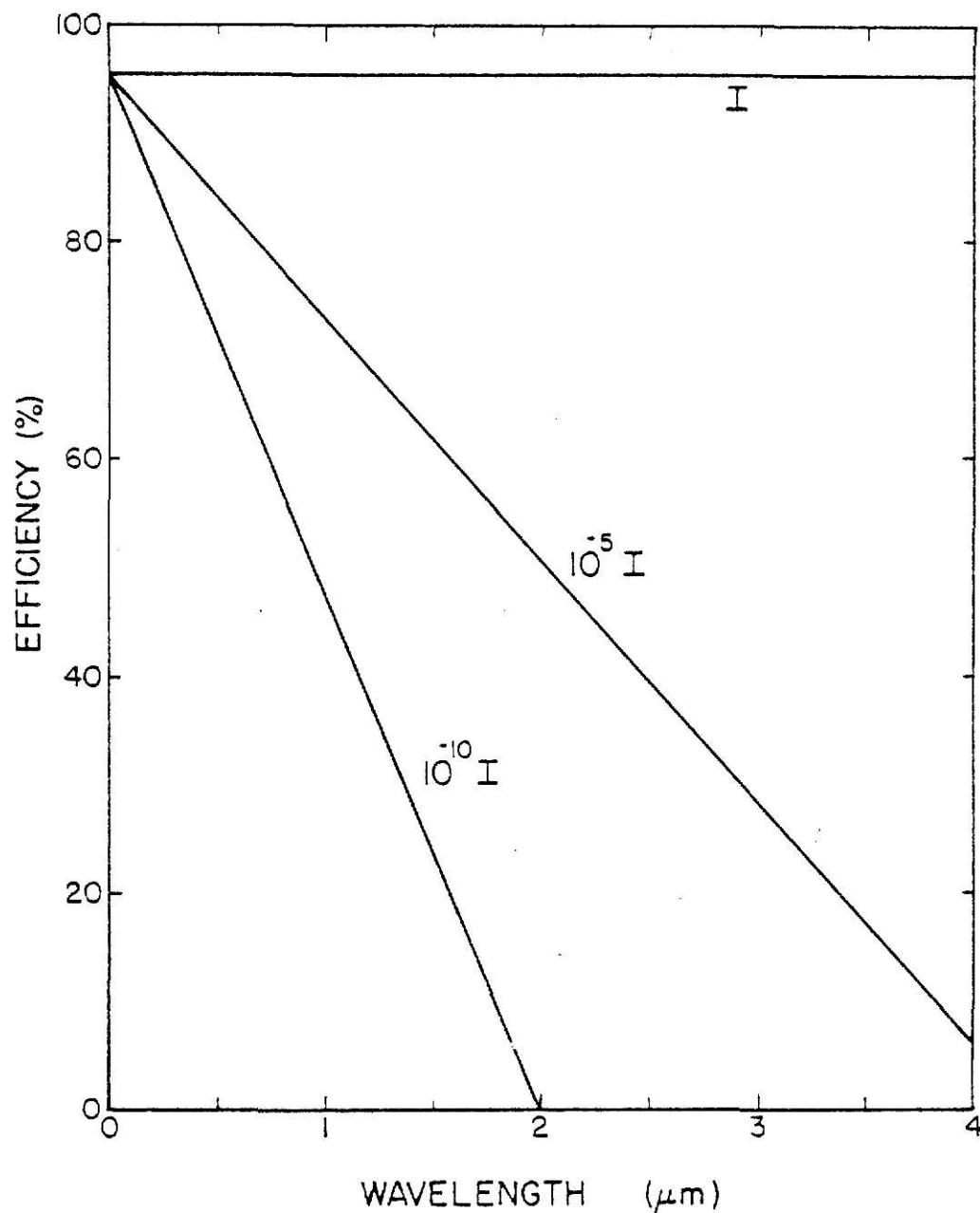


Figure 3. Maximum efficiency from a narrow-band absorber illuminated by a 6000°K blackbody source, with efficiency calculated on the basis of net absorbed light intensity. Top curve is for full blackbody intensity; middle curve is for intensity reduced by 10^5 (solar equivalent); bottom curve is for reduction by 10^{10} [54].

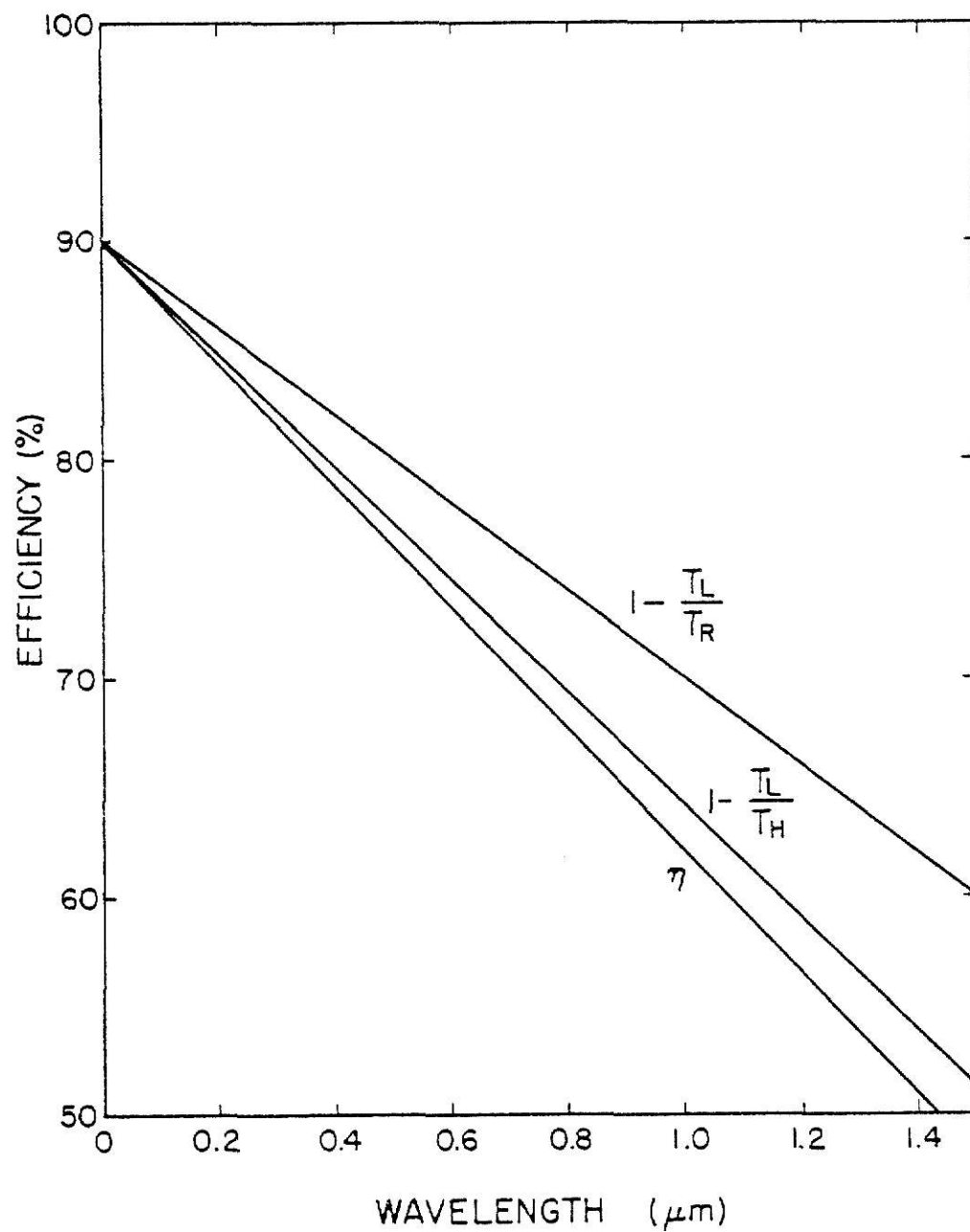


Figure 4. Effect of reradiation on the efficiency from a narrow-band absorber on Earth illuminated by a 6000 blackbody sun. $1 - T_L/T_R$ is maximum Carnot efficiency; middle curve is Carnot efficiency_R for maximum power storage, $1 - T_L/T_H$; lower curve is maximum calculated efficiency for incident light intensity, η [54].

CHAPTER IV

DEVELOPMENT OF REGULARITIES AND
CHARACTERIZATION OF RENEWABLE ENERGY RESOURCES

INTRODUCTION:

This Chapter presents a comprehensive review of literature with respect to regularities involved with various groups of organic compounds and renewable energy resources. Chapters II and III have illustrated some applications of these regularities to various biochemical engineering processes. This chapter is concerned with the identification of regularities for renewable energy resources. The work in this chapter also illustrates the use of regularities in the area of data consistency. In the final section an effort has been made to characterize renewable energy resources including emphasis on the bulk density and moisture content of the substances.

ANALYSIS OF HEATS AND FREE ENERGIES OF COMBUSTION FOR ORGANIC COMPOUNDS:

One of the most important regularities is the heat of combustion per equivalent of available electrons, Q_O . A second closely related regularity is the free energy of combustion per equivalent of available electrons, Q_G . Experimental data available in the literature [1-6] for the heats and free energies of combustion of various organic compounds has been analyzed in this section. Free energy of combustion data has been calculated using experimental free energy of formation data for the compound and its products of combustion.

Table 1 in Chapter II and Table 8 in Chapter III summarize heat of combustion and free energy of combustion properties respectively for several groups of organic compounds. Tables 1-30 in this chapter list the Q_O and Q_G

values for each organic compound for which experimental data was found. Q_o is the heat of combustion per equivalent of available electrons (kJ/eq.a.e.) while Q_G is the free energy of combustion per equivalent of available electrons (kJ/eq.a.e.). Figure 1 is a graphical presentation of the heat of combustion data for the various compounds. The ordinate represents the heating value in kJ/g mole while the abscissa gives number of equivalents of available electrons per g mole of the compound. The letters indicate the observation density or the number of observations centered at a particular point. The regression line for this data, when forced through the origin, gave a slope of 110.43 kJ/eq.a.e. with a 95% confidence interval from 110.27 to 110.59, and a coefficient of determination value of 0.99967 for the 627 values. Figure 2 presents free energy of formation data for 237 compounds. The regression line for this data has a slope of 106.93 kJ/eq.a.e. with a 95% confidence interval from 106.66 to 107.20, and a coefficient of determination of 0.99961. Tables 31 and 32 summarize the heat of combustion and free energy of combustion properties respectively for the various groups. Also presented in these tables are the 95% confidence intervals for the Q_o and Q_G values.

Figures 1 and 2 illustrate the linear variation of heat and free energies of combustion with equivalents of available electrons. Regression analysis of these data with the lines forced through the origin gave slopes which are good estimates of the Q_o or Q_G regularities (Equation 1). Another approach to estimating these regularities is to find the overall means for the Q_o and Q_G values of individual substances (Equation 2). The differences between these two approaches is discussed here.

$$\text{slope} \approx \frac{\sum(\text{Heat or free energy of combustion})_i}{\sum(\text{equivalents of available electrons})_i} \quad (1)$$

$$\text{mean} = \frac{\sum_{i=1}^n \left(\frac{\text{Heat or free energy of combustion}}{\text{equivalents of available electrons}} \right)_i}{n} \quad (2)$$

A compound which is further away from the origin in Figures 1 and 2 would dominate in calculating the slope. Thus the estimates of Q_O and Q_G obtained using the slope do not give equal weighting to the different compounds. Since values of Q_O are more regular for larger compounds than for smaller compounds, as shown in Chapter II, narrow confidence intervals are obtained for the Q_O regularity when estimated using the slope. The mean on the other hand is estimated using individual Q_O or Q_G values; thus the weighting is equal for the various compounds irrespective of their sizes. The confidence intervals are 110.43 ± 0.16 and 106.93 ± 0.27 respectively for Q_O and Q_G using slopes as estimates. However, they are 110.81 ± 0.24 and 108.07 ± 0.55 respectively for Q_O and Q_G when estimated using means. Graphical presentation of data, as in Figures 1 and 2, helps in identifying values which are irregular.

ANALYSIS OF ELEMENTAL COMPOSITIONS AND HEATS OF COMBUSTION FOR RENEWABLE RESOURCES:

One purpose of this study is to better understand the properties of renewable energy resources. In Chapter II, Tables 5-9 analyzed the properties of some woods, coals and solid wastes. In this section results are presented for a detailed list of such substances which have been divided into ten groups (Tables 33-42) according to their basic characteristics. Elemental compositions were used to calculate the values of γ ; i.e.,

$$\gamma = \frac{\%C(4/12) + \%H - \%O(2/16) + \%S(4/32)}{\%C(1/12)} \quad (3)$$

In Equation (3), the values of reductance degree $C=4$, $H=1$, $O=-2$, $N=0$, $S=4$

are used; thus, CO_2 , H_2O , SO_2 , and N_2 have reductance degrees of zero. Values of Q_o were calculated using heat of combustion data; that is,

$$Q_o = \frac{Q}{\%C \gamma (10/12)} \quad \text{kJ/g.eq.a.e.} \quad (4)$$

where, Q is in kJ/kg. The values of Q_o and γ are independent of ash and moisture content; however, both Q and $\%C$ depend on these quantities.

The regularity among the Q_o values within each group is obvious from these results. However, a few substances do show some irregularity with respect to their Q_o values. Any significant deviation of the experimentally obtained Q_o or Q_G value from established regularities may be due to experimental error.

The Q_o value for feedlot waste in Table 38 is higher than the value for other animal wastes. The low γ value of 3.82 would explain this discrepancy. This indicates a possible experimental error in the measurement of elemental composition. Also carbon percentage is lower for feedlot waste as compared to other wastes. In Table 39 the Q_o values for leather, raw sewage (dry), rubber and sewage sludge (dry) are exceptionally low. This indicates experimental error either in the elemental analysis or in the enthalpy measurements. The Q_o value could be low either due to an underestimated heat of combustion or because of a high value for the number of equivalents of available electrons. In the case of leather the error could be attributed to the high values of σ and γ as compared to the values for leather shoes. This indicates experimental error in elemental analysis of leather. In the case of rubber and sewage sludge the γ values appear to be consistent and the low Q_o values could be due to an error in enthalpy measurements. Q_o values for mixed plastics and municipal solid waste II are higher than expected. The value of γ for mixed plastics is reasonable so an overestimated enthalpy might be the cause of a high Q_o .

value. However, for municipal solid waste II the per cent carbon is lower as a result of which γ is low which explains the high value for Q_o . In the case of green logs in Table 42 the Q_o value is considerably below the expected value of around 111 kJ/eq.a.e. though the γ value is consistent with other woods. This could be either due to an error in enthalpy measurements or an error in correction for heat used to remove moisture, which was 50%.

Table 43 summarizes the properties and gives the 95% confidence intervals for the respective groups. Paper, which is mostly cellulose, has an average Q_o value of 115.6 kJ/eq.a.e. which is very close to the Q_o value of 118.03 for cellulose given in Table 2, Chapter III. However, wood which is mostly carbohydrate but has considerable amounts of oils has an average Q_o value of 111.1 kJ/eq.a.e. which is in between the 109.01 for plant fats (Table 7, Chapter III) and 118 for carbohydrates (Table 2, Chapter III). Agricultural residues have properties which are very similar to those for woods.

Figure 3 is a graphical presentation of the heat of combustion variation with respect to the equivalents of available electrons on a unit mass basis. Regression gave a slope of 107.68 kJ/eq.a.e. with a 95% confidence interval from 106.12 to 109.24. The larger confidence here compared to Figure 1 is expected. For known compounds the number of equivalents of available electrons per molecule is known precisely while for most renewable resources, the number of equivalents of available electrons per unit of mass is estimated based on elemental analysis measurements.

Figure 3 illustrates the use of such plots in checking data consistency. The three points on the plot marked by asterisks indicate significant deviations from expected values. Unlike Figures 1 and 2, where the quantities measured were on a per mole basis, in Figure 3 the measurements are per unit mass. In Figures 1 and 2, the data for large molecules with greater numbers of equivalents of available electrons per mole was farther from the origin;

and consequently, the slope of the curve was more dependent on the data associated with these large molecules. In Figure 3, the data for substances with higher energy density lies farther from the origin.

The results presented so far show that carbohydrates have some of the highest Q_o values. As a result, substances like wood, paper, etc., which are relatively high in carbohydrates have higher Q_o values as compared to substances like coals and chars which have higher quantities of carbon in the free form. Most renewable energy resources have Q_o values a little over 110 kJ/eq.a.e. The γ value for renewable energy resources averages around 4.4. Substances with a higher lipid content have higher γ values while carbohydrates decrease the γ values. Values of σ have been presented on a dry basis. The higher the ash content, the lower the σ value will be for the substance. On a dry ash-free basis, σ for most substances is greater than 0.4. The summary of results presented in Table 43 can be used effectively in material and energy balance calculations involving renewable energy resources.

CHARACTERIZATION AND COMPARISON OF RENEWABLE ENERGY RESOURCES:

Most renewable energy resources can be divided into broad categories as shown below:

- 1). Products of photosynthesis
 - forest products
 - crop residues
- 2). Solid waste products
 - garbage (food wastes)
 - rubbish (domestic solid waste)
 - ashes (from heating units)
 - trash (bulky refuse items)
 - animal waste

There is some overlap between the two categories, e.g. solid wastes do include items like plant trimmings, logging residue, sawdust, etc. which actually are products of photosynthesis. The work presented in this section uses the energy value approach to classify various renewable energy resources.

The quality, Q , of an energy source may be defined as follows:

$$Q = Q_1 + Q_2$$

where,

$$Q_1 = \text{Heat of combustion ratio}$$

$$= \frac{\text{Heat of combustion of substance}}{\text{Heat of combustion of cord wood}^*}$$

$$Q_2 = \text{Energy density ratio}$$

$$= \frac{\text{Energy density of substance}}{\text{Energy density of cordwood}^*}$$

$$\text{Energy density} = \text{Heat of combustion} \times \text{Density}$$

The parameter Q is important because it accounts for both, the bulkiness of the substance through its density ratio, Q_2 , and the heating value per unit mass through the heat of combustion ratio, Q_1 . The importance of Q is not realized when applied to fossil fuels because these are superior fuels with high Q_1 and Q_2 values. Even in case of gaseous fuels, the very high Q_1 value gives rise to a high Q value. When applied to alternate energy sources such as forest products and solid wastes, the value of the quality parameter Q is more easily apparent. This is due to the inferiority of such fuels as compared to fossil fuels.

* The heat of combustion of cordwood is taken as 20018 kJ/kg and the energy density is 8.016×10^6 kJ/m³ based on a true density of 400 kg/m³.

Tables 44 to 48 present detailed quality analysis for five groups of renewable energy resources. The Q_1 and Q_2 data for these groups is graphically presented in Figure 4. The fossil fuels presented in Table 46 are not included in the figure since they are of a comparatively higher quality and would lie at a greater distance from the origin. Thus, the higher the quality of a fuel, the further away it will be from the origin.

In Tables 44 to 48 and Figure 4, the most appropriate density to use in estimating Q_2 is the bulk density; however, for woods the true density is less variable and more widely available. Most of the densities in Table 48 are true densities.

Two processes which would improve fuel quality are drying and densification. Drying would result in a reduction of the "non-fuel" portion of the substance, thus increasing its heat of combustion per unit mass, resulting in a higher Q_1 value. Examples are woods, as shown in Figure 4. On changing moisture content of woods from 50% to 0% the Q_1 value increases from around 0.5 to 1.0 while Q_2 remains the same.

Densification increases the value of Q_2 by increasing the bulk density.

Oil shale is another important fuel that needs a considerable amount of processing before it can be used. The calorific value of kerogen, which constitutes 10 to 30% of shale, is 47170 kJ/kg* and the bulk density of quarried shale is 1474 kg/m³ [23]. Thus oil shale with 20% kerogen has a Q_1 value of 0.47 and a Q_2 value of 1.73 as shown on Figure 4.

The overall value of an energy resource is a function of its quality, quantity available, point of origin, etc. The quality would serve as a guideline in deciding the transportability of a fuel. A low quality fuel should be used close to its origin while fuels with higher Q values can be transported without incurring high expenses. The Q_1 vs Q_2 plot is thus a practical way of classifying renewable energy resources.

* Calculated using elemental composition [23] and Thornton's method [24].

Tables 44-48 show an efficient way of listing data on fuels. Using data from such tables it would be possible to make the Q_2 vs Q_1 plot and also one can identify the areas in which improvements can be made so as to increase the Q value.

In the above work no allowance has been made for pollution costs. Due to the sulfur content in some resources, pollution control costs could be considerable and this would influence the quality of a fuel.

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Table 1. Values of Q_0 for Aromatic Acid Amides
(kJ/eq.a.e.).

NAME	Q_0
Benzamide	107.47
Formanilide	109.16
Monophenylurea	108.24
Acetanilide	108.40
Phenylpropiolamide	111.81
Hippuric acid	108.61
Propionanilide	108.56
Benzoylalanine	108.61
Benzoylsarcosine	109.70
O-Toluylglycine	108.57
M-Toluylglycine	108.51
P-Toluylglycine	108.55
Phenaceturic acid	108.31
P-Anisylglycine	110.46
Phenacetin	109.74
O-Toluyllalanine	108.43
P-Toluyllalanine	108.25
Benzanilide	108.06
Diphenylurea	108.79
Succinanilide	108.48
Benzalhippuric acid lactone	109.14
Benzoylphenylalanine	108.33
Benzalhippuric acid	108.93

Table 2. Values of Q_O and Q_G for Organic Acids (kJ/eq.a.e.)

NAME	Q_O	Q_G
Acetic		111.71
Acrylic		114.27
Lactic		114.79
Pyruvic		118.28
Benzoic		107.55
O-Hydroxybenzoic acid		108.95
M-Hydroxybenzoic acid		108.91
P-Hydroxybenzoic acid		108.89
Propionic	109.86	109.54
Butyric	110.00	108.68
N-Valeric	109.80	108.21
Caproic	109.73	107.91
Isobutyl acetic	109.60	
Diethyl acetic	109.60	
Ethyl propyl acetic	109.61	
Dipropyl acetic	109.62	
Lauric	109.12	
Palmitic	109.18	106.52
Glycollic	116.32	122.02
Crotonic	111.39	111.75
Tiglic	109.31	
Angelic	110.74	
Allyl acetic	111.97	
Hydrosorbic	111.04	
Sorbic	111.13	
Geranic	111.08	
Oxalic	125.94	
Malonic	108.47	
Succinic	106.69	110.19
Methyl malonic	108.37	
Glutaric	107.78	
Ethyl malonic	108.41	
Diethyl malonic	108.97	
Pimelic	107.62	
Citric	110.41	
Ethyl propyl malonic	108.95	
Azelaic	108.59	
Dipropyl malonic	109.06	
Fumaric	111.68	117.05
Maleic	113.81	
Citraconic	113.41	

Table 2. contd.

NAME	Q_O	Q_G
Itaconicic	110.67	
Mesaconic	110.97	
Alpha,Beta-hydromuconic	109.73	
Beta,Gamma-hydromuconic	109.78	
Allyl malonic	111.29	
Aconitic	110.55	
Hexahydro-m-totyl acid	108.21	
Cyclooctane acid (act.)	108.51	
Laevulinic	109.81	
Heptyl malonic	109.09	
Cyclohexane-carbon acid	108.55	
Cycloheptane acid	108.38	
Cyclobutane-carbon acid	111.43	

Table 3. Values of Q_0 for Aliphatic Amines (kJ/eq.a.e.)

NAME	Q_0
PRIMARY:	
Methylamine	119.43
Ethylamine	115.23
Allylamine	116.29
Propylamine	114.02
N-Butylamine	110.12
Isobutylamine	110.58
Sec.-butylamine	110.49
Ter.-butylamine	110.95
Isoamylamine	109.90
1,1-Aminocyclopropylethane	111.12
Hexylamine	109.66
Benzylamine	109.21
1-Methylcyclohexylamine-3	108.85
Heptylamine	109.61
Camphylamine	108.72
SECONDARY:	
Dimethylamine	116.65
Diethylamine	113.22
Diisobutylamine	110.62
Benzylethylamine	110.12
Dibenzylamine	109.20
Diisoamylamine	110.27
TERTIARY:	
Trimethylamine	115.46
Triethylamine	111.23
Triisobutylamine	110.10
Triisoamylamine	110.64
Tribenzylamine	110.06

Table 4. Values of Q_0 for Aliphatic Nitriles (kJ/eq.a.e.)

NAME	Q_0
Acetonitrile	118.07
Glycollic nitrile	119.34
Malononitrile	117.99
Cyanoacetic acid	113.65
Cyanoacetamide	112.46
Propionitrile	112.33
Ethylidene lactonitrile	117.46
Succinic acid nitrile	114.16
Allyl cyanide	114.54
Trimethylene nitrile	115.86
Crotononitrile	113.94
Isocrotononitrile	114.32
Methyl cyanoacetate	116.07
Diglycolamidic nitrile	117.67
N-Butyronitrile	111.57
Glutaric nitrile	112.58
Ethyl cyanoacetate	114.61
Isovaleronitrile	111.40
Triglycolamidic nitrile	117.99
Methyl acetylcyanoacetate	114.64
Propyl cyanoacetate	113.83
Ethyl cyanoacetylacetate	112.91
Amyl propiolic nitrile	113.28
Cyanocamphor	109.77

Table 5. Values of Q_0 for Alkaloids (kJ/eq.a.e.).

NAME	Q_0
Coniine	108.91
Nicotine	110.62
Thebaine	112.25
Papaverine	111.49
Strychnine	110.17
Narcotine	114.07
Brucine	111.56

Table 6. Values of Q_O and Q_G for Alkanes (kJ/eq.a.e.).

NAME	Q_O	Q_G
2-Methylbutane	109.48	105.63
2-2-Dimethylpropane	109.20	105.62
2-Methylpentane	109.41	105.62
3-Methylpentane	109.47	105.82
2-2-Dimethylbutane	109.17	105.65
2-3-Dimethylbutane	109.34	105.78
2-Methylhexane	109.35	105.80
3-Methylhexane	109.41	105.83
3-Ethylpentane	109.46	105.97
2-2-Dimethylpentane	109.15	105.76
2-3-Dimethylpentane	109.27	105.75
2-4-Dimethylpentane	109.23	105.82
3-3-Dimethylpentane	109.24	105.80
2-2-3-Trimethylbutane	109.19	105.85
2-Methylheptane	109.31	105.87
3-Methylheptane	109.36	105.89
4-Methylheptane	109.38	105.95
3-Ethylhexane	109.40	105.95
2-2-Dimethylhexane	109.17	105.74
2-3-Dimethylhexane	109.36	105.98
2-4-Dimethylhexane	109.27	105.87
2-5-Dimethylhexane	109.20	105.85
3-3-Dimethylhexane	109.26	105.90
3-4-Dimethylhexane	109.37	105.97
3-Ethyl-2-methylpentane	109.42	106.05
3-Ethyl-3-methylpentane	109.35	106.02
2-2-3-Trimethylpentane	109.27	105.98
2-2-4-Trimethylpentane	109.23	105.93
2-3-3-Trimethylpentane	109.34	106.01
2-3-4-Trimethylpentane	109.31	106.01
2-2-3-3-Tetramethylbutane	109.04	106.06

Table 7. Values of Q_O and Q_G for Alkyl Benzenes (kJ/eq.a.e.)

NAME	Q_O	Q_G
BRANCHED:		
O-Xylene	108.40	105.99
M-Xylene	108.38	105.92
P-Xylene	108.40	105.98
Isopropylbenzene	108.66	106.19
1-2-3-Trimethylbenzene	108.29	105.83
1-2-4-Trimethylbenzene	108.23	105.73
1-3-5-Trimethylbenzene	108.19	105.76
2-Ethyl-1-methyl benzene	108.55	106.03
3-Ethyl-1-methyl benzene	108.50	105.95
4-Ethyl-1-methyl benzene	108.48	105.95
NORMAL:		
Benzene	110.05	106.92
Toluene	109.67	106.44
Ethylbenzene	109.69	106.47
Propylbenzene	109.68	106.46
Butylbenzene	109.67	106.46
Pentylbenzene	109.68	106.48
Hexylbenzene	109.69	106.49
Heptylbenzene	109.70	106.51
Octylbenzene	109.71	106.52
Nonylbenzene	109.71	106.53
Decylbenzene	109.72	106.54
Undecylbenzene	109.72	106.55
Dodecylbenzene	109.73	106.56
Tridecylbenzene	109.73	106.56
Tetradecylbenzene	109.73	106.57
Pentadecylbenzene	109.74	106.57
Hexadecylbenzene	109.74	106.58

Table 8. Values of Q_O and Q_G for Alkynes (kJ/eq.a.e.)

NAME	Q_O	Q_G
Ethyne	129.96	123.52
Propyne	121.10	115.71
1-Butyne	118.03	113.24
2-Butyne	117.18	112.48
1-Pentyne	116.26	111.81
2-Pentyne	115.71	111.25
3-Methyl-1-butyne	115.98	111.65
1-Hexyne	115.25	110.90
1-Heptyne	114.32	110.26
1-Octyne	113.73	109.79
1-Undecyne	112.62	108.91
1-Dodecyne	112.38	108.72
1-Tridecyne	112.17	108.56
1-Tetradecyne	112.00	108.42
1-Pentadecyne	111.85	108.30
1-Hexadecyne	111.72	108.20
1-Heptadecyne	111.60	108.10
1-Octadecyne	111.50	108.02
1-Nonadecyne	111.41	107.95
1-Eicosyne	111.32	107.91

Table 9. Values of Q_0 for Amides (kJ/eq.a.e.).

NAME	Q_0
Phthalimide	107.82
Glycocoll	108.51
Alanin	108.25
Isoserin	110.62
Asparagine	107.81
Glycyl glycine	109.51
Barbituric acid	107.29
Uric acid	107.25
4-Methyl uracil	107.66
Leucine	108.78
Veronal	108.34
Skatol	108.91
Alpha-methyl indol	108.75
O-Methyl hippuric	108.68
M-Methyl hippuric	108.62
P-Methyl hippuric	108.66
P-Methoxy hippuric	110.57
Methyl hydrouracil	107.77

Table 10. Values of Q_O and Q_G for Aliphatic Amides (kJ/eq.a.e.)

NAME	Q_O	Q_G
Formamide	112.88	
Urea	105.72	111.98
Oxamic acid	107.61	
Oxamide	106.27	
Formylurea	108.26	
Acetamide	107.49	
Oxaluric acid	108.52	
Methyl oxamate	116.16	
Malonamide	107.23	
Acetylurea	107.86	
Hydantoic acid	107.60	
Propionamide	108.27	
Urethane	110.79	
Ethylurea	109.71	
Ethyl oxamate	112.55	
Creatinine	112.25	113.27
Succinamide	106.53	
D-Tartramide	111.66	
Mesotartramide	111.56	
N-Butyramide	108.42	
Isobutyramide	108.40	
Creatine	111.53	113.35
Dimethylmalonamide	110.36	
Isovaleramide	108.42	
Diethylmalonamide	109.53	
Amylpropiolamide	111.94	
D-Tartaricdiethylamide	111.31	
DL-Tartaricdiethylamide	111.33	
Mesotartaricdiethylamide	111.43	
Hexylpropiolamide	111.69	

Table 11. Values of Q_O and Q_G for Amino Acids (kJ/eq.a.e.)

NAME	Q_O	Q_G
AMINO ACIDS:		
Phenylglycine	108.00	
Anilidoacetic acid	109.15	
Phenylalanine	108.13	108.06
Tyrosine	109.21	109.34
ALIPHATIC AMINO ACIDS:		
Glycine	109.02	112.32
Sarcosine	111.88	
Alanine	108.14	109.44
D-L-Alanine	108.09	
Isoserine	110.62	115.56
D-Alanine	108.09	
Diglycolamidic acid	110.49	
Aspartic acid	107.36	
L-Aspartic acid	107.56	112.42
Asparagine	107.67	111.07
Glycylglycine	109.41	
Glycylglycinecarboxylic acid	109.55	
DL-Alpha-aminoisovaleric acid	108.60	
Glutamic acid	108.07	110.25
Triglycolamidic acid	111.49	
Alanine anhydride	109.68	
D-Alanine anhydride	109.62	
Diglycineglycyl	109.99	
Glycylglycine ethyl ester	112.02	
Leucine	108.48	108.02
Formyl-D,L-Leucine	109.67	
D-L-Leucylglycine	109.11	
Triglycylglycine	110.02	
Leucylglycylglycine	109.37	
Leucineimide	109.28	
L-Arginine		111.36
Cysteine		103.86
Cystine		103.39
Glutamine		109.50
Isoleucine		108.00
Methionine		99.14
Tryptophane		108.62
Valine		108.13

Table 12. Values of Q_0 for Aromatic Amines (kJ/eq.a.e.).

NAME	Q_0
PRIMARY	
Aniline	109.69
P-Aminophenil(S)	109.65
P-Phenylenediamine(S)	110.28
O-Toluidine	109.04
M-Toluidine	109.16
P-Toluidine	108.38
P-Anisidine	110.46
1-Amino-2,4-xylene	107.81
Pseudocumidine	108.09
Alpha-naphthylamine	107.89
Beta-naphthylamine	107.67
Benzidine	108.51
O,P-Diaminodiphenyl	108.91
Triaminotriphenylcarbinol	111.73
SECONDARY:	
Methylaniline	110.84
Ethylaniline	109.13
Diphenylamine	108.94
Phenyl-alpha-naphthylamine	108.88
Phenyl-beta-naphthylamine	108.57
TERTIARY:	
Dimethylaniline	111.19
Diethylaniline	110.43
Triphenylamine	109.06

Table 13. Values of Q_0 for Aromatic Ethers (kJ/eq.a.e.)

NAME	Q_0
Anisol	111.49
Phenetole	110.66
M-Cresol methyl ether	110.67
Hydroquinone dimethyl ether	111.83
Resorcin dimethyl ether	112.70
Phenyl propyl ether	110.45
P-Cresol ethyl ether	110.42
M-Xylenyl methyl ether	110.48
P-Xylenyl ethyl ether	110.22
Thymol methyl ether	110.07
Methyl chavicol	111.79
Anethole	110.88
Alpha-ethoxy styrol	110.14
Isoeugenol	111.47
Eugenol	112.25

Table 14. Values of Q_0 for Aromatic Nitriles (kJ/eq.a.e.).

NAME	Q_0
Benzonitrile	109.74
Benzyl cyanide	109.80
O-Tolunitrile	110.53
Benzoyl cyanide	112.39
Cyanoacetophenone	110.78
Phenylpropionic nitrile	114.07
Alpha-naphthonitrile	108.80
Beta-naphthonitrile	108.37

Table 15. Values of Q_O and Q_G for Carbohydrates (kJ/eq.a.e.).

NAME	Q_O	Q_G
Arabinose	116.73	
Xylose	117.47	
Levoglucozan	118.15	
Rhamnose	115.53	
Fucose	114.56	
D-Glucose	117.33	119.67
L-Fructose	117.78	119.74
Sorbinose	116.51	
Galactose	116.72	119.40
Glucoheptose	117.08	
Rhamnose triacetate	113.01	
Pentaacetylglucose	112.86	
Pentaacetylgalactose	112.81	
Sucrose	117.64	120.61
Lactose	117.75	
Lactose(cryst.)	117.21	121.38
Maltose(S)	117.69	121.76
Maltose(cryst.)	116.73	
Mycose	117.62	
Trehalose(cryst.)	116.93	
Cellobiose(anhyd.)	117.68	
Sucrose octaacetate	113.32	
Maltose octaacetate	113.22	
Cellobiose octaacetate	113.29	
Lactose octaacetate	113.17	
Raffinose(S)	117.73	
Raffinose(cryst.)	117.32	
Melezitose	118.66	
Stachyose(anhyd.)	118.05	

Table 16. Values of Q_0 for Carbylamines (kJ/eq.a.e.).

NAME	Q_0
Methyl carbylamine	120.73
Ethyl carbylamine	117.42
Allyl carbylamine	121.36
Propyl carbylamine	116.35
Isobutyl carbylamine	114.84
Isoamyl carbylamine	113.51
Benzyl carbylamine	112.27

Table 17. Values of Q_O and Q_G for Cyclic Ureides (kJ/eq.a.e.).

NAME	Q_O	Q_G
Parabanic acid	111.09	
Hydantoin	108.68	
Barbituric acid	107.20	
Aminobarbituric acid	105.74	
Allantoin	108.13	
Oxypurine	112.55	
Xanthine	107.65	114.02
Uric acid	106.97	116.07
Guanine	106.67	113.55
4-Methyluracil	107.66	
5-Methyluracil	107.42	
Dimethylparabanic acid	112.61	
Pseudouric acid	105.58	
4-Methylhydrouracil	107.77	
7-Methylpurine	107.35	
7-Methylhypoxanthine	113.55	
Theobromine	110.52	
Murexide	109.96	
Caffeine	111.67	
Veronal	108.24	
4-Phenyluracil	107.55	
Desoxyamalic acid	110.63	
Tetramethylalloxanthine	112.72	

Table 18. Values of Q_O and Q_G for Cyclohexanes (kJ/eq.a.e.).

NAME	Q_O	Q_G
BRANCHED:		
1,1-Dimethylcyclohexane	108.67	105.82
1,Cis-2-Dimethylcyclohexane	108.81	105.92
1,Trans-2-Dimethylcyclohexane	108.68	105.79
1,Cis-3-Dimethylcyclohexane	108.58	105.70
1,Trans-3-Dimethylcyclohexane	108.73	105.82
1,Cis-4-Dimethylcyclohexane	108.73	105.86
1,Trans-4-Dimethylcyclohexane	108.59	105.74
NORMAL:		
Cyclohexane	109.81	106.14
Methylcyclohexane	109.54	105.91
Ethylcyclohexane	109.65	106.08
Propylcyclohexane	109.65	106.14
Butylcyclohexane	109.67	106.20
Pentylcyclohexane	109.68	106.25
Hexylcyclohexane	109.69	106.28
Heptylcyclohexane	109.70	106.31
Octylcyclohexane	109.71	106.34
Nonylcyclohexane	109.71	106.36
Decylcyclohexane	109.72	106.38
Undecylcyclohexane	109.72	106.39
Dodecylcyclohexane	109.73	106.41
Tridecylcyclohexane	109.73	106.42
Tetradecylcyclohexane	109.73	106.43
Pentadecylcyclohexane	109.73	106.44
Hexadecylcyclohexane	109.74	106.45

Table 19. Values of Q_O and Q_G for Cyclopentanes (kJ/eq.a.e.).

NAME	Q_O	Q_G
BRANCHED:		
1,1-Dimethylcyclopentane	109.13	106.06
Cis-1,2-Dimethylcyclopentane	109.29	106.19
Trans-1,2-Dimethylcyclopentane	109.15	106.03
Cis-1,3-Dimethylcyclopentane	109.22	106.10
Trans-1,3-Dimethylcyclopentane	109.17	106.05
NORMAL:		
Cyclopentane	110.65	106.55
Methylcyclopentane	110.26	106.26
Ethylcyclopentane	110.20	106.32
Propylcyclopentane	110.14	106.36
Butylcyclopentane	110.11	106.40
Pentylcyclopentane	110.08	106.43
Hexylcyclopentane	110.05	106.45
Heptylcyclopentane	110.03	106.47
Octylcyclopentane	110.01	106.48
Nonylcyclopentane	110.00	106.49
Decylcyclopentane	109.98	106.50
Undecylcyclopentane	109.97	106.51
Dodecylcyclopentane	109.96	106.52
Tridecylcyclopentane	109.95	106.53
Tetradecylcyclopentane	109.94	106.54
Pentadecylcyclopentane	109.93	106.54
Hexadecylcyclopentane	109.93	106.55

Table 20. Values of Q_O and Q_G for Olefins (kJ/eq.a.e.).

NAME	Q_O	Q_G
DIOLEFINS:		
1-2-Butadiene	117.90	113.07
1-2-Pentadiene	116.30	111.83
1,Cis-3-Pentadiene	113.90	109.52
1,Trans-3-Pentadiene	113.88	109.64
1,4-Pentadiene	114.87	110.39
2,3-Pentadiene	116.05	111.66
3-Methyl-1,2-butadiene	115.74	111.40
NORMAL MONOOLEFINS:		
Ethene	117.58	110.94
Propene	114.36	108.75
Butene	113.22	108.24
Pentene	112.53	107.91
Hexene	112.07	107.70
Heptene	111.74	107.55
Octene	111.50	107.44
Nonene	111.31	107.35
Decene	111.16	107.28
Undecene	111.03	107.23
Dodecene	110.93	107.18
Tridecene	110.84	107.14
Tetradecene	110.77	107.11
Pentadecene	110.70	107.08
Hexadecene	110.64	107.05
Heptadecene	110.59	107.03
Octadecene	110.55	107.01
Nonadecene	110.51	106.99
Eicosene	110.47	106.97

Table 21. Values of Q_0 for Esters (kJ/eq.a.e.).

NAME	Q_0
Methyl iso-butyrate	111.58
Dimethyl acrylic methyl ester	112.30
Methyl benzoate	109.76
Methyl P-oxabenzoate	110.30
Methyl salicylate	110.65
Methyl anisate	111.90
Methyl ester cyclohexenyl acetic acid	110.18
Cyclohexylidene acetic methyl ester	110.76
Methyl cinnamate	110.44
Methyl pinonate	110.49
Dimethyl carbonate	118.83
Diethyl carbonate	112.95
Ethyl benzoate	109.56
Ethyl salicylate	110.07
Ethyl P-oxabenzoate	109.31
Cyclo hexenyl acetic ethyl ester	109.56
Propyl benzoate	109.46
Propyl P-oxybenzoate	109.31
Isobutyl benzoate	109.47
Isobutyl salicylate	109.98
Amyl benzoate	109.56
Dimethyl acrylic methyl ester	112.30
Cyclohexylidene acetic methyl ester	110.76

Table 22. Values of Q_0 for Imides (kJ/eq.a.e.).

NAME	Q_0
Succinimide	107.78
DL-N-Methyltartarimide	113.74
D-N-Ethyltartarimide	112.32
DL-N-Ethyltartarimide	112.33
N-Ethylmesotartarimide	112.58
Phthalimide	107.71
Hemipinimide	112.15
D-N-Phenyltartrimide	110.79
DL-N-Phenyltartrimide	110.78
D-N-Benzyltartrimide	110.19
DL-N-Benzyltartrimide	110.18
N-Benzylmesotartrimide	110.45

Table 23. Values of Q_0 for Isocyanates (kJ/eq.a.e.).

NAME	Q_0
Methyl isocyanate	125.24
Ethyl isocyanate	118.41

Table 24. Values of Q_0 for Ketones (kJ/eq.a.e.).

NAME	Q_0
Methyl ethyl ketone	110.74
Diethyl ketone	109.92
Methyl propyl ketone	109.77
Methyl isopropyl ketone	109.67
Pinakoline	109.74
Methyl butyl ketone	110.16
Ethyl allyl ketone	112.20
Allyl acetone	112.14
Dipropyl ketone	109.88
Methyl hexyl ketone	109.61
Beta-methyl cyclo pentanone	108.97
Beta-methyl cyclo hexanone	109.53
Cycloheptenone	109.74
Diallyl acetone	111.77
Acetyl trimethylene	111.20
Ethyl cyclo pentenone	109.05
1,3-Dimethyl cyclopentenone	108.98
1,3-Dimethyl cyclohexenone	109.80
1,3-Dimethyl cyclohexanone	107.43

Table 25. Values of Q_O and Q_G for Normal Alkanes (kJ/eq.a.e.).

NAME	Q_O	Q_G
Methane	111.29	102.25
Ethane	111.42	104.82
Propane	111.00	105.42
Butane	110.66	105.63
Pentane	110.51	105.83
Hexane	110.39	105.96
Heptane	110.31	106.05
Octane	110.24	106.13
Nonane	110.20	106.18
Decane	110.16	106.23
Undecane	110.12	106.27
Dodecane	110.10	106.30
Tridecane	110.07	106.33
Tetradecane	110.05	106.35
Pentadecane	110.04	106.37
Hexadecane	110.02	106.39
Heptadecane	110.01	106.41
Octadecane	110.00	106.42
Nonadecane	109.99	106.43
Eicosane	109.98	106.44

Table 26. Values of Q_O and Q_G for Alcohols (kJ/eq.a.e.).

NAME	Q_O	Q_G
POLYHYDROXY:		
Glycerol	118.74	118.20
Erythritol	117.34	
Arabitol	116.17	
Mannitol	117.20	118.61
Galactitol	117.46	
Perseitol	116.68	
Sorbitol	118.61	
PRIMARY:		
Methyl alcohol	118.97	115.55
Ethyl alcohol	114.03	109.88
Propyl alcohol	112.92	108.67
Isopropyl alcohol		108.10
Butyl alcohol	111.28	107.98
Isobutyl alcohol	111.07	
Heptyl alcohol	109.98	
Benzyl alcohol	110.24	
Cyclobutyl carbinol	111.74	
Cyclohexyl carbinol	109.54	
Saligenin	110.67	

Table 27. Values of Q_O and Q_G for Ring Nitrogen Compounds
(kJ/eq.a.e.).

NAME	Q_O
Pyrrole	113.11
Diketopiperazine	110.32
Pyridine	110.21
Piperidine	111.56
Hexamethylenetetramine	117.00
Alpha-picoline	110.03
Beta-picoline	109.62
Gamma-picoline	110.11
Lutidine	109.46
Isatin	110.03
Indole	109.66
Dioxindol	109.47
Tetrahydroquinoline	109.38
Skatole	108.83
Alpha-methylindole	108.66
Quinoline	109.32
Phenylpyrrole	109.60
Quinaldine	109.32
Opianic acid oxime anhydride	117.50
Tetrahydroquinaldine	109.11
Carbazole	108.27
Undugo	108.49
Amygdalin	115.60

Table 28. Values of Q_o and Q_G for Styrenes (kJ/eq.a.e.).

NAME	Q_o	Q_G
Styrene (vinylbenzene)	110.97	107.90
Alpha-Methylstyrene	110.52	107.41
Beta-Methylstyrene	110.70	107.63
o-Methylstyrene	110.64	107.52
m-Methylstyrene	110.57	107.40
p-Methylstyrene	110.55	107.51

Table 29. Values of Q_O and Q_G for Tertiary Alcohols and Phenols (kJ/eq.a.e.).

NAME	Q_O	Q_G
Trimethyl carbinol	109.71	
Dimethyl ethyl carbinol	109.43	
1,3-Dimethyl cyclohexanol	108.47	
Ethyl dipropyl carbinol	107.39	
Phenol	109.52	108.22
Catechol	110.31	
Resorcinol	110.02	110.33
Hydroquinone	110.01	
Phloroglucinol	107.72	
O-Cresol	108.72	108.01
M-Cresol	108.46	107.90
P-Cresol	108.71	108.15
O-Xylenol	108.38	
M-Xylenol	108.62	
P-Xylenol	108.40	
Pseudocumenol	108.46	
Thymol	108.95	
Carvacrol	109.09	
Diphenyl carbinol	109.12	
Triphenyl carbinol	108.92	
Allyl methyl ethyl carbinol	109.84	
Benzyl alcohol		108.18

Table 30. Values of Q_0 for Unsaturated Hydrocarbons
(kJ/eq.a.e.).

NAME	Q_0
TYPE I:	
Cycloheptene	109.82
Methyl-1-cyclohexene-1	108.88
Methyl-1-cyclohexene-3	109.06
1,3,5-Trimethyl benzene	109.12
1,2,4-Trimethyl benzene	107.98
Naphthalene	107.74
Biphenyl	107.85
Biphenyl methane	108.30
1,6-Diphenyl hexadien-1,5	109.01
Triphenyl methane	108.63
Triphenyl methyl	109.47
Tetrahydrobenzene	110.02
Dihydrobenzene	110.95
2,4-Hexadien	109.04
Lauroleone	108.65
1-Methyl-3-Methane cyclohexene-1	109.43
1,5-Dimethyl-3-methene cyclohexene-1	108.71
1-Ethyl-5-dimethyl cyclohexene-1	108.69
Isobutenyl cyclohexene-1	108.69
1,5-Dimethyl-3-Ethene cyclohexene-1	108.89
1,5-Dimethyl-3-Isopropene-cyclohexene-1	108.71
1,3-Dimethyl-dihydrobenzene	109.18
TYPE II:	
Trimethyl ethylene	111.02
Camphene	109.79
Methylene cyclohexene	110.04
Ethylene cyclohexene	109.99
Sylvestren	109.57

Table 31. Summary of Heat of Combustion Properties of Various Groups of Organic Substances.

Group Name	Mean γ	Mean $Q_{O,e}$ (kJ/eq.a.e.)	95% C.I. for Q_O^*	No. of compounds
Acid amides (Aromatic)	4.6162	108.83	108.44, 109.22	23
Acids	4.3301	110.31	109.44, 111.17	46
Aliphatic amines (Primary)	6.6594	111.61	109.86, 113.36	15
Aliphatic amines (Secondary)	6.2402	111.68	108.76, 114.60	6
Aliphatic amines (Tertiary)	6.1900	111.50	108.69, 114.31	5
Aliphatic nitriles	4.9793	114.60	113.55, 115.65	24
Alkaloids	5.0019	111.29	109.78, 112.81	7
Alkanes	6.2797	109.30	109.27, 109.34	31
Alkyl benzenes	5.3083	108.41	108.30, 108.51	10
Alkynes	5.6963	114.80	112.70, 116.89	20
Amides	4.5171	108.54	108.07, 109.02	18
Amides (Aliphatic)	4.8277	109.78	108.88, 110.67	30
Amino acids	4.6458	108.62	107.60, 109.65	4
Amino acids (Aliphatic)	4.8715	109.33	108.80, 109.86	25
Aromatic amines (Primary)	5.1218	109.09	108.41, 109.77	14
Aromatic amines (Secondary)	5.0405	109.12	108.41, 109.83	5
Aromatic amines (Tertiary)	5.2361	110.23	107.55, 112.90	3
Aromatic ethers	4.9842	111.04	110.58, 111.49	15
Aromatic nitriles	4.6529	110.56	108.99, 112.14	8
Carbohydrates	4.0287	116.23	115.48, 116.97	29
Carbalamines	5.5250	116.64	113.44, 119.84	7
Cyclic ureides	4.1604	109.04	108.00, 110.08	23

Table 31. contd.

Group Name	Mean γ	Mean Q_o (kJ/eq.a.e.)	95% C.I. for Q_o *	No. of compounds
Cyclohexanes	6.0000	108.68	108.61, 108.76	7
Cyclopentanes	6.0000	109.19	109.11, 109.27	5
Diolefins	5.5857	115.52	114.19, 116.85	7
Esters	4.7442	110.79	109.95, 111.64	24
Imides	4.1494	110.92	109.74, 112.09	12
Isocyanates	4.7500	121.82	78.41, 165.24	2
Ketones	5.4787	110.02	109.45, 110.58	19
Normal alkanes	6.3598	110.33	110.12, 110.53	20
Normal alkylbenzenes	5.5032	109.73	109.68, 109.77	17
Normal alkyl cyclopentanes	6.0000	109.70	109.67, 109.73	17
Normal alkyl cyclohexanes	6.0000	110.07	109.98, 110.16	17
Normal monoolefins	6.0000	111.71	110.86, 112.56	19
Poly hydroxy alcohols	4.4075	117.31	116.48, 118.15	6
Primary alcohols	5.7039	112.04	110.05, 114.04	10
Ring nitrogen compounds	4.9429	110.66	109.54, 111.79	23
Styrenes	5.0926	110.66	110.48, 110.83	6
Tertiary alcohols and phenols	5.0262	108.96	108.62, 109.31	21
Unsaturated hydrocarbons (Type I)	5.3912	108.98	108.65, 109.30	22
Unsaturated hydrocarbons (Type II)	5.7329	110.08	109.39, 110.77	5
All compounds		110.81	110.58, 111.05	627

* C.I. = confidence intervals

Table 32. Summary of Free Energy of Combustion Properties of Various Groups of Organic Substances.

Group Name	Mean γ	Mean Q_G (kJ/eq.a.e.)	95% C.I. for Q_G^*	No. of comp
Acids	4.3301	111.48	109.24, 113.72	17
Alkanes	6.2797	105.87	105.82, 105.91	31
Alkyl Benzenes	5.3083	105.93	105.84, 106.03	10
Alkynes	5.6963	110.68	108.95, 112.42	20
Amides (Aliphatic)	4.8277	112.87	110.96, 114.78	3
Amino acids	4.6458	108.70	100.56, 116.84	2
Amino acids (Aliphatic)	4.8715	108.74	106.47, 111.01	15
Carbohydrates	4.0287	120.43	119.40, 121.45	6
Cyclic ureides	4.1604	114.55	111.22, 117.87	3
Cyclohexanes	6.0000	105.81	105.74, 105.87	7
Cyclopentanes	6.0000	106.09	106.01, 106.16	5
Diolefins	5.5857	111.07	109.89, 112.26	7
Normal alkanes	6.3598	105.91	105.46, 106.36	20
Normal alkylbenzenes	5.5032	106.54	106.49, 106.60	17
Normal alkyl cyclohexanes	6.0000	106.29	106.21, 106.37	17
Normal alkyl cyclopentanes	6.0000	106.47	106.42, 106.51	17
Normal monoolefins	6.0000	107.58	107.12, 108.03	19

Table 32. contd.

Group Name	Mean γ	Mean Q_G (kJ/eq.a.e.)	95% C.I. for Q_G^*	No. of comp.
Polyhydroxy alcohols	4.4075	118.47	117.88, 119.06	3
Primary alcohols	5.7039	110.04	106.09, 113.98	5
Styrenes	5.0926	107.61	107.43, 107.80	6
Tertiary alcohols and phenols	5.0262	108.74	107.71, 109.77	7
All compounds		108.07	107.52, 108.61	237

*C.I. = confidence intervals

Table 33. Elemental Analysis and Heat of Combustion Properties of Agricultural Crop Residues

Name	Elemental Composition *					σ^{**}	γ	Q_o^*	ΔH_c^*	ASH **	MOIST.†	REF.
	%C	%H	%O	%N	%S							
Bagasse	48.21	6.67	45.13	0.00	0.00	0.470	4.255	115.6	19753	2.50	48.00	16
Brava cane	46.27	6.00	45.25	0.53	0.16	0.446	4.094	118.8	18755	3.65	6.05	7
Coconut shell	49.00	6.00	44.00	1.00	0.00		4.122	111.8	18817			20
Coir dust	46.00	7.00	46.00	1.00	0.00		4.326	101.8	16887		85.00	20
Cotton thread	42.91	6.34	50.75	0.00	0.00		3.999	118.5	16945			11
Peanut shells	54.30	7.90	37.80	0.00	0.00	0.530	4.702	96.2	20469	2.48	7.20	19
Rice hulls	45.56	6.75	47.10	0.59	0.00	0.385	4.226	113.4	18195	15.50		12
Rice hulls (dry)	45.56	6.75	47.10	0.59	0.00	0.385	4.226	113.4	18195	15.50	7.60	8
Rice straw	48.51	6.31	44.31	0.74	0.12	0.392	4.195	111.0	18827	19.20		12
Straw	49.89	6.49	42.66	0.96	0.00	0.469	4.278	111.3	19796	6.00		13

* dry ash free basis

** dry basis

+ as is basis

Table 34. Elemental Analysis and Heat of Combustion Properties of Grasses, Leaves and Brush

Name	Elemental Composition *					σ **	γ	Q_o *	ΔH_c *	ASH **	MOIST. +	REF.
	%C	%H	%O	%N	%S							
Brush	46.38	6.44	44.94	2.18	0.05	0.425	4.213	123.0	20032	8.33	40.00	9
Citrus rinds and seeds	49.68	5.88	43.16	1.15	0.12	0.480	4.122	113.1	19299	3.46	78.70	9
Evergreen shrubs	49.81	6.72	41.52	1.76	0.20	0.485	4.373	114.9	20849	2.61	69.00	9
Flowering plants	49.15	6.96	42.33	1.27	0.27	0.466	4.417	108.7	19657	5.09	53.94	9
Lawn grass I	49.42	6.38	38.98	4.77	0.45	0.462	4.379	114.7	20676	6.55	75.24	9
Lawn grass II	46.47	6.48	44.70	2.31	0.05	0.433	4.232	117.0	19177	6.75	65.00	9
Mixed greens	46.33	6.48	44.83	2.30	0.06	0.403	4.230	115.8	18910	13.00	62.00	9
Ripe leaves I	54.46	6.38	31.96	7.30	0.17	0.521	4.538	104.5	21530	4.25	9.97	9
Ripe leaves II	44.12	6.48	49.13	0.22	0.05	0.405	4.094	118.9	17898	8.20	50.00	9

* dry ash free basis

** dry basis

+ as is basis

Table 35. Elemental Analysis and Heat of Combustion Properties of Coals

Name	Elemental Composition *					σ^{**}	γ	Q_O^*	ΔH_C^*	ASH ^{**}	MOIST. [†]	REF.
	%C	%H	%O	%N	%S							
Anthracite I	94.39	1.77	2.13	0.71	1.00	0.868	4.207	104.6	34614	8.06	2.80	11
Anthracite II	92.20	3.12	2.76	0.96	0.00	0.768	4.361	106.1	35566	16.70	5.40	16
Bituminous	88.98	5.05	3.71	1.65	0.00	0.864	4.618	106.2	36358	2.90	3.40	16
Bituminous (high grade)	85.09	4.99	6.99	1.80	1.13	0.827	4.600	111.2	36263	2.85	2.18	11
Bituminous (low grade)	76.11	4.03	16.14	0.84	2.88	0.532	4.374	104.3	28932	30.16	10.88	11
Bituminous (medium grade)	82.08	5.40	5.98	1.32	5.22	0.709	4.776	106.3	34710	13.65	4.99	11
Cannel	85.29	7.13	7.57	1.33	1.38	0.761	4.894	105.7	36752	10.74	2.36	11
Coke breeze	94.79	1.51	1.48	1.19	1.03	0.820	4.184	101.8	33631	13.50	10.77	11
Lignite I	68.32	4.00	25.54	1.42	0.72	0.565	4.158	108.4	25656	17.30	23.30	11
Lignite II	71.43	4.69	21.43	1.00	1.45	0.640	4.368	107.0	27808	10.40		12
Pittsburgh seam	84.17	5.57	5.46	1.34	3.46	0.755	4.759	106.0	35396	10.30		12
Semi-anthracite	92.15	3.76	2.17	1.18	0.74	0.812	4.466	104.8	35953	11.90	3.38	11
Semi-bituminous	89.79	4.76	2.47	2.00	0.98	0.835	4.611	106.8	36865	6.98	2.60	11
Sub-bituminous	69.17	4.46	24.35	1.66	0.36	0.660	4.254	111.2	27263	4.55	18.41	11

Table 35. contd.

Name	Elemental Composition *					σ^{**}	γ	Q_o^*	ΔH_c^*	ASH **	MOIST. +	REF.
	%C	%H	%O	%N	%S							
Utah coal	81.23	6.26	10.32	1.56	0.63	0.779	4.745	107.0	34369	4.10		12
West kentucky coal	80.26	5.50	8.52	1.62	4.10	0.744	4.740	105.9	33570	7.30		12
Wyoming elköl coal	74.63	5.53	17.64	1.25	0.94	0.715	4.554	109.0	30860	4.20		12

* dry ash free basis

** dry basis

+ as is basis

Table 36. Elemental Analysis and Heat of Combustion Properties of Chars

Name	Elemental Composition *					Y	Q _O *	ΔH_c^*	ASH **	MOIST. [†]	REF.
	%C	%H	%O	%N	%S						
Animal waste	67.38	4.30	15.43	3.71	1.76	0.345	4.461	98.8	24759	48.80	12
Charcoal I	83.13	3.21	11.70	0.21	0.00	0.803	4.252	109.3	32193	3.40	12
Charcoal II	95.88	2.58	0.00	0.80	0.74	0.949	4.334	100.3	34727	1.00	2.00 11
Fir bark	63.49	5.09	31.17	0.13	0.13	0.499	4.228	109.3	24444	21.40	12
Grass straw	67.37	4.89	26.02	0.66	1.06	0.510	4.315	105.3	25503	24.30	12
Municipal solid waste	93.37	1.36	3.06	1.87	0.34	0.549	4.131	98.7	31725	41.20	12
Oak I	78.11	2.54	18.74	0.48	0.12	0.646	4.033	106.2	27873	17.30	12
Oak II	79.55	2.82	16.92	0.47	0.24	0.677	4.111	106.9	29136	14.90	12
Redwood I	82.17	3.65	13.76	0.21	0.21	0.788	4.286	108.3	31773	4.10	12
Redwood II	77.38	3.38	18.83	0.20	0.20	0.756	4.163	110.0	29521	2.30	12
Rice hull	70.87	5.12	23.03	0.79	0.20	0.360	4.383	107.9	27930	49.20	12

* dry ash free basis

** dry basis

+ as is basis

Table 37. Elemental Analysis and Heat of Combustion Properties of Petroleum Fuels *

Name	Elemental Composition						σ	γ	Q_o	ΔH_c	ASH	MOIST. REF.
	%C	%H	%O	%N	%S							
Fuel, kerosene	85.80	14.20	0.00	0.00	0.00		0.858	5.986	108.4	46388	0.00	0.00 11
Naphtha, Alaska	86.30	13.70	0.00	0.00	0.00		0.863	5.905	106.8	45359	0.00	0.00 11
Naphtha, aromatic	90.10	9.80	0.00	0.00	0.00		0.901	5.305	108.1	43041	0.00	0.00 11

* all values are on as is basis

Table 38. Elemental Analysis and Heat of Combustion Properties of Animal Wastes

Name	Elemental Composition *				σ^{**}	γ	Q_O^*	ΔH_C^*	ASH **	MOIST. ⁺	REF.
	%C	%H	%O	%N							
Animal waste	51.95	6.69	38.08	2.92	0.36	0.427	4.457	108.2	20883	17.80	12
Cattle manure (dry)	49.76	6.88	40.22	2.78	0.36	0.412	4.459	108.0	19973	17.20	8
Feedlot waste	42.60	5.50	49.10	2.80	0.00	0.321	3.820	136.6	18529	24.68	15

* dry ash free basis

** dry basis

+ as is basis

Table 39. Elemental Analysis and Heat of Combustion Properties of Municipal/Domestic Wastes

Name	Elemental Composition *					σ^{**}	γ	Q_O^*	ΔH_C^*	ASH ^{**}	MOIST. [†]	REF.
	%C	%H	%O	%N	%S							
Fried fats	73.14	11.54	14.82	0.43	0.07		5.591	112.3	38275	0.00	0.00	9
Grass, dirt and leaves	51.77	6.79	38.09	3.00	0.37	0.362	4.483	108.0	20890	30.08	35.00	9
Leather	66.74	8.90	12.79	11.12	0.44	0.600	5.322	77.3	22884	10.10	10.00	9
Meat scraps (cooked)	62.78	9.98	25.97	1.07	0.20	0.596	5.291	110.1	30472	5.08	38.74	9
Mixed garbage I	53.56	7.65	34.24	3.93	0.62	0.450	4.774	110.2	23475	16.00	72.00	9
Mixed garbage II	53.40	7.36	35.35	3.80	0.32	0.417	4.670	103.8	21560	21.87		9
Mixed garbage III	53.31	6.33	40.35	0.00	0.00	0.528	4.290	108.7	20723	1.00		10
Mixed plastics	66.82	8.02	25.17	0.00	0.00	0.600	4.875	137.0	37190	10.20	2.00	9
Municipal refuse (dry)	51.29	7.76	38.47	2.16	0.32	0.476	4.700	110.9	22282	7.20	4.90	8
Municipal refuse (wet)	29.25	8.82	61.08	0.75	0.11	0.272	4.491	110.3	12073	7.00	43.30	8
Municipal solid waste I	54.09	6.82	37.39	1.36	0.34	0.476	4.485	111.7	22589	12.00		12
Municipal solid waste II	46.76	5.60	44.84	0.74	0.00	0.317	4.000	127.8	19925	32.20	20.80	16
Municipal solid waste III	55.45	7.04	41.37	0.87	0.21	0.336	4.410	115.4	23513	39.33	25.10	10
Pathological waste ^{††}	50.80	9.35	39.85	0.00	0.00	0.387	5.032	96.3	20515	23.75	62.10	10
Plastic battery cases	87.30	12.40	0.20	0.00	0.10	0.859	5.703	107.4	44558	1.60	0.20	8
Plastic film	72.05	10.42	16.96	0.49	0.08	0.672	5.384	106.7	34502	6.72	15.00	9

Table 39. contd.

Name	Elemental Composition *						σ **	γ	Q_O^*	ΔH_c^*	ASH **	MOIST. [†]	REF.
	%C	%H	%O	%N	%S								
Rags	44.31	6.16	49.46	0.00	0.00		0.439	3.993	111.4	16432	0.93	10.00	10
Raw sewage (dry)	56.17	8.40	31.85	2.96	0.62		0.455	4.959	87.6	20331	19.00	4.20	8
Rubber	86.28	11.50	0.00	0.00	2.22		0.776	5.638	72.2	29260	10.00	1.20	9
Sewage sludge (dry)	49.65	7.34	36.71	3.85	2.45		0.142	4.739	84.6	16591	71.40	4.40	8
Shoe, heel and sole	76.13	10.14	11.10	0.72	1.92		0.532	5.418	106.7	36663	30.09	1.15	9
Textiles	47.70	6.62	43.22	2.25	0.21		0.462	4.313	112.5	19293	3.17	25.00	9
Tires I	88.54	7.64	2.34	0.32	1.17		0.834	5.016	106.8	39507	5.80	0.40	17
Tires II	84.69	7.28	6.32	0.11	1.61		0.791	4.948	99.1	34610	6.60	1.02	9
Upholstery	48.46	6.28	44.86	0.31	0.10		0.471	4.169	106.2	17885	2.80	6.90	9
Vegetable food waste	51.58	6.96	39.48	1.77	0.21		0.491	4.477	105.0	20210	4.89	78.29	9

* dry ash free basis

** dry basis

+ as is basis

++ dead animals

Table 40. Elemental Analysis and Heat of Combustion Properties of Papers and Paper Products

Name	Elemental Composition*					σ^{**}	γ	Q_O^*	ΔH_C^*	ASH**	MOIST. [†]	REF.
	%C	%H	%O	%N	%S							
Cardboard	47.21	6.31	46.18	0.17	0.15	0.455	4.140	116.1	18913	3.57	5.00	10
Corrugated boxes	46.20	6.02	47.46	0.10	0.22	0.437	4.030	117.6	18241	5.34	5.20	9
Junk mail	43.89	6.27	49.54	0.20	0.10	0.379	4.025	116.7	17181	13.72	4.56	9
Newsprint	49.90	6.19	43.69	0.05	0.16	0.491	4.181	115.1	20015	1.52	5.97	9
Packaging waste	68.54	9.38	58.86	0.28	0.19	0.498	4.358	116.3	28935	27.37	8.47	10
Paper I	46.17	6.17	47.13	0.32	0.21	0.434	4.079	119.4	18737	6.00	3.00	12
Paper II	47.64	6.66	45.10	0.47	0.13	0.440	4.261	116.0	19628	7.65		10
Paper mill sludge (dry)	34.41	7.80	57.02	0.56	0.22	0.309	4.243	113.9	13858	10.20	23.20	8
Paper, brown	45.39	6.15	47.85	0.00	0.11	0.449	4.047	118.3	18105	1.07	5.83	9
Paper, food cartons	48.07	6.55	45.04	0.16	0.17	0.447	4.236	113.8	19304	6.93	6.11	9
Paper, plastic coated	46.59	6.35	46.80	0.19	0.08	0.453	4.130	114.8	18413	2.77	4.71	9
Paper, sulfite	44.79	6.33	48.88	0.00	0.00	0.443	4.060	117.7	17833	1.00		10
Paper, tissue	44.31	6.16	49.46	0.00	0.00	0.439	3.993	111.4	16432	0.93	7.00	10
Paper, mixed	46.18	6.19	47.15	0.27	0.21	0.434	4.084	119.1	18726	6.00	10.24	9
Trade magazine	42.98	6.46	50.35	0.09	0.12	0.329	4.052	114.6	16633	23.43	4.11	9
Waxed milk cartons	59.91	9.36	30.50	0.12	0.10	0.592	5.114	108.1	27608	1.22	3.45	9

* dry ash free basis

** dry basis

+ as is basis

Table 41. Elemental Analysis and Heat of Combustion Properties of Proteins

Name	Elemental Analysis *					σ **	γ	Q_o *	ΔH_c *	ASH **	MOIST. +	REF.
	%C	%H	%O	%N	%S							
Gliadin protein	52.70	6.90	21.70	17.70	1.00	0.527	4.982	114.5	25045	0.0		11
Milk casein, protein	53.00	7.00	22.65	15.70	0.80	0.530	4.967	108.2	23723	0.0		11

* dry ash free basis

** dry basis

+ as is basis

Table 42. Elemental Analysis and Heat of Combustion Properties of Woods

Name	Elemental Composition*				σ^{**}	γ	Q_o^*	ΔH_c^*	ASH**	MOIST.*	REF.
	%C	%H	%O	%N	%S						
Alabama oak waste	51.19	5.89	42.71	0.21	0.00	0.495	4.130	112.8	19883	3.30	12
Ash	49.46	6.31	44.16	0.07	0.00	0.492	4.192	114.5	19774	0.57	53.70 11
Bark, Douglas fir	56.88	5.97	37.15	0.00	0.00	0.562	4.280	110.2	22365	1.20	6.50 12
Bark, pine	53.86	5.97	39.96	0.21	0.00	0.523	4.218	111.1	21032	2.90	5.60 12
Beech I	49.34	6.15	44.42	0.09	0.00	0.491	4.145	117.6	20046	0.57	11
Beech II	51.98	6.30	41.72	0.00	0.00	0.516	4.251	111.4	20509	0.65	18
Beech III	51.91	6.34	41.75	0.00	0.00	0.516	4.259	111.3	20499	0.60	12
Birch	49.02	6.08	44.80	0.10	0.00	0.489	4.118	118.8	19979	0.29	46.24 11
Birch, white	49.91	6.51	43.58	0.00	0.00	0.498	4.255	114.0	20178	0.29	18
Cypress	55.20	6.57	38.23	0.00	0.00	0.550	4.389	114.2	23050	0.40	18
Demolition softwood	51.41	6.25	42.14	0.10	0.10	0.510	4.232	102.3	18550	0.80	7.70 9
Elm	50.73	6.62	42.66	0.00	0.00	0.503	4.304	113.5	20645	0.74	18
Fir	51.81	6.09	43.51	0.05	0.00	0.517	4.151	117.6	21079	0.28	11
Fir, Douglas I	52.72	6.35	40.83	0.00	0.00	0.523	4.284	112.7	21220	0.80	18
Fir, Douglas II	52.72	6.35	40.62	0.10	0.00	0.523	4.290	112.6	21220	0.80	12
Furniture wood	50.41	6.19	43.20	0.10	0.10	0.497	4.190	104.7	18421	1.40	6.00 9
Ash, white	49.88	6.95	43.17	0.00	0.00	0.497	4.374	114.5	20810	0.30	50.00 18

Table 42. contd.

Name	Elemental Composition *						σ^{**}	γ	Q_O^*	ΔH_c^*	ASH ^{**}	MOIST. [†]	REF.
	%C	%H	%O	%N	%S								
Green logs	50.63	6.46	42.69	0.14	0.08		0.501	4.270	54.8	9873	1.00	50.00	9
Hickory I	50.04	6.54	43.43	0.00	0.00		0.497	4.266	114.2	20315	0.73		18
Hickory II	50.05	6.55	43.40	0.00	0.00		0.497	4.269	114.1	20309	0.70		12
Hornbeam	49.24	6.23	44.47	0.06	0.00		0.490	4.164	116.1	19841	0.50		11
Lignin, hardwood	60.00	6.00	34.00	0.00	0.00			4.350	113.5	24686	0.00		11
Lignin, softwood	64.00	6.00	30.00	0.00	0.00			4.422	111.8	26359	0.00		11
Maple I	52.55	6.15	40.77	0.52	0.00		0.504	4.241	107.0	19866	4.10	44.44	11
Maple II	51.33	6.10	42.31	0.00	0.25		0.506	4.198	112.7	20230	1.35	44.44	18
Maple III	51.32	6.09	42.29	0.30	0.00		0.506	4.187	113.0	20240	1.40	44.44	12
Oak	50.35	6.04	43.52	0.09	0.00		0.502	4.143	110.9	19284	0.37		11
Oak, black	48.85	6.10	45.05	0.00	0.00		0.488	4.115	113.7	19055	0.15		18
Oak, hardwood	49.56	6.63	43.56	0.25	0.10		0.495	4.293	114.1	20225	0.15		10
Oak, red	49.56	6.63	43.81	0.00	0.00		0.495	4.279	114.5	20243	0.15		18
Oak, white	50.56	6.61	42.83	0.00	0.00		0.504	4.297	113.5	20541	0.24		18
Pine, pitch	59.67	7.27	33.05	0.00	0.00		0.590	4.632	115.6	26631	1.13		18
Pine, softwood	52.61	6.09	40.95	0.25	0.10		0.525	4.224	115.1	21308	0.12		10
Pine, white	52.61	6.09	41.30	0.00	0.00		0.525	4.211	112.3	20726	0.12		18

Table 42. contd.

Name	Elemental Composition *						σ^{**}	γ	ΔH_c^*	Q_o^*	ASH ^{**}	MOIST. [†]	REF.
	%C	%H	%O	%N	%S								
Pine, yellow	52.76	7.04	40.19	0.00	0.00	0.526	4.459	22422	114.4	0.31		18	
Poplar I	51.98	6.30	41.72	0.00	0.00	0.516	4.251	20884	113.4	0.65		18	
Poplar II	51.91	6.34	41.75	0.00	0.00	0.516	4.259	20873	113.3	0.60		12	
Redwood I	53.61	5.91	40.38	0.00	0.00	0.535	4.193	21069	112.5	0.20		18	
Redwood II	53.61	5.91	40.38	0.10	0.00	0.535	4.193	21069	112.5	0.20		12	
Rotten timber	53.81	5.66	40.12	0.21	1.23	0.523	4.178	15229	81.3	2.80	26.80	9	
Sawdust	45.90	6.60	46.50	1.00	0.00	0.455	4.206	19073	118.6	0.79	11.40	19	
Sawdust pellets	47.68	6.57	45.86	0.00	0.00	0.472	4.210	17149	102.5	1.00		12	
Spruce, Balsam	55.13	6.87	36.25	1.54	0.20	0.534	4.515	23037	111.1	3.19	74.35	11	
Spruce, Norway	50.50	6.22	43.24	0.04	0.00	0.503	4.194	21309	120.7	0.37		11	
Waste hardwood	49.70	6.14	43.96	0.10	0.10	0.494	4.158	17073	99.1	0.60	12.00	9	
Western Hemlock I	51.53	5.93	41.41	0.00	0.10	0.504	4.179	20501	114.2	2.20		18	
Western Hemlock II	51.53	5.93	42.33	0.10	0.10	0.504	4.152	20501	115.0	2.20		12	
White cedar	48.98	6.39	44.63	0.00	0.00	0.488	4.200	19611	114.4	0.37		18	
Wood and bark	50.97	6.03	42.80	0.15	0.05	0.505	4.162	20223	114.4	1.00	20.00	9	
Wood I	49.74	6.15	43.70	0.30	0.11	0.483	4.169	19727	114.2	2.89		10	
Wood II	52.18	6.09	41.62	0.10	0.00	0.514	4.204	20863	114.1	1.50	46.90	16	

* dry ash free basis

** dry basis

+ as is basis

Table 43. Summary of Heat of Combustion Properties of Various Groups of Renewable Energy Resources.

Group Name	Mean σ	Mean γ	Mean Q_o (kJ/eq.a.e.)	95% C.I. for Q_o *	No. of comp.
Agricultural crop residues	0.439	4.242	111.2	106.1, 116.2	10
Grass, leaves and brush	0.453	4.289	114.5	110.3, 118.7	9
Coals	0.744	4.510	106.6	105.4, 107.8	17
Chars	0.626	4.245	105.5	102.7, 108.4	11
Petroleum fuels	0.874	5.732	107.7	105.7, 109.8	3
Animal wastes	0.387	4.245	117.6	76.8, 158.5	3
Municipal/Domestic wastes	0.506	4.812	105.8	100.5, 111.1	27
Papers and paper products	0.439	4.190	115.6	114.0, 117.1	16
Proteins	0.529	4.974	111.3	71.2, 151.5	2
Woods	0.509	4.245	111.1	108.3, 113.9	51
Overall	0.529	4.414	110.0	108.5, 111.5	149

* C.I. = confidence intervals

Table 44. Quality Analysis for Grasses, Leaves and Brush *

Name	% Moist.	Bulk Density (kg/m ³)	$\frac{\Delta H_c}{\text{kJ/kg}}$	$\frac{\Delta H_c}{\text{kJ/m}^3}$	Q ₁	Q ₂	Ref.
Brush	40.00	30	11018	330543	0.550	0.041	9
Citrus rinds and seeds	78.70	640	3969	2539840	0.198	0.316	9, 21
Lawn grass I	75.24	130	4784	621933	0.239	0.077	9
Lawn grass II	65.00	130	6259	813644	0.313	0.101	9
Ripe leaves I	9.97	160	18559	2969488	0.927	0.369	9
Ripe leaves II	50.00	160	8215	1314448	0.410	0.163	9

* all values are on as is basis.

Table 45. Quality Analysis for Municipal/Domestic Wastes *

Name	% Moist.	Bulk Density (kg/m ³)	ΔH_c		Q ₁	Q ₂	Ref.
			kJ/kg	kJ/m ³			
Leather	10.00	180	18516	3332790	0.925	0.414	9
Leather shoe	7.46	320	16835	5387168	0.841	0.670	9,21
Mixed garbage	72.00	185	5521	1021459	0.276	0.127	9
Pathological waste**	62.10	355	5929	2104688	0.296	0.262	9,10
Plastic film	15.00	30	27356	820674	1.367	0.102	9
Rags	10.00	115	14652	1684945	0.732	0.210	9,10
Rubber	1.20	300	26018	7805430	1.300	0.971	9
Textiles	25.00	180	14011	2522016	0.700	0.314	9
Tires	1.02	240	31996	7679016	1.598	0.955	9
Vegetable food waste	78.29	355	4173	1481379	0.208	0.184	9

* all values are on as is basis

**dead animals

Table 46. Quality Analysis for Petroleum Fuels *

Name	% Moist.	Bulk Density (kg/m ³)	ΔH_c		Q ₁	Q ₂	Ref.
			kJ/kg	kJ/m ³			
Kerosene fuel	0	965	46388	44764420	2.317	5.566	9,11
Naptha, Alaska	0	965	45359	43771145	2.266	5.442	9,11
Naptha, aromatic	0	965	43041	41534372	2.150	5.164	9,11

* all values are on as is basis

Table 47. Quality Analysis for Papers and Paper Products *

Name	% Moist.	Bulk Density (kg/m ³)	ΔH_c		Q ₁	Q ₂	Ref.
			kJ/kg	kJ/m ³			
Cardboard	5.00	140	17326	2425682	0.866	0.302	9, 10
Corrugated boxes	5.20	112	16370	1833384	0.818	0.228	9, 21
Newsprint	5.97	112	18534	2075819	0.926	0.258	9, 21
Paper	3.00	140	17084	2391774	0.853	0.297	9, 12
Paper, brown	5.83	112	16867	1889160	0.843	0.235	9, 21
Paper, plastic coated	4.71	112	17060	1910731	0.852	0.238	9
Trade magazine	4.11	561	12213	6851269	0.610	0.852	9, 21
Waxed milk cartons	3.45	80	26331	2106440	1.315	0.262	9, 21

* all values are on as is basis

Table 48. Quality Analysis for Woods *

Name	% Moist.	True Density (kg/m ³)	ΔH_c		Q ₁	Q ₂	Ref.
			kJ/kg	kJ/m ³			
Ash	53.70	860	9103	7828580	0.455	0.973	11,22
Ash, white	0	550	20748	11411345	1.036	1.419	18,22
Bark, Douglas fir	6.50	256	20661	5289139	1.032	0.658	12,21
Beech I	0	560	19931	11161528	0.996	1.388	11,22
Beech II	0	560	20376	11410448	1.018	1.419	18,22
Beech III	0	560	20376	11410448	1.018	1.419	12,22
Birch	46.24	950	10709	10173835	0.535	1.265	11,22
Birch, white	0	510	20120	10261149	1.005	1.276	18,22
Elm	0	460	20492	9426366	1.024	1.172	18,22
Fir, Douglas I	0	470	21050	9893641	1.052	1.230	18,22
Fir, Douglas II	0	470	21050	9893641	1.052	1.230	12,22
Furniture wood **	6.00	50 **	17073	853650	0.853	0.106	9
Green logs **	50.00	320 **	4887	1563808	0.244	0.194	9
Maple I	44.44	970	10584	10267256	0.529	1.277	11,22
Maple II	44.44	970	11088	10755554	0.554	1.337	18,22
Maple III	44.44	970	11088	10755554	0.554	1.337	12,22
Pine, white	0	340	20701	7038476	1.034	0.875	18,22

Table 48. contd.

Name	% Moist.	True Density (kg/m ³)	ΔH_c kJ/kg	$\frac{\Delta H_c}{\text{kJ/m}^3}$	Q ₁	Q ₂	Ref.
Redwood I	0	420	21027	8831340	1.050	1.098	18,22
Redwood II	0	420	21027	8831340	1.050	1.098	12,22
Western Hemlock I	0	380	20050	7619038	1.002	0.947	18,22
Western Hemlock II	0	380	20050	7619038	1.002	0.947	12,22
Wood and bark **	20.00	256**	16016	4100198	0.800	0.510	9,21

* all values are on as is basis

** bulk densities used for these substances

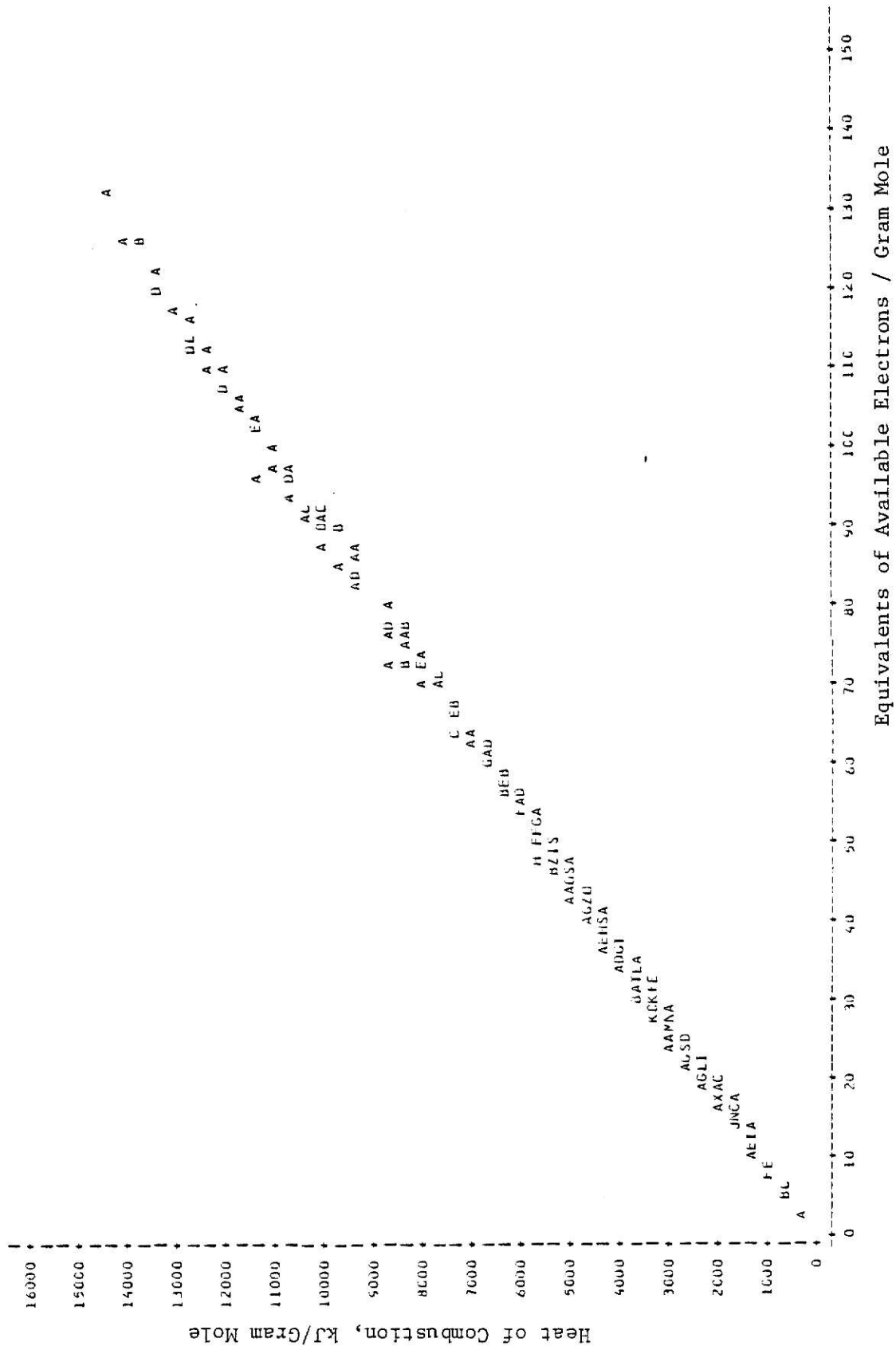


Figure 1. Linear variation of heat of combustion with number of equivalents of available electrons.
(for organic compounds)

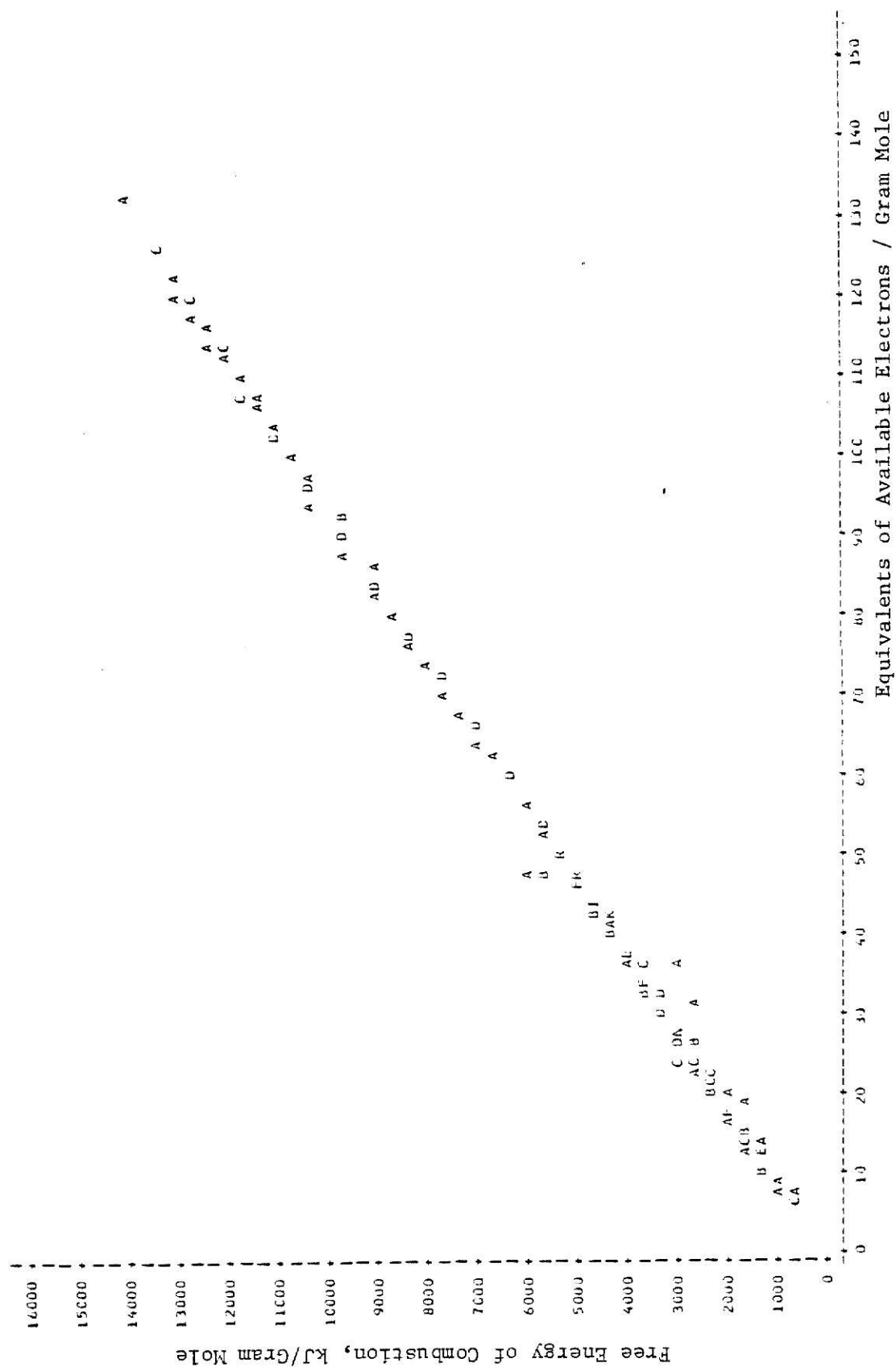


Figure 2. Linear variation of free energy of combustion with number of equivalents of available electrons. (for organic compounds)

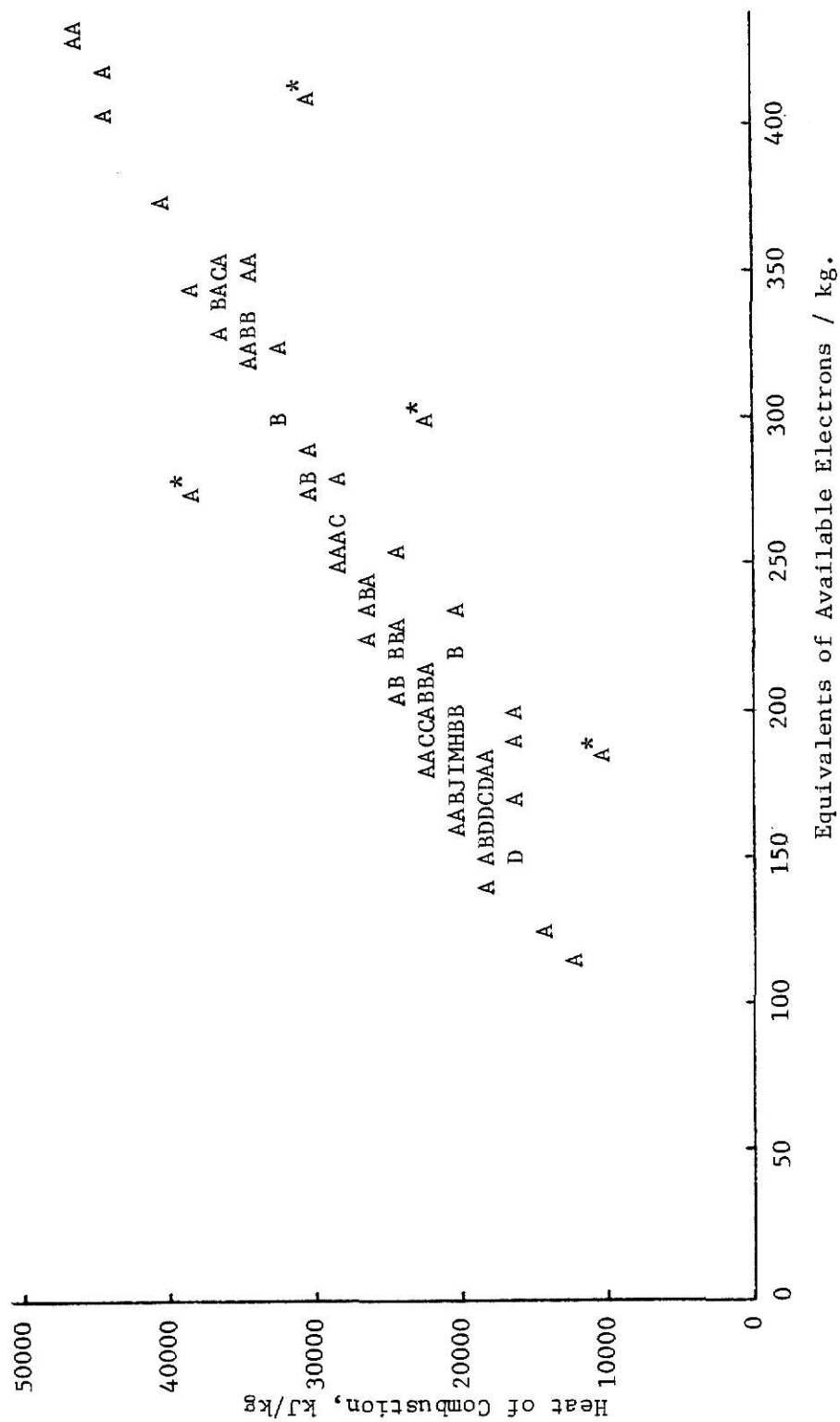


Figure 3. Linear variation of heat of combustion with number of equivalents of available electrons (for renewable energy resources). Asterisks (*) indicate deviations from regular behavior.

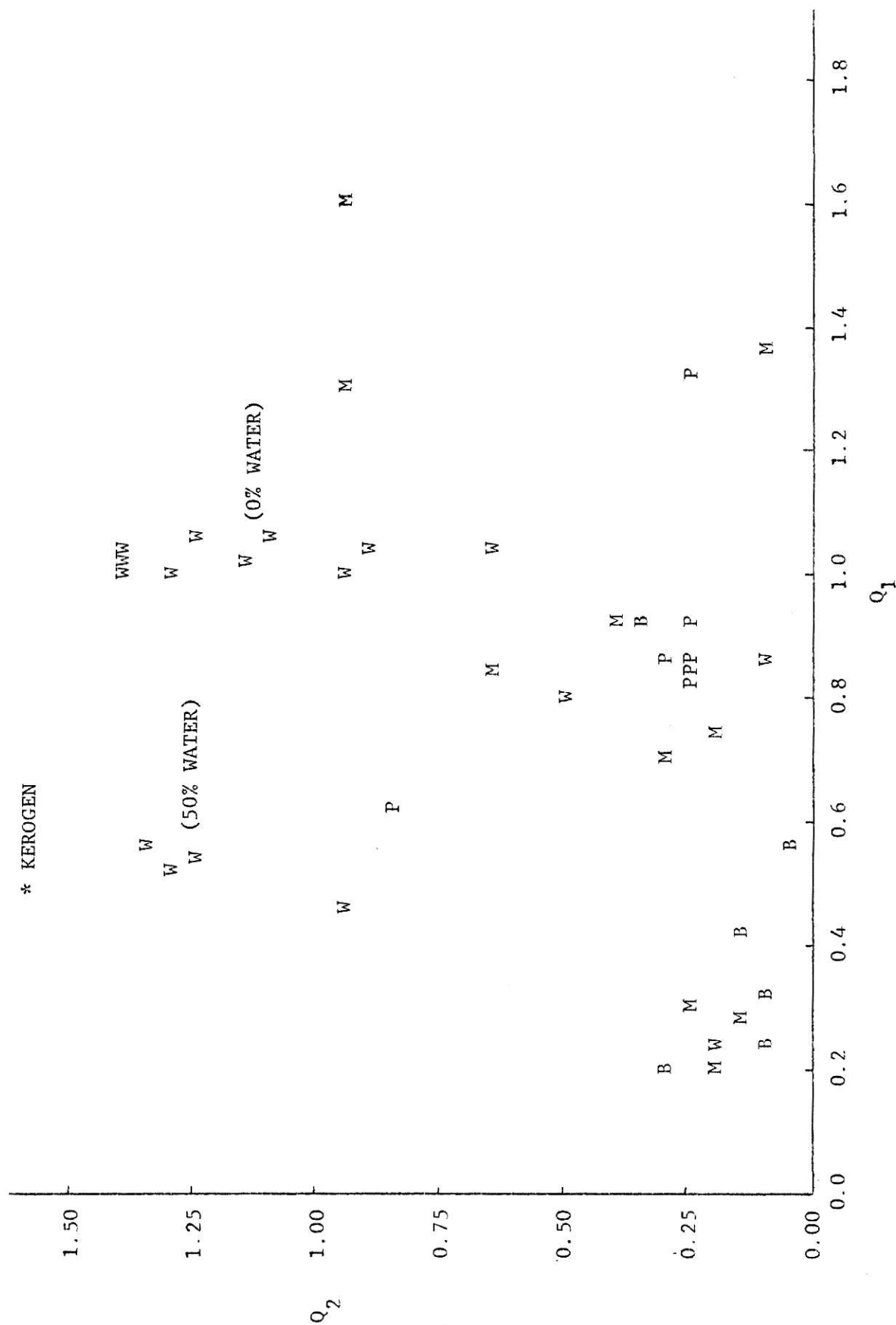


Figure 4. Quality distribution for renewable energy resources. W = woods, P = paper and paper products, B = grasses, leaves and brush, M = municipal/domestic waste (for details see Tables 44 - 48).

A STUDY OF REGULARITIES ASSOCIATED WITH
BIOCHEMICAL PROCESSES AND RENEWABLE ENERGY RESOURCES

by

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the
requirements for the degree

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1981

In biochemical engineering, the weight fraction carbon in microbial biomass, the number of equivalents of available electrons per g atom carbon in biomass, and the heat of reaction per electron transferred to oxygen are nearly constant. These regularities are used in material and energy balance calculations associated with microbial growth processes with considerable success. In this work they are used to identify and characterize renewable energy resources and analyze process efficiencies in living systems. Thornton's method which utilizes the weight fraction carbon on a dry basis and the reductance degree to predict the heat of combustion of renewable resources is presented. For most renewable resources Thornton's method gives a better estimate for the heat of combustion than Dulong's formula. Values of regularities are presented for carbohydrates, proteins, fats, organic compounds and renewable energy resources and use of the regularities in the area of data consistency is illustrated. The free energy of reaction per electron transferred to oxygen is also examined as a regularity. Results of prior work with regularities in living systems are reviewed. The importance of bulk density and moisture content in renewable energy resource characterization is discussed and illustrated.