Human Body Exergy Metabolism^{*}

C. E. K Mady^{**1}, S Oliveira Junior²

Polytechnic School of the University of São Paulo, Av. Prof. Mello Moraes, 2231 05508–900 São Paulo, Brazil, E-mail. ¹cekm@usp.br, ²soj@usp.br

Abstract

The exergy analysis of the human body is a tool that can provide indicators of health and life quality. To perform the exergy balance it is necessary to calculate the metabolism on an exergy basis, or metabolic exergy, although there is not yet consensus in its calculation procedure. Hence, the aim of this work is to provide a general method to evaluate this physical quantity for human body based on indirect calorimetry data. To calculate the metabolism on an exergy basis it is necessary to define the reference reactions and obtain their exergy variation. The reference reactions of the energy substrates are represented by the oxidation of the glucose, palmitic acid and a representative amino acid. Hence, from the exergy variation of these reactions and the consumption rate of the substrates, the metabolic exergy is determined. Results, for basal conditions and during physical activities, indicate that the difference between exergy and energy metabolisms is lower than 5%. Moreover, the body converts approximately 60% of the exergy of nutrients into available exergy to perform work.

Keywords: Human Body; exergy analysis; metabolic exergy.

1. Introduction

The application of the exergy analysis to the human body may be used to assess the quality of the energy conversion processes that take place in its several systems, organs and even cells. Several authors applied the analysis for the human body and some of the methods were revised by Mady et al., (2012). To perform the exergy analysis it is necessary to calculate the metabolic exergy of the human body, but there is not yet a consensus in its calculation.

Initially, the second law of thermodynamics was applied to living organisms as an attempt to confirm the principle of minimum entropy production or Prigogine & Wiame (1946) principle. In this principle it is stated that all living organisms tend to a minimum of entropy production. Therefore, Zotin & Zotina (1967), Balmer (1984), Aoki (1991), Silva & Annamalai (2008, 2009) and Mady et al. (2012) confirmed the principle of minimum entropy production for different types of species, ranging from fish to humans.

Batato et al. (1990) were one of the first authors that applied the exergy analysis to the human body. In their analysis the energy and exergy metabolism were calculated from indirect calorimetry results, where representative reactions of oxidation of three types of substance (carbohydrates, lipids and proteins) were selected. A comparison between metabolisms in both basis indicates that the difference is not higher than 5%.

Prek (2005, 2006), Prek and Butala (2010) and Simone et al. (2011) performed the exergy analysis for the human body to obtain relations between the destroyed exergy and thermal comfort and thermal sensation conditions. In their analyses the metabolic exergy was considered as a heat source, therefore the metabolism on energy and exergy basis have one order of magnitude of difference. Finally, Silva & Annamalai (2008, 2009) applied the concept of maximum available work to biochemical reactions based on the concept of metabolic efficiency. Lems (2009) performed the exergy analysis of the cellular metabolism where it was presented a very detailed methodology to calculate the exergy of the different processes involved in the cellular metabolism. The results obtained account for efficiencies up to 60% considering the conversion of carbon fuels into ATP (adenosine triphosphate) in living cells. However, the way in which the ATP is used was not considered.

Although there is a consensus in literature to calculate the metabolism on energy basis, there is not a consensus in its calculus on exergy basis. In this work it is proposed a method to calculate the metabolic exergy from indirect calorimetry results, based on Batato et al. (1990) and Diener (1997). Moreover, it will be held a discussion of the methods of literature to calculate this physical quantity to eventually establish a procedure and an equation to calculate the metabolism in both bases.

2. Model description

Figure 1 indicates a model with a schematic representation of the human body, where it is indicated the heat transfer rate and mass flow rates associated with radiation (Q_r) , convection (Q_c) , vaporization (H_e) , respiration $(H_{ex}-H_a)$, food intake, food wastes, water intake and urine. The term Q_M is the heat released to the body caused by the cellular metabolism. In Figure 1, the human body is divided in two control volumes, CV1 and CV2. The first one represents the thermal system and respiratory system and the second the cellular metabolism.

*This paper is an updated version of a paper published in the ECOS'12 proceedings. It is printed here with permission of the authors and organizers.

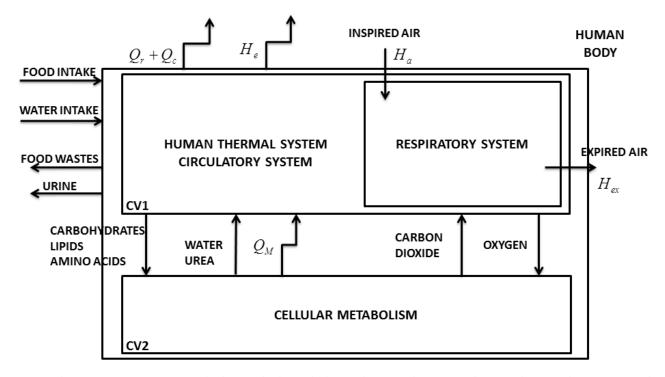


Figure 1. Schematic representation of the human body, with the intake of food, water and inspired air; and output of food, urine, expired air, vaporization trough skin and heat release due to radiation and convection.

According to Rahman (2007) in a period of one day the mass input (food, liquids and inspired gases) is equivalent to the mass output (food wastes, urine, expired gases and vaporization). In shorter periods of time this may not be verified. In this article, for the sake of simplicity, the variation of body mass due to food and water intake, wastes and accumulation are neglected.

The energy and exergy analyses are applied to the control volume shown in Figure 1, with given environment and reference conditions such as temperature $(T_0 = T_a)$, pressure $(P_0 = P_a)$ and relative humidity $(\phi_0 = \phi_a)$. Thus, Eq. (1) indicates a general equation of the exergy balance

$$\frac{d\mathbf{B}}{dt} = \sum B_{in} - \sum B_{out} + \sum_{k} Q_k \left(1 - \frac{T_0}{T_k} \right) - W - B_{dest}$$
(1)

where **B** is the exergy of the body.

The energy (*M*) and exergy (B_M) metabolisms for the whole body are part of the total internal energy (dU/dt) and exergy ($d\mathbf{B}/dt$) variation of the body over time

$$\frac{dU}{dt} = -M + \frac{dU}{dt}\Big|_{\Delta T}$$
(2)

$$\frac{d\mathbf{B}}{dt} = -B_M + \frac{d\mathbf{B}}{dt}\Big|_{\Delta T} = -B_M + \left(\frac{dU}{dt}\Big|_{\Delta T} - T_0 \frac{dS}{dt}\Big|_{\Delta T}\right)$$
(3)

where $dU/dt|_{\Delta T}$ and $d\mathbf{B}/dt|_{\Delta T}$ are the internal energy and the exergy variation of the body due to a variation in environmental conditions, respectively. In these equations it is assumed that the variation of the volume of the body is negligible. The energy and exergy variation of the body over time due to transient conditions are considered only in CV1.

The energy and exergy balances for CV1, and the exergy intake of this control volume are indicated in Eq. (4) to (6). In Eq. (4) the energy intake Q_M is the heat released to CV1 due to the metabolism. The terms Q_c , Q_r are the heat transfer rates to the environment associated with convection

and radiation, H_e and ΔH_{res} are the enthalpy flow rate related to vaporization and respiration. The exergy rate B_{QM} is calculated by Eq. (6). It is the exergy transferred to CV1 caused by the exergy metabolism, T_0 is the environment/reference temperature and T_b the body temperature. The terms B_c , B_r , B_e and $\Delta B_{res}(B_{ex}-B_a)$ are the exergy rates and flow rates associated with convection, radiation, vaporization and respiration, previously determined in Mady et al. (2012).

$$\left. \frac{dU}{dt} \right|_{\Delta T} = Q_M - \left(Q_c + Q_r + H_e + \Delta H_{res} \right) \tag{4}$$

$$B_{dest}^{CVI} = B_{Q_M} - \left(B_c + B_r + B_e + \Delta B_{res}\right) - \frac{d\mathbf{B}}{dt}\Big|_{\Delta T}$$
(5)

$$B_{Q_M} = Q_M \left(1 - \frac{T_0}{T_b} \right) \tag{6}$$

The cellular metabolism is a representation of the human cells energetic behavior. In this control volume (CV2) the reactions of oxidation of the energy substrates, also called metabolism, take place. The energy and exergy balance(s) for CV2 are

$$Q_M = H_{reac} - H_{prod} - W \tag{7}$$

$$B_{dest}^{CV2} = B_{reac} - B_{prod} - Q_M \left(1 - \frac{T_0}{T_b} \right) - W$$
(8)

where, H_{reac} is the enthalpy of the reactants (carbohydrates, lipids, amino acids and oxygen), H_{prod} is the enthalpy of the products (urea, liquid water and carbon dioxide), B_{reac} is the exergy content of the reactants, B_{prod} is the exergy content of the products and W is the performed work.

The metabolisms on energy and exergy basis are defined by

$$M = H_{reac} - H_{prod} \tag{9}$$

$$B_M = B_{reac} - B_{prod} \tag{10}$$

Int. Centre for Applied Thermodynamics (ICAT)

Finally, the energy and exergy analysis for the whole body are

$$\left. \frac{dU}{dt} \right|_{\Delta T} = \left(M - W \right) - \left(Q_c + Q_r + H_e + \Delta H_{res} \right) \tag{11}$$

$$B_{dest}^{body} = \left(B_M - W - \frac{d\mathbf{B}}{dt} \Big|_{\Delta T} \right) - \left(B_c + B_r + B_e + \Delta B_{res} \right) \quad (12)$$

Note that Eq. (5) takes into account only the thermal part of metabolism. Eq. (12) is similar to the analysis proposed by Batato et al. (1990). The difference between these two approaches is that all the exergy released to the body in CV2 is neglected if Eq. (6) is used as the metabolic exergy. Although, from the energy analysis, Eq. (4) is equal to Eq. (11), because $M-W=Q_M$.

2.1 Energy metabolism

As indicated by Diener (1997), the metabolism is defined as a set of chemical reactions that release energy from the oxidation of energy substrates and allow the vital processes in human body. Figure 1 indicates the cellular metabolism with the input of glucose, lipids, amino acids and oxygen; and the output of carbon dioxide, urea and liquid water. Moreover, there is a heat rate released to the body caused by the metabolism (Q_M).

Diener (1997) described a procedure to calculate the metabolism based on the indirect calorimetry technique. In order to calculate metabolic energy and exergy, it is assumed that the oxidation of carbohydrates, lipids and protein are represented, respectively, by the reactions of oxidation of glucose ($C_6H_{12}O_6$), palmitic acid ($C_{16}H_{32}O_2$) and a representative amino acid with average thermodynamic properties ($C_{4.98}H_{9.8}N_{1.4}O_{2.5}$).

The oxidations of these three organic compounds are indicated in Eqs. (13) to (15). Note that the oxidation of glucose and palmitic acid results in the formation of carbon dioxide and liquid water, while the oxidation of amino acid results in the formation of carbon dioxide, liquid water and urea. In humans and most of mammals, the excretion of nitrogen content in the amino acids is mostly through urea.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$
 (13)

$$C_{16}H_{32}O_2 + 23O_2 \rightarrow 16CO_2 + 16H_2O$$
(14)

$$C_{4.98}H_{9.8}N_{1.4}O_{2.5} + 5.13O_2 \rightarrow 4.28CO_2 + 3.5H_2O + 0.7CH_4N_2O$$
(15)

It is important to define the respiratory quotient (RQ) that is the ratio of the carbon dioxide production and oxygen consumption (on molar basis). This value is 1 for glucose, 0.7 for palmitic acid and 0.83 for aminoacids. In basal conditions RQ is approximately 0.83, during heavy aerobic activities it becomes close to 1, as indicated in ASHARAE (2009). This quotient gives a clue whether the oxidation which prevails is of only one type of substance (physical activities) or of a combination (basal conditions).

From the stoichiometry of the reactions, it is possible to obtain the consumption of carbohydrates, lipids and proteins in unity of mass, as indicated by Eq. (16) to (18), based on Diener (1997). In this equation, oxygen consumption (m_{O_2}) and carbon dioxide production (m_{CO_2}) are usually measured with the aid of a respirometer (indirect calorimetry). The nitrogen excreted from the body

 (m_N) is measured from the urine analysis. In the literature, there is a convention adopted that each gram of nitrogen excreted in the urine represents the oxidation of 6.25g of amino acids as discussed in Batato et al. (1990) and Diener (1997).

$$m_{carb} = -2.14m_{O_2} + 2.24m_{CO_2} - 3.39m_N \tag{16}$$

$$m_{lip} = 1.14m_{O_2} - 0.83m_{CO_2} - 1.50m_N \tag{17}$$

$$m_{ami} = 6.25m_N \tag{18}$$

The energy metabolism can be calculated as indicated in Eq. (19), where Δh is the enthalpy variation of the reactions indicated in Eqs. (13) to (15). Note that this procedure is well established on literature and used to calculate the metabolism from indirect calorimetry results.

$$M = -\left(m_{carb}\Delta h_{carb} + m_{lip}\Delta h_{lip} + m_{ami}\Delta h_{ami}\right)$$
(19)

It is important to mention that in literature exists a discussion that in basal conditions the oxidation of proteins may be neglected, because it represents only 2% of the total metabolism if the person is healthy.

2.2 Exergy metabolism

To calculate the metabolic exergy it is necessary to define reference reactions that are indicated in Eqs. (13) to (15). The exergy variation of the reactions of oxidation (ΔB) can be calculated as indicated in Eq. (20), where Δb is the specific exergy variation of each reaction. The consumption rate of the energy substrates is determined from Eqs. (16) to (18).

$$\Delta B = m_{carb} \Delta b_{carb} + m_{lip} \Delta b_{lip} + m_{ami} \Delta b_{ami}$$
(20)

The definition of the metabolism on exergy basis is not as simple as on energy basis. Some authors adopted the metabolic exergy as B_{QM} , similarly to Eq. (5). Herein the metabolic exergy will be considered as the exergy variation of the reactions of the oxidation.

2.3 ATP hydrolysis

According to Nelson & Cox (2008) the degradation of carbohydrates, lipids and amino acids in human cells, occur gradually with the contributions of several enzymes to reduce the activation energy of the reactions. Thus, the energy is gradually captured with certain efficiency adding an inorganic phosphate group (P_i) to adenosine diphosphate (ADP) to form adenosine triphosphate (ATP) according to Eq. (21). The Gibbs free energy change in biochemical standard conditions (Δg^{0}) is 30.5kJ/mol. As indicated by Lems (2009) the reversal reaction plays the key role in many cell processes by acting as an intermediate carrier of useful energy. So, to perform any kind of work, the human body obtains energy from the reversal reaction known as ATP hydrolysis.

$$ADP + P_i \leftrightarrow ATP + H_2O$$
 (21)

Lems (2009), Alberty & Goldberg (1992), Alberty (1998) and Nelson & Cox (2008) affirm that the actual condition of the human body is different from biochemical standard conditions. These authors propound methods to take into account effects of reactants and products concentration, acid and base dissociation, free magnesium ion interaction, ionic interactions, effects of electrical potential, and so on. Based on these authors' results, the

actual free energy change of ATP formation (Δg_{ATP}) in Eq. (21) is 56kJ/mol.

Silva and Annamalai (2008, 2009) used the concept of metabolic efficiency (η_M) to calculate the maximum energy that is available on to perform work (Eq. 22). Where, ΔG_{oxi} is the Gibbs free energy of the complete oxidation of the nutrient.

$$\eta_M = \left| \frac{\Delta G_{ATP}}{\Delta G_{oxi}} \right| \tag{22}$$

After the complete oxidation of the nutrient in the cells certain quantity of ATP is formed. One mole of glucose forms 32 moles of ATP, one mole of palmitic acid forms 106 moles of ATP and 1 mol of amino acid forms 8 moles of ATP (this last result obtained by Silva and Annamalai (2008, 2009)). Hence, the maximum available power to the human body performs any kind of physical activities, can be calculated from Eq. (23). Where the rate in which ATP is hydrolyzed (n_{ATP}) is obtained from Eq. (24).

$$W_{MAX} = -\Delta G_{ATP} = \sum_{i=1}^{3} (\eta_M \, \Delta G_{oxi})_i \tag{23}$$

$$n_{ATP} = 32 \frac{m_{carb}}{M_{carb}} + 106 \frac{m_{lip}}{M_{lip}} + 8 \frac{m_{ami}}{M_{ami}}$$
(24)

3. Experimental data and thermodynamic properties **3.1** Thermodynamic properties

To calculate the metabolism on energy and exergy basis, it is necessary to obtain thermodynamic properties of the energy substrates such as enthalpy variation (Δh) and Gibbs free energy variation (Δg) of the reactions of oxidation. The references where these data were obtained are Diener (1997), Hayne (2008) and Cortassa, Aon, Iglesias & Lloyd (2002). Table 1 indicates the values of these thermodynamic properties for the complete oxidation of glucose and palmitic acid, and partial oxidation to the formation of liquid water, carbon dioxide and urea for the amino acids. The Δh of the reaction of oxidation of urea (CH₄N₂O) is obtained from Doran (1995) (10527 kJ/kg) and the chemical exergy is obtained from Szargut, Morris & Steward (1988) (11483 kJ/kg).

Cortassa et al. (2002) provides the value of enthalpy variation and Gibbs free energy variation of the complete oxidation for different amino acids. Table 2 indicates the value of these thermodynamic properties for several amino acids and from these, the calculated chemical exergy.

Nelson & Cox (2008) provide the average occurrence of each amino acid in nature, indicated in Table 2 representing approximately 96% of the common amino acids found in proteins (exception of methionine and cysteine). These percentages are used to calculate the mean molecular formula ($C_{4.98}H_{9.8}N_{1.4}O_{2.5}$) and mean thermodynamic properties.

3.2 Experimental data 3.2.1. Basal conditions

To calculate the metabolism on energy and exergy basis, for basal conditions the O_2 consumption, the CO_2 and H_2O production are considered, respectively: 1.79×10^{-4} , 1.46×10^{-4} and 5.47×10^{-4} mol/s. The RQ is 0.82 (close to basal conditions defined in ASHRAE (2009)). These data were obtained from Hardy & Du Bois (1938), for basal conditions and were also used by Aoki (1991). Furthermore, it is possible to assume that in one day there is an excretion of 12 g of nitrogen in the urine Diener (1997) due to the oxidation of amino acids.

3.2.2 Physical activities

The experimental results for subjects under physical activities were obtained from Sports medicine group and FIFA Medical Center of Excellence of institute of Orthopedics and Traumatology of the University of São Paulo Medical School. During the experimental procedure, the individuals are submitted to increasing levels of velocities, where it was measured the respiratory gas exchange (oxygen consumption and carbon dioxide production) and the tympanic temperature (representative of the body temperature). Results of treadmill velocities, oxygen consumption rate and carbon dioxide production rate are indicated in Figure 2, for one runner. After the connection of the subject with the measurement system, 5 minutes of data were collected for control, with the subject standing over the treadmill. Then the subject ran for 3 minutes to warm-up with 30% of his long distance training speed. After that the speed was set to 70% of the training speed. The speed was incremented by 1km/h every 4 minutes until the subject becomes exhausted. During the experiment, the treadmill was set to 1% of inclination. The experimental procedure was approved by the Ethics Committee for Analysis of Research Projects (CAPPesq) of the Faculty of Medicine of USP.

4. Results and Discussion

4.1 Thermal properties and metabolism equation

In the present analysis it is important to detach that, carbohydrates and lipids are represented by one substance (glucose and palmitic acid, respectively), but amino acids are represented by one theoretical amino acid with mean thermodynamic properties and composition (based on the average occurrence in nature). Sorguven & Özilgen (2010) obtained the chemical exergy for three types of fatty acids with 18, 20 and 22 carbons in its chain; the difference of the specific chemical exergy (on mass basis) was not larger than 1%. Table 2 indicates that the difference of the chemical exergy of the amino acids may achieve values as high as 50%. Each amino acid has a different type of chain, with different ramifications.

Table 1. Enthalpy and Gibbs free energy variation of the complete oxidation of glucose, palmitic acid and a representative amino acid

	Δh (kJ/kg)				Δg (kJ/kg)	
	Glucose	Palmitic Ac.	Amino Ac.	Glucose	Palmitic Ac.	Amino Ac.
Diener (1997) Hayne (2008) Cortassa et al. (2002)	-15648 -15600 -15594	-39581 -39200 -39020	-18075 -19000 -	_ -15946 -15956	-38212 -38281	- - -

Table 2. Thermodynamic properties of the complete oxidation of each amino acid and the average occurrence of each amino acid in nature. Obtained in Cortassa et al. (2002) and Nelson & Cox (2008)

Substance	Molecule	% Nature	$\Delta h \left(kJ/kg ight)$	$\Delta g \ (kJ/kg)$	$b_{ch} (kJ/kg)$
Glycine	$C_2H_5NO_2$	7.2	-12987	-13480	14150
Alanine	$C_3H_7NO_2$	7.8	-19180	-18449	18991
Serine	$C_3H_7NO_3$	6.8	-13857	-14305	14783
Aspartic Acid	$C_4H_7NO_4$	5.3	-12090	-12677	13189
Asparagine	$C_4H_8N_2O_3$	4.3	-14667	-15144	15643
Threonine	$C_4H_9NO_3$	5.9	-17681	-17899	18446
Proline	$C_5H_9NO_2$	5.2	-23783	-24205^{***}	24856**
Glutamic Acid	$C_5H_9NO_4$	6.3	-15306	-15748	16312
Glutamine	$C_5H_{10}N_2O_3$	4.2	-17603	-18000	18553
Valine	$C_5H_{11}NO_2$	6.6	-24957	-24957	25623
Histidine	$C_6H_9N_3O_2$	2.3	-22103	-22039***	22629^{**}
Leucine	$C_6H_{13}NO_2$	9.1	-27389	-27214	27921
Isoleucine	$C_6H_{13}NO_2$	5.3	-27389	-27206	27914
Lysine	$C_6H_{14}N_2O_2$	5.9	-25233	-25951***	26541**
Arginine	$C_6H_{14}N_4O_2$	5.1	-21517	-21759	22294
Phenylalanine	$C_9H_{11}NO_2$	3.9	-28200	-28164	29021
Tyrosine	$C_9H_{11}NO_3$	3.2	-24514	-24768	25560
Tryptophan	$C_{11}H_{12}N_2O_2$	1.4	-27608	-27691	28540
Average Value	$C_{4.98}H_{9.8}N_{1.4}O_{2.5}$	95.8	-20965	-21164	21784

*The chemical exergy of these amino acids were calculated for this article ** Chemical exergy calculated using group contribution method, from Szargut et al. (1988) *** Calculated from chemical exergy

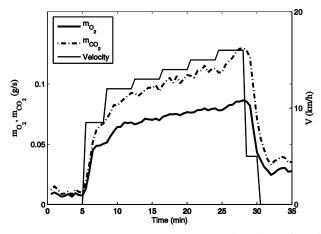


Figure 2. Oxygen consumption rate and carbon dioxide production rate as a function of time for different exercise levels (velocity at left axis) for one subject.

Table 3 indicates the Δh , Δg and Δb_{ch} of the reactions of partial oxidation (carbon dioxide, liquid water and urea) of several amino acids. The mean values are weighted by the occurrence in nature of each amino acid (Table 2). Furthermore, these results indicate a value of $\Delta b_{ch}/\Delta h$ of 1.04 and $\Delta g/\Delta h$ of 0.99. Note that Δb_{ch} is a combination of chemical exergy of the amino acid and urea.

In Table 1 the only value that Hayne (2008) does not provide is the Gibbs free energy of the oxidation of amino acids. Applying the result of $\Delta b_{ch'}\Delta h$ and $\Delta g/\Delta h$, it is possible to obtain that Δb_{ch} of the oxidation of amino acids is 18317kJ/kg and Δg of -18694kJ/kg.

In Table 4, it is indicated the values of Δb of the reactions of oxidation as they occur in humans (glucose and palmitic acid the oxidation is complete, amino acids the oxidation is partial). From the values of Δh and Δb it is

possible to formulate an equation of the metabolism on energy basis (which differ from Diener (1997) because of the oxygen consumption and carbon dioxide production are per unity of mass) and on exergy basis.

Table 3. Enthalpy, Gibbs free energy and exergy variation			
of the reactions of partial oxidation (liquid water, carbon			
dioxide and urea) of the amino acids.			

Substance	Molecule	Δh (kJ/kg)	Δg (kJ/kg)	Δb_{ch} (kJ/kg)
Glycine	$C_2H_5NO_2$	-8776	-8996	9556
Alanine	$C_3H_7NO_2$	-15631	-14671	15121
Serine	$C_3H_7NO_3$	-10850	-11102	11502
Aspartic Acid	$C_4H_7NO_4$	-9716	-10148	10599
Asparagine	$C_4H_8N_2O_3$	-9882	-10049	10424
Threonine	$C_4H_9NO_3$	-15027	-15073	15551
Proline	$C_5H_9NO_2$	-21037	-21280	22110
Glutamic Acid	$C_5H_9NO_4$	-13158	-13461	13969
Glutamine	$C_5 H_{10} N_2 O_3$	-13277	-13393	13834
Valine	$C_5H_{11}NO_2$	-22258	-22083	22678
Histidine	$C_6H_9N_3O_2$	-15991	-15530	16517
Leucine	$C_6H_{13}NO_2$	-24979	-24647	25291
Isoleucine	$C_6H_{13}NO_2$	-24979	-24639	25284
Lysine	$C_6H_{14}N_2O_2$	-20907	-21344	24378
Arginine	$C_6H_{14}N_4O_2$	-14257	-14028	14375
Phenylalanine	$C_9H_{11}NO_2$	-26286	-26126	26933
Tyrosine	$C_9H_{11}NO_3$	-22769	-22910	23657
Tryptophan	$C_{11}H_{12}N_2O_2$	-24512	-24394	25162
Average Value	$C_{4.98}H_{9.8}N_{1.4}O_{2.5}$	-17597	-17578	18317

Table 4. Exergy variation of the reactions of oxidation of glucose, palmitic acid and proteins.

		Δb (kJ/kg)	
Reference	Glucose	Palmitic Ac.	Amino Ac.
Hayne (2008)	-16506	-39141	-18964
Cortassa (2002)	-16516	-39223	-17578

Finally, the metabolisms on energy and exergy basis using the data from Hayne (2008) and from Cortassa et al. (2002) are

 $M_{Hayne} = 11371m_{O_2} + 2366m_{CO_2} + 6891m_N \tag{18}$

 $B_{M,Hayne} = 9501m_{O_2} + 3963m_{CO_2} + 6979m_N \tag{19}$

$$M_{Cortassa} = 11179m_{O_2} + 2502m_{CO_2} - 1580m_N \tag{20}$$

$$B_{M,Cortassa} = 9558m_{O_2} + 3928m_{CO_2} - 1823m_N \tag{21}$$

4.2 Energy and exergy metabolism 4.2.1 Basal conditions

Results in Table 5 indicate the metabolism on energy and exergy basis, considering the oxidation of proteins (M_p and B_{Mp}) and disregarding the oxidation of proteins (M_p and B_{Mp}) for the energy measurements obtained by Hardy & Du Bois (1938). For this condition, the authors obtained that the metabolism is 79.8W. In all cases the difference between this value and the ones calculated herein was not larger than 2%. Furthermore, the difference of the metabolism using the two different references of thermodynamic properties did not differ more than 2%. The ratio of metabolism on energy and exergy basis (considering and disregarding the oxidation of proteins) did not exceed 1.02. Hence, as in Batato et al. (1990), the approximation $B_M \approx M$ for basal conditions is valid.

Table 5. Metabolism in energy and exergy basis with the oxidation of amino acids (M and B_M) and without the oxidation of amino acids (M_p and B_{Mp}).

	Hayne (2008) (W)	Cortassa et al. (2002) (W)
М	81.3	79.9
M_p	80.3	80.1
B_M	80.8	79.7
B_{Mp}	79.9	80.0

4.2.2 Physical activities

For the experimental results of Figure 2 the metabolism in energy and exergy basis was calculated, using the values of thermodynamic properties of Cortassa et al. (2002) indicated in Eqs. (20) and (21), due to the small difference between results in Table 5.

Figure 3 indicates M, B_M and B_{QM} for the experimental data of Figure 2. The difference of B_M and B_{QM} is one order of magnitude, indicating that when the metabolism is calculated as B_{QM} (taking into account only the thermal exergy), more than 95% of the exergy content of metabolism is disregarded. Therefore, most of the available exergy to perform work would be disregarded.

In Figure 4 it is demonstrated the ratio of the metabolism on energy and exergy basis as a function of time. In the first five minutes, the ratio B_M/M ranged from 1.04 to 1.01 (time when the subject controlled the

respiration and was adapting to the respirometer). Between 5 and 30 minutes, the ratio remained between the same limits. Finally, at the end of the test the ratio increased to values as close as 1.05. This result indicates that the approximation $B_M \approx M$ may be also valid during physical activities.

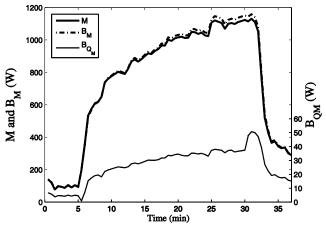


Figure 3. Result of M, B_M and B_{QM} as a function of time during the treadmill test. The first two properties are indicated in the left axis, the last on in the right side axis.

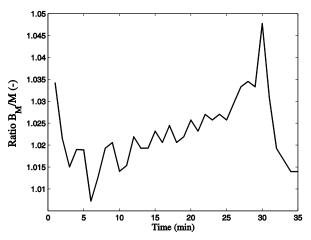


Figure 4. Ratio of the metabolism in energy and exergy basis during the treadmill test.

Figure 5 indicates the ratio of the metabolism considering the oxidation of proteins (M) and disregarding the oxidation of this type of substance (M_p). The ratio was very close to 1 (5–30 min), indicating that during the exercises the body uses more carbohydrates and lipids as energy source. In the beginning of the test the ratio was approximately 99.9%. Nevertheless, this figure indicates that for a healthy person under physical activities the oxidation of proteins can be disregarded.

Based on the results of Tables 1 to 4 and the number of ATP that are formed for each nutrient, it is possible to calculate the metabolic efficiency. This value is 62% for glucose, 61% for palmitic acid and 20% for amino acids.

Figure 6 shows a comparison of the metabolism on exergy basis, maximum available work and exergy released to the body associated with metabolism. These results indicate that the body maintains approximately 60% of the exergy content of the nutrients in the chemical bound of the phosphate group in ATP and these exergy is available to perform work. If the metabolism was considered as a heat source this efficiency would be only 5%.

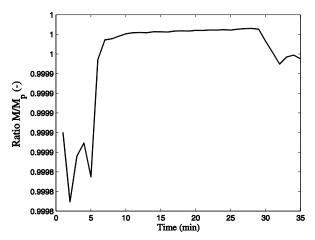


Figure 5. Ratio of the metabolism considering and disregarding the oxidation of proteins during the treadmill test.

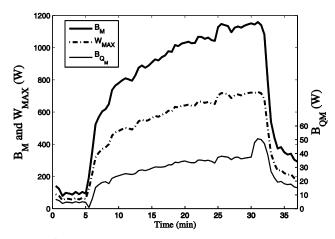


Figure 6 Result of B_M , W_{MAX} and B_{QM} as a function of time during the treadmill test. The first two properties are indicated in the left axis, the last on in the right side axis.

Table 6 indicates the metabolism on exergy basis, the maximum available work, the exergy rate associated with metabolism (B_{QM}) and the ratio B_M/M . It is possible to note that the thermal portion of metabolism is approximately 5% of exergy metabolism and the maximum available work from ATP hydrolysis corresponds to 60% of exergy metabolism. Hence, for the 11 runners more than 95% of the exergy released from the oxidation of nutrients would be neglected if B_{QM} be considered as the exergy source of the body, whereas in fact the body uses 60% of the exergy and

exergy basis ranged from 1.01 to 1.03, indicating that the approximation $B_M \approx M$ is valid for physical activities.

5. Conclusions

In this work analyses of the human metabolism on energy and exergy basis were performed and it was proposed a method and an equation to calculate the metabolic exergy. From the range of tests analyzed it was possible to conclude that:

• For basal conditions results the metabolism on energy and exergy basis did not differ more than 2%, for the different thermodynamic properties. For basal conditions, results obtained from Batato et al. (1990) were verified;

• For the treadmill running tests, the metabolism on energy and exergy basis are very close. The ratio is equal to 1.05 in only one point; in the rest of the test the ratio was lower.

• Finally, the contribution of proteins did not exceed 3% of the total metabolism (energy and exergy basis) during physical activities and in basal conditions. Hence, the oxidation of proteins may be disregarded in a healthy person in basal conditions and under physical activities.

• The exergy released in ATP hydrolysis is the maximum available work that the body can obtain from the oxidation of energy substrates. Hence, the body keeps approximately 60% of the exergy content of nutrients in the chemical bounds of ATP.

Acknowledgments:

The authors acknowledge FAPESP (São Paulo Research Foundation) for his PhD grant 09/17578–0 and CNPq (National Research Council) for grant 306033/2017-7. The authors also acknowledge the Sports medicine group and FIFA Medical Center of Institute of Orthopedics and Traumatology of the University of São Paulo Medical School.

Nomenclature:

ADP	adenosine diphosphate
ATP	adenosine triphosphate
b	specific exergy, J/kg
B	body exergy, J
В	exergy rate and flow rate, W
g	specific free energy, J/kg
G	Gibbs free energy rate, W
h	specific enthalpy, J/kg
H	enthalpy flow rate, W
M	metabolism, W
m	mass flow rate, kg/s

Table 6. Integration for 11 runners of metabolism in energy basis, metabolism in exergy basis, maximum available work, exergy rate associated with metabolism and ratio of metabolism on energy and exergy basis.

Subject	Time	M (kJ/kg)	B_M (kJ/kg)	$W_{MAX}(kJ/kg)$	B_{QM} (kJ/kg)	B_M/M
1	24.0	16851	17307	10651	439	1.03
2	44.0	17617	17897	10911	457	1.02
3	27.0	15729	16150	9916	383	1.03
4	48.0	17026	17308	10585	437	1.02
5	33.0	27088	27712	17091	843	1.02
6	21.0	30434	30951	18990	880	1.02
7	33.0	25312	26019	16086	617	1.03
8	23.0	29907	30351	18586	868	1.01
9	51.0	22699	23037	14100	796	1.01
10	34.0	20826	21343	13165	702	1.02
11	25.0	42545	43504	26825	1174	1.02

P_i	phosphate group
\hat{Q}	heat transfer rate, W
RQ	respiratory quotient, -
Т	temperature, K
t	time, min
V	velocity, m/s
W	work, W
Greek symbols	
η	exergy efficiency, %
$\dot{\phi}$	relative humidity, %
Subscripts and	l superscripts
0	reference
ami	amino acids
ATP	adenosine triphosphate
b	body
С	convective
carb	carbohydrates
dest	destruction
е	evaporative
ex	expired
in	inspired
lip	lipids
M	metabolic
MAX	maximum
oxi	complete oxidation
p	disregarding proteins
r	radiative
res	respiration

References:

- Alberty, R. A. (1998). Calculation of standard transformed gibbs energies and standard transformed enthalpies of biochemical reactants. *Archives of biochemistry and biophysics*, 353, 16–130.
- Alberty, R. A., Goldeberg, R. N. (1992). Standard thermodynamic formation properties for the adenosine 5'-triphosphate series. Biochemistry. ACS Publications, 31, 10610–10615.
- Handbook ASHRAE (2009). Fundamentals. American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., Atlanta GA.
- Aoki, I. (1991). Entropy principle for human development, growth and aging. *Journal of Theoretical Biology*, 150, 215-223.
- Balmer, R. T. (1984). Entropy and aging in biological systems. *Chemical Engineering Communications*, 17, 171-181.
- Batato, M., Borel, L., Deriaz, O., Jequier, E. (1990). Analyse exergétique théorique et expérimentale du corps humain. *Entropie*, 26, 120-130.
- Coratassa, S., Aon, M. A., Iglesias, A. A., Lloyd, D. (2002). *An introduction to metabolic and cellular engineering*. London: World Scientific Pub Co Inc.
- Diener, J. R. C. (1997). Indirect calorimetry (in Portuguese). AMB Revista da Associação Médica Brasileira, 43, 245–253.
- Doran, M. D. (1995). *Bioprocess Engineering Principles*. Cambridge, UK: Cambridge University Press.

- Hardy, J. D., Du Bois, E. F. (1938). The technique of measuring radiation and convection. *Journal of Nutrition*, 15, 461-475.
- Hayne, D. T. (2008). *Biological Thermodynamics*. Cambridge, UK: Cambridge University Press.
- Lems, S. (2009). Thermodynamic explorations into sustainable energy conversion – Learning from living systems. (Doctoral dissertation), Technische Universiteit, Delft, Netherlands.
- Mady, C. E. K., Ferreira, M. S., Yanagihara, J. I., Saldiva, P. H. N., Oliveira Jr, S. (2012). Modeling the exergy behavior of human body. *Energy*, 45, 546–553.
- Nelson, D. L., Cox, M. M. (2008). *Lehninger Principles of Biochemistry*, (5th ed.). New York, NY: Wh Freeman and company.
- Prek, M. (2005). Thermodynamic analysis of human heat and mass transfer and their impact on thermal comfort. *Int. J. Heat and Mass Transfer, 48*(3–4), 731–739.
- Prek, M. (2006). Thermodynamical analysis of human thermal comfort. *Energy*, *31*, 732–743.
- Prek, M., Butala, V. (2010). Principles of exergy analysis of human heat and mass exchange with the indoor environment. *Int. J. Heat and Mass Transfer*, 48, 731– 739.
- Prigogine, I., Wiame, J. (1946). Biologie et Thermodynamique des phenomenes irreversibles. *Experimentia*, 2, 451–453.
- Rahman, M. A. (2007). A novel method for estimating entropy generation rate in human body. *Thermal Science*, 11, 75–92.
- Silva, C., Annamalai, K. (2008). Entropy generation and human aging: lifespan entropy and effect of Physical Activity Level. *Entropy*, *10*, 100–123.
- Silva, C., Annamalai, K. (2009). Entropy generation and human aging: lifespan entropy and effect of diet composition and caloric restriction diets. *Journal of Thermodynamics*, 2009, 1–10,
- Simone, A., Kolarik, J., Iwamatsu, T., Asada, H., Dovjak, M., Schellen, L., Shukuya, M., Olesen, B. W. (2011). A relation between calculated human body exergy consumption rate and subjectively assessed thermal sensation. *Energy and Buildings*, 43, 1–9.
- Sorguven, E., Özilgen, M. (2010). Thermodynamic assessment of algal biodiesel utilization. *Renewable Energy*, *35*, 1956–1966.
- Szargut, J., Morris, D. R., Steward, F. R. (1988). Exergy analysis of thermal, chemical and metallurgical processes. New York: Hemisphere Publishing Corporation.
- Zotin, A. I., Zotina, R. S. (1967). Thermodynamics aspects of developmental biology. *Journal of Theoretical Biology*, 17, 57–75.