Energy 35 (2010) 77–84

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Chemical exergy assessment of organic matter in a water flow

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ARTICLE INFO

Article history:
Received 29 December 2008
Received in revised form
27 August 2009
Accepted 27 August 2009
Available online 7 October 2009

Keywords:
Physical Hydronomics
Exergy assessment
Exergy of organic matter

ABSTRACT

In recent years, exergy analysis has been successfully applied to natural resources assessment. The consumption of any natural resource is unavoidably joined to dispersion and degradation. Therefore, exergy analysis can be applied to study the depletion of natural resources and, particularly, to water resources. Different studies range from global fresh water resources evaluation to specific water bodies' detailed analysis.

Physical Hydronomics is a new approach based on the specific application of Thermodynamics to physically characterize the state of a river and to help in the Governance of water bodies. The core task in the methodology is the construction of the exergy profiles of the river and it requires the calculation of the different specific exergy components in the water body: potential, thermal, mechanical, kinetic and chemical exergy.

This paper is focused on the exergy assessment for the organic chemical matter present in water bodies. Different parameters such as chemical oxygen demand (COD), biological oxygen demand (BOD) or total organic carbon (TOC), among others, can be used as raw data for the calculation.

Starting from available sampling data, previous approaches are analyzed, completed and compared. The well-known and most simple average molecule representing the organic matter in the river (CH_2O) is proposed. Results show that, considering surface waters, TOC parameter is the most convenient one, but also that the BOD and COD can be reasonably useful.

1. Introduction

Exergy function was initially developed in the fields of engineering and it can be considered as the most useful function to solve cost-optimization problems and to analyze energy conversion systems (through the evaluation of the efficiency of energy systems and the detection of causes of thermodynamic imperfection in thermal or chemical processes). In addition, it attracts escalating interests in environmental resource accounting, environmental impact assessment, ecological cost evaluation, and ecological modelling studies. It has also been successfully applied to natural resources assessment [1–9]. The discipline that applies the Second Law of Thermodynamics in the evaluation of natural fluxes and resources on Earth is called Exergo ecology [10]. Since the consumption of any natural resource is unavoidably joined to dispersion and therefore to exergy destruction, exergy analysis could perfectly be applied to study the degradation of any natural resource and, in particular, of water bodies. In recent years it has been applied for global fresh water resources assessment [11,12] and locally to water bodies' analysis [13]. In particular, several research works [14,15] among others have tried to devise unified objective measures for environmental impact assessment based upon exergy, via either estimating the chemical exergy associated with a waste stream or the total exergy consumption associated with its corresponding wastewater treatments. Hellström [16,17] estimated and compared the exergy consumption of physical resources in some wastewater treatment plants and sewage systems.

On the other hand, Chen and Ji [9] developed a unified assessment of water quality, the chemical exergy based evaluation method. As opposed to the specific standard chemical exergy based on the global reference substances, he proposed an indicator called specific relative chemical exergy with reference to a spectrum of substances associated with the specified water-quality standard.

The work presented in this paper provides some keys to apply the Physical Hydronomics (PH) methodology, the branch of Exergo ecology devoted to water issues. It is focused on the physical cost of water assessment through the construction of the exergy profiles of the current and the desired (objective) states of the

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doi:10.1016/j.energy.2009.08.032

Nomenclature

Acronyms

BOD	biological oxygen demand
COD	chemical oxygen demand
IM	inorganic matter
ISM	incompressible substance model
NP	nitrogen and phosphor
OM	organic matter
PH	physical hydronomics
RE	reference environment
TOC	total organic carbon
TOD	total oxygen demand

Symbols

a	activity
b	specific exergy (kJ/kg)
B	total exergy (kJ)
C	velocity (m/s)
Cond	conductivity (μS/cm)
C_p	specific heat capacity (kJ/kg K)
g	gravitational acceleration of the earth (m/s^2)
m	mass (kg)
ml	molality (mol/kg)
n	mole number (kmol)
P	pressure (kPa)
R	universal gas constant (kJ/kg K)
s	specific entropy (kJ/kg K)
T	temperature (K)
u	specific internal energy (kJ/kg)
v	specific volume of the aqueous solution (m^3/kg)
x	molar fraction of the substance i in the solvent
y	relative molality (kmol/kg)
z	height (m)
ΔG_f	formation of Gibbs energy (kJ/kmol)
γ	activity coefficient

Subscripts

biol	biological
ch	chemical
ch,c	chemical (concentration)
ch,f	chemical (formation)
e	each element forming the substance i
i	any of the considered substances
k	kinetic
living_matter	living matter in the river
mch	mechanical
p	potential
0	under reference conditions
salts	dissolved salts in the river
t	thermal

river are built. Then, the exergy gap among them is calculated and the exergy required to drive the river from the current eventually damaged state to the legally established objective state is estimated. Further details about the PH methodology, as well as some application examples, can be found in Valero et al. [18] and Martínez et al. [19].

2. Organic compounds in water and their measurement

Water organic compounds are usually composed of a combination of carbon, hydrogen, and oxygen, together with nitrogen in some cases. Natural organic chemicals occur in nature as the result of decomposition of plants and animals and they are commonly found in surface waters. These organic chemicals can naturally evolve to nitrates, nitrites, and ammonia.

Besides, along with the proteins, carbohydrates, fats and oils, and urea, wastewater typically contains small quantities of a very large number of different synthetic organic molecules, forming from simple to extremely complex structures. Synthetic organic chemicals are not found naturally and are generally developed for mass production in industrial laboratories.

Over the years, a number of different analyses have been developed to determine the organic content of waters and wastewaters. In general, the analyses may be classified into those used to measure aggregate organic matter comprising a number of organic constituents with similar characteristics that cannot be distinguished separately, and those analyses used to quantify individual organic compounds.

In general, the analyses used to measure aggregate organic material may be divided into those used to measure gross concentrations of organic matter greater than about 1.0 mg/l and those used to measure trace concentrations in the range of 10^{-12}–1.0 mg/l. Laboratory methods commonly used today to measure gross amounts of organic matter (OM) in water include biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) and total oxygen demand (TOD). Trace organics in the range of 10^{-12}–10^{-3} mg/l are determined using instrumental methods including gas chromatography and mass spectroscopy [20].

This paper is focused on the exergy assessment for the organic chemical matter content in water flows. Then, the attention is devoted to the mentioned measurements of gross amounts of organic matter: TOC, COD, BOD and TOD, which are in turn the parameters that could be measured in water-quality monitoring networks.

2.1. Total organic carbon (TOC)

The TOC test is used to determine the total organic carbon in an aqueous sample. The test methods utilize heat and oxygen, ultraviolet radiation, chemical oxidants, or some combination of these methods to convert organic carbon into carbon dioxide which is measured with an infrared analyzer or by other means.

TOC is often used when levels of organic matter are low; it is a good parameter to measure and, actually, a more accurate indication of some of the pollutants that cause the majority of the problems to the BOD test.

The TOC of a wastewater can be used as a measure of its pollutional characteristics, and in some cases it has been possible to relate TOC to BOD and COD values. The TOC test is also gaining in favour because it takes only 5–10 min to complete. If a valid relationship can be established between results obtained with the TOC test and the results of the BOD test for a given wastewater, TOC test for process control is recommended [21].

2.2. Biochemical oxygen demand (BOD)

The most widely used parameter of organic pollution applied to both wastewater and surface water is the 5-day BOD (BOD_5). This determination involves the measurement of the dissolved oxygen