The use of exergy analysis to benchmark the resource efficiency of municipal waste water treatment plants in Ireland

M.Horrigan
Department of Mechanical Engineering
Dublin City University, Dublin, Ireland
e–mail: matthewhorrigan@gmail.com

B.Corcoran, Y.Delauré, T.Phelan, G.Mcnamara, L.Fitzsimons*
Faculty of Mechanical & Manufacturing Engineering
Dublin City University, Dublin, Ireland
e–mail: lorna.fitzsimons@dcu.ie

ABSTRACT

Exergy Analysis has been identified in the literature as a powerful tool to benchmark the resource efficiency of thermal systems. The exergy approach provides a rational basis for process optimisation, where, in theory, the processes with the greatest exergy destruction represent the greatest energy efficiency opportunities. Exergy analysis of a Waste Water Treatment Plant (WWTP) has been performed. In addition, two separate reference environments for WWTPs are defined based on plant location. Biological oxygen demand was identified as the most useful parameter when calculating the chemical exergy of organic matter in waste water. The results of this study indicate that organic matter is the principal contributor to chemical exergy values and that exergy analysis is a useful approach to identify inefficient processes within a WWTP.

KEYWORDS

Exergy Analysis, waste water, water treatment, resource efficiency, reference environment, benchmark, optimisation.

INTRODUCTION

When considering the resource efficiency of a Waste Water Treatment Plant (WWTP) factors such as effluent quality, carbon footprint and increasing electricity rates act as driving force for the sustainable design of these facilities. The US EPA states that the energy consumption for waste water treatment systems is expected to rise by 20% by 2020 [1]. Therefore, there is an urgent need to characterise and optimise energy consumption in WWTPs. Exergy analysis has been identified as an important tool in the analysis of thermal and chemical processes [2]. However, to date, this approach has seldom been the applied to study of WWTP optimisation. Exergy is a thermodynamic property, which combines the first and second law of thermodynamics, and can be defined as the maximum theoretical work obtainable as two systems interact to equilibrium [3]. By conducting an exergy balance across plant processes, the exergy destruction in each process can be quantified, and in turn used to focus energy efficiency efforts. Several researchers have used this approach to identify inefficiencies in thermal and chemical systems [4, 5]. Furthermore, exergy analysis can be used to quantify the work potential of waste streams. In WWTPs the generation of waste streams is unavoidable and exergy analysis may provide invaluable insight into their potential to do useful work. Exergy analysis can therefore be used to quantify waste streams enabling informed design decisions with regard to optimisation of WWTPs.

Initial works by Tai [6] related the chemical exergy of organic matter to wastewater indices Total Oxygen Demand (TOD) and Total Organic Carbon (TOC). In recent years exergy analysis has been applied to the quantification and optimisation of the environmental performance of a WWTP [7]; it has also been used to quantify chemical exergy assessment of organic matter in water flow [8]. Hellström [9] showed that exergy analysis can be used to estimate the flow and consumption of physical resources within WWTPs.

The objective of this paper is to conduct an exergy analysis of a WWTP, quantifying the exergy content or work potential of process streams. Consequently, a hierarchy of wastewater treatment plant processes with the greatest exergy destruction will be established.

TOTAL SPECIFIC EXERGY

The total specific exergy (b_T) of a wastewater body is defined by six variables, characterising its thermodynamic status: temperature, pressure, composition, concentration, velocity and altitude [10]. Each variable is associated with its corresponding exergy component: thermal (b_t), mechanical (b_m), chemical (b_{ch}), kinetic (b_k) and potential (b_z). The total specific exergy (b_T) of a waste water is defined in Eq. (1) below:

$$\underbrace{b(kJ/kg)}_{b_T} = \underbrace{C_{p,\,H2O}\,[T_p - T_o - T_o \ln (T_p/T_o)]}_{b_t} + \underbrace{V_{H2O}\,(p_p - p_o)}_{b_m} + \underbrace{\Sigma_i\,[y_i(\Delta G_f + \Sigma n_e b_{ch})]}_{b_{ch,f}} + \underbrace{[RT_o \Sigma x_i \ln a_i/a_o]}_{b_{ch,c}}$$
$$+ \underbrace{1/2\,(C_p^{\,2} - C_o^{\,2}/1000)}_{b_k} + \underbrace{g(z_p - z_o)}_{b_z} \qquad (1)$$

The nomenclature at the end of the paper provides a definition of terms and their units for Eq. (1). Assumptions of incompressible fluid with a constant specific heat capacity have been made in Eq. (1)

As the majority of WWTPs operate isothermally, thermal exergy is negligible. Mechanical exergy is also negligible as pressure changes within WWTPs are minute. Potential exergy is often insignificant, depending on plant configuration. Therefore, when calculating the total specific exergy (b_T) of a waste water body, it is sufficient to focus on its chemical exergy component. The total chemical exergy ($b_{ch,\,T}$) component combines two chemical exergy components: formation ($b_{ch,\,f}$) and concentration ($b_{ch,\,c}$) exergy. Detailed in Eq. (2):

$$\underbrace{b(kJ/kg)}_{b_{ch,T}} = \underbrace{\Sigma_i\,[y_i(\Delta G_f + \Sigma n_e b_{ch})]}_{b_{ch,f}} + \underbrace{[RT_o \Sigma x_i \ln a_i/a_o]}_{b_{ch,c}} \qquad (2)$$

Reference environment

The chemical exergy of a substance is dependent on the environmental model that is selected as its Reference Environment (RE). The RE from a technical perspective should be as close as possible to the natural environment [11]. Therefore, when defining the RE for a WWTP its composition should be as close as possible to that of its receiving waters. If a substance is not contained within the defined RE, its formation chemical exergy is the only component

considered. If a substance is already contained within the defined RE its concentration chemical exergy is the only component required [8]. Martinez [12] analysed a number of different RE scenarios in calculating the chemical exergy of river water, in particular:

- Sea water without organic matter and nutrients
- Sea water with organic matter and nutrients
- A completely degraded RE, with very high organic matter and nutrient concentrations
- Pure Water

As the final discharge location for Martinez's river case study is located on the eastern Spanish coast, sea water without organic matter was chosen as the RE. Pure water and the completely degraded RE models were easily discarded as they are not representative of the rivers final discharge location in that case. Sea water with organic matter and nutrients was also discarded as only trace elements of nutrients and organic matter exist in sea water.

When analysing the RE for a WWTP its discharge location impacts greatly on the selection of a suitable RE. For example, a WWTP discharging to an inland river would have a significantly different RE than a WWTP discharging to the sea. Therefore, two different REs are defined for WWTPs below:

WWTP discharging to inland rivers

Nutrients and organic matter have higher concentrations in river water than in sea water. Thus, they are included in the RE as they are representative of the real environment. Therefore, the RE for a WWTP discharging to inland rivers is defined as: river water containing organic matter a nd nutrients (Table 1) [13, 14]. If organic matter and nutrients are not included in the defined RE their exergy contribution will be their composition chemical exergy. If this option is selected the exergy value of nutrients and organic matter is increased when compared with the defined RE. Clearly, pure water and any form of sea water are non-realistic REs for WWTPs discharging to inland rivers.

Table 1. RE for WWTPs discharging to inland rivers

RE - River Discharge	Cl	HCO_3	K	Mg	Na	SO_4	Ca	Fe	S_iO_2	PO_4	NH_3	NO_3
ppm	6.9	95	1.7	5.6	5.4	24	31.1	0.8	7.5	0.03	0.083	1.46

WWTP discharging to the sea

The RE for WWTPs discharging to the sea will have identical characteristics to that of rivers whose final discharge location is the sea [8]. The defined RE is found several kilometres from the coast where complete mixing of waste water and sea water has occurred. Therefore, as previously detailed above the RE is defined as: sea water (Table 2)

Table 2. RE for WWTPs discharging to the sea

RE - Sea Discharge	Cl	HCO_3	K	Mg	Na	SO_4	Ca
ppm	19,345	145	390	1,295	10,752	2,701	416

The chemical exergy of nutrients and disinfectants within this paper are calculated using the above methodology. Hellström [9] stated that nitrogen concentration within wastewater should be considered as ammonium. Therefore, it is assumed that all ammonia values obtained from the WWTP exist as ammonium for the purpose of calculations. Disinfectants such as sodium hypochlorite and sodium hydroxide are clearly not contained within either RE detailed above; therefore the formation exergy component will be used when calculating the chemical exergy of these two disinfectants.

ORGANIC MATTER IN WASTEWATER

Organic compounds in waste water are generally composed of a combination of carbon, hydrogen, and oxygen. Typical waste water constituents are sugars, carbohydrates, fats, soluble proteins, and urea. Various techniques have been established to determine the organic content of waste water. Gross quantities of organic matter in waste water can be measured by laboratory analysis such as Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Theoretical Oxygen Demand (THOD), TOC and TOD. These measurement parameters are defined below; as they are of paramount importance when assessing the organic chemical matter present in waste water.

Organic matter parameters

Biological oxygen demand (BOD). BOD is the quantity of dissolved oxygen consumed by aerobic biological organisms in the oxidation of organic matter present in waste water.

Chemical oxygen demand (COD). COD is the quantity of oxygen required to chemically oxidise all organic and inorganic compounds in waste water. The COD value is usually larger than BOD, as some organic substances are oxidised more easily chemically than biologically.

Theoretical oxygen demand (THOD). THOD represents the quantity of oxygen required to oxidise a compound to its final oxidation products.

Total organic carbon (TOC). TOC represents the quantity of organic carbon contained within an aqueous sample. It can be used to measure the pollution characteristics within waste water.

Total oxygen demand (TOD). TOD is a measure of all matter oxidised in a sample of waste water, determined by measurement of the depletion of oxygen after chamber combustion.

ORGANIC MATTER CALCULATION METHODOLGY

Tai [6] established a relationship between the standard chemical exergy of a 138 organic compounds and the organic matter measurement parameter TOD and TOC, as indicated below by Eqs. (3) and (4):

$$b_{ch}\,(J/l) = 13.6\,(kJ/g) \times TOD\,(mg/l) \quad (3)$$

$$b_{ch}\,(J/l) = 45\,(kJ/g) \times TOC\,(mg/l) \quad (4)$$

Tai stated that it is very difficult to identify and determine every organic compound found in wastewater. Therefore, he conveniently expressed a generic organic compound as $C_aH_bO_c$ and established a pattern of oxidation to obtain Eqs. (3) and (4). He stated that organic matter parameters BOD and COD could also be used as approximate measures of effective energy, as TOD indirectly represented the magnitude of utilisable energy from wastewater. Hellström [9], on the other hand, suggested that BOD is the most reliable indicator of available exergy within waste water because it represents the amount of easily biodegradable organic matter. Martinez [8] demonstrated that using the COD and BOD parameters provided coherent results when compared with TOC in calculating the chemical exergy of organic matter in surface waters. Khosravi [7] proposed that THOD could be used to estimate the chemical exergy of organic matter in waste water. As THOD signifies the quantity of oxygen required to oxidise a compound to its final oxidation products, it therefore represents an unrealistic and worst case scenario of oxygen requirements. The actual oxygen demand of any organic compound is its biodegradability; therefore BOD will be used to estimate the chemical exergy of organic matter in waste water in this paper. The chemical exergy of sludge, return liquors and mixed liquor suspended solids in this paper will also be calculated using Eq. (5), indicated below:

$$b_{ch}\,(J/l) = 13.6\,(kJ/g) \times BOD\,(mg/l) \qquad (5)$$

WWTP EXERGY ANALYSIS

Exergy analysis was conducted on the plant detailed in Figure 3. It has a Population Equivalent (PE) > 100,000. The inlet works consists of four one metre-wide channels for the purpose of screening. Sand and grease are removed from the screened water within the pre – treatment building. The plant's biological reactor consists of initial anaerobic treatment followed by aerobic treatment. Waste water is pumped from the secondary clarifier to the sludge pump station, with return activated sludge pumped to the inlet of the biological reactor.

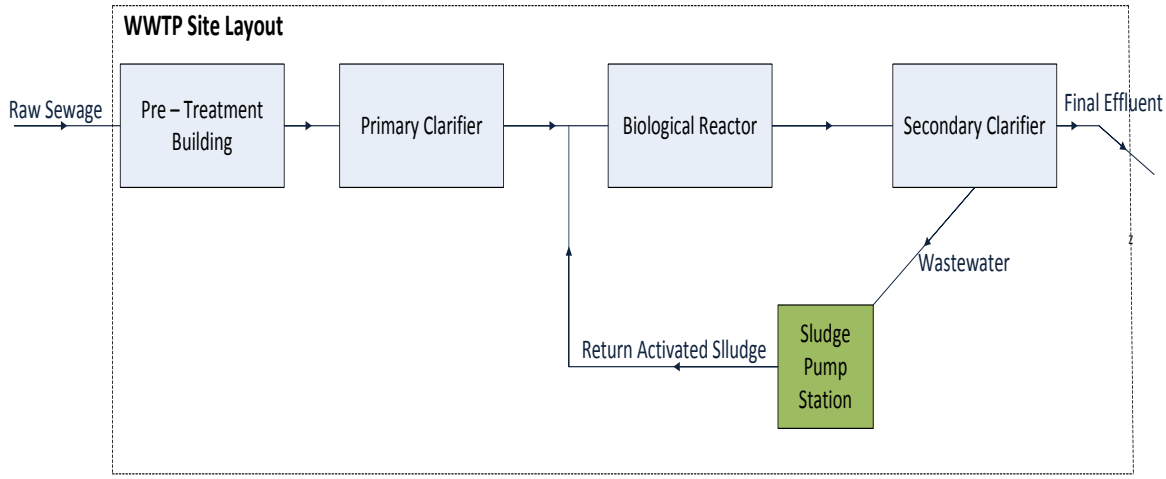


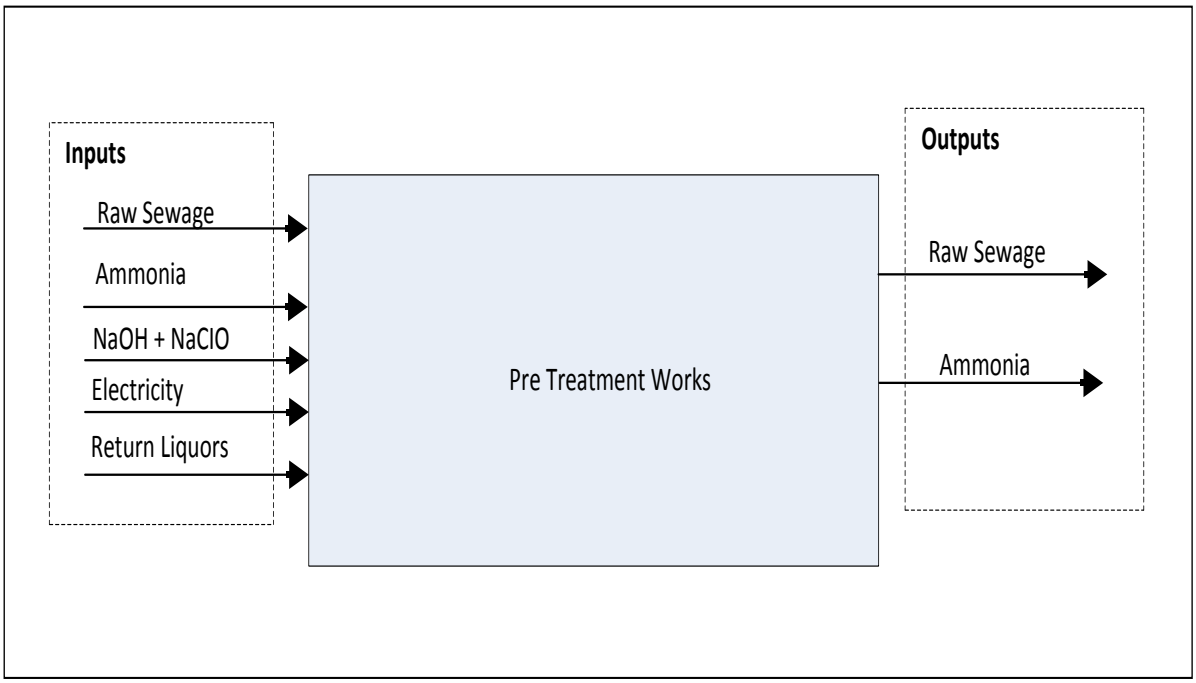
Figure 1: waste

Calculation Assumptions

- The plant's final effluent is discharged to sea, therefore sea water is selected as the RE
- Return liquors, sodium hydroxide, sodium hypochlorite and mixed liquor suspended solids are drip fed into the WWTP

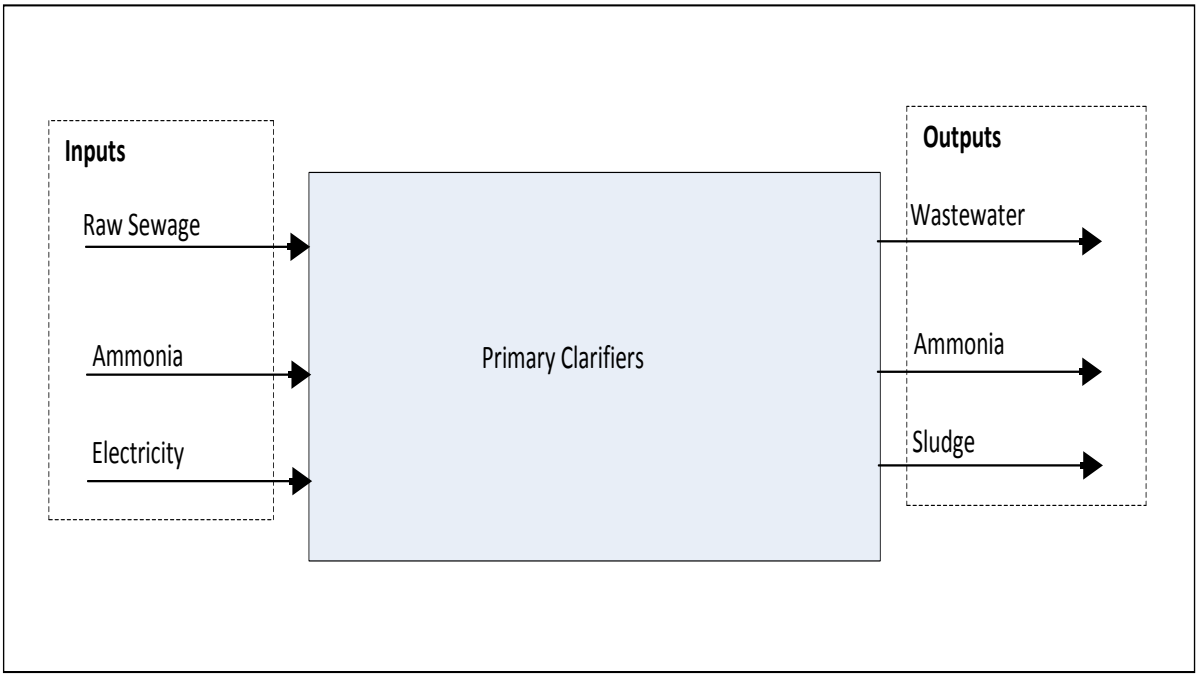
- All ammonia within the plant exists as ammonium for the purpose of exergy calculations
- Electricity (kW) usage is split evenly between the pre-treatment building and primary clarifier
- There is a 20.88% reduction in ammonia across the WWTP, however a 5.22% reduction in ammonia was assumed across each process for the purpose of calculations
- The chemical exergy of sludge, return liquors and mixed liquor suspended solids in this paper will be calculated using Eq. (5). Simply, multiply the BOD value (mg/l) by the coefficient of 13.6 (kJ/g) and divide by a 1000 to obtain the value in kJ/l.
- The chemical exergy of electricity (kJ/l) is simply found by multiplying its value in (kW) by a time period of a day in seconds and dividing by the flow through the plant in litres.
- The chemical exergy of nutrients and disinfectants (kJ/mol) has been previously calculated by Szargut [15]. This value obtained from Szargut (kJ/mol) is multiplied by the concentration of the component in (mol/l). Providing the exergy value in kJ/l.

Table 3. Exergy destruction across the pre – treatment works



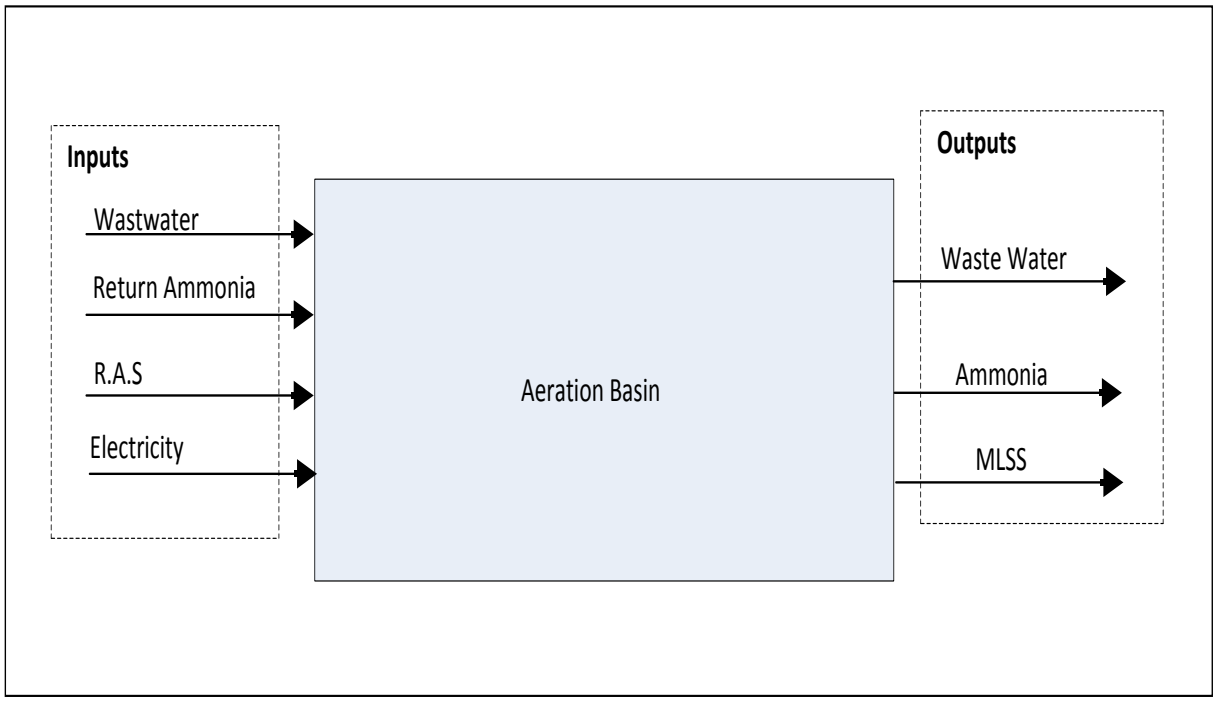
Inlet & Outlet Exergy of Pre - Treatment Works					
Process	Exergy Flow	Type & Unit Flow			Exergy (kJ/l)
Pre - Treatment Works	Inputs	**Raw Sewage**	Organic matter (BOD) (mg/L)	355.79	4.8387
		Other inputs	Ammonium (mg/l)	32.75	0.7137
			Sodium Hydroxide (NaOH) (mg/l)	1.04	0.0020
			Sodium Hypochlorite (mg/l)	2.21	0.0106
			Return Liquors (mg/l)	417.20	5.6739
			Electricity (kW)	23.88	0.0756
		Total Exergy @ Inlet			11.3146
	Outputs	**Raw Sewage**	Organic matter (BOD) (mg/L)	218.77	2.9753
		Other Outputs	Ammonia (mg/l)	31.04	0.6781
		Total Exergy @ Outlet			3.6534
Total Exergy Destruction					**7.6612**

Table 4. Exergy destruction across the primary clarifier



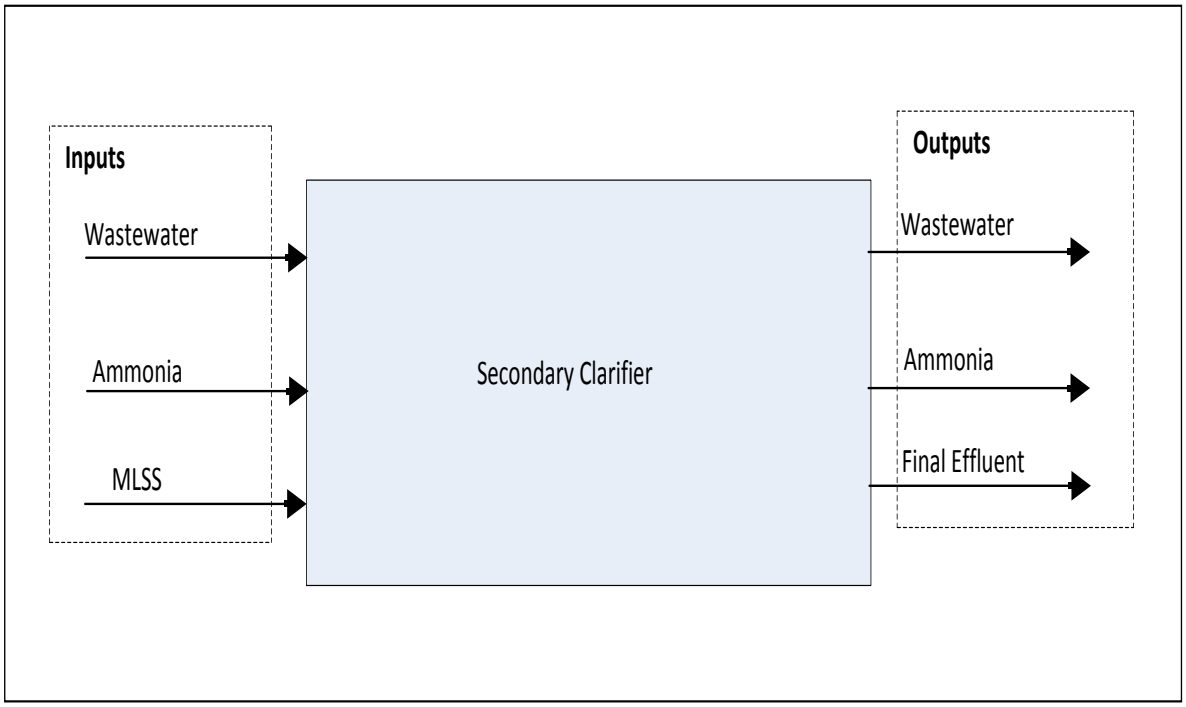
Inlet & Outlet Exergy of Primary Clarifiers					
Process	Exergy Flow				Exergy (kJ/l)
Primary Clarifier	Inputs	**Raw Sewage**	Organic matter (BOD) (mg/L)	218.77	2.9753
		Other inputs	Ammonia (mg/l)	31.04	0.6781
			Electricity (kWh)	23.88	0.0756
		Total Exergy @ Inlet			3.7290
	Outputs	**Waste Water**	Organic matter (BOD) (mg/L)	98.24	1.3361
		Other Outputs	Ammonia (mg/l)	29.33	0.6424
		Sludge	Organic matter (BOD) (mg/L)	81.00	1.1016
		Total Exergy @ Outlet			3.0800
Total Exergy Destruction					**0.6490**

Table 5. Exergy destruction across aeration basin



Inlet & Outlet Exergy of Aeration Basin					
Process	Exergy Flow				Exergy (kJ/l)
Aeration Basin	Inputs	**Waste Water**	Organic matter (BOD) (mg/L)	98.24	1.3361
		Other inputs	Return Ammonia (mg/l)	29.33	0.6424
			R.A.S (mg/l)	229.47	3.1208
			Electricity (kWh)	54.42	0.1724
		Total Exergy @ Inlet			5.2716
	Outputs	**MLSS**	Mixed Liquor Suspended Solids (mg/l)	328.30	4.4649
		Waste Water	Organic matter (BOD) (mg/L)	3.90	0.0530
		Other Outputs	Ammonia (mg/l)	27.62	0.6067
		Total Exergy @ Outlet			5.1246
Total Exergy Destruction					**0.1470**

Table 6. Exergy destruction across secondary clarifier and overall plant exergy destruction



Inlet & Outlet Exergy of Secondary Clarifiers					
Process	Exergy Flow				Exergy (kJ/l)
Secondary Clarifier	Inputs	**MLSS**	Mixed Liquor Suspended Solids (mg/l)	328.30	4.4649
		Waste Water	Organic matter (BOD) (mg/L)	3.90	0.0530
		Other inputs	Ammonia (mg/l)	27.62	0.6067
		Total Exergy @ Inlet			5.1246
	Outputs	**Final Effluent**	Organic matter (BOD) (mg/L)	42.54	0.5786
		Other Outputs	Ammonia (mg/l)	25.91	0.5647
		Waste Water to SPS	Organic matter (BOD) (mg/L)	31	0.4274
		Total Exergy @ Outlet			1.5706
Total Exergy Destruction					**3.5540**

Overall Exergy Plant Destruction	**12.0112**

RESULTS

The pre-treatment works account for 63.78% of the exergy destruction across the whole WWTP. In addition to the reduction in return liquors, there is a 38.5% reduction in the BOD of the raw sewage across the process. The secondary clarifier has the second highest exergy destruction with 29.59%, there is minimal exergy destruction associated with the primary

clarifier and aeration basin. Khosravi [7] noted similar losses across the secondary clarifier with 31.41% and minimal losses across the aeration basin were also noted. The aeration basin has traditional been seen as the chief consumer of energy within WWTPs [16]. However, the results in this paper clearly indicate that the chemical exergy value associated with electricity is minimal in comparison with the chemical exergy value of organic matter in waste water. Mixed liquor suspended solids for example are destroyed across the secondary clarifier; this loss of organic matter should clearly be avoided When exploring the resource efficiency of the WWTP, the pre – treatment works followed by the secondary clarifier should be focused on to achieve increased efficiency. Efforts should be made to utilise the embedded energy in the return liquors and mixed liquor suspended solids. A system such as a combined heat and power plant could be used to utilise the embedded within the sludge. The sludge could also be applied to the land as fertiliser. However, this is a contentious issue as sludge application to land could contribute to potential eutrophication.

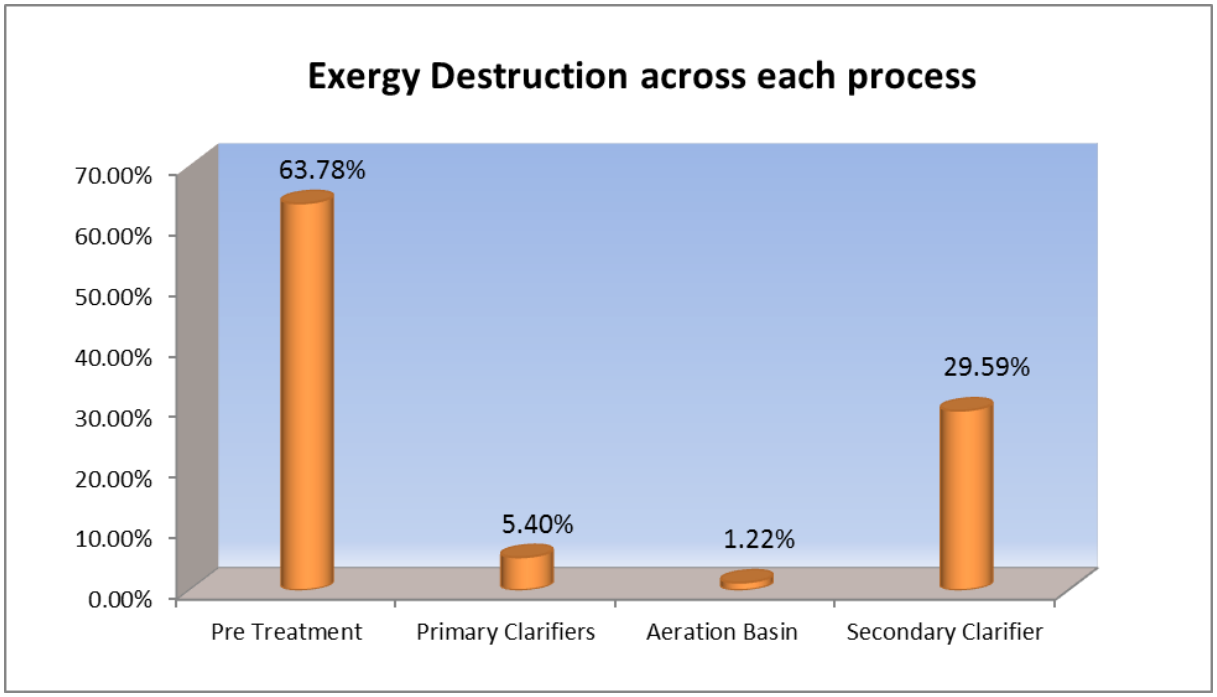


Figure 2. Exergy destruction across WWTP

CONCLUSION

An exergy balance of a WWTP has been completed; the chemical exergy of waste streams such as organic matter, nutrients, disinfectants and electricity has been quantified. Based on the findings of this study, the greatest value of exergy destruction occurs in the pre-treatment works and thus, in theory, this should be the focus area for optimisation. Organic matter has been identified as the chief contributor to the chemical exergy of wastewater. Therefore, when considering the optimisation of the WWTP one must also take into account the exergy value of waste streams, and primarily the organic matter content of waste streams that are not utilised.

The RE selection for WWTPs was also analysed, as the discharge location of a WWTP significantly effects the selection of suitable RE. Therefore, two different REs were defined for WWTPs.

- WWTP that discharge to the sea
- WWTP that discharge to an inland river

Previous methods to calculate the chemical exergy of organic matter were analysed; with BOD identified as the most reliable indicator of the chemical exergy of organic matter for waste water treatment.

NOMENCLATURE

Acronyms			
BOD	biological oxygen demand	v	specific volume of the aqueous solution (m^3/kg)
COD	chemical oxygen demand	x	molar fraction of the substance i in the solvent
RE	reference environment	y	relative molality (kmol/kg)
THOD	theoretical oxygen demand	z	height (m)
TOC	total organic carbon	ΔGf	Gibbs free energy (kJ/kmol)
TOD	total oxygen demand		
WWTP	wastewater treatment plant	Subscripts	
		ch	chemical
Symbols		ch,c	chemical (concentration)
a	activity	ch,f	chemical (formation)
b_T	total specific exergy (kJ/kg)	e	each element forming the substance i
c	velocity (m/s)	i	any considered substances
$c_{p, H20}$	specific heat capacity of water (kJ/kg K)	k	kinetic
g	gravitational acceleration of the earth (m/s^2)	m	mechanical
m	mass (kg)	o	under reference conditions
n	mole number (mol/kg)	p	under ambient conditions
p	pressure (kPa)	t	thermal
R	universal gas constant (kJ/kg K)	z	potential
T	temperature (K)		

REFERENCES

[1] R. Goldstein and W. Smith, "Water & sustainability (volume 4): U.S. electricity consumption for water supply & treatment - the next half century," Electric Power Research Institute, United States of America, 2002.

[2] J. Szargut, D.R. Morris and F.R. Steward, “Exergy analysis of thermal, chemical and metallurgical processes. New York: Hemisphere; 1988.

[3] M. Moran and H. Shapiro, *Fundamentals of Engineering Thermodynamics* , vol. 5, John Wiley & Sons Ltd, U.K., Ed. 2006, pp. 273.

[4] G. Tsatsanonis, “Thermeconomic analysis and optimization of energy systems,” Program energy combustion science, vol. 19, pp 227- 257, 1993.

[5] L. Wang, Y. Yang, T. Morosuk and G. Tsatsaronis, “Advanced Thermodynamic Analysis and Evaluation of a Supercritical Power Plant,” Energies, vol. 5, pp 1850 – 1863, 2012.

[6] S. Tai, K. Matsushige and T. Goda, "Chemical exergy of organic matter in wastewater," *International Journal of Environmental Studies*, vol. 27, pp. 301-315, 1986.

[7] S. Khosravi and M. Panjeshahi, "Application of exergy analysis for quantification and optimisation of the environmental performance in wastewater treatment plants," *International Journal of Exergy,* vol. 12, pp. 119-138, 2013.

[8] A. Martínez and J. Uche. (2010). Chemical exergy assessment of organic matter in a water flow. *Energy 35(1),* pp. 77-84.

[9] D. Hellström. (1997 Jan. - Feb.). An exergy analysis for a wastewater treatment plant: An estimation of the consumption of physical resources. *Water Environ. Res. 69(1),* pp. 44-51. Available: http://www.jstor.org/stable/25044841

[10] A. Zaleta-Aguilar, L. Ranz and A. Valero. (1998). Towards a unified measure of renewable resources availability: The exergy method applied to the water of a river. *Energy Conversion and Management 39(16–18),* pp. 1911-1917.

[11] R. Rivero and M. Garfias. (2006). Standard chemical exergy of elements updated. *Energy 31(15),* pp. 3310-3326.

[12] A. Martinez, "Exergy cost assessment of water resources: physical hidronomics, University of Zaragoza, Zaragoza, Spain." pp. 145-149, 2009.

[13] D. Livingston, "Chemical composition of rivers and lakes," vol. 6, 1963, pp. 64.

[14] M. Lehane and B. O'Leary, "Ireland's environment 2012 - an assessment," Environmental Protection Agency of Ireland, 2012.

[15] J. Szargut, "Chemical exergies of the elements," applied energy, 1989, pp 269-286.

[16] D. Trifonov and O. Tzarnoretcki, "A possibility for the investigation of dissolved oxygen quantity in a laboratory aeration model with computer system," Cybernetics and information technologies, vol. 5 pp.126