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Supplementary data for

A synergistic combination of algal wastewater treatment and hydrothermal biofuel production maximized by nutrient and carbon recycling

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1. E^2-Energy model

1.1. Model Objectives

In order to better understand the long-term steady-state impacts of nutrient and carbon recycling in the E^2-Energy system, a mathematical mass balance model was developed to simulate a continuously operating system in terms of energy and material flows, as well as environmental impacts (wastewater treatment performance and greenhouse gas capture).

1.2. Modelling approach

A mathematical model of the E^2-Energy process was developed using STELLA® (Strongly Typed Lisp-Like Language) modelling platform (http://www.iseesystems.com). STELLA® facilitates the building of a model for dynamic systems by creating a pictorial diagram of the system and then assigning values and mathematical functions to various components of the system.The key features of STELLA® consist of the following four tools (Fig. S1): (1) Stocks, which are the state variables for accumulation. They collect anything that flows into and out of them; (2) Flows, which are the exchange variables, control the arrival or exchanges of information between state variables; (3) Converters, are the auxiliary variables. These variables can be represented by constant values or by values dependent on other variables, curves, or functions of various categories; and (4) Connectors, which are used to connect modeling features, variables, and elements. STELLA has been widely used in biological, ecological, and environmental sciences. An elaborate description of the STELLA package can be found in Isee Systems.

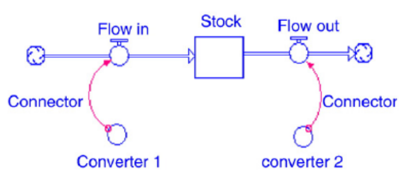


Fig. S1. A schematic diagram showing the four key features of STELLA: (1) stock, (2) flow, (3) converter, and (4) connector.

The approach taken in this analysis is to use the STELLA® software to model a multi-component mass balance for two scenarios of the E^2-Energy system based on a specific amount of municipal wastewater coming into the system. One scenario uses parameters obtained from the experimental results of this study, and the second scenario uses some "improved" parameters to investigate the potential to improve overall system performance via optimizing individual system components. The final outputs of the model include mass flows, energy production, pollutant treatment efficiency, and greenhouse gas (GHG) emissions, which are then compared between the two scenarios and with the performance of conventional municipal wastewater treatment and algal cultivation systems.

In this model, we simulate mass flow, carbon flow, and nitrogen flow, as they are all very important for understanding the process impacts. Mass flow of biosolids determines the energy production capacity of the E^2-Energy system as biosolids is the feedstock of HTL that ultimately produces usable bioenergy. Carbon includes both organic carbon and inorganic CO_2 in this model. Organic carbon is perhaps the most important target pollutant in wastewater, and it is also the major form of energy in wastewater. Dissolved organic carbon in wastewater is converted to CO_2 and particulate organic carbon during heterotrophic biomass production. CO_2 is the only carbon source for autotrophic microbial growth, and it is also one of the most important GHGs. Both heterotrophic and autotrophic biomass is used as an HTL feedstock and thus the carbon flow determines the mass flow of the E^2-Energy system. The key feature of E^2-Energy is multiple cycles of nutrient reuse to maximize biomass production. Nitrogen is also one of the most essential nutrients to support biological activity and various forms of nitrogen are also considered to be pollutants in wastewater. Therefore, nitrogen flow determines the biomass amplification ratios and would provide comparison criteria with other biofuel production systems. Other nutrients such as phosphorus are also going to be recycled in the E^2-Energy system, and future modelling work is expected to study additional nutrients.

1.3. Model description

The E[2]-Energy model consists of three sub-models for carbon, nitrogen, and mass, which are interrelated. Each sub-model contains three major compartments: waste pretreatment (PT), algal-bacterial cultivation (AC), and hydrothermal liquefaction (HTL), as shown in Fig. 1 in the paper. The following bulletized list provides a general description of the model assumptions, formulations, and the transformation processes occurring within each compartment. The specific processes and equations governing these transformations are shown in Table S1 for the carbon and mass sub-model (equations for nitrogen sub-model were provided in the main paper). The two sets of parameters used (baseline and improved) are listed in Table 3.

(1) For the pretreatment (PT) compartment

- The incoming total nitrogen or carbon includes soluble substrate nitrogen ($S_{N\,INF}^{\,PT}$) or carbon ($S_{C\,INF}^{\,PT}$) and nitrogen or carbon in suspended solids ($SS_{INF}^{PT} \times f_N^{SS}$ or $SS_{INF}^{PT} \times f_C^{SS}$)
- Nitrogen or carbon removal in this stage is only achieved by suspended solids removal as primary sludge; no dissolved component was removed

(2) For the algal cultivation (AC) compartment

- The incoming total nitrogen or carbon includes two parts: nitrogen or carbon in the PT effluent (TN_{EFF}^{PT} or TC_{EFF}^{PT}) and the dissolved nitrogen or carbon in the recycled post-hydrothermal liquefaction wastewater (PHWW) ($TN_{PHWW}\ or\ TC_{PHWW}$)
- The suspended solids in PT effluent is hydrolyzed into soluble substrate to support biomass production; the particulate nitrogen or carbon contained in these suspended solids is released into the water as soluble substrate nitrogen or carbon
- Nitrogen removal is achieved by being taken up by microbes which include autotrophic microbes (X_{AUTO}^{AC}) and heterotrophic microbes (X_{HETO}^{AC}) (Mixotrophic biomass growth was very limited in our system and was neglected for simplicity)
- Nitrogen or carbon removal efficiency ($RR_N^{AC}\ or\ RR_C^{AC}$) is decided by the nitrogen or carbon biodegradability of the two incoming streams ($\alpha_N^{RW}, \alpha_N^{PHWW}$ or $\alpha_C^{RW}, \alpha_C^{PHWW}$)
- Heterotrophic biomass was defined as microbes that can only utilize organic carbon substrate as a carbon and energy source. Available organic carbon ($TC_{INF}^{AC} \times RR_C^{AC}$) is the only limiting factor for heterotrophic biomass production*. Heterotrophic microbes have priority in using available nitrogen since they generally grow faster than autotrophs ($TN_{AUTO}^{AC} = TN_{BS}^{AC} - TN_{HETO}^{AC}$).
- Autotrophic biomass was defined as phototrophic microbes that utilize CO_2 as the only carbon source, and light as the only energy source in our model. Nitrogen availability is considered as the only limiting factor for autotrophic growth ($X_{AUTO}^{AC} = Y_{AUTO}^{OBS} \times TN_{AUTO}^{AC}$)*.
- Autotrophic microbes utilize inorganic carbon from three resources: respiration from heterotrophic microbes (assuming 100% is captured by autotrophic microbes), recycled HTL gaseous product (mainly CO_2), and CO_2 from ambient air or point source.

Table S1 Governing equations for carbon and mass sub-models.

Pretreatment (PT)

Inputs: From incoming waste stream: TSS, TC_{INF}^{PT}, Q

$$TC_{INF}^{PT} = (SS_{INF}^{PT} \times f_C^{SS} + S_{C\,INF}^{\,PT}) \times Q$$
$$TSS_{INF}^{PT} = SS_{INF}^{PT} \times Q$$

Processes:
- Carbon removal through primary sludge settling (assuming no soluble nitrogen removal)

$$SS_{EFF}^{PT} = SS_{INF}^{PT} \times (1 - RR_{SS}^{PT})$$
$$TSS_{PS}^{PT} = (SS_{INF}^{PT} - SS_{EFF}^{PT}) \times Q$$
$$TC_{PS}^{PT} = TSS_{PS}^{PT} \times f_C^{PS}$$

Outputs: To AC: $TSS_{EFF}^{PT}, TC_{EFF}^{PT}, Q_L$

To HTL: $TSS_{PS}^{PT}, TC_{PS}^{PT}, Q_s$

Algal-bacterial Cultivation (AC)

Inputs: From PT: $TSS_{EFF}^{PT}, TC_{EFF}^{PT}, Q_L$

From HTL: $TC_{PHWW}, Q_{PHWW}, TC_{GAS}$

From atmosphere: $TC_{AUTO}^{CO_2\_Seq\_Atm}$

$$TC_{INF}^{AC} = TC_{EFF}^{PT} + TC_{PHWW}$$
$$TSS_{INF}^{AC} = TSS_{EFF}^{PT}$$

Processes:
- Hydrolysis of residual suspended solids from PT

$$TS_{C\,INF}^{\,AC} = TC_{EFF}^{PT} + TC_{PHWW}$$

- Soluble carbon removal in the form of heterotrophic biomass

--Removal efficiency depends on nitrogen biodegradability of two incoming waste stream

$$RR_C^{AC} = \frac{TC_{EFF}^{PT} \times \alpha_C^{RW} + TC_{PHWW} \times \alpha_C^{PHWW}}{TC_{EFF}^{PT} + TC_{PHWW}}$$

--Carbon utilization to support heterotrophic growth

$$X_{HETO}^{AC} = Y_{HETO}^{OBS} \times TC_{INF}^{AC} \times RR_C^{AC}$$

--CO_2 emission from respiration of heterotrophic microbes

$$TC_{HETO}^{CO_2\_RES} = TC_{INF}^{AC} \times RR_C^{AC} - TC_{HETO}^{AC}$$

- CO_2 fixation from ambient air/point source to support autotrophic growth

$$TC_{AUTO}^{CO_2\_Seq\_Atm} = TC_{AUTO}^{AC} - TC_{HETO}^{CO_2\_RES} - TC_{GAS}$$
$$TC_{AUTO}^{AC} = X_{AUTO}^{AC} \times f_C^{AUTO}$$

- Biosolids increased in the form of biomass

$$TSS_{BS}^{AC} = X_{HETO}^{AC} + X_{AUTO}^{AC}$$

--Heterotrophic microbes growth

$$X_{HETO}^{AC} = Y_{HETO}^{OBS} \times TC_{INF}^{AC} \times RR_C^{AC}$$

--Autotrophic microbes growth

$$X_{AUTO}^{AC} = Y_{AUTO}^{OBS} \times TN_{AUTO}^{AC}$$

- Biomass harvesting

$$TSS_{Harv}^{AC} = TSS_{BS}^{AC} \times RR_{SS}^{AC}$$
$$TC_{Harv}^{AC} = TC_{BS}^{AC} \times RR_{SS}^{AC}$$

Outputs: To treated water: $TSS_{EFF}^{AC}, TC_{EFF}^{AC}, Q_{AC}$

To HTL: $TC_{Harv}^{AC}, TSS_{Harv}^{AC}$

Hydrothermal Liquefaction (HTL)

Inputs: From PT: $TSS_{PS}^{PT}, TC_{PS}^{PT}, Q_s$

From AC: $TSS_{Harv}^{AC}, TC_{Harv}^{AC}$

$$TSS_{FEED}^{HTL} = TSS_{Harv}^{AC} + TSS_{PS}^{PT}$$
$$TC_{FEED}^{HTL} = TC_{Harv}^{AC} + TC_{PS}^{PT}$$

Processes:
- Hydrothermal liquefaction

$$M_{OIL,\ PHWW,\ GAS\ or\ RES} = TSS_{FEED}^{HTL} \times Y_{OIL,\ PHWW,\ GAS\ or\ RES}$$

- Carbon release into HTL product

$$TC_{OIL,\ PHWW,\ GAS\ or\ RES} = TC_{BS}^{AC} \times y_C^{OIL,\ PHWW\ GAS\ or\ RES}$$

Outputs: To bio-crude oil: M_{OIL}, TC_{OIL}

To residue: M_{RES}, TC_{RES}

To PHWW: $M_{PHWW}, TC_{PHWW}, Q_{PHWW}$

To waste gas: M_{GAS}, TC_{GAS}

Please see Table 3 in main article for nomenclature, process parameter definitions and values used in the model.

- Biomass containing removed nitrogen or carbon (TN_{BS}^{AC} or TC_{BS}^{AC}) was harvested with an efficiency of RR_{SS}^{AC} and sent to HTL as feedstock

*Only one limiting growth factor related to carbon or nitrogen is assumed for each kind of microorganism in this model, as the current model focuses more on the nutrient and carbon recycling potential rather than detailed biological activity.

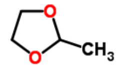
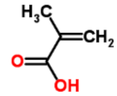
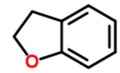
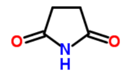
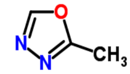
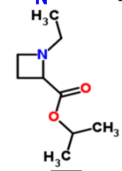
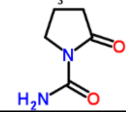
(3) For the HTL compartment

- The total incoming nitrogen, carbon, or solids includes the nitrogen, carbon, or solids in the primary sludge from PT (TN_{PS}^{PT}, TC_{PS}^{PT} or TSS_{PS}^{PT}) and that from biosolids harvested in AC (TN_{Harv}^{AC}, TC_{Harv}^{AC} or TSS_{Harv}^{AC})
- Nitrogen or carbon are released into different products during HTL and PHWW containing soluble nitrogen or carbon (TN_{PHWW} or TC_{PHWW}) was recycled back to AC. The partitioning ratio ($y_N^{OIL,\ PHWW,\ GAS\ or\ RES}$ and $y_C^{OIL,\ PHWW,\ GAS\ or\ RES}$) only depends on temperature and pressure, but not feedstock composition.

2. Recalcitrant compounds identification

Preliminary study has identified some of the recalcitrant/slow – degrading compounds by comparing the GC-MS analysis (method described previously [1]) result of the influent and effluent of the continuous operating photobioreactor [2] fed by 1% PHWW-Spi (with hydraulic retention time of 5 days and solid retention time 20 days), part of which (with relatively large chromatic peaks) are listed in Table S2 below. More detailed information will be published elsewhere.

Table S2 Identified recalcitrant/slow-degrading compounds

No	Name	Formula	Structure
1	1,3-Dioxolane, 2-methyl	$C_4H_8O_2$	
2	2-Propenoic acid, 2-methyl-	C_4H_6O2	
3	Benzofuran, 2,3-dihydro-	C_8H_8O	
4	2,5-Pyrrolidinedione	$C_4H_5NO_2$	
5	Pyrazolo[5,1-c][1,2,4]benzotriazin-8-ol	$C_9H_6N_4O$	
6	2-Methyl[1,3,4]oxadiazole	$C_3H_4N_2O$	
7	N-Ethyl-2-isopropoxycarbonylazetidine	$C_9H_{17}NO_2$	
8	l-Pyrrolid-2-one, N-carbamoyl-	$C_5H_8N_2O_2$	

Reference

1 G. Yu, Hydrothermal liquefaction of low-lipid microalgae to produce bio-crude oil, University of Illinois at Urbana-Champaign, 2012.
2 Y. Zhou, L. C. Schideman, Y. Zhang and G. Yu, Environment-Enhancing Energy: A Novel Wastewater Treatment System that Maximizes Algal Biofuel Production and Minimizes Greenhouse Gas Emissions, WEFTEC 2011, Los Angeles, CA, 2011.