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### DISTRIBUTED MARINE BIOREFINERIES FOR DEVELOPING ECONOMIES

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#### ABSTRACT

In the coming decades, developing countries will be responsible for significant increases in liquid fuel demand. There is an urgent need to develop alternative, preferably carbon-neutral, transportation fuels to supplement limited fossil fuel resources and minimize undesirable climatic change. While biofuels present a promising alternative to fossil fuels, sustainable biorefinery process design remains challenging. Efficiencies of scale realized by large centralized facilities are offset by increased feedstock collection and fuel distribution logistical costs. In this work, we use a thermodynamic balance approach to derive the optimal serviced territory size for a single biorefinery. We find that the optimal size decreases with increasing population density and per capita fuel consumption. We propose a modular, scalable, and sustainable biorefinery design based on the marine macro algae Ulva sp. To demonstrate the design principal, we provide an example marine biorefinery design for a coastal town of 20,000 inhabitants in rural India. Beyond basic biorefinery design, we consider biorefinery integration into distributed power sources and environmental impacts.

#### INTRODUCTION

The major growth in liquid fuel demand over the next 20 years will be predominantly due to developing countries [1]. While Gross Domestic Product (GDP) and primary energy production in Organization for Economic Co-operation and

Development (OECD) countries is not linearly correlated, GDP growth in developing countries requires increases in primary energy production [1, 2]. The World Energy Council predicts that India and China will overtake developed countries in transportation fuel consumption by 2025 [3]. Due to climatic, economic, and fossil fuel resource constraints, there is an urgent need for the sustainable, cost-effective production of carbon-neutral transportation fuels [3, 4].

Biofuels present an alternative to fossil fuels [4]. First generation biofuel technologies utilize established processes and currently produce biofuels on a commercial scale. First generation feedstocks include sugar beet, starch-bearing grains, and conventional vegetable oil crops, and first generation fuel products include ethanol and biodiesel [4]. Second and third generation biofuel technologies, currently in research and development, utilize animal fat, lignocellulosic biomass, and algae feedstocks, and produce hydrotreated vegetable oil, cellulosic-ethanol, biomass-to-liquids (BtL)-diesel, bio-butanol, and advanced drop-in replacement fuels such as fatty-acid ethyl esters, mono- and sesquiterpenes, alkanes, alkenes, terpenes and methyl ketones [4-9].

Although biofuels may collectively supply a portion of future transportation fuel demand, competition between "energy crops" and "food crops" for land and water resources is a growing concern [4, 10]. Furthermore, the extents to which land erosion, potable water consumption, fertilizers, pesticides, and

climate change impact biofuel sustainability have yet to be evaluated [11].

While significant efforts are being directed towards developing feedstocks and conversion technologies, biorefinery design remains in its infancy [12]. The optimization of biorefinery size, feedstock, technology, and serviced area will be required to reduce the costs of the resulting biofuel products.

Recent research in constructal design shows that the optimal distribution of flows of products and services across a populated area depends on a balance between the size of the production centers with the sizes of distribution networks that connect these centers to end users [13-16]. Although larger systems are thermodynamically more efficient in production, they serve greater areas; thus, the collection and distribution logistical costs also increase with size [16-18]. Therefore, a balance exists between efficiencies of scale, and distribution system losses. This balance has been investigated both for the thermodynamics of energy sources [14-16] and the economics of agricultural/biofuel systems [12, 19, 20]. Applications of the balance principle have been demonstrated for the thermodynamic optimization of hot water flow and heating [14], refrigeration [15], combined solar power and desalination [16], and agricultural product processing economics [19]. The balance principle has also lead to proposals for distributed energy systems to optimize energy production size and service area [16].

The goal of this work is to show that the balance between thermodynamic efficiency of system size, collection and distribution, is valid for biorefineries. This work also aims to demonstrate that population characteristics, such as density and per capita liquid fuel consumption, play critical roles in the design of biorefinery scale, technology choice and serviced area size.

We report a model macro algae biorefinery design for midsize towns in low to medium income countries with low liquid fuel consumption per capita. We targeted these populations since the majority of new fuel systems built in future years will serve their growing demands [3]. We focus our model on marine macro algae, a promising biofuel crop feedstock that does not compete with food crops for arable land or potable water [6, 21]. Furthermore, macro algae, which do not contain lignin, are convenient candidates for cost effective processing with current technology [6, 21]. We analyze biorefinery production of a transportation biofuel from the green macro algae Ulva sp, and demonstrate the integration of this model biorefinery into the distributed energy system proposed by Lorente et al. [16]. Finally, in the context of a single biorefinery, we compare macro algae with corn grain and cassava feedstocks.

#### NOMENCLATURE

D	[m]	service area characteristic length		
n		proportion of the service area		
		characteristic length allocated to fuel		
		crops		
Ν	[person]	population size		
ρ	[person·m <sup>-2</sup> ]	population density		
$m_1$	[L year <sup>-1</sup> person <sup>-1</sup> ]	annual per capita fuel consumption rate		
m	[L year <sup>-1</sup> ]	total fuel produced by a single		
		biorefinery		
$Q_{solar}$	$[Wh m^{-2}]$	solar energy flux		
$W_{O}$	[Wh]	photosynthesis energy loss		
$W_{I}$	[Wh]	feedstock collection energy loss		
$W_2$	[Wh]	fuel conversion energy loss		
$W_3$	[Wh]	fuel distribution energy loss		
$W_{u}$	[Wh]	useable transportation energy		
W	[Wh]	total energy loss		
$L_t$	[m]	feedstock collection transport length		
$L_d$	[m]	fuel distribution transport length		
α		efficiency scale factor		
CSI		crop sustainability index		
PW	[ton]	ton of potable water used		
Ch	[ton]	ton of chemicals leaked to the		
		environment		
J		number of jobs created		

# OPTIMIZATION OF BIOREFINERY SCALE AND SERVICE AREA SIZE

The goal of this section is to determine the optimal service area size for a single biorefinery for a given population density and per capita transportation fuel consumption rate.

#### A Model for Biorefinery Scale Optimization

Previously, Lorente *et al.* [16] developed a model for an area served by a distributed energy system, consisting of a centralized solar power station and distributed desalination plants. Here, we add biorefineries to the distributed energy network.

Each biorefinery collects feedstock biomass from the surrounding farming area of characteristic length scale nD, processes it to liquid biofuel, and then distributes the biofuel to population at specific locations within the service area. The scheme of the local biorefinery serving a network of biomass producers and liquid biofuel consumers is depicted in Figure 1. The service area is parameterized by characteristic length D, population size N, population density  $\rho$ , and per capita transportation fuel consumption rate  $m_1$ . The area  $D^2$ , through which the population is homogeneously spread, provides space for food and fuel crops, and solar energy systems. The rate of biorefinery transportation biofuel production that exactly meets the population's demand is given by:



Figure 1. Scheme of a single biorefinery service area with characteristic length D. Feedstock is supplied by multiple local producers concentrated within an area of characteristic length scale nD around the biorefinery. The produced liquid fuel is consumed within the service area.

Figure 2 depicts the thermodynamic model of the biorefinery service area shown in Figure 1. Fuel crops (residing in a fractional allocated area  $(nD)^2$ ) collect solar flux  $Q_{solar}$ . Photosynthesis, the conversion of solar energy to chemical energy stored in biomass, has limited efficiency (4-6%) [22].  $W_0$  is the photosynthesis solar energy loss. The resulting fuel crop biomass is harvested and transported to the biorefinery, requiring a truck, train or a boat, which consumes a certain amount of fuel per km of transport.



**Figure 2.** Thermodynamic model of a biorefinery producing liquid transportation biofuel.  $Q_{solar}$  is the solar energy flux,  $W_0$  is the photosynthesis energy loss,  $W_1$  is the biomass collection energy loss,  $W_2$  is the fuel conversion energy loss,  $W_3$  is the fuel distribution energy loss, and  $W_u$  is the total useable transportation fuel energy supplied to the population.

The feedstock collection energy loss  $W_1$  is related to transport length  $L_t W_1$  by:

$$W_1 = c_1 L_t N m_1 \tag{2}$$

where  $c_1$  is the transportation vehicle efficiency coefficient. French [19] has shown that the total transportation length is proportional to the characteristic length of the area:

$$L_t = c_2 n D \tag{3}$$

where  $c_2$  is a proportion coefficient.

Once delivered to the biorefinery, the fuel crops are converted to liquid fuels. The conversion efficiency depends on multiple factors such as crop type and processing technology. Previous analyses of biorefineries [23] and other power conversion systems [18, 24] suggest that conversion efficiency increases with biorefinery size.  $W_2$  is the energy lost during the crop to fuel conversion process:

$$W_2 = c_3 m^{\alpha}$$
 (4)

where  $\alpha$  is a scale factor ( $\alpha < 1$ ) and  $c_3$  is a proportion coefficient.

Finally, the produced biofuel is distributed to consumers (Figure 1). The biofuel distribution energy loss is given by:

$$W_3 = c_1 L_d N m_1 \tag{5}$$

where the length of distribution roads  $(L_d)$  depends on the service area characteristic length as follows [19]:

$$L_d = c_4 D \tag{6}$$

where  $c_4$  is a proportion coefficient.

The following equation describes the overall energy balance for conversion of solar energy to transportation fuel in our model:

$$W_u = Q_{solar}(nD)^2 - W_0 - W_1 - W_2 - W_3$$
(7)

In order to maximize the total useful energy  $(W_u)$ , it is necessary to minimize the energy losses. We assume that the photosynthetic energy losses are location and bioenergy crop specific. A review of photosynthetic efficiency optimization can be found in [22]. Here, we seek to minimize *W*, the aggregate feedstock collection, conversion, and fuel distribution energetic losses:

or:

$$W = W_1 + W_2 + W_3$$
 (8)

$$W = c_1 L_t N m_1 + c_3 m^{\alpha} + c_1 L_d N m_1 \tag{9}$$

Equations 1 to 9 lead to the total energy loss per consumer for producing and distributing biofuel:

$$WN^{-1} = c_1 c_2 n D m_1 + c_3 D^{2\alpha - 2} m_1^{\alpha} \rho^{\alpha - 1} + c_1 c_4 D m_1$$
(10)

With increasing service area characteristic length D, the first and the third terms of Equation 10 increase, while the second term decreases (Figure 3). In order to find the optimal service area leading to minimal energy loss per consumer, we differentiate  $WN^{1}$  with respect to D and solve for  $D_{opt}$ , zeroing the derivative:

 $D_{opt} = \left\{ \frac{c_1 c_2 n + c_1 c_4}{(2 - 2\alpha) c_2} (m_1 \rho)^{1 - \alpha} \right\}^{\frac{1}{2\alpha - 3}}$ 

or:



(11)



Figure 3. Useful energy loss per consumer in the biorefinery service area.

The scale factor  $\alpha$  was found to be approximately 0.7 for biorefineries [25]. Thus for  $D_{opt}$  and  $m_{opt}$ , we have:

$$D_{opt} = 0.73 \left(\frac{c_1}{c_3}\right)^{-0.63} \left(m_1 \rho\right)^{-0.19} \left(c_2 n + c_4\right)^{-0.63}$$
(13)

$$m_{opt} = m_1 \rho D_{opt}^2 \tag{14}$$

or:

$$m_{opt} = 0.53 (\frac{c_1}{c_3})^{-1.26} (m_1 \rho)^{0.62} (c_2 n + c_4)^{-1.26}$$
(15)

From Equations 14 and 15, it follows that the optimal service area decreases with increasing population density and per capita fuel consumption rate. In addition, the optimal biorefinery size grows as  $m_1^{0.62}$  for the per capita fuel consumption rate and as  $\rho^{0.62}$  for the population density. Thus, as population density and per capita fuel consumption increase, we anticipate that biorefinery density and size will also increase.

In summary, we find that the optimal service area of a biorefinery decreases with increasing population density and per capita fuel consumption. This finding is in agreement with previously reported economic analyses [12, 19].

#### Crop sustainability index (CSI)

As soon as biofuel crops began to play a significant economic role, concerns were immediately raised over their possible competition with food crops for arable land and potable water (and thus their potential threat to global food prices), as well as their potential adverse impact on the environment due to increased fertilizer and pesticide use [28]. Following triple-P (Profit, Planet and People) bottom line sustainability accounting principles, we propose a sustainability metric for a biofuel feedstock crop as follows:

$$CSI = s_1 W_0^{-1} + s_2 W_2^{-1} + s_3 P W^{-1} + s_4 C h^{-1} + s_5 J$$
(16)

where *CSI* is the crop sustainability index, *PW* is the potable water used for irrigation, *Ch* are the accumulative tonnage of chemicals introduced to the environment during cultivation, and *J* is the number of new jobs created. Each society may differentially weigh ( $s_1$ - $s_5$ ) the separate factors contributing to the CSI according to its unique set of circumstances.

#### MODULAR MACROALGAE BIOREFINERIES

Modular biorefineries

Previous economic analyses [12, 19], along with the thermodynamic findings reported here, suggest a need for modular biofuel production systems. Distributed modular systems can be centrally manufactured, and are rapidly adoptable due to low technological complexity and modest upfront capital requirements. Here, we report the design of a modular biorefinery based on the marine green macro algae *Ulva sp.* First, we compare marine macro algae with other energy crops. Second, we describe a modular intensive feedstock cultivation system with high biomass yields. Third, we present a sustainable design for an integrated solar-biomass biorefinery that fully supplies the transportation fuel demands of an average-sized town in India.

#### Macro algae as an energy crop

Concerns over net energy balance, land and potable water use, and environmental hazards, question the sustainability of a corn/sugar cane biofuel future [4, 10, 11, 24-27]. While lignocellulosic feedstock alternatives do not directly compete with the food supply, they may not be able to fully address land and potable water use, and environmental hazard concerns. Furthermore, the technology required to release fermentable sugars from lignocellulose remains immature [29].

Macro algae, lacking lignin content and not competing with food crops for arable land or potable water, are leading alternative candidates for future transportation fuel feedstocks [6, 30]. Both developed and developing countries have recently reported efficient conversion of macro algae to transportation fuels [6, 31]. Various green, red and brown macro algae species are under evaluation for inland and off shore cultivation [6, 21, 30]. The macro algae *Ulva sp.* is of particular interest due high growth rates [32, 33].

#### Intensive Ulva sp. cultivation

There are three major approaches to macro algae biomass production. The first is the direct harvest of drifting macro algae from shore. Although the production cost of this approach is low, material availability and composition vary with climate, season, local agricultural effluents, etc., making it unsuitable for continuous fuel production. Extensive and intensive macro algae cultivation (reviewed in [34]) constitute the second and third approaches. While extensive macro algae cultivation does not require mechanical mixing or active fertilization, it yields 3-4 times less than intensive cultivation [35, 36]. Intensive *Ulva sp.* cultivation systems have been previously reported [32, 37]

Yantovski [33] has proposed zero emission electricity generation from land grown *Ulva sp.*, but the extremely large scale of the requisite cultivation areas (~100 km<sup>2</sup> per GW of power) has limited immediate implementation. It is possible with current technology, however, to design and build smaller scale systems for developing economies.

The basic system components include:

- 1) Cultivation.
- 2) Refinery and conversion.
- 3) Energy supply.
- 4) Chemicals supply.
- 5) CO<sub>2</sub> supply.

Recently, a successful development of brown macro algae polysaccharide scarification by an engineered microbe has been reported [6]. Several projects have attempted to decompose *Ulva sp.* to fermentable sugars and biofuel [21, 38].

Achieving intensified biomass yields in on-shore macro algae cultivation ponds requires additional electrical power for mechanical mixing during active photosynthesis [36]. Since this additional power is only required during the day, we propose solar photo-voltaic (PV) systems to generate the required energy, thus integrating solar electrical power generation with intensive macro algae cultivation. Based on previous analyses of distributed desalination systems [16], we suggest a central solar power station to supply electricity to the network of local cultivation facilities and refineries (Figure 4). Thus, modular biorefineries will be integrated into distributed energy networks, with electricity supplied from a large central facility (as proposed by Lorente et al. [16]) and potable water and biofuels produced locally at each biorefinery. An additional assumption made in this model is that it is possible to use waste CO<sub>2</sub> from local industry. Combining CO<sub>2</sub> mitigation with macro algae cultivation has been reported [39]. Fertilization can be achieved through direct fertilizer input, circulating combined aquaculture systems [37, 40], or by circulating fresh sea water with natural nutrients.



**Figure 4.** Modular design of transportation biofuel production. Lorente *et al.* [16] have shown the advantages of centralized electrical power generation with distributed desalination stations to produce drinking water. Here, we show that modular biorefinery liquid biofuel production can be integrated within an analogous network.

Although intensive cultivation demands mixing energy and fertilization, the system leads to controllable, year round production of biomass with constant chemical composition. The macro algae cultivation system proposed here consists of multiple ponds with mixing wheel and fertilization systems. Due to its high efficiency, the relatively low tech system can be manufactured on site in developing countries without sophisticated equipment. The basic system demands appear in Appendix A. We propose the following design of a biorefinery network to supply liquid fuel to coastal communities in developing countries.

#### Model design of a scalable, modular biorefinery that supplies the liquid fuel needs for an average town in coastal India

In 2005, the annual per capita transportation fuel consumption in India was 9.9 L [41]. The population distribution for India appears in Figure 5. Here, we assume that



**Figure 5.** City population histogram for India [42]. The *y*-axis represents the number of cities, town or villages and *x*-axes represents the population size.

economic growth has driven an increase in the annual per capita consumption to 50 L. Table I summarizes the model assumptions. Fuel demand analysis reveals that a single biorefinery should supply  $1.5 \cdot 10^6$  L per year fully cover transportation fuel demand in a coastal town in Gujarat, India.

Table I. Fuel demands for an average town in India.

Population parameters	Coastal India characteristics		
Ν	20,000 person		
Р	300 person/km <sup>2</sup>		
$M_{I}$	50 L gasoline/(person·year)		
М	10 <sup>6</sup> L gasoline/year		

Several projects attempt to decompose Ulva sp. to fermentable sugars and biofuel [21, 38]. Recently, Wargacki et al. [6] reported an engineered microorganism that metabolizes brown macro algae polysaccharides and produces ethanol at a conversion rate of 1: 3.55 (w:w) ethanol: macro algae (DW). Assuming 200  $W/m^2$  solar irradiance, 18 kg Ulva sp D.W./(m<sup>2</sup>·year), and 1:1.5 (v:v) gasoline:ethanol energy equivalence,  $5.3 \cdot 10^3$  ton (DW) of *Ulva sp* is required to provide 100% of transportation fuel demand. Given previously achieved yields of intensive biomass production, a cultivation facility of ~30 ha is required. Ninety percent of the allocated area will be occupied by macro algae ponds and ten percent by roads and supporting buildings. An additional 8 ha are required for supporting Photo-Voltaic panels to provide electricity needed for facility operation. Table II describes the 38 ha  $(0.38 \text{ km}^2)$ facility energy and basic materials inputs. Calculation assumptions appear Appendix A.

 Table II. Basic materials and energy demands. Intensive macro algae cultivation required to supply 100% of the transportation fuel demand of a 20,000 population town in Gujarat, India.

Output	Value	Units	
Biomass	5.3·10 <sup>3</sup>	ton year <sup>-1</sup>	
Input			
Land (total)	38	ha	
Land (solar)	8	ha	
Land (ponds/roads/buildings)	30	ha	
Paddle wheels	138	wheels	
PVC pipes	1.5	km	
Power for farm operation	2.9	MW	
Ammonium sulphate	530	ton year <sup>-1</sup>	
Phosphoric acid	192	ton year <sup>-1</sup>	
CO <sub>2</sub>	$2.8 \cdot 10^3$	ton year <sup>-1</sup>	
Labor	30	operator	

It is important to emphasize the differences between macro algae-based refineries and arable plants. We briefly compare the usage of land, potable water, fertilizers and pesticides in both systems. First, macro algae ponds can be installed on marginal land not otherwise used for food crop cultivation. Second, unlike arable plants, macro algae demand only sea water for cultivation, resolving one of the most serious concerns of biofuel production – competition for drinking water [26]. Finally, macro algae cultivation does not require pesticides. Pimentel et al. [11] have shown that the estimated cost of pesticides on human health is approximately \$1.3B in the U.S. alone. In Table III, we compare the environmental aspects of macro algae biomass with corn and cassava for the production of  $1.5 \cdot 10^6$  L of ethanol per year. From Table III, it is evident that while having higher fertilizer demands, macro algae feedstocks may require an order of magnitude less land, do not require potable water, and have a near zero pesticide/herbicide footprint.

Table III. Feedstock environmental footprint comparison.Feedstock required to supply  $1.5 \cdot 10^6$  L ethanol per year.

	Com mains	Cassava	Maara Alaaa
	Corn grains [26, 27, 43]	Fresh roots [27, 44, 45]	Macro Algae (Ulva sp., DW)
Starting material (ton)	$4 \cdot 10^{3}$	$3.75 \cdot 10^3$	$5.3 \cdot 10^3$
Kg Biomass/L ethanol	2.69	6.6	2.57
Biomass yield (ton ha <sup>-1</sup> year <sup>-1</sup> )	8.9	40	15
Land ha	453	250	38
Potable water (ton)	$4.3 \cdot 10^{6}$	1.8·10 <sup>5</sup>	-
Fertilizers (NPK) (ton)	133	112	723
Lime	498	500	-
Pesticide/Herbi cide (ton)	4.5	0.5	-

#### CURRENT RESEARCH AND DEVELOPMENT NEEDS

There is urgent need for the biofuel sector to get estimate on energy expenses for feedstock collection, transportation and final product distribution. Currently, there is a rule of thumb that ~25 miles is the optimal size of area for feedstock collection. Thermodynamic and economic studies are needed to find the optimal collection distances as a function of local fuel demand and conversion technologies. Very few studies comparing the efficiency of biorefineries at different scales are available. These studies are essential for better future design.

Due to the yields and sustainability advantages measured in use of land, potable water and chemicals, macro algae are an excellent feedstock for transportation biofuels. However, their cultivation and decomposition technologies require further improvement. Recent reports on engineered microbes which digest the majority of brown macro algae polysaccharides have shown that macro algae are a practical and available feedstock for biofuels. Green macro algae (Ulva sp.) have an enormous advantage in higher growth rates. We believe that modern synthetic biology and molecular engineering approaches can lead to low cost biological methods for the decomposition of Ulva to fermentable sugars.

Finally, a great challenge for any new technology is field implementation. Bringing new energy technologies to rural communities in developing countries has economic and social challenges. Specific policy development and the integration of distributed biorefineries in to coastal community business networks will be required. The implementation of initial pilot facilities will significantly reduce barriers to entry as well as and train personal.

#### CONCLUSIONS

In this work, we analyzed the optimal size of biorefineries. Our model, based on basic thermodynamic balance, suggests that the optimal scale and service area of a biorefinery depends upon per capita transportation fuel consumption, population density, and the land area allocated to energy crops. We find that the serviced area size will decrease with economic growth. This finding led us to propose macro algae-based modular biorefineries to serve local communities in developing countries.

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Appendix A Table 1A. Basic Parameters for intensive Ulva sp. cultivation assumed in this model

assumed in this model		
Yield	Value	Units
Solar irradiance	200	W m <sup>-2</sup>
Biomass (D.W.)	18	kg (DW) m <sup>-2</sup>
DW .: wet weight	1:4.5	
Construction		
Pond:total allocated area	0.9:1	
PVC Pipes	1	$m/(200 m^2 pond)$
Paddle wheels	1	wheel/(200 m <sup>2</sup> pond)
Chemicals		
Ammonium Sulphate	10	g/(kg DW biomass)
Phosphoric Acid	3.6	g/(kg DW biomass)
$CO_2$	0.53	kg/(kg DW biomass)
Electricity		
Power for mechanical mixing	0.1	kWh/(10 hr operating per day)
Power for ethanol processing	0.5	kWh/(L ethanol)
Solar PV conversion efficiency	20	%
Labor		
Operator	0.2	operator/pond