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Commercial Development of Bio-Combustible Fuels from Hydrothermal Liquefaction of Waste using Solar Collectors

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Abstract. Current methods to improve the viability of microalgae based biofuel production depend on improved microalgae strains, biorefinery concepts and identification of higher value applications such as cosmetics and nutraceuticals. Despite such efforts, the energy inputs into the microalgae conversion process remain high. The technical approach presented is to design, deploy and field test an integrated set-up of Concentrated Solar Power and Hydrothermal Liquefaction systems to produce bio-oil and evaluate the production and conversion processes. Phycofeeds' approach is to integrate CSP and HTL technologies into the conversion process to improve the energy efficiency and the economic case for scaling microalgae based biofuel production. Further sustainability enhancements are achieved by integrating wastewater feedstock and market integration of output by-products for the aquaculture feed industry. This paper presents the microalgae harvesting and HTL bio-oil formation analysis procedures on a pre-pilot field scale. Solar concentrating captors are described and theoretical values obtained prior to experimental work that will be carried out in India.

INTRODUCTION

In order to respond to an increase in energy demand, biofuels are being considered to complement fossil fuels. Third generation renewable liquid biofuels derived from waste and microalgae could potentially supplement incremental global energy demand. Microalgae grow rapidly and produce energy dense lipids. They are able to utilise marine, freshwater and wastewater, to grow on non-agricultural land and remediate wastes and atmospheric carbon dioxide. Microalgae biomass feedstock for HTL bio-oil production benefits from reduced energy requirements for complete dewatering [1–20].

This project provides alternative biofuel using waste feedstocks by integrating CSP and nutrient recycling. Solar heat and pressure convert feedstock into liquid bio-combustible fuels. Post-reactant water-soluble by-products contain nitrate, ammonia and phosphate which are recycled into algal production ponds for aquaculture feed markets. Three technologies are integrated: Concentrating Solar Power (CSP), Hydrothermal Liquefaction (HTL) and waste remediation to convert waste and algae feedstock into biofuel and higher value co-products.

Solar Integrated Hydrothermal Liquefaction

Hydrothermal Liquefaction (HTL) is a biomass transformation process that can occur between 280-370°C and 10-25 MPa. There are unique physio-chemical properties of sub-critical and super critical water at these temperatures and pressures, which produce water and bio-oils as the main products. The dielectric constant decreases from 78.5 Fm-1 at 25°C and 0.1 MPa to 14.07 Fm-1 at 350°C and 25 MPa [1] (comparable to some polar organic solvents at normal conditions, e.g. acetone and ethanol) so the solubility of hydrophobic organic compounds

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in subcritical water is increased [2]. A Techno-economic analysis of solar integrated HTL of microalgae using solar parabolic trough hypothesized that microalgae biofuel could be produced with a minimum fuel sales price of $1.23/kg [3]. This project will field test the operational parameters of the integration of this multi-disciplinary research proposition. Figure 1 shows the integration concept of the parabolic trough and the aligned orientation of the HTL reaction vessel [3].

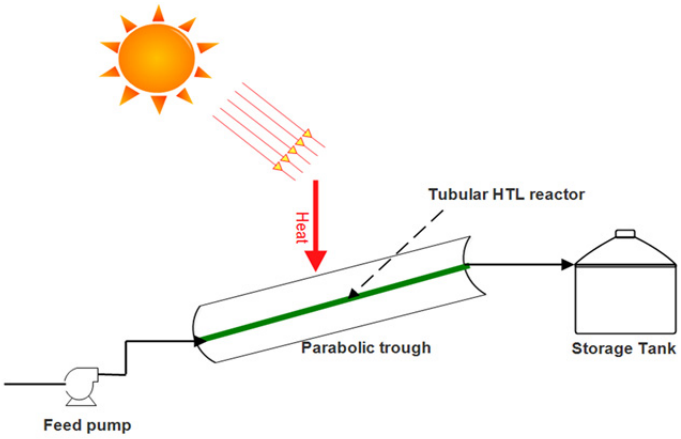

FIGURE 1. CSP Parabolic trough integrated with solar receiver as the tubular HTL reaction core [3]

Feedstock Materials

Different product constituents of feedstock materials show the general trend for biofuel product formation Lipids >Protein>Carbohydrates [4]. Swine manure conversion into biofuel had only a moderately lower yield (30.2%) than *Spirulina* microalgae (32.6%) [5]. HTL has also been used with lignite, wheat straw, coal and poly-ethylene terephthalate fractions [6]. The energetics of the HTL process are dominated by the energy required to heat the reactor, 6.51 MJ (kg microalgae)$^{-1}$[7]. As multiple carbon containing feedstock materials could viably be used in HTL, a reduction in the economic cost of choice of feedstock material, combined with the provision of solar heat for efficient conversion could decrease the minimum fuel sales price further, potentially closer to cost parity with conventional fossil fuels. Attainment of a suitable processing temperature is essential for product formation.

Table 1 describes the appearance and physical characteristics of the reactant products biofuel and solid residue "raw oil" [8].

TABLE 1. Appearance of raw oil products from different temperatures [8]

Reaction Temperature °C	Raw oil product appearance	Carbon recovery in biofuel
< 180	Green algal cake	<5%
180-200	Black solid, looking like a bio-char product	3 – 43%
200-240	High viscosity asphalt/bitumen-like product	3 – 43%
240-300	Self-separating, flow-able oil phase on the top of the aqueous phase	40 – 55%

Liquid bio-oil or bio-crude is a complex mixture of oxygenated hydrocarbons. Biomass thermo-treated via HTL directly converts biomass into liquid bio-oil, avoiding pre-steps of drying and oil extraction. The processing pathway of HTL is particularly applicable to wet biomass feedstocks, such as microalgae, which reduces the necessity for additional drying energy of the feedstock prior to processing, as required in alternative thermochemical conversion processes [9]. Temperature is the most influencing parameter for conversion of biomass into liquid biofuel, a temperature range of between 300-330°C is advisable for cellulose, hemicelluloses, grasses and algae [10].

A further benefit of HTL is that it destroys any pathogenic or any other potential contaminating organisms which may have been present during the non-axenic batch culture of microalgae and/or waste feedstocks. Yield of bio-oil was greater than the amount of lipid FAME present in the microalgae biomass, suggesting that bio-oil yield was incremented from protein hydrolysis [11]. Previous research has compared HTL of both high protein and highly

oleaginous microalgae species. *Nannochloropsis salina,* an oleaginous microalgae and *Spirulina platensis,* a protein rich species. Both have a protein content of around 50%, yet post-HTL, bio-oil yields are near 40% for both species, indicating that species-nascent oil content is not the prevailing factor for HTL conversion to bio-oil. Rather, it was concluded that HTL bio-oil yield was more determined by the growth rate of the species than by the protein, lipid and oil composition of the algae [12]. Volumetrically at 80-90%, water is the major component of HTL reactants. With substantial dissolved carbon in the form of organic compounds, much of this carbon is available for recycling into successive batches of microalgae culture. *Botryococcus braunii* liquefaction by HTL at 300˚C and 10MPa in the presence of sodium carbonate yielded 57-64% oil with a calorific value of 45.9 MJ/kg, close to that of petrodiesel [13]. Similarly, *Dunaliella tertiolecta* with a 78.4% water content using HTL at 340˚C and 10MPa in H_2 for 60 min yielded 35-37% oil with an energy density of 35-36 MJ/kg^{-1} [14]. Key issues for future R&D of microalgae biofuels include both the utilisation of co-products and development of energy efficient thermo-conversion processes [15]. Parameters affecting product yield of HTL derived bio-oil include microalgae species, feed ratio of solids to liquid, reaction temperature, holding time, heating rate, cooling rate, presence of catalysts and effective product separation [12]. Microalgae biomass of concentration 10-20% (w/v) is optimal for HTL boundaries of solids loading [16].

Market Potential

The proposed technique addresses the need for cost-effective biofuel production from waste and microalgae using solar renewable energy. The primary product is biofuels – obtained by converting waste and microalgae into bio-crude and then into biofuels. The secondary product is a nutrient rich water by-product, with nitrate, phosphate and carbon, as well as other minor constituents, for use as a nutrient feedstock for microalgae growth – for direct feed applications or as a secondary feedstock into the animal feed sector.

The market value for bio-oil aligns with conventional crude oil prices of USD $500/ton or USD $70/barrel, while the market price of microalgae as a feedstock is in the region of USD $1200/ton. Incremental added value is attained from product development that includes fish feed formulation and integrated aquaculture. The first major segment targeted by Phycofeeds is biofuels whose global market is valued at USD $168 billion in 2016 and expected to reach USD $246 billion by 2024, at 4.9% CAGR [17]. Within the EEA, the market is expected to reach €30 billion (USD $33 billion) in 2020, based on its use in the transport sector and projected price developments [18].

The next segment targeted is feed for aquaculture, from microalgae produced as a co-product from the Phycofeeds process. The global aquafeed market is set to grow to USD $155 billion by 2022, with CAGR of 13.2%. The Asia-Pacific region has the highest projected growth rates, of which China and Indonesia account for more than 75% [19]. A conservative 5% penetration of this market with aquafeed from bio-sources puts the market size for such products at $7.8 billion globally. Further refinement of the Phycofeeds production process and additional capabilities in downstream processing expands the scope of the market applications into high value chemicals and nutraceuticals.

EXPERIMENTAL EQUIPMENT AND EXPERIMENTS

Prior to developing the full-scale prototype solar receiver, a small-scale pressure vessel was built and used to evaluate bio-oil and by-products produced from various components.

Small Scale Reactor Pressure Vessel Experiments

A 10 ml stainless steel Swagelok reactor pressure vessel was immersed in a heated sand bath. The pressure tube was ½-inch Hoke Gyrolock (SS 316 grade), 170 mm in length with an inner diameter of 10.28 mm. According to the manufacturer, the design temperature range of the material is between (-235˚C to +426˚C). The insulated ceramic hot plate with a basal heat source attained a maximum temperature of 450˚C [20, 21]. Microalgae samples analysed included *Chlorella vulgaris*, *Chlorella salina*, *Nannochloropsis salina* and *Tetraselmis chui*. These species were chosen for being oleaginous, representative of both seawater and freshwater and with a previous research focus directed towards microalgae biofuels. Microalgae stock culture volumetric availability and the logistical timing of experimentation also influenced the decision of which species to investigate for the effect of harvesting processes on lipid profile.

The batch reactor was loaded at 20% (w/v) with 1.8 g of dried microalgae biomass and 9 ml of de-ionised water and sealed. 20% (w/v) proportion has been used by other author's in microalgae HTL experiments [16]. On

attainment of 280˚C the batch reactor was quickly introduced for 20 min for HTL to occur. Post-HTL, the reactor vessel was quenched in a water bucket. On return to room temperature, gases were vented and liquids retained for Gas Chromatography (GC) and Total Organic Carbon (TOC) analysis.

The data analysis showed chromatogram peak values from Gas Chromatography (GC) analysis of Fatty Acid Methyl Esthers (FAME) 37 Supelco® standard lipids between C6 and C24 were quantified using area normalisation by Shimadzu® lab solutions software. Known peaks correlating to the FAME mix standard were quantified as total lipid percentage FAME, unclassified peaks were grouped as other unknown lipids.

Solar Captors and Central Receiver

The type of solar captors selected for this project are shown in Figure 2.

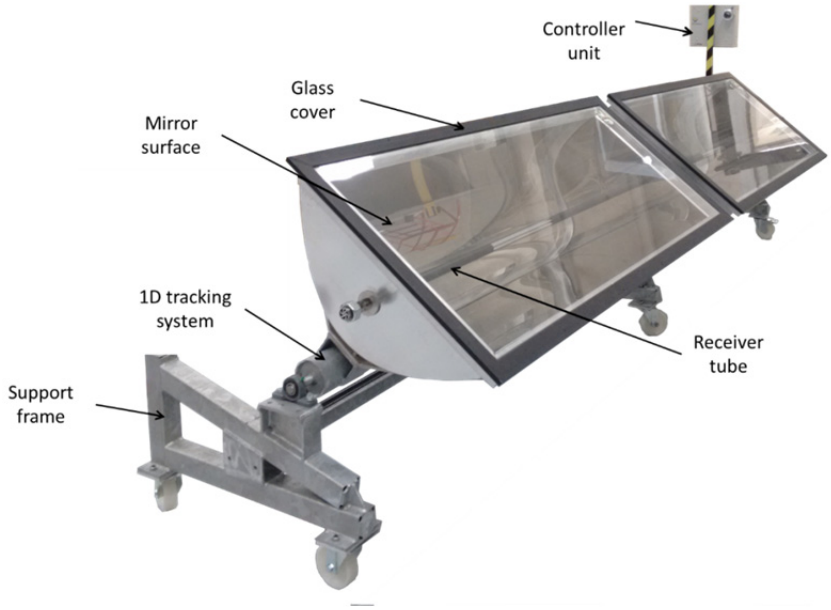

FIGURE 2. Solar collectors - Global CSP Ltd

These collectors are designed and manufactured by Global CSP Ltd (UK). Compared to commercial parabolic troughs, these smaller versions are aimed at either individual users or community scale energy demands. They have a manually controlled single axis tracking capability. The reflective surface has a parabolic shape with a focal length of 120mm. The captor aperture dimensions are 690 mm and 1960 mm width and length respectively. The original receiver is 32 mm diameter stainless steel black painted tube with a 2mm wall thickness. A glass cover is placed on top of the captor to protect the reflective surface. Cleaning the glass cover surface of the captor alone reduces any possible scratches on the receiver and optical surfaces. These captors are installed in Kota University (Rajasthan, India) for outdoor testing and performance evaluation.

New receiver tubes had to be designed in order to handle the high pressures and temperatures necessary for bio-oil production as previously mentioned. Each new receiver tube is made of stainless steel material with pressure valves and innovative internal arrangements. These pressure vessels configurations are currently being evaluated using Ansys FEA software and outdoor tests will then be carried out in India. Data collected such as weather conditions, DNI and temperatures, will be compared to the theoretical model.

Following on from the culmination of the 2017 Indian monsoon, different raw material mixtures comprising algae, PET plastic, sugar cane bagasse and animal manure will be pumped into the receiver and tested. Once temperature is reached and maintained for a minimum of 30 mins, the obtained mixture will be extracted into a tank. Series of experiments will be carried out such as heating, cooling and reactant retention times to confirm post-reactant content of bio-oil and by-products. A more dedicated tracking system will also be implemented to facilitate heliostat tracking accuracy.

RESULTS AND DISCUSSION

Bio-oil Evaluation

A prominence of C14-C15, C16-C17 and C20 lipids were detected across all microalgae groups. Bio-oil via HTL has a range of chemical reactions re-polymerising hydrocarbon complexes. Lipid fractions and other chemical compounds distinct from those in FAME 37 are formed. Such compounds cannot be quantified because their associated peaks were at different retention times to the FAME 37 standard, as also commonly comprised in a homogenous mixture of crude oil analysed by GC. Consequently, these peaks were therefore grouped together as unclassified lipids. Area normalisation was chosen for quantification purposes rather than the inclusion of an internal standard, because of the high composition of unknown lipids in the sample profiles. Figure 3 shows the GC peaks of major lipids in comparison to direct microalgae oil extraction FAME.

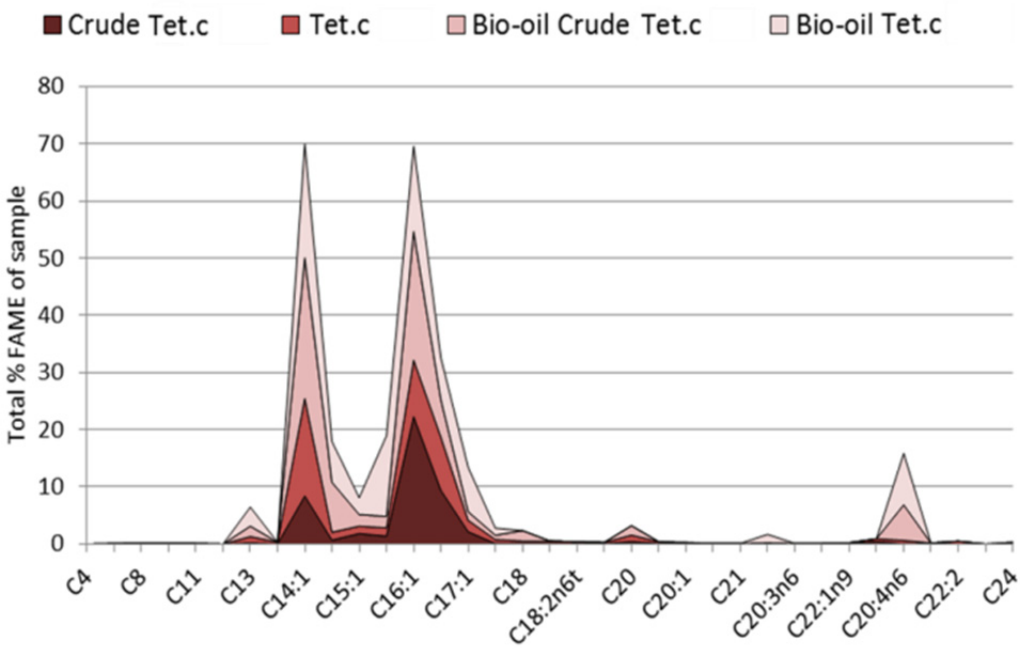

FIGURE 3. Total % FAME of crude *Tetraselmis* centrifuged & freeze dried *Tetraselmis*, harvested oils and HTL Bio-oils

Pressure Vessel – Temperatures and Pressures

HTL requires to attain temperatures in the range of 300˚C and pressures of 15-20 MPa [1]. This pressure is achieved by heating unpressurised water in a pressure proof vessel to 300˚C. No additional pre-pumping or pre-pressurisation is required. Figure 3 shows the experimental comparison between pressure and temperature in a 250 ml lab-scale HTL pressure vessel (Parr Instrument Company) with 100 ml of water.

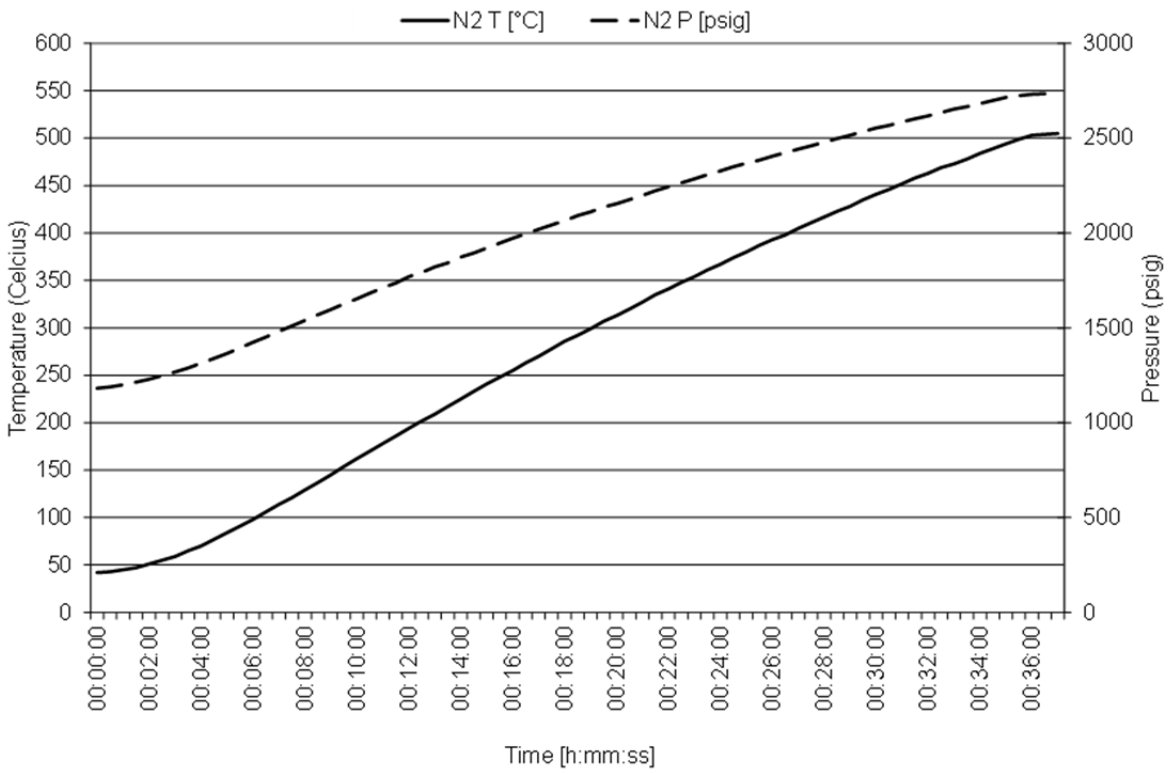

FIGURE 4. Pressure vessel – Temperatures versus pressures

The pressure vessel supported pressures up to 465˚C before attainment of pressure limit threshold, corresponding to 4650 psig (32 MPa). Therefore, the range of pressures and temperatures required for HTL of microalgae biomass is well within the specifications of this manufactured pressure vessel. Heat applied to a self-contained pressure vessel alone is the requirement for HTL reaction kinetics. Therefore, integrated energy processing technologies using CSP offers a viable solution to attain required temperatures. CSP parabolic receivers normally containing a heat transfer fluid (HTF) such as water or oil can be replaced with a mixture of feedstock and water. The most important characteristics of HTF are specific heat capacity, density, corrosivity, viscosity, freezing temperature and thermal stability [22].

Solar Irradiance and Environment

Using data available from a prior paper which investigated the feasibility of CSP and bio-oil production [3], the amount of time required to heat up one batch of feedstock was calculated. The main CSP solar collector operational parameters are combined in Table 2.

TABLE 2. CSP solar collector operational parameters.

Description	Experimental system	Units
Direct Normal Irradiance (DNI)	750	W/m^2
Total heat absorbed by the reacting fluid (after losses)	462	W/ m^2
Solar collector area	1.35	m^2
Power input (after losses)	623.7	W
Heat required to attain 350 °C	1.886×10^6	J
Mass of feedstock	1.57	kg
Time required to attain 350 °C (feedstock)	51	min
Mass of receiver	2.7	kg
Time required to attain 350 °C (including receiver)	137	min

The value of Direct Normal Irradiance (DNI) of 750 W/m^2 is a conservative number, representative of locations with high concentrations of direct sunlight on an average basis (e.g. desert regions of North Africa, the Middle East, and the Americas).

With mass m = 1.57 kg of feedstock within the reactor tube, the heat required to heat the mixture up by 350 °C would be 1.886×10^6 J. This assumes a specific heat of 3640 J/kg K (based on values of 4200 J/kg K for water and 1400 J/kg K for biomass in water, and a mixture containing 20% biomass in water). The ambient temperature is assumed to be 20 °C. Therefore, it would take $1.886 \times 10^6/623.7$ s, or 51 min to provide the heat necessary to raise the temperature by 350 °C. With a metal receiver tube, the additional mass to heat is 2.5kg and heating time is expected to rise by an additional 1.4h. The feedstock temperature needs to be maintained at 350 °C for a minimum of 30 min then the mixture is pumped into a tank to cool down.

CONCLUSIONS

This paper highlights bio-oil production at a field scale level from different waste feedstocks. Using direct solar radiation technology, such as a solar captor, heat provision and pressure is sufficient for the thermo-conversion of biomass and waste into liquid bio-oil and nutrient-rich aqueous waste outputs. This results in significant cost savings in the biofuel conversion process. The integration of wastewater treatment with algal biomass production processes increases the potential to be even more cost effective.

In this early phase and with small scale production volumes, this project focuses on demonstrating scaling up of the process from a lab-scale pressure vessel to dedicated large receiver tubes. The design of the receiver tube, integrated as part of the solar captor, should have a positive impact on cost and complexity of the overall process.

Such system could help to reduce reliance on fossil fuels through developing an integrated approach to producing biofuels from waste and microalgae sources, leading to lower emissions and carbon mitigation. An added benefit is the use of wastewater in the biofuel production process. By using microalgae, there is the potential to improve energy supply security and move away from the food versus fuel debate surrounding the use of agricultural land for biofuels.

An assessment of the revenue generating potential of Phycofeeds and licensing of larger scaled technology worldwide will be carried out based on production rate from field test results. This technology has scope to significantly improve general public household waste recycling through the availability of biofuels and aquafeeds. The primary target markets are countries that are closer to the equator (i.e. Asia, Southern Europe) with high levels of solar energy. The production of bio-oil to be used as feedstock for bio-fuel production in rural communities will help improve local energy access. For a full-scale system, the location of waste nutrients, ponds, solar collectors and bio-oil remediation technologies, in close proximity to each other, will reduce both transportation costs and the complexity of commercial equipment layout.

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