CHAPTER 6

LIFE CYCLE ASSESSMENT OF MICROALGAE GREEN DIESEL PRODUCTION SYSTEM

6.1.Introduction

This sixth chapter, based on the value chain and various agronomical practices and the techniques of green diesel production as reviewed in Chapter 4, will aim to find out if the net energy balance can further be increased by using a combination of many available agronomical practices and the techniques of green diesel production from microalgae. It also talks about the cost economics of the best route.

Many viability studies, with net energy balance (NEB) or net energy ratio (NER) as the viability indicator, have already been carried out for the production of green diesel i.e. biodiesel or liquid fuel from microalgae. Most of the studies have found very low or even negative values for net energy balance. Moreover, the one with very low values for net energy balance have not included energy inputs from most of the important activities. Many have not included the entire value chain, and the others have considered only a few of many available ways and techniques of green diesel production from microalgae. Net energy ratio depends on the type of techniques used for cultivation, harvesting and oil processing (conversion). Considering the same, the current study aims to find out if the net energy balance can further be increased by using a combination of many available agronomical practices and the techniques of production from microalgae.

6.2. Life Cycle Energy Balance

6.2.1. Goal, scope and system boundaries

Every activity involved in the production of biofuels from microalgae is energy intensive, and also produces green house gases. Many viability studies, with net energy balance (difference of energy input and energy output) or net energy ratio (ratio of energy output to energy input) as the viability indicator, have already been attempted for the production of liquid fuels from microalgae [86, 81]. Most of the studies have found very low [81] or even negative values [84, 82] for net energy balance.

Many have not included the entire value chain [86], and the others have considered only a few of many available methods and techniques of biofuel production from microalgae [81, 84, 82].

Net energy ratio depends on the type of techniques used for cultivation, harvesting and oil processing (conversion) [220]. Considering the same, the current study aims to find out if the net energy balance can further be increased by using a combination of many available agronomical practices and the techniques of biofuel production from microalgae.

The functional unit of the study is one hectare. Figure 6.1 shows the system boundary with various possible combinations and routes for green diesel production from microalgae. Energy requirements for items with many years of useful life have not been included in the study.

A. Open pond description

The design specifications of the raceway ponds considered for the current study comprise 10 units of open ponds, each 100 m long, 10 m wide and 30 cm in depth.

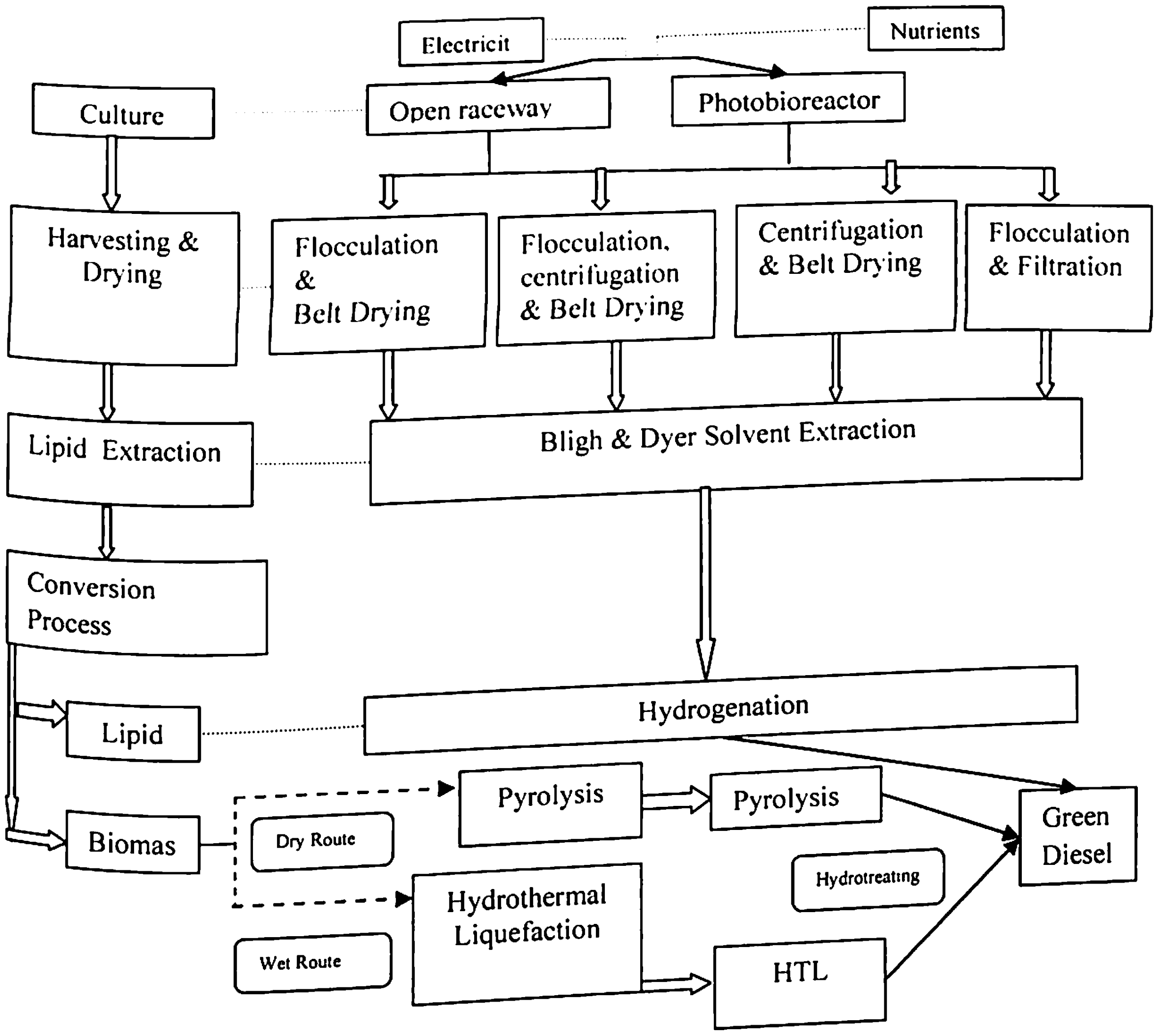

Figure6. 1: System boundary, showing the various possible combinations and routes for green diesel production from Microalgae

B. Photobioreactor description

Flat -plate airlift photobioreactors have been considered for the current study. Two cases have been considered:

Case 1: The design specifications comprise of 20 flat reactors each with 105 units. Each unit is 4.53 m long, 1 m high and 10 cm thick. Reactors are 1 m apart from each other to avoid shading. A part of the light energy required for illumination was from sunlight and rest from the fluorescent tubes on both sides of the reactors.

Case 2: The design specifications comprise 39 flat reactors each with 105 units. Each unit is 4.53 m long, 1 m high and 10 cm thick. The reactors were illuminated on both the sides using fluorescent tubes.

The culture conditions for flat plate reactors were kept similar to that by Pruvost et al, 2011 [70]. For all reactors the temperature was controlled at 25 °C and pH was set at 7.5 by air and CO_2 injections. The incident photon flux density was 270 μmole $m^{-2}s^{-1}$. The number of fluorescent tubes was adjusted accordingly to provide the required photon flux density. In addition, algae were grown under stressful condition of nitrogen depletion, which increased the total lipid content from 20% to 23%.

6.2.2. Microalgae (*Chlorella vulgaris*)

Chlorella vulgaris is a freshwater species, and is also known for lipid accumulation [70]. Chlorella is a single celled, spherical non-motile green alga 2.0–10.0 μm in diameter. Chlorella occurs in both fresh and marine water. Due to its occurrence in various different habitats it is also called ubiquitous [60].

According to various studies on *Chlorella vulgaris*, it is an ideal microalga for the production of biodiesel. The features which make it an ideal strain for biodiesel production are [235]:

1. Saturated fatty acids which give biodiesel good cetane number and high oxidation stability.
2. Contains palmitic and stearic acid, which are most common fatty acid contents of biodiesel.
3. Length of hydrocarbon chain is between C10 and C18.

4. Has good biomass productivity.

Moreover, it has been significantly studied and quantitative estimates of productivities and composition in various conditions are available.

6.2.3. Methodology

Life cycle assessment (LCA) has been used to calculate energy balance and green house gas emissions from the energy use for microalgae (*Chlorella vulgaris*) based biofuel (Biodiesel and biogas) production and their uses in the internal combustion engine for transportation. In LCA, a product is followed from its cradle to grave. Natural resource use and pollutant emission are described in quantitative terms [85]. This study includes all the major activities and various inputs/outputs in every stage of microalgae green diesel production. The whole life cycle of *Chlorella vulgaris* has been divided into four major stages:

a. Microalgae culture & harvesting
b. Oil extraction
c. Oil & Biomass residue processing
d. End combustion of green diesel

Since microalgae biofuel industry is still in infancy, data on large scale algae production is lacking. For accurate LCA study large scale production data is required. Therefore, laboratory data has been extrapolated to meet the requirements of the current study.

6.2.3.1. Method of data collection

Laboratory observations and published data of known industrial processes have been used and extrapolated.

6.2.3.2. Assumptions

a. Only CO_2 emissions from fossil fuel electricity and fertilizer use have been considered. While N_2O emissions have only been considered from fertilizer use.

b. According to Indian centre for science and environment in 2007–2008, 78% of India's urea production came from natural gas as the feedstock and rest from fuel oil and naphtha contributing 11% each [211]. Since the maximum urea in India is produced from natural gas, so have assumed 100% urea production from natural gas.

c. Electricity production has been assumed to be from 100% fossil fuel fired power plants in India. Fossil fuel share in electricity generation in India is 64%. Coal is by far the most important fuel source for power generation, with 52% of electricity generated in coal-fired power plants and rest from natural gas (11%), oil (1%), hydro (23%), nuclear (3%), and renewable (10%) [212].

d. Per kWh of only the direct electricity use, has been made equivalent to 10.69 MJ.

e. Considering that sulphur is produced as a byproduct in petroleum and steel industry [236], accordingly, specific energy consumption for sulphur as a component in Aluminium sulphate has not been considered.

f. As CO_2 is formed as a by-product during electrical power generation [237], and the same has been used to provide CO_2 requirements of the microalgae during its culture in the current study, therefore, specific energy consumption for CO_2 production has not been considered.

g. Initial temperature of biomass and water has been considered to be at 20 °C.

h. Specific heat of microalgae has been considered to be the same as that of cellulose, because it is the main component of plant cell wall [222].

i. Energy required for maintaining high pressure in certain processes has not been considered.

j. 98% solvent recovery after Bligh and Dyer process has been assumed.

k. Hydrogenation is a part of hydrotreating, therefore, the energy consumption for hydrogenation has been assumed to be same as that for hydrotreating.

l. The heating value of HTL is twice to that of pyrolysis oil. Therefore, it has been assumed that the amount of hydrogen required to upgrade per kg of HTL will be half as that required for pyrolysis oil upgradation.

m. Offgas contains 80% of propane [213], therefore, the calorific value of offgas was assumed to that of propane.

6.2.4. Calculations and study parameters

The various study parameters considered are given in Table 6.1 and calculation methods are shown in Table 6.2.

Table6. 1: Various parameters considered for study

Parameters	Value	Unit	References
Average energy consumed per Mton of fertilizer produced in India (Nitrogen and phosphorous fertilizer)	34.20	GJ/Mton of fertilizer	[216]
Fossil fuel energy per 1 kWh electricity, considering the conversion efficiency	10.69	MJ	[31]
Specific energy consumption of Indian Aluminium industry	85	GJ/MT	[238]

Parameters	**Value**	**Unit**	**References**
CO_2 emission from electricity	980	gCO_2/kWh of electricity produced	[212]
Energy required for CO_2 injection , from a power plant 100 km away	22.2	kWh/ton of CO_2	[237]
Amount of Aluminium sulphate required for flocculation	25 (8.55)	mmol L^{-1}(g/L)	[239]
Energy consumption for pumping water	0.05	kWh/m^3 of water pumped	[240]
Average annual evaporation losses	2.25	m	[241]
Energy required to process 1m^3 of culture during air sparging assisted coagulation flocculation (ASACF)	8.35	kJ	[84]
Energy consumed by Belt dryer per kg of evaporated water	3.35	MJ	[82]
Specific heat of cellulose	1.5	$J°C^{-1}g^{-1}$	[222]
Heating value of Bio-oil	17	MJ/kg	[232]
Specific latent heat of vaporization of chloroform	247	kJ/kg	[242]
Specific latent heat of vaporization of methanol	1100	kJ/kg	[243]
Energy consumed in Hydrogen production	50.9	kWh/kg of Hydrogen	[220]
Density of hydrogen at NTP	0.0899	Kg/m^3	[223]
Hydrogen required for hydrotreatment /kg pyrolysis oil	400	NL(normal litre)	[224]
Hydrogen required for hydrogenation/kg algal oil	1.5	wt% of algae oil	[213]
Average energy consumed in hydrotreating/hydrogenation process	0.32	kWh/kg of oil processed	[220]
Lower heating value of Hydrogenated oil (LHV)	44	MJ/kg of hydrogenated oil	[113]

Parameters	**Value**	**Unit**	**References**
Approx enthalpy of water at 350 °C and at 207 bar pressure	2540	kJ/kg	Steam table
Density of chloroform	1.48	g/cm^3	
Density of methanol	791.8	Kg/m3	
1 MMBTU of natural gas	1.055	GJ	[244]
Power required by raceway pond for mixing	4	W/m^3	[86]
Specific heat of water at 20 °C	4.182 kJ/kg °C	kJ/kg °C	[245]
Power required by Flat-plate air reactor for mixing	53	W/m^3	[246]
Average sunshine hours/year in India	2750	Hours/year	[247]
% DW obtained after centrifugation	16	% DW	[240]
The concentration of the harvested culture after 19 hrs of gravitational settling of flocculated microalgae culture	40	times	[239]
Heating value of gas obtained during pyrolysis and liquefaction	12	MJ/kg	[221]
Calorific value of Naphtha	10500	kCal/kg	[219]
Calorific value of Propane	10792777.3	kCal/ton	[225]

Table6. 2: Various calculation methods

Parameters	**Calculation methods**
Calculation for CO_2 emissions Hydrogenated oil	Hydrogenated oil have following chemical structure C_nH_{2n+2} [113], which gave 0.75 kg of carbon/kg of hydrogenated oil CO_2 emission = Fuel combusted * carbon content coefficient * Fraction oxidized* (44/12) Where 44 is molecular weight of CO_2 and 12 is molecular weight of carbon. If we consider fraction oxidized = 1 [As per IPCC, 2006 guidelines [248]] CO_2 emission from 1 kg of Hydrogenated oil = 1*0.75*1*(44/12) =2.75 kg of CO_2

<table>
<tr><th>Parameter</th><th>Calculation method</th></tr>
<tr><td>Calculations for direct N_2O emissions from fertilizer uses</td><td>N_2O emission = Fertilizer consumption * Emission coefficient

Emission Coefficient = 17.68 kg/ton of fertilizer consumed [227].</td></tr>
<tr><td>NEB and NER calculation</td><td>NEB = Total Energy Output - Total Energy Input
NER = Total Energy Output/Total Energy Input</td></tr>
<tr><td>CO_2 emission from DAP</td><td>The share of various feedstocks used to produce fertilizer in India is. Natural gas: Naphtha: Fuel oil: External ammonia is 50:25:10:15 [215]. And therefore, for CO_2 emissions from DAP use, individual CO_2 emissions of each feedstock has been calculated based on their share and data given in reference number [215]</td></tr>
<tr><td>Light energy supplied to the flat-plate reactors</td><td>Energy (W) = 0.2176* Incident light Intensity (μmole m^{-2} s^{-1})* Surface area (m^2) [249]</td></tr>
<tr><td>Electricity consumption by heat exchanger</td><td>Average temperature in the four seasons of India [250]:
<table>
<tr><th>Season</th><th>Months</th><th>Total number of Days</th><th>Average temperature (°C)</th></tr>
<tr><td>Winter</td><td>December to March</td><td>121</td><td>22</td></tr>
<tr><td>Summer</td><td>April to June</td><td>91</td><td>36</td></tr>
<tr><td>Monsoon</td><td>July to September</td><td>92</td><td>29</td></tr>
<tr><td>Post-monsoon</td><td>October to November</td><td>61</td><td>26</td></tr>
</table>
To simplify the calculation, the increased or decreased temperature of the flat-plate photobioreactors has been assumed to be the same as that of the atmospheric temperature.
Power (heat load) consumed by heat exchanger (both for heating and cooling) for temperature control in order to maintain culture temperature at 25°C [245]
Power (kW) = Mass flow (kg/s)*Specific heat (KJ/kg/°C) *Difference between inlet and outlet temperatures on one side (°C).
The amount of electricity consumed can further be calculated by multiplying the power with the number of working hours of heat exchanger.</td></tr>
<tr><td>Energy use by centrifuge [240]</td><td>Energy (kWh) = [Dry weight of microalgae to be processed (kg)* Power consumed by centrifuge (kW)]/ [Concentration of the algae culture (kg m^{-3}) * Throughput capacity of the centrifuge (m^3 h^{-1})]

For the current study, the specifications considered for the centrifuge were same as that by Xu et al, i.e. throughput capacity of 85 m^3 h^{-1} and motor power of 45 kW</td></tr>
</table>

Parameter	Calculation method
Energy required for Pyrolysis	Energy for pyrolysis (J/g) =Specific heat of biomass* (temperature rise in biomass)* amount of biomass
Heating value of char [228]	The experimental results have demonstrated that heating value of char increases with increase in temperature. HHV = 0.0069T + 24.68 [MJ/kg] Heating value of char produced at around 500 °C was estimated to be 28 MJ/kg.
Energy required for heating the microalgal culture up to the reaction temperature of 350 °C	Energy = Mass of water (kg) * (Enthalpy of water at 350 °C and pressure of 3000 psi - enthalpy of water at 20 °C) + Algal biomass (kg) *Specific heat of algal biomass*(350°C-20°C).

6.2.5. Microalgae culture & Harvesting

A. Microalgae culture

Based on the reactor types and configuration considered for the present study, Table 6.3 shows the biomass production over 5 years. The biomass concentration for raceway pond was assumed to be 0.5 kg/m^3 [83] while for flat-plate photobioreactor it was assumed to be 1.9 [70]. Dilution rate for raceway pond was assumed to be 0.1 d^{-1} [86]. The specific growth rate for flat-plate photobioreactor was calculated with the help of the equation (6.1) [71] and values for the various variables were taken from the work done by Pruvost et al, 2011 [70].

$$\mu = 1/t \ln [X_m/X_0] \quad \ldots (6.1)$$

where X_m and X_0 are the concentrations of biomass at the end and at the beginning of a batch run, respectively, and t is the duration of the run.

Table6. 3: Based on the Reactor Type and Configuration, Biomass Production over 5 years

Variables	Units	Raceway Pond	Flat-plate photobioreactor	
			Case 1	*Case 2*
Five year biomass production	kg	273750	989589.8	1929700
Annual biomass production	kg/year	54750	197917.97	385940
Volumetric productivity	kg/m^3*d	0.05	0.57	0.57
Total illuminated surface area	m^2	10000	19026	37100.7
Flow in 5 years	m^3	547500	520836.8	1015631.7
Biomass concentration	kg/m^3	0.5	1.9	1.9
Dilution rate	d-1	0.1	0.3	0.3
Space	m^2	10000	10000	10000
Reactor volume	m^3	3000	951	1855.
Flow rate	m^3/d	300	285.	556.5

As specific growth rate under stationary condition is equal to the dilution rate, therefore, dilution rate for flat-plate reactor was assumed to be equal to the specific growth rate calculated from equation (6.1).

Volumetric productivity was calculated using equation (6.2) [86].

$$Pv = \mu X \qquad \text{... (6.2)}$$

Where Pv is volumetric productivity, μ is specific growth rate (which here is equal to dilution as growth rate has been considered to be stationary) and X is biomass concentration.

Flow rate was calculated using equation (6.3) [86]

$$F = D*V \qquad \text{... (6.3)}$$

where F is flow rate, D is dilution rate and V is reactor volume.

Annual biomass production was calculated using equation (6.4)

$$ABP = F*X \qquad \dots (6.4)$$

where ABP is annual biomass production, F is flow rate and X is biomass concentration

Total illuminated surface area for flat-plate reactor was calculated using equation (6.5) [70]

$$TIS = 2*l*h*U*R \qquad \dots (6.5)$$

Where TIS is total illuminated surface area, l is length of each unit of the reactor, height of each unit of the reactor, U is number of units per reactor and R is the number of reactors.

Furthermore, during culture, water, light and nutrients are required. For uniform distribution of nutrients and light, the culture should be properly mixed. In flat-plate reactors, the mixing was achieved by air injection, while in photobioreactors by paddlewheels.

Table6. 4: Composition of the Biomass Obtained from Culture of Microalgae

Biomass fractions	**Composition [185]**	**Biomass fractions in N-deprived medium (%) [70]**	**Biomass fractions in normal medium (%) [70]**	**Molar mass (g/mol)**
Protein	$(C_6H_{13.1}O_1N_{0.6})$	20	60	109.5
Carbohydrates	$(C_6H_{10}O_5)_n$	40	20	162
Lipid	$(C_{57}H_{104}O_6)$	23	20	884

Table 6.4 shows the composition of the biomass obtained from the culture of microalgae. Based on the biomass composition, it was calculated that the amount of carbon required per kg of biomass is 487 g, thus, the amount of CO_2 required to fulfill this requirement is 1787 g (41 mols). The amount of nitrogen required per kg of biomass was calculated to be 15 g, and thus, amount of Di Ammonium phosphate [$(NH_4)_2HPO_4$] required to provide nitrogen requirement per kg of biomass will be 70.7 g. Di Ammonium phosphate will also provide the phosphorous requirement of algal biomass. Table 6.5 shows the nutrient requirement based on the biomass composition.

Table6. 5: Nutrient requirement based on the biomass composition

Nutrient requirement	**Open raceway pond**	**Flat-plate reactor**	
		Case 1	***Case 2***
Carbon dioxide (CO_2)	489191.25 kg	1768397.33 kg	3448374 kg
Di Ammonium Phosphate	19354.13 kg	69964 kg	136430 kg

Further, the temperature of the water in open pond was controlled by evaporation. Considering the average annual evaporation losses, total water lost through evaporation over 5 years, was estimated to be around 112500 m³. Therefore, in order to maintain the culture concentration, extra 112500 m³ of water was pumped in the culture medium, over a period of 5 years. Table 6.6 shows the total energy input during microalgae culture in the various reactors, whereas Table 6.7 shows the CO_2 and NOx emissions due to fertilizer and electricity use during microalgae culture.

Table6. 6: The Total Energy Input during Microalgae Culture in the Various Reactors

		Open raceway pond	**Flat-plate reactor**	
			Case 1	***Case 2***
Electricity consumed during water pumping in reactors (culture water+ water lost through evaporation) (kWh)		33000	26041.84	50781.6
Nutrients	**Electricity consumed during CO_2 injection (kWh)**	10860	39258.4	76553.9
	Energy use for Di Ammonium Phosphate (GJ)	661.9	2392.8	4665.9
Electricity consumed during mixing (paddlewheel/Airlift) (kWh)		525600	2208348	4306197
Electricity consumed by Tubelight (kWh)			33590357	95472626
Electricity consumed by heat exchanger for temperature control (kWh)			596423.5	922521.6
Total electrical energy input (kWh)		569460	36460429	100828680
Total energy input (GJ)		6749	392155	1082524

Table6. 7: CO_2 and NOx Emissions due to Fertilizer and Electricity use during Microalgae Culture

		Open raceway pond	Photobioreactor	
			Case 1	*Case 2*
CO_2 emissions from DAP (Mton)	Natural Gas	15.7	56.6	110.4
	Naphtha	12.13	43.85	85.50
	Fuel oil	5.12	18.52	36.11
	Ammonia	6.76	24.42	47.62
CO_2 emissions from electricity use (Mton)		558	35731	98812
NOx emissions from fertilizer use (Mton)		0.34	1.24	2.41
Total CO_2 emission (Mton)		597.71	35874.39	99091.63

B. Microalgae Harvesting & Drying

After culture, microalgae need to be harvested and dried for further processing. The dry weight % (DW %) required will depend on the routes followed for further processing of microalgae for biofuel production. There are two routes for biofuel production from microalgae, i.e:

I. **Dry Route:** Dehydration is needed to obtain 90% dry weight (DW) of microalgae, because biomass left after lipid extraction will further be processed by pyrolysis method for which moisture levels of 5-10 wt% are generally considered acceptable [232].

II. **Wet Route:** Dehydration is needed to obtain 20% DW of microalgae as Bligh and Dyer method for lipid extraction can applied to any tissue containing water up to 80% [251].

Depending on the two routes, following combinations of harvesting and drying, techniques were used to reach the required dry weight. The amount of Aluminium sulphate required for flocculating algae culture obtained from the open raceway pond, photobioreactor (Case 1) and photobioreactor (Case 2) was estimated to be 4681 ton, 4453 ton and 8684 ton simultaneously. After 10 hours of gravitational settling the concentration of the harvested culture is found to be 40 times higher than the initial culture [239], and was estimated to give 7.6 % DW algae culture.

The various combinations are as mentioned below:

1. **Combination 1:** It includes flocculation followed by belt drying. The details of the energy requirement for this combination are given in Table 6.8.
2. **Combination 2:** It includes flocculation followed by centrifugation and belt drying. The details of the energy requirement for this combination are given in Table 6.9.
3. **Combination 3:** It includes centrifugation followed by belt drying. The details of the energy requirement for this combination are given in Table 6.10.
4. **Combination 4:** It includes flocculation followed by filtration. Cell size of chlorella being very small, micro filtration alone won't be effective. Therefore, filtration must be done after flocculation.

Based on the energy requirements of the various combinations, when Tables 6.8, 6.9 and 6.10 were compared, Table 6.10 showed that combination three i.e. centrifugation followed by belt drying is the most energy efficient combination. Moreover, it is clear from Tables 6.8 and 6.9 that, flocculation alone contributes more energy input than the total energy input in Combination 3. Therefore, Combination 4 is not an energy efficient route. Therefore, for further calculations the energy requirements of the Combination 3 have been considered.

Table6. 8: Energy Requirements for Flocculation Followed by Belt Drying

		Dry Route (90% DW)			**Wet Route (20% DW)**		
		Open raceway pond	**Photobioreactor**		**Open raceway pond**	**Photobioreactor**	
			Case 1	***Case 2***		***Case 1***	***Case 2***
Energy required for pumping in flocculation chamber (kWh)		27375	26042	50782	27375	26042	50782
Air sparging assisted Coagulation Flocculation (ASACF) (7.6% DW)	**Energy consumed to produce the required amount of $Al_2(SO_4)_3$ for flocculation (GJ)**	397885	378505	738140	397885	378505	738140
	Energy required for air sparging(kWh)	1270	1208	2356	1270	1208	2356
Energy required for pumping in belt dryer (kWh)		684	651	1270	684	651	1270
Belt Dryer (kWh)	**Energy required to obtain 90% DW**	12453935	11093501	21632328			
	Energy required to obtain 20% DW				11463281	7512347	14649076

		Dry Route (90% DW)			***Wet Route (20% DW)***		
		Open raceway pond	**Photobioreactor**		**Open raceway pond**	**Photobioreactor**	
			Case 1	***Case 2***		*Case 1*	*Case 2*
Total electrical energy input (kWh)		12483264	11121402	21686736	11492610	7540248	14703484
Total energy input (GJ)		531331	497393	969971	520741	459110	895320
CO_2 emissions from electricity use (MT)		12234	10899	21253	11263	7389	14409

Table6. 9: Energy Requirements for Flocculation Followed by Centrifugation and Belt Drying

		Dry Route (90% DW)			**Wet Route (20% DW)**		
		Open raceway pond	**Photobioreactor**		**Open raceway pond**	**Photobioreactor**	
			Case 1	***Case 2***		***Case 1***	***Case 2***
Electricity required for pumping in flocculation chamber (kWh)		27375	26041.84	50781.58	27375	26041.84	50781.58
Air sparging assisted Coagulation Flocculation (ASACF) (7.6% DW)	**Energy consumed to produce the required amount of $Al_2(SO_4)_3$ for flocculation (GJ)**	397885	378505	738140	397885	378505	738140
	Energy required for air sparging (kWh)	1269.9	1208	2355.7	1269.9	1208.1	2355.7
Energy required for pumping in centrifuge (kWh)		684	651	1269.5	684.4	651	1269.5
Centrifugation after flocculation (16 % DW) (kWh)	**Energy required to obtain 16% DW**	7246	6893	13442	7246	6893	13442

		Dry Route (90% DW)			***Wet Route (20% DW)***		
		Open raceway pond	**Photobioreactor**		**Open raceway pond**	**Photobioreactor**	
			Case 1	*Case 2*		*Case 1*	*Case 2*
Energy required for pumping in (kWh)		85.6	309	603	85.6	309	603
Belt drying (kWh)	**Energy required to obtain 90% DW**	1309078	4732240	9227868			
	Energy required to obtain 20% DW				318424.4	1151085	2244616
Total electrical energy input (kWh)		1345739	4767343	9296320	355085	1186188	2313068
Total energy input (GJ)		412271	429468	837518	401681	391185	762867
CO_2 emissions from electricity use (MT)		1319	4672	9110	348	1163	2267

Table6. 10: Energy Requirements for Centrifugation Followed by Belt Drying

		Dry Route (90% DW)			Wet Route (20% DW)		
		Open raceway pond	**Photobioreactor**		**Open raceway pond**	**Photobioreactor**	
			Case 1	***Case 2***		***Case 1***	***Case 2***
Energy required for pumping culture in centrifuge (kWh)		27375	26041.84	50781.58	27375	26041.84	50781.58
Centrifugation (16% DW)(kWh)	**Energy requires for obtaining 16% DW**	289853	275737	537687	289853	275737	537687
Energy required for pumping water in Belt dryer (kWh)		85.5	309	603	85.5	309	603
Belt Drying (kWh)	**Energy required to obtain 90% DW**	1309078	4732240	9227867.8			
	Energy required to obtain 20% DW				318424.4	1151085.4	2244616.5

		Dry Route (90% DW)			***Wet Route (20% DW)***		
		Open raceway pond	**Photobioreactor**		**Open raceway pond**	**Photobioreactor**	
			Case 1	*Case 2*		*Case 1*	*Case 2*
Total electrical energy input (kWh)		1626392	5034328	9816939.38	635737.9	1453173	2833688
Total energy input (GJ)		17386	53817	104943	6796	15534.4	30292
CO_2 emissions from electricity use (MT)		1593.9	4933.6	9620.6	623	1424	2777

6.2.6. Oil Extraction

Chemical solvent has been reported to be more efficient method of lipid extraction than mechanical press [252]. Lam and Lee compared four different chemical solvents for lipid extraction, ethanol, methanol, n-hexane and Bligh and Dyer method (mixed methanol-chloroform with volume ratio of 2:1). They found Bligh and Dyer method to have highest lipid extraction efficiency and n-Hexane, which is one of the widely used solvent for lipid extraction, to have lipid extraction efficiency [252]. Bligh and Dyer method of lipid extraction, yields ≥95% of total lipid and further to it, this method can be used for any tissue containing water up to 80% [251]. Therefore, for lipid extraction, Bligh and Dyer method has been considered for both dry and wet route.

The critical ratios of methanol, chloroform and water should be 2:1:1.8 and that of solvent to tissue should be 3:1. After the solvent and culture are mixed, in the given ratio, they are homogenized to form a monophasic system and then re-homogenized with another similar quantity of chloroform. Therefore, the overall ratio of methanol, chloroform and water should be 2:2:1.8, and that of solvent to tissue is {(3+1):1} [251]. Considering the critical ratios, for dry route, since water content is insignificant in comparison to biomass, solvent to tissue ratio of {(3+1):1} should be considered, while for wet route, because of high water content, methanol, chloroform and water, ratio of 2:2:1.8 should be considered.

The homogenization was done by centrifuge, which also separates the biphasis layer (lipid dissolved in chloroform and methanol dissolved in water) formed in the process. Thereafter, the lipid is separated from chloroform and methanol from water by fractional distillation (heat energy was assumed to be provided by burning of natural gas). During this process the solvents are recovered. Table 6.11 shows the energy requirements for oil extraction from microalgae by Bligh and Dyer method.

Table6. 11: Energy Requirements for Oil Extraction from Microalgae by Bligh and Dyer Method

	Dry route			Wet route		
	Open raceway pond	Flat-plate Reactor		Open raceway pond	Flat-plate Reactor	
		Case 1	*Case 2*		*Case 1*	*Case 2*
Total culture mass (mass of algae + water left after harvesting & drying) (kg)	577917	2089134	4073811	1642500	5937539	11578201
Water (kg)	304167	1099544	2144111	1368750	4947949	9648501
Chloroform (l)	547500	1979180	3859400	1520833	5497721	10720557
Methanol (l)	547500	1979180	3859400	1520833	5497721	10720557
Energy required for homogenization and separation by centrifuge(kWh)	740.7	2677.7	5221.5	2334.9	8440.6	16459
Lipid recovery after Bligh and Dyer method (kg)	59814.4	216225.4	421639.5	59814.4	216225.4	421639.5
Energy required for chloroform recovery (GJ)	200	723.5	1410.8	556	2009.7	3919
Energy required for methanol recovery (GJ)	118	426.7	832	328	1185	2311

	Dry route			Wet route		
	Open raceway pond	Flat-plate Reactor		Open raceway pond	Flat-plate Reactor	
		Case 1	*Case 2*		*Case 1*	*Case 2*
Total energy input (GJ)	325.92	1178.82	2298.62	908.96	3284.93	6405.95
CO_2 emissions from electricity use (MT)	0.73	2.62	5.12	2.29	8.27	16.13
CO_2 emissions from NG (MT)	15	54.4	106	42	151.2	295
Total CO_2 emissions (MT)	15.73	57	111	44.3	159.5	311

6.2.7. Oil and Biomass processing

A. Oil Processing

The oil ages and tends to phase separate upon prolonged standing. As a consequence, it is not suitable for direct application in (non-stationary) internal combustion engines and requires upgrading to fulfill the stringent specifications for (bio-) fuels [224].

Out of the total 23% lipid content, TAG was only 14% [70] and only TAG can be converted to biodiesel via transesterification process. The rest are polar lipids and are unwanted in the biodiesel process, as they strongly influence the processing and the quality of the product. Therefore, in order to produce a biofuel with more favorable properties, hydro-processing is a better process. It converts entire lipid content, even the polar lipids [253]. Hydro-processing produces green diesel, naphtha and offgas in the ratio of 78:2:6 [213].

The energy produced by naphtha and offgas can be used to produce electricity required for hydrogenation process, thus decreasing the net energy input for the entire process. Table 6.12 shows the energy requirements during oil processing via hydrogenation.

Table6. 12: Energy Requirements During Oil Processing via Hydrogenation

	Dry route			**Wet route**		
	Open raceway pond	**Flat-plate Reactor**		**Open raceway pond**	**Flat-plate Reactor**	
		Case 1	***Case 2***		***Case 1***	***Case 2***
Oil recovery after Bligh and Dyer method (kg)	59814	216225	421640	59814	216225	421640
Amount of hydrogen required (kg)	897	3243	6325	897	3243	6325
Energy consumed in hydrogen production(GJ)	164	594	1159	164	594	1159
Energy required for hydrogenation (kWh)	19140	69192	134925	19140	69192	134925
Amount of hydrogenated oil/green diesel obtained (kg)	46655	168656	328879	46655	168656	328879
Total electrical energy consumed (kWh)	19140	69192	134925	19140	69192	134925
Total electrical energy consumed (GJ)	205	740	1442	205	740	1442
Total energy consumed (GJ)	369	1334	2601	369	1334	2601

	Dry route			Wet route		
	Open raceway pond	Flat-plate Reactor		Open raceway pond	Flat-plate Reactor	
		Case 1	*Case 2*		*Case 1*	*Case 2*
CO_2 emission from electricity use (MT)	19	68	132	19	68	132
Amount of Naphtha obtained (kg)	1196	4325	8433	1196	4325	8433
Amount of Offgas obtained (kg)	3589	12974	25298	3589	12974	25298
Energy content of Naphtha (GJ)	52	190	370	52	190	370
Energy content of Offgas (GJ)	161	584	1138	161	584	1138
Net energy consumed (GJ)	156	560	1093	156	560	1093

B. Biomass processing

1) Dry Route (Pyrolysis)

It involves heating biomass in the absence of air or oxygen [38] to around 500 °C to form liquid fuel (Bio-oil), charcoal and gaseous fraction [124]. Depending on the pyrolysis time or heating rate, it is of two types i.e., slow and fast pyrolysis [229]. Slow pyrolysis forms more of char [229, 232], while fast pyrolysis dramatically alters and shifts the reaction to form more of liquid bio-oil. According to National renewable energy laboratory (NREL) report, slow pyrolysis produces liquid, gas and char in the ratio of 30:35:35, while fast pyrolysis produces them in the ratio of 75:13:12 [232]. The bio-oil also contains about 15 wt% water [232] and higher oxygen content, which decreases the heating value of bio-oil to about 15- 19 MJ/kg. Also, it is not suitable for direct application in diesel engines and need to be further upgraded [224].

Table6. 13: Energy Requirement During Pyrolysis of Dry Biomass and Oil Up-gradation via Hydrotreating

	Open raceway pond	Flat-plate reactor	
		Case 1	*Case 2*
Remaining biomass after lipid extraction (kg)	213936	773365	1508061
Bio-oil obtained (kg)	160452	580023.8	1131046
Char obtained (kg)	25672.32	92803.8	180967.3
Gas obtained (kg)	27811.68	100537.5	196047.9
Energy required for pyrolysis (kWh)	42777.78	154722.2	301611.1
Amount of hydrogen required for hydrotreating (kg)	5760	20857.7	40672.4
Energy consumed in hydrogen production (GJ)	1055	3822	7453
Energy required to upgrade bio-oil (Hydrotreating) (kWh)	51344.64	185607.6	361934.7
Amount of upgraded oil/Green diesel obtained (kg)	96271.2	348014.28	678627.6
Total electrical energy input (kWh)	94122	340330	663546
Total electrical energy input (GJ)	1006	3638	7093
Total energy input (GJ)	2062	7460	14546
Energy content of char (GJ)	718.82	2598.51	5067.08
Energy content of gas (GJ)	333.74	1206.45	2352.58
CO_2 emission from electricity use (MT)	0.99	3.57	6.95
Net energy consumed (GJ)	1009	3655	7126

One of the technologies used for upgrading is catalytic hydrotreatment, which is carried out at about 200-400 °C and 100-200 bar pressure. The Ru/C catalyst was found to be superior, with yield of about 60 wt% upgraded oil [224]. Since the green diesel obtained by up-gradation of pyrolysis oil was assumed to be upgraded via hydrotreatment, its calorific value was assumed to be same as that of the green diesel obtained via hydrogenation i.e. 44 MJ. This heating value of 44 MJ/kg [113] is almost more than twice the heating value of bio-oil obtained after pyrolysis. Table 6.13 shows the energy requirement during pyrolysis of dry biomass and oil up-gradation via hydrotreating.

Feed particle size can significantly affect the balance between char and liquid yields. Larger particles are beneficial in processes targeting char production, and small particles are preferred to maximize liquid yields in fast pyrolysis. Fast pyrolysis is characterized by high heating rates and short vapour residence times. This generally requires a feedstock prepared as small particle sizes and a design that removes the vapours quickly from the presence of the hot solids [182].

2) Wet Route (Hydrothermal Liquefaction)

The remaining wet algae culture, after lipid extraction, can be further processed to obtain oil by hydrothermal liquefaction. Hydrothermal liquefaction converts carbohydrates and proteins, left after lipid extraction, into oil. 10% DW to 20% DW microalgae, i.e. wet algae, is an excellent substrate for hydrothermal liquefaction. No drying or cellular disruption is required [254].

The wet algal slurry is heated to approximately 250 °C to 350 °C at 1500 to 3000 psi. Water catalyses the reaction and the algal cells liquefy. Hydrothermal liquid (HTL) obtained is 38 wt% of total biomass feedstock and 15 wt% gas is also formed [254].

Table6. 14: Energy Requirement during Hydrothermal Liquefaction Wet Biomass and Oil Up-gradation via Hydrotreating

	Open raceway pond	Flat-plate reactor	
		Case 1	*Case 2*
Remaining biomass after lipid extraction (kg)	213936	773365	1508061
Total water content of the culture (kg)	1368750	4947949	9648501
Energy required for Hydrothermal liquefaction (kWh)	963194.4	3481944	6789722
HTL obtained (kg)	81295.68	293878.7	573063.18
Gas obtained(kg)	32090.4	116004.8	226209.2
Amount of hydrogen required for up-gradation (Hydrotreating) (kg)	1461.70	5283.94	10303.68
Energy consumed in hydrogen production (GJ)	268	968	1888
Energy required to upgrade HTL (Hydrotreating) (kWh)	26014.62	94041.18	183380.2
Amount of upgraded oil/green diesel obtained (kg)	65036.54	235102.96	458450.54
Total electrical energy input (kWh)	989209	3575985	6973102
Total electrical energy input (GJ)	10575	38227	74542
Total energy input (GJ)	10842	39196	76431
Energy content of gas (GJ)	385	1392	2714.5
CO_2 emission from electricity use (MT)	969	3504	6834
Net energy consumed (GJ)	10457	37804	73716

The hydrothermal liquid (bio-crude), obtained from hydrothermal liquefaction, is not suitable for direct engine application. That is because of high oxygen and nitrogen content [254]. HTL is not comparable with fossil products, such as, diesel [253]. Therefore, the oil needs to be upgraded [254].

HTL has a higher heating value of 33.3– 39.9 MJ/kg and, thus, are higher than for pyrolysis oils [253]. Since the heating value of HTL is twice to that of pyrolysis oil, it has been assumed that the amount of hydrogen required to upgrade per kg of HTL will be half as that required for pyrolysis oil up-gradation. After up-gradation 80% renewable diesel is be obtained [254]. Table 6.14 shows the energy requirement during hydrothermal liquefaction of wet biomass and its up-gradation via hydrotreatment.

6.2.8. End combustion of Green diesel

The details of the total green diesel produced over 5 years; from hydrogenation of algal oil and pyrolysis and up-gradation of oil extracted algal biomass is shown in Table 6.15. This table also shows the total energy and total carbon dioxide emissions, which it would release on combustion.

Table6. 15: Total Green diesel, Energy Content, & CO_2 Emissions obtained over Five years span from Microalgae

	Dry route			Wet route		
	Open raceway pond	Flat-plate Reactor		Open raceway pond	Flat-plate Reactor	
		Case 1	*Case 2*		*Case 1*	*Case 2*
Green diesel obtained by hydrogenation of algal oil (kg)	46655	168656	328879	46655	168656	328879
Energy content of hydrogenated (Green diesel) algal oil(GJ)	2053	7421	14471	2053	7421	14471
Green diesel obtained by hydrotreatment of bio-oil obtained by pyrolysis (kg)	96271	348014	6786278			
Energy content of hydrotreated (Green diesel) bio-oil obtained by pyrolysis (GJ)	4236	15313	29860			
Green diesel obtained by hydrotreatment of HTL obtained by Hydrothermal Liquefaction (kg)				65036.54	235102.96	458450.54
Energy content of hydrotreated (Green diesel) HTL (GJ)				2862	10345	20172
Total energy content of Green diesel obtained by different processes (GJ)	6289	22734	44331	4915	17766	34643
Total CO_2 emissions from combustion of Green diesel (MT)	393	1421	2771	307	1110	2165

6.2.9. Results & discussion

Table 6.16 shows the final stage wise energy input/output, NEB and NER over 5 years, while Table 6.17 shows the total CO_2 emissions over 5 years from the different routes. It is clear from Table 6.16 that none of the proposed routes in the current study has positive NEB. But still, when compared on the basis of present values production of green diesel via open raceway pond, both in dry as well as wet route, have less negative NEB and comparatively higher NER than the photobioreactors. As per Table 6.3, though the photobioreactors produce far more biomass than the open pond in the same time period, yet, this extra energy produced by them is compensated by the high energy requirements by the tube lights and the heat exchangers to support this high biomass production in the photobioreactors.

Table6. 16: Stage wise Energy input/output, NEB and NER over 5 years

		DRY ROUTE			WET ROUTE		
		Open raceway pond	Photobioreactor		Open raceway pond	Photobioreactor	
			Case 1	*Case 2*		*Case 1*	*Case 2*
Microalgae culture & Harvesting (GJ)	Culture	6749	392155	1082524	6749	392155	1082524
	Harvesting & Drying	17386	53817	104943	6796	15534	30292
Oil Extraction (GJ)	Extraction	326	1179	2299	909	3285	6406
Oil & biomass processing (GJ)	Oil processing	156	560	1093	156	560	1093
	Pyrolysis/ liquefaction of biomass	1009	3655	7126	10457	37804	73716
Total energy input (GJ)		25626	451366	1197985	25067	449338	1194031
End combution of Green diesel (GJ)	Hydrogenated algal oil	2053	7421	14471	2053	7421	14471
	Hydrotreatment of Pyrolysis oil /HTL	4236	15313	29860	2862	10345	20172
Total energy output (GJ)		6289	22734	44331	4915	17766	34643
NEB (GJ)		-19337	-428632	-1153654	-20152	-431572	-1159388
NER		0.25	0.05	0.04	0.20	0.04	0.03

Table6. 17: Total CO$_2$ Emissions over 5 years from the Different Routes

		DRY ROUTE			WET ROUTE		
		Open raceway pond	Photobioreactor		Open raceway pond	Photobioreactor	
			Case 1	*Case 2*		*Case 1*	*Case 2*
Microalgae culture & Harvesting (MT)	Culture	598	35874	99092	598	35874	99092
	Harvesting & Drying	1594	4934	9621	623	1424	2777
Oil Extraction (MT)		16	57	111	44	160	311
Oil & biomass processing (MT)	Oil processing	19	68	132	19	68	132
	Pyrolysis/ liquefaction of biomass	0.99	3.57	6.95	969	3504	6834
End combution of Green diesel (MT)	Green diesel obatined via hydrogenation of algal oil	128	464	904	128	464	904
	Green diesel obtained via hydrotreatment of Pyrolysis oil /HTL	265	957	1866	179	647	1261
Total Carbon dioxide emissions (MT)		2621	42357	111734	2560	42140	111311

Further, on comparison between the two open raceway pond routes, dry route has slightly higher value for NER than the wet route. Even the total CO$_2$ emissions for dry route is only slightly more than that of wet route. The reason for this could be attributed to the huge energy requirements during hydrothermal liquefaction process in the wet route, which compensates the entire energy savings, made during harvesting and drying process. Moreover, compared to other conversion technologies, research on pyrolysis of algal biomass is quite extensive and has achieved reliable and promising outcomes that could lead to commercial exploitation [255]. And, despite rising interest in HTL, many of its operational parameters are uncertain [254] and moreover, reactors for thermo-chemical liquefaction and fuel-feed systems are complex and are, therefore, expensive [255].

Even with the best possible route, as per the current study, the total energy use is almost four times more than the energy produced with a highly negative NEB of 19337 GJ and very low NER value of 0.25. Figure 6.2 shows that among the various stages, microalgae culture and harvesting consumes the highest energy, followed by oil and biomass processing. Oil extraction stage consumes the least energy. The main factor resulting in excessive energy use during microalgae culture & harvesting stage is the drying process. A lot of energy is required to dry the algal biomass up to 90% DW. Though centrifugation followed by belt drying has been shown to have the least energy requirements, yet it is important to develop more efficient dryers so that this energy requirement can further be reduced.

If we look at Figure 6.3, microalgae culture and harvesting produces maximum CO_2 followed by end combustion of green diesel. The two major CO_2 contributors, during culture and harvesting stage, are use of large quantity of fertilizer and electricity. Fertilizer used for algae growth and culture is highly energy intensive, by the virtue of which, culture stage alone should be the major CO_2 contributor among the two i.e. culture and harvesting stage. But Table 6.17 shows that harvesting stage, which consumes far more electricity than culture stage, emits more carbon dioxide. It is so because major share of electricity in India is produced from coal, while major share of fertilizer produced in India is from natural gas, which is a clean fuel.

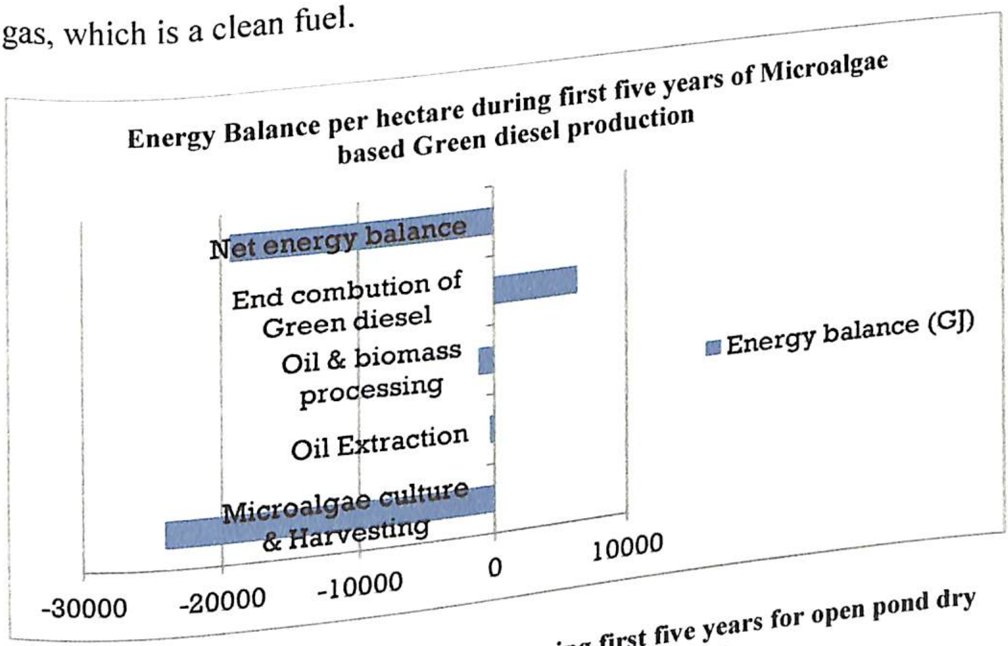

Figure6. 2: Energy balance per hectare during first five years for open pond dry route algae based green diesel production

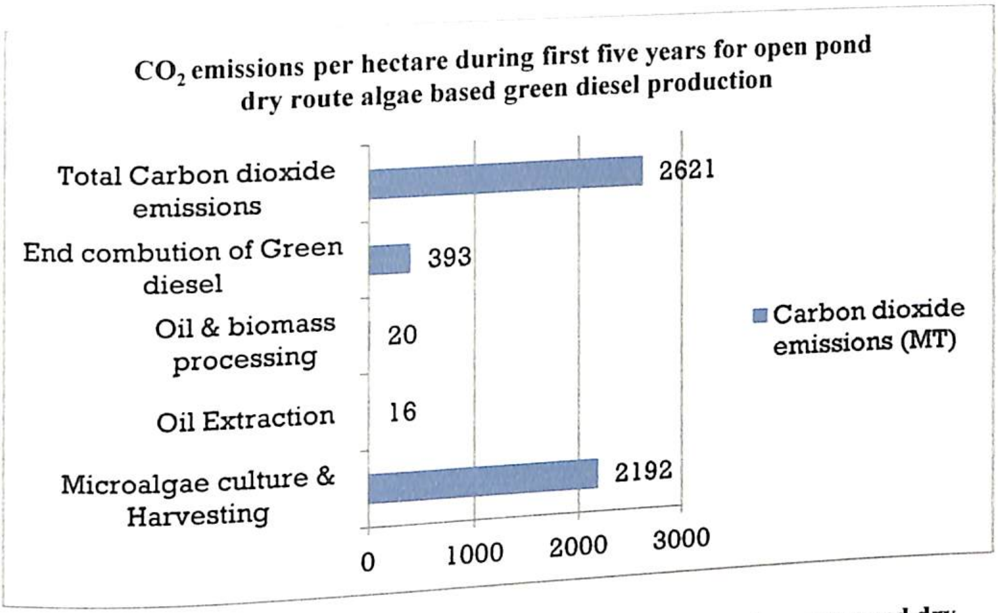

Figure6. 3: CO_2 emissions per hectare during first five years for open pond dry route algae based green diesel production

6.3. Cost of Green Diesel production

All costs for green diesel production from algae were estimated based on vendor quotes, prior literature studies and present market costs. With the assumption that capital cost has 20 years of life, the operational cost was also estimated for over 20 years.

It is clear from Tables 6.18 and 6.19 that operational cost over 20 years is much more than the capital cost. The highest contributor to the operational cost is the electricity uses, followed by the cost of methanol used as solvent for oil extraction during Bligh & Dyer process. Electricity uses alone accounts for 64% of total operational cost, and 56% of the total operational cost and 50% of the overall cost. According to the current study, the cost per kg of green diesel production from algae is ₹ 140. This cost can be further brought down by finding out more energy efficient processes for oil production from algae and its further processing to produce green diesel.

Table6. 18: Capital Cost Investment over 20 years, for Green Diesel Production from Algae

Capital cost	Rate	Cost (₹)
Land (1 hectare for cultivation & 0.5 acres for nursery)	₹125000/acre	371250
Raceway pond	₹ 1706/m^3	5118000
Water pump(2 units)		8000
Centrifuge(2 units)		2000000
Extraction unit		200000
Hydrotreating unit(2 units)		180000
Pyrolysis unit		60000
Total Capital cost (20 years life)		**7937250**

Table6. 19: Operational Cost Investment over 20 years, for Green Diesel Production from Algae

Operational cost	Rates	Cost (₹)
Fertilizer	₹ 650/50 kg	1006415
Manpower (3 skilled labor)	₹ 150/day for skilled labor	3285000
Chloroform (with 2% loss every operation)	₹ 500/liter	9196881
Methanol (with 2% loss evergy operation)	₹ 300/liter	10314259
Hydrogen	₹ 75/kg	1997100
Electricity	₹ 5/unit	46197094
Natural gas	₹ 233.65/mmbtu	281709
Total Operational cost (over 5 years)		**72278457**

Table6. 20: Total invest over 20 years, for Green diesel production from Jatropha

Total Capital cost (₹)	**7937250**
Total operational cost(₹)	**72278457**
Total cost (₹)	**80215706.6**
Total green diesel production (kg)	**571704.8**
Cost /kg of green diesel produced (₹/kg)	**140**

6.4. Concluding Remarks

Both raceway pond and flat-plate reactors showed negative NEB and NER values less than 1. Fertilizer uses during culture, and electricity uses during harvesting and drying, were the major energy consuming stages. As far as fertilizer uses are concerned, a lot of work has already been done on use of waste water from various sources for algae culture. However, the growth rates have shown to be very less in comparison to use of fertilizer. Further research is needed to develop a source of water, which could provide the same growth rate as that by fertilizer use. A lot of energy, which is used for production of these fertilizers, can be saved, and also, the environmental hazards caused by this water disposal can be minimized. Further, an efficient harvesting and drying technology, which can reduce the electricity uses especially for drying water, is required. Though wet route is available, yet the use of excessive amount of chemicals during oil processing reduces its overall efficiency.

It can be concluded from the current study that though microalgae has huge potential as an alternative source of renewable energy, yet research and development in the area of green diesel production from microalgae has to go a long way to come out with technologies, which can further reduce the huge energy requirements during green diesel production from microalgae.