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CERTIFICATION COURSE

# WASTE TO ENERGY CONVERSION

## ENERGY PRODUCTION FROM ALGAL BIOMASS-2

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- Biodiesel as an important route for energy production from algal biomass
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- Factors affecting biodiesel yield
- Upgradation of algal oil to bio diesel using homogenous and heterogeneous catalysts
- Quality parameters of algal bio diesel and its stability
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# Upgradation of algal oil to biodiesel.

## Homogeneous catalysts

| Microalgae species(dry or wet)                 | Oil extraction method          | Catalyst                       | Lipid content (%) | Biodiesel Conversion (%) | References       |
|------------------------------------------------|--------------------------------|--------------------------------|-------------------|--------------------------|------------------|
| <i>Nannochloropsis gaditana</i> (dry biomass)  | Stirring extraction            | HCl                            | 13.1              | 14.8                     | Rios et al. 2013 |
| <i>Chlorella vulgaris</i> ESP-31 (dry biomass) | Ultrasonic assisted extraction | Lipase (Burkholderias p.)      | 63.2              | 72.1                     | Tran et al. 2012 |
| <i>Chlorella vulgaris</i> (dry biomass)        | Stirring extraction            | H <sub>2</sub> SO <sub>4</sub> | -                 | 95.0                     | Lam et al. 2013  |
| <i>Chlorella protothecoides</i> (dry biomass)  | Soxhlet extraction             | Lipase (Candidia sp. )         | 44 - 48.7         | 98.1                     | Li et al. 2007   |



# Upgradation of algal oil to biodiesel

## Homogeneous catalysts

| Microalgae species(dry or wet)           | Oil extraction method                  | Catalyst                       | Lipid content (%) | Biodiesel Conversion (%) | References          |
|------------------------------------------|----------------------------------------|--------------------------------|-------------------|--------------------------|---------------------|
| <i>Chlorella vulgaris</i> (dry biomass)  | Soxhlet extraction                     | lipase ( <i>P. expansum</i> )  | 40.7              | 90.7                     | Li et al. 2012      |
| <i>Chlorella sp. KR-1</i> (dry biomass)  | Stirring extraction                    | Lipase (Novozyme 435)          | 38.9              | 75.5                     | Lee et al. 2013     |
| <i>Tribonema minus</i> (wet biomass)     | Subcritical ethanol extraction         | H <sub>2</sub> SO <sub>4</sub> | 20.2              | 96.5                     | Wang et al. 2013    |
| <i>Nannochloropsis sp.</i> (80%moisture) | Microwave assisted transesterification | NaOH                           | 38.3              | 86.4                     | Wahidin et al. 2014 |

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## Homogeneous catalysts

| Microalgae species(dry or wet)                                                      | Oil extraction method                     | Catalyst                       | Lipid content (%) | Biodiesel Conversion (%) | References         |
|-------------------------------------------------------------------------------------|-------------------------------------------|--------------------------------|-------------------|--------------------------|--------------------|
| <i>Chlorella</i> sp. KR-1 (dry biomass)                                             | -                                         | -                              | 40.9              | 89.7                     | Jo et al. 2014     |
| <i>Tetraselmis suecica</i> (dry biomass) <i>Chlorella sorokiniana</i> (dry biomass) | -                                         | H <sub>2</sub> SO <sub>4</sub> | 23.0              | 78.0                     | Wahlen et al. 2011 |
| <i>Nannochloropsis oceanica</i> (65% moisture)                                      | In situ transesterification in water bath | H <sub>2</sub> SO <sub>4</sub> | 19.1              | 90.6                     | Lam et al. 2014    |

| Feed stocks | Solvent used                            | Catalyst                                 | Operating conditions |          |         |        | YBD (%) |
|-------------|-----------------------------------------|------------------------------------------|----------------------|----------|---------|--------|---------|
|             |                                         |                                          | T (°C)               | ATOR     | CL wt % | RT (h) |         |
| Algal oil   | Methanol                                | CaO Supported on $\text{Al}_2\text{O}_3$ | 50                   | 6:1/30.1 | 2       | 4      | 23/97.5 |
| Algal oil   | Methanol                                | MgO Supported on $\text{Al}_2\text{O}_3$ | 50                   | 6:1      | 2       | 4      | 16      |
| Algal oil   | Methanol-methylene dichloride (3:1 V/V) | Mg-Zr solid base catalyst                | 65                   | -        | 10      | 4      | 28      |

T: Temperature; ATOR: Alcohol to oil ratio; RT: Reaction time; YBD: Yield of biodiesel',  
CL: Catalyst loading

Soni et al., 2012



# Homogeneous vs. heterogeneously catalyzed transesterification

| Factors                            | Homogeneously catalysis                                                                | Heterogeneously catalysis             |
|------------------------------------|----------------------------------------------------------------------------------------|---------------------------------------|
| Reaction rate                      | Fast and high conversion                                                               | Moderate conversion                   |
| Post treatment step                | Catalyst cannot be recovered, must be neutralized leading to waste chemical production | Can be recovered                      |
| Processing methodology             | Limited use of continuous methodology                                                  | Continuous fix bed operation possible |
| Presence of water/free fatty acids | Sensitive                                                                              | Not sensitive                         |
| Catalyst reuse                     | Not possible                                                                           | Possible                              |
| Cost                               | Comparatively costly                                                                   | Potentially cheaper                   |



# Quality of biodiesel

Hanna, 1999; Lang et al., 2001; Antolin et al., 2002 & ASTM

| Properties                                                            | Biodiesel from algae oil | Diesel Oil      | ASTM Biodiesel standard          |
|-----------------------------------------------------------------------|--------------------------|-----------------|----------------------------------|
| Density ( $\text{kg L}^{-1}$ )                                        | 0.864                    | 0.838           | 0.84-0.90                        |
| Viscosity ( $\text{mm}^2 \text{s}^{-1}$ , cSt at $40^\circ\text{C}$ ) | 5.2                      | 1.9-4.1         | 3.5-5.0                          |
| Flash Point ( $^\circ\text{C}$ )                                      | 155                      | 60              | Min 100                          |
| Solidifying point ( $^\circ\text{C}$ )                                | -12                      | -50 to 10       | -                                |
| Cold filter plugging point ( $^\circ\text{C}$ )                       | -11                      | -3.0 (max -6.7) | Summer max 0<br>Winter max < -15 |
| Acid value ( $\text{mg KOH g}^{-1}$ )                                 | 0.374                    | Max 0.5         | Max 0.5                          |
| Heating value ( $\text{MJ kg}^{-1}$ )                                 | 41                       | 40-45           | -                                |



# Stability of biodiesel

- Biodiesel from oils and other feedstocks is found more susceptible to oxidation due to exposure to oxygen of the air and higher temperature, the magnitude of which depends on the extent of unsaturation in the fatty acid molecules.

## The stability is divided into:

- Oxidation stability
- Thermal stability
- Storage stability



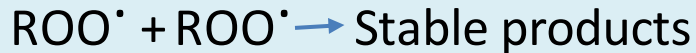
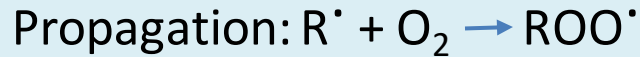
# Oxidation stability

$\text{ROO}^\bullet$  : Lipid peroxy radical;

$\text{ROOH}$ : Lipid peroxide

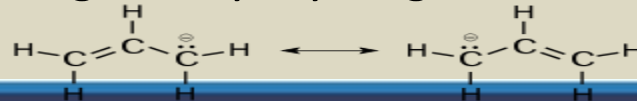
- ✓ Oxidation of biodiesel is due to the unsaturation i.e. the presence of double bonds in fatty acid chain.
- ✓ These double bonds offer high level of reactivity with  $\text{O}_2$ , especially, when it is placed in contact with air/water by indirect/direct exposure.

## Primary oxidation



- The initiator is a free radical that is generally produced by the decomposition of hydroperoxide present in the fat, which in turn is produced by photooxidation,
- High temperature/ metal ions in the lipid's environment helps its formation.

- A free radical attacks the lipid, abstracting an allyl hydrogen atom and generates an allylic radical.



# Oxidation stability

## ■ Secondary Oxidation

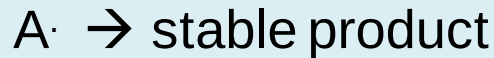
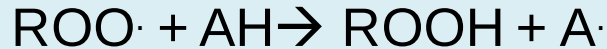
- Once the fatty oil hydroperoxides are formed, they ultimately decompose to form aldehydes.
- As hydroperoxides decompose, oxidative linking of fatty acid chains can occur to form species with higher molecular weights, i.e. oxidative polymerization resulting in an increase of viscosity of the oil fuel.
- Increased in poly-unsaturated fatty acid chains enhance the oxidative polymerization in the fatty oils resulting in the formation of insolubles.



## Methods to increase the stability

- Use of antioxidants as additives: These may be:
  - ✓ Natural, e.g., tocopherols, vitamin E etc
  - ✓ Synthetic, e.g., Pyrogallol, Propyl Gallate, Butylated  
hydroxyanisole, Butylated hydroxytoluene, Tert-butyl  
hydroquinone etc.

The mechanism of improving the stability of fuel is given as:

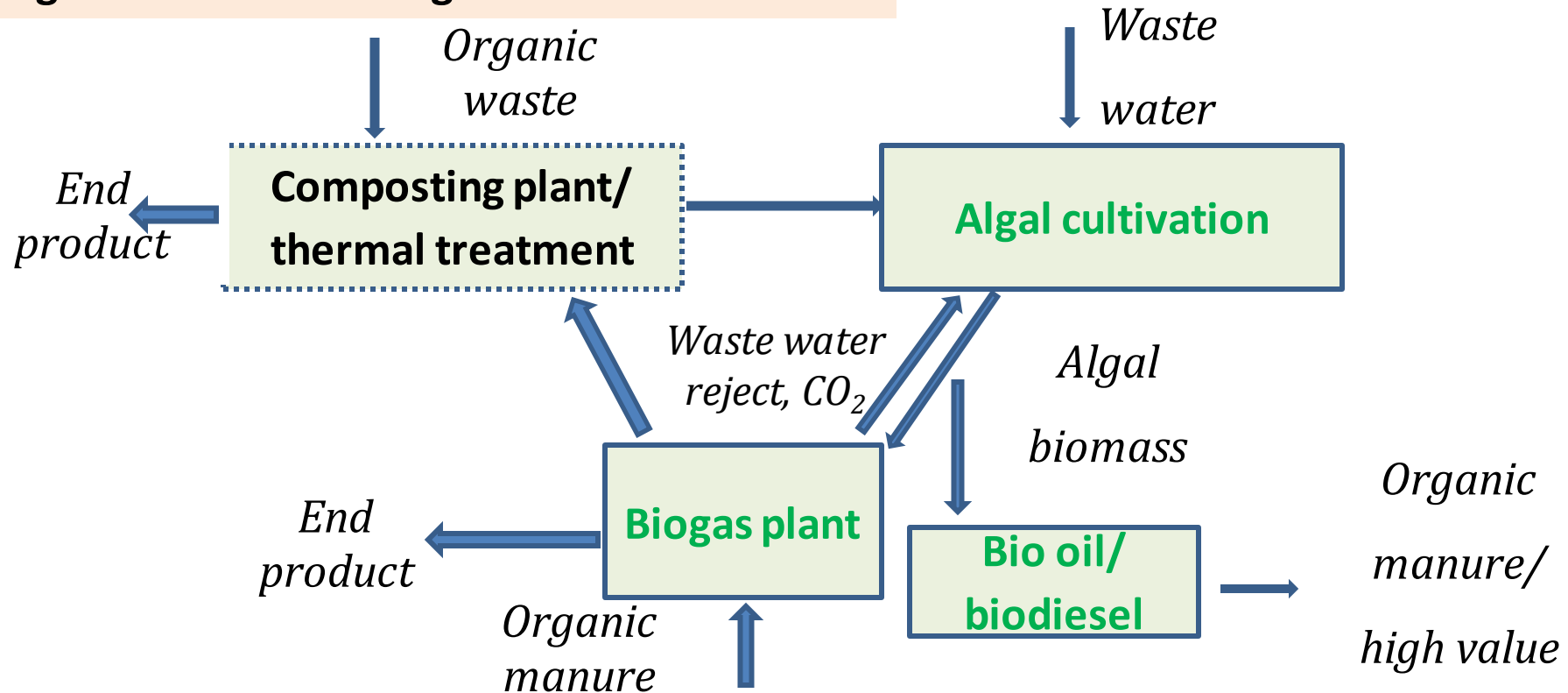


## Challenges for micro algae

- One of the biggest challenges in culturing microalgae for biodiesel is to find a suitable strain that grow fast and capable to produce as much lipid as possible during its culture.
- Another major challenge in algae culture is to design a cost effective photo bioreactor, which mitigates contamination risks and enhances high growth.
- High cost of oil extraction from microalgae.
- Even with all these challenges, biodiesel from microalgae looms as the only renewable biofuel that can substitute petro diesel completely (Chisti, 2007 and 2008; Brown et al., 1993). An additional advantage of microalgae is the capability to capture CO<sub>2</sub> and reduce greenhouse gas effects.



## Integrated scheme for algal biomass utilization



Source: International seminar on sustainable industrial algae production and related business opportunities, New Delhi, March 27, 2014 (Organized by Team Finland and ONGC)

### Civil/Commercial Jet fuel

Type1: Jet A-1: It is based on Kerosene grade fuels, which are suitable for mostly turbine engine aircraft. Flash point above 38°C.

Freezing point maximum of (-47°C). Net heat of combustion minimum of (43.15 MJ/kg).

Density at 15°C is 804 kg/m<sup>3</sup>.

Type2: JET A: It is another Kerosene based fuel. Flash point above 38°C ; Freezing point maximum (-40°C)

### Military Jet Fuel

Type1: JP-4: This is the military equivalent grade fuel of Jet B with the addition of corrosion inhibitor and anti-icing additives, has high efficiency.

Type2: JP-5: These types of fuel possess high flash point type kerosene based fuel.

### Civil/Commercial Jet fuel

Type3:TS-1: Kerosene type BP Jet TS-1 with higher volatility (for lower temperatures and **flash point is 28 °C minimum**), Net heat of combustion is 43.2 MJ/kg, density at 15°C is 787 kg/m<sup>3</sup>.

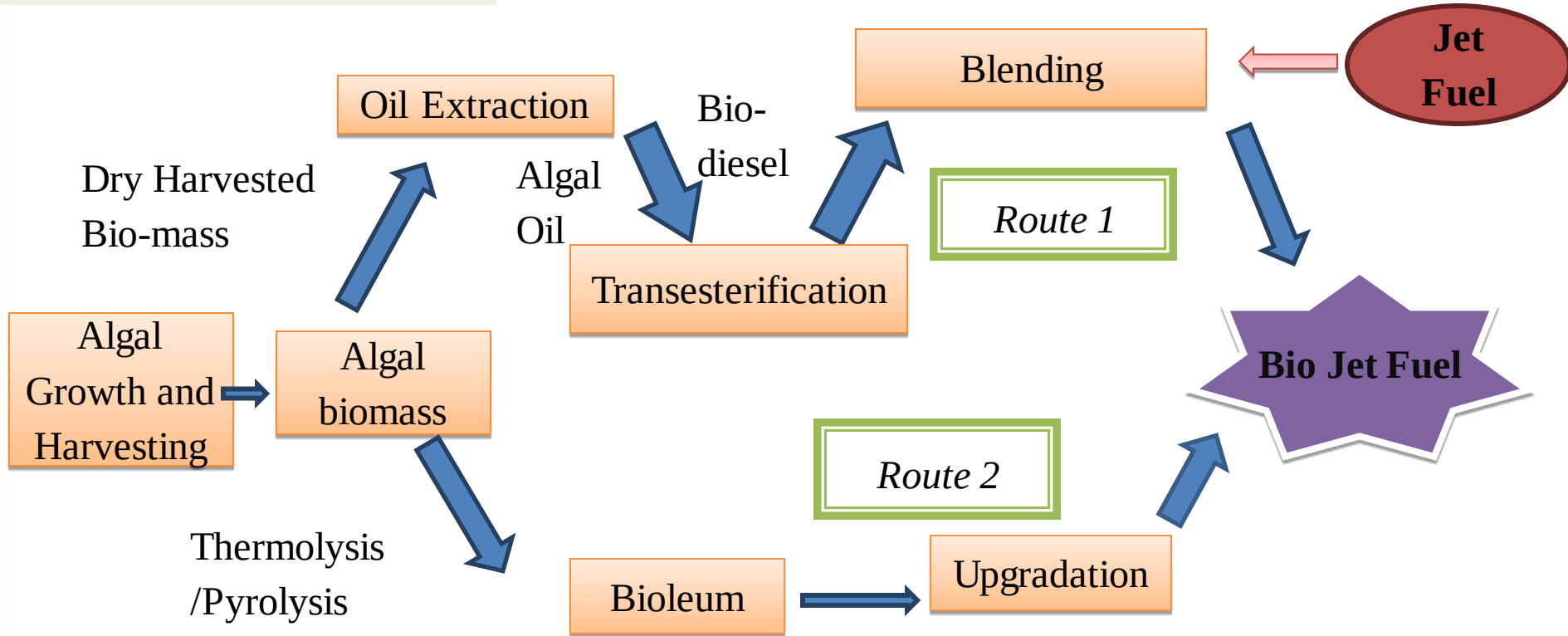
Type4: JET B: It is distillate product covering the naphtha and kerosene fractions component. Freezing point maximum of (-50°C). Minimum of (42.8MJ/kg) net heat of combustion. Very high flammability. Significant demand in high cold climates and such climatic region.

### Military Jet Fuel

Type2: JP-5: These types of fuel possess high flash point type kerosene based fuel.

Type3: JP-8: This is military equivalent of Jet A-1 with the addition of corrosion inhibitor with anti-icing additives.

# Bio jet fuel routes



## Institutes and Industries focusing on research in the field of algal fuel

| Industry/Institute                                   | Country   | Research area                                                                                                                       | Reference                         |
|------------------------------------------------------|-----------|-------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------|
| The Bioeconomy Institute (BEI) Iowa State University | USA       | Cost effective harvesting of microalgal cells                                                                                       | IOWA State University. 2016       |
| Leibniz University, Hannover                         | Germany   | Development of disposable photobioreactors                                                                                          | Leibniz University Hannover. 2016 |
| Murdoch University                                   | Australia | Industrial production of oil and carotenoids from microalgae, Efficient use of solar energy by microalgae, Sponge-algae interaction | Murdoch University. 2016          |



## Institutes and Industries focusing on research in the field of algal fuel

| Industry/Institute                                         | Country     | Research area                                                                                   | Reference                 |
|------------------------------------------------------------|-------------|-------------------------------------------------------------------------------------------------|---------------------------|
| University of Texas, Austin                                | USA         | Extraction of oil and other high value products from algae,                                     | University of Texas. 2016 |
| CFTRI Mysore<br>(Central food technological res. Inst.)    | India       | Enhancing lipid accumulation in microalgae, isolation and characterization of native microalgae | CFTRI. 2016               |
| Korea Advanced Institute of Science and Technology (KAIST) | South Korea | Using genome editing techniques for increased biofuel production from microalgae                | KAIST. 2014               |
| IIT Roorkee                                                | India       | Biofuel, genetic modification,                                                                  | IIT Roorkee. 2016         |

## Institutes and Industries focusing on research in the field of algal fuel

| Industry/Institute                       | Country   | Research area                                          | Reference               |
|------------------------------------------|-----------|--------------------------------------------------------|-------------------------|
| Monash University                        | Australia | Bioremediation and biofuel production by algae         | Monash University. 2016 |
| Indian Institute of Technology Kharagpur | India     | Increasing biofuel production from microalgae          | IIT Kharagpur. 2016     |
| Cellana Inc.                             | USA       | Developing biodiesel production system from microalgae | Cellana Inc. 2013       |
| Algenol                                  | USA       | Cost effective ethanol production from microalgae      | Algenol. 2015           |

## Industries producing algal biofuel at commercial scale

| Industry        | Country | Product                                | Production capacity                                | Reference             |
|-----------------|---------|----------------------------------------|----------------------------------------------------|-----------------------|
| Algenol         | USA     | Ethanol, gasoline, jet fuel and diesel | 8000 gallons/acre/year                             | Algenol. 2015         |
| Solazyme        | USA     | Renewable Biofuel                      | -                                                  | Solazyme. 2016        |
| BioFuel Systems | Spain   | Bio-oil and ethanol                    | -                                                  | Planet Ark. 2006      |
| Cellana Inc.    | USA     | Biproducs of biofuels                  | -                                                  | Cellana Inc. 2013     |
| Sapphire Energy | USA     | Crude oil from algae                   | 100 barrels/day in 2012 (5000 barrels/day by 2018) | Sapphire Energy. 2013 |
| Reliance        | India   | Biofuel                                | 66800 barrels/day (projected)                      | Biofuels Digest. 2015 |



# Thanks

