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Advances in Biofuel Technology: A Review

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Abstract
Anthropogenic Greenhouse Gas Emissions and Energy Security are one of the major problems faced by modern era. There are many factors which are the source of their production and accelerate their intensity of damage, among which the major one is high reliance on fossil fuels for our day-to-day activities. Renewable Energy although has started to share a considerable portion of energy production and utilization; but still there is need to focus on new and improved sources of Renewable Energy for future supplementation in terms of energy needs. In this context, Microalgae have emerged as a promising source as a sustainable and secured energy source which offers a additional perk of fast recovery. This article reviews the state-of-art of algal biomass production and conversion into various economically important fuels, which can be used.
Keywords: Algal biomass production, Biofuels, Renewable Energy, Energy Security.

I. INTRODUCTION

Energy security is one of the major factor to access the economic development of any country. According to IEA, Energy Security can be defined as uninterrupted energy supply to everyone at affordable prices in the present along with safeguarding the energy resources for future generations. If a country is secured in terms of energy, it ought to progress and develop in future as it has already resources to fulfil the needs of present and has safeguarded for future needs. In Indian context, this aim has still a long way to go but being blessed with ample number of renewable resources of energy this aim seems to be achievable with little steps to be taken.

Renewable energy resources are sources which can be used again and again and are abundantly available in nature that too without any cost. Some of the sources are Solar Energy, Biomass Energy, Wind Energy, etc. With the use and implication of appropriate technology and knowledge these resources can do wonders in providing energy security. These resources are environment- friendly also which is an added advantage for their use. As per the recorded data on November 2020, the total installed capacity of India to generate electricity from renewable sources is 38% of the total capacity. This data is still increasing with time in India because as per research till September 2020; 89.22 GW capacity projects were operational and 48.21 GW capacity projects are at various stages of implementation whereas 25.64 GW capacity projects are under various progress of implementation or approval. These data clearly indicates that the share of renewable energy resources in Indian context is increasing exponentially.

Since 19th century the production of biofuels is reported. It was when bioethanol was first derived from corn. At the same time first Rudolf Diesel's engine ran on fuel comprising of peanut oil. Until the 1940s, biofuels were seen as viable option for transportation fuels, but at that time their high cost of production and low calorific values as compared to fossil fuels acted as inhibitory factors for their further development. In 1970s biofuels again gained attention with the production of ethanol from sugarcane bagasse in Brazil and from corn in United States. In both the countries their production started on commercial levels by mid-1970. But their production gained its growth from the last few decades only after the support from government policies and subsidies. People were made aware of the positives and advantages of biofuels with the help of NGOs and other help groups. It was made them understand that besides energy security, biofuels also offer sustainable development with the reduction of CO_2 emissions. However, biofuels still have to go a long way to gain popularity.

Biofuels as earlier stated are derived from biomass sources, which are again renewable sources of energy. Production of chemical energy from sunlight is regarded as one of the most important processes for life to sustain on this planet. This conversion is responsible for plant reproduction. "Biomass" term is used for all the organic resources that can be used for the production of bioenergy, mainly including forests, agricultural crops and residues resulting from agroforestry and livestock. Biomass can be classified under two major groups: Traditional option and Modern option. In traditional option, the biomass is directly burned to produce energy whereas, in the modern option, the biomass is converted into high calorific fuels with the help of various biological or chemical conversion routes. The examples of biomass under traditional use can be combustion of fuelwood, etc. which produces pollution and low energy content whereas examples of biomass under modern use can be biogas production, bio-oil production and biofuels production.

Biofuels are energy products produced from biomass using modern route of conversion. Their production occurs by means of physical, chemical and/or biological processes. The American National Biofuels Action Plan points to five strategic areas in the biofuels production chain that should have federal investment:

- Production of Raw Materials
- Logistics of Raw Materials
- The Best Conversion Process
- Fuel Distribution Systems
- Technologies for the Efficient Use of Fuel

In India, it is aimed to replace at least 20 % of the total diesel requirement with biodiesel with the help of National Biodiesel Mission (NBM). In 2003, the government has taken steps towards the use and popularity of biofuels by making it mandatory to blend the fossil fuel with 5% biofuel. This is known as E5 blend throughout the country. In compliance to this Andhra Pradesh, Daman, Diu, Goa, Dadra, Nagar Haveli, Gujarat, Chandigarh, Haryana, Pondicherry, Karnataka, Maharashtra, Punjab, Tamil Nadu and Uttar Pradesh using it commercially. T was in 2005 that India ranked fourth in the production of ethanol by producing 1.6 billion liters. These data are increasing exponentially every day with the increase in the awareness and popularity of biodiesel with the help of National Biodiesel Mission (NBM). NBM was implemented in two stages:

1. Demonstration project: It was working from 2003-2007. The main objective of this project was to cultivate 400,000 hectares of Jatropha, which were expected to yield about 3.75 tons of oilseed per hectare annually. The project also accompanies other objectives such seed collection, oil extraction and establishment of government aided transesterification plant.
2. Commercialization period: it lasted from 2007 to 2012 with its main focus on Jatropha cultivation and installation of transesterification plants with the aim to meet at least 20 percent of India's diesel needs through biodiesel.

Considering this entire scenario, it will be apt to state that technological advances in the production and conversion of biofuels can lead to more competitive fuels. The development of chemical and biological sciences, along with new crops for energy production, new enzymes and artificial simulation of biological processes (anaerobic digestion, fermentation, etc.) can reduce their production. This review is done with the objective to discuss some of the recent advances in the production of biofuels.

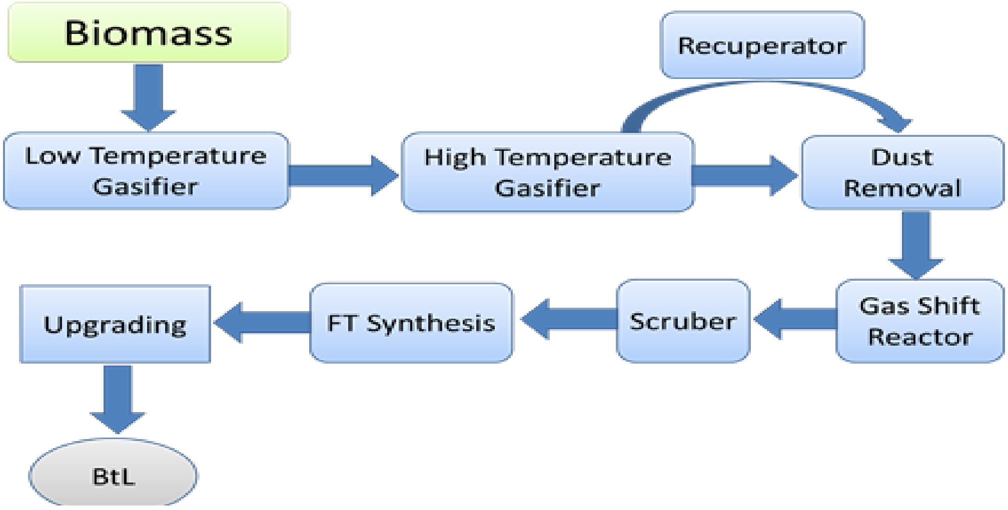
Advanced Biofuel Technologies

It is clear till now that the term Biofuel is quoted to refer all the fuels produced from biomass. Biofuels are commonly divided into first-, second- and third-generation biofuels, but these can also be classified depending on the technical advancement, GHG emission balance or feedstock used. The classes based on such classification are often termed as "Conventional" and "Advanced".

Conventional biofuels are those fuels which have been commercially well established and have well developed technologies for their production and processing. These mostly includes first-generation biofuels which are made from edible food products which are mainly sugar- and starch-based ethanol, oil-crop based biodiesel and straight vegetable oil, as well as biogas produced by anaerobic digestion.

Advanced biofuels mainly include second and third generation biofuels which still are under development either technologically or commercially. This category includes hydrotreated vegetable oil (HVO), lignocellulosic biomass biofuels, cellulosic ethanol, biomass-to-liquids (BtL) diesel and bio-synthetic gas (bio-SG). Algal biofuels are also included in this category.

The hydro-processing of oils into hydrocarbons using an appropriate catalyst and appropriate operating conditions leads to the production of Green Diesel, which can be blended with diesel fractions of petroleum origin. Besides a much higher cetane number, the advantage of green diesel compared with conventional biodiesel is the higher stability. BtL is the most used process to produce second generation biodiesel. The BtL biodiesel may be derived from any biomass, especially lignocellulosics with low moisture content. A typical process for producing BtL biodiesel is shown below:



The main catalytic process to convert the syngas into a liquid fuel is known as Fischer-Tropsch (FT). This process occurs at high temperatures; it consists of a reaction between hydrogen and carbon monoxide that is explained by the following equation:

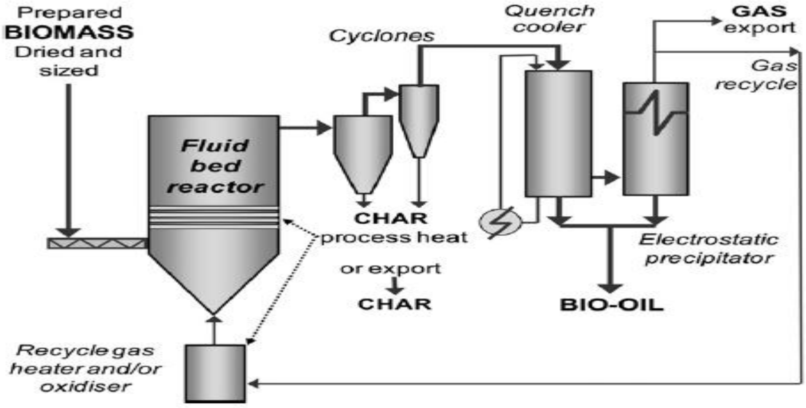
$$(2n+1)H_2+n(CO) \rightarrow C_nH_{2n+2}+n(H_2O)$$

The catalysts most commonly used are Mo, W, Co and Ni, and the recent studies have been focusing on new and more efficient catalysts. The FT process results in the synthesis of the BtL biodiesel. While the FT process has been commercially available for decades, some efficiency and environmental issues associated with syngas production from biomass still need to be addressed; therefore, key recent efforts have been focusing on these issues. Moreover, in recent years hydro-processing in subcritical and supercritical water mediums as well as in supercritical alcohols have been attracting attention. Finland and Singapore have the first large-scale plants producing HVO.

Some innovative processes have been evaluated for biodiesel production, such as enzymatic hydrolysis and cracking (pyrolysis), which are frequently pointed out as breakthroughs for vegetable oil conversion to fuels. The H-Bio process patented by Petrobras is a special case of the cracking process, which involves a catalytic hydro-conversion of a mixture of diesel fractions and vegetable oil to linear hydrocarbon chains, similar to what already exists in conventional diesel, with a very high conversion yield, at least 95%, without residue generation and a small amount of propane produced as a by-product.

Bio-oil from Pyrolysis

Pyrolysis has been applied for thousands of years to charcoal production but it is only in the last 3 decades that fast pyrolysis at moderate temperatures and with very short reaction times has become of considerable interest. Fast pyrolysis is a thermal decomposition process consisting of rapidly (2-3 s) heating the ground biomass to temperatures between 400 °C and 600 °C in the absence of air, followed by rapid cooling. Crude pyrolytic oil or commonly known as bio-oil, is a dark brown coloured liquid which resembles the elemental composition of biomass.



Scheme of the Fast Pyrolysis Process

Reprinted from Biomass and Bioenergy, 38, A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, 68-94, 2012.

Bioconversion technologies have lower capital costs than thermal conversion methods as they do not require the long-distance transport of biomass. The product obtained in the form of oil is a more opt option for long-distance transport than the raw materials required in the process. Along with bio-oil, a solid material is also produced known as Biochar which is a great source of soil amendment. Alternatively, the bio-oil and the biochar can be treated as raw materials in the production of BtL.

On the other hand, the information related to the pyrolysis of animal fats, vegetable oils and sewage sludge is still limited. This may be, at least partly, attributed to the loss of valuable liquid hydrocarbons to gas and coke, generally observed during pyrolysis of biomass. Moreover, because of the high content of guaiacols and phenols, liquids from pyrolysis are not stable. Therefore, in situ catalysts are being used to improve the quality of pyrolysis liquids. The use of suitable catalysts significantly increase the yields and also optimize the composition of the output products.

Bio-oils also exhibit some undesired properties, such as acidity, thermal instability, high oxygen content (35-40%), low heating value, high viscosity, corrosiveness, and chemical instability, which limits their application for vehicle fuels. Upgrading bio-oil to replace petroleum-based transportation fuels requires deoxygenation and refining, which can only be done by integrated catalytic pyrolysis, hydrotreatment, esterification (biodiesel), gasification (hydrogen, syngas), blending or other processes.

This technology has been successfully demonstrated on a small scale and is on the verge of commercial application but its economic feasibility is still low as compared with fossil fuels and thus it faces economic and other non-technical barriers.

Bio-Oil from Hydrothermal Process

Biomass processed in liquid medium; mostly water, under pressure at temperatures of 200-450°C produces oil and solids that have low water content. This process offers higher yeild than those of pyrolysis. This process can be done with or without a catalyst. Under sub/supercritical conditions, water acts as a reactant, catalyst, and solvent for typically acid- or base-catalyzed reactions. Apparently, water may also supply hydrogen for cracking, which is the hydrolysis of triglycerides, followed by decarboxylation.

A recent trend in hydro-processing is using polar protic solvents (e.g., methanol, ethanol, diethylene glycol, etc.), as the homogeneity of the bio-oil may be improved by diluting it in these solvents. This may be critical for bio-oils derived from municipal solid waste. The homogeneity of the medium can be further improved under supercritical conditions. This technology is being developed for use on algae and waste biomass. Developers of this technology include Changing World Technologies (West Hampstead, NY, US), EnerTech Environmental Inc. (Atlanta, GA, US) and Biofuel B.V. (Heemskerk, Netherlands).

Dimethyl ether (DME)

Dimethyl ether (DME) can be produced from methanol by catalytic dehydration or from syngas. DME is a simple ether that have the potential to replace propane in liquefied petroleum gas. It is a promising fuel in diesel engines with high cetane number. This technology is still in the demonstration stage, and in 2010 at Sweden the first plant running with this technology started.

Hydrogen from biomass

Hydrogen, the “fuel of the future”, has long been considered a good source of energy due to its high energy density and sustainability, and may finally become an important component of the energy balance. Hydrogen gas is also used for the production of chemicals, hydrogenation of fats and oils, processing steel and desulfurization and reformulation of gasoline in refineries. Difficulty in handling and expensive storage are the main disadvantages of hydrogen.

Green algae, cyanobacteria, anoxygenic photosynthetic bacteria, obligate anaerobic, and nitrogen-fixing bacteria are some of the organisms blessed with the capability for H_2 production but in less efficiency. The low-cost hydrogen-based fuel cells which have different processing routes for hydrogen production from biomass can be broadly classified as:

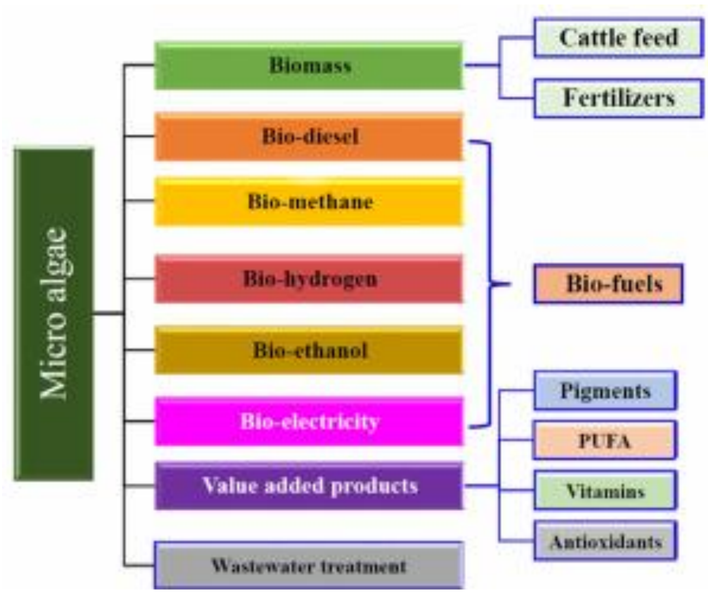
- Thermochemical gasification coupled to water gas shift;
- Fast pyrolysis followed by reforming of carbohydrate fractions of bio-oil;
- Direct solar gasification;
- Miscellaneous novel gasification processes;
- Conversion of syngas derived from biomass;
- Supercritical conversion of biomass;
- Microbial conversion of biomass.

The hydrogen obtained from renewable biomass is a sustainable source of energy, and is therefore known as Biohydrogen, which is still an underdeveloped technology. Areas of research for enhanced biohydrogen production includes:

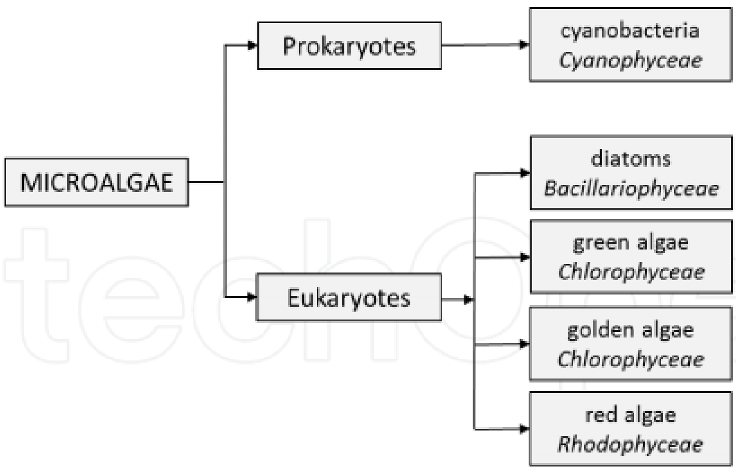
- Reengineering of photosynthetic microorganisms
- Development of effective technique for separating and refining the hydrogen formed
- Integrated systems for biohydrogen production with techno-economic analyses.

The Microalgae

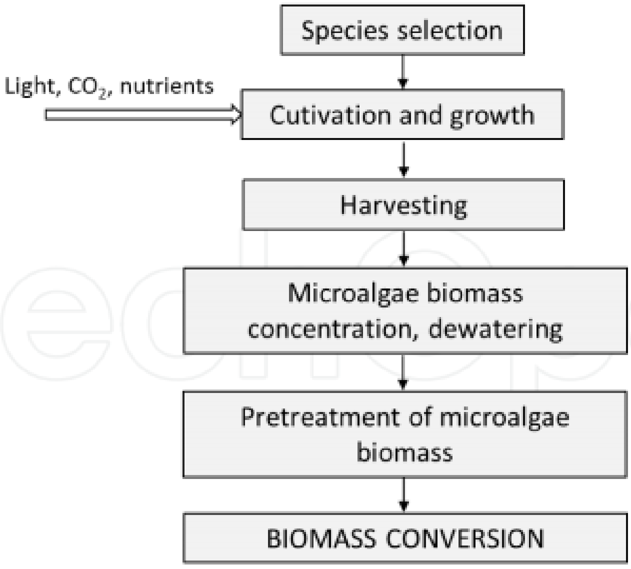
Microalgae have been used since a long time from being used by Chinese people during the famine situation to present where there is a variety of commercial as well as industrial applications of the algae. Some of the main uses of microalgae are listed below.



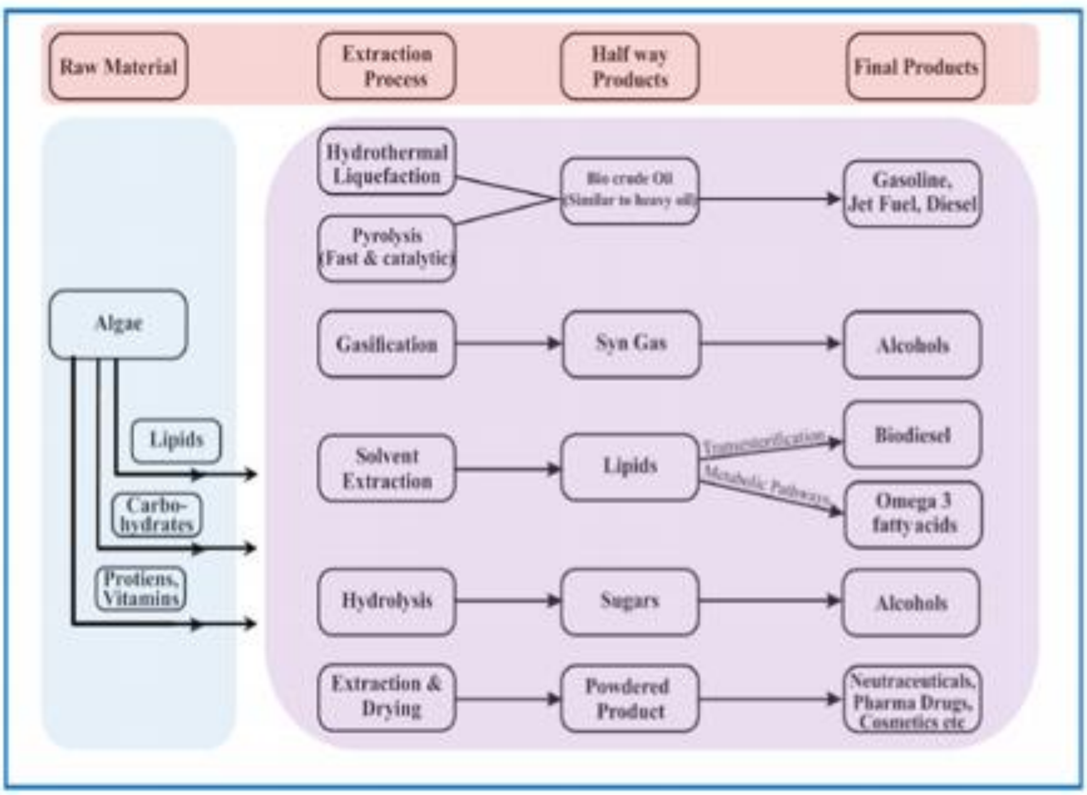
It is estimated that there are over 100 000 species of microalgae which can be divided as Prokaryotes and Eukaryotes. The following flowchart helps to understand this classification better.



Microalgae are being preferred source over plant sources because:
(a) They have a high photosynthetic efficiency.
(b) Can grow in water with different levels of nutrients.
The various processes to use algae for bio-chemical conversion routes can be summarised as:



A variety of fuels other than biodiesel can be obtained from algae. Some of them are shown in figure below.

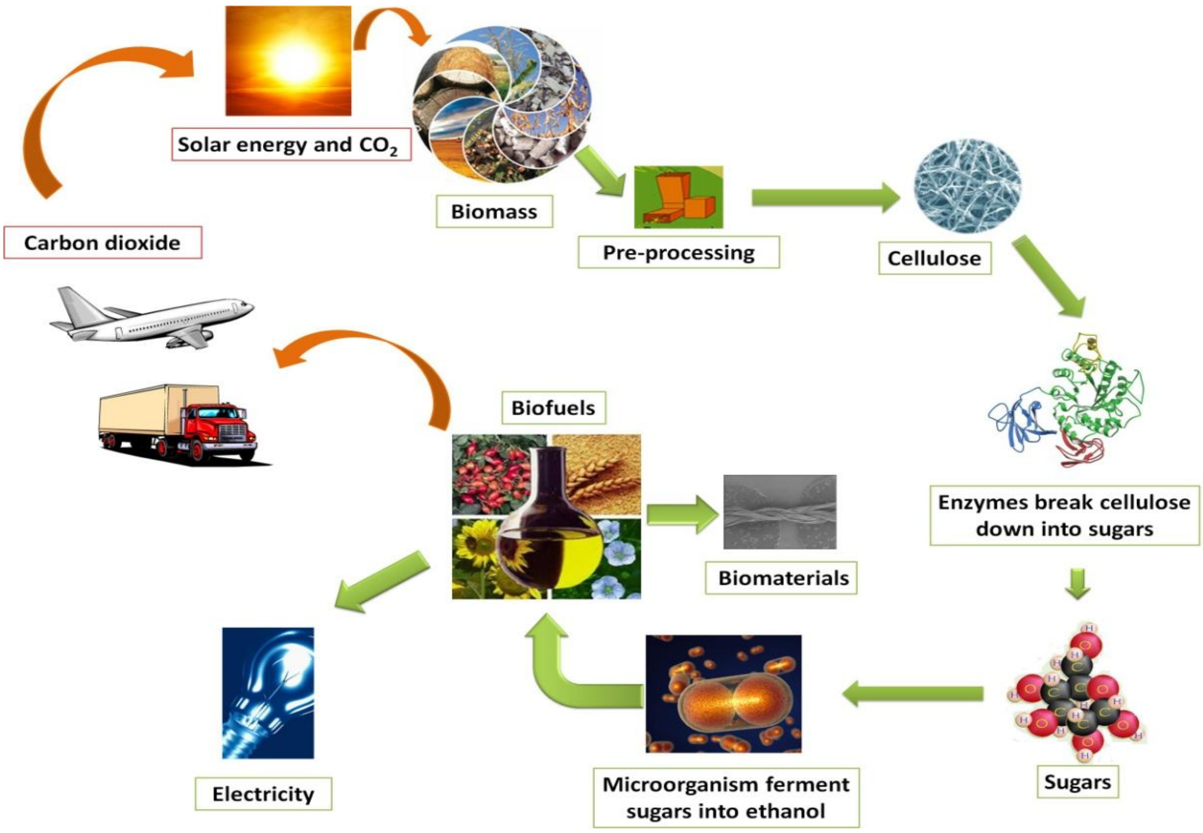


Different products of Algae from different extraction process

There are startup companies who are working on the commercialization of algae fuels in US, New Zealand and Israel.

Bio-refineries

The concept behind the term biorefinery is similar to traditional oil refineries. In biorefinery; co-production of fuels, chemicals and energy from different biomass feedstocks is seen. It will be appropriate to state that biorefinery optimally uses biomass for materials, chemicals, fuels and energy applications. Biorefineries contributes in the sustainable and efficient use of biomass by providing a variety of products. An overview of biorefineries' production technologies and products is shown below:



Neste Oil Corp. is the only refinery which produces biofuels from vegetable oil. A commercialization stage is also approaching the UOP/Eni Ecofining process developed by Honeywell's UOP.

II. CONCLUSIONS

Biofuels, although have been produced since a long time and now is one of the fastest growing research interests for most of the researchers. The full replacement of fossil fuels by biofuels is not deemed to be achievable but, nonetheless, modern biofuels have a crucial role to fulfil in the long term to help limit the growth of GHG emissions and to lead the transition of the current petroleum-based society towards a more sustainable one. Recently advanced options for biofuel production have gained more interest due to their promising role of replacing fossil fuels. The technology used for production of these advanced options still needs attention and improvement before being used on a commercial scale, which can take few more years. Their commercialization requires advanced laboratory-scale processes to improve yields and productivities.

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