DIRECT TRANSESTERIFICATION FOR BIODIESEL EXTRACTION FROM MICRO-ALGAL BIOMASS: A REVIEW

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Abstract  
The biodiesel production has gone through fast growth over the past decade. Microalgae have large scale cultivation resources. The non edible biodiesel resources have potential to meet the future energy demand without any environmental loss. Despite the umpteen advantages microalgal biodiesel is still facing technical and economical challenges. The complexity and the production cost related issues have been studied by many researches and scholars all over the globe for the optimum biodiesel extraction. This article reviews about the recent development and process parameters affecting the biodiesel production by insitu-transesterification. This article also reviews about the recent techniques which are being used for large scale production. It has been studied that insitu transesterification is being used for economic production of bio fuels and the process parameters viz. reaction temperature, reaction time, types of catalyst and methanol to algae ratio play a significant role in commercial biodiesel production. There is a focus on insitu transesterification which is most efficient and economic oil production process for wet as well as dry micro-algal biomass. Furthermore, all other issues related to the biodiesel production such as viscosity purification and processing time are taken into consideration.

Keywords: microalgae, innovation in biodiesel extraction, insitu transesterification, Biofuel Non-edible feedstock,

1. Introduction  
Biodiesel is derived from vegetables oil has a great potential as a substitute of diesel fuels. Biofuels are generated from mainly two sources namely edible and non edible biofuels. Edible biodiesel resources are usually employed for maximum biodiesel extraction. Almost 95% of world's total biodiesel is produced from edible biodiesel resources. However, edible biodiesel resources such as soybean, rapeseeds, sunflower and palm oil are associated with sever environmental problems like deforestation, vital land availability and climate change[1]. The limitations of edible resources can be minimized by the introduction of non-edible biodiesel resources viz. Jatropha Curcas, neem seeds, mahua and algae. Algae are kept in the category of third generation biofuel resources. These resources are most efficient and eco-friendly and excessively being adopted as sustainable future fuels. Algae are plant like organism without true roots, leaves and vascular bundle. They can be collected from different aquatic bodies such as pond, river and sea. Algae are of two types namely microalgae and macroalgae. Microalgae available in the size of micro to nano metre and known as single cell organisms[2]. Macroalgae on the other hand are known as seaweeds available in the size of 60 to 150 m in length.

2. Material and Method  
Various biodiesel extraction techniques have been introduced by the research scholars some of them are pyrolysis, gasification, micro-emulsification, two-step transesterification,
super critical transesterification and insitu transesterification. Out of these techniques insitu transesterification is the most useful economic and efficient process for biofuel generation from biomass. It is a chemical reaction in which triglyceride reacts with an alcohol in presence of homogenous or heterogeneous to produce free fatty alkyl ester (FFEAs). The transesterification reaction is shown below.

$$R'O'H + R'OR = R'O + R'OH + R'OR$$

Alcoholic Group + Triglycerides = Glycerol + Fatty Methyl Esters
Where R', R'' are alkyl groups [3].

3. Types of Transesterification
Commonly known Transesterification techniques are base catalyst, acid catalyst, enzyme catalyst and supercritical transesterification. Base catalyst method is broadly used for oil generation. It can't be reuse or recycled. It has been found that acid catalysts are slower than that of base catalyst and most suitable for high lipid containing oil. Enzyme catalyst technique is technique laborious in process and not useful for commercial production of biodiesel. Talking about supercritical transesterification high temperature around 250°C and pressure is required for the oil extraction. In this process use of catalyst is optional.

Numerous researches have been reported on transesterification process. Chamola R et al.[4] have been conducted insitu transesterification of dry algae with Methanol, acid catalyst (H$_2$SO$_4$) and base catalyst (NaOH). they found that acid catalyst has significant role in biodiesel extraction than that of base catalyst, reported maximum yields of 89.58% and 87.42% for acid and base catalyst respectively at 50°C in 60.4 min. Shirazi et al.[5] have been conducted insitu transesterification of dry algae with methanol, hexane and moisture content. 99.32% yields have been reported by using Response Surface Methodology (RSM) and Centre Deviation Method (CDM).

A Salam et al.[6] have worked with marine as well as fresh water microalgae for biodiesel generation. They used methanol, hexane and different catalyst to reduce the cost of the biodiesel production. Velasquez Orta and Harvey[7] conducted a research on chlorella Vulgaris oil in presence of methanol and a suitable catalyst. They claimed 77.6% yield with methanol to oil ratio 600. 94.9% fatty acid methyl ester (FAMEs) is obtained by Dong et al.[8] during two step transesterification and direct transesterification using amberlyst-15 and base catalyst. Spirulina Chlorella and pond water algae have been applied by Nautiyal et al.[9] for the oil extraction through transesterification process. It has been suggested that hexane could be better solvent for high yield.

Im et al.[10] reported biodiesel yield using supercritical transesterification with chloroform ethanol and H$_2$SO$_4$. They studied the involvement of moisture content decreases the output values. Transesterification of dry algae using solvents viz. n butanol, chloroform, ethyl ether, hexane, acetone and petroleum to check which has vital role on the output yield for oil production. Zhang et al.[11] found that n hexane and petroleum ether are best solvent due to miscibility with alcoholic products. Kaisim and Harvey [12] performed transesterification on jatropha curcus using alkali catalyst at 60°C. They reported maximum FAME yield of 95%. A research has been conducted by Hass and Wanger[13] using wet biomass and acid catalyst at 65°C. Maximum yield of 96% was recorded with methanol/oil ratio 308:1.

3. Process Parameters in Insitu Transesterifcation Process
Direct transesterification crucially depends upon process parameters like processing time, processing temperature, methanol/algae ratio and catalyst concentration. some of the study has take processing time in between 60 to 180 min and operating temperature range is suggested in between 60 to 80°C[14]. Effective methanol/algae ratio has been suggested as (8% to 20%)(W/W). Batch reactor is used to extract biodiesel from algal biomass which takes lots of steps are listed below in flow chart[15].

![Flow-Chart for Biodiesel Extraction](image)

Fig 3:- Flow-Chart for Biodiesel Extraction
Experimental procedures were done in a batch reactor as shown in the figure. The reactor was heated with an electric heater at
a constant temperature was sensed by a thermocouple, in a batch reactor mixture of methanol, algae, n-hexane and chloroform is prepared by weighing in chemical balance. A magnetic stirrer is used for the proper agitation and heat transfer rate along with a condenser.

According to research analysis, Oil production experiments are mostly decided by Response Surface Methodology (RSM) and Central Composite Design (CCD) through design expert software 11. The software has analysis of variance (ANOVA) feature to establish the statistical significance of process parameters on the output. The optimization is also conducted through the software in order to choose process variables to optimize the production yield.

![Diagram of Reactor](image)

Fig 4: Diagram of Reactor [4]

Statistical analysis is done by using regression equation, generated by the software. Furthermore, gas chromatography (GC) is used to optimize the experimental samples. The process is processed for 30 minutes at 230°C with nitrogen as a carrier gas. The study shows that GC analysis was performed by many research scholars using European standard EN 14103:2003.

The equation mentioned below is used to calculate the yield and stock solution i.e., Methyl heptadecanoate and n-heptane is used to determine the FFA content.

\[
\% \text{ of ME} = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} - V_{EI}}{m} \times 100
\]

Where,

- \( \sum A \) - Total peak area from the methyl ester in C14 to that in C24:1;
- \( A_{EI} \) - Peak area corresponding to methyl heptadecanoate;
- \( C_{EI} \) - Concentration of the methyl heptadecanoate solution (mg/ml);
- \( V_{EI} \) - Volume of the methyl heptadecanoate solution (ml);
- \( m \) - Mass of the sample (mg).

4. Factors Affecting Insitu Transesterification Process

FAME yields are influenced by the wet and dry algal biomass, reaction temperature, biomass grain size, agitation speed, reaction time and catalyst selection during insitu transesterification process.

4.1 Effect of Moisture Content

Some of the studies show that the output results are good with dry algae biomass. Actually the availability of water leads hydrolysis and as a result of which biodiesel disintegrates from solvent. Hass et al.[16] conducted a study on transesterification of soybean with 0% and 2.6% water content. They concluded that methanol consumption increased from 40% to 60% for dry and wet biomass respectively.

4.2 Effect of Biomass Particle Size

Biomass grain size has an important role in the consumption of solvent. Scholars have notes that as the particle size increases less solvent is required for the oil extraction. Methanol-to-dry algae ratio has crucial impact on the transesterification. Patil et al.[17] reported 85.75% of yield at 250°C in 30 minutes for wet biomass of Nannochloris. 5.82% methyl ester yield is collected in the processing of wet chlorella biomass (75% moisture) with methanol to dry algae ratio of 8:1.

4.3 Effect of Co-Solvent for the Process

Hexane and chloroform is most widely used co-solvent for the transesterification method. Hexane and chloroform improves the solubility of oil and enhance the output[18]. Hexane is preferred over chloroform because of its cost and availability.

4.4 Selection of Catalyst for the Oil Extraction

As it is already has been discussed that homogenous as well as heterogeneous catalyst can be used for the biofuel production. Selection of catalyst should be proper because it helps in fragmentation of hard micro-algae cell wall. NaOH, KOH, Ca(OH)\(_2\), Mg(OH)\(_2\), H\(_2\)SO\(_4\), NaOCH\(_3\) and HCl are some homogenous catalysts are being used by many researchers[19]. Furthermore, homogenous catalyst can be divided into two categories acidic and basic. Studies showed that H\(_2\)SO\(_4\) and HCl are most effective for utmost output. Commonly known heterogeneous catalyst are CaO, MgO, BaO, SrO, SrCO\(_3\) and MgCO\(_3\)[20]. According to some study both catalysts are outstanding to boost the oil production with the increase in consumption.

4.5 Effect of Agitation

Sivaramkrishnan and muthu kumar [21] reported as mixing speed increases from 150 to 180 rpm FAME also increase. They also suggested that output value doesn't change with
exceeding the mixing speed more than 450rpm.

4.6 Effect of Reaction Time and Temperature
It has been observed that reaction time for oil production is kept in a particular range from 60 to 180 min. Qian et al.[22] have conducted transesterification of rapeseed oil for 5 hour and they achieved output yield of 98%. They concluded that high reaction time doesn’t affect product yield. The best yield results are obtained for the range of 1 to 3 hours. Temperature on the other hand increases the solubility and high temperature reduces the viscosity of vegetable oil. According to a study when temperature changes from 35 to 55°C almost double value of output is obtained.

5. Conclusion
Recent developments in the in situ transesterification have been reviewed. The present study was emphasized on the use of direct transesterification for the sustainable development of fast and economic biodiesel extraction process. The numerous studies showed that the exploitation of edible biodiesel resources can be compensated by the application of microalgae because of high grade oil and widely abundant.

The research data indicated that direct transesterification resulted in maximum yields for FAEEs. In this case of in situ transesterification with methanol and ethanol almost equal yields are received but use of ethanol is a more economic, eco-friendly and efficient pathway. It was further observed that process variable had significant role on output. A comparison study of conventional process and in situ transesterification is discussed in this research.

5.1 Future Scope
Microagal biomass can be directly processed using a suitable catalyst and an alcohol in a batch reactor. Direct transesterification as the name implies, used to convert vegetable oil into fuel in one step. Mass production for commercial applications, oil purification and upgrading of fuel requires future attention and research.

References


