CHAPTER 5

SUMMARY AND CONCLUSIONS

5.1 SUMMARY

The growth in world population has resulted in a surge in energy demand and therefore, the need for secure energy sources. All the countries, including India and China are grappling with the problem of meeting the ever increasing demand of transport fuels within the constraints of international commitments, legal requirements, environmental concerns and limited resources. Biodiesel is an excellent substitute for conventional diesel fuel, because of being renewable, nontoxic and biodegradable. The availability of oil crops that serve as the sources for biodiesel production is limited. Macroalgae are a potential alternative source for the conventional feedstocks. Algal oil is suitable for esterification and transesterification reactions of biodiesel production. In this investigation, marine macroalgae were exploited as a feedstock for biodiesel production by two methods, namely, two-step process and in-situ transesterification under ultrasonic irradiation. Both methods have used to produce large quantities of high quality biodiesel.

5.2 CONCLUSIONS

Marine macroalgae were selected and processed to make them suitable for biodiesel production. The production of biodiesel from the selected macroalgae species was tried in two ways. In two-step process, algal oil was extracted with optimisation study. The extracted algal oil was characterized by GC-MS and $^1$H NMR analysis. The algal oil was treated by the acid esterification process to reduce the acid value and make it suitable
for the transesterification process. The optimisation study was conducted to
induce the reduction of acid value in algal oil. The pre-treated algal oil was
converted into biodiesel by the transesterification reaction using base catalyst.
The transesterification reaction conditions were optimised to increase the
conversion of the biodiesel. The produced biodiesel was confirmed and
characterised by analytical techniques. The fuel properties were analyzed
according to international standard specifications. A kinetic study was
conducted to experimental data and activation energy of the reaction was
calculated. In in-situ transesterification, a suitable catalyst and co-solvent
were selected for the specific biomass and the parameters were optimised to
increase the biodiesel yield. The conversion was calculated by $^{1}H$ NMR
analysis.

Based on the results the following conclusions were made:

- Marine macroalgae *Enteromorpha compressa*, *Ulva lactuca*
  and *Caulerpa peltata* were selected based on the oil quantity,
  availability, utility and toxicity.

- Ultrasonication pre-treatment (5 min) was found to be a
  suitable technique to isolate oil from the marine macroalgae
  biomass.

- Algal oil was extracted with a solvent system of 1% diethyl
  ether and 10% methylene chloride in n-hexane which
  produced highest oil extraction yield.

- The oil extraction yield (g/g) of 11.14% was achieved from
  *E. compressa* under the optimum extraction conditions of 5%
  moisture level, 0.149 mm particle size, 600 rpm mixing
  intensity, 55°C extraction temperature, 160 min contact time
  and 8:1 solvent-to-solid ratio. Palmitic acid (41.63) was found
  to be the predominant fatty acid in *E. compressa* algal oil
  composition. The acid value of the oil was found to be
12.6 mg KOH/g and it was reduced to 0.39 mg KOH/g by the acid esterification process with the optimum reaction parameters of 1.5 wt% H$_2$SO$_4$, 12:1 methanol to oil molar ratio, 400 rpm mixing intensity and 60°C for 20 min of ultrasonication time. *E. compressa* ME was produced from pre-treated algal oil by the transesterification reaction. The highest yield of 98.76% was obtained under the optimum conditions of 1% of NaOH concentration, 9:1 methanol to oil molar ratio and 600 rpm of mixing intensity at 60°C and 12 min of reaction time. The ultrasonication technique enhanced the acid value reduction and ME conversion, within a short duration of reaction time.

The optimized oil extraction parameters for *U. lactuca* were observed as 5% of moisture level, 0.12 mm of particle size, 500 rpm of mixing intensity, 55°C of extraction temperature, 140 min of contact time and 6:1 solvent-to-solid ratio. At this optimum condition, 10.88% of algal oil was produced from *U. lactuca* biomass. Palmitic acid (50.16%) was observed to be the chief fatty acid in the *U. lactuca* oil. The first pretreatment step was carried out to reduce the acid value from 14.27 mg KOH/g to 0.22 mg KOH/g with 1.75 wt% of H$_2$SO$_4$, 15:1 methanol to oil molar ratio, 25 min of reaction time at 55°C under 500 rpm. After the esterification reaction, the pretreated algal oil was subjected to the transesterification reaction and it reached the highest conversion of 95.92% with the optimized parameters of 0.75% NaOH, 6:1 methanol oil molar ratio and 600 rpm at 55°C for 14 min reaction time.

The optimum extraction parameters for *C. peltata* were identified as 6% moisture level, 0.105 mm of particle size, 600 rpm of mixing intensity, 55°C of extraction temperature, 180 min of contact time and 7:1 solvent-to-solid ratio to
produce 12.69% of algal oil. Among saturated fatty acids, palmitic acid was determined as a major fatty acid of 36.82% in algal oil. The reduction in the acid value from 19.35 mg KOH/g to 0.51 mg KOH/g was accomplished by pre-esterification process using 2 wt% of H₂SO₄, 15:1 methanol to oil molar ratio, 500 rpm mixing intensity and 65°C for 30 min reaction time. Up to 98.11% conversion of C. peltata algal oil into ME yield was achieved under the optimal reaction conditions of 1% NaOH, 12:1 methanol oil molar ratio and 600 rpm at 60°C for 16 min reaction time.

- GC-MS analysis confirmed the conversion of biodiesel based on the fatty acid composition of biodiesel produced from the algal biomass. NIR technique characterised the obtained biodiesel with the functional peaks corresponding to 6000 cm⁻¹ and 4425-4430 cm⁻¹. The standard retention time range in HPLC analysis validated the obtained biodiesel and algal oil samples. In HPTLC study, the Rᵢ value of the biodiesel and algal oil samples approved the formation of biodiesel from algal oil. The boiling point and the content of vaporisation materials verified the confirmation and conversion of the ME from algal oil.

- Kinetic studies revealed that the esterification reaction followed the first-order reaction kinetics and the rate constants were computed from the kinetics plot. The activation energies were determined as 78.52, 104.79 and 53.46 kJ/mol for E. compressa, U. lactuca and C. peltata, respectively.

- The transesterification reaction proceeds as a second-order kinetic mechanism. The reaction rate constants were increased with increase in the temperature and it was calculated from the slope of the linear equations. From the calculations using Arrhenius equation it was found that the selected macroalgae biomass E. compressa, U. lactuca and C. peltata required
115.02, 132.35 and 115.71 kJ/mol activation energy to actively participate in the transesterification reaction.

- The fuel properties of the algal biodiesel were found to be satisfied the limits of the ASTM standard specifications.

- In-situ methanolysis or direct transesterification eliminates the extraction step which could lead to a reduction in the overall production cost of biodiesel. An optimization study was conducted with in-situ parameters to get a higher yield and the conversion was confirmed by $^1$H NMR analysis.

- In-situ transesterification of *E. compressa* algal biomass produced 98.89% of ME yield, using 30 vol% of THF as a co-solvent, 10 wt% of H$_2$SO$_4$, 5.5:1 ratio of methanol to algal biomass and 600 rpm of mixing intensity at 65°C, for 90 min of ultrasonic irradiation time.

- The maximum yield of 98.74% of ME was derived from *U. lactuca* biomass, with the reaction parameters as 8% of H$_2$SO$_4$, 40 vol% of chloroform as a co-solvent, 6:1 methanol to biomass ratio, 700 rpm of mixing intensity, 65°C of temperature and 110 min of reaction time.

- The best result of 95.61% of ME yield was obtained from *C. peltata* biomass, under the optimum conditions of 14% H$_2$SO$_4$, 50 vol% of hexane as a co-solvent, 6:1 methanol to biomass ratio, 600 rpm mixing intensity, 60°C temperature and 100 min of reaction time.

- The biodiesel produced by in-situ transesterification method was analyzed by $^1$H NMR technique. The two characterized peaks from protons signal the methoxy groups in the ME (3.6 ppm, singlet) and those of the R-methylene protons present in all TG derivatives (2.3 ppm, triplet) authenticated the ME formation and conversion (%) of algal oil.
Both two-step and in-situ production methods were determined as efficient method to convert high FFA content feedstock into biodiesel. From this investigation, it has been proven that macroalgae could be used as a potential source to produce biodiesel. As a result, the utilization of marine macroalgae for biodiesel production provides dual benefits; it serves as a biomass for the production of biofuels and also saves our environment from detrimental effects.

5.3 SCOPE FOR FUTURE STUDY

The present investigation dealt with production of biodiesel from marine macroalgae using homogeneous catalytic system. The eco-friendly biodiesel can be used as a transport fuel by carrying out the following related works:

- These studies can be further extended to analyse the oxidation stability, corrosion and emission properties
- Methods to be improved the downstream processing and purification of synthesis biodiesel can be devised.
- Technical advances need to be improved to produce biodiesel from algal source using heterogeneous catalyst system with Nano-techniques.
- A novel process to develop for the commercial production of algal biodiesel can makes it affordable to consumers.

By products utilization

Crude glycerol is a key by-product of biodiesel production with a multitude of uses. Low price glycerol can become a major building block for bio-refinery. A simplified downstream separation is needed to improve the purity of the crude glycerol, so as to extend its usage in the food and pharmaceutical industries.