SUMMARY

- Rubber seeds required for the extraction of oil in the present study were collected from the rubber tree plantations of Kanyakumari District, Tamil Nadu, India.

- Physico chemical characteristics of the rubber seed oil were analysed and the results indicated that the rubber seed oil was closely equivalent to few edible vegetable oils in many respects.

- FFA content of the rubber seed oil was observed to be 25.15 ± 0.85 percent. Such high level of FFA was considered unfavourable for processing the same to produce biodiesel. Therefore attempts were made to reduce the FFA using acid catalysts. Homogeneous acid catalysts such as sulphuric acid, hydrochloric acid and orthophosphoric acid and heterogeneous catalyst such as ferric sulphate were evaluated to find their efficiency in reducing the FFA content.

- Maximum reduction of FFA (85.4 %) was obtained at 4.9 ml/l of sulphuric acid with 9 : 1 molar ratio of methanol to oil in 66 min at 60 °C. The relationship between the dose (y) and the reduction of FFA content (x) was $y = 0.0037x^2 - 0.5064x + 21.084$.

- During the treatment with hydrochloric acid at a dose of 4.3 ml/l with methanol to oil ratio of 9 : 1, 75 percent of FFA reduction was observed in 69 min. The relationship was $y = -1.3594x^2 + 204.17x - 7596.6$ at 60 °C.
• The optimum dose of orthophosphoric acid was 3.4 ml/l with 9 : 1 molar ratio of methanol to oil at 60 °C whose FFA reduction was 64.6 percent and the relationship established between FFA reduction(x) and dose(y) was \( y = 0.0722x^2 - 9.2698x + 300.78 \).

• The optimum dose of ferric sulphate was 2.5 g/l with a 9 : 1 molar ratio of methanol to oil which reduced the maximum percentage of FFA by 89.3 percent at 60 °C in 135 min. The functional relationship between the reduction of FFA (y) and dose (x) was \( y = -0.3992x^2 + 70.32x - 2961.9 \). When ferric sulphate was recycled, its efficiency slowly declined with every passing batch. It showed a marked loss of activity after four cycles.

• On comparison it was known that maximum reduction of FFA was obtained while using ferric sulphate as a catalyst. Though heterogeneous catalyst required longer duration of time than homogeneous catalysts its use was taken into positive consideration due to its reusability.

• After the reduction of FFA in the oil, the resultant material was tried on certain alkaline homogeneous catalysts such as sodium hydroxide, potassium hydroxide, sodium methoxide and heterogeneous catalyst such as calcium oxide so as to assess their efficiency in producing the methyl ester.

• Highest yield of methyl ester (83.8%) was obtained at a dose of 3.7 g/l of sodium hydroxide with 6 : 1 molar ratio of methanol to oil at 60 °C in 65 min with a functional relationship of \( y = -0.3823x^2 + 64.115x - 2623.2 \) where y was duration and x was yield of methyl ester.

• Similarly, maximum yield of methyl ester (78.5%) was reached at a dose of 4.1 g/l of potassium hydroxide with 6 : 1 molar ratio of methanol to oil at 60 °C
in 68 min. The relationship between the duration (y) and the yield (x) was
\[ y = -0.4083 x^2 + 64.138 x - 2451.9. \]

- During the treatment of sodium methoxide at a dose of 3 g/l, maximum yield
  of methyl ester (77.8%) was observed with 6 : 1 methanol to oil molar ratio at
  60 °C in 65 min. Their functional relationship between the duration (y) and the
  yield (x) was \[ y = -0.2966 x^2 + 46.176 x - 1732.2. \]

- When 2.3 g/l of calcium oxide was used, maximum yield of methyl ester
  (79.5%) was obtained in 132 min at 60 °C with a methanol to oil molar ratio of
  6 : 1. The functional relationship between duration (y) and ester yield (x)
  obtained was \[ y = -1.0577 x^2 + 168.31 x - 6564. \]

- Overall results of the base catalysts employed in the present study indicated
  that, sodium hydroxide exhibited higher catalytic activity than potassium
  hydroxide or sodium methoxide or calcium oxide in terms of their ester yield.

- Therefore, biodiesel from rubber seed oil could be produced by employing
  ferric sulphate (2.3 g/l) as an acid catalyst with 9 : 1 methanol to oil molar ratio
  in 135 min followed by 3.7 g/l of sodium hydroxide as an alkaline catalyst with
  6 : 1 methanol to oil molar ratio in 65 min at 60 °C.

- The biodiesel thus produced was subjected to analysis. It had an acid value of
  \[ 0.10 \pm 0.008 \text{ mg KOH/g}. \] The FFA was \[ 0.05 \pm 0.004 \text{ percent}. \] The standard
  acid value of biodiesel according to ASTM D 6751 was less than
  \[ 0.5 \text{ mg KOH/g}. \]
• Specific gravity of the biodiesel was observed to be 0.87 ± 0.0005 g/cm³ at 30 °C which satisfied the requirement (0.87 – 0.90 g/cm³) of ASTM D 6751 specifications.

• Kinematic viscosity of the biodiesel was 5.80 ± 0.004 cSt at 40 °C which was within the fuel specification (2 - 6 cSt @ 40 °C).

• The iodine value of the biodiesel was observed to be 123.0 ± 0.70 gI₂/100 g. Saponification value of the biodiesel was found to be 184 mg KOH/g. There is no specification for saponification value in ASTM D 6751 standards. Peroxidation studies of biodiesel was observed to be 8.0 ± 0.005 (meq/kg).

• Calorific value of the biodiesel produced in this study was 35.44 ± 0.08 MJ/kg and there was no standard specified for calorific value in ASTM D 6751 specifications. The calorific value of biodiesel was slightly lower than that of the raw oil due to the chemical changes that occurred after the transesterification process.

• The sulphated ash was 0.01 ± 0.004 percent by weight. The ASTM D 874 standard specifies that the samples can have a maximum of 0.02 percent of sulfated ash.

• The water and sediment present in the biodiesel was 0.01 ± 0.0008 percent and it was within the standard limit of the ASTM D 6751 specification.

• The copper strip corrosion test grouped it as 1a for the sample which was inferred as slight tarnish. It was in accordance with the specifications of ASTM D 6751.
The carbon residue of the biodiesel now produced was 0.021± 0.0005 percent. The maximum limit of carbon residue specified in ASTM D 6751 was 0.05 percent.

The flash point of the biodiesel was observed to be 134.8 ± 0.44 °C. It is to be noted that the minimum limit of the flash point of the biodiesel specified in ASTM D 6751 is 130 °C.

According to ASTM D 6751 there were no specifications for cloud and pour point. The reason for the absence of specification is that the climatic conditions in different parts of the world vary considerably, there by there cannot be a fixed standard. Pour point and cloud point in the present case was -8.8 ± 0.44 °C and 4.8 ± 0.44 °C.

The cetane number of the biodiesel in the present experiment was 48.73 ± 0.016. This value was higher than that of the conventional diesel. Consequently its ignition delay time was expected to be shorter than that of the diesel fuel.

Biodiesel had a low level of total glycerol (0.21 ± 0.005%). The permitted level of the total glycerol and free glycerol as per ASTM D 6751 was 0.24 percent. Low level of total glycerol in biodiesel ensures high conversion rate of triglyceride into fatty acid methyl esters. Biodiesel had 0.01± 0.0008 percent of free glycerol in the present case which showed that it was in agreement with ASTM D 6751 specifications.

The overall study suggested that all the biodiesel produced from rubber seed oil met the standard of ASTM D 6751.
Due to the fact that vegetable oils contained a significant amount of fatty acids with double bond, oxidative stability is of concern, especially when biodiesel is to be stored over an extended period of time. To check the stability of the biodiesel produced from rubber seed oil, major parameters that would change on account of storage were analysed every month for a period of one year.

It was observed from the storage study that the acid value of biodiesel increased with the increase in storage time. Minor changes were observed after 210 days. The data on the keeping quality of methyl esters (ASTM D 6751) was in accordance with the standard (0.5 mg KOH/g) even after 360 days. There was increase in the acid value which could probably be due to the typical fatty acids composition of the vegetable oils used as raw materials. The equation obtained between storage days (y) and acid value (x) was $y = 0.0012x + 0.0497$.

The FFA content of the biodiesel increased during the initial period of storage. The relationship between the FFA of the biodiesel during storage was $y = 0.0006x + 0.0265$ whose y axis referred to FFA and x axis referred to days.

Increase in the storage time and the absence of an antioxidant collectively caused an increase in kinematic viscosity. However, the ASTM D 6751 standard (6.0 cSt at 40 °C) was not exceeded during the course of the storage. The increase in the viscosity of the ester could be attributed to the structural variations of the ester. The functional relationship was $y = 0.0004x + 5.776$ where y was the kinematic viscosity and x was the duration in days.

Results obtained showed that the biodiesel produced had a specific gravity of 0.87 – 0.90 g/cm$^3$, thus meeting the ASTM D 6751 standards.
• Iodine value of the biodiesel decreased with the increase in storage time. The functional relation was $y = -0.0489x + 124.26$ where $y$ was the iodine value and $x$ was the number of days. The decrease could be due to the dehydrogenation and saturation. The decrease in the iodine value was an indication of the oxidation of lipid inferred by the decline in unsaturation during oxidation.

• Water and sediment of the biodiesel increased with the increase in storage time. The increase in water and sediments could be due to the very characteristics of the raw material involved. The maximum limit of water and sediment content specified in ASTM D 6751 standard was 0.05 percent. The values obtained were within the standard.

• Peroxide level of the biodiesel increased with the storage time. The relationship between the duration in days and peroxide value was $y = 0.0348x + 8.5055$ where $y$ referred to peroxide value and $x$ referred to number of duration in days.

• The overall results of this study suggest that the biodiesel produced from rubber seed oil is relatively stable for a total period of one year under normal environmental conditions.