INTRODUCTION

World at present is seriously confronted with the twin crises of fossil fuel depletion and environmental degradation. The petroleum fuels play a major role in industry, agriculture and transport besides meeting out many other basic human needs. As stock of fossil fuel is dwindling, the search for alternative fuels received greater attention (Lin et al., 2009). However, fossil fuels are limited in quantity and are depleting day by day as the consumption is increasing very rapidly.

India is importing around 80 percent of its fuel need by spending a huge amount as foreign currency (Basha et al., 2009). Consumption of diesel in India during 1994 - 95 was 28.3 million metric tonnes which rose to 40.3 million metric tonnes during 2000 – 01 (Murugesan et al., 2009). During the year 2006 - 07 the demand further increased to 52.3 million metric tonnes.

Active research is now in progress to identify alternate fuels to combat the above problems. Biodiesel is one such fuel in which there is a lot of hope. In the recent past, biodiesel received considerable attention as a renewable fuel. In India it has not been possible to produce biodiesel from edible oils since the same is very scarce. Hence the scope of opting to non-edible oils from plants as raw material for biodiesel production recently gained momentum (Devi and Raj, 2007).

It is estimated that India will produce around 288 million metric tonnes of biodiesel at the end of 2012 so as to supplement around 40 percent of the total diesel need and to provide employment for a total of 19 lakh rural people. The emission characteristics indicate that biodiesel causes low level of pollution compared to that
of diesel. Usage of biodiesel in automobiles does not require any internal modification of the engine (Freedman et al., 1986; Canakci and Gerpen, 1999; Ma and Hanna, 1999; Srivastava and Prasad, 2000; Fukuda et al., 2001; Meher et al., 2006; Sharma et al., 2008 and Murugesan et al., 2009).

Viscosity of biodiesel produced from various vegetable oils is reported to be closer to that of diesel. Its volumetric heating value is relatively lower, but it has high cetane number and flash point (Varese and Varese, 1996; Srivastava and Prasad, 2000 and Yamane et al., 2001). Since the characteristics of biodiesel are generally similar to that of diesel, the former is a strong candidate to replace diesel (Fukuda et al., 2001).

Depending upon the climate, soil conditions and availability, different countries employ different vegetable oils for the production of biodiesel (for example, soybean oil in the U.S., rape seed and sunflower oils in Europe, palm oil in South East Asia and coconut oil in The Philippines).

Several years ago, Rudolf Diesel tested vegetable oil as a fuel for his engine (Shay, 1993). In the 1930s and 1940s vegetable oils were being used as fuel in engines, especially during emergency (Ma and Hanna, 1999).

Since then vegetable oils occupy a prominent position in the development of alternative fuels although, there have been many auxiliary problems associated in using them directly in diesel engine (Murugesan et al., 2009). These include:

01 High viscosity which interferes with the fuel atomization.
02 Poor mixing of oil with air which causes incomplete combustion.
03 Change in emission characteristics.
04 High flash point causing low volatility.
05 Lube oil dilution.
06 High carbon deposits.
07 Ring sticking.
08 Scuffing of the engine liner.
09 Failure of injection nozzle.
10 Change in physico-chemical characteristics, according to climate.
11 Higher cloud and pour points.

These problems are mainly caused due to the largest size of the triglyceride molecules in the raw vegetable oil. Therefore such oils are being transesterified to make the oil as good as diesel (Barnwal and Sharma, 2005 and Murugesan et al., 2009).

There are many technical challenges which are needed to be addressed so as to make biodiesel a profitable one. The high cost of vegetable oil as a source of triglycerides plays a major role in the process profitability. To reduce the cost of production and make it competitive, low cost feed stocks such as non-edible oils, waste frying oils and animal fats are to be considered as raw materials.

A wide variety of non-edible oil crops are available in nature. The promising crops yielding non-edible oils are Jatropha curcas, Pongamia pinnata, Calophyllum inophyllum and Hevea brasiliensis. Non-edible oils from such crops are currently being used for making low cost soap. However at a broader sense, rubber seed oil at present has not attracted any major application and hence the natural production of seeds remain underutilized (Ramadhas et al., 2005). Therefore, an attempt is now made to investigate the scope of utilising rubber seed oil as a feedstock in the production of biodiesel.

Hevea brasiliensis (Rubber tree) which belongs to the family Euphorbiaceae is being cultivated in India since 1902 for extracting its latex. Latex is largely used to prepare natural rubber (Bringi, 1987; Kim and Winnink, 1994 and Aigbodion et al., 2003). The major rubber producing countries of the world are Brazil, Nigeria, India,
Sri Lanka, Burma, Cambodia, Vietnam, Malaysia and The Philippines (Johnson, 2002). In India, *H. brasiliensis* is being cultivated in the hilly slopes of the midlands and also in the foot hills of the Western Ghats.

Locations suitable for rubber cultivation in India are hinterlands of coastal Karnataka, Goa, Andhra Pradesh and Orissa, Konkan region of Maharashtra, Bastar district of Madhya Pradesh, northern parts of West Bengal, Tripura, Assam and lower hilly reaches of Meghalaya, Mizoram, Manipur, Nagaland, Arunachal Pradesh and Andaman and Nicobar Islands (Johnson, 2002).

*H. brasiliensis* is a perennial tree that grows up to a height of 40 m. The mature fruit is a hard, woody, trilobed capsule enclosing three seeds (Fig.1). The dry fruit dehisces with a characteristic loud noise, breaking the pericarp into six pieces and the seeds are normally dispersed to a maximum distance of 15 m.

Rubber seed is ellipsoidal in shape with its length varying from 2.5 – 3 cm, mottled brown, lustrous and weighing around 4 g each (Fig.2). Capsules which are seen scattered on the ground below the canopy can be collected during the fruit bearing season and also immediately thereafter.

Around 450 trees are grown in a hectare, each bearing more or less 500 seeds. The production per hectare is around 900 kg in a full year (Johnson, 2002). The estimated availability of rubber seeds in India is around 30,000 tonnes per annum, which has a
potentiality of yielding 5000 tonnes of raw oil (Ramadhas et al., 2005).

It is known that the seeds deteriorate very rapidly if it happens to stay long on the ground. Besides moisture, microbial infection and endogeneous lipase present in it are reported to alter the free fatty acids (FFA) content of the oil (Bringi, 1987). Therefore, it is essential to collect the seeds soon after they fall on the ground and dry them quickly so as to reduce the moisture content of the seed to a level less than 5 percent to prevent the rise in free fatty acids (FFA) levels.

The kernels are normally separated from the seeds by breaking the capsules mechanically. These kernels are then sun dried to expel the moisture. They are then crushed in the expeller and the resultant oil is filtered (Ramadhas et al., 2005). The kernel forms around 50 - 60 percent of the total weight of the seed (Bringi, 1987).

Seed kernels contain oil to the tune of 40 - 50 percent by weight. Drying the seeds at a higher temperature tends to polymerize the oil and as a result the pale colour of the oil often turns dark brown (Njoku et al., 1996b).

It is known that the seeds of rubber tree contain a lipolytic enzyme, which makes oil refining difficult. Normally, rubber seeds are pretreated before milling. Higher temperature during the extraction enhances the oil recovery (Uzu et al., 1986). This also helps to reduce the moisture content and control the negative role played by the lipase enzymes (Njoku, 1994 and Njoku et al., 1996a). The main characteristic of the rubber seed oil from the processing point of view is the presence
of a small amount of rubber-like material, which makes it extremely difficult to filter the oil.

Rubber seed oil is a rich source of essential fatty acids (Hilditch, 1956). C\textsubscript{18:2} and C\textsubscript{18:3} constitute 51 - 63 percent of the total fatty acids. The oil is used mostly in soap making. It is also employed as a substitute for linseed oil being used in paints and alkyl resins (Williams, 1966). Rubber seed cake rich in protein is used as a component in the supplementary feed of cattle and poultry (Rogers, 1981 and Adefariati, 1986). Rubber seed oil was observed to be non-toxic (Njoku et al., 1996a) and could be used for industrial purposes.

Biodiesel is developed by the transesterification of oil. Transesterification or alcoholsysis is the process of displacing the alcohol from an ester by another alcohol. This process has been widely used to reduce the high viscosity of triglycerides. Transesterification is a reversible reaction and proceeds essentially by mixing the reactants in the presence of a suitable catalyst which accelerates the conversion. The mechanism of transesterification reaction is shown below (Myint and EL-Halwagi, 2009).

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\begin{align*}
\text{CH}_2\text{–OOC-R}_1 & \xrightarrow{\text{Catalyst}} \text{CH}_2\text{–OH} \\
\text{CH} & \text{–OOC-R}_2 + \text{CH}_3\text{OH} & & \xlongleftarrow{\text{Methanol}} \text{CH}_2\text{–OOC-R}_2 + \text{CH}_3\text{–OOC-R}_1 \\
\text{CH}_2\text{–OOC-R}_3 & & \text{(Triglyceride)} & & \text{CH}_2\text{–OOC-R}_3 & & \text{(Diglyceride)} \\
\text{CH}_2\text{–OH} & \xrightarrow{\text{Catalyst}} \text{CH}_2\text{–OH} \\
\text{CH} & \text{–OOC-R}_2 + \text{CH}_3\text{OH} & & \xlongleftarrow{\text{Methanol}} \text{CH}_2\text{–OH} + \text{CH}_3\text{–OOC-R}_3 \\
\text{CH}_2\text{–OOC-R}_3 & & \text{(Diglyceride)} & & \text{CH}_2\text{–OH} & & \text{(Monoglyceride)} \\
\text{CH}_2\text{–OH} & \xrightarrow{\text{Catalyst}} \text{CH}_2\text{–OH} \\
\text{CH} & \text{–OOC-R}_2 + \text{CH}_3\text{OH} & & \xlongleftarrow{\text{Methanol}} \text{CH}_2\text{–OH} + \text{CH}_3\text{–OOC-R}_2 \\
\text{CH}_2\text{–OH} & & \text{(Monoglyceride)} & & \text{CH}_2\text{–OH} & & \text{(Glycerol)}
\end{align*}
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Chemistry of transesterification reaction.
From one triglyceride molecule, three esters are formed. The short chain alcohols that may be used for transesterification include methanol, ethanol, propanol and butanol (Demirbas, 2003; Canakci, 2007; Marchetti et al., 2007 and Sharma and Singh, 2008).

Biodiesel produced by transesterification reactions are catalysed by alkali or acid or enzyme. But the use of alkali and acid received more attention due to its short reaction time and low cost than the latter. Acid catalyses the reaction by donating a proton to the carbonyl group, while base catalyses the same reaction by removing a proton from the alcohol. The FFA and moisture content are one of the key parameters for determining the viability of the transesterification process of the vegetable oil. Choice of acid and alkali catalyst depends on the FFA content of the raw oil. FFA content should be in low level for transesterification reaction to occur using an alkali catalyst. Ramadhas et al. (2005) and Veljkovic et al. (2006) used rubber seed and tobacco seed oil having higher FFA content (17 %) for the production of biodiesel.

It is known that the variables influencing the transesterification process have to be optimized, as addition of excess catalyst may cause the formation of emulsion. This may further lead to the increase in viscosity and activate the formation of gels (Ramadhas et al., 2008 and Sharma et al., 2008). Romano (1982) and Canakci and Gerpen (2001) indicated that presence of even a small quantity of water during the transesterification reaction would decrease the ester formation from vegetable oil. Demirbas (2006) reported that a decrease in the yield of alkyl ester would have been caused due to the presence of water and high FFA as they end up in soap formation, consume large quantity of catalyst and reduce the effectiveness of the process.

One of the major criteria for the quality of a biodiesel is its storage stability. Biodiesel denatures more quickly than fossil fuel due to the vulnerable chemical structure of fatty acid alkyl esters present in it. The deterioration of the quality of
biodiesel during its long storage is observed to be greater than that of the commercial diesel.

Considering the above factors, the present work is initiated with the following objectives:

01 Assessing the free fatty acids content of rubber seed oil collected from various places in Kanyakumari district, Tamil Nadu, India and correlate FFA level with moisture content.

02 Evaluating the physical and chemical characteristics of rubber seed oil in the context of utilizing the same as a raw material for biodiesel production.

03 Comparing the homogeneous and heterogeneous acid and base catalysts to obtain suitable catalysts for the reduction of FFA and its yield on methyl ester.

04 Studying the fuel properties of the biodiesel prepared from rubber seed oil.

05 Assessing the stability of biodiesel from rubber seed oil for a period of one year.