ABSTRACT

Energy crisis is one of the grand problems that our planet is facing today. The growing energy demand, high oil prices, lack of oil in some countries, accelerated development of emerging nations and environmental problems all contribute to the world’s energy concerns. Therefore, the replacement of fossil fuels and petroleum products by renewable energy sources is becoming more and more prominent to provide a sustainable solution to the fuel demand of transportation sector. In this regard, biodiesel seems very promising. Biodiesel can be defined as a vegetable oil or animal fat based diesel fuel consisting of the alkyl monoesters of fatty acids. It is highly biodegradable and has minimal toxicity, can replace diesel fuel in many different applications such as boilers and internal combustion engines without major modifications. Production of biodiesel from non-edible sources is desirable because it minimises the risk of choosing fuel vs. food and besides, they can create huge rural employment. India has a vast potential of non-edible oil bearing plant species distributed throughout the country viz; Nahar (*Mesua ferrea*), Koroch (*Pongamia pinnata*), Terminalia (*Terminalia belerica*), Karabi (*Cascabela thevetia*) etc. as feedstock for biodiesel industries.

With all the virtues biodiesel has a limiting side that it may get degraded before it can be utilised because of its poor oxidation stability. The stability of a fuel refers to its resistance to the degradation process that can change its fuel properties and make it inapplicable as a fuel. Peroxides and hydroperoxides are the main products of oxidation in biodiesel with further degradation; these products form short-chain compounds like acids, aldehydes, ketones and alcohols. The presence of alcohols decreases the flash point and the presence of acids increases the total acidity and the risk of corrosion. Further reactions with the unstable hydroperoxide species with another fatty acid chain may form high molecular weight materials, such as dimer or trimer acids which may lead to filter blocking, injector failures and deposit formation (Karavalakis *et al.*, 2010). Therefore, oxidation stability of biodiesel is an essential quality criterion for its commercial possibility. In order to commercialize biodiesel, the oxidation stability of biodiesel produced from various feedstocks should be well understood and meet the standards. The quality of biodiesel is ensured by various standards like EN-14214 and ASTM D-6751 and oxidation stability is among the screened parameter as EN-14214 calls for determining oxidative stability at 110 °C with a minimum IP (induction period) of 6 h by Rancimat method (EN14112) and ASTM
standards D-6751 has a minimum IP limit of 3 h in 2006 by the same method. Indian standard IS-15607 also requires a minimum induction period of 6 h.

In order to overcome the issues associated with the stability of biodiesel and meet the standards, costly synthetic antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tert-butyl hydroquinone (TBHQ) have been used as additives. Addition of antioxidants has one more advantage other than increasing oxidation stability and restoring other fuel properties i.e. it can also reduce the NOx emission from biodiesel which is also one of the biggest biodiesel drawbacks. Therefore it is like win-win situation for applying antioxidant to biodiesel. However, use of these synthetic antioxidants are not encouraging because these antioxidant compounds are synthesized from petroleum products, which contaminates the renewable nature of biodiesel, increases production cost and also may implicate many health risks, including cancer and carcinogenesis (Karavalakis et al., 2010). Due to these safety concerns and search for a renewable alternative, there is an increasing trend to replace these synthetic antioxidants with natural ones, which, in general, are supposed to be safer. Phenols are one of the most important groups of natural antioxidants (Artajo et al., 2006). They occur only in material of plant origin and are known to protect easily oxidizable constituents from oxidation. Natural antioxidants can improve oxidation stability and increase the readily biodegradable, non-toxic component of fuel. Nevertheless, they are still not widely explored and used in practice for biodiesel.

Therefore, in our present work we have made an attempt to explore some unexplored nature-based antioxidant sources to be utilized in biodiesel produced from non-edible oils for enhancing the oxidation stability and also studied their potential in reducing NOx emission. Thus, the present thesis is divided into five Chapters.

**Chapter 1** gives an overview of the research topic. It starts by giving an introduction to the importance of energy, price hikes and expected depletion of fossil fuels, importance of biodiesel as a solution for the current world energy crisis. This is followed by a background that shows the history and evolution of biodiesel and gives some examples of biodiesel feedstocks around the world, followed by discussing the fuel properties and analytical methods to ensure the quality of biodiesel. It also discusses about biodiesel standards adopted by countries. Limitations of biodiesel and the possible methods to overcome the poor
oxidation stability and high NOx emissions. The objectives were presented in this Chapter and it includes the scope of the research work.

Chapter 2 presents the review of literature which gives an overview of the related work that has been carried out by various researchers around the world. This chapter helps to understand the earlier research outcomes and their limitations. The chapter focuses on various feedstocks that have been investigated for utilization as natural antioxidants and their potential use in biodiesel oxidation stability enhancement.

Chapter 3 presents the detail information about the materials and methodologies used to carry out the experiments during the research work. This chapter also gives a brief account on the feedstock utilised for the production of biodiesel and natural antioxidants followed by the experimental and characterization techniques adopted for the investigation.

Chapter 4 is dedicated to show all the results that have been obtained from the experimental work and presents the findings of the study followed by a detailed discussion and analysis. It consists of five sub-Chapters (A to E).

Chapter 4A delineates the characterization of Ginger extract, *Pongamia pinnata* seed oil and biodiesel produced from pongamia oil. This chapter also shows the results of the Rancimat test for the analysis of oxidation stability with different levels of Ginger extract concentrations in produced biodiesel.

Chapter 4B discusses the characterization of Thuja extract, waste cooking oil (WCO) and biodiesel produced from WCO. This chapter also shows the results of the Rancimat test for the analysis of oxidation stability with different levels of Thuja extract concentrations in produced biodiesel.

Chapter 4C describes another nature based antioxidant source i.e. Potato peels extract and its potential application in enhancing oxidation stability of biodiesel produced from Nahor (*Mesua ferrea*) oil. This chapter shows the results of the characterization of potato peels extract, *Mesua ferrea* oil and biodiesel produced from Nahor oil followed by the results of the Rancimat test for the analysis of oxidation stability with different levels of potato peels extract concentrations in produced biodiesel.
Chapter 4D demonstrates the comparisons of nature-based antioxidants studied viz; Ginger extract, Thuja extract and potato peels extract with synthetic antioxidant TBHQ (*tert*-butyl hydroquinone) in terms of oxidation stability and storage stability of biodiesel for 180 days.

Chapter 4E explains the results of the effect of nature-based antioxidant extracts as additive on NOx, CO, HC and CO$_2$ emissions from biodiesel produced from waste cooking oil (WCO).

Chapter 5 provides a summary of the key findings drawn out from all the respective experiments. Apart from the findings some left out work of the current study has also been suggested as future work in the field of nature-based antioxidant research for biodiesel oxidation stability enhancement.