CHAPTER 5

CONCLUSION AND SCOPE FOR FUTURE WORK

6.1 CONCLUSION

According to proposed National Mission on biodiesel in India, we have undertaken studies on the physico-chemical properties of biodiesel from tree borne non-edible oil seeds *Jatropha curcas* and *Pongamia pinnata*. Physico-chemical properties of palm biodiesel (PBD) synthesized from palm oil were also investigated. Research was conducted to investigate the influence of presence of transition metals, likely to be present in the metallurgy of storage tanks and barrels; on the oxidation stability (OS) and physico-chemical properties of biodiesel. Influence of the organic contaminants like vegetable oils, free fatty acids and glycerol likely to be present in biodiesel, on the OS and physico-chemical properties of biodiesel were also investigated. Further, research was conducted to establish the correlations between various physico-chemical properties of biodiesel with fatty acid methyl ester (FAME) composition. To minimize the use of biodiesels synthesized from edible oils like palm due to raising food versus fuel issue, PBD was blended in different weight ratios with biodiesels synthesized from tree borne non-edible oil seeds jatropha, and pongamia to examine the effects on OS and low temperature flow properties of biodiesel.

Biodiesel was prepared by transesterification process, involving reaction of oil with methanol under reflux conditions. Biodiesel samples were tested for physico-chemical properties as per Indian standard IS-15607, American standard test method ASTM D-6751 and European EN-14214 standards. Subsequent analysis showed no statistically significant difference between the measurements. The biodiesel standards IS-15607 and EN-14214 call for determining oxidative stability at 110°C with a minimum IP of 6h by the Rancimat method (EN-14112). Even ASTM standard D-6751 has recently introduced a minimum IP of 3h. Jatropha biodiesel (JBD) met all the specifications, except induction period (IP) of 6h. Neat pongamia biodiesel (PoBD) showed the IP of
2.54h so did not meet the minimum limit of 3h IP in accordance with recent ASTM D-6751 and minimum limit of 6h IP as required by EN-14112 standards.

PBD satisfied the aforementioned specifications of OS. Neat PBD exhibited an OS of 9.24h; thus it is highly stable but exhibited poor low temperature flow properties. The low temperature flow properties of biodiesel are characterized by cloud point (CP), pour point (PP) and cold filter plugging point (CFPP) and these must be considered when operating compression-ignition engines in moderate temperature climate during winter months. FAME composition of jatropha and pongamia biodiesel samples showed that these samples mainly consisted of unsaturated fatty acid methyl esters like oleic and linoleic fatty acid methyl esters. The contents of saturated fatty acids methyl esters for palm, jatropha, and pongamia biodiesel samples were 44.4, 21.1, and 16.0% respectively and the contents of unsaturated fatty acids methyl esters for three biodiesels were 55.6, 78.9, and 84.0% respectively. Therefore, jatropha and pongamia mainly consisted of unsaturated fatty acid methyl esters and palm consisted of approximately equal concentrations of saturation and unsaturation. Low OS and good low temperature flow properties of jatropha and pongamia can also be attributed due to more unsaturation.

Further, tests were done to improve the low OS of jatropha and pongamia biodiesels by doping different antioxidants with varying concentrations. Synthetic antioxidants namely tert-butylated hydroxytoluene (TBHT), tert-butylated phenol derivative (TBP), octylated butylated diphenyl amine (OBPA), and tert-butylhydroxquinone (TBHQ) and natural antioxidant α-tocopherol (α-T) were selected for this purpose. All the antioxidants were doped to the biodiesel samples with varying concentrations (ppm), and corresponding IPs were measured with the Rancimat test method to observe the effectiveness of different antioxidants. Synthetic antioxidants shown better antioxidant property than natural antioxidant. When compared all antioxidants, TBHQ was most effective in enhancing the IP of JBD. The antioxidant property of TBHQ is greater than other antioxidants investigated. This can be explained based on their molecular structures, which the former possesses two OH groups attached to the aromatic ring and thus, TBHQ offers more sites for the formation of complex between free radical and AO radical for lipid stabilization purpose.
Research was conducted to investigate the effect of presence of transition metals—iron, nickel, manganese, cobalt, and copper, likely to be present in the metallurgy of storage tanks and barrels, on the OS of biodiesel samples. Different transition metals were blended with varying concentrations (ppm) in biodiesel samples. It was found that influence of the metals were detrimental to OS and catalytic, as even small concentrations of metal contaminants showed nearly the same influence on OS as large amounts. Copper showed the strongest detrimental and catalytic effect on OS. Neat PBD exhibited an OS of 9.24h; thus it is highly stable and it was found that influence of metal was detrimental and catalytic even for stable palm. The presence of metals in biodiesel resulted in acceleration of free radical oxidation due to a metal-mediated initiation reaction and strongest catalytic effect of copper is due to its relative higher pro-oxidant effect.

It was found possible to meet the desired EN specification for the OS for neat biodiesel and metal-contaminated biodiesel by using antioxidants; it will have a cost implication, as antioxidants are costly chemicals. Research was conducted to increase the OS of metal- contaminated biodiesel by doping metal deactivator with antioxidant, with varying concentrations in order to meet the aforementioned standard required for the OS. It was found that usage of the antioxidant can be reduced by 30 – 50%, therefore the cost, even if very small amount of metal deactivator is doped in biodiesel to meet EN-14112 specification.

Effect of the minor contaminants like monoglycerides on the biodiesel physico-chemical properties was also investigated. These contaminants may be present in the crude oil and be carried through after incomplete conversion during transesterification and processing of the biodiesel product. Monoglycerides were measured according to EN ISO 14105 method and water is measured according to D-2709 methods of ASTM and Indian standards. Therefore, the effect of monoglycerides, water and soap contamination, on the biodiesel properties was investigated. It was seen that increase in levels of these minor contaminants has negative effect on the low temperature flow properties of biodiesel. These contaminants have minor effect on the stability of JBD. JBD has OS of 3.95h, the blends of these contaminants at different levels only decreases the OS to 3.26h.
Palm, jatropha, and pongamia biodiesels used in this work had CPs of 16.0, 4.0, and -1.0°C, PPs of 12.0, -3.0, and -6.0°C and CFPPs of 14, 1, and -2°C respectively. Therefore, palm had very poor low temperature flow properties. To minimize the use of biodiesels synthesized from edible oils like palm due to raising food versus fuel issue, PBD was blended with different weight ratios (%) with biodiesels derived from tree-borne non-edible oil seeds jatropha, and pongamia to examine the effect on CP, PP and CFPP of PBD. Blending PBD synthesized from edible oil with jatropha and pongamia biodiesel respectively, and with both, jatropha and pongamia biodiesels remarkably improved the CP, PP, and CFPP of PBD, so its use can be minimized.

Properties of various individual fatty esters that comprise biodiesel determine the overall fuel properties of the biodiesel fuel and in turn, the properties of various fatty esters are determined by the structural features of the fatty acid that comprise a fatty ester. The next objective of the study was to investigate the effect of the FAMEs compositions in the blended biodiesels on CP, PP, and CFPP and to determine the correlation between them. A good correlation between CP and palmitic acid methyl ester (PAME) was obtained as CP = 0.526(PAME) – 4.992 (0 < PAME < 45). For this equation, coefficient of correlation (R) was 0.981, coefficient of determination (R²) was 0.963 and standard error of estimate (σest) was 0.929. A high degree of correlation between PP and PAME was obtained as PP = 0.571(PAME) – 12.240 (0 < PAME < 45). For this equation, R = 0.929, R² = 0.863 and σest = 2.039.

The correlation between CP and total unsaturated fatty acid methyl ester (X) was also obtained as CP = -0.576(X) + 48.255 (0 < X ≤ 84). For this equation, R = 0.986, R² = 0.973 and σest = 0.788. The correlation between PP and X was PP = -0.626(X) + 45.594 (0 < X ≤ 84). For this equation, R = 0.935, R² = 0.874 and σest = 1.955.

A good correlation was also obtained between CFPP and contents of PAME (wt%) of three biodiesel blends as follows; CFPP = 0.511(PAME) – 7.823 (0 < PAME < 45). For this equation, R was 0.929, R² was 0.863 and σest was 1.831. A good correlation was obtained between CFPP and X of three biodiesel blends as follows; CFPP = -0.561(X) + 43.967 (0 < X ≤ 84). For this equation, R = 0.934, R² = 0.872 and σest = 1.762.
The aforementioned results showed that with regard to the effects of the individual unsaturated fatty acid methyl ester, the good correlation could not be found. However, when the effects of total unsaturated fatty acid methyl esters were determined, a good correlation was found.

Using these correlations, cloud, pour and cold filter plugging points of different biodiesel blends can be determined. Therefore, to improve the poor biodiesel low temperature flow properties, blending of biodiesels over two is a simple but effective method and also it can minimize the use of edible oils. With the help of correlations between biodiesel low temperature flow properties and the FAME compositions, the low temperature flow properties of biodiesels produced from new resources can be easily estimated.

Similarly, dependence of OS on esters of fatty acid composition was also examined. Good correlation between OS and PAME was obtained as \( OS = 0.214(\text{PAME}) + 0.671 \) (0 < PAME < 45). For this equation, \( R = 0.997 \), \( R^2 = 0.994 \) and \( \sigma_{\text{est}} = 0.149 \). A correlation between OS and X was also obtained as \( OS = -0.234(X) + 22.318 \) (0 < X ≤ 84). For this equation, \( R = 0.999 \), \( R^2 = 0.998 \) and \( \sigma_{\text{est}} = 0.091 \).

Using the above correlations, cloud, pour and cold filter plugging points of different biodiesel blends can be determined. Therefore, to improve the poor biodiesel low temperature flow properties, blending of biodiesels over two is a simple but effective method and also it can minimize the use of edible oils. With the help of correlations, the low temperature flow properties and OS of biodiesels produced from new resources can be easily estimated.

From the present research, it can be concluded that it will not be possible to use biodiesel having low OS, poor physico-chemical properties like CP, PP and CFPP. The effect of presence of transition metals, likely to be present in the metallurgy of storage tanks and barrels, was detrimental to OS and catalytic. The production of biofuel from edible oils has raised serious concerns on preserving the food security of the planet and therefore, more emphasize should be given on biodiesel derived from tree borne non-edible oil seeds due to rising food-fuel issues.
5.2 SCOPE FOR FUTURE WORK

Further investigations can be done on the influence of metal and organic contamination on the oxidative stability and other physico-chemical properties of biodiesel synthesized from new resources. Influence of the microbial growth on the biodiesel synthesized from non-edible seed oils can be investigated. More efficient and cheap methods can be derived to reduce the contamination.

Correlations derived in the present research can be applied further to check their accuracy. More correlations between various physico-chemical properties of biodiesel with their chemical structure like FAME can be derived.

Last but not the least, a carefully planned and executed national biodiesel program could provide energy security to countries like India and at same time uplift the rural economy.