CHAPTER 5

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Northeast India has adequate forest land and the prospect of some of its tree species as source of biodiesel feedstock could favourably complement the growth of both forestry and biodiesel as entrepreneur activities in this region. The present research work is carried out to investigate the prospect of non-edible seed oils from tree species available in forests of northeast India. The findings of the present investigation are summarized below.

5.1 Feedstock: description of the trees

Two forest origin oilseeds of Terminalia belerica R. and Sapindus mukorossi G. trees could be identified as a prospective source of biodiesel feedstock. Terminalia belerica is a large deciduous tree available in the forests of North-eastern region of India. It attains up to the height of 40 m, with a girth and clear bole of about 3 to 9 m, respectively. The fruit pulp of Terminalia belerica is traditionally used as medicinal ingredient for many ailments in India which includes dyspepsia, chronic diarrhea, dysentery, intestinal parasites, fever, sore throat, cough etc. Sapindus mukorossi is also a fairly large, deciduous tree, usually of height of up to 20 m tall with about 1.8 m girth. Sapindus mukorossi seed has high saponin content, therefore traditionally used as cleaning agent like soap. The pulp of Sapindus mukorossi also has medicinal usage. Thus, fruits of both the trees have existing utilities, and seeds remain as by-product. The total available forest area of Assam is 27,826 km². Part of this area, including the area needing replanting, could be considered for growing Terminalia belerica and Sapindus mukorossi tree so as to increase the biodiesel feedstock. However, appropriate planning will be required for extending the area for oil bearing trees in order to increase feedstock supply. The research effort of this present work is only to identify the potential tree species.
5.2 Oil contents and fatty acid profile of vegetable oils

Oil content (w/w% of kernels) of Terminalia belerica and Sapindus mukorossi are found as 43% and 39%, respectively. Fatty acid profile of vegetable oil is an important consideration as it influences the properties of oil and hence the biodiesel. Terminalia belerica oil composes of 39.5% saturated fatty acid and 60.5% unsaturated fatty acid. Palmitic (32.8%), oleic (31.3%) and linoleic (28.8%) acids are dominant in Terminalia belerica oil. On the other hand, Sapindus mukorossi oil composes of 16.5% saturated and 83.5% unsaturated fatty acids. Oleic (58.4%), linolenic (17.1%) and arachidic (7.5%) acids, are the major constituents of Sapindus mukorossi oil. Variations in fatty acid profile are observed amongst the new variety of oils and oils reported earlier. Overall, fatty acid profiles of both the new varieties of oil are suitable for biodiesel production.

5.3 Characterization of vegetable oils

Sapindus mukorossi oil is heavier (923 kg/m³) and more viscous (32.10 mm²/s) compared to Terminalia belerica (910 kg/m³, 25.60 mm²/s) oil. Densities of both the oils are lighter than some of the earlier reported tree seed oils such as Pongamia glabra (931 kg/m³), Mesua ferrea (935 kg/m³) and Madhuca indica (960 kg/m³). However, viscosities of both the oils are comparable with similar tree seed oils reported earlier. Calorific value of Terminalia belerica oil (37.5 MJ/kg) is marginally lower than the calorific value of Sapindus mukorossi oil (38 MJ/kg), and comparable with similar tree born oils reported earlier. Acid value of Terminalia belerica oil is found as 8.01 mgKOH/g, which is less than Sapindus mukorossi (15.6 mgKOH/g) oil, and comparable with similar tree born seed oils reported earlier. Sapindus mukorossi oil is relatively safer to handle with flash point of 159°C, compared to Terminalia belerica oil, which has flash point of 102°C. Terminalia belerica has less carbon and ash content as compared to Sapindus mukorossi. Comprehensively, results of vegetable oil characterization show both of these seed oils as prospective feedstock for biodiesel production.
5.4 Conversion of oil to biodiesel

Alkaline catalytic transesterification process is chosen for production of biodiesel from *Terminalia bellerica* oil. Repeated experiments are conducted with varying molar ratio (methanol: oil) and catalyst (NaOCH$_3$) concentration through standard transesterification procedure, maintaining 65°C temperature for 120 minutes. The optimum molar ratio (10:1) and catalyst concentration (1 wt%) could be ascertained for *Terminalia bellerica*, which ensure the highest possible yield (93%) of biodiesel amongst the series of experiments.

Two step transesterification is followed for *Sapindus mukorossi* as the acid value of *Sapindus mukorossi* oil is higher. In the first step, oil is reacted with H$_2$SO$_4$ (1 wt%), at 55°C, with 6:1 (alcohol to oil) molar ratio for 90 minutes. After removing the unreacted methanol and free fatty acid from the first stage reaction product, the remaining part is subjected to alkaline transesterification. The molar ratio and catalyst concentration for conversion of *Sapindus mukorossi* oil are 8:1 and 1 wt%, respectively, at 65°C for 120 minutes with a yield of 92.5%. The production of biodiesel is confirmed through $^1$H NMR and $^{13}$C NMR spectral analysis.

5.5 Fuel quality

Although *Sapindus mukorossi* oil is heavier than *Terminalia bellerica* oil, more reduction in density is observed in *Sapindus mukorossi* biodiesel (876 kg/m$^3$), as compared to *Terminalia bellerica* (882 kg/m$^3$) biodiesel. Moreover, density of both the biodiesels conform to EN 14214-07 standard specification. *Sapindus mukorossi* biodiesel is less viscous (4.63 mm$^2$/s) than *Terminalia bellerica* biodiesel (5.17 mm$^2$/s). The viscosity values obtained for both the biodiesels are similar to some other biodiesels reported earlier and also conform to ASTM D6751-07 specification. Calorific value of *Sapindus mukorossi* biodiesel (40.00 MJ/kg) is marginally higher than *Terminalia bellerica* biodiesel (39.22 MJ/kg), and is comparable with some other biodiesels obtained from tree seed oils. Acid values of both the oils are reduced after transesterification to 0.23 mgKOH/g and 0.14 mgKOH/g for *Terminalia bellerica* and *Sapindus mukorossi*.
biodiesel, respectively. *Sapindus mukorossi* biodiesel shows better fuel handling properties with higher flash point (140°C) as compared to *Terminalia bellerica* biodiesel (90°C). *Sapindus mukorossi* biodiesel also exhibits better cold flow properties compared to *Terminalia bellerica* biodiesel. Cloud points of *Terminalia bellerica* and *Sapindus mukorossi* biodiesels are 6°C and -1°C, respectively, whereas pour points are 3°C for *Terminalia bellerica* and -4°C for *Sapindus mukorossi*. Both the biodiesels are within the specific cloud point and pour point limits of EN 14214-07. In terms of ash and carbon residue contents, *Terminalia bellerica* biodiesel (0.0005 wt% ash, 0.0085 wt% carbon residue) is found superior than *Sapindus mukorossi* (0.003 wt% ash, 0.12 wt% carbon residue) biodiesel. Similarly, oxidation stability of *Terminalia bellerica* biodiesel (3.76 h) is relatively higher than *Sapindus mukorossi* (1.2 h) biodiesel. However, both the biodiesels fail to meet the EN 14214-07 specification, as far as oxidation stability is concerned. Lubricating property is also accessed using standard index (wear scar diameter). Lubricity of *Sapindus mukorossi* (0.181 mm) biodiesel is marginally better than *Terminalia bellerica* (0.193 mm) biodiesel and comparable with similar biodiesels, reported earlier. Cetane number of *Terminalia bellerica* (53) and *Sapindus mukorossi* (56) biodiesels are also found satisfactory to ensure proper ignition behavior. The distillation characteristic of *Terminalia bellerica* (130°C - 347°C) and *Sapindus mukorossi* (193°C - 383°C) biodiesel are comparable with similar biodiesels and also satisfies the ASTM D6751-07 standard specification. Sulphur content of *Sapindus mukorossi* biodiesel is 102 ppm which is more than *Terminalia bellerica* biodiesel (96 ppm).

Overall, density, viscosity, cetane number, ash content, carbon residue, flash point, pour point, acid value, copper strip corrosion, IBP/FBP for both the biodiesels are found to conform the existing biodiesel norms. However, two aspects of both the types of biodiesels, namely, sulphur content and oxidation stability would require further attention.

5.6 Storage behavior of biodiesel and identification of additives

Biodiesels obtained from *Terminalia bellerica* and *Sapindus mukorossi* oils and their blends with petro-diesel (B5, B10, B20 and B30) are stored in borosilicate glass
bottle in normal laboratory condition for 12 weeks. Viscosity, acid value and peroxide value are found to increase while measuring at 2 week interval. Viscosities of all the stored samples lie within the limit of ASTM D6751, except for 12th week old *Terminalia belerica* biodiesel.

Efficacy of six phenolic antioxidants viz., vitamin E (α-tocopherol), butylated hydroxyanisole (BHA), pyrogallol (PY), propyl gallate (PG), tert-butylhydroxytoluene (BHT) and tert-butylhydroxyquinone (TBHQ) and their concentrations (viz., 100 ppm, 500 ppm, 1000 ppm, and 1500 ppm) are investigated for freshly prepared samples of neat biodiesels on the basis of Induction period. PG treated biodiesel (B100) exhibited the highest IP amongst all the antioxidants for both *Terminalia belerica* and *Sapindus mukorossi* considered for present investigation. The higher the antioxidant concentration more is the IP, and this is true for both the biodiesels. Results show that treating with PG could enhance IP from 3.76 h to 14.67 h in *Terminalia belerica*, whereas in *Sapindus mukorossi* biodiesel, the increase in IP is from 1.2 h to 11.03 h. Overall, the efficacy of antioxidants are summarized as, PG>PY>TBHQ>BHT>a-tocopherol for *Terminalia belerica* biodiesel and PG>PY>BHT>TBHQ>BHA>a-tocopherol for *Sapindus mukorossi* biodiesel.

Oxidation stability of biodiesel (B100) and its different blends (B5, B10, B20, B30) are also assessed with and without antioxidant additives up to a storage period of 12 weeks considering three specific antioxidants viz., PG, TBHQ and BHT, with a concentration of 1000 ppm. For freshly prepared biodiesel blends, the activities of antioxidants are in the order of, PG>BHT>TBHQ for both the biodiesels. After 6 weeks of storage, IP of TBHQ treated B100 (1000 ppm) fails to meet the minimum required limit of EN 14214. Also, without antioxidants, B5 and B10 can be stored only up to 11 weeks and 4.5 weeks respectively. With addition of antioxidants, IPs of all blended samples lie well above the minimum limit, even after 12 weeks of storage. However, safe storage period for PG, TBHQ and BHT treated *Sapindus mukorossi* biodiesel are 6 weeks, 3 weeks and 6 weeks, respectively. Moreover, without antioxidant, B5 and B10 of *Sapindus mukorossi* can be stored safely only up to 7 weeks and 4 weeks, respectively.
5.7 Assessments of engine performance characteristics

The blended biodiesel (B5, B10 and B20) of both the types are tested in a 39 kW test engine and compared with the performance results of petrodiesel. The experiments are conducted at randomly varying loads with all levels of blending. Increase in brake thermal efficiency associated with decrease in specific fuel consumption by the increase in engine load has been the characteristics feature for all the biodiesel blends, as well as for petrodiesel. Overall, acceptable performances are observed for both the types of biodiesel (*Terminalia belerica* and *Sapindus mukorossi*) up to 20% blending.

At medium load condition, biodiesel sample of *Sapindus mukorossi* perform better compared to the biodiesel samples of *Terminalia belerica*. The Brake thermal efficiency (BTE) of the engine with B10 sample of *Sapindus mukorossi* was 27.1% whereas B10 sample of *Terminalia belerica* at relatively lighter load was 16.76%. The similar trend of variation of BTE was also observed at higher level of engine loading. At medium loading condition, performance of biodiesel blend was better than diesel as exhibited by relatively higher BTE.

In general, with increase in biodiesel percentage, CO emission level decreases. No definite trend could be observed for CO emission vs. engine loading while considering the entire set of results. However, overall emission of CO in biodiesel blended fuel is less than that of diesel. This is true for both *Terminalia belerica* and *Sapindus mukorossi*. In general, higher levels of NOx emissions were observed in biodiesel as compared to diesel. The maximum emission of NOx for diesel is 282 ppm, which is lower than B5, B10, B20 of both *Terminalia belerica* and *Sapindus mukorossi* biodiesel blends, respectively. The hydrocarbon (HC) emission resulted from *Terminalia belerica* and *Sapindus mukorossi* biodiesel blends are quite low as compared to diesel. As the biodiesel percentage in blends increases, overall HC emission decreases.

5.8 Conclusions

From the study the following conclusions are drawn.
1. Tree seed oils have potential for biodiesel production. Proper R & D intervention is required for promotion of biodiesel using these tree oils.

ii. Properties of biodiesels are the reflection of the fatty acid profile of the parent material. This is true for both *Terminalia belerica* and *Sapindus mukorossi* seed oils. Both the types of oils have distinguishing fatty acid profile, and can be converted into biodiesel. *Terminalia belerica* requires single stage alkaline transesterification whereas *Sapindus mukorossi* requires two stage transesterification (acid followed by alkaline).

iii. Alcohol to oil molar ratio required for *Terminalia belerica* oil (10:1) to result the highest yield (93%) was different than the molar ratio for *Sapindus mukorossi* (8:1) with a yield of (92.5%). However, for both the transesterification process require 1wt% catalyst (NaOCH₃) concentration.

iv. Most of the fuel properties of *Terminalia belerica* and *Sapindus mukorossi* conform to the ASTM and European standard specifications. However, oxidation stability and sulphur content do not conform to the norms.

v. Biodiesel produced from both the oils require additives to enhance oxidation stability (Induction Period). Specific phenolic antioxidants additives are identified for both the biodiesels.

vi. Short duration engine testing with blended biodiesels of both the oil seeds result satisfactory performances both in terms of efficiency and emissions. However, there are some differences between *Terminalia belerica* and *Sapindus mukorossi* biodiesel, which might be due to the differences in fuel characteristics of these biodiesel.

5.9 Suggestions for future works

i. Optimization of process parameters (viz., temperature, alcohol to oil molar ratio, catalyst type and concentration and reaction time) are important while transesterifying vegetable oil to biodiesel. In this study, limited numbers of parameters (alcohol to oil molar ratio and catalyst concentration) are varied for maximum yield of biodiesel. Future study is recommended to optimize the process
parameters incorporating all possible variable combinations of treatments and formulate a suitable mathematical model for better understanding.

ii. The results of the storage stability test of the present investigation are pertaining to 12 weeks of storage period with a few specific storage conditions. Future study is recommended for storing the sample for extended period of time, incorporating all possible storage conditions.

The remedy for higher sulphur level is not investigated in the present work and suggested as research for future work.

iii. Long duration engine performance testing at different load conditions including the impact on engine health is recommended, for future work both *Terminalia bejerrica* and *Sapindus mukorossi* biodiesel.