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Transesterification of Citrus maxima Seed Oil to Biodiesel using Heterogeneous Catalyst derived from Peel and Rhizome of Musa balbisiana Colla

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Abstract: Transesterification of *Citrus maxima* seed oil to its fatty acid methyl esters (FAME, biodiesel) was carried out in methanol by batch reaction using heterogeneous catalysts derived from the peel and rhizome of *Musa balbisiana* Colla at room temperature (32 °C). The yield of biodiesel with the catalysts from the peel and rhizome of *Musa balbisiana* Colla were 92 and 93 wt.% within 4 and 3.5 h respectively. Better catalytic activity is observed when the catalyst is activated.

Key words: Transesterification, Biodiesel, *Citrus maxima*, *Musa balbisiana* Colla, Banana plant.

1. Introduction

In recent times, due to depleting petroleum reserves and environmental concerns about air pollution caused by the combustion of fossil fuels, production of biodiesel and its application are gaining popularity throughout the world. Biodiesel is an alternative, renewable, and clean-burning fuel for diesel engines with less pollutant emissions produced from nontoxic, biodegradable and potentially inexhaustible sources such as vegetable oils, animal fats, and waste cooking oils[1-3]. Chemically, biodiesel is a mixture of fatty acid methyl esters (FAME) possessing similar physicochemical and fuel properties to that of petroleum based diesel fuels[4-6].

Biodiesel is generally produced by transesterification of vegetable oils or animal fats with short-chain alcohols in the presence of catalysts. The conventional catalysts for this transesterification reaction are homogeneous strong bases (such as alkali metal hydroxides and alkoxides) and homogeneous acids (such as H_2SO_4)[1,2,5,7,8]. However, basic catalysts are generally corrosive to equipment and also react with free fatty acid to form unwanted soap as by-products that require expensive separation[9,10]. Homogeneous acid catalysts are difficult to recycle and operate at high temperatures, and also give rise to serious environmental and corrosion problems[11,12]. Therefore, to overcome all these problems including cost, people are working on the development of economically viable as well as ecofriendly solid catalysts for biodiesel industries[12,13]. Recently, several naturally derived heterogeneous catalysts have been reported in various literatures and showed potentials to be used as a low-cost biodiesel production catalyst[14-21].

Citrus maxima Merr. (Fig. 1), locally called *Robab tenga* in Assamese, is an important source of non-conventional oil having 48% of oil content[22]. The plant bears edible fruits spherical in shape (14–20 cm in diameter, weighing 0.75–2.0 kg) with a good number of small seeds inside (Fig. 1). Fruits are popular but yet to be commercially exploited. Commercial exploitation of the fruits would yield large quantities of seeds which can be used for the production of oil and biodiesel. The chemical composition of biodiesel obtained from *Citrus maxima* seed oil determined by GC-MS analysis was reported by Barua *et al.*[22] and it consists of 29.7 wt.% of methyl palmitate (C16:0), 25.7 wt.% of methyl linoleate (C18:2), 39.6 wt.% of methyl oleate (C18:1), and 4.9 wt.% of methyl stearate (18:0).

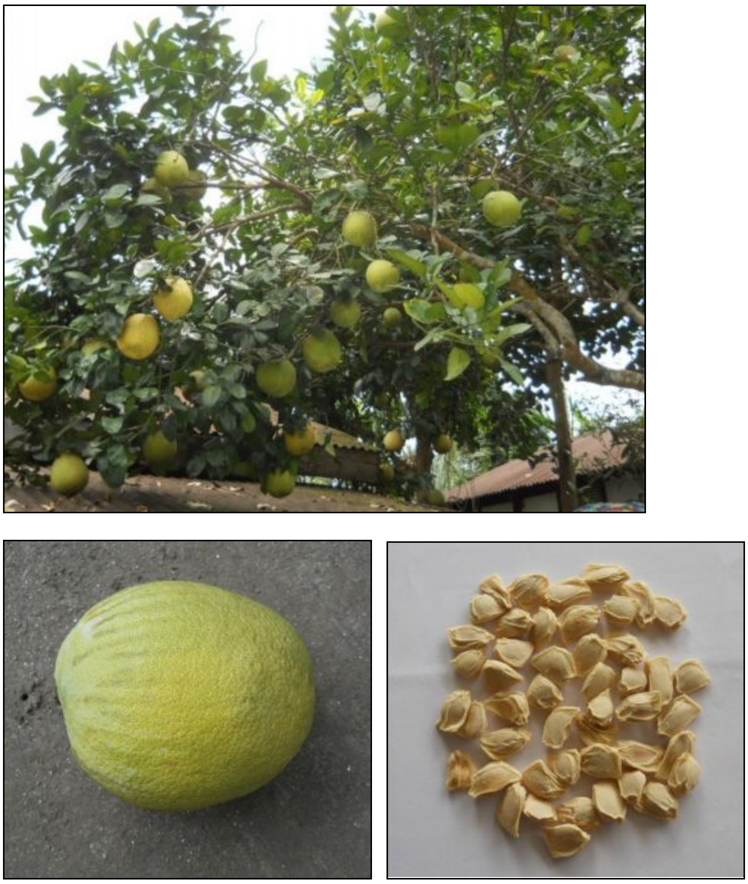

Fig. 1. ***Citrus maxima*** **plant, fruit and seed**

In this study, an environmentally friendly and active heterogeneous catalyst derived from the peel and rhizome of *Musa balbisiana* Colla for biodiesel synthesis is reported. It is observed that the catalysts can catalyze transesterification of *Citrus maxima* seed oil into its corresponding fatty acid methyl esters with methanol in a highly efficient manner at room temperature (32 ºC).

2. Experimental Section

2.1 Materials

Citrus maxima seeds were collected from plants from Bongaigaon District of Assam, India during its availability of the season. The seeds were dried in sunlight, deshelled and the kernel crushed using a grinder prior to oil extraction. The peel and rhizome of *Musa balbisiana* Colla were collected from the nearby villages of Gauhati University (Guwahati, Assam) for the preparation of the catalyst. Methanol used was of analytical grade (Merck, Mumbai, India). All other solvents and chemicals used were of analytical grade, and they were procured from commercial sources and used as such without further treatment.

2.2 Oil Extraction

Crushed kernel in petroleum ether (bp 40-60 ºC, 10 mL/g) was magnetically stirred at room temperature for 3 h, filtered and solvent was removed at 45 ºC using a rotary vacuum evaporator to yield the crude oil. The oil was purified prior to transesterification done, by column chromatography over silica gel (60-120 mesh) using a mixture of petroleum ether and ethyl acetate (20:1) as the eluent. *NMR data of the Oil*: ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ= 0.88 (m, 3H: -C-C$\boldsymbol{H}_3$), 1.26 (m, -(C$\boldsymbol{H}_2$)$_n$-), 1.61 (m, 2H: -C$\boldsymbol{H}_2$-C-COO-), 2.04 (m, 2H: -C$\boldsymbol{H}_2$-C=C-), 2.29 (m, 2H, -C$\boldsymbol{H}_2$-COO-), 2.77 (t, 2H, ^3J = 5.8 Hz: -C=C-C$\boldsymbol{H}_2$-C=C-), 4.15 (dd, 2H, -C$\boldsymbol{H}_2$-CO_2R [methylene protons at C1 & C3 of glycerides], ^3J=5.8, 11.9 Hz), 4.31 (dd, 2H, -C$\boldsymbol{H}_2$-CO_2R [methylene protons at C1 & C3 of glycerides], ^3J=4.2, 12.0 Hz), 5.27 (m, 1H, -C$\boldsymbol{H}$-CO_2R [methine proton at C2 of glycerides]), 5.35 (m, 2H, -C$\boldsymbol{H}$=C$\boldsymbol{H}$-). ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ= 14.07–34.17 (-($\boldsymbol{C}H_2$)$_n$, -$\boldsymbol{C}H_3$), 62.07 & 68.88 (methylene [-$\boldsymbol{C}H_2$-CO_2R] & methine [-$\boldsymbol{C}$H-CO_2R] carbons of glycerine moiety), 127.87–130.19 (olefinic carbons), 173.25(-$\boldsymbol{C}$O-O-, carbonyl carbon). FT-IR (thin film): 722, 915, 1032, 1096, 1162, 1238, 1351, 1381, 1462, 1528, 1606, 1665, 1746, 2854, 2925, 3009 cm^{-1}.

2.3 Catalyst preparation

The peel and rhizome of *Musa balbisiana* Colla (one variety of banana plant) was cut into thin pieces and air dried under sun for several days. Dry material was ignited, and allowed to burn and cool down to ambient temperature in its own. The ash was then preserved in an air tight plastic container for use as and when necessary.

2.4 Composition of the catalyst

The chemical composition of the catalyst was estimated by chemical analysis, atomic absorption spectroscopy and flame photometry[23]. Major components present are K^+, Na^+, CO_3^{2-} and Cl^- along with eleven other metals *viz.* Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb, which are present only in trace amounts (ppm level). Metals are present as their carbonates, chlorides or oxides. Finely divided carbon particles are also present[14].

2.5 Activation of catalyst

The catalyst was activated by heating at 400 ºC and 700 ºC in a programmable muffle furnace (LAB TECH). About 1.5–2.0 g of the catalyst was taken in a silica crucible (preheated and weighted) and then heated in a muffle furnace to either 400 ºC for 2 h or 700 ºC for 3.5 h, and kept at the temperature for about 1.5 h. After the heating was completed, the catalyst was allowed to cool to room temperature inside a desiccator, and preserved there until used.

2.6 Transesterification of oil

The purified oil was transesterified to fatty acid methyl esters (biodiesel) using the heterogeneous catalyst derived from the peel and rhizome of *Musa balbisiana* Colla. A mixture of oil in methanol (10 mL/g of oil) and the catalyst (20 wt.% of oil) was magnetically stirred at room temperature (32 ºC) and the conversion was monitored by TLC. The reaction mixture was filtered under vacuum pump and the residue washed with petroleum ether and the combined filtrate was partitioned between water and petroleum ether. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum to yield the crude product which was further purified by column chromatography over silica gel using 20:1 petroleum ether and ethyl acetate as the eluent. The purified product was further subjected to high vacuum to remove the last traces of solvents to yield pure biodiesel. *NMR data of the FAME mixture*: ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ= 0.88 (m, 3H: -C-C$\boldsymbol{H}_3$), 1.25 (m, -(C$\boldsymbol{H}_2$)$_n$-), 1.61 (m, 2H: -C$\boldsymbol{H}_2$-C-COOMe), 2.03 (m, 2H: -C$\boldsymbol{H}_2$-C=C-), 2.29 (t, 2H, ^3J = 7.5 Hz: -C$\boldsymbol{H}_2$-COOMe), 2.76 (t, 2H, ^3J = 5.7 Hz: -C=C-C$\boldsymbol{H}_2$-C=C-), 3.66 (s, 3H: -CO-OC$\boldsymbol{H}_3$), 5.33 (m, 2H, -C$\boldsymbol{H}$=C$\boldsymbol{H}$-). ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ= 14.04–34.06 (-($\boldsymbol{C}H_2$)$_n$, -$\boldsymbol{C}H_3$), 51.40 (-O$\boldsymbol{C}H_3$), 127.86–130.16 (olefinic carbons), 174.29 (-$\boldsymbol{C}$O-OCH_3). FT-IR (thin film): 722, 870, 1023, 1116, 1172, 1248, 1366, 1451, 1528, 1597, 1660, 1743, 2842, 2926, 3018 cm^{-1}.

2.7 Analysis of oil and FAME

All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz respectively using Bruker Avance III 300 MHz/54 mm NMR spectrometer. IR spectra were recorded with a Perkin Elmer RX I FT-IR spectrometer as a thin film on KBr plate.

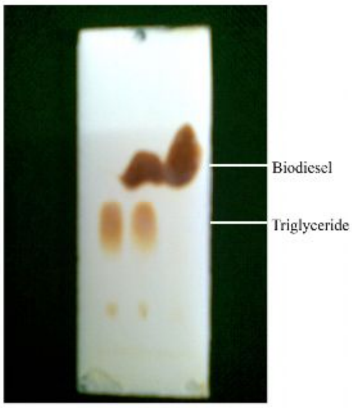

Fig. 2. TLC showing the conversion of triglyceride to biodiesel

3. Results and Discussion

Conversion of oil to biodiesel is achieved by reacting with methanol in presence of a catalyst. Biodiesel is mixture of methyl esters of long chain fatty acids. In this paper, transesterification of *Citrus maxima* seed oil to fatty acid methyl esters (FAME, biodiesel) using heterogeneous catalysts derived from the peel and rhizome of *Musa balbisiana* Colla are presented (Table 1). For transesterification reaction, a mixture of oil in methanol (10 mL/g of oil) and the catalyst (20 wt.% of oil) was taken in 250 mL RB flask and magnetically stirred at room temperature (32 ºC). The conversion of seed oil to biodiesel was monitored by TLC (Fig. 2). *Citrus maxima* seed oil is successfully converted to biodiesel at room temperature (32 ^{o}C) and the yield of FAME (biodiesel) with the catalysts derived from the peel and rhizome of *Musa balbisiana* Colla were 92 and 93 wt.% within 4 and 3.5 h respectively (Table 1).

The catalysts derived from the peel and rhizome of *M. balbisiana* were activated at 400 °C and 700 °C in a muffle furnace and transesterification reaction of oil was performed with the activated catalyst under nitrogen atmosphere. It is seen from the Table 1 that a maximum of 93 wt.% conversion could be achieved with both normal and activated catalysts but activated catalysts demand slightly lower duration of reaction time. Activation temperature, 400 °C *vs*. 700 °C practically makes no difference except that reaction time with the catalyst activated at 700 ºC is marginally reduced. The increase in activity after heating the catalyst at 400 °C may be due to more free surface area availability for catalytic activity. As the catalyst is hygroscopic, it absorbs moisture from the atmosphere which is easily removed by heating the catalyst[24]. Only a marginal increase in activity of the catalyst after heating at 700 ºC reaffirms our hypothesis. There is no substantial change either in physical state or chemical structure of the catalyst after heating either at 400 °C or 700 °C.

Table 1. Activity of catalyst in transesterification of *Citrus maxima* seed oil to its FAME

Catalyst		Reaction time (h)	Yield (wt.%)
From Rhizome of *M. balbisiana*	Normal	3.5	93
	Activated at 400 ºC	3.0	93
	Activated at 700 ºC	2.5	94
From Peel of *M. balbisiana*	Normal	4.0	92
	Activated at 400 ºC	3.5	93
	Activated at 700 ºC	3.0	93
Reaction conditions: *Citrus maxima* seed oil (2 g); catalyst (20 wt.%); methanol (20 mL); reaction temperature (32 ºC).			

The ^{1}H, ^{13}C NMR and IR spectra of *Citrus maxima* seed oil are respectively shown in Figs. 3, 5 & 7 and that of biodiesel in Figs. 4, 6 & 8. It should be noted that the major difference between the ^{1}H NMR spectra of the oil (Fig. 3) and the biodiesel (Fig. 4) is the disappearance of the signals representing protons of the glycerol moiety of the glyceride at δ 4.15 (dd), 4.31 (dd) and 5.27 (m) and the appearance of a singlet signal at δ 3.66 ppm representing methoxy protons ($-CO-OCH_3$) of the ester functionality on conversion of the oil to biodiesel. The signals at δ 62.07 and 68.88 ppm in the ^{13}C NMR spectrum of *Citrus maxima* seed oil depicted in Fig. 5

revealed the presence of methylene (-$C\text{H}_2$-CO_2R) and methine (-$C\text{HCO}_2\text{R}$) carbons of glycerine moiety in the triglyceride molecules. In the ^{13}C NMR spectrum of biodiesel (Fig. 6), disappearance of these two signals (δ 62.07 & 68.88) and appearance of new one at δ 51.40 ppm due to methoxy carbon (-$\text{O}C\text{H}_3$) are indicative enough for the desired transformation. In IR spectra, sharp signals at 1746 cm^{-1} in case of the oil (Fig. 7) and at 1743 cm^{-1} in case of the biodiesel (Fig. 8) are indicative of strong absorptions by respective carbonyl stretching frequencies.

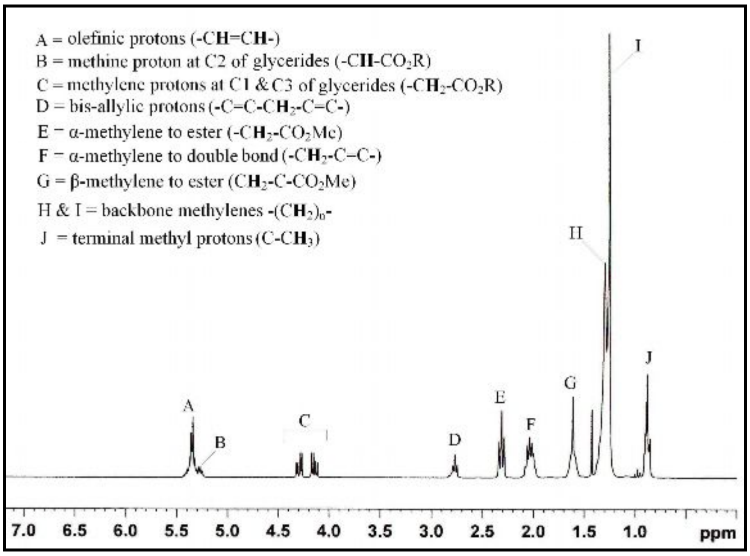

Fig. 3. ^{1}H NMR spectrum of *Citrus maxima* seed oil

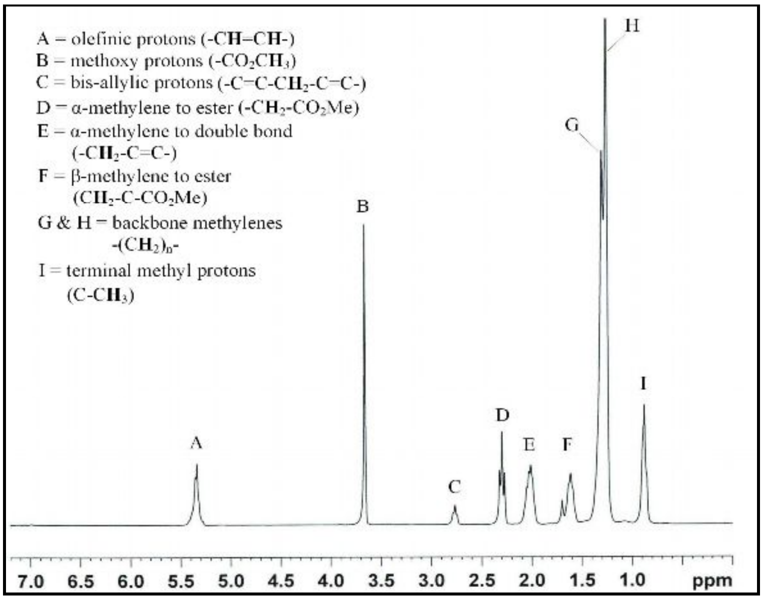

Fig. 4. ^{1}H NMR spectrum of biodiesel from *Citrus maxima* seed oil

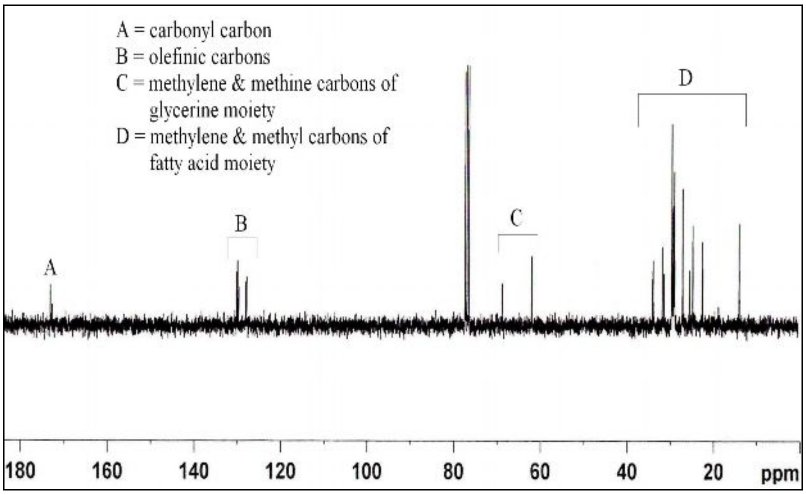

Fig. 5. ^{13}C NMR spectrum of *Citrus maxima* seed oil

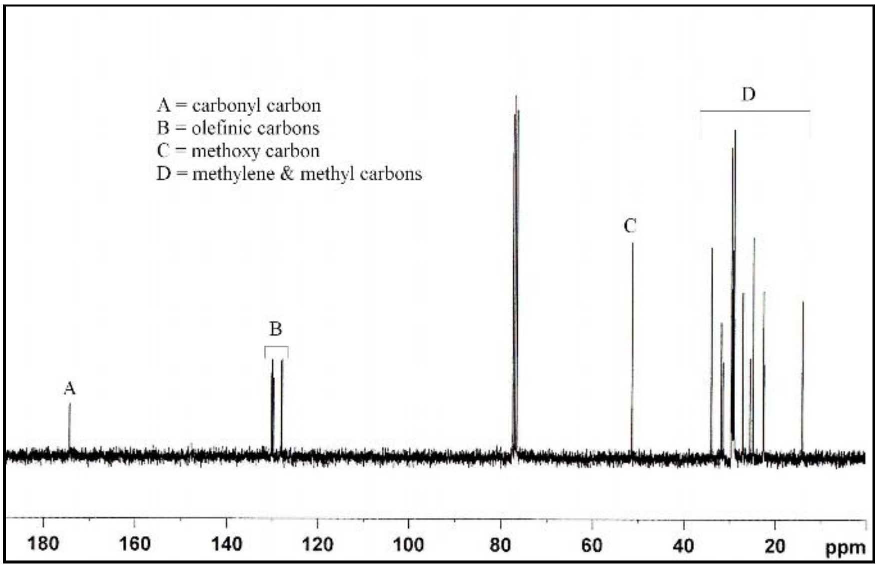

Fig. 6. ^{13}C NMR spectrum of biodiesel from *Citrus maxima* seed oil

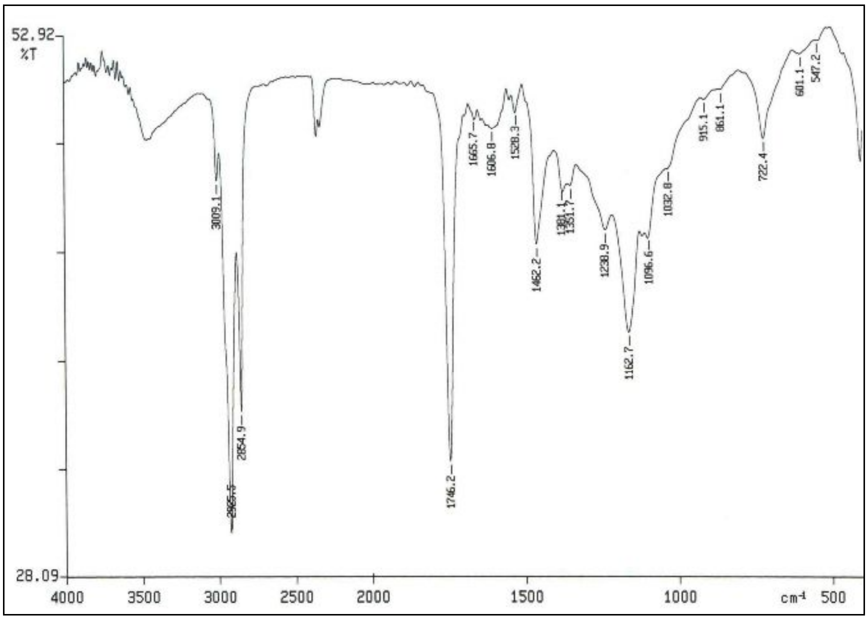

Fig. 7. IR spectrum of *Citrus maxima* seed oil

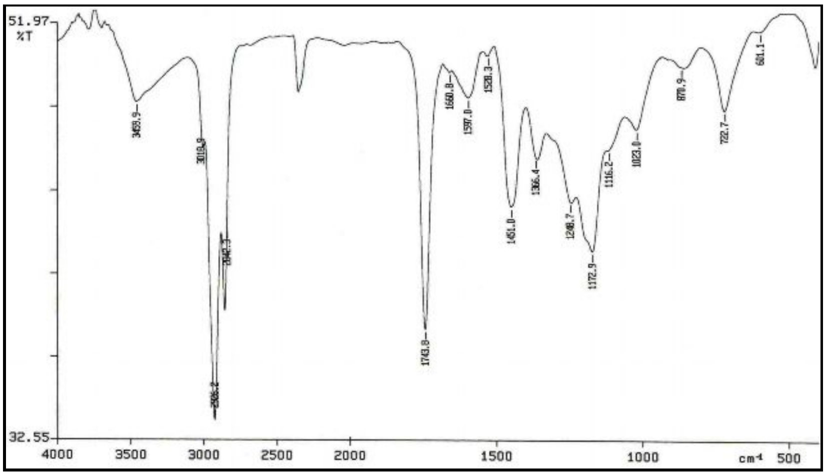

Fig. 8. IR spectrum of biodiesel from *Citrus maxima* seed oil

4. Conclusion

In this study, a low-cost heterogeneous catalyst derived from the peel and rhizome of *Musa balbisiana* Colla is used for the conversion of *Citrus maxima* seed oil to biodiesel. The yield of biodiesel with the catalysts from the peel and rhizome of *Musa balbisiana* Colla were 92 and 93 wt.% within 4 and 3.5 h respectively. Better catalytic activity is observed when the catalyst is activated by heating in the range of 400 °C to 700 °C. This plant is a potential raw material for the large scale preparation of the catalyst for biodiesel production due to its easy availability. Biodegradability and environmental acceptability are other two factors in favour of the catalyst as its large scale use will pose no disposal problem. *Citrus maxima* seed oil may be considered as potential non-edible feedstock for biodiesel production and for other purposes. Hence, further research needs to be done to explore its potential for future industrial oilseeds crop.

5. References

1. Ma, F., Hanna, M.A., Bioresour. Technol., 1999, 70, 1-15.
2. Leung, D.Y.C., Wu, X., Leung, M.K.H., Appl. Energ., 2010, 87, 1083-1095.
3. Kulkarni, M.G., Dalai, A.K., Ind. Eng. Chem. Res., 2006, 45, 2901-2913.
4. Srivastava, A., Prasad, R., Renew. Sust. Energ. Rev., 2000, 4, 111-133.
5. Meher, L.C., Sagar, D.V., Naik, S.N., Renew. Sust. Energ. Rev., 2006, 10, 248-268.
6. Schuchardt, U., Sercheli, R., Vargas, R.M., J. Braz. Chem. Soc., 1998, 9, 199-210.
7. Fukuda, H., Kondo, A., Noda, H., J. Biosci. Bioeng., 2001, 92, 405-416.
8. Barnwal, B.K., Sharma M.P., Renew. Sust. Energ. Rev., 2005, 9, 363-378.
9. Wen, Z., Yu, X., Tu ST., Yan J., Dahlquist E., Bioresour. Technol., 2010, 101, 9570-9576.
10. Song, R., Tong, D., Tang, J., Hu, C., Energ. Fuel, 2011, 25, 2679-2686.
11. Brahmkhatri, V., Patel, A., Ind. Eng. Chem. Res., 2011, 50, 6620-6628.
12. Zabeti, M., Daud, W.M.A.W., Aroua, M.K., Fuel Process. Technol., 2009, 90, 770-777.
13. Semwal, S., Arora, A.K., Badoni, R.P., Tuli, D.K., Bioresour. Technol., 2011, 102, 2151-2161.
14. Deka, D.C., Basumatary, S., Biomass Bioenergy, 2011, 35, 1797-1803.
15. Nakatani, N., Takamori, H., Takeda, K., Sakugawa, H., Bioresour. Technol., 2009, 100, 1510-1513.
16. Wei, Z., Xu, C., Li, B., Bioresour. Technol., 2009, 100, 2883-2885.
17. Boey, P.L., Maniam, G.P., Hamid, S.A., Bioresour. Technol., 2009, 100, 6362-6368.
18. Viriya-empikul, N., Krasae, P., Puttasawat, B., Yoosuk, B., Chollacoop, N., Faungnawakij, K., Bioresour. Technol., 2010, 101, 3765-3767.
19. Xie, J., Zheng, X., Dong, A., Xiao, Z., Zhang, J., Green Chem., 2008, 11, 355-364.
20. Boey, P.L., Maniam, G.P., Hamid, S.A., Ali, D.M.H., Fuel, 2011, 90, 2353-2358.
21. Chakraborty, R, Bepari, S, Banerjee, A., Bioresour. Technol., 2011, 102, 3610-3618.
22. Barua, P., Dutta, K., Basumatary, S., Deka, D.C., Deka, D.C., Natural Product Research, 2014, 28(8), 577–580.
23. Deka, D.C., Talukdar, N.N., Ind. J. Traditional Knowledge, 2007, 6, 72-78.
24. Basumatary, S., Deka, D.C., Int. J. ChemTech Res., 2014, 6(4), 2377-2384.

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