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K_2CO_3 in NH_4OH as an Effective Catalyst Mixture for the Transesterification of High Acid Value Mahua Oil

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In present study, biodiesel was synthesized from high free fatty acid content Mahua oil using K_2CO_3 in NH_4OH catalyst mixture through transesterification process. Addition of NH_4OH to K_2CO_3, enhanced the basic strength of the catalyst (K_2CO_3) by generating *in-situ* KOH in ammonium carbonate medium. The presence of ammonium carbonate in the reaction medium controlled the generation of intermediate water during methoxide formation and thereby increased the biodiesel yield. The maximum yield of 98.5% with a fatty acid methyl ester (FAME) content of 98.95% was obtained at the optimized condition of catalyst mixture of 1g K_2CO_3 in 0.5 g of NH_4OH, oil to methanol molar ratio 1:7 at 55 ºC in 75 min. Characterization of the obtained biodiesel has been carried out using GC-MS and ^{1}H NMR techniques. The physico-chemical properties of the oil and the synthesized biodiesel were tested according to the ASTM D6751 standards and the values are within the range.

Keywords: Mahua oil, Potassium carbonate, Ammonium hydroxide, Ammonium Carbonate, Catalyst mixture, Biodiesel.

INTRODUCTION

Fuels derived from renewable resources are one of the greatest solutions to alleviate the current reliance on diminishing fossil fuels [1]. Biodiesel is the most common substitute for petroleum diesel because it is a stable alternative energy source with the advantages of renewability, non-toxicity, lower pollution and biodegradability [2]. Commercial biodiesel is currently produced from first-generation edible oils such as soybean, rapeseed, palm and sunflower oil. However, the amount of edible oil feedstock available is insufficient to fulfil global fuel demand [3]. Biodiesel production from edible oils causes a conflict between energy and food, as well as deforestation and ecological imbalance, because it requires a considerable amount of fertile land for cultivation [4]. As a result, it is preferable to produce biodiesel from non-edible second generation feedstocks such as Mahua, Pongamia, Jatropha, Caster and others [5]. These biofuel crops can grow in non-agricultural and marginal lands with low maintenance cost [4].

Presently, commercial biodiesel is produced through base catalyzed transesterification process, as the method is more feasible and effective [5]. However, catalysis of transesterification reaction using conventional direct KOH catalyst despite of its faster rate of reaction leads to increased soap formation due to the formation of intermediate water molecules and presence of unreacted KOH in the reaction medium [6]. Many researchers used K_2CO_3 as an alternative catalyst to KOH as it does not produce water during the alkoxide formation reaction and also tolerant of free fatty acid (FFA) content in the feedstock [6-8]. Since, K_2CO_3 is a mild base [9] and sparingly soluble in methanol [10], the process consumes a large quantity of catalyst. As a result of the greater catalyst load, secondary saponification occurs and reduces the biodiesel yield [9]. To address this, an experiment was carried out utilizing K_2CO_3 in

NH_4OH as a transesterification catalyst for Mahua oil. When K_2CO_3 was treated with NH_4OH, an *in-situ* KOH was formed in $(NH_4)_2CO_3$ medium. *In situ* produced KOH strongly participated in the production of methoxide with methanol for the transesterification, presence of $(NH_4)_2CO_3$ in the reaction medium controlled intermediate water forma-tion and made the process less susceptible to saponification. No significant works have been carried out previously on biodiesel synthesis from high free fatty acid content Mahua oil feedstock using K_2CO_3 in NH_4OH catalyst mixture.

In present study, the cost effective and easily available Mahua oil was used as a feedstock for the biodiesel production. Mahua is indigenous to India, Sri Lanka, Nepal and Myanmar. It is a frost resistant species that can grow in marginal areas of dry tropical and subtropical forests up to an altitude of 1200-1800 m. It grows well where annual rainfall is between 500 mm to 1500 mm and where temperatures are in the range of 2-46 ºC. Mahua seeds contain up to 50% oil and can be effectively extracted using oil seed expellers [9]. In the present study, production optimization has been carried out with Mahua oil using K_2CO_3 in NH_4OH catalyst mixture. Reaction conditions were optimized for the maximum biodiesel yield. The obtained biodiesel was analyzed with the help of GC-MS and ^{1}H NMR techniques for its yield and quality. The physico-chemical properties of the oil and the synthesized biodiesel were tested according to the ASTM 6751 standards for the appropriateness of obtained biodiesel as an alternative fuel for diesel engine.

EXPERIMENTAL

Mahua oil was purchased from local market of Gauribidanur town, India. The reagents such as anhydrous methanol with 99.9 % purity, Concentrated H_2SO_4 of 98.9% pure, KOH (85 % purity), Anhydrous K_2CO_3 (99.9% purity), NH_4OH (25% liquor ammonia) of analytical grade are used in the process of biodiesel production. All the reagents were purchased from Sigma-Aldrich, India.

The fatty acid composition of Mahua oil was determined using GC-MS (Shimadzu QP2020 model) instrument at an injection temperature of 240 ºC using helium gas as a mobile phase and a DB-wax column of length 30 mm, thickness 0.25 µm, diameter 0.32 mm and the composition is summarized in Table-1. It is clear that Mahua oil was composed highly of saturated fatty acids (49.9%) and the similar composition has been reported by Singh & Singh [11]. Conversion of oil to biodiesel (methyl esters) was analysed using ^{1}H NMR-Agilent (VNMRS-400). The free fatty acid content in the feedstock was determined by the modified AOCS Cd 3d-63 method [12]. Other physico-chemical properties of oil and derived biodiesel was determined according to ASTM standard methods.

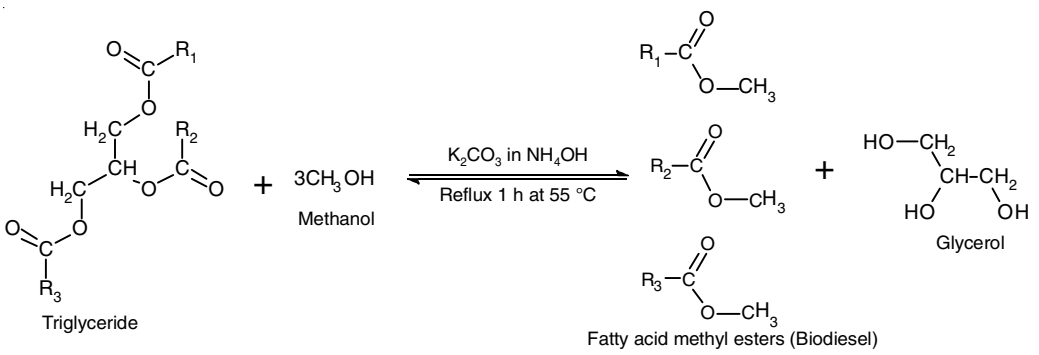
TABLE-1
FATTY ACID COMPOSITION OF MAHUA OIL

Fatty acid	Common acronym	Mahua (wt.% of fatty acid)
Palmitic acid	C 16:0	18.05
Stearic acid	C 18:0	22.71
Oleic acid	C 18:1	34.4
Linoleic acid	C 18:2	14.86
α-Linolenic acid	C 18:3	0.57
Arachidic acid	C 20:0	1.06
11-Ecosenoic acid	C 20:1	0.27
Behenic acid	C 22:0	1.13
Other saturated fatty acids		6.95

Biodiesel production

Acid pre-treatment: The initial acid value of Mahua oil was determined titremetrically and found to be 36 mg KOH/g. Two-step acid esterification was performed to lower the acid value to the desirable limits. The quantity of methanol and H_2SO_4 needed for each stage was estimated based on the amount of FFA in the feed oil [2.5 g methanol/FFA (g) and 0.05 g H_2SO_4/FFA (g)] [13]. The acid esterification was carried out by refluxing 100 g of crude Mahua oil with the required amount of methanol and H_2SO_4 at 60 ºC for 1 h at a constant stirring speed of 600 rpm. After the reaction, the mixture was allowed to settle for 8 h and the methanol-water-H_2SO_4 fraction that separated at the top was removed from the separating funnel. The final product, having an acid value of 2.0 mg KOH/g, was subjected to base catalysed transesterification.

Base catalyzed transesterification: In base catalyzed transesterification (eqn. 1), 1 g of K_2CO_3 was initially treated with 0.5 g (0.6 mL) of NH_4OH (1:2 K_2CO_3 to NH_4OH molar ratio), followed by 35 mL (1:7 oil to methanol molar ratio) of methanol. The reaction mixture was stirred for 5 min followed by th esterified oil and refluxed for 1 h at 55 ºC with a stirring speed of 600 rpm. The transesterified product was separated from the glycerol and subjected to a water wash to remove water soluble impurities. After a water wash, the biodiesel was dried in a microwave oven at 100 ºC. Biodiesel yield in terms of weight percent was calculated by using eqn. 2. A maximum yield of 98.5% of Mahua oil biodiesel was obtained. Fig. 1 depicts the steps involved in the synthesis of biodiesel.



(1)

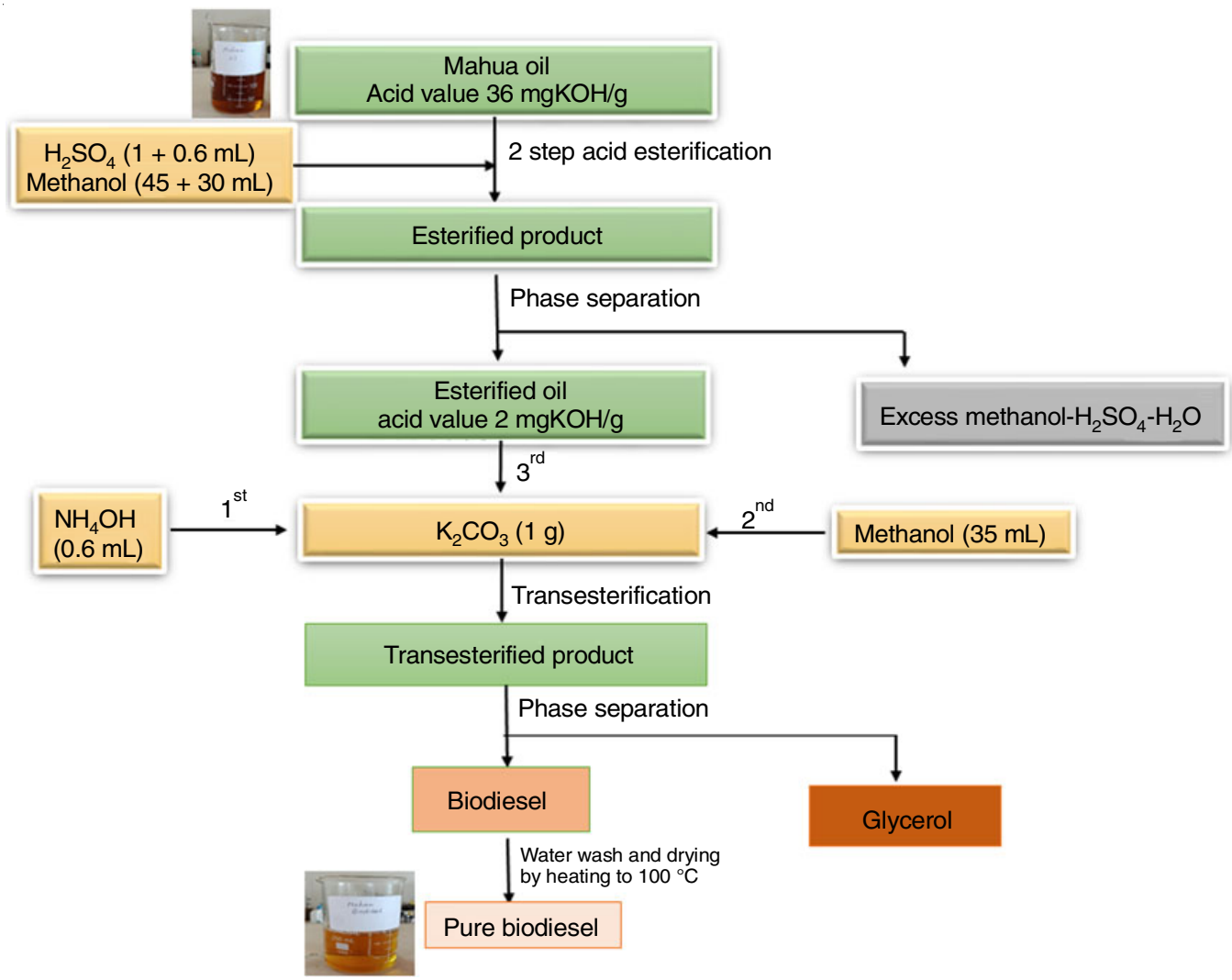


Fig. 1. Steps involved in the synthesis of Mahua oil biodiesel using K_2CO_3 in NH_4OH catalyst

$$\text{Yield in weight (\%)} = \frac{\text{Weight of biodiesel obtained}}{\text{Weight of oil taken}} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Physio-chemical properties: The physico-chemical properties of Mahua oil and the biodiesel was investigated according to standard methods and tabulated in Table-2. Transesterification of highly saturated fatty acid containing Mahua oil to its fatty acid methyl esters resulted in an improved oxidation stability, cold flow, and kinematic viscosity in the biodiesel. The properties of produced biodiesel using K_2CO_3 in NH_4OH catalyst were according to the specified ASTM 6751-02 values.

Role of NH_4OH in transesterification: Efficiency of transesterification (methanolysis) is primarily determined by the effectiveness of methoxide formation and its concentration in the reaction medium. Potassium carbonate has a great potential to be a catalyst for transesterification as it does not produce water during methoxide formation (eqn. 3). However, the reaction between K_2CO_3 and methanol is a reversible temperature dependent reaction. As the temperature increases, the reaction shifts towards the left and hence, the concentration of active methoxide species decreases [10]. It is evident from earlier reports that more K_2CO_3 is necessary to get adequate methoxide for the maximal methyl ester conversion. The addition of more catalyst caused a secondary saponification reaction, lowered the biodiesel yield [7,10].

$$K_2CO_3 + CH_3OH \rightleftharpoons CH_3OK + KHCO_3 \quad (3)$$

To prevent this, K_2CO_3 was treated with NH_4OH before being treated with methanol. On adding NH_4OH, K_2CO_3 ionized to produce *in situ* KOH and $(NH_4)_2CO_3$. *in situ* KOH assisted in the successful production of methoxide with methanol for transesterification of Mahua oil. Whereas hydrophilic $(NH_4)_2CO_3$ absorbed water molecules in the reaction medium and generated $KHCO_3$ and NH_4OH without permitting free water molecules to develop for the saponification side reaction. Eqn. 4 shows the reaction mechanism for methoxide formation using K_2CO_3 in NH_4OH catalyst. The increased Mahua oil biodiesel yield of 98.5% validates that K_2CO_3 in an NH_4OH catalytic mixture is one of the best options to synthesize biodiesel from high acid value feedstocks.

TABLE-2
PHYSIO-CHEMICAL PROPERTIES OF MAHUA OIL AND ITS BIODIESEL

Property	Testing method	Biodiesel-ASTM 6751-02	Crude Mahua oil	Mahua biodiesel
Density at 15 °C (kg/m^3)	ASTM-D1298	880 Max	960	898
Kinematic viscosity at 40°C (mm^2/s)	D445	1.9-6.0	24.58	4.344
Flash point (°C)	D93	130 min	232	160
Cetane number	D613	47 min	36	52
Cloud point (°C)	D2500	-3 to 12	19	5
Pour point (°C)	D97	-15 to 10	15	2
Calorific value (MJ/kg)	D240	–	36	38.502
Ester content (mass %)	EN 14103	96.5 min	–	98.95
Acid value (mg KOH/g)	AOCS-Cd3d-63-Oil D664-Biodiesel	0. 80 max	36	0.52
Copper strip corrosion for 3 h at 100 °C	D130	No. 3 max	< No.1	< No.1
Oxidation stability, at 110 °C (h)	EN14112	Min. 3 h	–	10.5
Saponification value (mg KOH/g oil)	D1962	–	194.2	190.5
Iodine value (mg I_2/100g)	EN 14111	Max 120	62	64.4
Methanol content (% vol.)	EN14110	0.2 max	–	Nil
Water content (% vol.)	D2709	Max 0.05	1.6	Nil
Sulphur content (% mass)	D5453	0.05 max		0.01
Carbon residue (% mass)	D4530	0.05 max	3.70	0.1545
Ash content (% mass)	D0482	0.05 max	0.9	0.01

$$K_2CO_3 + 2NH_4OH \longrightarrow 2[KOH] + (NH_4)_2CO_3$$
$$\xrightarrow{CH_3OH} CH_3OK + KHCO_3 + 2NH_4OH \quad (4)$$

Effect of K_2CO_3 and NH_4OH amounts on the biodiesel yield: The generation of *in-situ* KOH depends on the amounts of both K_2CO_3 and NH_4OH. In order to optimize the total amount of catalyst mixture required for the synthesis of Mahua oil biodiesel, experiments were conducted by varying the K_2CO_3 amount from 0.5 to 1.5 g and the K_2CO_3 to NH_4OH molar ratio from 1:1 to 1:4 by keeping other experimental parameters constant. Experimental observation revealed that a maximum of 98.5% biodiesel yield was obtained when 1 g of K_2CO_3 was treated with a 1:2 NH_4OH molar ratio (Fig. 2). A further rise in the catalyst amount, reduction in the biodiesel yield was observed. This is due to the excessive release of KOH at the beginning because of the complete ionization of K_2CO_3. Where in the case of a lower catalyst amount, even by adding a higher molar ratio of NH_4OH, a lower yield was observed as the quantity of K_2CO_3 was insufficient for the process. At the molar ratio of 1:2 (1 g of K_2CO_3 in 0.5 g of NH_4OH), the catalyst endured partial dissolution to produce only the required amount of KOH in ammonium carbonate medium for the methanolysis without releasing free water molecules (eqn. 4). The obtained yield was higher compared to the yield obtained in the case of the direct K_2CO_3 method, in which using 3 g of K_2CO_3 catalyst, 90.13% of the canola oil biodiesel yield was achieved [8]. Also, the obtained yield was better than the yield obtained in the case of the conventional NaOH catalytic method as reported by Puhan *et al.* [14], in which 92% Mahua oil biodiesel was obtained using 1 g NaOH catalyst. An increase in the yield in the present method is due to the less scope for intermediate water formation and a reduction in the hydrolysis of esters and saponification side reaction.

Impact of oil to methanol molar ratio on biodiesel yield: Extent of methanolysis mainly depends on the oil (triglycerides) to methanol molar ratio. Stoichiometrically for every one mole of triglyceride, three moles of methanol (eqn. 1) is required. Since the reaction is reversible, this ratio was inadequate. A higher methanol ratio was used to push the reaction towards the product side and achieve the process in a shorter reaction time [15,16]. The yield of Mahua oil biodiesel increased as the methanol ratio increased up to 1:7 and reached maximum (Fig. 3). On further rise in the methanol ratio, there was an insignificant change in the biodiesel yield.

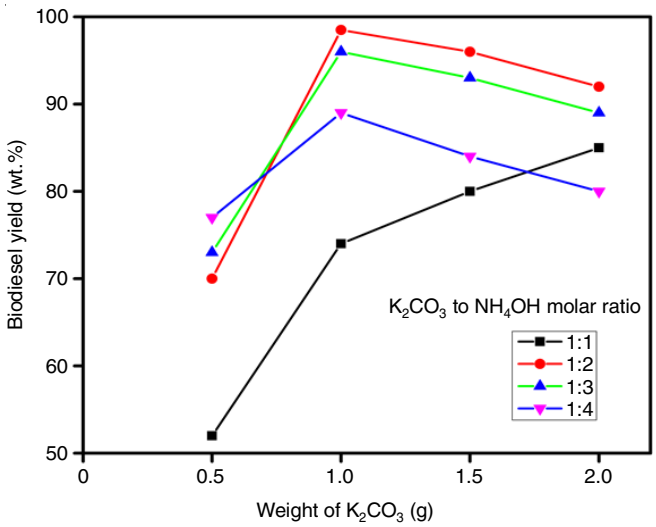


Fig. 2. Impact of K_2CO_3 and NH_4OH amounts on yield of Mahua oil biodiesel

Impact of reaction time and temperature on biodiesel yield: Experiments were conducted at temperatures ranging from 45 to 65 ºC, with a reaction time ranging from 30 to 105 min, while catalyst (1.g K_2CO_3 in 0.5 g NH_4OH) and methanol (1:7) quantities remained constant. At 55 ºC, a maximum yield of 98.5% biodiesel was obtained in 1 h. A slightly decrease in yield is observed as the temperature increased, since saponification is more favourable than transesterification at higher

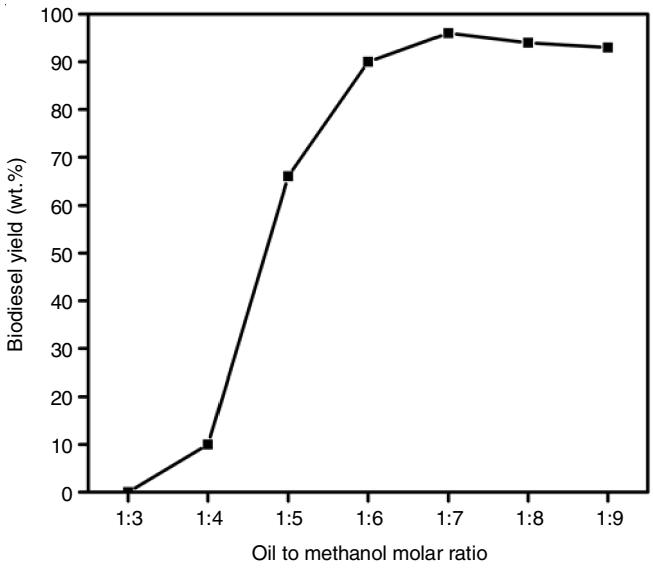


Fig. 3. Impact of oil to methanol molar ratio on the yield of Mahua oil biodiesel

temperatures [17]. Additionally, increasing the reaction time resulted in a negligible change in yield (Fig. 4).

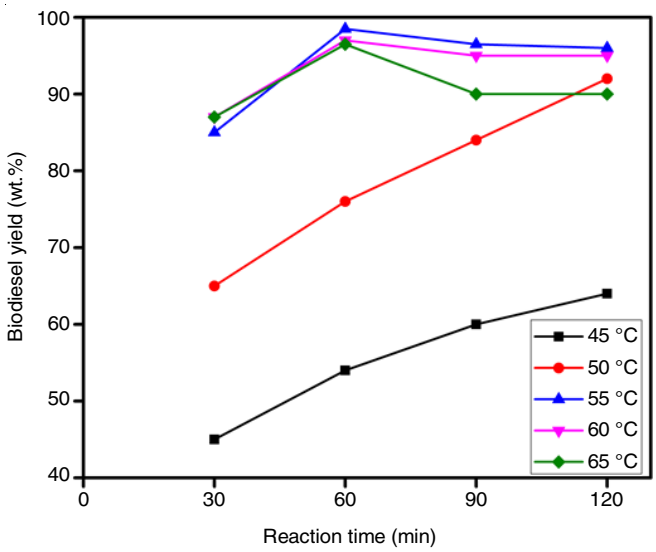


Fig. 4. Impact of reaction time and temperature on the yield of Mahua oil biodiesel

GC-MS analysis: Fatty acid methyl ester (FAME) content of Mahua oil biodiesel was estimated through GC-MS analysis according to EN14103 standard method. Percentage of FAME content in the biodiesel was determined by comparing methyl esters peak areas (Fig. 5) with internal standard (methyl margarate) peak area obtained in GC-MS analysis using eqn. 5 [18]. The maximum of 98.95% FAME content was achieved.

$$C = \frac{(\Sigma A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \quad (5)$$

where C = methyl ester content (mass fraction in percentage), ΣA = Total peak area of methyl esters, A_{EI} = peak area of internal standard, m = mass(mg) of sample, C_{EI} and V_{EI} are the concentration (mg/mL) and volume (mL) of internal standard, respectively.

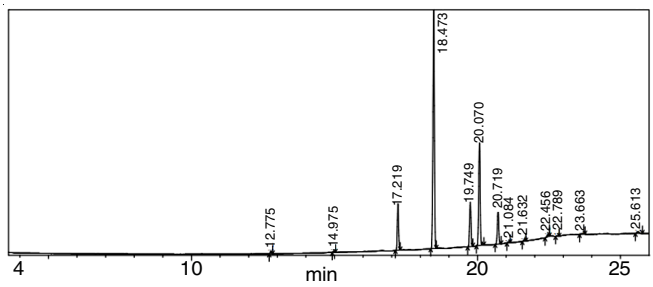


Fig. 5. GC-MS spectrum of Mahua biodiesel

^{1}H NMR analysis: ^{1}H NMR spectrum of the Mahua oil (a) and its biodiesel (b) are depicted in Fig. 6. In Fig.6a, multiplets in the δ range from 4 to 4.3 ppm indicates the presence of glycosides protons in the oil. Disappearance of these peaks in the biodiesel spectrum (Fig. 6b) and appearance of sharp singlet at 3.627 ppm in the biodiesel spectrum confirmed the transformation of triglycerides to fatty acid methyl esters (FAME) [19-21]. In Fig. 6b, a sharp intense peak at 3.627 ppm, clearly indicates the presence of methoxy proton and triplet at 2.284 ppm indicates the presence of α-CH_2 protons [22,23]. Appearance of these two characteristic peaks confirms the formation of methyl esters. Conversion percentage of triglycerides to methyl esters was calculated from eqn. 6 [24], where 98.19% FAME conversion was achieved.

$$C = 100 \times \frac{2A_{ME}}{3A_{\alpha-CH_2}} \quad (6)$$

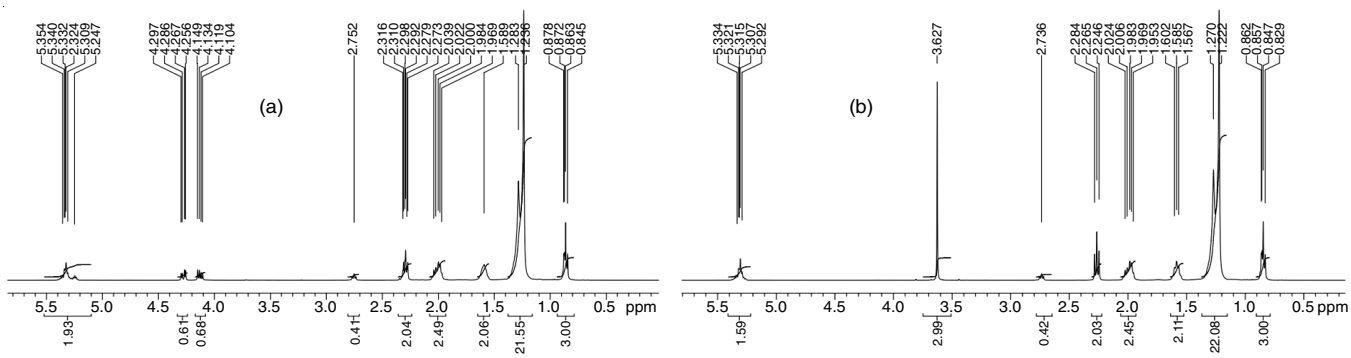


Fig. 6. ^{1}H NMR spectrum of Mahua oil (a) and its biodiesel (b)

where C = conversion percentage of triglycerides (oil) to methyl esters (biodiesel), A_{ME} = integral value of methoxy protons (OCH_3), Aα-CH_2-integral of methylene protons. Integer 2 and 3 are the proton number in methylene and methyl ester, respectively.

Conclusion

Biodiesel synthesis from Mahua oil feedstock is one of the easiest and cost-effective method to overcome dependency on edible oil feedstock and also to get optimum properties in the biodiesel. Maximum reduction in the free fatty acids (FFA) content in the crude oil was achieved through two step acid pretreatments. In current study, a new experimental approach was made to generate *in situ* KOH in ammonium carbonate medium using K_2CO_3 in NH_4OH catalyst mixture for the catalysis of transesterification reaction. *In-situ* KOH increased the catalysis of Mahua oil transesterification whereas $(NH_4)_2CO_3$ in the reaction media absorbed water molecules, limiting the amount of free water molecules available for the hydrolysis and saponification side reactions. Maximum yield (98.5%) was obtained by using catalyst mixture of 1.0 g K_2CO_3 in 0.5g of NH_4OH, 1:7 oil to methanol molar ratio at 55 ºC in a reaction time of 1 h. The GC-MS and ^1H NMR analysis confirmed the high degree of FAME conversion in the derived Mahua oil biodiesel. This research demonstrates that K_2CO_3 in NH_4OH catalyst mixture can be effectively applied to produce biodiesel with improved yield and enhanced fuel properties from high FFA content feedstock. However, catalyst was not recovered in the process, but lesser water wash was required compared to KOH and K_2CO_3 catalytic methods as the process is less sensitive to secondary saponification reaction. By further improving the reaction conditions in terms of large-scale biodiesel production, economically viable biodiesel from low-cost feedstock Mahua oil can be manufactured and used as an alternative fuel in existing diesel engines without any modifications to satisfy the ever-increasing oil demand.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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