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Research paper



Effect of Quaternary Ammonium Salt Addition to Conventional Biodiesel Production Process

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Abstract

Biodiesel on a commercial scale is largely produced by transesterification using a conventional homogeneous catalyst like KOH and NaOH. The major problem associated with conventional homogeneous transesterification process is that it is prone to water & FFA content. This problem can be mitigated with some process modification using quaternary ammonium salts. In the present study, the reaction between waste palm oil & methanol was carried in a batch reactor at 65^{o}C & various molar ratios of oil to methanol. Further, the effect of various dosages of tetramethylammonium bromide (TMAB) addition to this reaction was studied. Results show that there is a strong influence of TMAB (a phase transfer catalyst) on the methanol requirement during the reaction and also on the washability characteristics of the produced biodiesel. It was observed that there is a considerable decrease in the molar ratio of methanol to oil requirement during the reaction. Moreover, the addition of TMAB has enhanced the washability of the final biodiesel product by forming less foam. This has a direct advantage of decreasing the water requirement during the purification process.

Keywords: *Biodiesel; Phase transfer catalyst; Quaternary ammonium salt; Tetramethylammonium bromide; Transesterification.*

1. Introduction

The limited resources of fossil fuels alarm to look for an alternative replacement. Biodiesel is considered to be the best alternative to the fossil-derived diesel fuel[1]. Biodiesel production using waste vegetable oil is considered to be the tech-savvy and environmentally benign approach[2].

According to the corporate catalyst[3], the food processing industry in India is the 5th largest one and it contributes as much as 9-10% of GDP growth in agriculture products manufacturing sector. Indian food processing industry has reached the business of US $ 39.03 billion in 2013 and by 2018, it is expected to touch the US $ 64.31 billion at an expected growth rate of 11%. Thus it suggests that there is an exponential increase in the generation of waste vegetable oil. Therefore, it is required to develop an economical, environmentally benign and sustainable process which may utilize the generated waste oil for the production of biodiesel.

Transesterification of triglyceride in vegetable oil with short-chain alcohol like methanol is widely used to produce biodiesel in the presence of a catalyst as shown in Equation-1[4]. There are many types of catalysts used in the biodiesel production like alkali, acid, and enzyme[5][6]. The alkali-catalyzed transesterification mechanism is most widely used because it is simple to carry out and gives high yield at mild reaction conditions. Biodiesel on commercial scales is largely synthesized using a homogeneous catalyst (KOH & NaOH) due to its cheaper cost[7]. Presence of water during the transesterification process fragments the triglycerides to diglyceride (DG) and free fatty acid (FFA) as given in Equation-2. As a consequence, the FFA reacts with the alkali to form soap and water as shown in Equation-3.

$$TG+3CH_3\ OH \leftrightharpoons 3FAME+Glycerol \quad (1)$$

$$TG+Water \dashrightarrow DG+FFA \quad (2)$$

$$FFA+NaOH \dashrightarrow Water+Soap \quad (3)$$

Transesterification reaction is the main reaction mechanism in forming biodiesel. The formation of soaps during transesterification not only hinders the reaction progress but also increases the loss of produced biodiesel to byproduct phase (glycerol) during washing. This results in higher water requirement in purification step and this increases the cost of biodiesel production[4]. The main reason behind this disadvantage is due to the reaction between TG and water, alkali and FFA and also due to the formation of alkali soaps. Since oil and alcohol are two dissimilar species used in the biodiesel production and suffers from very least solubility during the reaction[8]. Therefore, the usage of the catalyst is unavoidable.

Most of the reactions occurring in conventional, homogeneous conditions require each of the dissimilar species (organic & inorganic) must have some solubility within the reaction medium and its efficacy largely depends on their mutual solubility's[9]. These disadvantages in direct organic synthesis reaction raise the need for phase transfer catalytic processes. Transesterification using base-catalyst requires strict anhydrous conditions whose mechanism involves the nucleophilic attack[10]. Therefore, it is expected that the usage of quaternary ammonium salt can assimilate the water content and facilitates the smooth reaction between the vegetable oil and alcohol.

Tetramethylammonium (TMA) salts are known to possess phase transfer catalytic properties. TMA salts are positively charged simplest quaternary ammonium cation with four methyl groups attached to the central nitrogen atom and are often associated with some anion groups like bromide, chloride, iodide, and

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hydroxide[4]. There is no reported data for the role played by TMA compounds in the biodiesel production to date.
The current work focuses on the base-catalyzed batch scale production of biodiesel using waste palm oil (WPO) & methanol as feedstocks, NaOH & KOH as a catalyst and tetramethylammonium bromide as the production process enhancer. The effect of oil to methanol molar ratios & TMAB on the production of biodiesel was studied.

2. Materials & Methods

2.1. Materials

WPO was collected from the selected households. It was dark brown in color containing food contaminants. The other chemicals such as methanol, sodium hydroxide, potassium hydroxide, glacial acetic acid, hexane, diethyl ether, potassium permanganate, chloroform, iodine monochloride, potassium iodide, sodium thiosulphate, ethanol, hydrochloric acid, phenolphthalein indicator and tetramethylammonium bromide were purchased from Fluka chemicals and were used without further purification. caprilic, decanoic, lauric, myristic, palmitic, palmitoleic, stearic, oleic, linoleic, linolenic, arachidic, behenic, lignoceric acid, Internal standards: butanetriol, tricaprin; reference standards: mono-olein, di-olein, and triolein; derivatizer: N- methyl-N-trifluoroacetamide (MSTFA) of Sigma-Aldrich were used for chromatographic analysis. All the standards are used with pyridine solvent. The instrument grade helium, hydrogen, and zero-air were supplied by Sigma-gases and services, New Delhi, India.

2.2. Experimental procedure

The contaminants in WPO were removed by screening with fiber cloth placed on Buchner funnel and then the moisture was removed by heating at 120^{o}C for 45 minutes with continuously stirring.
Experiments were conducted in a 250ml three-neck round bottom flask fitted with a reflux condenser at various methanol to oil molar ratios (3:1, 6:1, 7.5:1, and 9:1) using KOH and NaOH as a catalyst. The KOH and NaOH amounts were varied in the range of 0.5 to 2 wt. % and 0.25 to 1.5 wt. % of feed oil, respectively. The reaction mass was heated at 65^{o}C with constant stirring at 500 rpm.
Another set of transesterification experiments were performed using various dosages of TMAB (0.2-1.0 grams) to study the effect of TMAB on the process.
After completion of the reaction (90 min), the batch was poured into the separating funnel and left for 24h. On cooling & separating the formation of two layers (ester and glycerin) were observed. Glycerin formed was separated from the ester layer and the ester layer was subjected to further purification.
The ester layer was subjected to remove the catalyst (KOH/NaOH/TMAB) and excess methanol. The catalyst present in the ester layer was removed by adding a small amount of glacial acetic acid to neutralize the ester followed by washing with hot distilled water (60^{o}C). The pure ester was heated at 120^{o}C for 10 minutes to remove any moisture present. Then the samples were stored for analysis using gas chromatograph (GC).
GC analysis of biodiesel was carried out following the methodology of ASTM® D6584 which require five-level calibration curve at five different known amounts of standards. The internal standards (IS) like butanetriol (IS1) for glycerin identification and tricaprin (IS2) and the calibration standards like monoolein, diolein & triolein were used for individual glycerides quantification.
Before analysis derivatization of the standard and samples were carried out using MSTFA whose reaction involves the replacement of active hydrogen of the hydroxyl group by the trimethylsilyl-group. Usually, samples and standards having molecules like monoglycerides, diglycerides, triglycerides, and glycerin are derivatized to reduce their polarity and improve the thermal stability of this molecules. After derivatization, the hexane was added to each vial containing samples and standards and the vial was capped and shaken. 1µL of this sample from vial was injected through the injector of a gas chromatograph with flame ionization detector (GC-FID). The GC-FID used was Perkin Elmer make (model: Clarus-580) with a Zebron made capillary column (30m x 0.25 mm x 0.25 µm). Helium was used as a carrier gas. The flow of H_2 and zero-air was maintained as 45 mL/ min & 450 mL/min respectively.
The oven of GC was programmed as per the following conditions: Oven program initial temperature was maintained at 50^{o}C with a first hold time of 1 min against ramp-1 at 15^{o}C/ min. Then the temperature was increased to 180^{o}C with the second hold time of 0 min against ramp-2 at 7^{o}C/ min. Further, the temperature was set to increase up to 230^{o}C with a third hold time of 0 min, against ramp at 10^{o}C/ min. Finally, the oven program temperature was set at 370^{o}C with a hold time of 5 min and equilibrating time of 0 min.
Each analyte was identified using the retention times (in minutes) of reference standards and are given according to their appearance of a peak in ascending order of the chromatogram:
Glycerin (5.379), butanetriol (6.259), total monoglycerides (17.872), tricaprin (19.903), diglyceride (21.653), triglyceride (25.013).
A calibration curve was generated to identify the unknown amount of analyte in the produced biodiesel. Reference standards at five different amounts are taken to ensure a linear relationship between FID response (Area) and the weight percentage of the analyte. The calibration curve for each analyte demonstrated R^2 value greater than 0.99: total monoglycerides (0.9963), total diglycerides (0.9991), total triglycerides (0.9963) and glycerin (0.9991). The total chrome workstation software was used to find the chromatograph area generated.

3. Results & Discussions

The waste vegetable oil used in this study has the acid value of 1.8 mg KOH/g oil, the specific gravity of 0.923 and viscosity of 38.7 c.St. Composition of oil was found to be caprilic (C8:0)-0.024, Capric (C10:0)-0.016, Lauric (C12:0)-0.216, Myristic (C14:0)-0.794, Palmitic (C16:0)-44.1, Palmitoleic (C16:1)-0.208, Stearic (C18:0)-4.121, Oleic (C18:1)-39, Linoleic (C18:2)-10.52, Linolenic (C18:3)-0.132, Arachidic (C20:0)-0.146, Behenic (C22:0)-0.060, Lignoceric (C24:0)-0.054, Others-0.61. Overall, 49.531 wt% of saturated fatty acids are present in the feed oil.

3.1. Effect of methanol molar ratio on %Yield and properties

The effect of methanol mole ratio was studied in the range of 3:1 to 9:1. It was found that increasing methanol mole ratio favorably shifts the reaction towards the product formation. Since oil is the limiting reactant, providing the methanol in excess shifts the equilibrium towards higher product formation which increases the percentage yield. The data in Table 1 represents this behavior. The optimum methanol to oil molar ratio was found to be 9:1. Beyond this ratio, the yield is going down. It is due to the fact that the presence of excessive methanol dilutes the concentration of the catalyst in the total reaction mixture and decreasing the probability of contact between reactants and the catalyst. Similar trends were observed in the case of Leung & Guo [11] and Zhang et.al.[12].
Biodiesel kinematic viscosity was found to vary with a molar ratio of methanol to oil as well as with the type of catalyst used (Fig.1). It was observed that, increasing molar ratio of methanol to oil from 3:1 to 9:1 decreases the viscosity from 4.5 cSt to 3.8 cSt in the case of KOH and 4.8 to 4.2 cSt in the case of NaOH catalyst. The viscosity of the biodiesel in the range of (3.4- 4.5 cSt) is close to the viscosity of mineral diesel (2 - 4.5 cSt) which indicates that it can be used in the diesel engine without modifications. On one hand, the higher viscosity of the fuel can result in poor vaporiza-

tion, poor fuel atomization, and blocks filter during the flow of fuel from fuel storage tank to the combustion chamber of the engine. On the other hand, lower viscosity of fuels may results in wear in injection pump and pump leakages. Therefore, the kinematic viscosity has complied with the standards given in Table 2.
Flashpoint is the important property of a fuel, describing the minimum temperature at which the fuel catches the fire. According to safety norms, it is mandatory to specify the flashpoint for every fuel. Flashpoint was found to vary considerably with methanol to oil molar ratio from 173^{o}C (3:1 methanol/oil) to 160^{o}C (9:1 methanol/oil) for KOH catalyzed samples & from 180^{o}C (3:1 methanol/oil) to 174^{o}C (9:1 methanol/oil) for NaOH catalyzed samples. It was observed that increasing the molar ratio of methanol to oil, decreases the flash point of the produced biodiesel.
The cloud point of the obtained fuel represents the temperature at which the wax formation takes place (hazy cloud as an indicator) and can clog the fuel filter as well as flow lines. The cloud point of obtained biodiesel samples was found to be 9.2^{o}C and showed the negligible change due methanol to oil molar ratio.

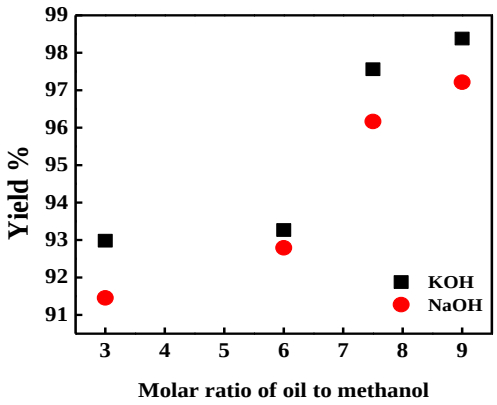


Fig. 1: Effect of catalyst type on biodiesel yield

3.2. Effect of TMAB addition on biodiesel production

It was observed that there is a considerable increase in the yield when TMAB was added to the reaction as shown in the Fig.2. There was a decrease in the optimum methanol requirement from 9:1 (in case of either KOH/NaOH) to 7.5:1 molar ratio (in case of TMAB along with either KOH/NaOH) was observed. During washing of biodiesel synthesized in presence of TMAB it was observed that a relatively very lesser amount of water was required (reduced nearly half). During washing & separation, there was no disturbance in settling was also observed. Alkali-catalyzed transesterification reaction is greatly affected by the presence of water which makes the reaction partially shift towards saponification[4]. Therefore, adding TMAB to the process suppresses & diminishes the soap formation. Thus, the crude biodiesel can be handled easily. Diminishing the soap formation can be directly related to the less water requirement for washing, making the process relatively more economical than the existing commercial process. The reason behind these positive results is due to the fact that TMAB assimilates the water content during the reaction. Since, biodiesel production is the organic synthesis reactions the use of TMAB might dissolve each ionic and valence species, thereby effectively increasing the basic strength and nucleophilicity of anions. This can be postulated by the fact that decreasing ion-pairing and removing the associating impact of a hydroxylic solvent obviously increases the base strength and nucleophilicity of anions[13]. A similar phenomenon can also be observed using dipolar, aprotic solvents like dimethyl sulfoxide (DMSO)[14] or dimethylformamide (DMF)[15]. However, these solvents are not readily separable from the reaction product[16][17]. Separation might require a lengthy work- up like washing with a larger volume of water, distillation of reaction solvent followed by product filtration, centrifugation, and further washing or multiple extractions with a unique water-immiscible solvent, washing with water followed by evaporation of the extraction solvent. Such procedures are time- consuming, volume-inefficient and in many instances generate large volumes of effluent containing solvent mixtures and are tough to recycle. TMAB used here adds the advantage of easy separation of the products rather than lengthy workup as in the case of DMSO or DMF. Therefore, the use of TMAB is recommended in order to make the process economically and technically feasible. Moreover, in the system consisting of two mutually-insoluble phases, either liquid-liquid or solid-liquid the distinct attribute of the phase-transfer process is that it forms an intermediate complex, which is soluble in organic solvents to transfer inorganic ions into the organic phase. Such techniques are notably useful in base-catalyzed reactions, nucleophilic displacements, and oxidations of water-insoluble compounds by inorganic reagents.
Industrial processes widely adopt these techniques due to their faster, cleaner reactions and greatly simplified ramp up without the necessity for strictly anhydrous conditions. They also provide an advantage of comparatively less expensive and easily recyclable solvent than dipolar aprotic solvents. Therefore, the water content prone homogeneous-catalytic process can be made simple by just conducting the reaction in the presence of TMAB.
The work carried out by Qi et.al.[18], using SO_3H-functionalized quaternary ammonium ionic liquid as a catalyst to synthesize biodiesel from waste cooking oil reported 95% of biodiesel yield in 1h. They reported the optimum reaction conditions as methanol/oil/IL molar ratio = 10/1/0.063, temperature= 120°C. TMAB used here is being a quaternary ammonium salt comparable to their reported ionic liquid gives a yield greater than 95% in 1.5h under mild reaction conditions of 65^{o}C, 7.5/1 molar ratio of methanol/oil and 0.8g TMAB. Therefore, use of TMAB offers the triple facet benefits like economical (less expensive), technically feasible (lesser water requirement for washing) & environmentally viable (lesser water effluent).
When compared with the compositions of samples of the biodiesel without TMAB, a very less relative decrease in the percentage of MG, DG, TG and overall Glycerides were observed. Their values are presented in Table 1 (only KOH catalyzed samples data is given).

3.3. Effect of TMAB on properties of biodiesel

Table 2 is the comparison between the Properties of the produced biodiesel (without TMAB and KOH as a catalyst) and biodiesel (with TMAB and KOH as a catalyst) with standards set by ASTM D6751-12 & EN 14214:2012. From Table 2, it was observed that addition of TMAB has a considerable effect on flash and fire point of biodiesel and is lowering the flash and fire point of the biodiesel. However, these values are within the limits set for biodiesel standards. This can be attributed to the unusual behavior exhibited by the quaternary ammonium salts in various types of solvents & in different types of the reactions[9].

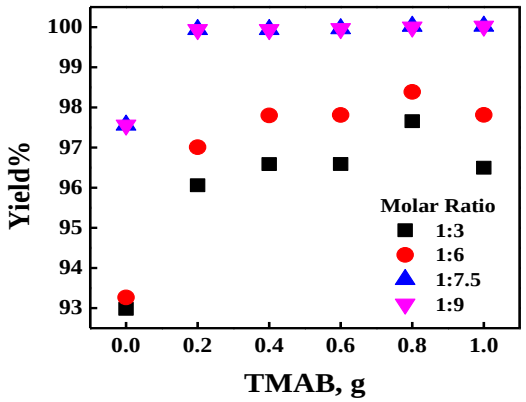


Fig.2: Effect of TMAB on biodiesel yield

Table 1: Composition and properties of biodiesel samples

TMAB (g)	TG (%mass)	DG (%mass)	MG (%mass)	Flash point (°C)	Fire point (°C)
0	0.546	0.583	1.452	175	187
0.2	0.543	0.589	1.456	175	187
0.4	0.546	0.589	1.454	176	186
0.6	0.545	0.586	1.454	176	186
0.8	0.545	0.584	1.452	175	186
1.0	0.545	0.584	1.452	175	186
0	0.459	0.428	1.256	175	186
0.2	0.459	0.425	1.248	159	163
0.4	0.445	0.425	1.248	159	164
0.6	0.445	0.425	1.246	158	165
0.8	0.446	0.425	1.246	159	165
1.0	0.445	0.425	1.246	158	165
0	0.021	0.022	0.196	177	191
0.2	0.015	0.025	0.012	129	137
0.4	0.022	0.020	0.007	129	137
0.6	0.019	0.032	0.013	129	137
0.8	0.107	0.035	0.022	128	136
1.0	0.073	0.020	0.004	128	136
0	0.011	0.014	0.177	179	194
0.2	0.015	0.026	0.012	129	136
0.4	0.025	0.020	0.007	129	136
0.6	0.020	0.032	0.013	129	136
0.8	0.110	0.036	0.022	129	136
1.0	0.071	0.023	0.004	129	136

Table 2: Comparison of produced biodiesel with standard

SI.No.	Properties	Biodiesel Standard[4]	Biodiesel (with TMAB)	Biodiesel (without TMAB)
1	Kinematic viscosity (cst.)	1.9 - 6.0	3.5	3.8
2	Flash point, (°C)	130	129	175
3	Fire point, (°C)	-	137	186
4	Acid value (mg KOH/gm)	0.5 (max)	0.112	0.112
5	Density (gm/cc)	0.860-0.900	0.8608	0.8628
6	Distillation Temperature (°C)	360 (max)	300	320
7	Free glycerin (mass %)	0.020	0	0.023

4. Conclusion

1. The optimum methanol to oil molar ratio was found to be 9:1 when KOH/NaOH was used. Beyond this ratio, the yield is going down.
2. The decrease in the methanol requirement from 9:1 to 7.5: 1molar ratio was observed when TMAB was added. The decrease in the excess methanol requirement has a positive effect on the purification of the biodiesel.
3. Addition of TMAB improves the washability characteristics of crude biodiesel and lowers the wash water requirement by half of that used in the conventional transesterification.

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