IMPROVED BIODIESEL PRODUCTION FROM FEEDSTOCKS OF VERY HIGH FREE FATTY ACID AND PROCESS OPTIMIZATION WITH TRANSESTERIFICATION

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ABSTRACT

In spite of extensive use of Diesel fuel world over, researchers are very keen for it's viable alternative, because of fast depletion of fossil fuels, increasing import bill on it, & it's notorious emissions. Biodiesel, has emerged as an alternative, because of reduced emissions, and various other suitability upto a substantial extent. But still various technical issues are needed to be addressed regarding adoption and popularization of Biodiesel. The different physico-chemical properties of biodiesel are required to be under acceptable limits of different quality norms, as many technical and economic issues are encountered during the process of biodiesel production. The above difficulties can be overcome by optimizing the process parameters which are likely to affect the yield as well as quality of biodiesel. One such technical issue is with largely available non-edible oils and fats, which contain high proportion of free fatty acids (FFA). These free fatty acids quickly react with the alkaline catalyst to produce soaps that inhibit the separation of the ester and glycerin. So, direct transesterification in such cases is difficult. A two stage Integrated pre-esterification of free fatty acid and base catalyzed transesterification process was adopted for conversion of these feedstocks into methyl ester.

In the present work, an attempt has been made to optimize the process parameters of biodiesel production from high FFA feedstocks of Acid oil and Animal Tallow. The operating parameters studied were molar ratio, concentration of catalyst, temperature and agitation speed for both the stages. The optimized process parameters during esterification of free fatty acid of Animal Tallow are : molar ratio of 12:1, catalyst concentration (PTSA) 5%, temperature 65°C, agitation 375 rpm and the yield was found to be 64% after 3 hrs, and for Acid Oil are : molar ratio 12:1, catalyst concentration (PTSA) 7%, temperature 65°C, agitation 375 rpm and the yield was found to be 73%. after 3 hrs. The optimized process parameters in base catalyzed transesterification process for Animal Tallow are : molar ratio 6:1, catalyst concentration (KOH) 1%, temperature 65°C, agitation 375 rpm and the yield was found to be 91% after 1.5 hrs. and for Acid Oil are : molar ratio 6:1, catalyst concentration (KOH) 1%, temperature 65°C, agitation 375 rpm and the yield was found to be 92% after 1.5 hrs. The results suggest that PTSA was found to be better acid catalyst as compared to sulfuric acid during esterification stage. After optimizing the process parameters, the physico-chemical properties were evaluated in accordance with ASTM Standards and were found to be under the specified limits.

Keywords*-Biodiesel, Feedstocks, Free Fatty Acid, Transesterification*

1. INTRODUCTION

Biodiesel, defined as the mono-alkyl esters of vegetable oils and animal fats, has undergone rapid development and acceptance as an alternative diesel fuel. There are different processes for producing Biodiesel, like transesterification of vegetable oil or fat, (chemical and enzymatic) [1-4]. The transesterification is assisted by either base or acid catalyst. However, base catalyzed transesterification reaction is generally preferred because of low temperature & pressure conditions and high yield with no intermediate compounds. Also in case of base catalyst, lower molar ratio is required [5]. Different reaction parameters such as moisture content and free fatty acids in vegetable oils, alcohol to vegetable oil molar ratio, catalyst type and concentration, reaction time and temperature affect the transesterification.

The common base catalysts include sodium hydroxide, potassium hydroxide, sodium hydride, potassium hydride, sodium amide, potassium amide and sodium methoxide. Alkaline catalysts due to faster reaction rates and being less corrosive to industrial equipments as compared to acidic catalysts are having better commercial viability. Use of heterogeneous catalysts for biodiesel production has also been reported by many researchers. [6-10]. The advantages of heterogeneous catalyst over homogenous catalysts are easy separation of catalyst, no effluent water and less sensitivity to free fatty acid content of oil. The critical aspects of production to ensure smooth operation of diesel engine include completion of transesterification reaction, proper removal of glycerin, catalyst & alcohol and absence of free fatty acids. These are the crucial steps to ensure the physico-chemical properties of biodiesel to be close to the standard specifications (BIS/ASTM).

The countries like USA and EU, can afford using edible oil as the feedstock for biodiesel production, because of it's overproduction. But, it would be not acceptable to India due to scarcity of edible oils. In this context, it is relevant to use other multi feedstocks (Vegetable oils or Animal fats) available in India and assess their suitability for biodiesel production. Several Non-edible oils, such as Jatropha Curcas, Pongamia Pinnata ('Honge' or 'Karanja') are suitable for biodiesel production in Indian conditions. However, the potential availability of these oils is not very attractive and efforts are underway for large scale cultivation of these species all over India. It is also relevant to mention that 80-85% of the cost of the biodiesel is attributed to the cost of the feedstock. Therefore, other feedstocks such as animal tallow, acid oil should also be investigated which are low priced. Hence it makes a sense to explore the possibility of using these feedstocks for biodiesel production at a competitive price. So, low priced Non edible feedstocks of animal tallow and acid oil with high free fatty acid, were selected for the present research work, and biodiesel was produced from these feedstocks.

2. TRANSESTERIFICATION

Out of the various processes, the transesterification has been extensively used for biodiesel production all over the world. In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. Higher molar ratio results in higher yield, however, an excessive amount of alcohol makes glycerol recovery difficult, so that the ideal alcohol/oil ratio has to be established experimentally, considering each individual process. Also, with an effort to evolve the appropriate yield of biodiesel, several routes of biodiesel production have been adopted as, 'Base catalyzed' transesterification, two stage integrated pre-esterification of free fatty acid & base catalyzed transesterification and heterogeneous catalyzed transesterification

Molar ratio of 6:1 is normally used in industrial processes to obtain biodiesel yield higher than 98% by weight [4]. During transesterification, the starting materials (oil or fats) should have lower content of FFA and water. The presence of higher amount of moisture in the reaction mixture produces soap which lowers the yield of biodiesel. FFA also consumes the catalyst and reduces the catalyst efficiency. The yield of transesterification reaction is affected by parameters such as alcohol to triglyceride molar ratio, catalyst type & concentration, mixing intensity, reaction temperature, free fatty acids in oil and water content of oils. Acid catalysts are found to be considerably slower than base catalysts [11]. Mixing intensity between the alcohol and triglyceride phases play a very important role in transesterification process. Triglyceride and alcohol phases are not miscible and form two separate liquid layers in the reactor. The reaction is diffusion-controlled and poor diffusion between the phases results in a slow reaction rate. Mechanical mixing is normally applied to increase the contact between the reactants, resulting in an increased mass transfer rate. Variations in mixing intensity alter the

kinetics of transesterification reaction. The maximum yield of biodiesel is generally obtained at temperatures ranging from 60 to 70°C [4].

For this study, acid oil and animal tallow of higher FFA content were taken, as feedstock. Acid oil is by-product of the vegetable oil refining process and contains a very high amount of FFA. Also, the animal tallow selected for the present work had a high FFA. The concentration of free fatty acid in Animal tallow and Acid oil were 65% and 75% respectively. Therefore, these feedstocks were not found suitable for direct transesterification and require pre-treatment for quality and economical biodiesel production.

Biodiesel production through any route is dependent upon a combined effect of different operating parameters. Therefore, the optimization of various parameters is necessary for maximizing the biodiesel yield during any biodiesel production. The yield of biodiesel production was optimized by optimizing the operating parameters: Reaction Temperature, Catalyst Type, Concentration of Catalyst, Molar Ratio, Level of agitation, and Reaction Time. As feedstocks used in this study were not suitable for direct transesterification, a two stage integrated pre-esterification of free fatty acid and base catalyzed transesterification route was selected for this research work.

3. TWO STAGE INTEGRATED PRE-ESTERIFICATION OF FREE FATTY ACID AND BASE CATALYZED TRANSESTERIFICATION

The free fatty acids can be esterified by alcohols in the presence of a suitable acidic catalyst [12].The esterification process for conversion of free fatty acid into methyl ester was carried out using methyl alcohol with H_2SO_4 / PTSA as a catalyst. During esterification, FFA present in the oil is esterified in presence of an acid catalyst. The oil is heated to 60-65ºC and methanol with a suitable acid catalyst is added to the oil and stirred. The FFA converts into fatty esters lowering down the acid number of the oil. After the acid number has reached lower than 2.0, the base catalyzed transesterification process for biodiesel production can be adopted.High FFA oils were converted by a two stage process i.e. pre-esterification of FFA followed by transesterification as already elaborated. In Esterification process, sulphuric acid and PTSA (Para Toluene Sulfonic Acid) were used as a catalyst in the initial phase of the experiments. However, during the initial phase of the experiments, it was found that the PTSA is a better catalyst than sulphuric acid. Therefore, PTSA was used as an acid catalyst in subsequent experimentation. However in the transesterification stage, KOH was used as a catalyst.

3.1. ESTERIFICATION OF FREE FATTY ACID PROCESS

The different process parameters selected for optimization during the acid catalyzed esterification in case of the different feedstocks are summarized in Table 1. The acid catalyzed reactions are preferred in case of glycerides with high molecule and free fatty acid content but if this reaction is carried out in base medium, soap formation also takes place as the result of a side reaction [13-16].

The esterification reaction was carried by heating the oil/fat to different temperatures. Methyl alcohol in different molar ratios for 1000 g of oil was used with different catalyst concentration. The molar ratio of alcohol to oil was evaluated by determining the saponification number of the oil sample. Agitation speed was also varied. Samples (10ml) were collected at every 10 minutes from esterified mixture. The samples drawn were quickly quenched with potassium carbonate solution to neutralize the acid catalyst and stop the reaction. The determination of biodiesel yield was done with the help of gas chromatograph. Para Toluene Sulfonic Acid (PTSA) was used as a catalyst for converting free fatty acids of the oil into methyl esters after series of initial experiments. After esterification of free fatty acid, aqueous methanol layer which remained at the top of the reactants was removed and samples were dried using vacuum distillation and converted into biodiesel using base catalyzed

transesterification process.

3.2. BASE CATALYZED TRANSESTERIFICATION PROCESS

After the esterification process, base-catalyzed transesterification was carried out in a moisture-free environment at atmospheric pressure with KOH as a catalyst. The variables affecting transesterification such as catalyst concentration (0.25-1.0 % wt/wt of oil), alcohol/oil molar ratio (3:1 to 12:1), temperature (50-65°C), rate of agitation (125-500 rpm) and reaction time were studied over a wide range to get higher conversion under optimal reaction conditions. The transesterification reaction was carried out by heating the lower FFA feedstock (obtained by the procedure mentioned above) to different temperatures. Methyl alcohol in different molar ratios for 1000 g of oil was used with different catalyst concentration. The molar ratio of alcohol to oil was evaluated by determining the saponification number of the oil sample. The accurately weighed catalyst was gently shaken and stirred with methanol until it was dissolved. The reaction was commenced by adding the alcohol-catalyst mixture to the stirred tank containing the oil/fat at the reaction temperature. Agitation speed was also varied. Samples (10ml) were collected at every 5 minutes in the first hour of reaction and thereafter the samples were taken at 10 minutes interval.

The samples drawn were quickly quenched in 0.5 mL of 1M HCL solution to neutralize the base catalyst and stop the reaction. The determination of biodiesel yield was done with the help of Gas Liquid Chromatograph. The different process parameters selected for optimization during base catalyzed transesterification in case of different feedstocks are summarized in Table 2.

4. RESULTS AND DISCUSSIONS

The optimized process parameters for pre-esterification of free fatty acid and base catalyzed transesterification are summarized in table 3 & 4 respectively. A representative graph showing variation of yield of acid oil biodiesel with time for different molar ratios during pre-esterification and transesterification (when other process parameters are held constant) are shown in figure 1 and 2 respectively. The fatty acid composition of AOME (Acid Oil Methyl Ester) and ATME (Animal Tallow Methyl Ester) was evaluated with the help of Gas Chromatograph and figure 3 represents fatty acid composition of Acid Oil Methyl Ester. The values of different fatty acids present in AOME and ATME are given in the table 5. Figure 4 shows the ester content of acid oil biodiesel. Figure 5 shows samples of biodiesel derived from Acid oil and Animal Tallow.

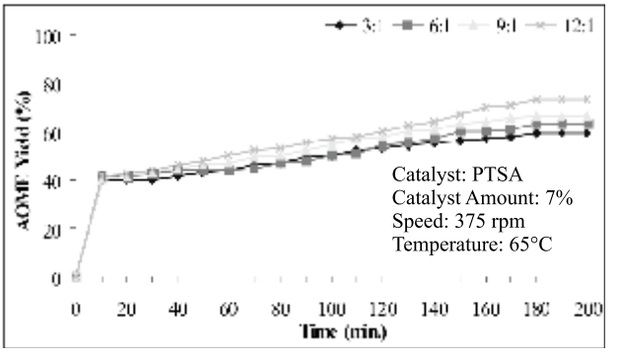

Fig. 1. Variation of AOME yield with time for different molar ratio (in Acid Catalyzed)

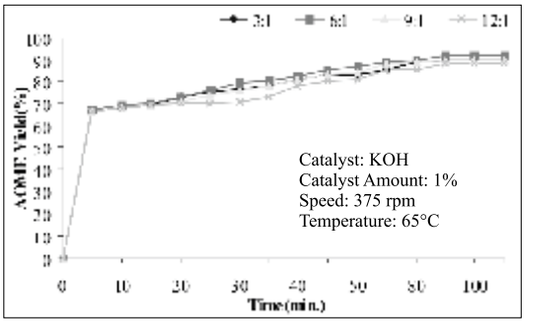

Fig. 2. Variation of AOME yield with time for different molar ratio (in Base Catalyzed)

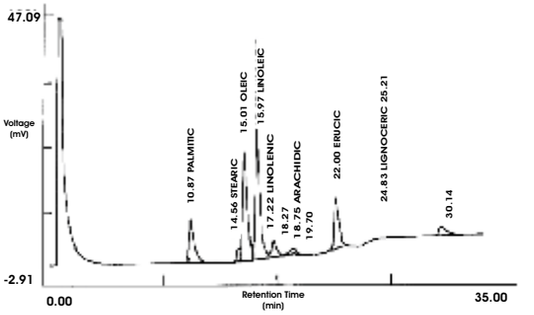

Fig. 3. Chromatograph showing fatty acid composition of acid oil methyl ester

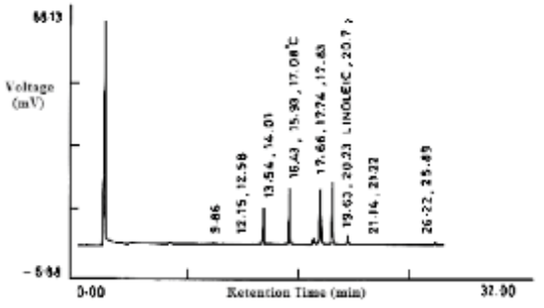

Fig. 4. Chromatograph showing methyl ester yield of acid oil

Fig. 5. Photograph of multi-feedstock derived biodiesel

The different Physico-chemical investigations involving different biodiesel were carried out and results are summarized in Table 6. From the result, it is clear that the specific gravity of the two methyl esters is slightly higher than the mineral diesel fuel. The flash point of the methyl esters is considerably higher than the diesel. The minimum value of flash point for biodiesel according to ASTM D 93 is 130°C. Biodiesel produced from Acid oil have low CFPP (cold filter plugging point) which enhances its suitability for use in cold weather also. However, in case of Animal Tallow methyl esters, the value of cold filter plugging point is 9°C which is not suitable in cold climatic conditions. Therefore, a CFPP depressant may be used. The value of Cetane index for AOME and ATME is above 47 suggesting better ignition quality. The values of initial boiling point (IBP) of diesel, AOME and ATME have been found to be159°C, 304°C & 303°C respectively. It signifies the low volatility of biodiesel as compared to diesel fuel. The 90% volume has been found to be recovered at a temperature in the range of 345°C to 355°C for AOME and ATME which is also less than the maximum temperature of 360°C as prescribed in ASTM D-6751. It is clear that there has been no trace of high boiling point substance in the biodiesel samples. For different B100, the values of IBP have been found to be higher than 290°C. It suggests that with addition of biodiesel in diesel, the initial boiling temperature of diesel increases making it less volatile. From the above result, it is also clear that the values of water content in the biodiesel based fuels have been found to be higher than diesel (120ppm). Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel. Micro method Carbon Residue for biodiesel is more important than that in diesel fuel because it show a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids, inorganic impurities and even to the additives used for pour point depression. The values of carbon residue were higher in case of all biodiesel than diesel. Sulfur content was in the range of 10 ppm in all biodiesel samples. It was found that all the physico-chemical properties of biodiesel derived from the feedstocks of Animal tallow and Acid oil were under prescribed limits of ASTM.

Catalyst Type	Catalyst Conc. (% wt/wt of FFA)	Alcohol/oil molar Ratio	Temp. (°C)	Speed (rpm)
	1	3:1	50	150
PTSA	2	6:1	55	225
	3	9:1	60	300
	4	12:1	65	375

Table 1. Selected process parameters for acid catalyzed esterification process

Oil	Alcohol/oil molar ratio	Catalyst	Catalyst Amount wt/wt of FFA (%)	Temp. (°C)	Time (hrs)	Speed (RPM)	Yield (%)
Animal Tallow	12:1	PTSA	5%	65	3 hrs	375	64
Acid Oil	12:1	PTSA	7%	65	3 hrs	375	73

Table 2. Optimized process parameters in esterification for free fatty acid process for the feedstocks

Catalyst Type	Catalyst Conc. (% wt/wt of oil)	Alcohol/oil molar ratio	Temp. (°C)	Speed (rpm)
KOH	0.25	3:1	50	150
	0.50	6:1	55	225
	0.75	9:1	60	300
	1.00	12:1	65	375

Table 3. Selected process parameters for base catalyzed transesterification process

Oil	Alcohol/oil molar ratio	Catalyst	Catalyst Amount Wt/wt of oil (%)	Temp. (°C)	Time (hrs)	Speed (RPM)	Yield (%)
Acid Oil	6:1	KOH	1%	65	1.5	375	92
Animal Tallow	6:1	KOH	1%	65	1.5	375	91

Table 4. Optimized process parameters in base catalyzed transesterification process for different feedstocks

	14:0 (Myristic)	16:0 (Palmitic)	16:1 (Palmitolic)	18:0 (Stearic)	18:1 (Oleic)	18:2 (Linoleic)	18:3 (Linolenic)	22:1
AOME	----	12.46	----	2.5	26.71	33.50	5.029	12.64
ATME	2.49	24.61	2.11	0.66	31.94	30.79	1.52	----

Table 5. Different fatty acid percentage

Property	*ASTM Method*	*Diesel*	*Acid Oil Biodiesel*	*Tallow Biodiesel*
Higher Calorific Value (kJ/Kg)	*D-4809*	42232	38990	38568
Density (kg/m ^{3})	*D-4052*	0.831	0.894	0.881
Kinematic Viscosity @ 40°C(mm^2/s)	*D-445*	3.21	5.95	5.97
Acid No. (mg.KOH/gm)	*D-664*	*0.2*	*0.5*	*0.48*
Cloud Point °C	*D-2500*	*-12*	-2	10
Pour Point °C	*D-97*	*-17°C*	-9	6
Cold Filter Plugging Point (CFPP), °C	*D-6371*	*-15*	-8	9
Flash Point °C	*D-93*	*76*	*179*	*183*
Water Content (Karl Fisher),	*D-1744*	*120*	*176*	*195*
Copper Strip Corrosion	*D-130*	*1A*	*1A*	*1A*
Micro Method Carbon Residue (% wt)	*D-4530*	*0.1%*	*0.13*	*0.125*
Distillation Characteristic				
IBP	*(D-86)*	*159*	304	303
T10, °C		*222*	338	330
T50, °C		*241*	349	343
T90, °C		*309*	354	353
FBP		*336*	358	359
Cetane Index	*D-976*	*47.14*	47.77	48.60

Table 6. Physico-Chemical characterization of the biodiesel produced from different feedstocks

5. CONCLUSIONS

The following conclusions have been drawn from the exhaustive series of the experimental work.

- The feed stocks of Animal tallow and Acid oil used for biodiesel production have higher values of FFA and requires pre-treatment for their conversion into biodiesel. A two stage integrated pre-esterification of free fatty acid and base catalyzed transesterification process was found to be an effective method for converting high FFA feedstock into biodiesel.
- H_2SO_4 (Sulphuric acid) and PTSA (Para Toluene Sulfonic Acid) were evaluated as an acid catalyst for esterification and PTSA was found to be the better catalyst.
- Optimized parameters for production of biodiesel through two stage integrated acid-catalyzed pre-esterification of FFA and base-catalyzed transesterification results in maximum yield.
- Physico-chemical properties of biodiesel

- produced from, Acid oil and Animal tallow were found to be within acceptable limits of ASTM standards.

  As can be seen from Table No. 6 the Carbon
- Residue in case of both the Biodisels (AOME and ATME) are marginally higher compared to that of the pure Biodiesel. Also, the Kinematic Viscosity of both the Biodisels (AOME and ATME) are more than that of the pure Biodiesel. So, to achieve minimum droplet size with Biodiesel higher Injection Pressure may be required, which will give desired droplet size for better combustion and reduced Carbon deposits.

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