Optimization of Parameters for Purification of Jatropha Curcas Based Biodiesel using Organic Adsorbents

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Abstract-This paper discusses purification of biodiesel by using organic adsorbents instead of traditional water washing technique. The efficiency of different organic adsorbents under different conditions was compared with each other as well as traditional water washed biodiesel for the purification of Jatropha curcas based transesterified biodiesel. The proposed methodologies were based on the use of Amberlite BD10 DRY, Purolite PD 206 and Tulison T-45BD as adsorbents. The response of each adsorbent was measured through the determination of all the potential impurities like, free alkali, residual alcohol, moisture content, soap content and free and bonded glycerol; present in the biodiesel as per ASTM/EN Standard test method. As a result, it is observed that increasing the temperature from room temperature to 65° C decreases the time of contact as well as the amount of adsorbent required for the removal of impurities. On comparing the results of conventional acid water washing with that of organic adsorbents (at 3% (w/w) concentration with stirring time 25 min at 65°C), these matrices are found to be equally appropriate for the removal of contaminant species from biodiesel. The values for free potassium, residual methanol and free and bonded glycerol are found within the EN 14214 maximum limits.

Keywords-Biodiesel, Dry wash, Amberlite BD-10 Dry, Purolite PD-206, Tulison T-45BD

1. Introduction

Recently, the area of alternative fuels has been increasingly researched; one it is due to increase in greenhouse gas (i.e. CO_2) concentrations from burning petroleum-based fuels secondly the energy crisis during an era of growing energy consumption.

Vegetable oils are an alternative form of renewable fuel to diesel engines. But direct application of vegetable oil as fuel to diesel engines is not possible due to its higher viscosity. The use of transesterified vegetable oil called biodiesel does not require any modification in engine. The production of biodiesel would be cheap as it could be extracted from non-edible oil sources. Jatropha curcas (Linaeus).Also production of biodiesel plays a major role in terms of economy and employment, as it offers chances for social and rural development amongst the poorest people.

The physiochemical properties, energy value, fatty acid composition and oil content of Jatropha curcas oil are strongly influenced by the processing, season, climate and geography during the growth of the seed, storage etc. [1-3]. Improper handling and storage conditions lead to deterioration of Crude Jatropha curcas oil quality (CJCO) and cause the water content to increase. Exposing the CJCO to air and sunlight for a long time increases the free fatty acid (FFA) content significantly. Since, the rainfall, soil type, nutrition content of the soil, temperature and other factors vary from region to region, the physiochemical properties of the Jatropha curcas oil produced are region specific. The primary parameters relevant to biodiesel production by transesterification of vegetable oils by alcohol using a base catalyst are the FFA content and moisture content [1]. The FFA content of CJCO will vary and depends on the quality of the feed stock [4]. During alkali catalyst based transesterification, higher the FFA content of the oil requires more alkali to neutralize the FFA and it leads to soap formation and the separation of products becomes difficult and as a result low yields of biodiesel are produced [5].Some time the presence of FFA will interfere with the process reaction and lead to an incomplete reaction. Another technique to increase the biodiesel yield is acid catalyst based esterification [6], however, it is much slower than the alkali catalyst based trans esterification.

To avoid side reactions due to the presence of FFA in the feedstock an acid catalyzed trans esterification or an alkali catalyzed process with an oil pre-esterification step can be considered. When alkali catalyzed transesterification is used, the feedstock used should not contain more than 1wt. % of FFA [7, 8] to avoid side reactions such as soap formation that would adversely affect subsequent separation processes. Low grade oils are usually pre-treated using acid catalysts to reduce the FFA contents to < 1% prior to the trans esterification reaction. This process consists of direct esterification of the FFA acids with an alcohol, for example methanol, forming methyl ester and water. The effect of water on the esterification of FFA has been reported in literature [9, 10]. The rate of esterification was found to decrease upon increase in water contents. Yingying et al. [9] studied the pre esterification of Jatropha curcas oil before the alkali catalyzed trans esterification reaction. They found that water remarkably lowered the catalytic activity of sulphuric acid due to the reduction of proton concentration and acid strength. Fatty acid methyl esters thus obtained usually contain contaminant materials that are detrimental to the quality of the fuel, and must be eliminated from the product. Key aspects of the quality of the fuel strongly depend on the content of free and bound glycerol [11], thus removal of glycerol and glycerides from biodiesel is an important step of the process. Although it is slightly soluble in biodiesel, glycerol can be found dispersed as small droplets in biodiesel [12,13] High concentrations of glycerol in biodiesel can cause problems during storage due to its separation, and in usage by forming deposits on injection nozzles and promoting an increase in aldehyde emissions. The presence of water in the biodiesel can cause engine corrosion or side reactions with glycerides to produce soaps and glycerol [14]. Soaps and free fatty acids cause the deterioration of certain components of engines. Thus, the determination of free fatty acid and water content are essential for the feasibility of biodiesel use and also for the choice of the raw materials (vegetable oil or animal fat) used in the trans esterification process. Sodium and potassium contamination in biodiesel can be caused by the use of catalysts in biodiesel production (KOH or NaOH). Both of these ions can cause the formation of insoluble soaps, which can be deposited in the motor and also promote catalytic polymerization reactions[15-17].

Water-soluble contaminants are traditionally removed by water washing of the biodiesel. Washing is commonly done using mist wash system [18]. All washings can be done after initial settling time (18 h) and after draining glycerin layer, but better results can be obtained by waiting at least 36-48 h or longer before first wash [18]. Another approach is to spray a fine water mist over fuel; as water settles to base of container, impurities are removed. However, the water-wash method results in an effluent, which can then cause a harmful environmental impact [19]. Water washing process has the disadvantage of using large amounts of water, generating waste matter. This large amount of waste matter can reach at least 3 g of water per gram of biodiesel [20].

The conventional "wet" methods of purification can be replaced by "dry" purification with adsorbents or ion exchange resins [21, 22]. Different adsorbents (magnesium silicate (Magnesol), calcium magnesium silicate and organic ion exchangers (AMBERLITE XAD)) can be used more conveniently. Resulting biodiesel is of higher quality than traditional water washing. Yoriet et. al. [11] and Predojevic[14] studied the removal of glycerol from biodiesel from waste frying oils with elevated acid values using silica and achieved high purity of the resultant biodiesel[11, 14].

The present study aimed to compare the efficiency of different organic resins (Amberlite BD10 DRY, Purolite PD 206 and Tulison T-45BD) as adsorbents in the biodiesel purification process and to compare this dry purification process with the conventional wet purification process.

2. Materials and Methods

2.1. *Chemicals Required*

The Jatropha oil was procured from the Vikas Sansthan, New Delhi and was analyzed for the free fatty acid content. The organic adsorbents used for the purification were Amberlite BD-10 DRY from Rohm and Haas; another was Purolite PD-206 and Tulison T-45BD. Other chemicals used for the production and analysis of biodiesel sample were, sulphuric acid, isopropyl alcohol, NaOH, bromophenol blue indicator, hydrochloric acid, KOH and toluene.

2.2. *Biodiesel Production*

Biodiesel synthesis by a transesterification reaction

Acid value of Jatropha oil was evaluated by ASTM D974 to quantify the free fatty acid content (17 mg/g) in oil. Due to very high FFA content, Jatropha Curcas was converted to methyl ester by two step process. In the first step oil was reacted with methanol in the presence of sulphuric acid as a catalyst to convert free fatty acid into fatty ester. 1000 g of Jatropha oil was taken in three necked round bottom flask and the oil was heated to 60-65°C with constant stirring. In a separate flask (507 g) of methanol was mixed with 1 %(V/V) sulphuric acid and then transferred to three necked flask containing Jatropha Curcas Oil. The mixture was stirred for two hrs and temperature was maintained at 60°C. The mixture was allowed to cool overnight and separate into two different layers in separating funnel. The lower layer was separated and was analyzed for free fatty acid content. The free fatty acid content was found to get reduced to 1.12 mg/g. In the second step, this lower layer (1000g) was transferred to three necked flask and the contents were heated to 65°C with constant stirring. Methanol (300 ml) and KOH (5.5 g) were mixed in separate flask and was then transferred to the three necked flask containing pretreated oil from the first step. The contents of the flask were stirred constantly for 90 min at 60°C and then allowed to cool overnight. The reaction mixture was transferred to a separatory funnel to promote the separation of the glycerol and biodiesel phases. The glycerol phase was recovered after phase separation, carrying most of the dissolved catalyst with it. He lower biodiesel layer was then purified under different conditions using organic adsorbents and acid water washing method.

2.3. Biodiesel Purification

Wet purification process

The unpurified biodiesel was washed thoroughly with 10% acid water. The acid water was prepared by adding 10% (v/v) Phosphoric acid to distilled water. This washing step was performed with constant stirring over 5 minutes. Afterwards, the mixture was transferred to a separating funnel and the waste water and biodiesel phases were separated. The bottom layer (waste water) was removed and the biodiesel was washed three times with portions of 10% (v/v) water. The upper layer, containing the purified biodiesel, was stored for further analysis.

Dry purification process

The dry purification conditions were based on the literature; [23] the unpurified biodiesel was heated and stirred slowly until reaching 65°C. At this point, 1%, 2% and 3% (w/w) of each adsorbent (Amberlite BD 10 DRY, Purolite PD-206 and Tulison T-45 BD), related to the mass of biodiesel, was added maintained 65°C. At this temperature, samples were stirred for 25 min. Another set of purification was carried out by stirring the biodiesel sample with 10 % (w/w) of the adsorbent at room temperature using all the three adsorbents separately.

Analysis of biodiesel

Samples of purified and unpurified biodiesel were analyzed by their acid number, potassium, soap, water and residual methanol content. The analysis of glycerol and glycerides was only done for biodiesel unpurified sample and the sample purified with 3% (w/w)Amberlite BD 10 dry at 65°C for 25 minute. The potassium content and residual methanol was also determined for unpurified biodiesel, sample purified with acidic water and the samples obtained by using 3% (w/w) adsorbents (Amberlite BD 10 DRY, Purolite PD-206 and Tulison T-45BD) at 65°C for 25 min. The acid value was determined according to ASTM D974. The soap and catalyst content were determined with the method AOCS Cc 17-95 and water content by the Karl Fischer method, based on EN ISO 12937. The potassium content was determined by EN 14538 method using Inductive Coupled Plasma Optical Emission Spectroscopy (Optima 3300 RL Perkin Elmer ICP-OES).The determination of glycerol and glycerides was performed according to EN 14105/ASTM D-6584 method using GC/FID (Agilent 7890A). The methanol determination was performed according to European standard EN 14110 by using GC/FID (DANI -1000).

3. Results and Discussion

The results for the analysis of acid number, soap content, Potassium, residual methanol, moisture content, pH and density of purified and unpurified biodiesel samples are presented in Table 1.The density of all the purified samples was found in the range of 0.870g/l to 0.872g/l. The pH value was also determined for unpurified and purified samples. The adsorbent concentration has its affect on the pH value of the biodiesel samples. The soap content of the unpurified sample was 1920 mg/Kg, which decreases considerably as the adsorbent concentration was increase from 1% to 3%(w/w) at 65°C for 25 min stirring time. This decrease in soap content at 10 %(w/w) adsorbent concentration with stirring time 1 hr at room temperature was comparable with that of 2% (w/w) adsorbent concentration at 65° C for 25 min stirring time as shown in Figure 1, although legislation does not define the limit of soap contamination in biodiesel for commercial use. Figure 2 shows the results for moisture content and increase in adsorbent concentration results in decrease in moisture content for all the adsorbents. Results for Potassium content of unpurified biodiesel sample were compared with that of water washed sample and the samples purified by using 3%(w/w) organic adsorbent at 65° C for 25 min stirring time. The potassium content in all the purified samples were found within the limits but purolite PD 206 showed better removal as compared to water washed sample as well as other two adsorbents Amberlite BD 10 Dry and Tulison T-45BD as shown in Figure 3. The %age of residual methanol also showed a significant removal from 5% in crude biodiesel to0.05% 0.1%, 0.12% and 0.07% for acid water washing, 3 % (w/w) Amberlite BD 10 Dry, PurolitePD-206 and Tulison T-45BD respectively at 65°C for 25 min stirring time whereas the EN 14214 limit is 0.2% as shown in Figure 4. The acid value for unpurified biodiesel was 0.7 mg of KOH/g.

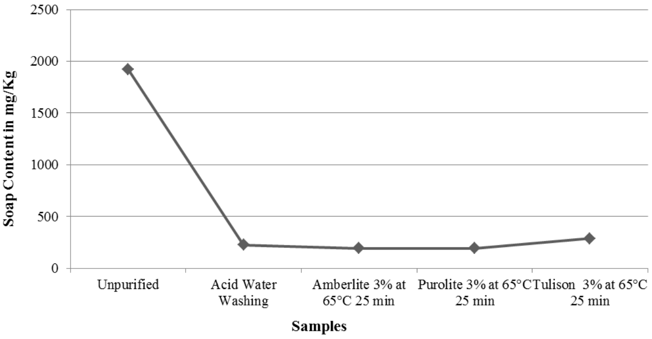

Fig. 1. Effect of different adsorbents on the soap content of Biodiesel and its comparison with acid water washed biodiesel sample and unpurified sample of biodiesel

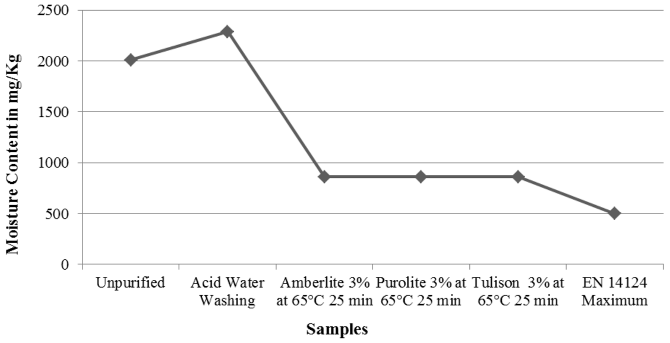

Fig. 2. Effect of different adsorbents on the moisture content of Biodiesel and its comparison with acid washed biodiesel sample and unpurified sample of biodiesel

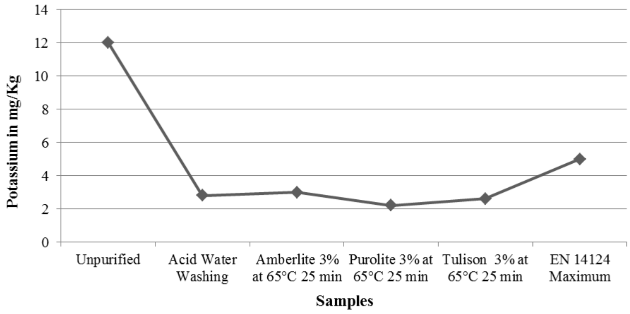

Fig. 3. Effect of different adsorbents on the Potassium removal from the biodiesel sample and its comparison with the acid water washed biodiesel sample and unpurified sample of biodiesel

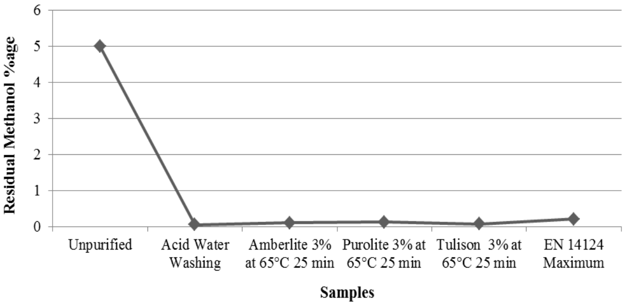

Fig. 4. Effect of different adsorbents on the residual methanol content of biodiesel and its comparison with the acid water washed biodiesel sample and unpurified sample

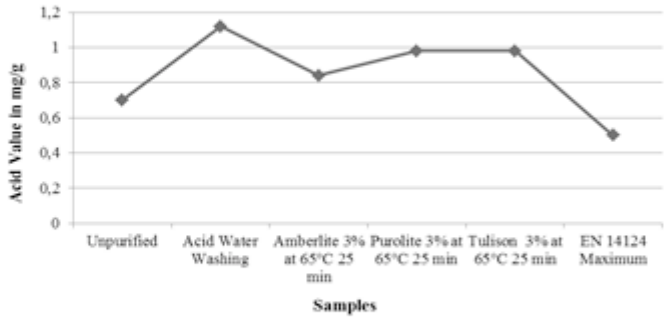

Fig. 5. Effect of different adsorbents on the Acid number of Biodiesel and its comparison with acid water washed biodiesel sample and unpurified sample of biodiesel

Table 1. The results of analysis of density, pH, acid number, potassium, soap, water, potassium and residual methanol of purified and unpurified biodiesel samples for different adsorbents under different conditions

Samples	**Density**	**pH at 27.4° C**	**Soap (mg/Kg)**	**Acid Value (mg/g)**	**Water (mg/Kg)**	**K (mg/Kg)**	**Meth-anol (%)**
Unpurified	0.8700	10.03	1920	0.7	2010	12	5
Acid Water Washing	0.8720	7.01	224	1.12	2290	2.8	0.05
Amberlite 1% at 65°C 25 min	0.8718	7.7	608	0 .84	1430	-	
Amberlite 2% at 65°C 25 min	0.8721	7.63	256	0 .84	860	-	
Amberlite 3% at 65°C 25 min	0.8717	6.61	192	0 .84	860	3	0.1
Amberlite 10 % at room Temp 1 hr	0.8710	6.5	256	1.26	860	-	
Purolite 1% at 65°C 25 min	0.8717	8.4	448	0.84	1140	-	
Purolite 2% at 65°C 25 min	0.8717	7.8	224	0.84	860	-	
Purolite 3% at 65°C 25 min	0.8713	7.3	192	0.98	860	2.2	0.12
Purolite 10 % at room Temp 1 hr	0.8710	6.88	224	1.12	570	-	
Tulison T-45BD 1% at 65°C 25 min	0.8717	8.3	608	0.84	1430	-	
TulisonT-45 BD 2% at 65°C 25 min	0.8715	8.9	448	0.84	860	-	
Tulison T-45BD 3% at 65°C 25 min	0.8716	8.8	288	0.98	860	2.6	0.07
TulisonT-45BD 10 % at room Temp 1 hr	0.8706	8.1	192	1.12	1140	-	
EN 14124 Maximum	-	-	-	0.5	500	5	0.2

The acid value for water washed sample and the samples purified using different concentrations of organic adsorbents are found to increase slightly [23] as shown in Figure 5. An increase in acid value indicates that when soap is removed the potassium/sodium portion of the soap molecule is being held by the resin, releasing the FFA into the effluent biodiesel.

Total glycerol and free glycerol was determined for unpurified sample and the sample purified with 3% (w/w) Amberlite BD 10 dry at 65°C for 25 min stirring time. On purification the value for total and free glycerol was found to be very much within limits as shown in Table 2. In most of the studies it has been observed that the performance of inorganic adsorbents is better as compared to organic adsorbents due to chemical characteristic of the inorganic matrices, which present a more rigid and cross linked structure. In this study, when the results of total and free glycerol for the biodiesel sample purified with organic adsorbent, Amberlite BD-10 dry (3%(w/w) at 65°C for 25 min stirring time)are compared with Soy Oil based biodiesel sample purified using 2% (w/w) Magnesol / Silica (at 65°C for 20 min stirring time)[24]; organic adsorbent are showing better removal of total and free glycerol as shown in Table 2.

Table 2. The result for the analysis of free and bonded glycerol with 3% Amberlite BD 10DRY as an organic adsorbent

Sample	**Total Glycerol %**	**Free Glycerol %**	**Mono Glycerides %**	**Di Glycerides %**	**Triglycerides %**
Unpurified	3.117	0.068	1.48	1.06	0.570
Amberlite 3% at 65°C 25 min	0.201	0.0074	0.071	0.094	0.035
EN 14214 Maximum	0.25	0.02	-	-	-

4. Conclusion

The main advantages of using dry purifications are the drastic reduction of aqueous effluents, making the process environmentally friendly and considerable reduction in the total time of production. This study has shown that Purolite PD-206 and Amberlite BD10 Dry are the effective adsorbents at 3% (w/w) concentrations with stirring time 25 min at 65°C. On increasing the adsorbent concentration, all the adsorbents are showing similar trend for the removal of impurities. The investigation has shown that increasing the temperature from room temperature to 65°C results in decrease in contact time as well as adsorbent concentration. Results for total and free Glycerol for Jatropha oil biodiesel might be due to better exchange, adsorption and filtration being facilitated by ion exchange resin based on four mode theory. With all the organic adsorbents (at 3% (w/w) concentration with stirring time 25 min at 65°C) the values for free potassium, residual methanol and free and bonded glycerol are found within the EN 14214 maximum limits. Based on these results, purification of biodiesel samples can be further investigated using blends of organic adsorbent in order to make it more effective.

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