Polymeric efficiency in remove impurities during cottonseed biodiesel production

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Abstract: This paper describes a new process for developing biodiesel by polymer from crude cottonseed oil. The study was conducted to examine the effectiveness of the alkali transesterification-flocculation-sedimentation process on fast glycerol and other impurities in the separation from biodiesel by using quaternary polyamine-based cationic polymers SL2700 and polyacylamide cationic polymer SAL1100. The settling velocity of glycerol and other impurities in biodiesel was investigated through settling test experiments; the quality of the biodiesel was investigated by evaluating the viscosity and density. The results revealed that SL2700, SAL1100 and their combination dramatically improved the settling velocity of glycerol and other impurities materials than traditional method. SL 2700 with molecular weight of 0.2 million Da and charge density of 50% then plus SAL1100 with molecular weight of 11 million Da and charge density of 10% induced observable particle aggregation with the best settling performance.

1. Introduction

The most common method of biodiesel production is by transesterification of vegetable oils or animal fats with methanol in the presence of an alkaline catalyst [1-3]. The primary concern for biodiesel producers is the steady availability of low-cost oil feedstock, which yields high quality biodiesel product that is competitive in price with diesel fuels. Unfortunately, the efforts expended to obtain and maintain high purity refined oil make the resulting biodiesel less economically viable alternative to diesel under the prevailing market conditions [4]. Therefore, there is considerable interest and economic benefit in using unrefined (crude) oil directly for biodiesel production. However, compared to the refined vegetable oils, their crude oil counterparts contain higher free fatty acids (FFA) and form higher amounts of soap during transesterification, which inhibits the separation of the glycerol from methyl esters using the traditional method [5]. During biodiesel production, the cottonseed oil is de-gammed following complicated steps of adding water and acid first to reduce the phosphorous content to a very low level and rewashing the oil with water. The glycerol produced by transesterification is separated and removed by gravity or

centrifugation because glycerol is insoluble in the biodiesel. The gravity method takes several hours, and the centrifugation process is very expensive [6]. Therefore, the developing alternative methods to efficiently remove glycerol, gossypol and other impurities from methyl esters are essential when crude cottonseed oil is used directly for biodiesel production. If this can be performed rapidly and inexpensively, the economic competitiveness of the biodiesel will improve significantly leading to widespread use of biodiesel in place of diesel. In addition, the phosphorous content of crude cottonseed oil adversely affects the biodiesel production process [7-9].

Herein we describe a polymeric flocculation method to improve the biodiesel production process by directly transesterifying crude cottonseed oil. The polymeric flocculants destabilize the particles through charge neutralization, electrical double layers and subsequent formation of particle-polymer-particle bridges, which generate a small volume of sludge output [10-13]. Previous studies have focused on thickening operations in mineral processing, with flocculant [14-18]. However, flocculation technology practice in making cottonseed biodiesel has not performed and little work has been reported. If phosphorus and other impurities can be coagulate and flocculate by polymers then sink from the biodiesel, it will save energy and time of the making process. Our objectives are: 1) investigate the effectiveness of using polymeric flocculants as a sedimentation aid during biodiesel production from crude cottonseed oil ,2) characterize the biodiesel properties and 3) molecular weight, charge density of polymer are analyzed to gain a better understanding of the flocculation mechanism. Cottonseed oil was chosen because transesterification of cottonseed oil produces methyl ester whose properties are comparable to those of the conventional diesel fuel [19-20].

2. Materials and methods

2.1. Materials
Crude cottonseed oil was obtained from Wisconsin, Madison. Methanol of 99.9% purity was purchased from Fisher Scientific (Fair Lawn, NJ). Sodium hydroxide of 98.2% purity was purchased from Wausau Chemical, China. Potassium hydroxide of 99.0% purity was purchased from Fisher Scientific (Fair Lawn, NJ). Two commercial grade cationic polymers of different molecular weight (Mw) and charge density (CD) were obtained (Soil Net LLC, WI). The polymers were designated as SL2700 (Mw=0.5x10^5 Da; CD=50 %) and SAL1100 (Mw=11x10^6; CD=10%). SL2700 is a quaternary polyamines-based polymer and SAL1100 is a polyacrylamide.

2.2. Transesterification of crude cottonseed oil
Free fatty acid (FFA) content of the biodiesel was determined by titration [21] to be 2.51 mg KOH/g; phosphorus content of crude cottonseed oil was between 200-330 mg/L [22]. Crude cottonseed oil was transesterified by methanol (molar ratio 1:6) with a basic catalyst (0.8 wt-% of NaOH to oil) in beaker. The reaction was carried out for 90 min at 60 °C while mixing thoroughly with a magnetic stirrer (~1000 rpm).

2.3. Flocculation and Sedimentation
The polymers SL2700, SAL1100, and their 1:1 (w/w) mixture (SL2700 added first, then SAL1100 the second by step) were added following transesterification as above. The following four polymer concentrations were used: 1.0, 2.0, 3.0, and 4.0 mg/L of oil. The polymers were mixed in thoroughly using magnetic stirrer (~300 rpm) under 60 ℃ for 10 min.

The samples were held at 30℃ undisturbed for settling of the flocs of gums, gossypol and other impurities formed. The settling rates of the flocs were determined by measuring the mud-line heights by taking the samples in 100 mL graduated cylinders. The cylinders were stoppered and carefully inverted

back-and-forth 8-10 times for thorough mixing and then held upright. Non-polymer amended samples were concurrently analyzed for transesterification using the same techniques. Results were then read, calculated, recorded and reported in units of cm / min. The measurements were conducted three times for each sample and the results were averaged. Unreacted methanol and water were removed in oven at 100 ºC until the constant weight was observed.

2.4. Effect of polymers on sample characterization

Free fatty acid (FFA) content of the biodiesel was determined by titration; Gossypol content of biodiesel was tested by UV–Vis absorption spectra in 1 cm cells using a UV- visible spectrophotometer (UV-1601PC, Japan); Trace elements were measured by wavelength dispersive X-ray fluorescence (WDXRF) spectrometry (S4 Pionees, Bruker AXS, Inc., Madison, WI)   all the samples were analyzed applying a measurement time of 1200 s; specific gravity of the biodiesel was precisely measured to investigate the glycerol settling in the biodiesel with polymer types and dosage, the measurements were done from 20 ºC to 100 ºC by using specific gravity meter (Precision hydrometer, Chase, USA, 233743), the measurements were conducted three times for each sample and the results were averaged; dynamic viscosity of the biodiesel samples were measured at 15-100ºC over a shear rate range of 1 to $100s^{-1}$ using rheometer (Anton Paar Instruments Inc., Physical MCR301) equipped with cup-and-bob geometry, three replicates were produced for each type of samples and the results were averaged.

3. Results and discussion

3.1. Flocculant dose and settling behavior

Figure 1 (a)-(d) shows the biodiesel/impurities settling velocity with different dosages of SL2700, SAL1100, and combination of SL2700+SAL1100 (1/1, w/w), respectively. From the settling graphs, it could be pointed out that impurities settling could be finished in around 90, 75, 50, and 50 min at 30 ºC when   polymer dosage was 1.0, 2.0, 3.0, and 4.0 mg/L, respectively. At polymer dosage of 1.0-3.0 mg/L, the higher velocity of solid settling is occurred by higher polymer dosages, but the settling velocity has no significant difference when different kinds of these polymers and dosages are used in this range. It can be seen in figure 3 that the addition amount of polymers (4.0 mg/L) does not help in enhancing the settling velocity. It is also observed that impurities settling could be faster by using polymers comparing no polymer is used at the same settling condition. When polymer is not added, the time to reach the stable compact heights of impurities is near 5 h at 30 ºC. In addition, the sequence of compact efficiency of impurities in canola blend by polymers is SL2700 + SAL1100 > SAL 1100 > SL2700 when same dosage polymers are used. The stable compact height of impurities in cylinder is 22.1, 23.6 and 24.3 cm after 90 min when SL2700+SAL1100, SAL1100, and SL2700 are used respectively.

The clarification process of crude cottonseed oil using polyamines-based flocculant polymers has been discussed by Aicardo et al. [23]. In the transesterification process of cottonseed crude oil, glycerin can form a uniform phase at any mixing ratio. Therefore, the glycerin layer from the biodiesel system has a higher density than the biodiesel resulting in a separation between the biodiesel layer and glycerin layer due to the difference in the density of both layers. At the same time, the use of the polymers causes the agglomeration soap formed in the process of neutralization or bridging. Soap can help to combine glycerin and gossypol, which greatly enhances the separation of the glycerin fraction from the biodiesel. A suitable amount of soap also reduces the interfacial tension between the biodiesel and the impurities aqueous phase (phosphorus and salts). This improves the reaction between polymer and the impurities.
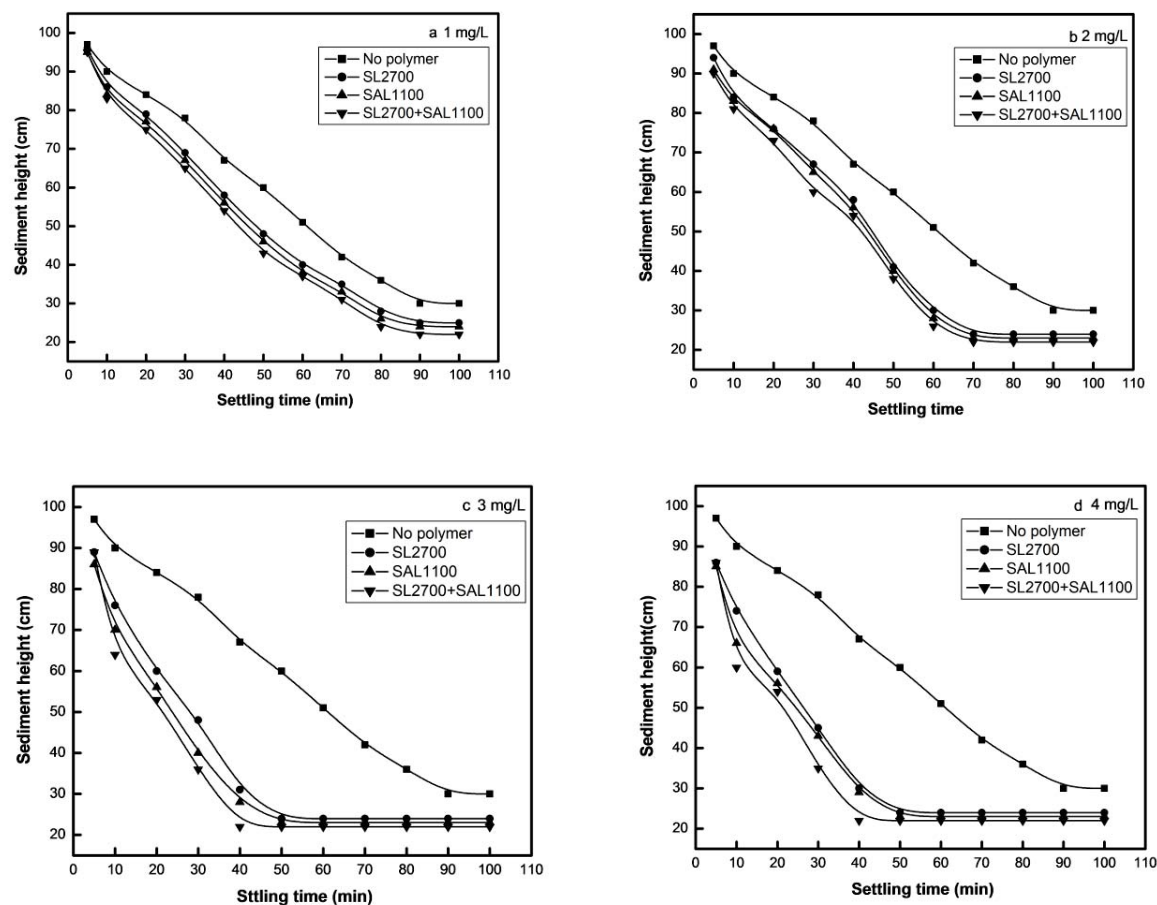
Figure 1. Settling behavior of cottonseed biodiesel suspension with polymers dosages of a,1.0; b,2.0; c,3.0; and d,4.0 mg/L at 30 ℃.

3.2. *Effect of polymer molecular weight and charge density on the flocculation process*

Figure 1 also shows that the combination of polymers SL2700 and SAL1100 induce observable particle aggregation with the best compact efficiency of impurities in canola biodiesel blend; SAL1100 induces particle aggregation with the second compact efficiency of impurities; and SL2700 induces particle aggregation with the third compact efficiency of impurities. SAL1100 is polyacylamide cationic polymer with lower charges and higher molecular weight, which can be ascribed to the strong bonds of polymer chains due to bridging. Some of the segments of SAL1100 chain can adsorb onto the surface of particles through electrostatic interactions, some of the reminder of the polymer extending into solution phase. As other particles approach the SAL1100 chain, they interact with SAL1100 chain, thus a bridge is formed between particles then flocculate. SL2700 is quaternary polyamine-based cationic polymer with higher charges and lower molecular weight, which can adsorb onto the surface of the anionic particles in cottonseed biodiesel through electrostatic interactions, most of the charged sites on the polymer attach to

the particle surface with oppositely charges then flocculate. The combination of SL2700 and SAL1100 function by charge neutralization and bridging, this adds the function of flocculation of particles then sedimentation.

3.3. Effect of polymers on gossypol, FFA and trace elements

It is established that the maximum absorption wavelength of gossypol on a spectrophotometer is 375 nm. Figure 2 showed that the clarified cottonseed biodiesel exhibited an absorption peak at 375 nm on a UV-vis spectrophotometer when no polymer was used. The cottonseed biodiesel clarified with various polymers didn't exhibit any absorption peak at this wavelength. The results indicate that gossypol contained in the biodiesel with polymer was sufficiently removed.
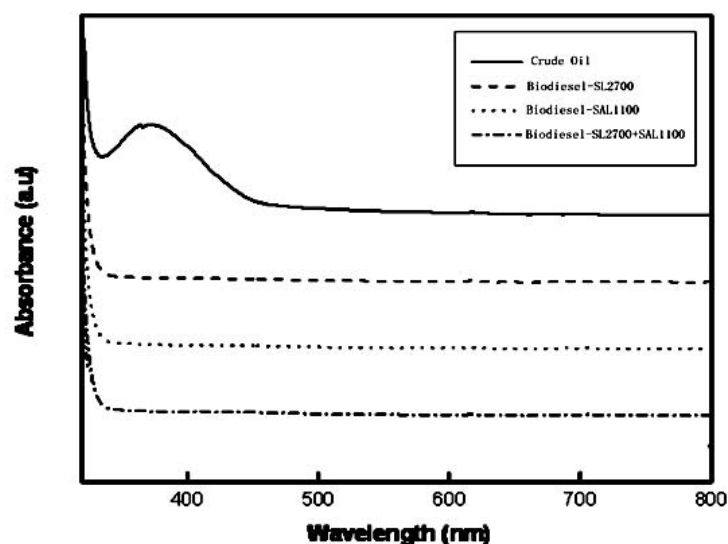

Figure 2. Changes in light absorbance of the crude cottonseed oil and cottonseed biodiesels at different wavelength.

Table 1. FA content in crude cottonseed oil and biodiesel (treated with polymer and no polymer). Values marked with the same superscript letters for the same test parameter indicate no significant differences at α=0.05.

	FFA (%)					
	1.0 mg/L	2.0 mg/L	3.0 mg/L	4.0 mg/L	0.0 mg/L	Crude oil
AL2700	0.33 ± 0.01^a	0.34 ± 0.01^a	0.33 ± 0.01^a	0.32 ± 0.01^a		
SAL1100	0.35 ± 0.01^a	0.34 ± 0.02^a	0.36 ± 0.04^a	0.33 ± 0.00^a	0.35 ± 0.04^b	2.51 ± 0.03^c
1:1 mixture	0.30 ± 0.02^a	0.35 ± 0.03^a	0.34 ± 0.02^a	0.32 ± 0.03^a		

FFA must be reduced to very low levels to improve the appearance and the oxidative stability of the vegetable biodiesel. According to EN14213 standard, the standard level of FFA in biodiesel is less than 0.5%. The effect of polymers types and polymer dosage on cottonseed biodiesel was reported in table 1.

There were no significance changes (p > 0.05) when different types and dosages (0.0-4.0 mg/L) polymers were used, FFA content in all cottonseed biodiesel was between in 0.30-0.36%, which met the biodiesel standard of FFA.   The result also means that FFA content in biodiesel from crude cottonseed oil is not influenced by polymers treatment.

Trace concentration of elements can influence emission and flow properties of biodiesel. Table 2 lists the mineral contents of cottonseed oil and biodiesel samples. P, S, C and Na + K were the most abundant minerals found in crude cottonseed oil. The around level of P (310 mg/L), S (100 mg/L), C (1.0 mg/L), and Na+K (119 mg/L) in crude cottonseed oil, which was reduced to 0.0, 0.0, 0.0 and <3.0 mg/L respectively after transesterification-flocculation-sedimentation, and reduced to 3.00, 0.0, 0.3 and 2.0 mg/L respectively after the process of transesterification-sedimentation (no polymer treatment). It is evident that elemental concentration existing in cottonseed biodiesel treated by polymers and no polymers meet the EN14213 standard, but the the transesterification-flocculation-sedimentation combined process were more effective in reducing the level of P, C, and Na+K than the process of transesterification-sedimentation. Both of these methods could reduce S to 0.0 mg/L. The other concentrations of major element like sulfur, carbon, sodium and potassium existing in cottonseed biodiesel was higher than concentration of samples treated by polymer.

Table 2. DXRF measurement results (3.0 mg/L polymer was used). Values marked with the same superscript letters for the same elemental test parameter indicate no significant differences at α=0.05.

concentration (mg/L)	SL2700	SAL1100	SL2700+SAL1100	No polymer	Crude oil	EN14213 standard
P	0.0 ± 0.00^a	0.0 ± 0.00^a	0.0 ± 0.00^a	3.0 ± 0.00^b	310.0 ± 0.94^c	<10
S	0.0 ± 0.00^a	0.0 ± 0.00^a	0.0 ± 0.00^a	0.0 ± 0.00^a	100.0 ± 0.97^b	<10
C	0.0 ± 0.00^a	0.0 ± 0.00^a	0.0 ± 0.00^a	0.3 ± 0.00^a	1.0 ± 0.12^b	<0.3(%)
Na+K	2.0 ± 0.00^a	3.0 ± 0.00^a	1.0 ± 0.00^a	2.0 ± 0.00^a	119.0 ± 0.23^b	<5

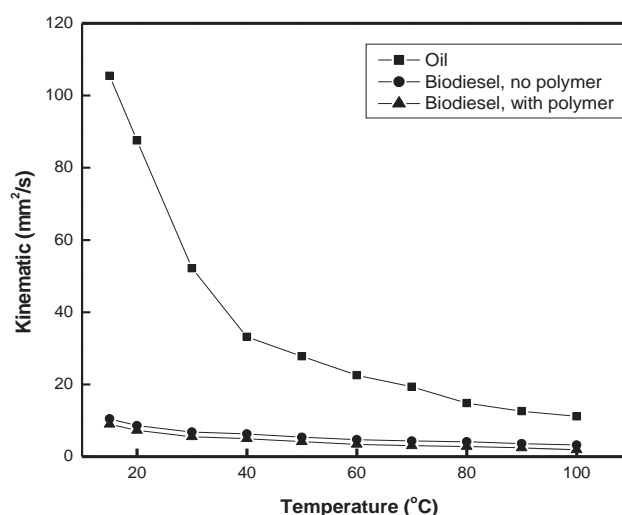*3.4. Effect of polymers on specific gravity*

Figure 3. Specific gravity of the cottonseed biodiesel with different temperature.

Specific gravity plays an important role of diesel combustion and exhaust emissions.The specific gravity of biodiesel depends on the fatty acid composition. The specific gravity of biodiesel usually varies between 0.86 and 0.90 [24]. In this study, the specific gravity of biodiesel obtained by three polymers and no polymer are measured from 20-100 ℃ (figure 3).   The testing result is approximately between 0.86-0.89. Regression analysis shows that the temperature depends of specific gravity to be linear over the measured temperature range. The regression line is in the form of

$$\rho = mT + b$$

where r is Specific gravity, T is temperature (℃), and m and b are given in Table 3 for all biodiesels. The average m value is -3.0×10^{-4} g/ml T. The straight line correlation fits the data very well, and R^2 is 0.99. Biodiesel has a density of 0.86-0.89. The specific gravity of biodiesel with no polymer and polymer treatment has no significant differences.

Table 3. Specific gravity correlation constants for cottonseed biodiesel.

Biodiesel type	m (g/ml ℃)	b (g/ml)	R^2
Biodiesel-no polymer	-3E-04	0.892	0.99
Biodiesel-SL2700	-3E-04	0.890	0.99
Biodiesel-SAL1100	-3E-04	0.888	0.99
Biodiesel-SL2700 + SAL1100	-3E-04	0.887	0.99

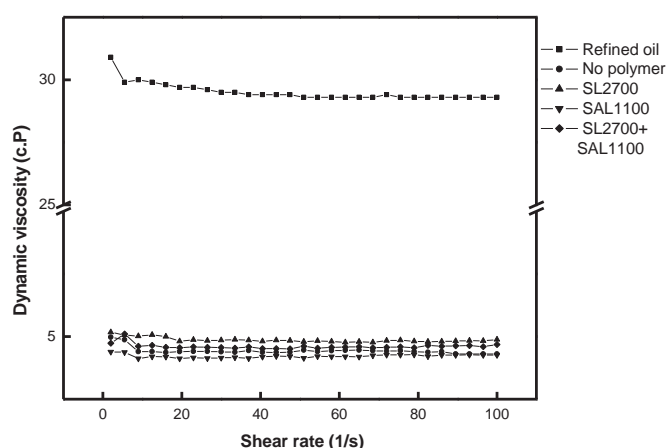*3.5. Effect of polymers on viscosity and flow behavior*

Figure 4. Viscosity curves of canola oil and biodiesel with different polymers treatment (settling 90 min) and no polymer treatment (settling 5 h)

Viscosity also plays an important role of diesel combustion and exhaust emissions. Accordingly, vegetable oil is converted to biodiesel primarily to reduce fuel viscosity. Figure 4 is the dynamic viscosity of refined cottonseed oil and biodiesel treated with SL2700, SAL1100 and SL2700+SAL1100 settling after 90 min and no polymers treatment after settling 5 h (methanol was removed also) at 40 ℃. These rheograms show approximately Newtonian behavior for cottonseed oil and biodiesel at 40 ℃ because of the evidenced of the linear curves. They show Newtonian flow behaviors approximately because of double bonds [25]. Cottonseed oil has a relatively high feedstock dynamic viscosity (around 30 mPa s). It was observed that the viscosity of biodiesel obtained from no polymer is around 8.8 mPa s after settling 90 min and 5.0 mPa s after settling 5 h. Biodiesel obtained from the three polymers has much lower and similar dynamic viscosity after settling 90 min (around 4.8 mPa s). There was no significant difference for the performance of three polymers to viscosity. There was no significant difference for the performance of three polymers and no polymer treatment to viscosity after the systems are stable.

4. Conclusions

The use of cationic polymers as flocculation aid can hasten the cottonseed biodiesel to separate from glycerin and other impure materials after transesterification process. At this moderate polymer dosage of 1.0-3.0 mg/L, the efficiency of solid settling occurred by higher polymer dosage is higher. The impurities settling could be finished in around 50 min at 30 ℃ when 3 mg/L of SL2700, SAL1100 and SL2700+SAL1100 (1:1, w/w) is used respectively. When polymer is not added, it needs at least 5 h to separate the impure materials from biodiesel. The use of cationic polymers could quicken the process of making cottonseed biodiesel.

Acknowledgments

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