Production of a Clay-Polymer Composite Aiming the Removal of Residual Sodium from Biodiesel

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Summary: Clay particles are frequently used in adsorption processes with aqueous solution, but the formed colloidal dispersion is responsible for several phenomena that hinder the flow. To overcome these problems, this work deals with adsorption experiments carried out using an adsorptive media prepared with clay immobilized on the surface of polymer pellets. The effect of biodiesel on three polymer pellets and on a clay-polymer composite was evaluated. Only the composite was not affected by the biodiesel, and its optimal operational conditions were determined. The composite was effective to remove residual sodium from biodiesel, attaining levels below law requirements.

Keywords: biodiesel; clay; composite; experimental planning; polymer; residual sodium.

Introduction

Consumption of fossil fuel has a great impact on the quality of the world-wide environment. Air pollution, climatic changes, oil spilling and toxic residues generation are results of the production and using of these fuels. Renewable fuels utilization, or biofuels (biodiesel), are directly related to the reduction of noxious substances such as carbon dioxide (CO_2), sulphur dioxide (SO_2), aromatic polycyclic hydrocarbons, nitrogen oxides (NO_x) and carbon monoxide (CO).[1–3]

European Union produces around 1 million ton biodiesel per year,[4] where Germany, France and Italy are the greatest producers. In Brazil, since the 20 decade, the Instituto Nacional de Tecnologia (INT) studies and developes techniques aiming to obtain alternative fuels from renewable sources. In the 70's, the INT, the IPT (Instituto de Pesquisas Tecnológicas) and the CEPLAC (Comissão Executiva do Plano da Lavoura Cacaueira) develop projects to use vegetable oils as fuels.

The National Biodiesel Board defines biodiesel as the long chain mono-alquil esther fatty acid obtained from renewable sources. It is produced by alcoholise of vegetable oils, using a catalyst. There are several routes to be followed and the catalyst used can be homogeneous (an acid or a base), heterogeneous or enzymatic. Reaction to produce biodiesel is shown in Figure 1.[4]

Alkoxides (sodium methoxide or sodium ethoxide) and alkaline metal hydroxides (sodiumor potassium hydroxides) can be used as catalysts, as well sodium or potassium carbonates.[1]

During the production process of biodiesel, the step of phase separation involves refining the products, but it can be a technical difficult step with a high production cost. The free fatty acids contents, alcohol, glycerin and water must be a minimum quantity and the purity of biodiesel must be higher than 96.5%.[5]

Clays are traditionally used in the vegetable oil industry to diminish impurity and coloring substances. The principal impurities removed from oil are pigments (chlorophyll and derivates, carotenes, and

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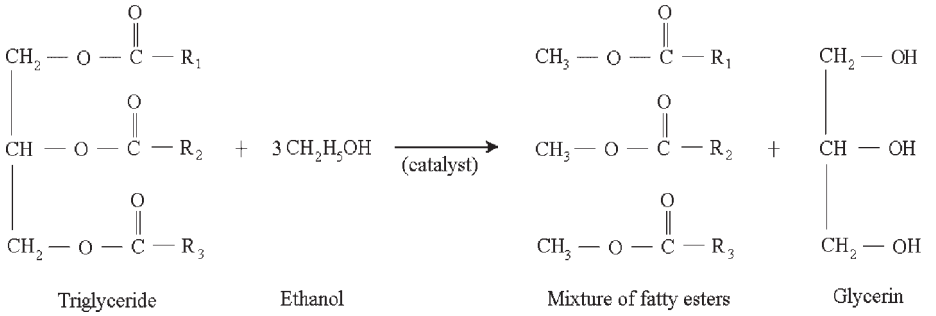

Figure 1.
Triglycerides transestherification. R_1, R_2 and R_3 are the fatty acids long chain.

so on), phospholipids, soap, oxidation products, metals and humidity.[6–8]

Sodium and potassium are soap residues from the biodiesel reaction when alkaline bases are used as catalyst. Even small quantities of that catalyst, in its free form or with water and residual oil, can produce soap that is the origin of several problems such as motor corrosion, besides favor the microorganism growing. The European Standard EM 14214 and Government Directive 255 from 15/09/2003 of the Brazilian National Oil Agency (ANP) limit the maximum value to the content of group I metals, including sodium in the fuel, to 5 mg kg^{-1}.[9]

This study aims to obtain the production optimal conditions of a composite that can be used in the separation of residual sodium present in the biodiesel using adsorption separation process.

Material and Methods

Adsorbents

Tonsil Terrana 580 FF clay was supplied by Süd Chemie do Brasil Ltda., and chemical composition is shown in Table 1.

Polymers

Pellets of 3 mm mean diameter of poly-(vinyl ethylene-co-acetate) - EVA, with a) 19% and b) 28% vinyl acetate contents, supplied by Politeno Ind. Com. S.A.; c) 3 mm mean diameter pellets of HD 7255 LS-L resin, a high density polyethylene (HDPE) supplied by Ipiranga Petroquímica S.A.; d) polystyrene pellets produced in the laboratory by suspension reaction using a monomer (Innova S.A.) with a purity degree higher than 99,6%, were used as clay support. The concentration of p-terc-butilcatechol inhibitor was 12 ppm, and the initiator was benzoil peroxide, BPO, supplied by Elf Atochem Chemicals. Polyvinylpyrrolidone, PVP, was used as stabilizing agent and was supplied by ISP Technologies Inc. Distilled water was the continuum medium.

Biodiesel

Biodiesel was provided by the Chemical Engineering Group from Federal University of Rio Grande (GEQ/FURG), Rio Grande, RS, Brazil and was produced by ethylic route/alkaline catalyst (NaOH). It was characterized by 1.0 Factor fatty acids, 192 saponification index and 130.5 iodine index.[10] Quantitative evaluation of

Table 1.
Chemical composition of Tonsil Terrana 580 FF clay.

Composition	Clay mass (%)
Silicon oxyde (SiO_2)	55.50
Aluminium oxyde (Al_2O_3)	16.36
Iron oxyde (Fe_2O_3)	7.53
Calcium oxyde (CaO)	2.45
Sodium oxyde (Na_2O)	0.11
Potassium oxyde (K_2O)	2.94
Mnaganese oxyde (MnO)	0.18
Titanium oxyde (TiO_2)	0.90
Magnesium oxyde (MgO)	2.28
Phosphorus oxyde (P_2O_5)	0.35
Weight loss ($T = 950\ ^\circ C$)	10.64

sodium and potassium was accomplished using AAS Vario 6 Spectrometer (Analytic Jena) atomic flame emission. The measures were carried out at 766.5 nm for potassium and 589.0 nm for sodium.

Clay-Polymer Composite

Polymer pellets covered with adsorbent matrix were obtained by heating a mixture of clay-polymer pellets 2:1 mass proportion at 210 °C for 2 hours.[11] After fixation, the pellets were washed and dried in order to remove any excess of adsorbent particles.

Manufacturing Clay-Polymer-Composite Optimization of the Process

Fixation process of Tonsil Terrana 580 FF clay at the surface of polymer pellets samples used a modified rotavapor, without condenser and condensed collector parts. In the modified system, a connecting rod and a rotation controls were adapted at the inner of the glass balloon (Figure 2) to better mix the clay and polymer, and to homogenize the samples. Polymer was first placed at the balloon, followed by clay at the proportion of 1:2.

In this system, a half fraction of an experimental factorial planning, 2_V^{5-1}, evaluated the influence of five factors: (A) Bath temperature (T, °C); (B) Processing time duration (t, minutes); (C) Rotation of the system (v, rpm); (D) Polymer mass (M, g); (E) EVA type. Table 2 shows the variation levels for the studied factors. Based on the resulting effects, inert factors were fixed at the more economic and/or convenient value for the optimization essays. The statistical significant factors were used in a compound experimental design aiming to produce a model to describe results. Operation optimal conditions were obtained by the Response Surface Methodology (RSM). Analysis of variance (ANOVA) was used to evaluate the model.

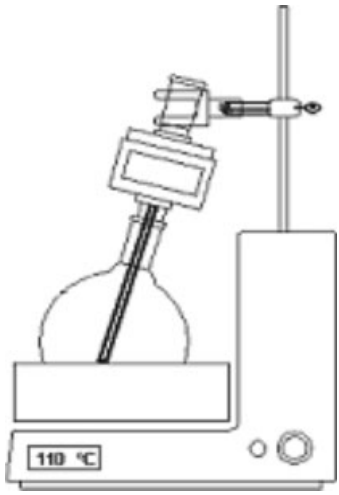

Figure 2.
Experimental system used for fixation of clay on polymer.

Table 2.
Factors levels for the 2_V^{5-1} partial experimental design.

Factors	Codification of the factors levels	
	−1	+1
(A) Temperature (°C)	110	150
(B) Time (minutos)	30	60
(C) EVA type	HM-2528	8019-PE
(D) Rotation (rpm)	100	150
(E) Polymer mass (g)	20	60

Particle's Morphology

Scanning electron microscopy - SEM, was used to evaluate the pellets surfaces before and after the biodiesel adsorption-desorption process. The microscope (PHILIPS, model XL-30) operates at 20 kV with a tungsten source. Images from both back scattered electrons were considered; the pellets were broken under liquid nitrogen action to show the inner polymeric matrix. Image analysis to evaluate and quantify the clay layer was accomplished using the software SizeMeter®.

Batch Experiments

Batch essays were carried out at 25 ± 1 °C. A known mass of polymer-adsorbent pellets and 50 mL biodiesel were mixed using a magnetic stirrer.

Results and Discussion

Stability of Biodiesel-Polymer System

Biodiesel is a mixture of carboxylic acid esters, which is able to dissolve a wide range

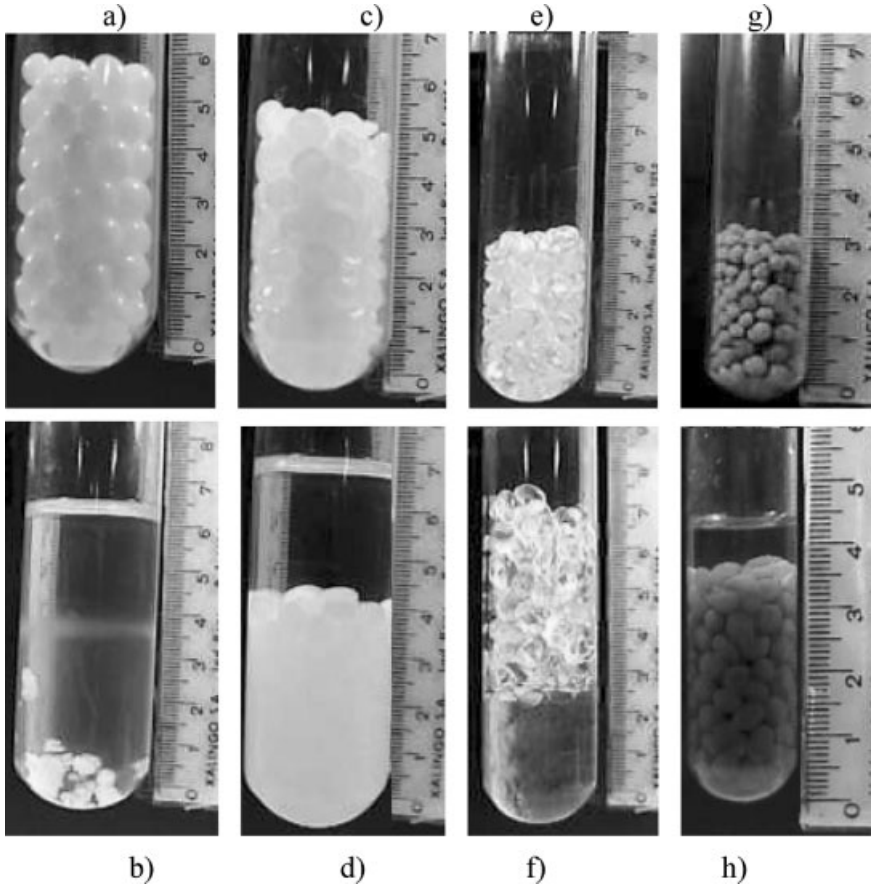

Figure 3.
Effect of biodiesel on polymer pellets: a) and b) polystyrene; c) and d) polyethylene; e) and f) EVA; g) and h) EVA-clay pellets.

of organic substances. To evaluate the chemical stability of polystyrene, polyethylene and EVA, preliminary tests were carried out immerging them in a biodiesel sample. Figure 3 shows the influence of biodiesel on polymers. Figures 3.a), 3.c), 3.e) and 3.g) refers to polymers before biodiesel contact, while Figures 3.b), 3.d), 3.f) and 3.h) refers to polymers after biodiesel contact.

Polystyrene and polyethylene were greatly affected by biodiesel. Polystyrenes was dissolved (Figures 3a, 3b), while polyethylene (Figures 3c, 3d) was partially dissolved and particles lost the form. Pure EVA pellets (Figures 3e, 3f) showed a two-fold increase in volume after 7 days of biodiesel contact. Otherwise, EVA-clay pellets (Figures 2g, 2h) were protected from

Table 3.
Residual sodium in biodiesel.

After purifying using	Sodium (ppm)	Potassium (ppm)
Nothing (pure biodiesel)	$4{,}2 \pm 0{,}2$	$<0{,}1$
Tonsil Terrana 580 FF clay	$<0{,}1$	$<0{,}1$
Organophilic Clay	$0{,}9 \pm 0{,}1$	$<0{,}1$
Silica	$2{,}1 \pm 0{,}1$	$<0{,}1$

Table 4.
Partial factorial design $2^5_V{}^1 5$ matrix, and experimental responses.

Essays	Factors					Response
	A (°C)	B (min)	C	D (rpm)	E (g)	Fixed clay (g)
1	110	30	HM2528	100	60	2.1490
2	150	30	HM2528	100	20	2.5659
3	110	90	HM2528	100	20	0.6372
4	150	90	HM2528	100	60	6.7209
5	110	30	8019-PE	100	20	0.7434
6	150	30	8019-PE	100	60	4.3347
7	110	90	8019-PE	100	60	3.5092
8	150	90	8019-PE	100	20	2.1454
9	110	30	HM2528	150	20	0.9049
10	150	30	HM2528	150	60	6.1379
11	110	90	HM2528	150	60	3.8302
12	150	90	HM2528	150	20	1.5196
13	110	30	8019-PE	150	60	2.4500
14	150	30	8019-PE	150	20	1.5741
15	110	90	8019-PE	150	20	1.5566
16	150	90	8019-PE	150	60	4.7254

biodiesel attack presenting a small volume increase. This qualitative evaluation indicates that the polymer-biodiesel interaction is a complex phenomena. It also indicates the EVA as best choice for the sodium adsorption experiments.

EISNER et al. also studied the elastomers compatibility in organic fluids. It was found that rubber swells in the ester fatty acids presence, as observed for EVA in this study. This effect is influenced by the fluid viscosity, the functional groups in the ester and rubber molecules, and the size of ester molecules.[12]

Adsorption Batch Essays Using Biodiesel

Table 3 shows the sodium contents after adsorption batch experiments using the three adsorbents immobilized on EVA pellets.

Good results for alkaline metals removal was given by EVA-Tonsil Terrana 580 FF composite. Tonsil Terrana 580 FF clay has potassium cations as a structural component, but they did not migrate to the liquid. Potassium was not detected in biodiesel samples after adsorption processes.

Optimization of the Operational Conditions for EVA-Clay Composite Production

As EVA was the more resistant polymer under biodiesel action, it was used to optimize the operational conditions for the production of the clay-polymer composite. Table 4 shows the experimental design matrix for a partial design $2^5 f^d$, and the response obtainedfor each essay. The calculated effects are shown in Table 5, and were evaluated for a significant level of 5%.

By the results in Table 5 it is observed that only temperature and polymer mass are the significant effects, as shown by the p-level < 0.05 and positive confidence intervals for the two factors. The other factors are

Table 5.
Factor effects on the fixed clay mass on EVA.

	Effect	Standard error	p-level	Confidence interval	
				Inferior	Superior
Mean	2.8440	0.2195	0.0000	2.3547	3.3333
(A) Temperature	1.7429	0.4391	0.0026	0.7643	2.7215
(B) Time	0.4730	0.4391	0.3067	−0.5055	1.4516
(C) EVA type	−0.4283	0.4391	0.3524	−1.4069	0.5502
(D) Rotation	−0.0133	0.4391	0.9763	−0.9919	0.9652
(E) Polymer mass	2.7762	0.4391	0.0000	1.7977	3.7548

Table 6.
Compound design applied to the temperature and polymer mass for the fixation process of clay on EVA.

Essay	Polymer mass (g)	Temperature (°C)	Clay fixed (g)
1	20	110	0.5678
2	60	110	2.601
3	20	150	1.5325
4	60	150	4.0991
5	11,8	130	0.4793
6	68,2	130	2.689
7	40	102	1.8089
8	40	158	2.4364
9	40	130	2.2356
10	40	130	2.1848

considered as inert variables, and constant values of 30 minutes heating time t, HM 2128 EVA type and 100 rpm rotation speed were used. The 16 experiments correspond to triplicated essays of a complete design 2^2. Addition of 6 experiments, at levels 0 and $\pm\alpha$, produced a compound design (Table 6) used to optimize the operation conditions. Table 7 shows the effects of the temperature and polymer mass on the process.

It can be observed that the linear (L) and quadratic (Q) terms of the polymer mass and the linear term (L) of the temperature are significant to the process, as shown by positives or negatives confidence intervals at a significant level of 5%. Regression by minimum squares gives the model coefficients, and the quadratic reduced model is shown in Equation (1). The determination coefficient R^2 was 0.8444.

$$\begin{aligned} MF = {} & 0,2644 + 0,0502M \\ & - 0,0005M^2 - 0,0214T \\ & + 0,0001T^2 + 0,0003\ MT \end{aligned} \quad (1)$$

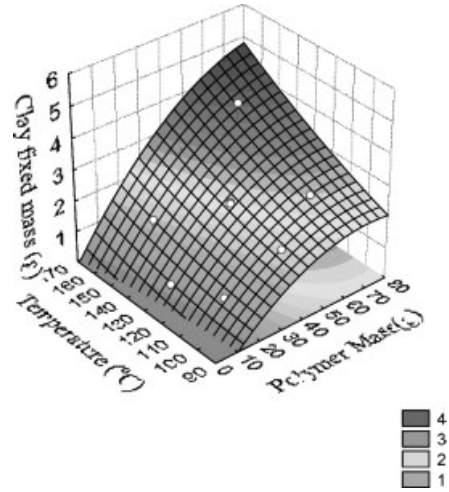

Figure 4.
Surface response of clay adhered mass as a function of temperature and polymer mass.

where MF is the clay fixed mass on the polymer, M is the polymer mass and T is the temperature.

Figure 4 shows the surface response generated by the model. At high temperatures and polymer mass, the clay fixed mass is at the maximum region for the process. The operational conditions range is 140 to 170 °C for the temperature and 50 to 80 g for the polymer mass. Table 8 shows the ANOVA for the resulting model.

From Table 8, the F test calculated for the regression is higher than the value found in tables, and the model can be considered as representative of the experimental results. The lack of fit is also neglectable ($F_{cal} < F_{tab}$).

Clay-EVA Particle Morphology

Figures 5 and 6 show the composite pellet completely covered by the clay layer, even

Table 7.
Effects of the factors on the fixation process of clay on EVA.

	Effect	Standard error	Confidence interval	
			Inferior	Superior
Mean	2.2081	0.0254	1.8853	2.5308
(1) Polymer mass(L)	1.9346	0.0254	1.6114	2.2578
Polymer mass(Q)	−0.4522	0.0337	−0.8808	−0.0236
(2) Temperature(L)	0.8393	0.0254	0.5161	1.1626
Temperature (Q)	0.0894	0.0337	−0.3391	0.5180
1Le2L	0.2667	0.0359	−0.1897	0.7231

Table 8.
ANOVA for the clay mass fixation on the polymer.

Source variation	Quadratic sum	Degrees of freedom	Quadratic mean	$F_{\nu,1,\nu,2calc}$	$F_{\nu,1,\nu,2tab}$
Regression	9.18043	5	1.83608		
Residue	0.81911	4	0.20477	8.96	6.26
Lack of fit	0.81782	3	0.27260		
Pure error	0.00129	1	0.00129	211.31	215.7
Total	10.10080	9			

R^2: 99,98%; R^2 fitted: 90,80%.

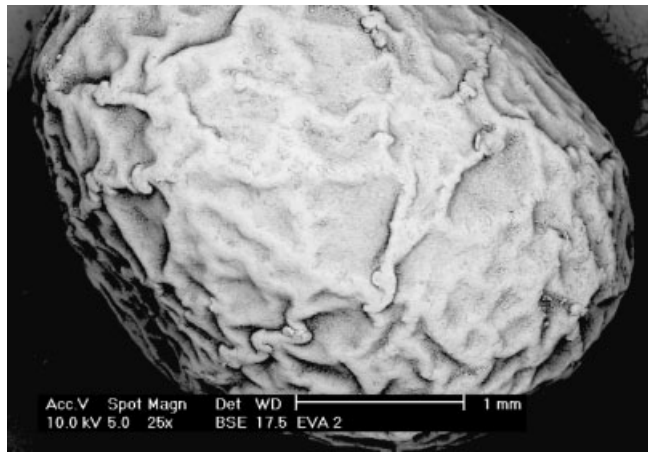

Figure 5.
Micrography of EVA pellet covered with Tonsil Terrana 580 FF (25×).

after 60 minutes under strong stirring in the sodium removal experiments The mean adsorptive layer thickness was estimated at 49.6 ± 6.6 μm, from 30 measures on 3 different pellets.

Conclusion

It was shown that clay-EVA composite was able to be immerged in biodiesel, showing neglectable changes. Optimization of the

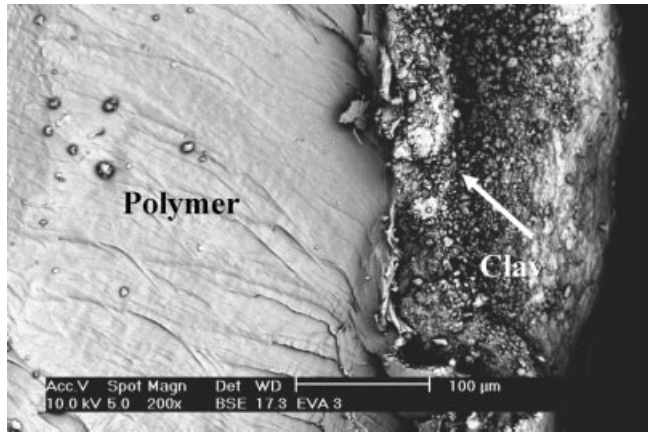

Figure 6.
EVA-clay pellet (200×). Conclusion.

operational conditions indicated 140 to 170 °C and 50 to 80 g EVA mass as the best ranges to produce the clay-polymer composite.

Removal of residual sodium from biodiesel was very effective. Final values of sodium content followed the law requirements, producing alkaline metal contents below 5 ppm.

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