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Evaluation of the Antioxidant Potential of Additives for Biodiesel produced from different processes

Avaliação do potencial Antioxidante de Aditivos para o Biodiesel produzido a partir de diferentes processos

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ABSTRACT
Soybean oil, used widely by its availability and accessibility as the principal feedstock for biodiesel production in Brazil, presents high susceptibility to oxidation, since it has high levels of unsaturated fatty acids.[1] Use of a synthetic antioxidant, actually feasible and effective, could delay the onset of oxidation or reduce its rate for esters derived from oils and fats, one of the major causes of not specified biodiesel in the Brazilian legislation. In order to collaborate with industry on the storage of biodiesel in Brazil, this study tested several additives (0 to 4000ppm) still underused or unused on the market for this purpose and compared them with an additive widely used in the food industry, the butylhydroxytoluene – BHT.[2-3] The research was divided in three steps. First step was established to verify the activities of pure additives and mixed with soybean biodiesel.[4] For that, it was also, three main transesterification routes used in the Brazilian biodiesel production scenario were also tested, varying the type of catalysts and washing, monitoring stability in long term storage, antioxidant kinetic study and evaluation of specification of the additivated biodiesel. Step 2 mixtures of better performance additives from the first stage were submitted to biodiesel produced by the best process and evaluated in long-term storage tests, in the third stage blends of different types of

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biodiesel (soy with palm or tallow) were tested in proportions different. Results from step 1 showed that process Company 1 is the less harmful to the activity of the tested additives, mainly during de first month of storage. Most of cases had Kerobit 3627, followed by Kerobit TP26, BHT and Keromet MD100. In tests comparing acid washing steps and types of raw material, the influence of these parameters on esters stability is clear. Less pure raw material (degummed oil) and less aggressive washing (Company 1 process) gave better results. In step 2, it was possible to obtain a blend of additives between Kerobit 3627 and Keromet MD100 (1: 1) capable of conserving the ester for more than 5 years when stored at 25 °C. Soybean biodiesel blends with palm or tallow, richer in saturated esters, seemed to be an interesting alternative, with a inferior effect in the stability comparing it to the additives. At low temperatures, content of saturated ester is a determinant factor in the oxidation stability. On the other hand, time of storage almost not influenced oxidation. When at highest temperatures of storage, the benefit effect of saturated esters amount is minimum, but the time of storage is crucial to guarantee the integrity of the mixture.

Keywords: Biodiesel, Oxidative stability, Kinetics, Molecular modeling.

RESUMO

O óleo de soja, amplamente utilizado por sua disponibilidade e acessibilidade como principal matéria prima destinada à produção de biodiesel no Brasil, apresenta grande suscetibilidade à oxidação, uma vez que possui altos teores de ácidos graxos insaturados.[1] O uso de um antioxidante sintético, realmente viável e eficaz, poderia adiar o início da oxidação ou diminuir sua taxa para os ésteres derivados de óleos e gorduras, uma das principais causas de biodiesel não especificado na legislação brasileira. No sentido de colaborar com o setor de estocagem de biodiesel no Brasil, o presente trabalho testou vários aditivos (0 a 4000ppm) utilizados no mercado para esse fim e comparou com um aditivo tradicional amplamente empregado no setor nacional, butilhidróxitolueno - BHT.[2-3] O estudo foi dividido em três etapas. A primeira foi estipulada para verificar a atividade antioxidante dos aditivos usados na forma pura e misturado ao biodiesel de óleo de soja.[4] Para isso, também foram testadas três principais rotas de transesterificação utilizadas no cenário brasileiro de produção de biodiesel, variando tipo de catalisadores e lavagem, monitoramento da estabilidade a longo prazo e avaliação das especificações do biodiesel aditivado. A etapa 2 misturas entre aditivos de melhor performance da primeira etapa foram submetidas ao biodiesel produzido pelo melhor processo e avaliadas em testes de estocagem à longo prazo, na terceira etapa foram testados blends de tipos diferentes de biodiesel (soja com palma ou sebo) em proporções distintas. Os resultados obtidos na etapa 1 mostraram que o processo Empresa 1 é o menos prejudicial à atividade dos antioxidantes, durante o primeiro mês de estocagem. A maioria dos casos teve como melhor antioxidante o Kerobit 3627, seguido de Kerobit TP26, BHT e Keromet MD100. Em testes de comparação entre etapas de lavagem ácida e tipos de matéria prima, é nítida a influência desses parâmetros na estabilidade dos ésteres. Matéria prima menos pura (óleo degomado) e lavagem menos agressiva (processo Empresa 1) deram melhores resultados. Na etapa 2, foi possível obter um blend de aditivos entre Kerobit 3627 e Keromet MD100 (1:1) capaz de conservar o éster por mais de 5 anos quando conservado à 25°C. As misturas entre biodiesel de soja e os ricos em ésteres saturados, como palma e sebo, mostraram-se uma alternativa interessante, porém com um efeito na estabilidade inferior aos aditivos. Em temperaturas baixas, o teor de ésteres saturados é o fator determinante na estabilidade, ao passo que o tempo de estocagem pouco influi na oxidação. Já em temperaturas elevadas de armazenamento, o efeito benéfico da quantidade de ésteres saturados é mínimo, mas o tempo de estocagem é crucial para garantir a integridade da mistura.

Palavras-chave: Biodiesel, Estabilidade à oxidação, Cinética, Modelagem molecular.

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1 INTRODUCTION

The consolidation of biodiesel on the world market as an alternative biofuel to diesel is increasingly evident over the years, both for the proven environmental benefits (in relation to fossil fuel) and for the viability of production through the various renewable sources that serve as feedstock. The fact that soybeans are the main raw material combined with the problems of logistics and storage of biodiesel constitutes an adequate scenario for targeted research in the storage of biodiesel that allows an increase in production for domestic supply and other markets. The sector, still little explored, strengthens the incentive for the development and application of synthetic compounds in biofuels.[5-8]

In the last five years, with the legal insertion of biodiesel in the energy matrix, the Brazilian production capacity has always been above what is necessary to meet the consumption of biofuel in the country. With the national energy market currently supplied with about 80% biodiesel from soybean oil, with the problems of logistics, storage and harvests due to weather conditions, it is indisputable to investigate compounds with greater antioxidant activity (or lower concentrations) and at more affordable prices than compounds already applied on an industrial scale. In addition, there is a growing interest in guaranteeing production and taking advantage of the installed capacity for extra production of biofuel, since Brazil is able to produce biodiesel in quantities much higher than our demand, being able to supply the domestic market and even export.[9-10]

Antioxidants can prevent unwanted problems caused by biodiesel rancification, such as deposit formation due to precipitation, drop in engine performance, increased susceptibility to corrosion and decreased engine life. The application of commercially available compounds with other purposes and new additives that meet the legislation established by the ANP - National Agency for Petroleum, Natural Gas and Biofuels - for the specification of stability to oxidation of biodiesel it can be important not only to avoid problems of rancification but also for diversification of the main raw material.[11]

In this research, three main biodiesel industrial production routes were adopted, the difference of which involves different raw materials, catalysts and washing steps, as well as contributing to the biodiesel storage sector in Brazil using the application of different economically viable and effective antioxidant additives for the biofuels market. In addition, the dependence on soy basically as a monoculture supply for biodiesel production encouraged the study with biodiesel mixtures of this oilseed with tallow, the second most explored raw material in the country, and with palm, which constitutes great potential for future markets.

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2 MATERIALS AND METHODS

2.1 SCHEME OF EXPERIMENTS

The research initially focused to trace the behavior of six compounds with potential antioxidant activity for biodiesel, comparing them with a standard additive. Based on this premise, seven additives were individually tested with soybean oil biodiesel, varying their quality and the type of production process used, called Step 1 (Figure 1 flowchart). The antioxidant activity was monitored for 60 days at 45 °C in the storage stability test, the preliminary stage of the study. The results of the antioxidant activity of these compounds made it possible to design three subsequent substeps (called Steps 1.2, 1.3 and 1.4). Step 1.2 is the test of total contamination of samples with the additive more efficient in preventing oxidation. Step 1.3 involves the selection of the most active additive, as well as the least aggressive production process for biodiesel for the development of a kinetic study aiming to compare the antioxidant activity of the additive in different qualities of the same raw material. The test of influence of the presence of the additive on the properties of the most properly prepared biodiesel (Step 1.4) was carried out for 60 days, aiming to monitor the behavior of the biofuel when added.

Once the best additive was detected, blends between 2 additives were produced for the study of Step 2 (flowchart of Figure 1), aiming to increase the performance of the antioxidant activity and guarantee the specification of the biofuel. For this purpose, an influence test was performed on the presence of the blend of additives in biodiesel (Step 2.1), kinetic study (Step 2.2) and molecular modeling (Step 2.3). The latter is related to the development of computational calculations for understanding, at the molecular level, the antioxidant behavior of substances used as additives.

In addition to tests with performance chemicals, tests were also carried out on mixtures of different types of biodiesel, with the same aim of increasing the useful life of soy biodiesel. Thus, raw materials with high commercial potential were used, the study of which was established in Step 3 (flowchart of Figure 1) through tests of influence on storage (Step 3.1) and the study of the response surface (Step 3.2).

The tested additives were BHT, Kerobit TP26, Kerobit 3627, Biodiesel Stabilizer N3627, Keromet MD100, Irgastab BD50 and Irgastab BD100. For the synthesis of biodiesel, commercial refined soybean oil, degummed soybean oil (Fertibom and Granol), methanol, potassium and sodium hydroxides, citric and hydrochloric acid were used.

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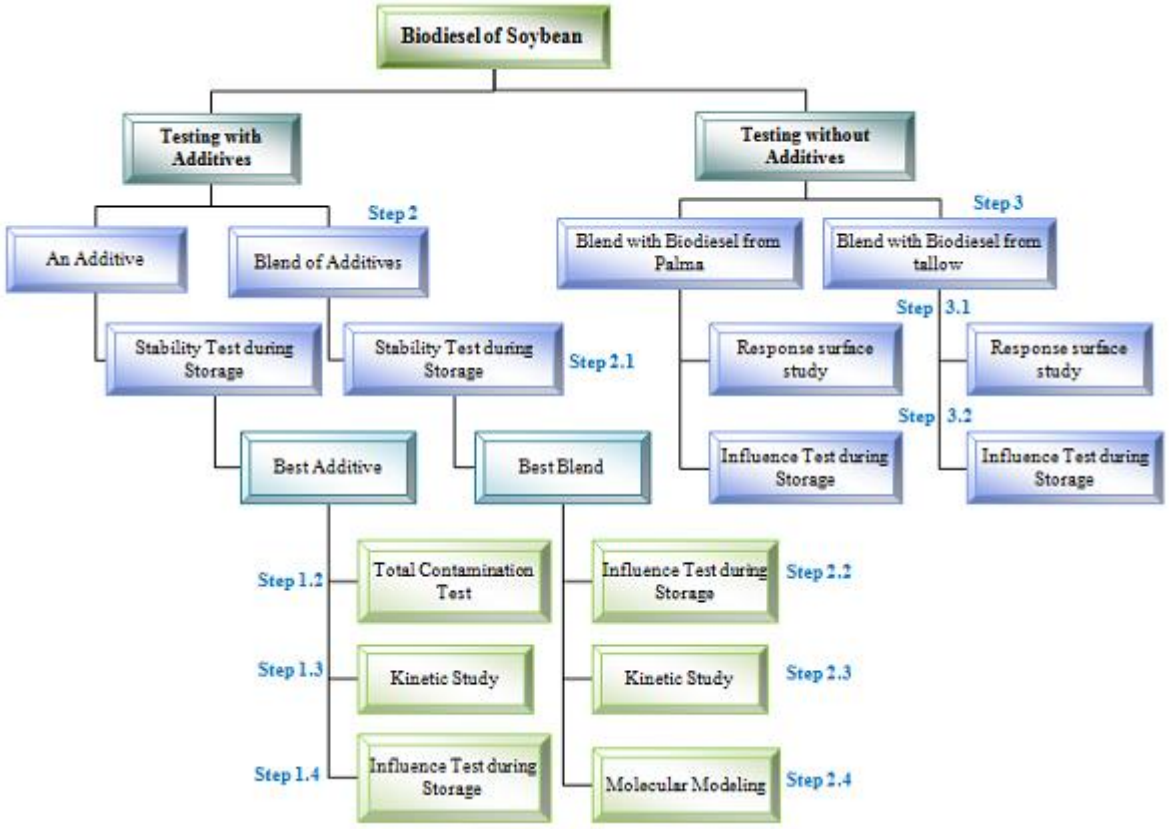
Figure 1 – Scheme of experiments carried out



2.2 SYNTHESIS OF BIODIESEL VIA DIFFERENT PROCESSES - STAGE 1

Were synthesized esters in three main transesterification routes used in the Brazilian biodiesel production scenario, which use alkaline transesterification of vegetable oil, varying the type of catalysts and washing. All of them use soy oil as raw material and methanol in the proportion of 35 % w/w of alcohol in relation to the oil. Potassium and sodium hydroxides were used as catalysts (0,75 % and 0,50 %, respectively).

For synthesis, all reactions were performed at room temperature and kept under mechanical agitation for 1 hour, in a closed system. After this period, the mixture was placed in a separating funnel for decanting the phases and separating biodiesel.

The washing step was then performed on the separate biodiesel, according to each process. For Company 1 and Company 3, 20% by volume in relation to the mass of biodiesel from a 0,3 % citric acid solution (m/m in relation to the amount of biodiesel) were used. For the Company 2 process, the acid used was hydrochloric, at a concentration of 0,05 %. After adding the acid, the mixture was stirred in a separating funnel so that any residual base was neutralized. Again separated, the biodiesel was washed with 20 % hot water (m/m of biodiesel) until the washing water was transparent, on average 2 more times. After the separation process, the washed biodiesel was dried and heated to 110 °C under constant agitation.

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2.2.1 Storage stability test

The storage stability test was performed with samples with and without additive, stored at 45 °C for two months. Oxidation stability analyzes were performed during the storage period to monitor the activity of each additive.

Seeking a real understanding of how the antioxidant activity of the additive varies with time and how it affects other specifications, after defined and interspersed periods of storage, allows monitoring the behavior of the sample, before and after storage, with respect to the properties that can be altered with oxidation such as acidity, viscosity, ester content, iodine index, precipitate formation (total contamination) and color change.

Tests at different oxidation temperatures will be carried out in order to verify the kinetics of the antioxidant activity of an additive, develop an extrapolation method to obtain the induction period, apply the Arrhenius law to calculate activation energy and analyze how the constant of reaction rate of antioxidant consumption varies depending on the temperature for each type of raw material tested.

The storage stability test, as well as the oxidation stability analyzes performed in the storage influence test and kinetic study, are based on the standard EN 14112 (2003).

2.3 KINETIC STUDY

Kinetic studies were performed to establish the durability of the antioxidant effect of the additive (or additive blend) in biodiesel. The data were obtained from oxidation stability at different temperatures (from 100 °C to 120 °C), both for biodiesel from refined and degummed soybean oil, both compound with additives best antioxidant activity.

Different curves IP x Concentration, ln C_0 (initial concentration) x IP, ln k x 1/T, ln IP x T were plotted, in order to comply with the consumption kinetics of the additive in each different concentration. The methodological analysis procedure in the case of Step 1 (Best additive) was identical for the kinetic study of Step 2 (Best Blend), varying only the type of biodiesel and the antioxidant compound.

2.4 MOLECULAR MODELING

Once the compounds with greater oxidation stability were designated, they were modeled at the molecular level in order to establish a link between structure-activity for potentially antioxidant molecules. The electronic structures were calculated using the DFT density functional method, with the Lee-Yang-Parr (Vale, 2011) correlation functional, the B3LYP. The 3-21G functions were used

due to its 3 bases for Gaussian functions for calculating internal orbitals and the set of 2 bases plus 1 for external orbitals. Parameters of boundary orbitals, ionization potential, electrostatic potential map and Mulliken charge distribution were calculated using the Gaussian 03W program and their results were visualized through the Gaussview interface for each of the modeled additives, the 3627, MD100, TP26 and BHT. The ionization potential of the molecule was obtained through the difference of energies between the radical cation of the molecule of the additive and its respective neutral species. The other parameters were calculated in the program for the most stable conformation, after optimization of the molecules.

3 RESULTS AND DISCUSSION

The results for the stored samples of biodiesel from degummed soybean oil at 45 °C are described in Table 1. The oxidation stability values obtained for biodiesel from fresh refined soybean oil and stored at 45 °C, with and without additive, in semi-closed container for 1 and 2 months are shown in Table 2. The same was done for fresh biodiesel from degummed soybean oil, shown in Table 3, where MPI means improvement of the induction period (percentage in relation to white).

Due to the structural similarity, the concentrations for the TP26 additive are the same as for BHT, as this is already widely cited in the literature. For the other additives, the concentrations adopted followed a suggestion for use by the manufacturer BASF.

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Table 1 – Oxidation stability values (h) for degummed biodiesel with degummed soybean oil, stored at 45 °C.

Antioxidants	Dosage in ppm		1st Month of Storage closed at 45 °C			2nd Month of Storage closed at 45 °C		
			Company 1	Company 2	Company 3	Company 1	Company 2	Company 3
BHT	Dose 1	100	1,34	7,31	4,06	0,83	7,05	4,36
	Dose 2	250	0,76	4,55	1,47	0	4,36	1,28
	Dose 3	500	2,5	5,76	1,81	2,94	4,65	1,86
Kerobit TP26	Dose 1	100	0,68	3,3	2,61	10,37	3,24	2,12
	Dose 2	250	0,64	3,9	1,88	9,02	3,34	1,77
	Dose 3	500	1,91	4,25	2,01	0,68	3,94	2,06
Kerobit 3627	Dose 1	50	1,63	5,09	2,04	1,91	4,5	1,83
	Dose 2	175	1,91	5,12	1,52	3,02	4,01	1,71
	Dose 3	300	3,09	4,75	1,95	2,62	4,33	1,51
Biodiesel Stabilizer N3627	Dose 1	50	1,47	2,26	1,26	1,84	2,15	1,41
	Dose 2	175	0,9	2,99	1,52	1,5	2,92	4,6
	Dose 3	300	1,06	3,32	3,63	19,87	3,02	3,03
Keromet MD100	Dose 1	50	3,79	2,97	1,89	6,46	2,75	1,85
	Dose 2	175	3,32	0,56	2,78	2,8	0,62	2,83
	Dose 3	300	4,18	5,94	1,59	2,59	5,24	1,19
Irgastab BD 50	Dose 1	50	2,68	4,84	3,02	3,37	4,76	2,89
	Dose 2	175	1,93	3,99	2,72	1,93	3,71	2,51
	Dose 3	300	1,36	4,79	2,73	15,41	4,15	2,43
Irgastab BD100	Dose 1	50	5,07	3,03	3,11	5,16	3,02	2,88
	Dose 2	175	1,61	6,88	3,43	2,49	3,83	3,18
	Dose 3	300	0,56	3,97	3,62	1,01	3,77	2,89

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Table 2 – Oxidation stability values (h) for refined soybean oil biodiesel, additive or not (white).

Antioxidants	Dosage in ppm		Fresh Methyl Biodiesel						1st Month of Storage at 45 °C			2nd Month of Storage at 45 °C		
			Company 1	White	Company 2	White	Company 3	White	Company 1	Company 2	Company 3	Company 1	Company 2	Company 3
BHT	Dose 1	100	5,65	5,28	4,80	4,53	6,75	6,27	4,90	0,62	0,55	4,83	1,02	0,62
	Dose 2	250	7,28	6,20	5,48	4,53	6,40	6,27	6,29	0,97	0,51	5,95	1,10	0,91
	Dose 3	500	7,19	5,28	6,06	4,53	8,37	6,27	2,93	1,08	0,48	0,61	0,89	0,73
Kerobit TP26	Dose 1	100	6,01	4,39	4,39	4,53	8,38	6,27	4,18	0,43	0,53	4,01	0,61	0,65
	Dose 2	250	6,43	4,39	4,76	4,69	6,59	6,27	4,39	0,39	0,36	3,78	0,51	0,71
	Dose 3	500	8,95	4,39	5,45	4,69	6,86	6,27	2,87	0,81	0,63	2,15	0,72	0,58
Kerobit 3627	Dose 1	50	11,76	4,39	5,05	4,69	6,66	6,23	4,29	1,14	0,90	3,84	1,62	0,62
	Dose 2	175	12,38	4,39	6,34	4,69	8,11	6,23	4,15	0,71	0,81	4,06	0,53	0,65
	Dose 3	300	13,47	4,39	7,31	4,69	10,74	6,23	5,39	0,75	0,89	4,48	0,67	0,76
Biodiesel Stabilizer N3627	Dose 1	50	5,04	5,03	4,75	4,90	6,24	6,23	3,94	2,60	0,51	2,43	3,61	0,49
	Dose 2	175	7,87	4,39	4,74	4,90	6,19	6,23	3,14	2,31	0,47	2,89	0,39	0,47
	Dose 3	300	7,52	4,39	4,98	4,90	6,12	6,23	6,26	2,76	0,59	3,83	0,45	0,49
Keromet MD100	Dose 1	50	5,08	5,03	3,94	4,90	5,76	5,92	4,93	0,69	0,45	4,86	1,42	3,53
	Dose 2	175	5,12	5,03	4,93	4,90	5,53	5,92	5,08	0,67	0,38	5,09	1,30	0,78
	Dose 3	300	5,04	5,03	4,90	4,90	4,74	5,92	4,36	0, 72	0.62	4,21	0,69	0,58

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Table 3 – Oxidation stability values (h) for fresh biodiesel from degummed soybean oil, additive or not (white).

Antioxidants	Dosage in ppm		Company 1			Company 2			Company 3		
			Biodiesel Methyl Additivated	White	MPI (%)	Biodiesel Methyl Additivated	White	MPI (%)	Biodiesel Methyl Additivated	White	MPI (%)
BHT	Dose 1	100	5,5	5,75	-4,35	5,62	3,94	42,64	4,73	4,41	7,26
	Dose 2	250	7,78	5,75	35,30	5,16	3,94	30,96	4,85	4,41	9,98
	Dose 3	500	6,72	5,75	16,87	5,83	3,94	47,97	5,63	4,41	27,66
Kerobit TP26	Dose 1	100	6,2	5,74	8,01	4,36	4,4	-0,91	5,41	5,32	1,69
	Dose 2	250	6,38	5,74	11,15	4,78	4,4	8,64	5,75	5,32	8,08
	Dose 3	500	6,85	5,74	19,34	5,16	4,4	17,27	6,46	5,32	21,43
Kerobit 3627	Dose 1	50	6,04	4,94	22,27	5,18	4,4	17,73	5,73	6,13	-6,53
	Dose 2	175	7,15	4,94	44,74	5,91	4,4	34,32	5,91	6,13	-3,59
	Dose 3	300	8,4	4,94	70,04	6,76	4,4	53,64	7,19	6,13	17,29
Biodiesel Stabilizer N3627	Dose 1	50	5,2	5,17	0,58	4,37	4,40	-0,68	4,26	6,13	-30,51
	Dose 2	175	6,1	5,17	17,99	4,03	4,40	-8,41	4,31	6,13	-29,69
	Dose 3	300	5,13	5,17	-0,77	4,39	4,40	-0,23	4,34	6,13	-29,20
Keromet MD100	Dose 1	50	6,46	5,75	12,35	8,91	3,94	126,14	4,89	4,89	0,00
	Dose 2	175	6,33	5,75	10,09	8,10	3,94	105,58	4,66	4,89	-4,70
	Dose 3	300	6,66	5,75	15,83	7,80	3,94	97,97	4,65	4,89	-4,91
Irgastab BD 50	Dose 1	50	7,33	7,19	1,95	4,55	5,03	-9,54	6,2	6,18	0,32
	Dose 2	175	8,52	7,19	18,50	6,36	5,03	26,44	5,78	6,18	-6,47
	Dose 3	300	7,7	7,19	7,09	6,01	5,03	19,48	6,31	6,18	2,10
Irgastab BD100	Dose 1	50	5,35	5,2	2,88	5,39	5,63	-4,26	6,15	6,18	-0,49
	Dose 2	175	4,81	5,2	-7,50	5,8	5,63	3,02	5,68	6,18	-8,09
	Dose 3	300	5,7	5,2	9,62	5,93	5,63	5,33	5,92	6,18	-4,21

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3.1 KINETIC STUDY

The kinetic study was carried out with blend 1 in the proportion of formula 2 (which uses the least amount of 3627) and with blend 3 in the proportion of formula 1, according to the best activities presented throughout their storage. The kinetic data were obtained by adding the blend in refined (commercial) soy oil biodiesel via Company 1, under the conditions of analysis described in Step 1, in order to standardize the white sample.

Through the results, it was verified that the antioxidant 3627 when used in mixture with another additive, in the case of blend 1 mixed with MD100 and in the case of blend 3 with BHT, presented a lower kinetic constant value when compared to those of additive blends (Table 4).

Table 4 – Values obtained from the kinetic study of blend additives 1 and 3.

Temperature (°C)	**Blend 1 - Formula 2**			**Blend 3 - Formula 1**		
	k	**C_{Cr}**	**R^2**	**k**	**C_{Cr}**	**R^2**
100	1,097	61,756	0,9934	1,170	57,271	0,9989
105	1,106	96,149	0,9938	1,186	84,622	0,9921
110	1,132	132,927	0,9933	1,193	98,760	0,9632
115	1,190	213,940	0,9957	1,211	213,427	0,9927
120	1,215	352,833	0,9933	1,220	363,361	0,9972

This shows that 3627 mixed with another additive had a lower antioxidant consumption rate than when used alone, as can be seen in Figure 2. That is, in their respective blends, MD100 and BHT can also compete with 3627 by the oxidizing radical. At 110 °C, for example, 3627 and its blend 3 has a kinetic constant k of 1,234 h^{-1} and 1,193 h^{-1}, respectively, while for blend 1 the constant k was equal to 1,132 h^{-1}.[12]

It is evident that the higher the temperatures, the higher the reaction rate of the additive or of its blend with the oxidizing agent to preserve the ester molecules from the oxidation process. All coefficients of determination (R^2) were greater than 0,96, demonstrating the high robustness and suitability of the models used to the experimental data (at 95 % confidence).

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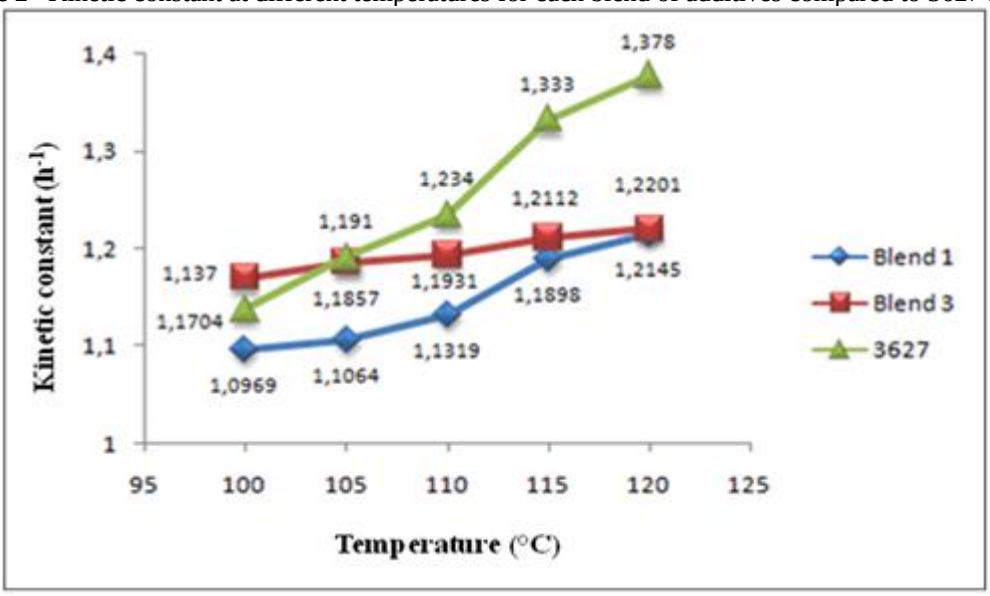
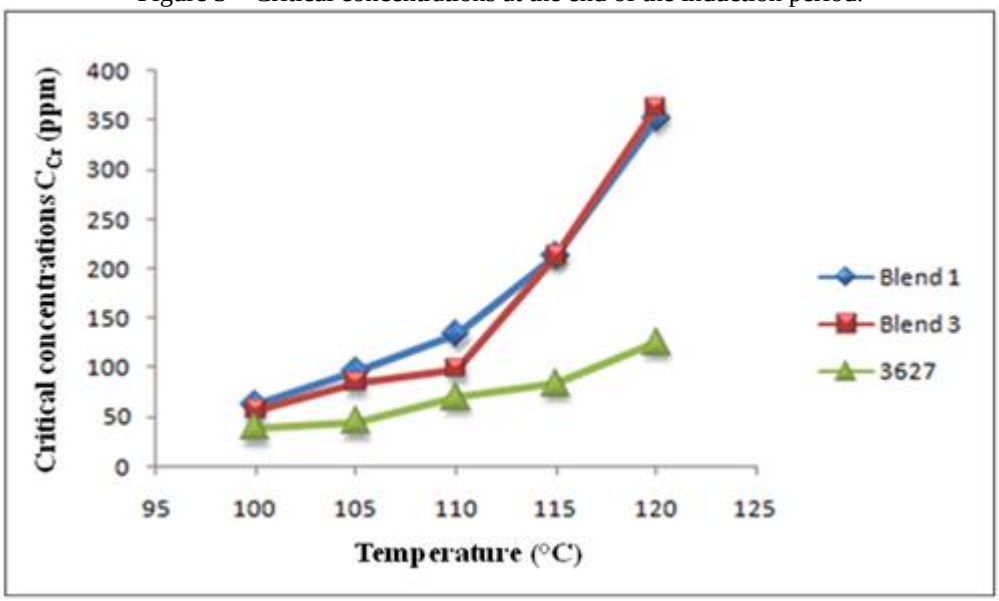
Figure 2 –Kinetic constant at different temperatures for each blend of additives compared to 3627 alone.



The critical concentration value, which measures the concentration of the additive or its blend at the end of the induction period, below which there is no antioxidant activity, was higher when 3627 was used alone due to competition from other additives used in blends. The higher the temperature, the greater the concentration of additive in the sample that remains inactive after the induction period for all cases (Figure 3). This can demonstrate the sensitivity (even some inactivation) of the additive blend with increasing temperature.

Figure 3 – Critical concentrations at the end of the induction period.



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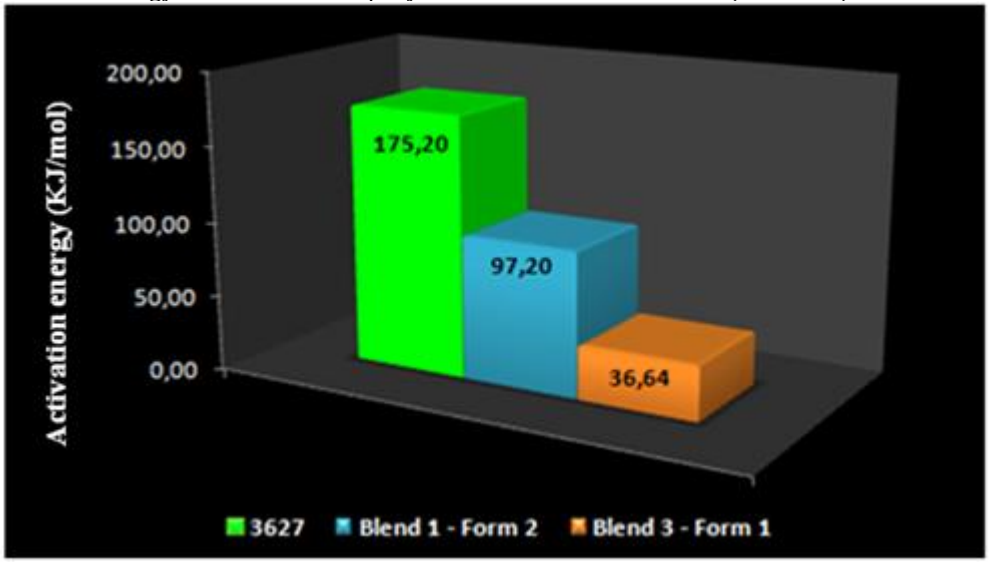
Through the Arrhenius equation to describe the temperature dependence with the reaction rate kinetic constant, it was possible to observe that both additive blends (1 and 3) decrease the activation energy in relation to the pure 3627 used (Figure 4) for BSR.

Figure 4 – Activation energy for BSR via Company 1 added with 3627, Blend 1 (formula 2) and Blend 3 (formula 1).



Blend 1 had an activation energy of 97,20 kJ / mol with R^2 0,9403, showing a reduction of 44,52% when compared to the energy of the 3627 isolated. The same was observed for blend 3, with an activation energy of 36,84 kJ / mol and R^2 0,9865, which means a reduction of 78,97%. The additive blends were able to reduce the thermo-sensitivity of biodiesel added with only 3627. However, blend 1 is more susceptible to degradation by high temperatures than blend 3, which is more resistant.

By the extrapolation method, the simulation of the stability behavior of the biodiesel added with blend 1 and blend 3 was carried out when stored at room temperature (25 °C). Figure 5 shows how the additive blends behaved in relation to additive 3627 alone, in 7 concentrations tested and comparing to the white called “0 ppm” (without additive).

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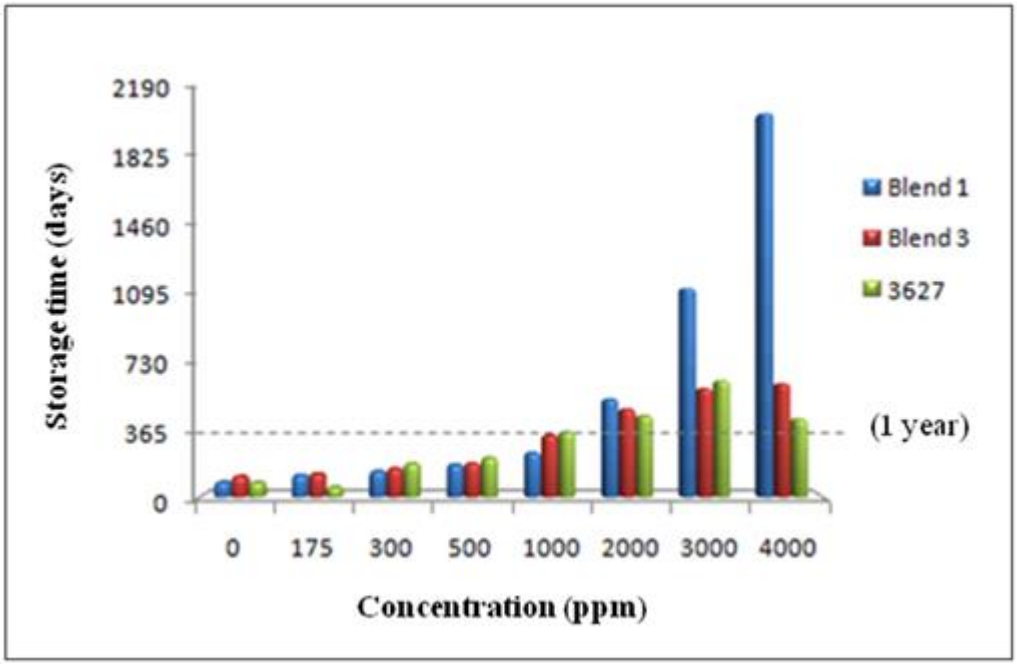
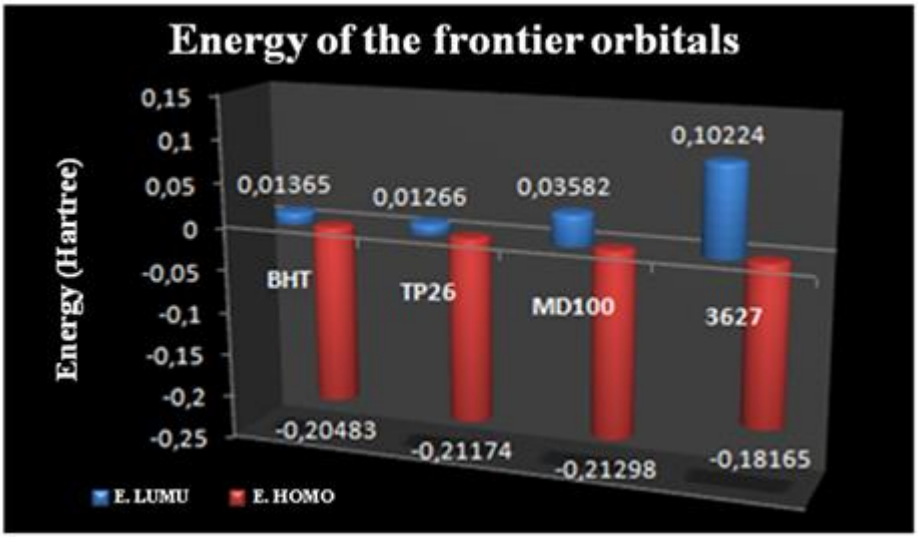
Figure 5 – Induction periods (in days) obtained by extrapolation for all used concentrations of additives 1 and 3 and 3627 blends.



3.2 MOLECULAR MODELING

The energy of the lowest energy unoccupied molecular orbital (LUMO) represents the electronic affinity of a molecule or its reactivity as an electrophile.[13] This orbital is related to the ability to receive electrons, indicating in module that the greater or lesser its energy, the greater or lesser its electrophilic character, respectively.[14-15] Figure 6 shows the comparison of the LUMO energies (in module) of the additives.

Figure 6 – Energy of the frontier orbitals for molecules of additives.



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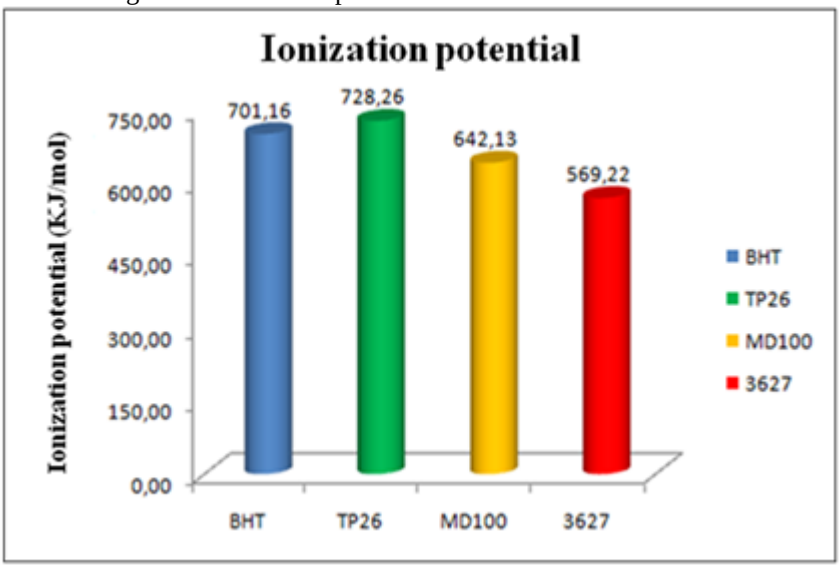
The ionization potential shows that the additive 3627 has the lowest energy required to remove an electron (or hydrogen) from the molecule in the gaseous state, that is, in the oxidation reaction, the oxidizing agent can more easily capture the H of the additive from the than the H of the ester. This trend is also seen, to a lesser extent, for the MD100, BHT and TP26, respectively (Figure 7).

Figure 7 – Ionization potential for the best active additives.



4 CONCLUSIONS

The results obtained in this work show that some tested additives showed excellent antioxidant activity.

More efficient production process and washing step with organic acid such as that of Company 1 contributed positively to the performance of the additives. Likewise, less pure raw material, but richer in tocopherol, showed better interaction with the additives and less heat sensitivity than refined oil biodiesel.

Kerobit 3627, BHT, TP26 additives were highlighted for their high activity, the first being the one with the best performance. However, the long-term stability test revealed that the MD100 must also be evidenced by its behavior.

Despite high stability, the presence of the additive can interfere with other biodiesel specifications. Total contamination analyzes showed that only when the biodiesel added with the amine compound is stored cold (5 °C) or when the raw material has a higher purity content was it possible to reach compliance. These conditions, however, are costly.

To circumvent this inconvenience, a blend of additives was proposed with a lower kinetic constant than when the additive was used alone. Blend 1, which has always shown a tendency to increase stability with increasing concentration, allowed the combination of the high stability provided by the 3627 with the durability of the induction period caused by the MD100.

Computational calculations made it possible to verify the molecular characteristics that led to such behavior. The additive 3627 can donate and receive electrons more easily. In addition, it is able to interact more quickly with the oxidizing agent (ROO•), as it has less ionization energy. On the other hand, MD100 has the lowest Gap (H-L) and therefore interacts with other compounds in order to better stabilize them. When mixed, MD100 seems to act as a synergist for 3627, regenerating and stabilizing its formed radicals.

The development of additives and / or mixtures with greater antioxidant activity could provide an increase in production in the biodiesel industries, which currently do not operate at maximum capacity. This currently means an increase of approximately 2,16 million m^3 of biodiesel produced in surplus in just six months, which could be supplying other markets. For this, new investments in capacity expansion would not be necessary, as only 38 % of installed capacity in the country is used. The surplus biodiesel could be exported to countries whose production is insufficient or expensive, if the Brazilian government allowed equal competition with foreign markets.

An additive that was more efficient and economical would be highly appreciable for the domestic market, which is basically supplied by oil with a high content of installation, such as soy, the main source of supply for the production of biodiesel.

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