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A new vehicle for herbicide application using crude glycerin, a by-product of biodiesel production

Rejanne Lima Arruda[1]*, José Iran Cardoso da Silva[1], Evilanna Lima Arruda[1], Marciane Cristina Dotto[2], Renato de Almeida Sarmento[3] and Eduardo Andrea Lemus Erasmo[3]

[1]Biotechnology, Marlebologia Laboratory of the Federal University of Tocantins, Brazil.
[2] Marlebologia Laboratory of the Federal University of Tocantins, Brazil.
[3]Federal University Tocantins, Brazil.

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The supply of glycerin derived from the pre-purification of biodiesel has increased considerably in Brazil, making it necessary to identify economic and environmentally friendly applications for this by-product. This work aimed to develop oil-in-water (O/W) emulsions using crude glycerin treated with H_3PO_4 for use as a vehicle for the application the herbicide Togar. The work was conducted in the laboratory of Marlebologia at the Federal University of Tocantins, Gurupi Campus. The preliminary emulsions were subjected to stability testing, and those that remained stable were diluted with the herbicide Togar (8% v v^{-1}) and characterized with respect to pH, conductivity, viscosity, density and surface tension. The crude glycerin was used to develop five stable emulsions with promising physicochemical characteristics for use as vehicle for herbicide application. The conductivity and viscosity of the emulsions were high compared to diesel.

Key words: Agrochemicals, residue, emulsions.

INTRODUCTION

Biodiesel is a mixture of straight-chain alkyl esters obtained from the transesterification of triglyceride oils and fats with short-chain alcohols (ethanol or methanol), and glycerol is a by-product of this process (Knothe, 2010). Biodiesel production has increased considerably in recent years. Europe is the largest producer of biodiesel, but Brazil has shown the greatest recent increase in production rate, from 736 m^3 in 2005 to 2.4 million m^3 in 2010 (Pimentel et al., 2006; Anp, 2014). The growth of biodiesel production in Brazil follows the trend in the consumption of diesel B6 (a mixture composed of 94% diesel A and 6% biodiesel) and B7 (composed of 93% diesel A and 7% biodiesel). The production of 2.9 billion litres of B6 and B7 in 2013 rose to 3.5 billion litres by December, and in 2015, production of B7 may reach 4.3 billion litres (Anp, 2014). For every 100 L of biodiesel produced, approximately 10 L of glycerin are generated. In 2010, 257,900 m^3 of glycerin were generated as a by-product of the total biodiesel production in Brazil (Anp, 2014). The demand for glycerin in Brazil is less than the amount that is produced, and the unused portion represents a major environmental liability.

*Corresponding author. E-mail: rejanne.lima.arruda@hotmail.com. Tel: (62)82245730.

Glycerin is a substance with a variety of applications; it can be used in the food industry as a food additive owing to its characteristic as a stabilizer, antioxidant, sequestering agent, emulsifier, and wetting agent (Bueno and Silva, 2012). The glycerin obtained by the transesterification of vegetable oils shows impurities such as water, alkaline catalysts, unreacted alcohol, and fatty acids (Motta and Pestana, 2011), which may limit its use in certain areas. Therefore, pre-purification is necessary and is usually performed using acids. Glycerin shows physicochemical properties that enable its use in agriculture, particularly as an adjuvant in bio-control products (Tinos et al., 2010).

The herbicide Togar is formulated for basal treatment, and is effective in controlling semi-woody shrubs and shrub weeds. It is applied via the stem and appears to be quite effective in controlling the weed *Memora peregrina*, which is difficult to control and has a high rate of infestation in pastures. It typically uses diesel oil as a vehicle for application, and this increases the cost of pulverization and causes serious environmental problems, since it is derived from petroleum. Given the surplus of glycerin and the need to replace diesel oil as a solvent for the application of Togar with a cheaper and less aggressive product, it is important to study the use of glycerin derived from the synthesis of biodiesel, and particularly its applications as a vehicle for applying the herbicide Togar. For herbicide applications, glycerin needs to undergo a process of adaptation with respect to its physicochemical characteristics, including a pre-purification process, mixing with emulsifiers to ensure viscosity, hydrophilic-lipophilic balance, surface tension, stability, and other essential features. Information regarding the use of glycerin in herbicide applications is limited. Therefore, it is necessary to conduct studies that contribute to environmentally sound applications of glycerin. This study aimed to develop oil-in-water (O/W) emulsions via crude glycerin treated with H_3PO_4 for use as a vehicle for application of the herbicide Togar.

MATERIALS AND METHODS

Crude glycerol was obtained from Biodiesel Biotins Industry (Paraiso-TO, Brazil). The glycerol was derived from transesterification by basic catalysis of biodiesel feedstock including soybean oil using sodium hydroxide as a catalyst, and the alcohol used was methanol. The work was developed in the laboratory of Marlebologia at the Federal University of Tocantins, Campus Gurupi. This work was divided into four steps: I, Pre-crude glycerin purification and physicochemical characterization; II, preparation of emulsions, physicochemical characterization, and stability testing; III, dilution of stable emulsions and physicochemical characterization of the grout application process; IV, incorporation of the herbicide Togar in dilute emulsions and physicochemical characterization. The characterization results were subjected to regression analysis using SigmaPlot 10.1.

Purification and characterization of pre crude glycerin

The pre-purification of glycerin was performed using two concentrations of phosphoric acid (85%) (4% and 6% v v^{-1}). The pre-purification reaction was performed according to the methods of Rehman et al. (2008) for a period of 1 h. Samples of glycerides and unsaturated fatty acids were separated and stored in sealed vials for later use in the preparation of emulsions. The crude glycerin and pre-purified glycerin with phosphoric acid (85% PA- A.C.S. SYNTH) concentrations of 4 and 6% were characterized based on pH (by inserting the electrode pHmeter model 210 MPa, to a constant value), conductivity (using of a portable conductivity meter, model 150 mCA calibrated with a standard solution) and viscosity (using rotary viscosity gauge analogic EEQ-9031 model range 1-20000 cP brand Edutec). The surface tension was determined by measuring the gout weight according to Lee et al. (2009) and the density was determined by using a pycnometer according to the methodology described by Rangel (2006). The soap level, ash, acidity, water content, methanol, matter organic non-glycerin (MONG), chlorides, saponification, and glycerol content were determined by a particular company, which follows the methodologies listed in Table 1.

Table 1. Methodologies used to characterize the glycerin.

Test	Method
Soap level	ASTM D 1613
Ash	ASTM D 874
Acidity	ASTM D 1613
Water content	ASTM E 203
Methanol	EN 14110
Matter organic non-glycerin (MONG)	ISO 2484
Chlorides	ADM
Saponification	ADM
Glycerol content	AOCS Ea 6-94 / Mod

*****Tests conducted by the laboratory Saybolt Croncremat.

Preparation of emulsions, characterization, and stability tests

Emulsions with pre-purified glycerin and 4 or 6% H_3PO_4 were prepared. The amount of distilled water used in the emulsions was 100 g. The emulsions were prepared in four replicates. Table 2 shows the amounts of each component used in each emulsion, that is, surfactants, fatty acids, and pre-purified glycerine.

Preparation of simple emulsion O/W

The O/W emulsions in the proportions described in Table 2 were prepared according to the methodology of Gharibzahedi et al. (2012) with some adaptations. The stability study was conducted according to the methods suggested by Brasil (2004). Centrifugation, heat stress, and ice thaw cycle tests were performed.

Dilution of emulsions, characterization, and physical chemistry

After the stability test, the emulsions were screened, and those that showed separation at the end of the stability process were discarded. After screening, five emulsions were considered stable if they showed no changes after treatment. Each of these was diluted with distilled water (50/50) to adjust the viscosity for subsequent field applications. After dilution, the emulsions were analysed for pH, conductivity, viscosity, density, and surface tension, according to the methodology described in step 1.

Table 2. Amounts of components used in each treatment. Further work will be performed to evaluate the efficiency of these emulsions in the field for weed control.

Treatment	SLS (10%) and AC (90%) / fatty acids / glycerin 4% (g)	Treatment	SLS (10%) and AC (90%) / fatty acids / glycerin 6% (g)	EHL
T01	6-20-30	T13	6-20-30	17.76
T02	8-20-30	T14	8-20-30	17.76
T03	10-20-30	T15	10-20-30	17.76
T04	12-20-30	T16	12-20-30	17.76
T05	6-30-20	T17	6-30-20	17.76
T06	8-30-20	T18	8-30-20	17.76
T07	10-30-20	T19	10-30-20	17.76
T08	12-30-20	T20	12-30-20	17.76
T09	6-40-10	T21	6-40-10	17.76
T10	8-40-10	T22	8-40-10	17.76
T11	10-40-10	T23	10-40-10	17.76
T12	12-40-10	T24	12-40-10	17.76

*SLS: Sodium lauryl sulphate; CA: Cetostearyl alcohol; EHL: hydrophilic lipophilic balance

Table 3. Representation of the physicochemical parameters of glycerin samples (Gurupi, 2013).

Parameter	Glycerin Samples		
	Crude	4%	6%
pH	6.4	4.8	2.5
Chloride (%)	6.86	2.53	5.18
Electrical conductivity (µS/cm)	1626.0	505.5	378.3
Ashes (%)	2.08	2.01	2.32
Soap content (KOH/g)	33.54	10.44	0.54
Viscosity (cP)	95	50	45
Total glycerol (%)	66.54	75.07	74.92
Acidity index (mg/KOH)	0.01	1.22	5.18
Density (g/cm^3)	1.36	1.17	1.15
MONG (%)	25.58	13.01	13.45
Methanol (%)	14.61	19.39	19.32
Humidity (%)	5.8	9.82	9.31
Surface tension (mNm^{-1})	28.5	28.3	29.6

4%, glycerin pre-purified with 4% H_3PO_4; 6%, glycerin pre-purified with 6% H_3PO_4; MONG, matter organic non-glycerin.

Addition of Togar in dilute emulsions

The Togar herbicide (8% v v^{-1}) was added to the distilled water emulsions. After the addition of the herbicide, the solutions were characterized for pH, conductivity, viscosity, density, and surface tension.

RESULTS AND DISCUSSION

Pre-crude glycerin purification and physicochemical characterization

Table 3 shows the experimental results regarding glycerin properties. The crude glycerin derived from the transesterification of soybean oil showed a slightly acidic pH because the biodiesel transesterification process occurred by basic catalysis. However, after the addition of phosphoric acid, the pH decreased, and the pre-purified glycerine with 4% H_3PO_4 showed a pH of 4.8 and with 6% H_3PO_4 showed a pH of 2.5. The chloride content was high in crude glycerin due to the salts of the catalyst (NaOH) used in the transesterification process. These salts also explain the high rate of conductivity in crude glycerin. Increased phosphoric acid in the samples caused decreased conductivity owing to the binding of the anion (PO_4^-) with the cation (Na^+), leading to sedimentation of the sodium phosphate salt in the bottom of the flask, and reducing the impurities and ions of the sample. With increased phosphoric acid, the glycerin reacts with the catalyst to form an insoluble salt, which is deposited at the bottom of the flask. The presence of the salts from the catalyst also explains the concentration of ash (inorganic material) (Quispe et al., 2013).

Lopes et al. (2014) studied the use of anionic and cationic resins for the removal of impurities from crude glycerine and noted that high conductivity indicates that a sample is rich in cations because rich anion solutions have lower conductivity. The soap content decreased when the amount of H_3PO_4 increased. The high soap content in the crude glycerin can be explained by the high amount of fatty acids in the sample. The soap results from an alkali reaction with a fatty material, and this occurs during biodiesel transesterification. With phosphoric acid, it is transformed again into free fatty acids, and these in turn are separated from the glycerin after pre-purification, resulting in a lower soap content in pre-purified glycerin (Gervajio, 2005). The viscosity decreased with increased phosphoric acid concentration. Thompson and He (2006) confirmed that this reduction

occurs because the fatty acids in crude glycerin react, thereby forming emulsions that increase viscosity; however, when glycerin is subjected to phosphoric acid, the fatty acids are separated and removed from the glycerin, resulting in a lower viscosity for pre-purified glycerin. As the concentration of phosphoric acid in glycerol increased, impurities were removed, and the purity of the samples increased.

In the pre-purified glycerine samples with 4 and 6% H_3PO_4, the acid values were 1.22 and 5.18 mg/KOH, respectively. The reaction of the acid with crude glycerin resulted in higher amounts of free fatty acids in the samples. The density of glycerin decreased during the process of pre-purification, also did the MONG, which dropped from 25.58% to less than 13.50%. After acidification, glycerin samples showed higher glycerol and lower MONG. Pre-purified glycerine with 4% H_3PO_4 had a MONG value of 13.01% and with 6% showed a MONG value of 13.45%. The difference in MONG values represents the value obtained by subtracting the glycerol content of ash and water contained in sample and multiplying by 100 (IUPAC, 1980).

Preparation of emulsions, characterization, and stability tests

Only five treatments were stable, two pre-cooked samples with purified glycerin with 4% H_3PO_4 and three pre-glycerin samples purified with 6% H_3PO_4. These stable samples were diluted 50:50 (50 g emulsion with 50 g of distilled water) and were analysed for pH, conductivity, viscosity, density, and surface tension before and after the addition of the herbicidal Togar (8% v v^{-1}). Figure 1 shows the results; we observed no significant difference between treatments in the pH, surface tension, or density. Treatments with pre-purified glycerine with 4% H_3PO_4 showed a pH of approximately 4.0 and those prepared with 6% H_3PO_4 showed pH values close to 2.0. Green and Beestman (2007) indicated that the changes in pH values of the vehicle for the application of herbicides after the addition of adjuvants varies widely and may increase, decrease, or remain steady. The final pH of the emulsions is of great interest because of the importance of this parameter for field applications of the herbicide. The vehicle generally exhibited an acidic pH value; some herbicides with low pKa reduce the pH of the solution and are therefore highly efficient. In addition, the lower pH is associated with a lower rate of hydrolysis and maintains moisture for longer periods (Rheinheimer and Souza, 2000). The current vehicle for the application of the herbicide Togar is diesel oil, which has a pH value of 4.36. Thus, the pH values of the emulsions of glycerin pre-purified with 4% H_3PO_4 were similar. The pH of 2.0 obtained in the preparation of emulsions with pre-purified glycerin with 6% H_3PO_4 are also satisfactory because it approaches the pKa of the herbicide that was subsequently added to the emulsions. By reducing the pH of the vehicle, K_{ow} values for the Togar herbicide increased, and thus lipophilicity increased. The addition of the herbicide reduced the conductivity of the samples. The amount of phosphoric acid used in the pre-purification of glycerine for the preparation of emulsions affected the conductivity, and the pre-purified glycerin with 6% H_3PO_4 increased conductivity. The conductivity is a factor that must be taken into account during the formulation of a vehicle to apply herbicides, since the amount of ions present in the solution interferes with the herbicide molecules, which can result in the formation of insoluble compounds and decrease its efficiency.

Carlson and Burnside (1984) and Rheinheimer and Souza (2000) examined the influence of high conductivity for vehicle herbicide application, and found that large amounts of ions may decrease the efficiency of herbicides and decrease the amount of active ingredient available for the reaction of 2,4-D ions Ca^{+2} and Mg^{+2} and the chelation of these ions by the herbicide glyphosate. The conductivity values of emulsions prepared with glycerin are relatively high, indicating a large amount of ions. This occurs because glycerin still contains large amounts of ions even after the process of pre-purification. None of the treatments showed a conductivity value close to the value of diesel (0.1 µS/cm). The viscosity of T8 increased after the addition of the herbicide, from a value of 27.13 to 64.98 cP, and the other treatments showed a reduced viscosity after the herbicide was added. The greatest reduction was observed in T24, which was reduced from 70.38 cP before adding the herbicide to 58.48 cP after adding the herbicide.

The pulverization process to convert a liquid into droplets and the final destination of these droplets depends on the physicochemical properties of the solutions used (Prokop and Kejklicek, 2002). The utility of the vehicle is directly related to the solution viscosity and flow. In addition, characteristics such as stability and density also influence the drop formation process, which is essential for the successful application of an herbicide (Carlson and Burnside, 1984). The viscosity is important in determining the droplet size and the flow of the solution, but higher values impede the passage of the solution through the spray nozzle. The viscosity of diesel oil when the temperature of 25°C is 4.9 cps. For the emulsions prepared, no treatment had viscosity values close to that of diesel. However, lower doses of surfactants were associated with lower viscosity values. The crude glycerin enabled the development of five stable emulsions with promising physicochemical characteristics for use as a vehicle for herbicide application. The viscosity and conductivity of the emulsions were slightly higher than those of diesel; however, the type of water and the amount and type of surfactant used during preparation may affect these parameter estimates.

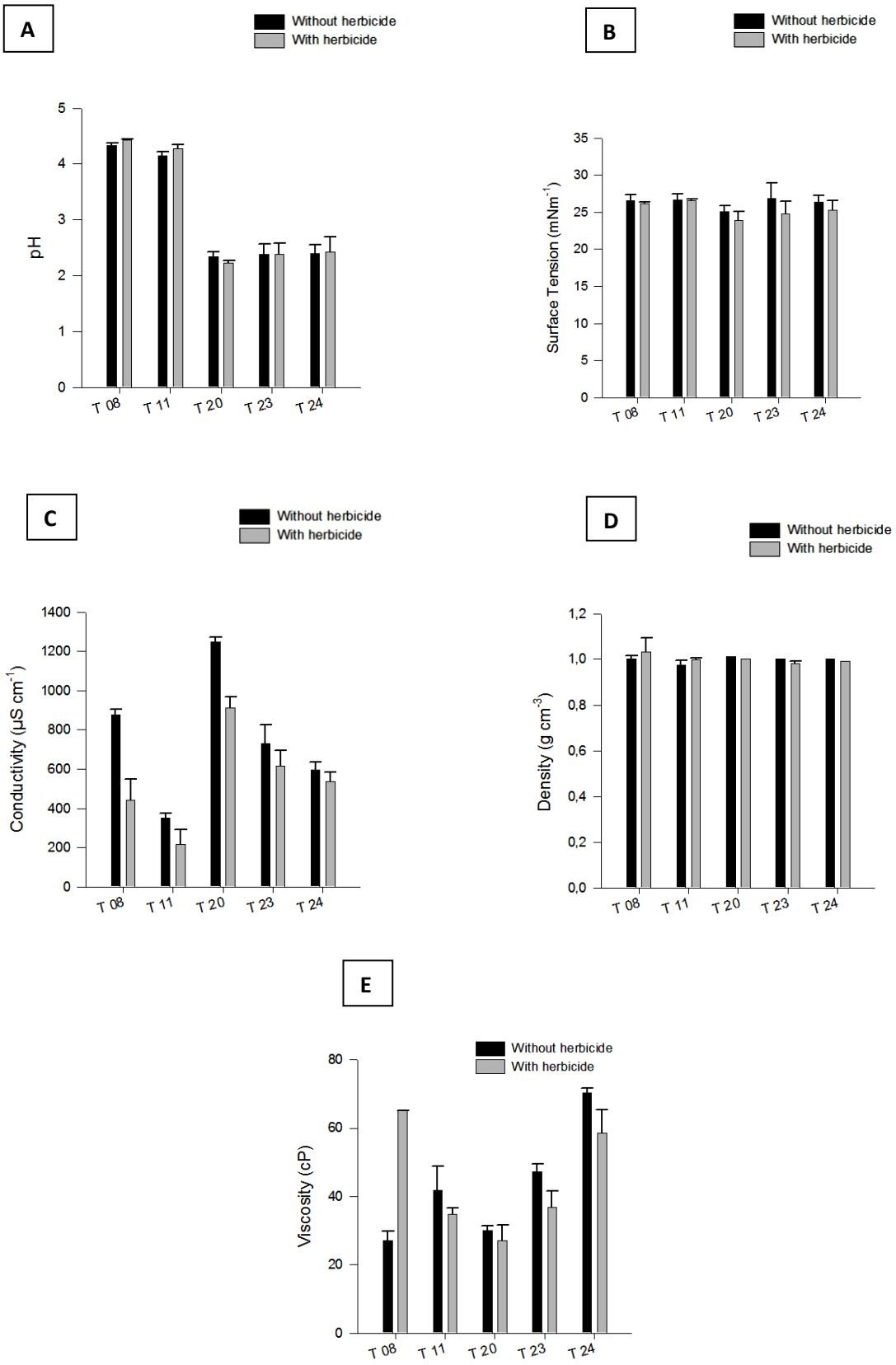

Figure 1. Characterization of the samples for each treatment group before and after the addition of the herbicide Togar. T6 and T11 (treatment with pre-purified glycerin with 4% H_3PO_4), T20, T23, and T24 (treatment with pre-purified glycerin with 6% H_3PO_4).

Conflict of interests

The authors did not declare any conflict of interest.

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