Produção de biodiesel utilizando cossolventes: uma revisão

Biodiesel production using co-solvents: a review

Producción de biodiesel utilizando cosolventes: una revisión

George Simonelli

ORCID: https://orcid.org/0000-0002-8031-1401

Universidade Federal da Bahia, Brazil

E-mail: gsimonelli@ufba.br

José Mario Ferreira Júnior

ORCID: https://orcid.org/0000-0003-4295-6417

Universidade Federal da Bahia, Brazil

E-mail:jmfj@ufba.br

Carlos Augusto de Moraes Pires

ORCID: https://orcid.org/0000-0003-4231-6495

Universidade Federal da Bahia, Brazil

E-mail: cap@ufba.br

Luiz Carlos Lobato dos Santos

ORCID: https://orcid.org/0000-0003-3824-7802

Universidade Federal da Bahia, Brazil

E-mail: lclsantos@ufba.br

Resumo

O biodiesel é um biocombustível renovável e biodegradável, obtido geralmente pela transesterificação de materiais graxos. Em razão de sua importância na diversificação da matriz energética dos países, diversas pesquisas têm sido realizadas para melhorar seu processo produtivo. Uma das tecnologias desenvolvidas consiste no uso de cossolventes no processo. Os cossolventes diminuem a resistência à transferência de massa entre o óleo e o álcool durante a reação química. Neste artigo, foi apresentada uma revisão da literatura sobre a produção de biodiesel utilizando cossolventes. A pesquisa reuniu informações sobre diversos trabalhos relevantes no tema, com o intuito de mostrar o estado da arte, as substâncias mais empregadas como cossolventes e as condições das variáveis de processo que resultam em elevados rendimentos em ésteres. Na catálise básica homogênea de óleos

vegetais, o hidróxido de potássio é o catalisador mais empregado. Sua faixa de aplicação varia normalmente de 0,5% a 1,8% em relação à massa de óleo. O tempo de reação pode variar de 10 minutos a 2 horas, a temperatura, de 25 °C a 100 °C, a razão molar de álcool para óleo, de 3:1 a 12:1, e a quantidade de cossolvente, até 30% (m/m), ou em algumas casos, até razão molar de cossolvente para álcool de 0,7:1.

Palavras-chave: Transesterificação; Ésteres de ácidos graxos; Variáveis de processo.

Abstract

Biodiesel is a renewable and biodegradable biofuel, generally produced by the fatty materials transesterification. Due to its importance in the diversification of the energy matrix of countries, various studies have been carried out to improve its production process. One of the technologies developed is the use of co-solvents in the process. The co-solvents decrease the mass transfer resistance between the oil and the alcohol during the chemical reaction. In this paper, a review of the literature on the biodiesel production using co-solvents was presented. The research gathered information about various studies that are relevant to the theme, aiming to show the state of the art, the substances most used as co-solvents, and the conditions of the process variables that result in high yields of fatty acid methyl esters (FAME). In the homogeneous basic catalysis of vegetable oils, potassium hydroxide is the most used catalyst. Its range of application normally varies from 0.5% to 1.8% in relation to the mass of oil. The reaction time may vary from 10 minutes to 2 hours, the temperature from 25 °C to 100 °C, the molar ratio (MR), from 3:1 to 12:1, and the amount of 30% (w/w) co-solvent, or in some cases up to 0.7:1 co-solvent to alcohol molar ratio.

Keywords: Transesterification; Fatty acid esters; Process variables.

Resumen

El biodiesel es un biocombustible renovable y biodegradable, generalmente obtenido atraves de la transesterificación de materiales grasos. Debido a su importancia en la diversificación de la matriz energética de los países, se han realizado varias investigaciones para mejorar su proceso productivo. Una de las tecnologías desarrolladas es el uso de cosolventes en el proceso. Los cosolventes disminuyen la resistencia de transferencia de masa entre el aceite y el alcohol durante la reacción química. En este artículo, presentamos una revisión de la literatura sobre la producción de biodiesel utilizando cosolventes. La investigación reune un compendio de información sobre varios trabajos relevantes, con el fin de mostrar los avances de investigación, de las sustancias más utilizadas como cosolventes y las condiciones de las

variables del proceso que dan como resultado altos rendimientos de ésteres. En la catálisis básica homogénea de aceites vegetales, el hidróxido de potasio es el catalizador más utilizado. Su rango de aplicación generalmente varía de 0,5% a 1,8% con respecto a la masa de aceite. El tiempo de reacción puede variar de 10 minutos a 2 horas, la temperatura de 25 °C a 100 °C, la relación molar de alcohol a aceite de 3:1 a 12:1 y la cantidad de cosolvente hasta 30% (p/p), o en algunos casos, hasta una proporción molar de 0,7:1 de cosolvente a alcohol.

Palabras clave: Transesterificación; Ésteres de ácidos grasos; Variables del proceso.

1. Introduction

In recent decades, increased fossil fuels consumption has been singled out as a major cause of air pollution and global warming. Negative impacts of global warming include, for example, the greenhouse effect intensification, the disappearance of species of flora and fauna, rising sea levels and climatic changes, such as prolonged droughts or heat waves, severe storms, windstorms and floods (Anuar & Abdullah, 2016; Chattopadhyay & Sen, 2013). In this context, the development of alternative fuels is a way of reducing dependence on fossil fuels.

Biofuels, such as bioethanol and biodiesel, are important alternatives for total or partial replacement of fossil fuels. Biodiesel is a renewable, biodegradable, non-toxic biofuel and can be used in diesel cycle engines without the need for modifications. Compared to petroleum diesel, biodiesel has a high flash point (>150 °C), higher combustion efficiency, good lubrication and lower emission of pollutants, such as CO, CO_2, SOx and particulates (Atabani et al., 2012; Martinot, 2006; Peters &Thielmann, 2008; Wassell Jr & Dittmer, 2006).

From the chemical point of view, biodiesel is defined as alkyl monoesters of long chain fatty acids. Generally, the same it is obtained from vegetable oils or animal fat. Soybean oil, canola oil, cotton oil, *jatropha* oil; bovine, swine, or fish fat, etc. may be used. Oil or fat accounts for approximately 70% of the total cost of biodiesel production. Therefore, the choice of raw material is an important factor for enabling the process (Balat, 2009; Ma & Hanna, 1999; Murugesan, Umarani, Subramanian, & Nedunchezhian, 2009).

The most commonly used chemical reaction for the transformation of oils and fats into biodiesel is transesterification, also known as alchololysis. The transesterification can occur as a non-catalytic process, or by acid, basic or enzymatic catalysis. The choice of the catalyst depends on the free fatty acids (FFA) amount and water content in the fatty materials, as well

as its availability and cost (Mwangi, Lee, Chang, Chen, & Wang, 2015; Qiu, Zhao, & Weatherley, 2010; Vyas, Verma, & Subrahmanyam, 2010).

For the production of biodiesel on a commercial scale, the basic catalysts (KOH or NaOH) are the most used because of the low cost. Basic catalysis results in high yields in biodiesel using short time and milder reaction conditions. However, for this to happen, it requires the raw material to be free of free fatty acid (FFA) and water. When the FFA amount is raised, above about 5%, soap formation may occur (Li, Qiu, Yang, Sun, & Li, 2012; Stojković, Stamenković, Povrenović, & Veljković, 2014).

The chemical equations (1) to (4) show the overall reaction of alkaline transesterification with methanol and its three consecutive steps (Leung, Wu, & Leung, 2010; Rabu, Janajreh, & Honnery, 2013).

Global reaction: TG   3 MeOH ↔ G   3 FAME   (1)

Step 1:TG + MeOH ↔ DG + FAME   (2)

Step 2:DG + MeOH ↔ MG + FAME   (3)

Step 3:MG + MeOH ↔ G + FAME   (4)

As observed in the chemical equations, the reaction of transesterification is reversible and the products formed are glycerol (G) and methyl esters of fatty acids (FAME or Biodiesel), reaction 1. In the first stage (reaction 2), the triglycerides (TG) are converted into diglycerides (DG) and FAME. The reaction takes place using excess alcohol, usually methanol (MeOH) or ethanol, so that the equilibrium is satisfactorily shifted towards the formation of products. In the second stage (reaction 3), the diglycerides are converted into monoglycerides (MG) and FAME. And finally, in the third stage (reaction 4), the monoglycerides are transformed into glycerol and FAME. When basic catalyst is used, the alcoholization of the triglyceride obeys the SN_2 mechanism. Industrially, the reaction generally occurs in batch reactors. The conditions normally controlled in the reaction are temperature, time, molar ratio, amount of catalyst and stirring speed (Brennan & Owende, 2010; Lim & Teong, 2010; Meher, Sagar, & Naik, 2006).

The soap formation (saponification) consumes the catalyst. Thus, it causes a decrease in the yield of alkaline transesterification and impairs the separation between biodiesel and glycerol. The water formed in saponification, or present in the raw materials, can hydrolyze the triglycerides to diglycerides, and consequently generate more FFA. In the biodiesel production by alkaline transesterification, the acid value of the raw material should be less

than 1 mg KOH / g, and the water content, less than 0.06 wt.%. The need for pre-treatment of the raw material raises energy consumption and the costs of operation and production.

Acid catalysis is used when there is high concentration of FFA in the raw material, so that there is no soap formation (Haas, Scott, Foglia, & Marmer, 2007; Helwani, Othman, Aziz, Fernando, & Kim, 2009; Marchetti, Miguel, & Errazu, 2007; Santori, Di Nicola, Moglie, & Polonara, 2012). This chemical route requires the use of high molar ratios (12:1) and high reaction times (around 48 hours). The reaction rate is 4000 times lower than that observed in the basic catalysis in homogeneous medium (Fukuda, Kondo, & Noda, 2001; Veljković, Stamenković, & Tasić, 2014).

In alcoholysis, regardless of the type of catalyst chosen, the reactants that participate in the reaction do not form a single phase in the reaction medium. Alcohol and oil are immiscible. This results in a heterogeneous reaction at the interface formed between these components, thus, the reaction rate is low (Araújo, de Andrade, e Silva, & Dupas, 2013; Atadashi, Aroua, Aziz, & Sulaiman, 2012; Sadeghinezhad et al., 2013). The difficulty of mass transfer between the immiscible components causes low reaction velocity, especially at the beginning of the process. The use of mechanical stirrers and the increase of the reaction temperature, close to the alcohol bubble point, can solve this problem; however, they increase energy consumption and operating costs. A temperature increase of 10 °C increases the solubility of the components (alcohol and oil) from 2 to 3% by mass (Atadashi et al., 2012; Ferella, Di Celso, De Michelis, Stanisci, & Vegliò, 2010; Khan, Yamsaengsung, Chetpattananondh, & Khongnakorn, 2015; Lotero et al., 2005; Ma, Clements, & Hanna, 1998).

A simple and effective technology that has attracted the attention of researchers to improve mass transfer is the use of co-solvents in transesterification. The co-solvent application, when in an adequate quantity, benefits the process by increasing the solubility between oil and alcohol mutually, and by being effective in reducing time, amount of catalyst, molar ratio and / or reaction temperature (Alhassan, Kumar, Bugaje, Pali, & Kathkar, 2014; Luu et al., 2014; Okitsu, Sadanaga, Takenaka, Maeda, & Bandow, 2013). Amid different studies, Thanh, Okitsu, Boi and Maeda (2012) and Okitsu et al. (2013) studied the use of acetone as a co-solvent. Alhassan et al. (2014) employed tetrahydrofuran as a cosolvent. Luu, Truong et al. (2014) investigated the use of diethyl ether, and Babaki, Yousefi, Habibi, Mohammadi and Brask (2015) studied chlorobenzene as a co-solvent. Other co-solvents present in scientific works are: 2-propanol, ethyl acetate, 1.4-dioxane, dibutyl ether, tert-butyl methyl ether and diisopropyl ether. Ethers are good co-solvents because they can lower the

interfacial tension between alcohol and oil because the molecules have a satisfactory balance between the polar and nonpolar parts (Casas, Fernández, Ramos, Pérez, & Rodríguez, 2010).

In this paper, our objective was to present the state of the art of biodiesel production using co-solvents. Furthermore, we show the most commonly used substances as co-solvents, and the conditions of the process variables that result in high yields of FAME.

2. Production of biodiesel using co-solvents

In biodiesel production process the co-solvents addition, when in adequate quantity, raises the specific mass of the mixture and the solubility between oil and alcohol. This is desirable because it provides a homogeneous reaction system and decreases the resistance to mass transfer in the boundary layer formed between the reactants. With the formation of an emulsion, it is possible to accelerate the chemical reaction by increasing the percentage of FAME in a short period of time. Through the use of co-solvents it is possible to reduce not only the reaction time, but also the alcohol:oil MR, the temperature, the amount of catalyst, and consequently the costs of production and operation. Some studies use room temperature satisfactorily when co-solvents are used Alhassan et al. (2014) and Luu et al. (2014).

It is advisable to choose co-solvents that have a bubble point close to the alcohol employed in the process. This facilitates recovery of the co-solvent since it can occur along with recovering excess alcohol. Some of the widely used co-solvents are: hexane, acetonitrile, petroleum ethers, isopropanol, tetrahydrofuran, ethyl acetate, etc. Because of their toxicity and danger, the co-solvents must be completely removed from biodiesel and glycerol (Abbaszaadeh, Ghobadian, Omidkhah, & Najafi, 2012; Mohammed-Dabo, Ahmad, Hamza, Muazu, & Aliyu, 2012; Pardal, Encinar, González, & Martínez, 2010). Through this research, we have found in the literature scientific works that use co-solvents in biodiesel production from different raw materials and chemical routes (Table 1).

Co-solvents have been used to produce biodiesel from different edible and non-edible fatty materials, such as soybean oil, sunflower oil, rapeseed oil, *jatropha curcas* oil, cottonseed oil, waste oil, palm oil, etc. The choice of the fatty material depends on the availability in each country. Using microreactors, Chueluecha, Kaewchada and Jaree (2017) investigated the production of biodiesel from palm oil with isopropanol as a co-solvent. The catalyst employed was calcium oxide. When investigating the influence of the co-solvent amount, methanol to oil MR and residence time in the microreactor, the authors observed that to produce 99% in DMF the optimum experimental conditions were 6.5 minutes, 65 °C,

14.5% of isopropanol relative to the mass of oil and molar ratio of 20:1. The use of microreactors increases the reaction rate in heterogeneous catalysis, decreases energy consumption and molar ratio. These reactors facilitate mass transfer by decreasing the distance required for diffusion of the molecules involved in the reaction.

Palm oil transesterification with methanol was performed by Roschat, Siritanon, Kaewpuang, Yoosuk and Promarak (2016) with calcium oxide as a catalyst and different co-solvents (acetone, 1-propanol, 2-propanol, tetrahydrofuran, ethanol and ethylene glycol). To produce $98.5 \pm 1.5\%$ in FAME they used 65 °C, 90 minutes reaction, tetrahydrofuran to methanol volumetric ratio of 10%, methanol to oil molar ratio of 12:1 and 5% CaO to mass of palm oil.

Using ultrasound for emulsification and increasing the interfacial area between the reactants, Thanh et al. (2012) and Okitsu et al. (2013) made use of acetone as a co-solvent in the transesterification of cooking oil, canola oil, catfish fat and jatropha curcas L. When studying the optimal reaction conditions, they verified that 98% of FAME is obtained after 30 minutes of reaction at 25 °C using a methanol molar ratio of 4.5:1, 1.0% KOH and 25% of acetone in relation to the mass of raw material. The use of ultrasound allowed the production of high quality biodiesel through a process with lower energy and material consumption. The authors pointed out that the separation time between biodiesel and glycerol was high (4 hours).

Fadhil, Al-Tikrity and Albadree (2015) produced biodiesel from transesterification of fish oil (*cyprimus carpio*) using hexane as a co-solvent. When studying the reaction conditions, they concluded that to obtain yields of 97.24 to 98.55% ($\pm$ 1.02%), one should use 50 °C, 30 minutes reaction, hexane to methanol molar ratio of 1.5:1, 5:1 methanol to oil MR and 0.60% KOH to the mass of oil. The authors stated that the production of biodiesel with co-solvent presented higher yield than the process without co-solvent. The biodiesel produced was as required by ASTM D6751 and EN 14214. When testing for blends between biodiesel and diesel, the authors verified that they were in accordance with ASTM D7467.

Encinar, Pardal and Sánchez (2016) investigated the use of rapeseed oil in biodiesel production with different co-solvents (diethyl ether, acetone, tert-butyl methyl ether, diisopropyl ether and tetrahydrofuran). Seven catalysts were used: KOH, Ba $(OH)_2$, LiOH, p-TsOH, $ZnCl_2$, $AlCl_3$ and BF_3. When studying the reaction conditions, they verified that 97-98% in FAME is obtained at the temperature of 30 °C, 120 minutes of reaction, 700 rpm, co-solvent to methanol molar ratio of 1:1, molar ratio of 9:1 and 0.7% KOH to the mass of oil.

Wu et al. (2016) used diethyl ether as a co-solvent in the biodiesel production of soybean oil. In addition, they employed bentonite as a moisture adsorbent during the chemical reaction. When studying the reaction conditions, they obtained a maximum FAME yield of 98.35% ± 0.69% for the molar ratio of diethyl ether to methanol of 0.56:1, molar ratio (methanol to oil) of 5.65:1 and 1.07% NaOH relative to the oil mass. By means of kinetic and thermodynamic analysis, they determined that the activation energy of the reaction is 23.73 kJ/mol.

Tetrahydrofuran is the most commonly used co-solvent when methanol is chosen as process alcohol. This is because the bubble temperature and the vaporization enthalpy of tetrahydrofuran have values close to those of methanol. Methanol has a bubble point of 64.6 °C and vaporization enthalpy of 28.72 kJ / mol. Tetrahydrofuran, however, has values of 65.8 °C and 28.83 kJ / mol. As a consequence, tetrahydrofuran can be readily recovered along with excess methanol by heating the mixture obtained at the end of the chemical reaction (Ataya, Dube, & Ternan, 2006; Boocock, Konar, Mao, & Sidi, 1996; Guan, Kusakabe, Sakurai, & Moriyama, 2009; Guan, Sakurai, & Kusakabe, 2009; Hancsók, Kovács, & Krár, 2004; Karmee & Chadha, 2005; Kumar, Ravi, & Chadha, 2011).

Soybean oil and rapeseed oil mixture transesterification using methanol and sodium hydroxide as the catalyst was studied by Qiu, Li, Yang, Li and Sun (2011). When studying the reaction conditions of the process, the authors observed that the optimum yield, 94% in DMF, was obtained for the bulk mixture of 50% of each oil, 55 °C, 5 grams of hexane, 2 hours of reaction, methanol to oil MR of 5:1 and 0.8% of catalyst (NaOH) relative to the mass of oil.

Guan, Sakurai and Kusakabe (2009) produced biodiesel from sunflower oil at 25 °C using KOH as a catalyst and various co-solvents as facilitators of oil-alcohol contact. The co-solvents used were dimethyl ether, diethyl ether, tetrahydrofuran and tert-butyl methyl ether. The results showed that the addition of co-solvent in the molar ratio of approximately 1:1 (dimethyl ether:methanol) improved the reaction rate to the 6:1 methanol:oil molar ratio. Dimethylether was considered the best co-solvent because it is readily recovered at the end of the process. The complete conversion of the oil into biodiesel occurred for 20 minutes of reaction. Without the co-solvent, under the same conditions the yield was 78%.

Transesterification *in-situ* of dehydrated sludge using hexane and xylene as the co-solvent was studied by Choi et al. 56 Using hexane as the co-solvent, the biodiesel yield was 3.28%, using xylene, the yield was 8.12%.

Table 1 - Experimental conditions of the papers of different authors

Reference	Feedstock	Catalyst	Time (min)	Temperature (°C)	Molar Ratio	Co-solvent	Yield (%)
Chueluecha, Kaewchada and Jaree (2017)	soybean oil	30 mg CaO	6.5	65	20:1	iso-propanol: 14,5 %m	99
Roschat et al. (2016)	palm oil	5% CaO	90	65	12:1	Tetrahydrofuran: 10 %V (in methanol)	98.5 ± 1.5
Okitsu et al. (2013)	various*	1% KOH	30	25	4.5:1	Acetone: 25 %m	98
Fadhil, Al-Tikrity and Albadree (2015)	cyprinus carpio fish oil	0.6% KOH	30	50	5:1	MR 1.5:1 (n-hexane:methanol)	97.24-98.55
Wu et al. (2016)	soybean oil	1.07% NaOH	30	34	5.65:1	MR 0.56:1 (diethyl ether:methanol)	98.35
Guan, Sakurai and Kusakabe (2009)	sunflower oil	1% KOH	10	25	8:1	MR 0.7:1 (Tetrahydrofuran:methanol)	100
Religia and Wijanarko (2015)	marine microalgae	2% KOH	240	60	400:1	VR 1:1 (n-hexane:methanol)	90.94
Zhang et al. (2015)	microalgal biomass	0.6 mL H_2SO_4	120	90	-	VR 1:2 (n-hexane:ethanol 75%)	90.02
Luu, Truong et al. (2014)	jatropha curcas oil	1% KOH	30	40	6:1	Acetone: 20 %m	99
Rahimi et al. (2016)	soybean oil	1% KOH	0.15	57.2	6:1	VR 1:0.45 (n-hexane:methanol)	98.8
Lam and Lee (2013)	crude microalgae lipid	31% H_2SO_4	180	60	60:1	MR 1:4 (tetrahydrofuran:methanol)	95
Alhassan et al. (2014)	cotton oil	0.75% KOH	10	55	6:1	10% (v/v): dichlorobenzene and acetone in methanol	98
Barekati-Goudarzi, Boldor and Nde (2016)	Chinese tallow tree seeds	1.74% NaOH	20	58.1	2.98:1	3% (v/m) (n-hexane/Chinese tallow tree seeds)	89.19
Guan et al. (2016)	waste vegetable oil	4% $AlCl_3$	90	120	20:1	5.1 MPa CO_2	72.21
Parida, Sahu and Misra (2017)	soybean oil	1% NaOH	30	50	3:1	30% (m/m) diesel:oil	92
Singh, Yadav and Sharma (2017)	waste vegetable oil	1.2% $Ca_2Al_2O_5$	25	55	6:1	20% (m/m) acetone	97.98
Han, Cao and Zhang (2005)	soybean oil	-	10	280	24:1	14.3 MPa of CO_2	98
Encinar, Pardal and Martínez (2012)	rapeseed oil	0.7% KOH	60	100	12:1	MR 1:0.7 (methanol:n-hexane)	99.9
Encinar, Pardal and Sánchez (2016)	rapeseed oil	0.7% KOH	120	30	9:1	Various** VR: 1:1 (co-solvent: methanol)	97-98
Qiu, Li, Yang, Li and Sun (2011)	soybean oil + rapeseed oil	0.8% NaOH	120	55	5:1	n-hexane: 5 g	94
Luu, Takenaka et al. (2014)	waste cooking oil	1% KOH	30	40	5:1	Acetone: 20 %m	98

*waste cooking oil. rapeseed oil. catfish and jatropha curcas oil

** acetone. diethyl ether. dibutyl ether. tert-butyl methyl ether. diisopropyl ether and tetrahydrofuran

- Does not apply to research

Luu, Takenaka et al. (2014) studied the production of biodiesel from kitchen waste oil in a small pilot plant (5 liters). Acetone was used as a co-solvent. Based on the research, the authors reported that the optimal transesterification condition occurred at 40 °C, 30 minutes, methanol to oil molar ratio of 5:1, 20% acetone to the oil mass and 1% KOH in relation to the oil mass.

Religia and Wijanarko (2015) studied the extraction of lipids from marine microalgae (Nannochloropsis sp) and the simultaneous transesterification using co-solvent (hexane). In the study, the researchers found that to produce high-yield biodiesel (90.9% in esters), methanol to hexane ratio of 1:1, methanol molar ratio of 400:1 and reaction time of 4 hours should be used.

Zhang, Li, Zhang and Tan (2015) investigated the direct transesterification of microalgae for biodiesel production. The process was studied using hexane to facilitate the extraction of lipids from the biomass and to increase the solubility between alcohol (ethanol) and triglycerides. To obtain the conversion of 90.02% ($\pm$0.55% by mass), the authors used 90 °C, 2 hours reaction, 6 mL hexane, 0.6 mL H_2SO_4 and volumetric ratio of hexane to ethanol of 1:2.

Luu, Truong et al. (2014) used jatropha curcas L. for the synthesis of biodiesel. As the oil used in the study had high acidity, the researchers esterified the raw material. The experimental conditions of esterification of free fatty acids were considered optimized at 65 °C, 60 minutes, methanol to oil molar ratio of 6:1, 1% H_2SO_4 and 30% acetonitrile as a co-solvent relative to the oil mass. After reducing the acidity of the material from 15.93% to 2% (by mass), 99% FAME was obtained for 30 minutes of transesterification reaction, 40 °C, methanol to oil molar ratio of 6:1, 1% of KOH and 20%, relative to the mass of oil, of acetone as a co-solvent. Taking into account standards EN 1424 and JISK 2390, the biodiesel produced was in accordance with the requirements for FAME yield, amount of water and free fatty acids.

Biodiesel was produced by Rahimi, Mohammadi, Basiri, Parsamoghadam and Masahi (2016) using a microtube reactor. The researchers used three different angles (45°, 90° and 135°) of confluency between oil, potassium methoxide and hexane (co-solvent). The effect of the type of mixture, volumetric ratio of oil:alcohol, residence time in the microtubes, reaction temperature and volumetric ratio of hexane to methanol was studied through an experimental design of the central composite design type. The optimal condition obtained by analyzing the empirical mathematical model was 98.8% in FAME for the confluence angle of 45°,

residence time of 9.05 seconds, hexane to methanol volumetric ratio of 1:0.45, temperature of 57.2 °C and volumetric ratio of methanol to oil of 3:1.

In investigating the kinetics and thermodynamics of the extraction of soybean oil using ethanol and mixtures of ethanol and biodiesel (co-solvent), Dagostin, Carpiné and Corazza (2015) concluded that the process is spontaneous ($\Delta S° > 0$), irreversible and endothermic ($\Delta H° > 0$). The higher molar ratios of biodiesel to anhydrous ethanol provided high yields at temperatures of 25 and 40°C. At 55 °C, the addition of biodiesel to ethanol did not improve the extraction yield. The researchers stated in their work that the second order kinetic model was the one that best fit the experimental data.

Lam and Lee (2013) investigated the production of biodiesel by esterification of viscous lipid from microalgae using H_2SO_4 as a catalyst. The researchers observed that the use of tetrahydrofuran as a co-solvent improved the reaction conditions of the process. Without co-solvent, 95% FAME yield required 60 °C, 6 hours, methanol molar ratio of 180:1 and 35% catalyst relative to the lipid mass. To obtain the same FAME yield using tetrahydrofuran, 60 °C, 3 hours, methanol:tetrahydrofuran:lipid molar ratio of 60:15:1, and 21% catalyst to mass of lipids was necessary.

Alhassan et al. (2014) produced cotton oil biodiesel by transesterification using different co-solvents (diethyl ether, dichlorobenzene and acetone). The researchers found that 55 °C, 10 minutes of reaction, 10% (v / v) dichlorobenzene and acetone in methanol and 0.75% (w / w) KOH over the mass of oil afforded high yields. The stirring speed and the oil:methanol molar ratio were maintained at 350 rpm and 1:6, respectively.

Using microwave, Barekati-Goudarzi, Boldor and Nde (2016) performed the optimization of biodiesel production from the seed fat of Chinese trees (Triadica Sebifera L.). The extraction of the fat occurred simultaneously with the transesterification using 60 mL of hexane. The authors stated that the optimum condition was obtained with 58.1 °C, 20 minutes, 3% (by volume) of methanol and 1.74% of NaOH in relation to fat mass.

Guan et al. (2016) produced biodiesel from waste cooking oil using ethanol, $AlCl_3$ as flocculant, for dehydration of the oil and as a catalyst (4% (m / m)). The CO_2 (5.1 MPa) was applied as a co-solvent. The authors achieved 72.21% conversion of oil to ethyl esters using 120 °C and 90 minutes of reaction. The mass ratio of ethanol to residual oil was 20:1.

Using ultrasound, Parida, Sahu and Misra (2017) investigated the production of biodiesel from soybean oil through transesterification. Diesel derived from petroleum was used as co-solvent of the process. A yield of 92% in FAME was achieved for ultrasound of 20 kHz and 750 W, methanol:oil molar ratio of 3:1, 50°C, 30 minutes, 1% NaOH and 30% diesel relative

to the mass of oil. The authors pointed out that the use of diesel as a co-solvent eliminated the need to remove it, making the process faster and cheaper.

Applying supercritical conditions, the Lim and Lee (2013) research showed that the use of co-solvents (CO_2 and pentane) improves the simultaneous extraction and transesterification of Jatropha Curcas L. oil. The simultaneous extraction and transesterification process is attractive for biodiesel production because it eliminates the pre-extraction and refining stages of vegetable oil. The choice of the co-solvent to be employed depends on factors such as availability and the conditions necessary for the process to result in satisfactory yields. The use of pentane, for example, enables the use of working pressures less than 8.0 MPa, unlike what occurs with CO_2.

When using acetone as co-solvent in the transesterification of cooking residual oil, Singh, Yadav and Sharma (2017) employed $Ca_2Al_2O_5$ as a catalyst. To obtain a high ester yield, 97.98%, it was necessary to use 55 °C, 25 minutes reaction, methanol molar ratio to kitchen waste oil of 6:1, 20% acetone to the mass of oil and 1.2% $Ca_2Al_2O_5$ in relation to the mass of oil.

Osmieri, Esfahani and Recasens (2017) designed and simulated in Aspen Plus[®] the continuous production of biodiesel by supercritical transesterification with methanol. The authors applied CO_2 as a co-solvent. The use of CO_2 allowed the reduction of the critical point of the reaction mixture.

Han, Cao and Zhang (2005) produced biodiesel under supercritical conditions using soybean oil, methanol and CO_2 as a co-solvent. The realization of the reaction under supercritical conditions with CO_2 led to the reduction of the methanol to oil MR, pressure and temperature. To obtain yields of 98% esters, 280 °C, 24:1 methanol to soybean oil MR, 10 minutes of reaction, 14.3 MPa and molar ratio CO_2 to methanol of 0.1:1, in the absence of KOH.

Encinar, Pardal and Martínez (2012) transesterified rapeseed oil using methanol under subcritical conditions, and hexane as a co-solvent. A 99.9% yield was obtained when using 100 °C, 0.7% catalyst to oil mass, 60 minutes and methanol to oil molar ratio of 12:1. The use of hexane as a co-solvent did not show improvement in yield for the conditions studied by the researchers (methanol to hexane MR from 1:0 to 1:0.7).

3 Process variables

3.1 Co-solvents

There are different co-solvents used in transesterification of fatty materials, for example, acetone, tetrahydrofuran, hexane, diethyl ether, chlorobenzene, 2-propanol, ethyl acetate, 1,4-dioxane, dibutyl ether, tert-butyl methyl ether and diisopropyl ether. Comparing the studied co-solvents, Roschat et al. (2016) found that tetrahydrofuran resulted in higher biodiesel yields than those obtained with the use of 1-propanol, 2-propanol, acetone, ethanol and ethylene glycol. Putting the co-solvents in order of increasing yield are: ethylene glycol <ethanol <acetone <2-propanol <1-propanol <tetrahydrofuran. From the chemical point of view, it can be stated that the higher the polarity, the lower the biodiesel yield. The polar solvents are readily solubilized in alcohol, but their solubility in oil is low.

In biodiesel production from the soybean oil and rapeseed oil mixture with methanol, Qiu et al. (2011) showed that the presence of small amount of hexane improved FAME yield.

Rahimi et al. (2016) observed that above the volumetric ratio of 1:0.45 hexane to methanol the FAME yield decreased. The authors attributed this to the dilution that the co-solvent causes in the reaction medium, which hinders the mass transfer of the starting reactants. Mass transfer affects the reaction rate because alcohol and oil are immiscible. The co-solvent can reduce the resistance to mass transfer, since it makes alcohol and oil miscible (Alhassan et al., 2014; Escobar, Demafelis, Pham, Florece, & Borines, 2008; Mohammed-Dabo et al., 2012; Zhang, Jin, Zhang, Huang, & Wang, 2012).

In studying the effect of hexane, ethanol, tetrahydrofuran, toluene, methyl acetate, ethyl acetate and chloroform as co-solvents, Lam and Lee (2013) chose tetrahydrofuran as the best co-solvent. In addition to having provided the highest yield among the chosen co-solvents, the authors highlighted the advantage of using tetrahydrofuran in methanol recovery. These two compounds have close boiling points, 66 °C and 64.6 °C, respectively. According to Lam and Lee (2013), increasing the co-solvent molar ratio (tetrahydrofuran) to methanol increases FAME yield to a certain extent. Up to the molar ratio of 0.25:1 the yield increased satisfactorily. For higher molar ratios (0.4:1 and 0.5:1) the yield changes were not significant in biodiesel production from microalgae viscous lipids. There is a certain amount of co-solvent required to completely solubilize the reactants. Above it, the addition of solvent does not improve the reaction rate because of the dilution of the reactants.

On the effect of the ratio between the amounts of hexane and methanol, Barekati-Goudarzi, Boldor and Nde (2016) stated that low amounts of methanol are favorable in increasing yield (3% by volume of hexane relative to fat mass). The increase in the amount of methanol in transesterification *in-situ* by microwaves decreases the yield due to the properties of the alcohol. Due to its high polarity, methanol absorbs microwave irradiation, preventing or limiting the absorption of irradiation by biomass seeds. This impairs the process of diffusion of the fatty material from the seeds to the reaction medium. Excess alcohol and low amounts of hexane and NaOH decrease the extraction rate and transesterification. Search results for Patil et al. (2011) show the same behavior.

When using acetone as a co-solvent, Luu, Takenaka et al. (2014) verified that by increasing its percentage in the reaction medium from 30 to 40%, there was a decrease in biodiesel yield. As the acetone concentration increased, the concentration of the reactants in the reaction medium decreased. Therefore, the reaction rate also decreased. In addition, excess acetone can dissolve part of the formed methyl esters, decreasing the yield.

Like other authors, Singh, Yadav and Sharma (2017) state that increasing the percentage of co-solvent increases yield to a certain extent. After this limit, there will be dilution of the starting reagents in the co-solvent. This raises the time required for the separation of biodiesel and glycerol. The separation of glycerol and excess alcohol is dependent on the concentrations of the components of the reaction mixture. At lower concentrations of co-solvent in the reaction medium, the chances of collisions between the co-solvent molecules and glycerol increase. This favors proper separation of glycerol by gravity.

 Parida, Sahu and Misra (2017) found that increasing the percentage of diesel as a co-solvent increases the transesterification yield. This is due to favoring the miscibility between oil and alcohol. The value of 30% of co-solvent was considered the best in the studied range of 10 to 40%.

According to Alhassan et al. (2014) In most cases, low volumes of co-solvents are used to improve yield in biodiesel production. An example of a co-solvent which is to be employed in higher percentages (30% v / v) is diethyl ether, which has little solubility in methanol.

By varying the volumetric ratio of methanol to hexane from 1:0 to 1:1 maintaining the other fixed reaction conditions, Religia and Wijanarko (2015) observed that the yield of the reaction increases by 6.2%. When the volumetric ratio is varied from 1:1 to 1:1.5 the yield of the reaction decreases. According to the researchers, excess hexane decreases the mass transfer between the lipid and methanol, which consequently decreases contact between the

reactants. The excess of co-solvent decreases the concentration of methanol and lipids in the reaction medium, also decreasing the heat transfer.

To perform the sludge transesterification, Choi, Song, Cha, and Lee (2014) found that replacing hexane with xylene as a co-solvent improved the mass yield of biodiesel production. The biodiesel mass yield was 3.28% when dehydrated slurry was transesterified using hexane. Transesterification of dry sludge using xylene as a co-solvent resulted in a mass yield of 8.12%. The researchers say that the use of xylene reduces the reaction time and methanol consumption when compared to that needed to obtain the same yield using hexane as a co-solvent. For Choi, Song, Cha, and Lee (2014), the use of xylene as a co-solvent reduces the reaction time and the consumption of methanol, being better than hexane at obtaining a certain yield. According to the researchers, the amount of methyl esters doubled when hexane was exchanged for xylene as a co-solvent.

When studying different co-solvents (acetone, butanol, ethyl ether, hexane, chloroform, carbon tetrachloride and petroleum ether) in the direct transesterification of microalgae, Zhang, Li, Zhang and Tan (2015) found that the best co-solvents were chloroform, petroleum ether and hexane. Hexane and petroleum ether are non-polar solvents miscible in triglycerides and in ethanol. The use of chloroform, due to its high polarity, allowed the breakdown of the cell wall of microalgae facilitating the extraction of lipids. Researchers have indicated hexane as the best co-solvent, because it is cheaper than petroleum ether, and more environmentally correct than chloroform. Like other researchers, Zhang, Li, Zhang and Tan (2015) agree that excess co-solvent reduces the mass transfer between lipids and methanol, also reducing heat transfer.

Guan, Sakurai and Kusakabe, (2009) observed that for each methanol to sunflower oil MR, there is a minimum molar ratio of co-solvent to methanol needed to make alcohol and oil miscible. The conversion of vegetable oil to biodiesel reaches maximum value in the minimum molar ratio of obtaining a single phase in the reaction medium. According to the researchers, excess co-solvent slows down the transesterification reaction due to dilution of the reactants. When the molar ratio of co-solvent to methanol is less than the minimum, the ester yield decreases because of the immiscibility between oil and alcohol. Combining the methanol to sunflower oil MR of 8:1 with the minimum molar ratio of any co-solvent (dimethyl ether, tetrahydrofuran, diethyl ether and tert-butyl methyl ether) to methanol, ten minutes is the time required to convert sunflower oil into biodiesel.

3.2 Molar ratio alcohol:oil

The alcohol:oil molar ratio can vary greatly. In this study, we observed values in the range of 2.98:1 to 400:1 (Table 1). The lowest molar ratio values (2.98:1 and 4.5:1) occur in the homogeneous basic catalysis using n-hexane and acetone as co-solvent (Barekati-Goudarzi, Boldor, & Nde, 2016; Okitsu et al., 2013). The highest values (400:1 and 60:1) were observed in the transesterification of microalgae (Lam & Lee, 2013; Religia & Wijanarko, 2015). According to the stoichiometry of the transesterification reaction, three moles of alcohol are required for each mole of triglycerides. Under the specific reaction conditions studied by Qiu et al. (2011), it was observed that the elevation of the molar ratio alcohol:oil up to 5.0:1 favors the increase in FAME yield. For molar ratios greater than 5.0:1, yield decreases. The excess of alcohol favors the displacement of the balance towards the formation of the products, but also favors the formation of monoglycerides. In turn, the monoglycerides increase the solubility of glycerol in biodiesel, decreasing the yield in FAME.

Lam and Lee (2013) concluded that in the presence of co-solvent (tetrahydrofuran) raising the methanol to lipids MR raises the FAME yield to a certain extent. For the molar ratios studied above 60 (80, 100 and 120) no significant changes in yield were observed. This was because the chemical balance was reached.

In the study by Singh, Yadav and Sharma (2017), the ester yield increased to the molar ratio of oil to methanol of 1:6. Above this molar ratio yield decreased. This occurred due to the solubilization of the glycerol in the excess alcohol, which hindered the separation between the phases (biodiesel and glycerol).

Parida, Sahu and Misra (2017) also stated that because the transesterification reaction is reversible, it is necessary to use excess alcohol. The increase of the molar ratio improved the yield of the chemical reaction using the ultrasound energy for the reaction mixture. The yield is raised for short reaction times as the molar ratio of alcohol:oil is increased. For high alcohol to oil molar ratios, the yield tended to be the same with or without the use of co-solvent.

According to Alhassan et al. (2014), the molar ratio oil:alcohol is one of the most important parameters of transesterification. The reaction is reversible, so excess methanol is needed to shift the balance towards the formation of products. The use of excess alcohol can considerably increase the time and energy consumption of the stage for separation between biodiesel and alcohol (Fadhil & Abdulahad, 2014; Feyzi, Hassankhani, & Rafiee, 2013). Religia and Wijanarko (2015), as well as other researchers, have also observed that increasing

the methanol to lipids MR shifts the equilibrium of the transesterification reaction towards the formation of the products.

Choi, Song, Cha, and Lee (2014) state that the use of xylene as a co-solvent reduces the consumption of methanol when compared to that required to obtain the same yield using hexane. Guan, Sakurai and Kusakabe, (2009) state that a high molar ratio is required to move the transesterification equilibrium towards the formation of the products. The chemical conversion of the oil into biodiesel decreases with the decrease of the methanol to oil MR, because the reaction is reversible. For the methanol to oil molar ratios of 6:1 and 8:1, the ester yield is raised with increasing reaction time.

3.3 Amount of catalyst

The production of biodiesel using co-solvents has been performed with homogeneous and heterogeneous catalysts. Most scientific research uses basic homogeneous catalysts, such as NaOH and KOH (Table 1). These catalysts have good availability and low cost. In addition, the use of NaOH and KOH allows the production of biodiesel under milder reaction conditions (Encinar, Pardal, & Sánchez, 2016; Parida, Sahu, & Misra 2017; Rahimi, Mohammadi, Basiri, Parsamoghadam, & Masahi, 2016; Wu et al., 2016; Zhang, Li, Zhang, & Tan, 2015). The homogeneous basic catalysts are used in approximately 1 % in relation to the mass of oil. Increasing the amount of catalyst causes an increase in biodiesel yield in the transesterification process to a certain extent. Qiu et al. (2011) showed that for 0.8% NaOH, relative to the oil mass, a yield of 94% was obtained. For higher amounts of catalyst, yield decreases. The explanation for this is that the high amount of base favors the formation of soap, which hinders the separation of glycerol and biodiesel. During the washing of biodiesel with warm water, more soap can be formed due to excess catalyst.

According to Lam and Lee (2013), the co-solvent increases the solubility of the reaction mixture and decreases the amount of catalyst required to accelerate the chemical reaction of biodiesel production. The researchers showed that 21% of H_2SO_4 in relation to the lipid mass of microalgae is sufficient to obtain a high yield in FAME (95%).

According to Barekati-Goudarzi, Boldor and Nde (2016), the excess catalyst in the reaction medium causes a decrease in biodiesel yield. The humidity of the reagents in the presence of excess alkaline catalyst leads to the formation of soap (saponification reaction), which explains the reduction of the yield in esters. Singh, Yadav and Sharma (2017) agree that yield increases with increasing amount of catalyst, but to a certain limit. In the study of

these authors, above 1.2% by mass of catalyst ($Ca_2Al_2O_5$) the yield decreases due to the formation of soap. This increases the viscosity of the reaction media and the resistance to mass transfer Oliveira Lima et al. (2012).

Parida, Sahu and Misra (2017) found that the increase in the percentage of catalyst (0.25, 0.5 and 1% NaOH) increases the proportion of methoxide ions that improves the yield of the reaction. Guan, Sakurai and Kusakabe, (2009) showed that the percentage of catalyst exerts a strong influence on the reaction rate. In the study of these researchers, the conversion of sunflower oil to esters increased with the increase of the amount of catalyst in the reaction medium. Alhassan et al. (2014) observed that increasing the catalyst mass from 0.25% to 0.5% relative to the mass of cotton oil considerably increases the yield of esters for different co-solvents. Above 0.75%, the yield of alcoholysis decreases dramatically for the different co-solvents studied (Feyzi, Hassankhani, & Rafiee, 2013; Takase et al., 2014).

3.4 Temperature

The transesterification temperature may vary widely (Table 1). The lower temperature (25 ° C) occurred in the homogeneous catalysis using KOH (Okitsu et al., 2013; Guan, Sakurai, & Kusakabe, 2009). The highest temperature (280 ° C) was used in biodiesel production with supercritical methanol Han, Cao and Zhang (2005). The transesterification rate is strongly temperature dependent. Qiu et al. (2011) have shown that the use of co-solvent provides increased yield by employing milder temperatures. Without the addition of co-solvent, at 150 °C, the authors obtained a yield of 80%. With the addition of 5 grams of hexane, varying the temperature from 40 to 70 °C, for the same raw material, and fixing the molar ratio and time, the yields ranged from 88.22 to 94.39%.

Raising the temperature increases the FAME yield to a certain extent. In the Lam and Lee (2013) study, the temperature rise was beneficial up to 60 °C. Above 60 °C, the methanol to lipids MR decreased due to the vaporization of methanol. This justifies the reduction of income in FAME. From 50 to 60 °C, the rise in temperature caused improvements in fat *Triadica Sebifera L.,* and increasing the solubility of the transesterification reagents with NaOH. Temperatures above 60 °C favored the formation of soap and evaporation of methanol, resulting in reduced yields of esters (Barekati-Goudarzi, Boldor, & Nde, 2016).

According to Brennan and Owende (2010) and Singh, Yadav and Sharma (2017), temperature is an important variable in the process of transesterification of oils and fats. The FAME yield increases to near the vaporization temperature of the alcohol employed in the

process. Above this temperature, the yield decreases due to the reduction of the amount of alcohol in the liquid phase (Yuan, Hansen, & Zhang, 2005).

Singh, Yadav and Sharma (2017) used acetone as a co-solvent. The authors showed that the yield of the reaction increased to 55 °C, ie, near the vaporization temperature of acetone, 56 °C. Above this, the yield decreased because the acetone evaporated and the reaction medium possibly started to have two phases, which made the mass transfer necessary for the occurrence of the chemical reaction difficult.

Alhassan et al. (2014) stated that the reaction temperature significantly affects FAME production. Depending on the co-solvents used, the reaction is favored by temperatures close to that of alcohol vaporization. Reaction temperatures above the alcohol vaporization condition usually reduce yield. While most studies report near-ambient temperatures for transesterification of vegetable oils with co-solvents, alcoholization of 10% (v / v) cotton-seed oil diethyl ether requires 55 °C for high yields to be achieved.

3.5 Time

The transesterification time can vary greatly. In this study, we observed a variation of 0.15 min to 240 min (Table 1). The lowest reaction times (0.15 min and 6.5 min) were obtained in microreactors using n-hexane and iso-propanol as co-solvents (Chueluecha, Kaewchada, & Jaree, 2017; Rahimi, Mohammadi, Basiri, Parsamoghadam, & Masahi, 2016). The largest transesterification times (180 min and 240 min) occurred in biodiesel production of from microalgae. This because it is necessary to extract the lipids from biomass (Lam & Lee, 2013; Religia & Wijanarko, 2015). Alhassan et al. (2014) found that the transesterification reaction using co-solvents can reach equilibrium and yield greater than 90% in a short time (10 minutes). For the use of diethyl ether, the ester yield was less than 80% in the first 10 minutes of reaction. In this case, the reaction balance took longer to be achieved.

The increase of the time favors the increase of the yield in biodiesel was observed by Qiu et al. (2011). For fixed reaction conditions, the authors showed the influence of reaction time. For 30 minutes, the production was 88% of biodiesel, for one hour, 93%, and for two hours, 94.32%. The researchers reported that there were no significant changes in yield for time greater than 2 hours.

When the transesterification time was raised from 4 to 6 hours, Religia and Wijanarko (2015) observed decreased yields of esters. The researchers explain in their study that this

may have occurred because of the shift of the equilibrium of the chemical reaction towards the formation of the reactants (reverse direction of the reaction), or the catalyst consumption with the saponification of FFA. Zhang, Li, Zhang and Tan (2015) also state that increasing the reaction time favors the reverse reaction and reduces the ester yield. Choi, Song, Cha, and Lee (2014) state that the use of xylene as a co-solvent reduces the consumption of methanol when compared to that required to obtain the same yield using hexane. Barekati-Goudarzi, Boldor and Nde (2016) did not observe significant changes in yield with the change in reaction time.

4. Conclusion

Co-solvents can be used in the transesterification to decrease the mass transfer resistance. The most studied co-solvents are acetone, tetrahydrofuran, hexane, diethyl ether, chlorobenzene, 2-propanol, ethyl acetate, 1,4-dioxane, dibutyl ether, tert-butyl methyl ether and diisopropyl ether. It has been observed that the ethers are good co-solvents.

The process variables that influence ester yield are: chemical species used as co-solvent, amount of co-solvent, time, temperature, amount of catalyst and molar ratio alcohol:oil. With the survey of the state of the art, it was observed that the studies dedicated to the use of co-solvents in the transesterification are concentrated in the investigation of the effectiveness of different co-solvents, as well as in the optimization of the operational conditions of the process, since the presence of the co-solvent can decrease the time, temperature and molar ratio of alcohol:oil required.

Most of the works found in the literature use homogeneous basic catalysis of vegetable oils. Potassium hydroxide is the most used catalyst. Its range of application normally varies from 0.5% to 1.8% in relation to the mass of oil. The reaction time may vary from 10 minutes to 2 hours, the temperature from 25 °C to 100 °C, the molar ratio, from 3:1 to 12:1, and the amount of co-solvent, to 30% (m / m), or in some cases up to 0.7:1 co-solvent to alcohol molar ratio.

Future papers should address the use of new co-solvents in biodiesel production. We believe that cheaper and non-toxic co-solvents are required. Furthermore, studies should be conducted to indicate the most suitable substances for different types of transesterification (enzymatic, homogeneous and heterogeneous).

Acknowledgement

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Porcentagem de contribuição de cada autor no manuscrito

George Simonelli – 25%

José Mario Ferreira Júnior – 25%

Carlos Augusto de Moraes Pires – 25%

Luiz Carlos Lobato dos Santos – 25%