Fusel Oil: Chemical Composition and an Overview of Its Potential Application

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Fusel oil (FO) is one of the by-products of the sugar-alcohol industry, which has application as an additional source of higher alcohols for the production of esters with flavoring, fuels and lubricants properties, as well as additives in petroleum-based fuels and in pesticide formulations. Thus, this review is focused on the characteristics of FO and its applications as an acyl acceptor in transesterification and esterification reactions for esters production, its addition to fossil fuels, and the herbicidal and fungicidal potential of the compounds presented in its chemical composition. The operating conditions of the process, results obtained, and patented applications in the food, cosmetic, transportation and agricultural sectors are also reported and discussed. Furthermore, main trends, challenges and recommendations are proposed in order to overcome the disadvantages of applying FO in the reported sectors, as well as alternatives for the development of new lines of research are suggested.

Keywords: acyl acceptor, by-products, esters, esterification, operating conditions, transesterification

1. Introduction

Ethanol is a biofuel derived from the fermentation of sugars, designed to reduce the environmental impacts resulting from fossil fuels. The main raw materials for the manufacture of ethanol are sugarcane, corn, sugar beet, potatoes, among others.[1] In Brazil, production is mostly made up of sugarcane, as the country is the largest producer of this crop in the world.[2]

Environmental and social concerns have had a beneficial impact on the Brazilian fuel ethanol program: pressures from nongovernmental organizations (NGO) and the United Nations (UN) on reduction of greenhouse gas (GHG) emissions have led to government regulations and incentives.[3] In this context, Brazilian legislation encourages, from Decree No. 76,593 of 1975 and Ordinance No. 75 of 2015, to meet the needs of the domestic and foreign market and the addition of 27% of anhydrous ethanol to gasoline,

respectively.[4,5] These incentives are aimed at complying with the agreement assumed by Brazil to reduce 43% of carbon emissions by 2030 signed to the Paris Agreement in 2015.[6]

The financial instability of the sugar, ethanol and electricity markets correspond to one of the most significant problems faced by ethanol production.[3,5-7] Thus, adding value to the by-products generated by the sugar-alcohol industry can contribute to maximizing profits in the manufacturing cycle. In obtaining 1000 liters of ethanol, 5 liters of fusel oil (FO) are generated,[8] which would correspond to ca. 165 million liters generated from the production of ethanol in Brazil in 2018,[1] which entails an environmental liability for companies, due to the high quantity and low demand.

FO is composed of a mixture of alcohols (isoamyl alcohol, ethanol, isobutanol and propanol) and water,[9,10] whose composition varies according to the raw material (for example: sugarcane, barley, corn, rice and sugar beet) used in the fermentation process of alcohol production, and to the efficiency of its separation from the fermented mixture.[11,12]

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FO has a high content of isoamyl alcohol (57.65-74%),[10,13,14] which enables its use as an acyl acceptor of trans- and esterification reactions for the production of esters with flavoring properties,[10,15] biolubricants,[16,17] and fuels,[18,19] as well as a fossil fuel additive.[20,21] In addition, FO can act as an herbicide, since its application causes the eradication of weeds,[22,23] and fungicide, as its chemical composition presents compounds with antimicrobial activity, such as coctanoic acid,[24] pyrazines,[25] nerolidol,[26] and farnesol.[27] Recently, Mendoza-Pedroza *et al.*[12] evaluated the phase equilibrium of the recovery process of isoamyl alcohol from FO and indicated that it is possible to obtain this alcohol at high purity and low cost using a dividing wall column, that represents a good option for FO distillation due to the benefits in terms of reduction in the total annual cost over the traditional distillation.

With that in mind, the purpose of this overview is to revisit the distinct features of FO and discuss its potential application. Therefore, the industrial process of which FO is depicted as well as its chemical composition are presented. Scientific papers and patent registrations were analyzed with the objective of providing bibliometric data of publications on the subject, emphasizing the potential of FO as an acyl acceptor for esters production, an attractive alternative for replacing fossil fuels. Hence, the operational parameters that maximize the transesterification and esterification reactions of FO in the production of such esters are raised and discussed. In addition, the herbicidal and fungicidal activity of its chemical constituents is also presented. Finally, aspects that are still considered to be explored are highlighted, which can be an encouragement factor for researchers to carry out such investigations.

2. Industrial Process of Ethanol Production

FO comes from the rectification column of the industrial process of ethanol production,[28] as shown in Figure 1 regarding the production of alcohol from sugarcane. The manufacturing process starts when the sugarcane is received by trucks and then goes through a dry-cleaning process to remove the dirt. The next step is to extract sugar from the crushed stalks. The extracted juice is treated to remove impurities and the clarified juice is shared between the ethanol distillery (50%) and the sugar factory (50%).[29] Then, the juice intended for the production of alcohol is sent to the fermentation vats, with the addition of yeasts. At the end of fermentation, the yeasts are separated by means of centrifuges that result in a solution called fermented wine (alcoholic content of 8 °GL) which is sent to the distillation process.[3,30]

In Brazil, the distillation process usually takes place through two sets of columns. The first, called distillation, is formed by three columns, where the fermented wine is fed in the intermediate column. As a result of the distillation, two streams are obtained, the phlegm which contains 50% by weight of ethanol (obtained in the upper column), and
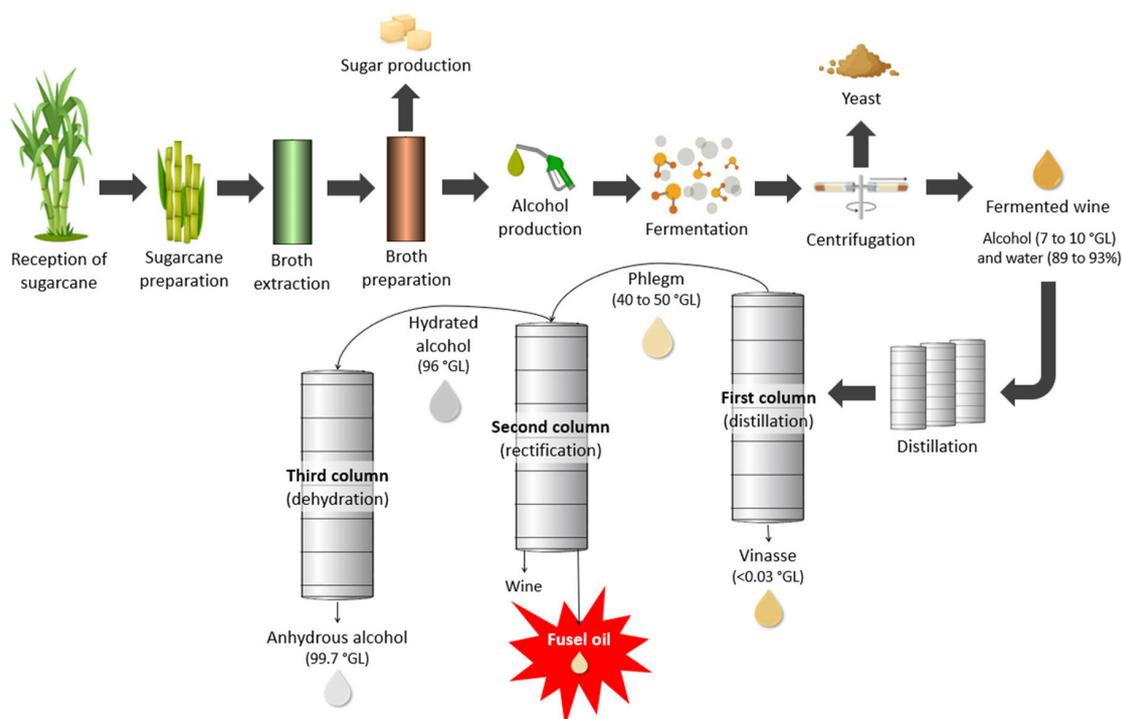

Figure 1. Flowchart of ethanol processing (adapted from reference 30).

the vinasse (obtained in the lower column), which is mainly composed of water.[3,30] Vinasse is considered an aqueous by-product of ethanol production that corresponds to about 10 to 15 times the volume of ethanol produced, which is used as fertilizer and source of energy in distilleries.[31] The phlegm is destined for the second set formed by two columns called rectification. In this step, hydrated ethanol (92.5-94.6 wt.%) is produced at the top of the upper column and the remaining water is removed at the bottom of the lower column. A mixture of organic compounds that contains isoamyl alcohol as the main component is produced as a lateral flow of the rectification columns, which is called FO.[30]

For the production of anhydrous ethanol (99.3 wt.%), it is necessary to employ alternative purification methods, since water and ethanol form an azeotrope with an ethanol concentration of around 95 wt.%. Thus, water can be removed by azeotropic distillation with cyclohexane, extractive distillation with monoethylene glycol and by adsorption of molecular sieves.[32] In order to maximize production, distilleries remove the ethanol present in the FO stream. The alcohol stream is collected from the rectifier column and goes to a decanter, in which the FO is backwashed with water. Subsequently, the FO is collected at the top of the decanter, while at the bottom, the phase combine a mixture rich in ethanol and water, which returns to the ethanol processing columns.[33]

3. Fusel Oil (FO)

As seen, FO is an oily fraction resulting from the removal of alcohol in the fermentation process of products such as sugarcane, barley, corn, rice and sugar beet.[8,34] Its composition consists of an azeotropic mixture between C_3-C_5 alcohols (isoamyl alcohol, isobutanol, propanol, butanol and others) and water,[33] in addition to small concentrations of aldehydes, fatty acids, esters and terpenes.[11] FO has an unpleasant odor and dark brown coloration,[8] less dense than water,[14] flammable, insoluble in water, and has a boiling temperature between 122 and 138 °C.[35,36]

During the processing stage, there are some factors that favor the FO formation during the fermentation process of ethanol production, such as: fermentation with low nitrogen content, long fermentation periods, and the long time between fermentation and distillation.[13,37] On the other hand, there are other factors that reduce its production, such as the large capacity of the fermenters, high ethanol yield and control of process variables that help in the selectivity of yeasts, resulting in greater ethanol production and lower FO formation.[9]

The diversity of the raw material, the fermentation process and the purification of ethanol influence the composition of the FO.[33] Table 1 presents a compilation of data referring to the composition of FO from sugarcane ethanol plants from four countries. As it can be seen in this table, the oil is mainly constituted by isoamyl alcohol (49.13-74.70%), ethanol (1.10-16.22%), isobutanol (1.30-11.30%) and water (4.10-16.40%).

From Table 1, it is possible to see that there is great variation in the composition of FO. This is due to the fact that the composition of alcohols formed depends on the amino acids available during fermentation and on the nitrogen concentration of the medium.[39,40] For example, from the amino acids isoleucine, valine and threonine there is the production of 2-methyl-1-butanol (isoamyl alcohol isomer), isoamyl alcohol and propanol, respectively.[39,41] In addition, the recovery of ethanol from FO performed by distilleries interferes in the composition of higher alcohols[9,33] as a result of the thermodynamic interactions present in FO (homogeneous and heterogeneous azeotropes).[12]

Table 1. Composition of fusel oil reported in the literature from ethanol plants of sugarcane processing

| Country | Composition of fusel oil / wt.% | | | | | | | | Reference |
	Isoamyl alcohol	Ethanol	Isobutanol	Propanol	Butanol	Pentanol	Methanol	Water	
Canada	70.85	3.44	nr	nr	nr	nr	nr	9.96	Montoya *et al.*[9]
Brazil	57.65	16.22	6.04	2.18	1.00	nr	nr	14.70	Dias *et al.*[10]
Turkey	74.70	1.10	11.30	3.80	4.90	nr	nr	4.10	Sozen *et al.*[11]
Colombia	70.40	12.06	1.30	nr	1.40	nr	nr	14.30	Mendoza-Pedroza *et al.*[12]
Turkey	62.29	11.09	8.71	0.74	0.12	nr	nr	10.30	Simsek and Ozdalyan[13]
Brazil	53.72	8.35	6.47	0.90	0.50	0.003	nr	14.76	Ferreira *et al.*[33]
Brazil	49.13	11.44	6.53	0.76	0.54	0.02	0.03	16.40	
Brazil	65.02	8.60	7.87	nr	nr	nr	nr	12.19	Li[38]

nr: not reported.

4. Fusel Oil Applications

4.1. Esters production

4.1.1. Esters with flavoring properties

Esters with flavoring properties are usually short-chain fatty acid esters (C_6 and C_8), and are essential flavor components in foods, beverages and cosmetics, due to the growing consumer demand for foods with natural flavors.[14,15,42,43]

The use of FO provides an additional source of higher alcohols for production of such esters, which is an alternative way to obtain natural acetate esters from low-cost agricultural residues. Due to the majority presence of isoamyl alcohol in FO, the main flavoring ester produced by esterification is isoamyl acetate, which has great applicability in the perfumery, food and pharmaceutical industries, particularly for presenting banana and pear flavors.[15,44]

It can be found in the specialized literature a wide application of FO as an acyl acceptor in esterification reactions, reacting with several carboxylic acids,[10,14,15,42,45] as well as reports of reactions using isoamyl alcohol, obtained from distillation of FO, as substrate for ester formation.[43,46]

Table 2 presents a compilation of the main research works published in the last 12 years regarding the production of esters with flavoring properties using FO as acyl acceptor, as well as the operating conditions indicated by the authors for the maximum product formation.

It is observed in Table 2 that the catalysts most used for esterification reactions are the heterogeneous biological ones, which have stood out for allowing easy separation and reuse,[43] besides being environmentally friendly.[51]

Working with a chemical catalyst, Tran *et al.*[15] showed that a heterogeneous catalyst in the third reuse cycle resulted in a yield 18% higher in esters compared to the homogeneous catalyst, a fact that corroborates the benefits obtained by the heterogeneous catalyst application.

In addition to the nature of the catalyst, Table 2 also shows a variation in the catalysts concentration in the reaction (2.5 to 11.65 wt.%), a variable of great importance in the process, since the addition of catalyst usually results in a percentage increase in esters yields. However, above certain concentration, the increase of catalyst can lead to a reduction in the esters formation, due to saturation of the reaction medium.[15,36]

Also, the reaction temperature is one of the essential parameters for the chemical esterification reactions for flavoring esters production, since in most cases, the reaction rate increases with increasing temperature. However, enzymes are considered thermosensitive, so the reaction temperature must be mild.[52]

Bi *et al.*[47] indicated that the increase from 30 to 40 °C resulted in a 3% increase in the esterification percentage, while the increase to 60 °C promoted the enzyme Novozyme® 435 degradation, which resulted in an esterification percentage reduction of 14%. However, when using a heterogeneous chemical catalyst, such as the Amberlyst® 15 cation-exchange resin,[48] reported in Table 2, the reaction temperature was higher than the reaction conducted by lipases, due to the fact that the chemical catalyst requires more energy to reduce the reaction activation energy.

Regarding the carboxylic (fatty) acid to alcohol molar ratio, shown in Table 2 as R, it is observed that, in most of the works reported, the synthesis of esters is favored with the increase of both reagent amounts. In some researches the increase was only in the FO amount[36,47,48,53] and in others only in carboxylic acid quantity.[14,15,43,49] In most cases, the increase in the reactants concentration tends to positively influence the reaction, shifting it to increased product formation.[43,47] Nevertheless, this increase must be evaluated, since an excess of FO can promote the dehydration of enzymatic catalysts, such as Novozyme® 435,[47] and the excess of carboxylic acid can cause the FO dilution, blocking the chemisorption of the substrates in the adsorbent agent.[15] Thus, the substrates amount and the reaction temperature are essential parameters to be determined, as they vary according to the type of catalyst used.

Table 2. Application of fusel oil (FO) as acyl acceptor in the esterification reaction for production of esters with flavoring properties

Substrates/catalyst	Product	Result / %	Ideal conditions				Reference
			Temperature / °C	R	C / wt.%	Reaction time / h	
Acetic anhydride and isoamyl alcohol from FO/Lipozyme® 435[a]	isoamyl acetate	88.4 (isoamyl alcohol conversion)	60	2:1	2.5	1	Dias *et al.*[14]
Acetic acid and FO/mesoporous silica KIT-6 functionalized with alkyl sulfonic acid	isoamyl acetate	95 (ester yield)	80	2:1	5	3	Tran *et al.*[15]

Table 2. Application of fusel oil (FO) as acyl acceptor in the esterification reaction for production of esters with flavoring properties (cont.)

Substrates/catalyst	Product	Result / %	Ideal conditions				Reference
			Temperature / °C	R	C / wt.%	Reaction time / h	
Butyric acid and FO/*Candida rugosa*	butyric esters	94.5 (esters yield)	30	1:2	10 mg mL^{-1}	24	Gamayurova *et al.*[36]
Lauric acid and FO/ *Rhizopus oryzae* lipase	isoamyl laurate	ca. 80 (lauric acid conversion)	45	1.5:1	11.65	24	Bôas *et al.*[43]
Acetic acid and isoamyl alcohol from FO/ Lipozyme® 435	isoamyl acetate	92 (esterification percentage)	40	1:2	9	6	Bi *et al.*[47]
Acetic acid and isoamyl alcohol from FO/cation-exchange resin H⁺ Amberlyst® 15	isoamyl acetate	97 (ester yield)	120	1:1.2	3.2	1	Bandres *et al.*[48]
Acetic anhydride and isoamyl alcohol from FO/cation-exchange resin H⁺ Amberlyst® 15		98 (ester yield)	120	1:2	1.6	2	
Acetic anhydride and FO/Novozyme® 435[b]	isoamyl acetate esters	95 (esterification yield)	40	2:1	1 g in a 10 mL-continuous reactor	1	Dias *et al.*[49]
Butyric acid and isoamyl alcohol from FO/Lipozyme® TL IM	isoamyl butyrate	95.6 (esterification percentage)	45	1:2	11.25	18	Garcia[50]

[a]Addition of supercritical CO$_2$ to the reaction medium at 15 MPa; [b]addition of supercritical CO$_2$ to the reaction medium at 10 MPa. FO: fusel oil; TL IM: *Thermomyces lanuginosus* immobilized; R: carboxylic acid to alcohol molar ratio; C: catalyst percentage in relation to substrate mass.

Given the context presented, it is observed that the variables temperature, substrates molar ratio, and concentration and type of catalyst influence the conversion into esters and the operating costs of the process, such as high reaction times when enzymatic catalysts are used. Thus, by means of alternative techniques, such as the supercritical fluids, it is possible to optimize operating conditions, as developed and reported in Dias *et al.*[10,14,49] in the enzymatic synthesis of flavoring esters in supercritical carbon dioxide (SC-CO$_2$). According to these results and comparing them to the other conditions presented in Table 2, it is observed that there was a reduction in the reaction times when compared to reactions conducted without supercritical conditions application, probably because SC-CO$_2$, which presents low viscosity and diffusivity, reduced the resistance to mass transfer in reaction mixtures, increasing conversion rates.[10,54,55] Moreover, the process efficiency is enhanced when operating in continuous mode[49] compared to batch mode,[14] due to the fact that the greater contact between substrates and enzyme surface in the longest residence time (36.5 min) reduced the mass transport limitations, thus increasing the isoamyl acetate conversion. However, the authors do not present any economic evaluation related to the costs of the technology using SC-CO$_2$, indicating that this may be the subject of studies to be conducted.

4.1.2. Esters with lubricating and fuel properties

Medium and long chain fatty acid esters are usually intended for the biodiesel production, in which short-chain alcohols (methanol or ethanol) are used,[56] and also for the formulation of biolubricants, where higher alcohols, with 8 to 14 carbons, are applied.[57]

Biodiesel production using FO as an acyl acceptor in the esterification of carboxylic acids and transesterification of vegetable oils results in obtaining fatty acid esters with a lower cold filter plugging point compared to esters conventionally produced from short chain alcohols,[18] which result in the reduction of clogging of engine pipes due to fuel solidification.[58] Recently, Monroe *et al.*[59] evaluated the performance of fatty acid fusel esters (FAFE) in diesel engines and report that the cetane value, heat of combustion, and cold flow performance from cloud point indicate that FAFE outperforms fatty acid methyl esters (FAME) and, despite FAFE having higher viscosity than FAME, remains within the acceptable range for biodiesel.

Biolubricants production stands out as an ecological alternative to the use of traditional petroleum-derived

lubricants, as they are obtained from vegetable oils.[17,60] Esterification of FO and oleic acid is carried out in order to obtain biolubricants through the formation of oleate esters, in which the resulting biolubricants have characteristics similar to the DB-32 type synthetic reference lubricating oil, and can be applied as a low viscosity lubricant.[60] Likewise, transesterification of FO and palm kernel oil results in lubricating esters, which have presented satisfactory values of viscosity and oxidation stability.[17]

The most significant parameters for the fatty acid esters production include those discussed above for obtaining esters with flavoring properties. In this sense, Table 3 compiles data reported in the literature regarding the formation of fatty acid esters for the biodiesel and biolubricants production using FO.

It can be seen from Table 3 that the reported ideal conditions vary significantly to achieve the best reaction yield because it involves other variables in the process that influence yield efficiency, such as the amounts of free fatty acid, pigments, and water[10] present in the reaction medium. Similarly, the composition of the fusel oil, which consists of a mixture of various alcohols, can interfere in the enzymatic activity, since the degree of lipase deactivation is inversely proportional to the number of carbons present in the alcohol molecule.[67]

By analyzing Table 3, it is observed that the reactions for biodiesel and biolubricants production can occur applying chemical catalysts,[19,61] but mainly enzymatic catalysts.[17,18,59,60,62-66] It is noteworthy to point out that the reaction temperature is one of the factors that needs to be checked when determining the nature of the catalyst to apply, as the temperature used for enzymatic catalysts must be mild,[17,18,58,59,62] due to enzyme denaturation at high temperatures that would lead to reduced esters yields.[18] The reactions conducted with homogeneous chemical catalysts are usually carried out at higher temperatures and according to the boiling temperature of the solvent applied.[68] Besides, it is also verified the use of acidic catalysts[61] and alkaline

Table 3. Application of fusel oil (FO) as acyl acceptor in the esterification and transesterification reactions for production of fatty acid esters for biodiesel and biolubricant formulations

Substrate	Catalyst	Product	Result / %	Ideal conditions				Reference
				Temperature / °C	R	C / wt.%	t / h	
Oleic acid and FO	Novozyme® 435[a]	isoamyl oleate	ca. 100 (ester yield)	70	1:9	30	5	Bányai et al.[16]
Palm kernel oil and FO	*Burkholderia cepacia*	isoamyl esters	98 (esters yield)	45	1:4	22	8	Cérón et al.[17]
Waste cooking oil and FO	Novozyme® 435	fatty acid esters	90 (esters yield)	40	1:3	14	24	Wang et al.[18]
Babassu oil and isoamyl alcohol	potassium hydroxide	fatty acid esters	94 (esters yield)	25	1:10	2	1	Tebas et al.[19]
Triolein and FO	*Pseudomonas cepacia*	oleic acid alkyl esters	ca. 100 (triolein conversion)	40	1:3	1.5	6	Salis et al.[58]
Triolein and FO	*Aspergillus oryzae*	fatty acid esters	97 (esters yield)	35	1:5	2	24	Monroe et al.[59]
Oleic acid and FO	Novozyme® 435	isoamyl oleate	ca. 100 (ester yield)	60	1:2	0.5	12	Dormo et al.[60]
Oleic acid and FO	sulfuric acid	oleate ester	97 (oleic acid conversion)	90	1:2	1.25	1	Özgülsün et al.[61]
Waste baked duck oil (WBDO) and FO	Novozyme® 435 and Lipozyme® TL IM	fatty acid esters	90 (WBDO conversion)	45	1:4	5	15	Liu et al.[62]
Coconut oil and FO	Lipozyme® TL IM	octanoic acid esters	38 (octanoic acid esters yield)	23	1:3	15	20	Sun et al.[63]
Microalgal oil and FO	*Burkholderia cepacia*	fatty acid esters	89 (esters yield)	45	1:8	4	120	Silva et al.[64]
Macaw palm oil and FO	*Burkholderia cepacian*		ca. 100 (esters yield)	45	1:8	4	96	
Oleic acid and FO	*Rhizopus oryzae*	isoamyl oleate	90 (ester yield)	45	1.5:1	10	24	Bôas et al.[65]
Stearic acid and FO	*Rhizopus oryzae*	isoamyl stearate	94 (isoamyl alcohol conversion)	45	1:1	12	24	Lima et al.[66]
Stearic acid and FO	*Candida antarctica*		91 (isoamyl alcohol conversion)					

[a]Addition of ionic liquids to the reaction medium. FO: fusel oil; TL IM: *Thermomyces lanuginosus* immobilized; T: temperature; R: fatty acid or oil to FO molar ratio; C: catalyst percentage in relation to substrate mass; t: reaction time.

catalysts,[19] and the choice is determined according to the free fatty acids content present in the raw material. Since the oleaginous matrixes are rich in free fatty acids, acid catalysts are used to avoid the saponification reaction caused by the addition of alkalis.[69]

Hence, it is observed that the use of homogeneous catalysts, despite favoring the reaction rate in relation to reactions catalyzed by enzymes, result in greater energy consumption, due to the high reaction temperature required and the drawback purification steps, leading to environmental disadvantages. Although biocatalysts are usually more expensive than homogeneous catalysts, separation processes can be easily carried out when applying immobilized enzymes,[51] as they are heterogeneous. Also, due to their specificity, there are practically no undesirable by-products formation, which eases product recovery, and enhances product yield and quality.[70]

Moreover, immobilized enzymes are more robust and resistant to environmental changes, when compared to free enzymes in solution. Additionally, with enhanced stability, immobilized enzymes can be reused for repeated cycles.[71,72] Therefore, these advantages prompt their applications in, among others, esterification and transesterification reactions.

According to the transesterification reaction stoichiometry, one mole of triglyceride is needed to react with three moles of alcohol. In this regard, it is necessary an alcohol excess to drive the reaction towards complete conversion.[73] Liu *et al.*[62] and Cérón *et al.*[17] performed the transesterification of waste baked duck oil (WBDO) and palm kernel oil, respectively, using FO as acyl acceptor of the reaction. In these studies, the use of the ester to alcohol molar ratio of 1:4, resulted in a WBDO conversion of 90% and maximum esters yield of 99%, respectively. Such results corroborate with the work carried out by Monroe *et al.*[59] in which the molar ratio increase from

1:3 to 1:5, resulted in a percentage increase of 8% in the esters yield. However, the alcohol addition should not be exorbitant, as its excess can hinder the final product recovery and increase the process costs. Moreover, at high concentrations of alcohol, lipase activity may be inhibited,[59] which was verified in the cooking oil transesterification with FO carried out by Wang *et al.*[18] where there was a 25% reduction in the esters yield while carrying the reaction in the maximum alcohol amount.

4.1.3. Patents

Table 4 presents patent registrations in which FO was used as an acyl acceptor in esterification and transesterification reactions for the production of esters with flavoring properties and for biodiesel and biolubricant formulations.

The research works reported in Table 4 used mainly acetic acid as acyl donor in the esterification reaction with FO for the production of esters with flavoring properties.[74-77] Moreover, the produced esters can have applications in the food and cosmetics sectors, such as in the development of nail polish[76] and nail polish remover.[75]

On the other hand, it can be seen in Table 4 that the works developed for biodiesel production describe the transesterification of vegetable oils with FO in patents MD 4173[78] and CN 105087170.[79] It is reported by the Chinese patent that, when mixing the resulting biodiesel with petroleum diesel, a reduction of engine clogging occurred.[79]

Furthermore, some works were patented regarding the production of lubricants from the FO. Sugita and Matsui[80] developed the Japanese patent JP 06304688 which consists of a lubricant formulation based on FO for low temperature press molding of aluminum. Finally, the production of lubricants used as additives to diesel fuels, from the esterification of fatty acids and FO is described in the patent WO 2002100987.[81]

Table 4. Compilation of patent data on the applicability of fusel oil for production of flavoring and fatty acid esters

Ester	Patent number	Title	Reference
Flavoring	RU 2174974 (C1)	Preparation of a fusel oil-based mixing solvent	Grevtsev *et al.*[74]
	RU 2194492 (C1)	Nail polish remover	Musienko and Petykhin[75]
	FR 2878157 (A1)	Solvent-based varnish composition containing a solvent of plant origin	Deswartvaegher *et al.*[76]
	RU 2471769 (C2)	Method for processing fusel oil waste from alcohol production by esterification with acetic acid in presence of sulfuric acid catalyst	Panteleev *et al.*[77]
Fatty acid	MD 4173 (B1)	Process for the production of biodiesel fuel	Covaliov *et al.*[78]
	CN 105087170 (A)	Manufacture method of biodiesel with low cold filter plugging point	Deng *et al.*[79]
	JP 06304688 (A)	Lubricant for low-temperature press molding of aluminum or aluminum alloys and method for press molding	Sugita and Matsui[80]
	WO 2002100987 (A1)	Fatty acids-fatty acid esters-aminated fatty acid mixtures as lubricant additives for diesel fuels	Fredrikson and Ahonem[81]

5. Fuel Formulation

Environmental concern due to the depletion of fossil fuels has a major impact on the increased use of biofuels.[82] Ethanol, methanol and biodiesel are preferred as clean energy sources, while alternative combustion models that provide high thermal efficiency have also been studied.[20] Among them, the use of FO in spark ignition (SI) engines as an alternative fuel can be promising as a new source of energy for internal combustion engines.[82] Thus, the concentration of FO used in the formulation of fuels, as well as the main parameters to assess the efficiency of combustion, need to be investigated.

To analyze fuel efficiency, the main variables to be determined are engine load test, fuel composition, and engine rotation speed, which will imply fuel consumption, gas emissions and torque. Therefore, Table 5 presents a selection of works reported in the literature showing the concentration of FO in fuel formulations, as well as some process characteristics such as engine system, engine speed, and engine load.

As can be seen in Table 5, there is a wide application of FO as a gasoline additive in SI engines. Among the variables investigated, the fuel formulation results in combustion efficiency, emission and engine performance.[82] Calam *et al.*[83] observed that increasing the concentration of FO added to gasoline from 20 to 50% contributed to the effective efficiency of the engine and reduction of nitrogen oxides (NOx) emissions, which are considered an atmospheric contaminant. Calam *et al.*[84] reported that as the amount of FO in the mixture increased from 20 to 30%, improvements were seen in engine torque compared to pure gasoline, due to the high amount of oxygen present in the FO which improves combustion characteristics. However, the high amount of water present in the FO influences combustion, favoring carbon monoxide (CO) and hydrocarbon (HC) emissions.[85]

Taking into account the disadvantage of FO used as a fuel due to the large amount of water in its composition, Awad *et al.*[34] investigated the fuel properties of FO with the reduction of moisture content and identified that, by decreasing the water content of FO from 13.5 to 6.5 wt.%, there was an improvement in the heating value of 13%, reducing the combustion duration and showing greater stability. Similarly, the studies carried out by Uslu and Celik[86] focused on the great potential of using isoamyl alcohol in the mixture with gasoline, observing a decrease in the emissions of hydrocarbons, carbon monoxide and nitrogen oxides, while the thermal efficiency of the brake, the torque and the effective power increased compared to the pure gasoline.

Correspondingly, FO can also be added to diesel fuel (Table 5), resulting in some similar features that have already been reported for gasoline mixture, such as a reduction in NOx emission and an increase in HC and CO emissions, justified by high water content of the FO.[20,80]

Akcay and Ozer[87] carried out a study on mixtures consisting of FO and diesel in one-cylinder compression ignition (CI) engine and identified that, for the higher concentration of FO used (20%), CO, NOx and smoke emissions reduced to 0.48%, 495 ppm and ca. 69.3%, respectively, compared to pure diesel. The same effect regarding the reduction of smoke emission was observed by Yilmaz,[21] which indicates that this effect is mainly caused by the high amount of oxygen present in the FO.

Furthermore, as can be seen in Table 5, the engine load and the rotation used are parameters to be specified, as they influence the emission of gases and combustion efficiency. With an increase of the fuel amount in the combustion chamber, the inefficiency of the process can occur, since the engine needs enough time to completely burn the amount of fuel injected.[88] And as engine speed increases, the mixture becomes more homogeneous, reducing CO_2 emissions.[84]

Table 5. Application of fuel oil (FO) in fuels

Fuel	FO concentration[a] / %	Engine	Rotation / rpm	Engine loads / %	Reference
	10 to 20	SI	4500	15 to 60	Awad *et al.*[34]
	0 to 50	SI	3500	100	Calam *et al.*[83]
Gasoline	0 to 30	SI	1500 to 5000	25 to 100	Calam *et al.*[84]
	0 to 100	SI	2500	25 to 100	Solmaz[85]
	0 to 30	SI	2600 to 3200	nr	Uslu and Celik[86]
	0 to 10	nr	2200	19 to 96	Yilmaz[21]
	0 to 20	SI	1200 to 2400	50 to 75	Awad *et al.*[82]
Diesel	0 to 20	CI	2600	2.5 to 12.5	Akcay and Ozer[87]
	10 to 20	CI	2000	15 to 60	Ağbulu *et al.*[88]

[a]In volume. SI: spark ignition; CI: compression ignition; nr: not reported.

Table 6 presents patented works aimed at the application of FO in fuels. As far as is known, the first patent implemented with the use of FO in fuels was carried out by Lan and Zhang[89] in which the fuel formulation consisted of methanol, ethanol or FO (72-85%), oils or gasoline (10-15%), ethanol (5-8%), acetone (5-8%), ferrocene (0.005-1.1%), ammonium hydroxide (0.5-1%) and water (8-12%).

In the other patents, FO was added to fuel formulations mixtures that are basically composed of vegetable oils and some petroleum-based fuels (gasoline, diesel or kerosene).[38,90-92] Patents CN 1303911[90] and CN 10398095[38] stand out, where the fuels developed had superior combustion performance and reduced soot formation, avoiding secondary pollution. Patent CN 1523083 reports the increase in engine power from 1.0 to 3.8% and the reduction of pollutants present in the exhaust gases achieved with the alternative fuel obtained in the present invention.[91] The partial replacement of kerosene, gasoline and diesel by FO is reported in both patents CN 1958744[92] and CN 103980959.[38]

Additionally, in some fuel formulations, the FO addition was treated in order to achieve a specific property: fuel mixture stabilizer,[93,99] heat enhancement agent,[94] fuel lubricity booster[95] and production of an additive resulting from the FO dehydration.[100]

6. Pesticide Formulation

FO presents in its chemical composition some compounds that have shown antimicrobial properties, such as octanoic acid (0.17 to 0.76%), 3,7,11-trimethyl-2,6,10-dodecatrienol (0.05 to 0.014%), 3,7,11-trimethyl-1,6,10-dodecatrien-3-ol (0.04 to 0.16%) and components belonging to the organic compounds known as pyrazines (ca. 4.50%).[34,53]

Octanoic acid, known as caprylic acid, has presented antimicrobial activity on several microorganisms, including: *Escherichia coli*, *Salmonella enterica*, *Staphylococcus aureus* and *Listeria monocytogenes*.[101] 3,7,11-Trimethyl-2,6,10-dodecatrienol, a terpene known as farnesol, has shown potential as an antimicrobial agent[27] and is used in agricultural crops as mite parapheromones.[102] For the compound nerolidol (3,7,11-trimethyl-1,6,10-dodecatrien-3-ol) there are also reports of acaricide activity[26] and insecticide.[103] And the compounds belonging to the pyrazines class behaved as fungicidal agents against a wide spectrum of diseases located in several plant species.[25,104]

Based on these characteristics, the application of FO in weed control is reported[22,23,28] as shown in Table 7. Analyzing the data presented in this table, it is observed that FO is applied as an herbicide, both alone and in formulations with traditional herbicides, in several weed species.

Regarding the studies presented in Table 7, it is highlighted that the seeds of *Brachiaria decumbens* and *Sida rhombifolia* did not germinate only at the highest concentrations of product (50 to 100% of FO).[22] Similar results are reported by Azania *et al.*[23] in which the evaluated weed species showed signs of intoxication only when subjected to the highest concentration of FO (500 L hectare^{-1}). When evaluating the application of FO in conjunction with traditional herbicides[28] it was observed

Table 6. Compilation of patent data on the applicability of fusel oil in fuel formulations

Patent number	Title	Reference
CN 103980959 (A)	Green diesel fuel and its preparation method	Li[38]
CN 1103659 (A)	Alcohol based synthetic household fuels and their manufacture	Lan and Zhang[89]
CN 1303911 (A)	Production of synthetic diesel fuels	Peng[90]
CN 1523083 (A)	Fuel oil with high alcohol content	Hu[91]
CN 1958744 (A)	Hydrocarbon fuel composite for vehicles and watercrafts	Hang and Huang[92]
LT 3299 (B)	Stable gasoline-ethanol-liquid water fuel composition	Pikunas *et al.*[93]
CN 1632074 (A)	Environmental friendly alcohol based liquid fuel	Zhang and Zhang[94]
BR 2006002633 (A)	Automotive biofuel composition comprising diesel fuel with additive alcohols distilled from fusel oil for combustion optimization and pollution reduction	Barreto and Mendes[95]
CN 102206519 (A)	Microemulsified diesel oil containing biomass component and preparation method thereof	Zhang and Link[96]
US 20130255141 (A1)	Miscible diesel fuel ethanol composition	Ried[97]
US 20180291296 (A1)	Methods of igniting a fuel source, lighter fluid compositions and self-lighting charcoal briquetes	Adolphson *et al.*[98]
CN 108034461 (A)	Fuel additive for enhancing the anti-phase separation of alcohol fuels and its preparation method	Lin[99]
WO 2019175393 (A1)	Preparation of olefin by alcohol dehydration, and uses thereof for making polymer, fuel or fuel additive	Richardson *et al.*[100]

Table 7. Application of fusel oil (FO) as an herbicide in weed species

FO concentration[a] / %	Flow application / (L *per* hectare)	Commercial herbicide concentration / (g *per* hectare)	Weed	Reference
12.5 to 100	nr	nr	*Brachiaria decumbens* *Sida rhombifolia*	Azania *et al.*[22]
0 to 100	50 to 500	nr	*Ipomoea hederifolia* *Ipomoea quamoclit* *Euphorbia heterophylla* *Digitaria* spp. *Cenchrus* *Echinatus* *Panicum maximum*	Azania *et al.*[23]
0 to 100	25	diuron + hexazinone: 819 + 231 to 1170 + 330 metribuzin: 1344 to 1920 amicarbazone: 980 to 1400	*Ipomoea quamoclit* *Amaranthus deflexus* *Panicum maximum* *Euphorbia heterophylla* *Brachiaria decumbens*	Pizzo *et al.*[28]
0 to 100	0 to 75	glyphosate: 0 to 6800	*Commelina benghalensis* *Cyperus* sp. *Digitaria* sp. *Eleusine indica*	Azania *et al.*[105]

[a]In volume. nr: not reported.

that the most efficient dose against weeds was constituted by 70 and 30% of traditional herbicide and FO, respectively. And when evaluated with the herbicide glyphosate, the addition of FO in the application mixture resulted in a 50% reduction in the use of the herbicide, resulting in an efficiency of 92.5% in the control of weeds.[105]

The effectiveness of FO in weed control (Table 7) is achieved when highly concentrated sample formulations are applied, or when it is added to a conventional herbicide. Thus, the application of FO as an herbicide is limited, since isoamyl alcohol in high doses can be toxic and lethal.[106,107] However, despite being toxic at high doses, it is noteworthy that the application of FO at a concentration of 150 m^3 hectare^{-1} did not change the chemical attributes of the soil essential for plant development.[108] Therefore, new studies need to be carried out in order to enhance the herbicidal activity of FO, without the need to add a concentrated product, as it does not interfere with the development of future plantations and has great herbicidal potential against several weeds.

In addition to the research mentioned above, patent registrations were found for the applicability of FO in pesticide, fungicide and herbicide formulations, according to the information presented in Table 8. Heyn[109] developed the patent DE 2701129 which contains the formulation of a mixture of several oils, including FO, and added it to herbicides, verifying that the process of absorption by plants was facilitated with the addition of the oils mixture.

In patents MD 3306, MD 3668 and MD 3610, focused on the pesticide activity of FO, its efficiency was evaluated in the composition of several solutions composed of sodium chloride, copper ferric hexacyanoferrate, bentonite and copper sulfate applied in the galls of cucumber plants infested with nematodes. They observed that the resulting liquid increased the fungicidal efficiency, similarly to other formulations tested by Galiakhmetov *et al.*[110] in which solutions prepared with FO also enhanced the fungicidal activity for agricultural use.

7. Conclusions and Future Perspectives

The use of FO presents numerous advantages, as it is considered a residue from the production of bioethanol

Table 8. Compilation of patent data on the applicability of fusel oil in herbicide pesticides and fungicides formulations

Patent number	Title	Reference
DE 2701129 (A1)	Plant-compatible oils for use with herbicides	Heyn[109]
RU 2424659 (C1)	Fungicidal formulation	Galiakhmetov *et al.*[110]
MD 3306 (F1)	Process for obtaining biologically active liquid	Covaliov *et al.*[111]
MD 3668 (F1)	Pesticide for plant spraying and process for its preparation	Covaliov *et al.*[112]
MD 3610 (F1)	Process for obtaining a liquid with pesticide action	Covaliov *et al.*[113]

and it is rich in higher alcohols, mainly isoamyl alcohol, and several components that have shown antimicrobial properties. Despite its high availability due to the large global production of ethanol, the applicability of FO is limited by some factors, mainly due to the high-water content, and only few studies focused on this area. In this study, a comprehensive review was conducted to present the characteristics, composition and potential applications of FO. According to the bibliometric data presented and discussed, it is possible to note that studies can be conducted in order to minimize the disadvantages of its application, and alternatives to explore new lines of research can be developed. In this sense, the following aspects can be highlighted:

(*i*) FO proved to be a promising fuel alternative, due to the reduction in the polluting gases emission. However, the high-water content present in the FO prevents it from being used as pure fuel, due to incomplete combustion. This fact also interferes with the catalytic activity of enzymes commonly applied when this co-product is used as an acyl acceptor in trans- and esterification reactions for esters production. Therefore, the opportunity arises for industrial plants to improve separation techniques to reduce the water content in the FO.

(*ii*) FO seems to be suitable for esters production from oleaginous matrices and carboxylic acids. However, there are no studies aimed to produce biodiesel from FO and soybean oil, which is one of the most traditional raw materials in the process. Thus, investigating the production of biodiesel through new substrates using FO as a reaction reagent becomes an attractive route in this market;

(*iii*) The compounds present in the FO composition have shown antimicrobial properties. However, the application range of FO as a fungicide and herbicide is still little explored; therefore, it is of great importance to investigate the FO effect on new microorganisms in order to assess its applicability in several areas;

(*iv*) As an herbicide, FO showed desiccant property against weeds. Nevertheless, elevated amounts applied lead to applicability disadvantages. Consequently, establishing chemical reactions that enhance the potential of the compounds present in the FO in order to reduce the amount applied in agricultural fields can be explored.

Acknowledgments
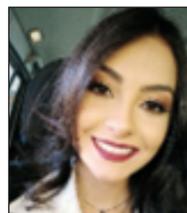
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