1 Subcritical ethylic biodiesel production from wet animal 2 fat and vegetable oils: a net energy ratio analysis

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14 Abstract

15 Ethylic transesterification process for biodiesel production without any
16 chemical or biochemical catalysts at different subcritical thermodynamic con-
17 ditions was performed using wet animal fat, soybean and palm oils as feed-
18 stock. The results indicate that 2h of reaction at 240°C with pressures vary-
19 ing from 20 to 45 bar was sufficient to transform almost all lipid fraction of
20 the samples to biodiesel, depending on the reactor dead volume and propor-
21 tions between reactants. Conversions of 100%, 84% and 98.5% were obtained
22 for animal fat, soybean oil and palm oil, respectively, in the presence of wa-
23 ter, with a net energy ration values of 2.6, 2.1 and 2.5 respectively. These
24 results indicate that the process is energetically favorable, and thus repre-
25 sents a cleaner technology with environmental advantages when compared to
26 traditional esterification or transesterification processes.

27 **Keywords:** Biodiesel, FAEs, subcritical, Animal Fat, Net Energy Ratio.

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28 *Nomenclature.*

29 AF: animal fat; FFA: free fatty acids; FAEs: fatty acid ethyl esters;
30 FAMES: fatty acid methyl esters; GC: gas chromatography; IS: internal
31 standard; NER: Net Energy Ratio; TG: triglycerides; TGpcar: TG peak
32 corrected after reaction; TGpar: TG peak area after reaction; TGpbr: TG
33 peak area before reaction; ISpbr: IS peak area before reaction; ISpar: IS
34 peak area after reaction; TGtc: TG total conversion; TGpcar: TG peak
35 corrected area after reaction; FAEsmax: Maximum possible formation of
36 FAEs peak area; FFApbr: FFA peak area before reaction; E_{FAEs} : Energy
37 obtained from FAEs; E_{cpm} : Energy consumption from the power meter;
38 E_{rfr} : Energy requirements for the reaction.

39 **1. Introduction**

40 The transesterification reaction of vegetable oils to produce fatty acid
41 methyl or ethyl esters (FAMES or FAEs) can be catalyzed by acids, bases
42 or enzymes, among other processes [1]. The predominant FAMES employed
43 in the biodiesel industry in the world are derived from soybean, rapeseed,
44 and palm oils [2]. Currently, most commercial processes employ methanol
45 to perform the transesterification of triglycerides, catalyzed by a strong base
46 (KOH) in a homogeneous process to produce FAMES. This is due to the
47 fast transesterification reaction in the presence of alcohol soluble bases and
48 to the low cost of alkaline material, but this process involves many treat-
49 ment steps previous to and post-reaction, with generation of large amounts
50 of effluents and waste. Besides, the use of a soluble base as a catalyst is
51 not suitable for processing low quality raw materials, such as animal fat and
52 palm oil that usually contain traces of water and high amounts of free fatty
53 acids which readily react via the saponification reaction, generating soaps
54 and hindering the separation of the products, consumes the catalyst and re-
55 duces its efficiency[3]. Likozar and Levec [4] performed a very detailed kinetic
56 study of the transesterification reaction of various vegetable oils, using vari-
57 ous alcohols, via homogeneous catalysis with KOH. The authors showed that
58 the alcohol influences the mass transfer rate-determining region through its
59 physical properties and the reaction rate-determining region depending on
60 its chemical properties and reactivity. Using methanol, the initial emulsion
61 formed, gradually becoming a pseudo-homogeneous phase with the progress
62 of the transesterification reaction may explain its better performance among
63 all alcohols tested. However, methanol is very toxic in comparison with

ethanol[5]. The transesterification reaction using ethanol is safer and an environmental friendly alternative. In Brazil, where ethanol is produced at large scale and is more cost effective, fatty acid ethyl esters (FAEEs) should be produced instead of fatty acid methyl esters (FAMES). The proposed reaction mechanism for the traditional alkaline transesterification occurs by a nucleophilic attack of the methoxide groups (resulting from the reaction of the alkali with the alcohol) at the triglyceride carbonyl groups. An undesirable saponification reaction occurs between the alkali and triglyceride, generating a fatty acid salt (soap) and glycerol. The use of acid catalysts solves this problem, but the kinetics of the reaction is much slower[1],[6],[7],[8],[9], and presents problems of corrosion of the equipment used in the process. The reaction mechanism for acid catalysis is initiated by an electrophilic attack of the acidic proton, generating protonic intermediate species, followed by a nucleophilic attack of the alcohol to the triglycerides[8]. Currently both the alkaline and acid transesterification processes feature a number of technological and environmental challenges among which are: a) the conditioning of the reactants with acids and strong bases prior to the alkaline transesterification reaction; b) the generation of large volumes of contaminated water resulting from the neutralization of the produced biodiesel; c) the generation of waste in the purification of glycerol's step; d) the lack of modularity of the processes; e) batch operation; f) the generation of soap when using the alkaline catalyst (KOH); g) the high toxicity of methanol; and h) the slowest kinetics of the reaction catalyzed by acidic or some heterogeneous catalysts.

Enzymatic process, on the other hand, has important advantages which include mild reaction conditions and the possibility of using feedstock with high free fatty acid content, but generally presents kinetics limitations. Mangas-Sanchez and Adlercreutz [10] recently proposed the use of silica particles, which permitted a larger surface area in the interphase, overcoming mass transfer limitations and thus increasing the rate of the triacylglycerol and free fatty acids conversion process to biodiesel. The authors used *Thermomyces lanuginosus* lipase as catalyst in an aqueous/organic two-phase system and a high oleic acid content starting material in order to simulate low-quality oil obtaining a biodiesel yield of 96%, with 2% monoacylglycerols and 2% diacylglycerols remaining after 5 h under the mild conditions used (37°C), but further increases in the efficiency of the enzymatic process are desired to make it attractive and suitable for large-scale applications.

Transesterification reactions in supercritical and subcritical thermodynamic conditions have been described in the literature, using methanol or

ethanol and avoiding most of the above-mentioned problems [11],[12], or trying to find, by mathematical modeling, the best thermodynamic conditions to produce biodiesel from triglycerides using methanol, subcritical or supercritical [13], [14],[15],[16],[17],[18],[19],[20],[21]. Generally, under subcritical thermodynamic conditions, short reaction times are sufficient to achieve conversion yields above 90% in the absence of catalysts. Compared to the alkaline and acid reaction mechanisms, the proposed mechanism for the supercritical (and perhaps subcritical) transesterification reaction [22] indicates a direct attack of the alcohol to the triglyceride's carbonyl groups, forming an intermediate diglyceride and then the methyl or ethyl esters of fatty acids. High yields and very low reaction time (about 5 min.) have been achieved, in which the major critical factors are the optimization of the mix between the reactants and the characteristics of the supercritical fluids. Water use in subcritical conditions is a technologically cleaner alternative that has been successfully applied in various processes such as extraction, hydrolysis [23], [24] and wet oxidation of organic compounds, including glycerol [25],[26]. Recently the production of biodiesel by transesterification using methanol and water in subcritical condition was described with conversion rates above 90% and reaction time of 4 hours [11]. The main problem of this process is the huge energy demand. Some authors of the same research group showed that wet activated sludge may be converted directly into biodiesel using only subcritical water as catalyst [24], but the long reaction time (24h) at 175 °C also implies in huge energy demand. More recently, they showed again that subcritical water act as a catalyst for esterification with methanol of fatty acids obtained from low quality feedstock oil [27], at 175-205 °C and 2.0-2.8 MPa. A catalyst-free two-step process has been proposed, with hydrolysis of triglycerides to fatty acids in subcritical water and subsequent methyl esterification of these acids in supercritical methanol [23]. This process presents some advantages, as glycerol is removed away prior to methyl esterification, avoiding backward reaction; moreover, because the fatty acids act as acid catalysts, smaller amounts of methanol are used. All these aspects may contribute to higher energy efficiency.

A key point for the production of any fuel is that the energy produced per product unit must be greater than the energy expended to obtain this product (which, in the present case, is biodiesel). The metrics used here to evaluate the energetic feasibility of the process is the net energy ratio (NER), which can be defined as "the ratio of the total energy production to the primary non-renewable energy requirements" [28].

140 In Brazil, the main feedstock used for biodiesel is soybean oil, varying
141 between 70 % and 85 % of the total biodiesel matrix each year, but animal
142 fat corresponds to 10 % in average, and reached 25 % in 2008. Animal fat
143 is abundant in Brazil, as this country is the second meat producer in the
144 world, but many biodiesel industries limit the addition of animal fat to 30
145 wt.% of the total feedstock, generally combined with the soybean oil, due to
146 its high acidity and high viscosity, which may cause clogging of pipes and
147 equipment. To achieve this ratio of 30 wt.% in the mixture, a pretreatment is
148 required to remove the free fatty acids from the animal fat. This treatment is
149 made through a reaction with sodium hydroxide, followed by centrifugation
150 and neutralization with hydrochloric acid, and all these steps generate more
151 fatty acid residues. The process presented here has no such limitations, as it
152 can use raw animal fat as feedstock, with no need for mixtures, and generates
153 almost no effluents and residues, compared to the all traditional processes.
154 This process has other intrinsic advantages due to the absence of catalysts,
155 as homogeneous alkaline catalysts causes the undesirable saponification reac-
156 tion, and the homogeneous acid catalysts may cause corrosion problems, and
157 both led to the intrinsic generation of effluents. Moreover, solid catalysts im-
158 plies on mass transfer limitations between phases and within the pores of the
159 catalyst itself, resulting in lower conversion of the feedstock. Enzymatic cat-
160 alysts also have limitations; mass transfer of substrate and products between
161 the phases constitutes a bottleneck to overcome in these bioprocesses.
162 In this study we report a biodiesel production technique using subcritical
163 thermodynamic conditions for ethylic transesterification reaction of wet ani-
164 mal fats and vegetable oils with high content of free fatty acids, investigating
165 the reaction conditions that enable a NER grater than one. Since no catalyst
166 is employed, the process presented here is simpler and environmental friendly
167 than traditional methods, mainly due to the very low generation of effluents
168 and residues.

169 **2. Materials and Methods**

170 **2.1 Chemicals.**

171 Animal fat (35 wt.% free fatty acids and 0.3 wt.% water) was supplied
172 by FOSFOCAL, a company located at Itapetinga, Bahia, Brazil. Refined
173 edible soybean oil (0.3 wt.% free fatty acids and 0.1 wt.% water) and palm
174 oil (5 wt.% free fatty acids and 0.1 wt.% water) were obtained from a com-
175 mercial source (local supermarket, Salvador, Bahia, Brazil). The detailed

composition of all feedstock is shown in Table 1. The standard mixture of fatty acid ethyl esters (FAEEs) (49454-U, C4-C24 Even Carbon Saturated FAEEs) was purchased from Supelco (Bellefonte, PA, USA). A standard triglyceride, namely glyceryl trioleate was purchased from Sigma-Aldrich. The standard mix of Mono, Di and Triglyceride (code 1787) was purchased from Supelco (Bellefonte, PA, USA). All other chemicals such as ethanol, hexane and methyl heptadecanoate were analytical grade reagent obtained from Sigma-Aldrich.

Table 1

2.2 Equipment for biodiesel production.

Biodiesel from animal fat and vegetable oils was obtained by a one-step subcritical process without catalyst addition, using water and ethanol according to the proportion indicated in the design of experiments described in the next section, using a 100 mL Parr reactor (Parr Instrument Company, Moline, Illinois) mounted as described in the Fig. 1. The total volume used for each experiment was 60 mL. The reactor was monitored and controlled (PID controller) through a program designed by the authors, using the Lab-View software (National Instruments). The reactor was operated in batch; the reagents (ethanol, triglycerides and water) were added and heated under mixing (stirring speed 1200 RPM) until the mixture reached the set point temperature, with a mean heating rate of 13.3 °C/min. The time to reach the highest temperature used in the experiments (240 °C) was around 40 min. No inert gas or co-solvent were used. The reaction time and the set point were pre-set for each experiment. The main controlled variable was the internal temperature, with variation lower than 1 °C, so the pressure varied with the ratio of reactants, from 20 to 45 bar. For comparison reasons, it was assumed that the reaction started when the desired temperature was reached. At the end of the reaction, the reactor was cooled to room temperature and the mixture was removed for subsequent chromatographic analysis.

Fig. 1

2.3 Experimental design.

A statistical two levels half factorial design with center point [29] was

212 used. The independent parameters considered were: temperature, reac-
213 tion time, water/fat or water/triglycerides molar ratio and ethanol/fat or
214 ethanol/triglycerides molar ratio. The rate of conversion of free fatty acids
215 and triglycerides to biodiesel was chosen as the main response variable, cal-
216 culated as shown below. Additionally, the FAEs's yield was estimated, and
217 the NER for each experiment was calculated as also shown below. The sta-
218 tistical analysis of the results was done using the software Minitab version 17.

219

220 2.4 GC analysis.

221 Qualitative and quantitative analysis of FAEs, monoglycerides, diglyc-
222 erides and triglycerides were performed using a Bruker Scion 456-GC equipped
223 with a split/splitless injector and a flame ionization detector (FID). Separ-
224 tion was carried out using a BR-biodiesel (5 % phenyl 95 % methyl polysilox-
225 ane stationary phase modified for high temperature) capillary column (10 m
226 x 0.32 mm internal diameter, 0.1 µm film thickness) supplied by Bruker. The
227 operation conditions were: split/splitless ratio 100:1, injector temperature
228 280°C, detector temperature 380°C, column temperature profile: 80°C for
229 1min., ramp to 300°C at 7°C/min., ramp to 370°C at 30°C/min., plus 10
230 min. at 370°C. The total runtime was 45 min., and the injection sample
231 volume was 1 µL. Helium was used as the carrier gas with a linear veloc-
232 ity of 55 cm/s at 80°C. The peak assignments were made by comparison
233 with standards samples of fatty acid ethyl esters (FAEs) and mono, di and
234 triglyceride (monoolein, diolein and triolein) (Fig. 2).

235

236 Fig. 2

237

238 2.5 Sample preparation.

239 The biodiesel sample obtained after the reaction was weighed (100 mg ap-
240 proximately) and dissolved in 1 mL of hexane. Prior to the injection in the
241 chromatograph, a known amount of internal standard (1 mg/mL of methyl
242 heptadecanoate) was added to the vial. The results presented in this study
243 represent the mean value of three injections of each sample obtained from
244 the experiments.

245

246

247 **2.6 Total conversion calculation.**

248 The peak areas of animal fat or vegetable oils triglycerides (TG) and
 249 free fatty acids (FFA) before and after reaction were determined as well as
 250 the areas of the internal standard (methyl heptadecanoate) peak for each
 251 injection. The total conversion of triglycerides was determined using the
 252 TG peak areas after the reaction corrected with respect to the areas of the
 253 internal standard peak (IS) as follows:

$$TG_{pcar} = TG_{par}(IS_{pbr}) / (IS_{par}) \quad (1)$$

254

255

256 Thus, the total conversion of triglycerides to biodiesel was calculated as:

$$TG_{tc} \% = ((TG_{pbr} - TG_{pcar}) / (TG_{pbr})) \times 100 \quad (2)$$

257 The conversion of free fatty acids (present significantly only in the animal
 258 fat samples) was calculated using a similar procedure.

259

260 **2.7 FAEEs yield estimation.**

261 Using the total conversion percentage of TG and observing that the fatty
 262 acids are easily esterified because their corresponding peaks disappear, the
 263 FAEEs yield for each experiment was estimated as follows, considering a
 264 similar molar response factor of the detector for molecules with equal number
 265 of carbon atoms:

$$FAEEs_{max} = 3 \times TG_{pbr} + FFA_{pbr} \quad (3)$$

266

267 . Thus, the estimated yield in FAEEs was calculated as:

$$FAEEs_{yield} = (1 - (FAEEs_{max} - ((TG_{tc} / 100 \times 3 \times TG_{pbr}) + FFA_{pbr}) / FAEEs_{max})) \times 100. \quad (4)$$

269 **2.8 Net energy ratio (NER) determination.**

270 The NER measures how much energy is produced per unit of energy
 271 spent, and for the production of biodiesel it is calculated as:

272

$$NER = \text{Energy content in biodiesel} / \text{all energy requirements} \quad (5)$$

273 To determinate the energy requirements for the transesterification process
 274 using the Parr reactor used here (Fig. 1), a volume of 60 mL of distilled water
 275 was placed inside the reactor, which was brought to the maximum operating
 276 temperature (240°C). The energy consumption in W.h was measured through
 277 a power meter (Kron model Mke-01). This amount of energy comprises the
 278 energy requirement for heating all parts of the equipment, heating the fluid
 279 to the desired temperature, for the stirring, and energy losses. Water was
 280 used for reference because it is a simple fluid, with great availability of ther-
 281 modynamic data. The theoretical amount of energy necessary to bring the
 282 liquid water at 30°C to superheated water at 240°C was calculated using the
 283 latent and sensible heat data, yielding 188 kJ or 55.3 W.h. The comparison
 284 between the measured value and the theoretical one indicated a loss of heat
 285 of 83 % in the reaction system, due to bad insulation of the whole apparatus.
 286 Obviously, this energy loss must be minimized in the development of a future
 287 industrial process. This loss must be deducted in order to determine the net
 288 energy requirement for the reaction itself. The energy consumption for each
 289 reaction was thus measured each time and corrected for this heat loss to de-
 290 termine the net energy requirement for the reaction itself and then the NER
 291 was calculated, taking in account the energy corresponding to the biodiesel
 292 produced. The biodiesel energy content (ethyl ester) was considered to be
 293 40.97 kJ/g [30]. Thus, the NER was calculate as:

$$E_{cpm} = W.h \times 3.6 \text{ (kJ)} \quad (6)$$

$$E_{rfr} = E_{cpm} \times 0.17 \text{ (1 - 0.83)} \quad (7)$$

$$E_{FAEEs} = \text{Feedstock (g)} \times TGtc \times FAEEs \text{ yield} \times 40.97 \text{ (kJ/g)} \quad (8)$$

294 .

$$NER = E_{FAEEs} / E_{rfr} \quad (9)$$

295 .

3. Results and Discussion

The experimental statistical and the main results of total conversion, NER, and yield of FAEs obtained from the nine experiments conducted for the transesterification of animal fat are showed in Table 2. The best operating condition was found at a temperature of 240°C and reaction time 120 min., using molar ratio water/fat = 5 and molar ratio ethanol/fat = 10, for which a full conversion of the feedstock was obtained, with almost no diglycerides and very low monoglycerides at the end of reaction, giving 98 % of FAEs's yield, and positive NER value (2.6).

Table 2

As the temperature was the main variable, a precise PID controller as described in the section materials and methods was used to control it, and the pressure varied freely, ranging from 20 to 45 bars among all experiments. At the lower level of temperature, 120°C, no conversion is observed in these experiments without using catalysts. Indeed, a statistical analysis of the results showed that the temperature is the most important parameter, with significant effect on the three responses, as shown in the Pareto's charts of the standardized main effects for 95 % of confidence (Supplementary file). None of the interactions between two parameters showed statistical significance, for the set of nine experiments considered for analysis.

Fig. 3 exhibits two chromatograms: a) Animal fat feedstock (AF), b) FAEs produced by the transesterification reactions of this feedstock with ethanol at the operating condition cited above.

Fig. 3

The esterification reaction of the free fatty acids present in the animal fat was complete, as well as the transesterification reaction of the triglycerides with ethanol, as seen in the Fig. 3. An overall conversion of 100 % is observed for this experiment. The standards peaks for monoglyceride (monoolein), diglyceride (diolein), and triglyceride (triolein) allowed us to conclude that: (a) all triglycerides present in the animal fat were converted; (b) no diglycerides remain at the end of reaction; and (c) only a small proportion (about 2 %) of the product remains as monoglycerides. The thermodynamic condi-

tions employed probably allowed a very good mixture between the reactants, which is a key factor in the esterification or transesterification reactions, as non-soluble compounds are involved. The presence of water, despite possible solubility problems in this complex system, was beneficial, as observed in the experiments. This positive effect of water can be seen comparing some results presented in Tab. 2. For example, runs 2 and 3 were conducted at the same temperature (240°C), same molar ratio ethanol/fat (6), and, despite of the very low time of reaction (30 min.) the total conversion and FAEs yield results found in run 2, using a molar ratio water/fat 10 times higher, were slightly higher than those of run 3, showing clearly the beneficial effect of the water in the reaction mechanism. One possibility is that water causes hydrolysis of part the triglycerides forming glycerol and fatty acids; these fatty acids, together with the free fatty acids present in the feedstock (very high content for the animal fat sample used in this work: 35 wt.%) react via the esterification reaction with ethanol to form the FAEs (biodiesel), and more water. This additional amount of water produced in the esterification reaction may cause hydrolysis of the remaining triglycerides, in a cyclic behavior, favoring the overall conversion process. The catalytic effect of subcritical water was explained by Go and co-workers [27] due to the better dissociation of the water molecule into hydroxonium and hydroxide ions, as the pH of water decreases from 7.4 at 0 °C to 5.5 at 250 °C, increasing the amount of H_3O^+ formed.

The esterification reaction is known to be much easier and faster than the transesterification reaction, which normally requires strong acidic or basic catalysts to activate and broke the carbon-oxygen bonds of the triglycerides. The presence of a very high amount of free fatty acids in this feedstock (35 wt.%) may explain the total conversion observed, as these acids are easily transformed to FAEs under the thermodynamic conditions employed here. There is also a possibility of catalytic action of the fatty acid itself, as observed by Minami and Saka [23], as they concluded that FA has an important role as acid catalyst in hydrolysis reaction of oils/fats in subcritical water. Moreover, these conditions may also facilitate the nucleophilic attack of the alcohol (ethoxy group) to the carbonyl group of part the triglycerides, forming an intermediate, and subsequently, diglycerides, monoglycerides and finally FAEs. This transesterification reaction mechanism was suggested by Sawangkeaw and co-workers [22], but under supercritical conditions. Experiments with soybean oil and palm oil were also conducted under analog conditions: temperature 240°C, reaction time 120 min., molar ratio water/TG

371 = 5 and molar ratio ethanol/TG = 10. Fig. 4 shows the results of the trans-
 372 esterification reaction using soybean oil as feedstock. This figure presents
 373 the chromatograms obtained for the control sample (soybean oil) and the
 374 products (FAEEs). In contrast with animal fat, soybean oil has almost only
 375 triglycerides, and very low amount of free fatty acids (0.3 wt.%). This led
 376 to the false conclusion that almost no esterification reaction had occurred,
 377 but the presence of water (molar ratio water/triglycerides = 5) suggests that
 378 the same two possible transesterification reaction mechanisms cited above
 379 did indeed take place: via hydrolysis of part of the triglycerides, or via the
 380 nucleophilic attack of the alcohol (ethoxy group) to the carbonyl group of the
 381 triglycerides. The reaction via hydrolysis produces glycerol and fatty acids;
 382 these acids, together with the free fatty acids present in the feedstock (very
 383 low content in this case) react via the esterification reaction with ethanol
 384 to form part of the FAEEs observed. As discussed in the case with animal
 385 fat, we believe that the transesterification reaction mechanism via the nu-
 386 cleophilic attack of the alcohol to the carbonyl groups of the triglycerides
 387 is also possible under the conditions employed here, as extra experiments
 388 conducted with very low amount of water (no extra addition of water and no
 389 catalysts at all) also allowed the reaction to occur, although at a lower rate,
 390 when compared to the abovementioned conditions. As seen in Fig. 4, not
 391 all triglycerides present in the feedstock were converted, and the calculated
 392 conversion was 84 %. Moreover, some diglycerides (very few) remain at the
 393 end of reaction, and a significant proportion (about 16 %) of the product
 394 remains as monoglycerides.

395
 396 Fig. 4
 397

398 Fig. 5 shows the results for the production of FAEEs using palm oil as
 399 feedstock, performed at the same experimental conditions. Similarly to the
 400 case using soybean oil, not all triglycerides present in the feedstock were
 401 converted, but the calculated total conversion was 98.5 % for this run. Anal-
 402 ogously, some diglycerides (very few) remain at the end of reaction, and a
 403 significant proportion (about 10 %) of the product persists as monoglyceride.
 404 It is important to stress, however, that the total triglyceride conversion was
 405 significantly higher, under the same reaction conditions. This result confirms
 406 the assumption made for the case of animal fat, i.e., that the presence of free
 407 fatty acids in much higher amount in palm oil (5 wt.% against 0.3 wt.%
 408 for soybean oil) results in the formation of FAEEs by direct esterification, a

much easier and faster reaction than the transesterification, consistent with the higher total conversion observed, in comparison to the soybean feedstock. This fact reinforces the possibility of catalytic action of the fatty acids in the hydrolysis reaction of oils/fats in subcritical water, as mentioned before.

Finally, it may be stressed that the FAEEs produced in all experiments with the three feedstocks ranged from 14 carbon atoms up to 22 carbon atoms, by comparison with the standards (Fig. 2), and the major part of them stayed at around 18 carbon atoms, as expected.

Fig. 5

The energy consumption, as well as the net energy ratio (NER), was determined in each one of the experiments performed. Table 3 presents the

NER for animal fat biodiesel, vegetable oils biodiesel and other sources for bioenergy production, for comparison [31],[32],[33].

Table 3

To achieve a positive energy balance, the energy content of the biodiesel produced must be greater than the total energy used to obtain it, meaning NER values greater than one. Many experiments performed in this study met this criterion, and the three cases presented in Tab. 3 were among the best ones, which qualifies this process as high potential for industrial application. Some operational conditions exhibited greater NER values, but with low conversion of feedstock, and higher by-products generation. Based on the results presented, we can conclude that crude, or used vegetable oils or animal fats may be used to produce biodiesel by this procedure, since the presence of free fatty acids accelerates the overall reaction rate, increasing the total conversion efficiency. Nevertheless, this process can operate with a broad range of water content in the feedstock, as high water content also showed a positive effect. The water/triglycerides molar ratio has an important role in the process. The presence of water at low ratios (less than 1.0) allowed the reaction to occur with very high values of NER (greater than 6.0), and excellent conversions (greater than 98 %), but the product exhibited high contents of mono and diglycerides. As the international specifications for biodiesel require very low content of both mono and diglycerides, the parameter water/triglycerides ratio must be optimized in a future work, aiming at a positive NER and final product specification meeting the standards, at

447 higher rates of production, to allow scale-up of the process.

448 **4. Conclusions**

449 The presence of water and free fatty acids improved the conversion in
450 the hydrolysis, esterification and transesterification reactions of animal fat,
451 soybean and palm oils in the presence of subcritical ethanol. The energy
452 content in the biodiesel produced was greater than the net energy require-
453 ments to the process (NER greater than one), at 240 °C, 2h of reaction, with
454 pressures varying from 20 to 45 bar. These results indicate that the pro-
455 cess is energetically favorable, and thus represents a cleaner technology with
456 great environmental advantages when compared to traditional esterification
457 or transesterification processes. The energetic feasibility using the net en-
458 ergy ratio (NER) should be considered to any process suitable for large-scale
459 applications.

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Tables

Table 1: Composition in percentage of Fatty Acids contained in the feedstock studied (animal fat, soybean oil and palm oil)

Fatty Acid Name	Formula	% Fatty Acid in the animal fat *	% Fatty Acid in the soybean oil**	% Fatty Acid in the palm oil**
Caproic acid	C6:0	0.69		
Caprylic acid	C8:0	1.80		
Capric acid	C10:0			
Onedecanoic acid	C11:0	0.52		
Lauric acid	C12:0	0.2		0.2
Miristic acid	C14:0	2.41	0.1	1.1
Miristoleic acid	C14:1	0.63		
Palmitic acid	C16:0	30.3	11	44.1
Palmitoleic acid	C16:1	1.52	0.1	0.2
Heptadecanoic acid	C17:0	1.13		
Cis-10-heptadecanoic acid	C17:1	0.33		
Stearic acid	C18:0	23.12	4	4.4
Oleic acid	C18:1n9c	24.05	23.4	39.0
Linoleic acid	C18:2n6c	0.24	53.2	10.5
Linolenic acid	C18:3n3	0.06	7.8	0.3
Araquidic acid	C20:0	0.15	0.3	0.2
Gadolinic acid	C20:1	0.7		
Eicosapentaenoic acid	C20:5			
Behenic acid	C22:0	4.6	0.1	
Euricic acid	C22:1n9	2.4		

Tricosanoic acid	C23:0	0.9		
Lignoceric acid	C24	0.44		

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**<http://web.cals.uidaho.edu/biodiesel/tools-for-producers/triglyceride-molecular-weight-calculator/>

Table 2: Experimental design and results of Total Conversion, NER, and yield of FAEEs for the esterification/transesterification of animal fat.

Run Order #	Temp (°C)	Time (min)	Molar ratio water/triglycerides	Molar ratio ethanol/triglycerides	Total Conversion %	NER	FAEEs yield %
1	120	30	0.5	6	0.0	0.0	0.0
2	240	30	5.0	6	93.7	6.1	94.3
3	240	120	0.5	6	93.1	4.8	93.7
4	180	75	2.8	8	19.7	1.2	74.2
5	240	120	5.0	10	100.0	2.6	98.0
6	120	120	0.5	10	0.0	0.0	0.0
7	240	30	0.5	10	93.6	6.2	94.3
8	120	30	5.0	10	0.0	0.0	0.0
9	120	120	5,0	6	0.0	0.0	0.0

Table 3: NER for animal fat biodiesel, vegetable oils biodiesel and other sources for bioenergy production.

Biofuel	NER	References
Animal Fat biodiesel	2.6	Authors*
Soybean oil biodiesel	2.1	Authors*
Palm oil biodiesel	2.5	Authors*
Corn grain ethanol	1.25	[31]
Soybean biodiesel	3.67	[31]
Biodiesel from Palm Fatty Acid Distillate	3.23	[32]
Biofuels from microalgae	1,54	[33]

*Temperature 240 °C, reaction time 120 min., molar ratio water/fat or TG = 5 and molar ratio ethanol/fat or TG = 10.

Fig. 1.
Scheme for the experimental setup used for biodiesel production from animal fat under subcritical wet conditions. 1, Parr reactor; 2, DAQ (data acquisition system); 3, computer and graphical interface (LabView); 4, temperature sensor in the reactor; 5, temperature sensor in the heat blanket; 6, magnetic stirrer; 7, heat blanket; 8, pressure sensor and transducer; 9 rupture disc; 10 sampling valve.

Fig. 2.
Chromatograms of the standards FAEEs, monoglyceride (monoolein), diglyceride (diolein) and triglyceride (triolein).

Fig. 3.

Chromatograms representing the FAEEs products obtained from the ethanol transesterification of animal fat (AF) at temperature 240 °C, reaction time 120 min., molar ratio water/fat=5 and molar ratio ethanol/fat=10.

Fig. 4.

Chromatograms showing the FAEEs obtained from the ethanol transesterification using soybean oil at temperature 240 0C, reaction time 120 min., molar ratio water/TG=5 and molar ratio ethanol/TG=10.

Fig. 5.

Chromatograms showing the FAEEs obtained from the ethanol transesterification of palm oil at temperature 240 0C, reaction time 120 min., molar ratio water/TG = 5 and molar ratio ethanol/TG=10.