



Article

Fatty Acid Alkyl Ester Production by One-Step Supercritical Transesterification of Beef Tallow by Using Ethanol, Iso-Butanol, and 1-Butanol

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Abstract: The effect of temperature was studied on the synthesis of fatty acid alkyl esters by means of transesterification of waste beef tallow using ethanol and, iso-butanol and 1-butanol at supercritical conditions. These alcohols are proposed for the synthesis of biodiesel in order to improve the cold flow properties of alkyl esters. Alcohol–beef tallow mixtures were fed to a high-pressure high-temperature autoclave at a constant molar ratio of 45:1. Reactions were carried out in the ranges of 310–390 °C and 310–420 °C for ethanol and iso-butanol, respectively; meanwhile, synthesis using 1-butanol was assessed only at 360 °C. After separation of fatty acid alkyl esters, these samples were characterized by nuclear magnetic resonance (NMR) and gas chromatography coupled to mass spectrometry (GC-MS) to quantify yields, chemical composition, and molecular weight. Results indicated that yields enhanced as temperature increased; the maximum yields for fatty acid ethyl esters (FAEEs) were attained at 360 °C, and for fatty acid butyl esters (FABEs) were achieved at 375 °C; beyond these conditions, the alkyl ester yields reached equilibrium. Concerning the physicochemical properties of biodiesel, the predicted cetane number and cloud point were enhanced compared to those of fatty acid methyl esters.

Keywords: fatty acid ethyl ester; fatty acid butyl ester; 1-butanol; ethanol; iso-butanol; supercritical; waste beef tallow; transesterification



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1. Introduction

Energy consumption changes according to the world population density and technological advances, as well as human needs and comforts. According to a projection for the year 2050 published in the latest report of the U.S. Energy Information Administration, energy utilization is going to increase in sectors such as electric power, transportation and industry in the next years. Moreover, residential and commercial segments are expected to keep the same consumption energy rate. In the early years, the three most produced energy sources are expected to be natural gas, oil, and renewable materials; furthermore, the maximum fossil oil demand will be achieved, followed by variable consumption in benefit of other energy sources. Natural gas and renewable materials will have a constant growing demand between the years 2022 and 2050, with a production of about 35 to 44 and 10 to 22 quadrillion of BTU, respectively [1].

Biodiesel is a liquid biofuel derived from biomass and is constituted by fatty acid alkyl esters mainly obtained by transesterification of fatty acids with methanol (FAME) in which the final product (100% biodiesel, B100) has similar properties to fossil diesel [2]. Biodiesel development has been focused on FAMEs, however exploration and development to use higher alcohols, such as ethanol and butanol, to obtain fatty acid ethyl and fatty acid butyl esters are also relevant [3,4]. Ethanol and butanol are gaining attention recently since these are potential additives for fuels and especially due to the fact that these could be produced by fermentation; therefore, a combination of biodiesel and green alcohol technologies would strengthen the development of sustainable fuels [5–7].

Transportation engines commonly use blends of biodiesel (B20: 20%) + diesel (80%) [8]. Fatty acids are supplied from feedstocks classified as renewable materials such as vegetable oils, animal fats, waste oil or fat, algae, among others [9,10]. Vegetable oils are the major source used around the world but are also destined for human consumption; then, the other materials are taking growing participation, i.e., beef tallow [11]. Non-edible tallow feedstock had a remarkable role in Brazil (13%) in 2018 and has been gaining presence with about 7% in the United States since 2021 where soybean oil was the main feedstock, at 50% [12–14].

Biodiesel production from non-edible tallow, under certain pathways, carries some benefits, such as low-cost feedstocks, and overweighs obstacles associated with the high content of free fatty acids (FFA) and moisture that reduce yields and affects its properties. Low yields on fat synthesis attract the interest of improving transesterification to attain new insights in basic, acid and enzymatic catalysis; each pathway has its own characteristics, and the conditions include moderated temperatures, low-cost catalysts, and novel catalysts [15–24].

Transesterification with alcohols at supercritical conditions is a viable option carried out at higher temperatures and pressure among the abovementioned methods [24]. Production of fatty acid alkyl esters from beef tallow with high FFA content can be enhanced since the mass transfer and the homogeneous medium are promoted at supercritical conditions. Among the alcohols, methanol is the most used in transesterification for several feedstocks, for instance fresh or used vegetable oils [25–46]. Ethanol and butanol are other alternative solvents for fatty acid alkyl esters production, and both can be transformed from chemical and biochemical processes [47,48]; bioethanol and biobutanol are generated as main or secondary by-products using biological methods from first, second and third generation feedstocks. These solvents have attracted much attention; hence, new developments have been reported recently [49–53].

Insights about the transesterification of animal fats with supercritical long carbon-chain alcohols are limited [29,42–45,54], and to the best of our knowledge, two contributions are specialized on beef tallow [34,55]. Marulanda-Buitrago and Marulanda-Cardona [55] evaluated the effect of temperature (320–400 °C), alcohol excess (9–15) in the feed molar ratio and time (8–40 min) in the transesterification of beef tallow with supercritical ethanol; the highest conditions were claimed to promote the ester production. Bolonio et al. [34] evaluated the fatty acid ethyl esters manufacture from beef tallow by two methods: one-step transesterification under supercritical ethanol, and two-step reactions consisting of hydrolysis and esterification. The one-step method was explored in ranges of 300–350 °C and 40–120 min, and 20 or 40 mol of ethanol per mol of animal fat. For the two-step method, reactions lasted 60 min and temperature ranged from 200 to 350 °C; hydrolysis needed a high water/tallow volume ratio (2/1) and esterification operated at 7/1 of ethanol/free fatty acids molar ratio. Both methods had their own advantages: the first was simple, the esters had low content of polyunsaturated compounds and reported few degradations, while the second generated FAEEs rich in unsaturated chemicals.

Due to the fact that the raw material composition affects the properties of the final product, our contribution is aligned with the valorization of beef tallow waste for the fatty acid alkyl esters production. The aim of this work was to study the effect of alcohols and temperature on the fatty acid alkyl ester yields using three different alcohols (ethanol, isobutanol, 1-butanol) at a fixed molar ratio of alcohol/tallow (45/1) during 60 min based on

our previous findings using supercritical methanol [56] and the literature compilation [34,55]. This research also presents the quantitative characterization of fatty acid alkyl esters.

2. Materials and Methods

2.1. Materials

ACS grade iso-butanol and n-butanol were provided by Reactivos Química Meyer, having 0.1% of water content. Commercial ethanol had a water content of 3.6%. A sample lot of beef tallow was picked up from different local markets in the State of Mexico, this waste did not have any further valorization. Then, meat residues were separated from beef tallow by a simple filtration following a previous melting stage. The external standard (49454-U) for quantification of fatty acid ethyl ester was provided by Sigma-Aldrich. Fatty acid content and physicochemical properties of waste beef tallow have been previously reported and are listed in Table 1. This raw material was analyzed by Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance ($^1\text{H-NMR}$ and $^{13}\text{C-NMR}$). Detailed analytical conditions can be found in an earlier contribution [56].

Table 1. Physicochemical properties of waste beef tallow (WBT) [56].

Property	Value
ρ at 308.15 K/g cm $^{-3}$	0.890
$MW_{WBT}/\text{g mol}^{-1}$	737.7 ± 2.0^a
$MW_{WBT}/\text{g mol}^{-1}$	742.5 ± 1.8^b
HHV/J g $^{-1}$	39,143.7
water content/ppm	200
SI	189.1
% FFA $_{C16:0}$	3.55 ± 0.04
% FFA $_{C18:0}$	3.94 ± 0.03
% FFA $_{C18:1\ n-9}$	3.91 ± 0.04

^a HPLC-MS; ^b Cryoscopy.

2.2. Transesterification

A batch autoclave made of Inconel 625 alloy with a volume capacity of 170 cm 3 was operated to implement the synthesis at supercritical conditions. The procedure briefly consisted of pouring 150 cm 3 of alcohol–waste beef tallow blend to the autoclave with a molar ratio of 45/1, sealing, degassing, and wrapping the autoclave in an electrical heating resistance, turning on the magnetic shaft stirrer (1000 rpm) coupled to a three-blade propeller. Then, autoclave temperature was set above the critical point of the alcohol (ethanol: $T_c = 240.77\text{ }^\circ\text{C}$, $p_c = 61.48\text{ bar}$; iso-butanol: $T_c = 274.63\text{ }^\circ\text{C}$, $p_c = 43\text{ bar}$; 1-butanol: $T_c = 289.9\text{ }^\circ\text{C}$, $p_c = 44.23\text{ bar}$) [57]. Furthermore, the temperature was monitored by a calibrated K-type thermocouple vertically immersed near the internal bottom of the autoclave. A gradual heating rate was established with the aim of minimizing the thermal degradation, particularly at elevated temperatures. Once desire temperature was reached, the synthesis lasted 60 min in order to guarantee the maximum yield [34,55,56]. Pressure changes in the constant volume autoclave were dependent on temperature and volume feedstock variations; moreover, the addition of a pressurizing agent (hydrogen, nitrogen, or carbon dioxide) was not considered since this component modifies the phase diagram. Thereafter, the heating was immediately stopped to inhibit further reactions by circulating cold water throughout an internal coil and removing the autoclave from the electrical resistance. Finally, the collected liquid sample was distilled for alcohol recovery, and the residual section was poured in a separation funnel. After stabilization of the residual, the glycerol-rich phase located on the bottom phase and the fatty acid alkyl esters in the upper phase were separated. Esters were stored into amber bottles for subsequent analyses. Reactions were performed thrice for each temperature by separating the total amount of waste beef tallow, thus, to avoid different composition on raw material for each set of experiments.

2.3. Quantification

The recovered fatty acid alkyl esters were characterized by nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) in a Bruker Ascend 750 MHz to determine yields, as well as gas chromatography coupled to mass spectrometry (GC-MS) to generate FAEEs and FABEs profiles and their molecular weight. Physicochemical properties, cloud point (CP), calculated cetane number (CN), color Gardner (CG) and free fatty acid content (FFA_S) were also reported with basis on standard methods and correlations detailed elsewhere [56].

3. Results and Discussion

Fatty acid alkyl esters were obtained at different temperatures and pressures above the critical point of the alcohol. Each reaction was performed thrice and the corresponding first run is summarized in Table 2. The transesterification reversibility caused the loading molar ratio, between the alcohol and waste beef tallow, to be established in excess (45/1); thus, the synthesis direction was displaced to promote esters production while a homogeneous phase was probably coexisting at the required conditions [54,58,59].

Table 2. Properties for each transesterification at 45:1 of molar ratio for A:BT.

Reaction	T/°C	P/bar	I _{FAEEs} Area	I _{FAEEs} Interval	I _{TAG} Area	I _{TAG} Interval	Y _{FAEEs} /%	CP/°C	CN	CG	FFA _S A /%
Ethanol											
E1S7	310	152.0	95,455.9	4.18–4.09	19,980.7	4.35–4.17	55.74	20	79.7	3.6	8.1
E2S7	320	171.6	101,315.3	4.17–4.10	18,443.4	4.35–4.17	59.96	18	79.2	4.0	7.2
E3S7	330	217.3	94,003.9	4.17–4.10	15,789.8	4.34–4.17	62.28	18	86.8	4.1	7.6
E4S7	340	254.9	86,045.8	4.17–4.09	7509.2	4.26–4.17	77.71	19	79.7	3.5	7.6
E5S7	350	280.4	77,754.0	4.17–3.97	3585.4	4.22–4.17	87.33	17	79.5	3.8	8.3
E6S7	360	344.6	141,698.7	4.17–4.09	2565.2	4.34–4.17	94.76	16	80.1	4.1	9.2
E7S7	360	344.2	83,930.6	4.17–4.07	1410.7	4.36–4.17	95.12	16	80.8	4.1	9.2
E8S7	370	397.1	81,931.6	4.17–4.09	4318.1	4.34–4.17	85.70	14	80.8	5.4	10.9
E9S7	380	397.9	50,956.1	4.17–4.10	2745.7	4.35–4.17	85.41	14	81.1	5.7	15.0
E10S7	390	397.1	70,722.1	4.18–4.10	9636.4	4.36–4.17	67.88	14	81.2	7.4	18.7
Iso-butanol											
E1S9	310	63.7	70,200.5	3.87–3.77	25,722.0	4.35–3.89	76.47	18		4.6	6.0
E2S9	335	147.1	73,763.8	3.90–3.79	5817.2	4.34–3.90	94.73	17		2.7	5.3
E3S9	350	205.9	68,245.6	3.90–3.79	7571.5	4.33–3.88	93.06	14		2.4	4.7
E4S9	375	269.6	65,417	3.89–3.77	1266.7	4.34–3.88	96.65	10		4.8	6.2
E6S9	390	279.4	71,736.0	3.89–3.80	1946.8	4.35–3.88	94.80	9		5.7	8.2
E5S9	420	343.2	34,260.4	3.90–3.78	12,063.0	4.37–3.89	35.55	11		7.3	8.2
1-butanol											
E1S10	360	210.7	237,318.6	3.01–4.10	20,289.96	4.31–4.11	87.70	8		5.0	6.4

3.1. Fatty Acid Ethyl Esters (FAEEs)

The isolated FAAEs were dissolved in deuterated chloroform and subject to $^1\text{H-NMR}$ analyses, and the corresponding spectra are depicted in Figure 1. The triplet (A) in the interval of 2.2–2.4 ppm denoted hydrogens of $\alpha\text{-CH}_2$. Three multiplets ranging from 1.55 to 1.70 ppm (B), 1.1 to 1.46 ppm (C) and 5.2 to 5.4 ppm (D) corresponded to the hydrogens of $\beta\text{-CH}_2$, $-(\text{CH}_2)_n$ - end and $-\text{CH}_2\text{-CH=}$, in the same order; this last hydrogen with a double carbon chain was also identified by the multiplet within 1.92–2.07 ppm (F). The CH_3 hydrogens were detected in two zones, one in a triplet ranging from 0.83 to 0.93 ppm (E) and the second peak in a multiplet at 0.3 ppm (K). Subsequently, a quartet in the interval from 3.97 to 4.18 ppm (EE) was related to $\text{CH}_3\text{-CH}_2\text{-OOC-}$ hydrogens.

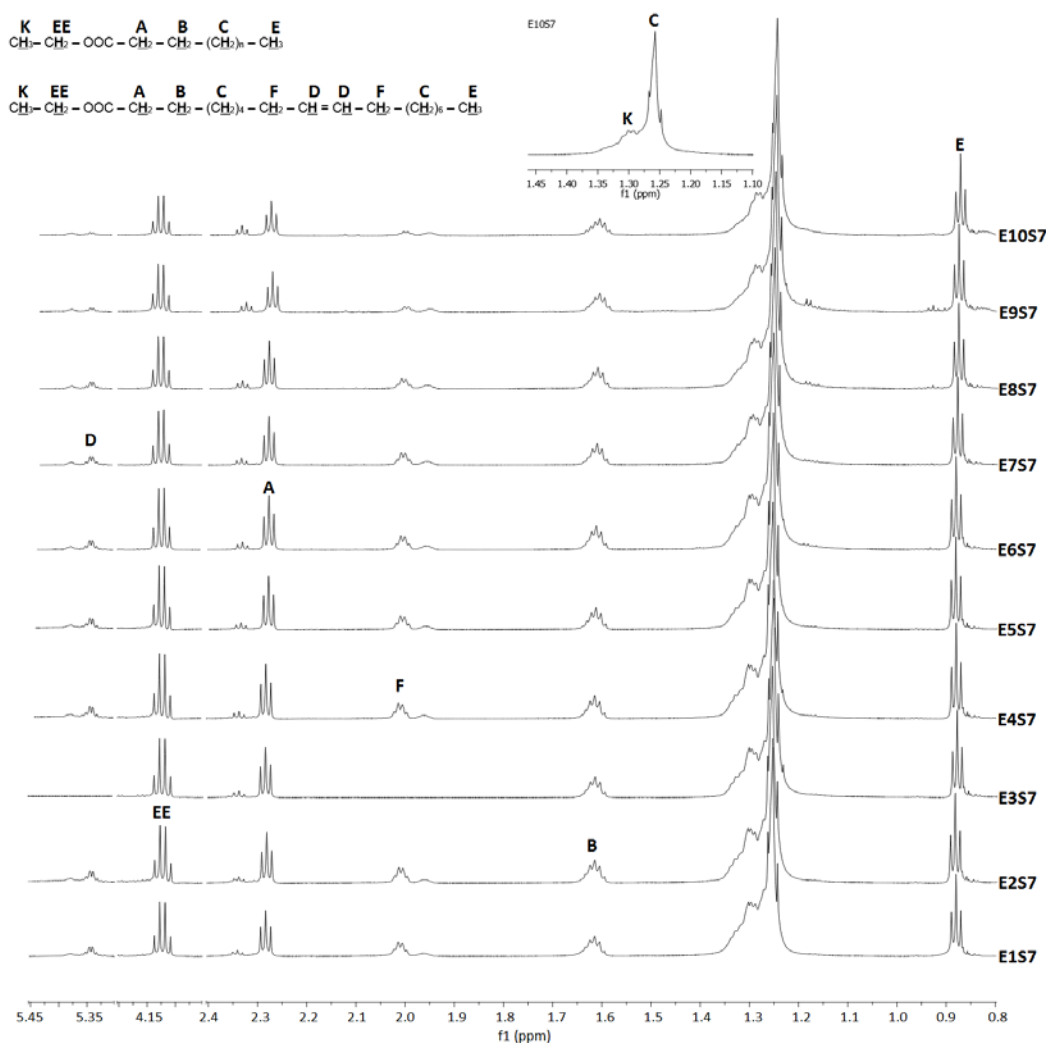


Figure 1. $^1\text{H-NMR}$ spectra for FAEE obtained from beef tallow by using supercritical ethanol.

Yield for FAEEs (Y_{FAEEs}) listed in Table 2 were estimated by integrating peak areas from the $^1\text{H-NMR}$ analyses and formulating the expression proposed by Ghesti et al. [60]:

$$Y_{\text{FAEEs}}/\% = \left(\frac{4 (I_{\text{FAEEs}} - I_{\text{TAG}})}{4 (I_{\text{FAEEs}} - I_{\text{TAG}}) + 6 (2 I_{\text{TAG}})} \right) \times 100 \quad (1)$$

where the number 4 in Equation (1) denoted the four glycerol methylene hydrogens in triacylglycerides or triacylglycerol (TAG), while the number 6 expressed the six hydrogens in the three FAEEs. From Figure 1, I_{FAEEs} corresponded to the quartet area observed in the range of 3.97–4.18 ppm and indicated as EE; it was assumed to belong to the two hydrogens of the $\text{CH}_3\text{-CH}_2\text{-OOC-}$ group presented both in FAEEs and TAG. Finally, I_{TAG} was evaluated from the double doublet area in the interval of 4.17–4.36 ppm, and was related to the hydrogens of $-\text{CH}_2$ hydrogens from glycerol in the TAG samples.

The temperature induced a promising effect on the Y_{FAEEs} , whose values enhanced in the range of 310–360 °C, the yield was 55.74% at 310 °C, then a high temperature led to a strong upgrading $Y_{\text{FAEEs}} = 77.71\%$ (at 340 °C), and the maximum yield (95.12%) was achieved at 360 °C, assigned as the proper temperature. Conversely, the performance of fatty acid ethyl esters was interfered beyond 370 °C since the yield decreased to 67.88%.

Quantification of FAEE constituents was investigated by GC-MS analyses and a compositional standard. The identified components were ethyl palmitate, ethyl stearate and ethyl oleate. Composition of different samples studied are reported in Table 3. The synthe-

sis named “E3S7” carried out at 330 °C did not generate the unsaturated ester (ethyl oleate) as can be seen in Table 3. It also presented in the ¹H-NMR spectrum shown in Figure 1, where the multiplet (F) was not detectable. The absence of the unsaturated ester could be related to the initial feedstock: oleic acid was probably not contained at the beginning regardless of the pretreatment of the feedstock for achieving a homogeneous sample lot. Out of this, ethyl stearate had the highest composition for all the reactions. The chemicals contribution below 360 °C had the following order: ethyl stearate > ethyl oleate > ethyl palmitate, while the order of chemicals of ethyl stearate > ethyl palmitate > ethyl oleate was noted at temperatures over 370 °C. The average molecular weight for FAEEs oscillated in the range of 302.84–304.22 g/mol, but the FAEEs for the “E3S7” experiment had 306.41 g/mol due to the absence of the unsaturated ester, as reported in Table 3.

Table 3. FAEE composition from beef tallow transesterification.

Experiment	Chemical	Formula	MW	wt%	mol%	MW _{FAEEs}
E1S7	Ethyl palmitate	C ₁₈ H ₃₆ O ₂	284.4772	26.492	28.306	303.960
	Ethyl stearate	C ₂₀ H ₄₀ O ₂	312.5304	41.598	40.458	
	Ethyl oleate	C ₂₀ H ₃₈ O ₂	310.5145	31.910	31.236	
E2S7	Ethyl palmitate	C ₁₈ H ₃₆ O ₂	284.4772	25.856	27.641	304.108
	Ethyl stearate	C ₂₀ H ₄₀ O ₂	312.5304	40.281	39.196	
	Ethyl oleate	C ₂₀ H ₃₈ O ₂	310.5145	33.862	33.164	
E3S7	Ethyl palmitate	C ₁₈ H ₃₆ O ₂	284.4772	20.239	21.800	306.415
	Ethyl stearate	C ₂₀ H ₄₀ O ₂	312.5304	79.761	78.200	
E4S7	Ethyl palmitate	C ₁₈ H ₃₆ O ₂	284.4772	26.650	28.472	303.921
	Ethyl stearate	C ₂₀ H ₄₀ O ₂	312.5304	41.835	40.683	
	Ethyl oleate	C ₂₀ H ₃₈ O ₂	310.5145	31.515	30.846	
E5S7	Ethyl palmitate	C ₁₈ H ₃₆ O ₂	284.4772	26.338	28.145	303.990
	Ethyl stearate	C ₂₀ H ₄₀ O ₂	312.5304	41.008	39.887	
	Ethyl oleate	C ₂₀ H ₃₈ O ₂	310.5145	32.654	31.968	
E6S7	Ethyl palmitate	C ₁₈ H ₃₆ O ₂	284.4772	25.985	27.782	304.143
	Ethyl stearate	C ₂₀ H ₄₀ O ₂	312.5304	43.961	42.782	
	Ethyl oleate	C ₂₀ H ₃₈ O ₂	310.5145	30.054	29.437	
E7S7	Ethyl palmitate	C ₁₈ H ₃₆ O ₂	284.4772	25.927	27.727	304.226
	Ethyl stearate	C ₂₀ H ₄₀ O ₂	312.5304	47.416	46.156	
	Ethyl oleate	C ₂₀ H ₃₈ O ₂	310.5145	26.658	26.118	
E8S7	Ethyl palmitate	C ₁₈ H ₃₆ O ₂	284.4772	29.913	31.868	303.069
	Ethyl stearate	C ₂₀ H ₄₀ O ₂	312.5304	43.568	42.249	
	Ethyl oleate	C ₂₀ H ₃₈ O ₂	310.5145	26.519	25.883	
E9S7	Ethyl palmitate	C ₁₈ H ₃₆ O ₂	284.4772	30.763	32.749	302.844
	Ethyl stearate	C ₂₀ H ₄₀ O ₂	312.5304	43.861	42.502	
	Ethyl oleate	C ₂₀ H ₃₈ O ₂	310.5145	25.376	24.749	
E10S7	Ethyl palmitate	C ₁₈ H ₃₆ O ₂	284.4772	27.426	29.291	303.817
	Ethyl stearate	C ₂₀ H ₄₀ O ₂	312.5304	47.416	46.094	
	Ethyl oleate	C ₂₀ H ₃₈ O ₂	310.5145	25.158	24.615	

3.2. Fatty Acid Butyl Esters (FABEs)

Regarding transesterification in the presence of iso-butanol, the spectra of fatty acid isobutyl esters analyzed by ¹H-NMR are illustrated in Figure 2. Peaks for the FABEs samples were similar to those formed on FAEs identified with the symbols from (A) to (F): the triplet in 2.2–2.4 ppm (A) ascribed to α-CH₂ hydrogens, the respective three multiplets in 1.55–1.70 ppm (B), 1.1–1.46 ppm (C) and 5.2–5.4 ppm (D) associated with hydrogens of β-CH₂, -(CH₂)_n- structure end and double carbon chain, the triplet within 0.83–0.93 ppm (E) assigned to the CH₃ hydrogens, and the multiplet 1.95–2.07 ppm (F) represented the CH₂ within the double carbon chain. The distinctive peaks for FABE were identified with the symbols (J), (BE), (L), and were classified as hydrogens using the same order: the doublet ranging from 0.9–0.96 ppm denoted CH₃ hydrogens, the doublet within 3.8–3.88 ppm belonged to CH₂ in the >CH-CH₂-OOC- structure, and the multiplet from 1.89 to 1.95 ppm indicated the -CH< hydrogens.

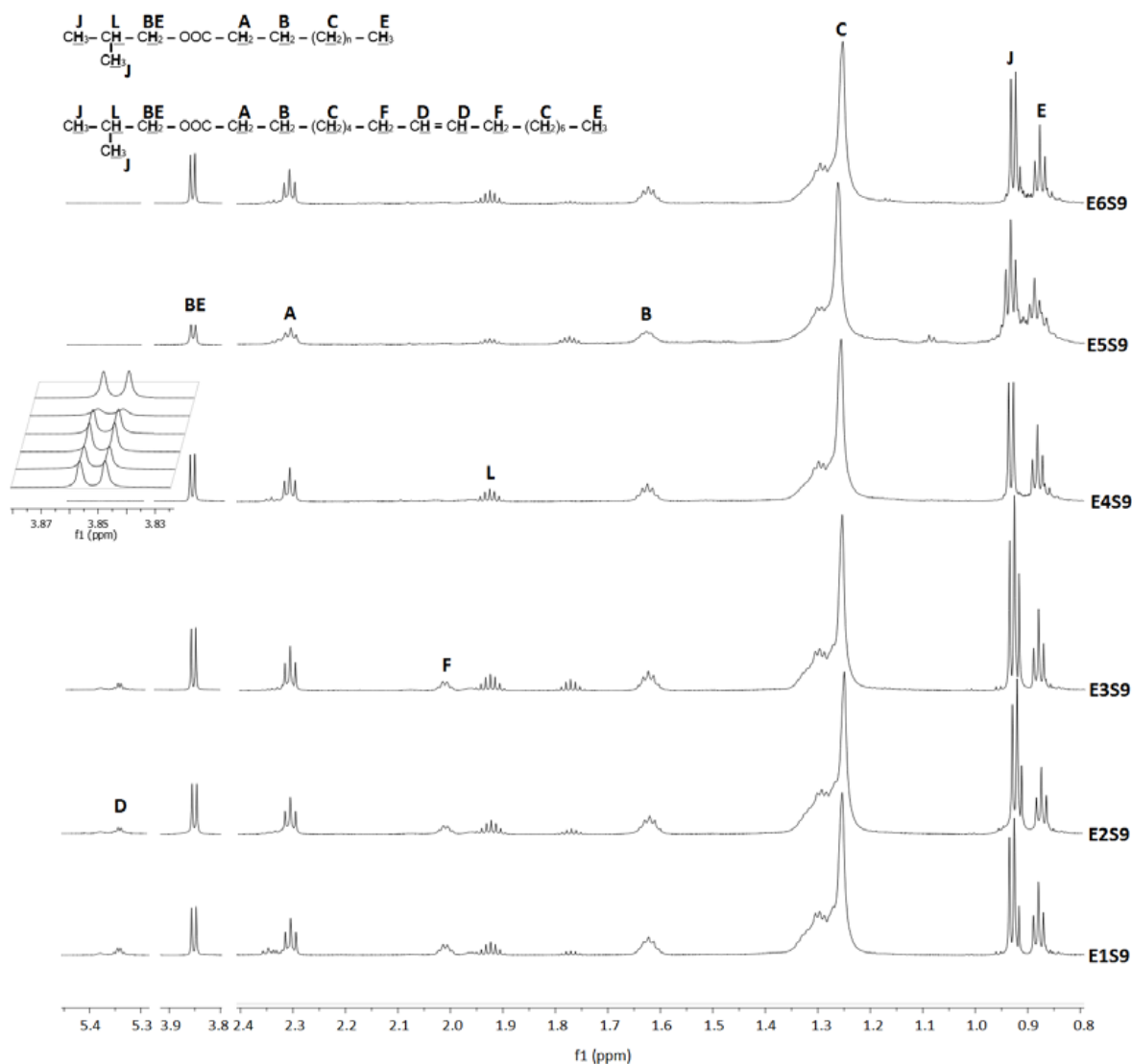


Figure 2. ¹H-NMR spectra for FABE obtained from beef tallow by using supercritical iso-butanol.

The production of fatty acid isobutyl esters was evaluated in terms of the yield (Y_{FABEs}). The calculated values listed in Table 2 were approached by using the Equation (2) and the integration of peak areas from ¹H-NMR analyses. The proposed equation was developed under the same considerations and notation given for yields of fatty acid ethyl esters:

$$Y_{\text{FABEs}}/\% = \left(\frac{4 (I_{\text{FABEs}} - I_{\text{TAG}})}{4 (I_{\text{FABEs}} - I_{\text{TAG}}) + 6 (2 I_{\text{TAG}})} \right) \times 100 \quad (2)$$

where the number 4 expresses the glycerol methylene hydrogens in triacylglycerides or triacylglycerol (TAG), the number 6 represents the hydrogens in the three FABEs, the area of the hydrogens in the $>\text{CH}-\text{CH}_2-\text{OOC}-$ structure from produced FABEs, and unreacted TAG is indicated with the I_{FABEs} notation that appears within 3.77–3.90 ppm. The hydrogens of $-\text{CH}_2$ hydrogens from glycerol contained in TAG are symbolized with I_{TAG} and are in the range of 3.88–4.37 ppm. The highest yield ($Y_{\text{FABEs}} = 96.65\%$) was attained at 375 °C, which was superior to the maximum value accomplished by using ethanol as solvent at 360 °C. Critical temperature for each alcohol played an important role in FAAEs synthesis; fatty acid isobutyl esters production was not satisfactory at 310 °C ($Y_{\text{FABEs}} = 76.47\%$) but it was superior to that reported for the FAAEs ($Y_{\text{FAEs}} = 55.74\%$), and this temperature was close to the critical temperature of iso-butanol.

Correspondingly, the FAbEs content via 1-butanol was assessed under the same conditions as the reported for the other alcohols at 375 °C. The yield calculated with Equation (2) was reported as 87.7%, which was lower than the produced FAbEs using iso-butanol (93.06% at 350 °C and 96.65% at 365 °C) or ethanol (94.76% at 360 °C). A higher effect of the thermal degradation was taking part in the involved system as a consequence of the additional competing reactions. The identified peaks from Figure 3 for the transesterification with 1-butanol were the same as those identified in the reaction using iso-butanol for the (A)–(F) and L notation. The exceptions were the multiplets (G) and (H), the triplet (J) and the doublet (BE) that denoted the hydrogens of CH₂, CH₂, CH₃, CH₂ assigned on the CH₃–CH₂–CH₂–CH₂–OOC– structure.

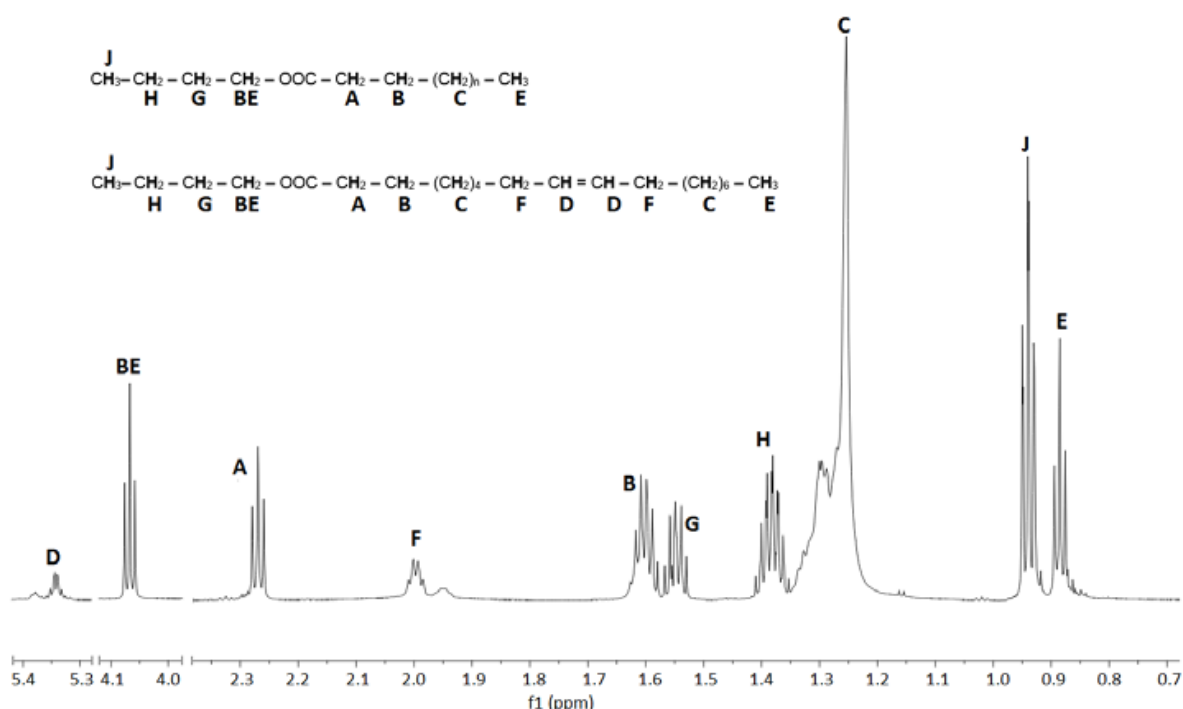


Figure 3. ¹H-NMR spectra for FAbE obtained from beef tallow by supercritical 1-butanol.

The components identified in the fatty acid isobutyl ester samples are summarized in Table 4. The existence of esters was confirmed with a carbon chain length from eight to twenty-two; with reference to the relative area, the major esters were those of high molecular weight: isobutyl stearate, isobutyl oleate, isobutyl palmitate, isobutyl margarate and isobutyl myristate. Other esters were produced above 390 °C where the yield did not enhance. At the maximum temperature (420 °C) used, the lowest yield 35.55% was obtained, and the formation of 4-methyl-2ethyl-pentanol and some alkanes confirmed the appearance of additional reactions; these chemicals could be obtained from simultaneous thermal cracking reactions apart from transesterification. Concerning the FAbEs sample using 1-butanol, the identified species by GC-MS were 2-methyl propyl octadecenoate, butyl hexadecanoate, pentyl octadecenoate and butyl myristate. Their composition followed the above sequence in terms of the relative area from high to low content as listed in Table 5.

Table 4. FASE profile from beef tallow transesterification using iso-butanol.

Experiment:		E1S9	E2S9	E3S9	E4S9	E6S9	E5S9
Chemical	Formula	MW	Area %				
isobutyl butyrate	C ₈ H ₁₆ O ₂	144.2114				1.293	1.698
4-methyl-2ethyl-pentanol	C ₈ H ₁₈ O	130.1800					3.237
isobutyl caproate	C ₁₀ H ₂₀ O ₂	172.2646			1.469	4.537	4.132
butyl heptanoate	C ₁₁ H ₂₂ O ₂	186.2912					1.567
isobutyl enanthate	C ₁₁ H ₂₂ O ₂	186.2912			1.133	1.765	
isobutyl caprylate	C ₁₂ H ₂₄ O ₂	200.3178	0.067	0.119	0.735	1.472	1.523
3-methyl-undecane	C ₁₂ H ₂₆	170.3300					2.958
isobutyl pelargonate	C ₁₃ H ₂₆ O ₂	214.3443			0.687	1.226	1.424
tridecane	C ₁₃ H ₂₈	184.3700					1.867
isobutyl caprate	C ₁₄ H ₂₈ O ₂	228.3709	0.095	0.168	0.972	1.418	1.914
tetradecane	C ₁₄ H ₃₀	198.3900					1.225
isobutyl undecylenate	C ₁₅ H ₃₀ O ₂	242.4030				1.798	1.555
n-butyl laurate	C ₁₆ H ₃₂ O ₂	256.4241					1.314
isobutyl laurate	C ₁₆ H ₃₂ O ₂	256.4241	0.158	0.247		1.953	
hexadecane	C ₁₆ H ₃₄	226.4100					4.342
isobutyl tridecanoate	C ₁₇ H ₃₄ O ₂	270.4570				1.559	4.458
isobutyl myristate	C ₁₈ H ₃₆ O ₂	284.4772	6.065	5.477	5.019	5.016	4.010
isobutyl pentadecanoate	C ₁₉ H ₃₈ O ₂	298.5038	1.291	3.106	2.918	1.131	5.148
nonadecane	C ₁₉ H ₄₀	268.5100					4.981
2-methyl-octadecane	C ₁₉ H ₄₀	268.5100					0.874
isobutyl palmitate	C ₂₀ H ₄₀ O ₂	312.5304	27.119	27.507	27.652	25.951	28.426
isobutyl margarate	C ₂₁ H ₄₂ O ₂	326.5570	4.738	6.105	5.938	5.182	
2-methyl-eicosane	C ₂₁ H ₄₄	296.6000					0.797
isobutyl oleate	C ₂₂ H ₄₂ O ₂	338.5677	24.679	22.784	23.499		
isobutyl stearate	C ₂₂ H ₄₄ O ₂	340.5836	33.536	31.609	32.185	47.921	41.353
							32.125

Table 5. FASE profile from beef tallow transesterification using 1-butanol.

Experiment	Chemical	Formula	MW	Area %
E1S10	Butyl myristate	C ₁₈ H ₃₆ O ₂	284.4772	1.904
	Butyl hexadecanoate	C ₂₀ H ₄₀ O ₂	312.5304	25.549
	2-Methyl propyl octadecanoate	C ₂₂ H ₄₄ O ₂	340.592	50.282
	Pentyl octadecenoate	C ₂₃ H ₄₄ O ₂	352.5940	22.264

Our findings could be explained based on the phase diagram for the mixture where non-catalytic transesterification takes advantage of the FAAEs synthesis made at supercritical conditions. Aside from the alcohol excess with respect to the oil or fat, the possible location of the complex mixture out of a homogenous phase impeded mass transfer; then, the mixture was feasible to coexist in the vicinity of its phase transition at the lowest temperature and pressure studied in the reactions [24,59,61].

Concerning the yields falling beyond optimal temperatures, cracking of chemicals was competing with transesterification along with other kinds of reactions, such as those associated with a possible polymerization and isomerization. Under the same experimental conditions of alcohol/waste beef tallow in molar ratio, the generated fatty acid alkyl esters with different alcohols as a function of temperature are compared in Figure 4. The maximum yields were accomplished at 365 °C for methanol (98.3%) [56], 360 °C for ethanol (95.12%) and 375 °C for iso-butanol (96.65%); meanwhile the additional reaction made under 1-butanol seemed to provide a low ester content, but an acceptable yield (87.7%). The high ester portion at supercritical conditions is suggested to occur within the homogenous phase. This was verified by the reduction of the hydrogen bonds of the alcohol occurring as the temperature was increased, where its dielectric constant diminished at supercritical conditions; then, a higher solvation of the non-polar chemicals in the alcohol generated a unique fluid phase where the particle interaction was enhanced [54,58,62]. The longer

carbon chain for ethanol and butanol could contribute to a weakening of hydrogen bonds and obstructing interactions between functional groups. Furthermore, the higher yield reached via methanol could be ascribed to its easier reactivity with lipids due to the shorter carbon chain compared to higher alcohols; thus, the interaction is simpler between the oxygen atom from methanol with the carbon atom of the carbonyl functional group from successive glycerides (tri-, di- and mono-) [63]. This mechanism allowed the generation of the respective chemicals: diglycerides, monoglycerides and glycerol. Comparing FAAEs values, those obtained via butanol and methanol were similar but the reaction via ethanol seemed to be less effective, probably caused by its high-water content; the valuable advantage via ethanol and butanol over methanol was the lower glycerol formation observed at the end of the reaction.

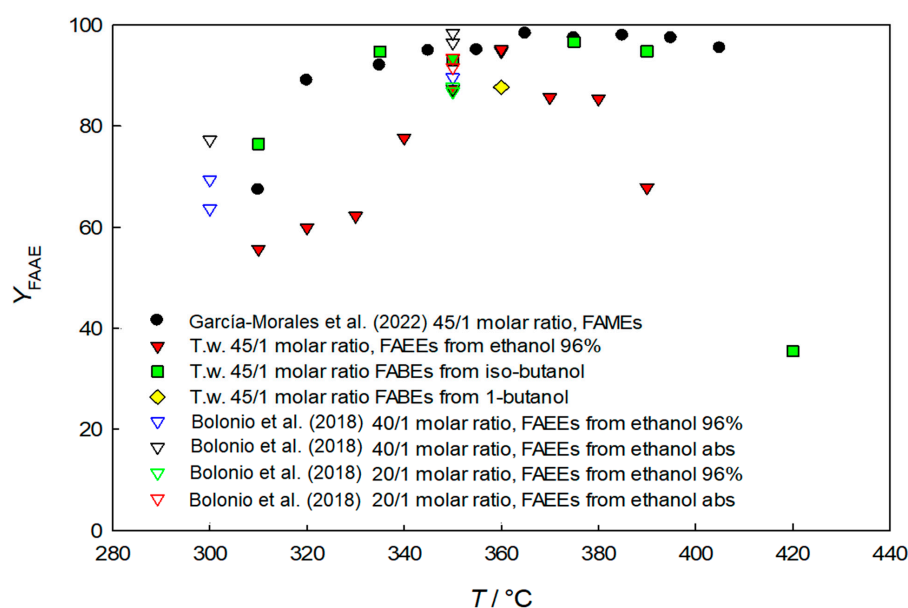


Figure 4. Production of fatty acid alkyl esters from waste beef tallow with different alcohols and feedstock ratios [34,56].

The yield results from this work are in agreement with those insights reported by Bolonio et al. [34] for a one-step reaction performed at 300 and 350 °C, as depicted in Figure 4; water as the main impurity in ethanol (4%) and low ethanol/beef tallow molar ratio (20/1) reduced the FAEEs yield. Moreover, the successful ester production via supercritical alcohols in this work was also contrasted with the catalytic methods, which have pros and cons; for instance, the basic catalysis that commonly used KOH and 6/1 (methanol/beef tallow) molar ratio yielded >91% beyond 35 min [20,64], the acid catalysis lasted 90 min with a 6/1 (methanol/beef tallow) molar ratio, and reached a yield of 96.3% [65], and the enzymatic catalysis performed during 48 h and 50 °C that yielded 89.7% [66].

3.3. Fatty Acid Alkyl Ester Properties

The cloud point (CP), cetane number, color Gardner and free fatty acid content are summarized in Table 2. Cloud points for esters tended to diminish as the temperature of the reaction was increased, even for the samples with the lowest FAEEs content. The exception was detected for the highest temperature (420 °C) for FABEs via iso-butanol, whose cloud point (CP = 11 °C) was superior to that reported at reactions undertaken at 390 °C (CP = 9 °C); the generation of other functional groups on the reaction performed at 420 °C could contribute on the opalescence. Cloud point values for FAEEs started at 20 °C and were lowered at 16 °C for the highest yield; the cloud point lowered to 14 °C for the reactions that were prone to thermal degradation. FABEs via iso-butanol attained a CP ranging from 18 to 9 °C. Cloud points from FAEEs and FABEs indicated good transport

properties under cold ambient temperatures since these values were lower than those reported for fatty acid methyl esters (FAMES) that ranged from 18 to 20 °C using the same raw material [56].

The cetane number (CN) for FAEEs was estimated by adding the contribution of the cetane number of pure fatty acid ethyl ester as reported in the literature [56] and the composition ($CN = \sum w_i CN_i$) as reported elsewhere [67,68]. The esters from the optimal reaction temperature (360 °C) achieved a CN = 80.8, where the cetane number varied within 79.2 to 86.8. Under the same feedstock, the produced fatty acid ethyl esters seemed to have a CN superior to that reported for FAMES in our preceding contribution (65.5 to 74.9) [56]. Concerning fatty acid butyl esters, this parameter was not able to be estimated under the same method because of the absence of mass composition and the insufficient cetane number data for pure esters (FABEs); based on our literature review, the existing cetane number values for butyl esters were: 73 for n-butyl laurate, 84.8 for isobutyl palmitate, 59.6 for isobutyl oleate, 99.3 for isobutyl stearate, 69.4 for butyl myristate, 82.6 for butyl hexadecanoate, and 86.3 for 2-methyl propyl octadecenoate [63,69].

The color Gardner with values of 7.3 and 7.4 demonstrated thermal decomposition at high temperature, where the production of esters diminished. The color Gardner below 5.7 seemed to have an acceptable appearance before it reached darker above 380 °C. Equal to the first property, the color Gardner had lower values for FAEEs and FABEs in contrast with FAMES.

Finally, a certain content of free fatty acids, appraised as stearic acid (FFASA) [70], was still contained in the esters, as indicated in Table 2. An increase in the free fatty acids was noticeable with rising temperature, and the ethyl esters exhibited superior values in comparison with the butyl esters. Hydrolysis as a possible additional reaction at supercritical conditions took place among the lipids and fatty acid alkyl esters: a simultaneous hydrolysis of glycerides generated free fatty acids, which was competing with transesterification, while the produced fatty acid alkyl esters were also hydrolyzed to generate again free fatty acids [71,72]. This was ascribed to the elapsed thermal exposure and the water content of materials, mainly for ethanol, which contained 3.6 wt% of water. The formation of FFA is beneficial to supercritical transesterification since these could be converted to FAAEs, but this was not possible in our experiments; the free fatty acid formation from FAMES during biodiesel obtainment was also proposed by catalytic thermal decomposition throughout a different mechanism of successive reactions [73]. Therefore, the analysis of short residence times should be considered to avoid secondary reactions which are related to thermal exposure.

4. Conclusions

The effect was analyzed of three supercritical alcohols, ethanol, iso-butanol and 1-butanol, accompanied by temperature variations, on the conversion of waste beef tallow via transesterification for the fatty acid alkyl esters production. Ester content decreased dramatically at the highest temperature in each case, and this drop in yields might be caused by the appearance of additional reactions attributed to long thermal exposure. The maximum yields were attained at 360 and 375 °C for ethanol and iso-butanol (temperatures were lower than those via methanol) without any apparent thermal degradation and the preservation of the yellowish coloring on the samples; physicochemical properties for FABEs via 1-butanol were kept but with a lower yield against with the reported for iso-butanol. Our findings suggested a better solvation to the detriment of the restriction of the mass transfer associated with the existence of a homogenous phase. Transesterification of waste beef tallow via supercritical ethanol and butanol seemed to be better than using supercritical methanol under the same conditions in terms of the physicochemical properties. The longer carbon chain alcohols reduced the glycerol formation and allowed the FAAEs synthesis with low cloud points (for instance 14 °C for FAEEs, 10 °C and 8 for FABEs) and a high predicted cetane number (80.8 for FAEEs); nevertheless, the produced

esters via methanol were slightly higher than the other alcohols, emphasizing that the dissolved water in ethanol did not restrain yields dramatically.

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