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INFLUENCE OF FUSEL OIL COMPONENTS ON THE DISTILLATION OF HYDROUS ETHANOL FUEL (HEF) IN A BENCH COLUMN

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Abstract - The components of fusel oil form azeotropes with water, resulting in challenges in obtaining hydrous ethanol fuel (HEF) and increasing investment and operating costs. The aim of this study was to evaluate how the presence of fusel oil affected HEF distillation. Mixtures of ethanol (6.0 to 6.5 % w/w) and water (93.0 to 94 % w/w) containing different concentrations (zero to 0.5 % w/w) of 3-methyl-1-butanol, 2-methyl-1-propanol, propan-1-ol and propan-2-ol were distilled in a laboratory apparatus. Under total reflux conditions, HEF concentrations in compliance with Brazilian legislation specifications were obtained, but the desired concentration could not be attained under continuous operation. All of the experiments resulted in a high loss of ethanol in the bottom product under multiple operating conditions. The results demonstrated that fusel oil affects HEF distillation, but that HEF concentrations can still be obtained in compliance with Brazilian legislation.

Keywords: Fuel ethanol; Distillation; Fusel oil.

INTRODUCTION

The terms fusel oil, fousel oil, finkel, faints, higher alcohols or congeners all refer to high-molecular-weight compounds, particularly higher chain alcohols, that are obtained by distilling fermented carbohydrates (Garcia, 2008). Fusel oil is dark green in color and has an acrid smell (Rasovsky, 1979). Fusel oil is formed during yeast metabolic processes in fermentation. The composition of fusel oil depends on the fermentation medium conditions (i.e., the presence of amino acids, assimilable nitrogen compounds, the temperature, aeration and the inoculum concentration) and the type of inoculums used (Webb and Ingraham, 1963; Borzani *et al*., 1981; Gutierrez, 1993; Walker, 1998; Patil *et al*., 2002). The composition of fusel oil also depends on the feedstock used to obtain the fermentation substrate (Brau, 1957; Webb

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*To whom correspondence should be addressed and Ingraham, 1963). Webb and Ingraham (1963) demonstrated that fusel oil can contain up to 97 different substances. Table 1 presents the composition of fusel oil samples obtained from the fermentation of sugarcane carbohydrates. The proportion of fusel oil in the fermented broth ranges between 0.1 and 0.6% (Küçük and Ceylan, 1998; Patil *et al.*, 2001; Pérez *et al.*, 2001; Lima *et al.*, 2001; Amorim *et al.*, 2005). Brau (1957) reported fusel oil contents between 0.1 and 1.1%. Table 2 shows the average composition for fermented sugarcane juice, as given by Batista and Meirelles (2011).

Fusel oil has a high boiling point between 130 and 132 °C (Webb and Ingraham, 1963) and must be removed from the low volatility fractions during distillation. In batch distillation (for the production of distilled spirits), the obtained fusel oil is diluted in the “head” "tail" stream with high water and ethanol concentrations. This operational procedure is used in *cachaça* (sugarcane spirit) distillation, to remove undesired compounds from the beverage (Scanavini *et al.*, 2012). In continuous distillation, fusel oil is withdrawn from the lower portion of the rectification column. In addition to the aforementioned factors, the concentration of each component of the fusel oil depends on the method by which the component is removed from the distillation column.

After being removed from the rectifying tower, the fusel oil is cooled and washed with water to recover residual ethanol. The fusel oil is then distilled to recover the products, primarily amyl alcohol (3-methyl-1-butanol). Amyl alcohol is the primary component (at approximately 60%) in fusel oil (Table 1). The term amyl alcohol originates from when fusel oil was first identified in distillates obtained from starch (*amylum*) fermentation (Simmonds, 1919).

Table 1: Composition of fusel oil samples from sugarcane broth (%w/w).

Component	**Reference**		
	Pérez *et al.* (2001)[a]	**Patil (2001)**	**Brau (1957)**
Water	-	5.93	0.00
Ethanol	7.82	1.23	0.00
3-methyl-1-butanol[b]	63.39	60.00	55.30
Propan-1-ol	2.42	3.20	24.30
Propan-2-ol	-	19.00	0.60
Butan-1-ol	4.5×10^{-4}	4.53	8.10
2-methyl-1-propanol	22.19	1.83	7.40
Pentan-1-ol	2.84×10^{-4}	-	4.30
Others	4.17	3.62	0.00

[a] Values converted to mass fractions

[b] Corresponds to fractions of 3-methyl-1-butanol (amyl alcohol) and optically active amyl alcohol (2-methyl-1-butanol)

Table 2: Composition of fermented sugarcane juice (Batista & Meirelles, 2011).

Component	**Concentration range (% w/w)**
Water	92.0 – 95.0
Ethanol	5.0 – 8.0
Methanol	$0.0 – 3.0 \times 10^{-6}$
3-methyl-1-butanol[a]	$(2.7 – 18.8) \times 10^{-3}$
Propan-1-ol	$(2.1 – 6.8) \times 10^{-3}$
Propan-2-ol	1.02×10^{-4}
Butan-1-ol	$0.0 – 2.4 \times 10^{-4}$
2-methyl-1-propanol	$(1.3 – 4.9) \times 10^{-3}$
Pentan-1-ol	NA
Ethyl acetate	$(5.5 – 11.9) \times 10^{-4}$
Acetaldehyde	$(1.0 – 8.3) \times 10^{-3}$
Propanone[a]	10.4×10^{-4}
Acetic acid	$(3.3 – 99.3) \times 10^{-4}$
Carbon dioxide	-

NA: Not available

[a] Values calculated from Dias (2008)

Fusel Oil Removal in Beverages

The characteristics of fusel oil and its effect on distillates first attracted interest in the beverage industry. Records of fusel oil in both fermented and distilled beverages date back to the XVIII century (Webb and Ingraham, 1963). In 1853, Charles M. Wetherill (Wetherill, 1853) reported on a series of studies in which fusel oil was detected in beverages derived from fermentation. The Lancet (The Lancet, 1901) reported: “*It has intoxicating and poisonous properties superior to those of ordinary spirits, and is said to be known in some of the northern counties of Europe to the consumers of corn brandy who frequently ask to be served with a ‘glass of good fusel’.*” The compounds 3-methyl-1-butanol, butan-1-ol, propan-1-ol and propan-2-ol are primarily responsible for the aroma of distilled spirits (Batista and Meirelles, 2011; Scanavini *et al.*, 2012), but high concentrations of these compounds can cause health problems (Opdyke, 1978; Lachenmeier *et al.*, 2008).

Fusel oil removal has motivated technological changes for various continuous distillers of beverage following the development of the Coffey still (or the Patent still) in 1830 (Gaiser *et al.*, 2002; Russel, 2003). The configuration of the Coffey still is very similar to that of current ethanol distillation towers for high grade fuel ethanol production. This still is divided into two sections: stripping and rectification. This type of distiller was modified to remove a side stream from the trays with the highest fusel oil concentration. Patil *et al.* (2001) reported that this removal is a complex process because of the volatility of fusel oil. At low ethanol concentrations, fusel oil has a higher volatility than that of ethanol, and the fusel oil becomes trapped in the region of the column where the ethanol concentration ranges between 40 and 47 % w/w. Kirschbaum (1948) reported the same range. The removed oil stream may or may not split into two liquid layers depending on the prevailing conditions (i.e., the mass and energy balance) at the point of fusel oil removal. Separation below the point of removal in the column may be impossible. Unfortunately, it is not known when this phenomenon will occur during operating conditions.

Two to 6.5% of the total feed ethanol must be purged to remove fusel oil from the distillate (neutral distillate) (Valderrama *et al*., 2012). Batista and Meirelles (2011) reported that, in the distillation of drinking ethanol, the higher alcohols become more concentrated in the distillate at low distillate flow rates and low reflux ratios. The equilibrium curve of the ethanol/water/3-methyl-1-butanol system at a temperature of 25 °C shows that there is a wide concentration range over which two phases co-exist in the system, which can be used to separate and remove 3-methyl-1-butanol (Kadir *et al*. 2008). However, this biphasic region decreases as the minimum temperature in the tower is approached (near 78 ºC, at the top of the rectifying section), which limits fusel oil separation.

Russel (2003) reported that the presence of 3-methyl-1-butanol in the lower portion of the rectification column prevents ethanol condensation. This condensation reduces the tray efficiency and increases the ethanol concentration in the bottom product of the column. Rectification has been reported to be unhindered above a certain stage. Russel (2003) identified another significant issue, i.e., the relative volatility of 3-methyl-1-butanol is higher than that of ethanol for ethanol concentrations below 40% v/v. Gaiser *et al*. (2002) developed simulations showing that the peak concentration of 3-methyl-1-butanol coincides with an ethanol concentration of 20% w/w (approx. 25% v/v).

Fusel Oil Removal from Hydrous Ethanol Fuel (HEF)

Fusel oil is removed during HEF distillation using a similar but rougher operation than that used for beverages. This removal usually involves a side withdraw that is cooled prior to phase separation and from which the aqueous phase, containing ethanol and water, is returned to the distillation column.

The presence of fusel oil can perturb ethanol distillation operation via "cyclic flooding" from the formation of a second liquid phase (Kister, 1990). Shinskey (1984) reported that the higher alcohols form azeotropes with water during the distillation process. These alcohols accumulate up to the solubility limit, forming a second liquid phase. This behavior generates instability in the distillation operation because the total vapor pressure in the column results from two liquid phases. Therefore, the upward vapor flow doubles instantaneously and lowers the column temperature. This flooding usually carries the fusel oil to the top of the column. The column heating inlet may be raised by using a temperature control to manipulate the boilup. In both cases, the fusel oil tends to be purged at the top of the column, after which the distillation returns to normal operation in a few hours or few days (Shinskey, 1984).

Is it really necessary to remove fusel oil from ethanol for use in fuel? As previously mentioned, the removal of fusel oil requires multiple constructive modifications to the distiller (i.e., side streams, the fusel oil removal column and the ethanol recovery column). These additions lead to higher construction and operating costs. Currently, all major ethanol distilleries remove fusel oil during distillation, but it may not be necessary in small scale ethanol production. A simple, cost-effective distillation system is essential for the economic feasibility of small-scale ethanol production. Mayer *et al*. (2013) conducted tests on a single column distillation system using a hydroalcoholic solution (ethanol + water), which yielded a distillate that satisfied the required ethanol concentration of the ANP. However, the effect of fusel oil on the process was not evaluated in Mayer *et al*.'s study.

In addition, the Brazilian legislation that regulates the commercialization of fuel ethanol (ANP Resolution Nº 07, dated February 9, 2011) does not directly control the levels of fusel oil or its components in HEF. This resolution states that the maximum permitted level for hydrocarbons is 3.0% v/v, as analyzed using the standard from ABNT NBR 13993. However, this standard only assesses the presence of gasoline in the sample, i.e., higher alcohols may also be present in HEF. The Technical Regulation CNP-07/82 (IBP, 1987) from the former National Petroleum Council defined the maximum allowed concentration of higher alcohols as 6.0% w/w; however, this regulation is no longer valid. The European Union allows the addition of up to 7% oxygenates in gasoline, including 3-methyl-1-butanol (Council Directive of the European Communities 85/536/CCE). Cataluña *et al*. (2008) compared the effectiveness of different oxygenates as fuel in internal combustion engines, indicating that 3-methyl-1-butanol has a lower specific fuel consumption and produces more power than pure ethanol.

More recently, ANP Technical Notes 04- and 97-/2013/SBQ/CPT-101-DF have stated that the presence of higher alcohols in HEF does not affect engine performance. These Notes report that the commercial price of fusel oil is higher than that of ethanol. Thus, removing fusel oil in larger distilleries is economical, unlike in small-scale ethanol production.

The aim of this paper is to evaluate the effect of fusel oil in ethanol distillation using a bench column, as developed by Mayer *et al*. (2013). These findings will provide operational information to support the development and improvement of a pilot still.

MATERIALS AND METHODS

Analytical Procedures

Apparatus

To monitor the progress of the distillation process, the ethanol concentrations in the top and bottom products were analyzed using a digital density meter (Anton Paar DMA 4500 M) with temperature control and a repeatability of 0.00001 g.cm^{-3}. The digital density meter directly converted the density measurement to the ethanol concentration with a typical accuracy of 0.025 % w/w.

Gas chromatography was used to analyze the concentration of the higher alcohols and was developed and applied using a Perkin Elmer Instruments model Auto System XL GC equipped with a flame ionization detector. The data acquisition was performed using Perkin Elmer Turbochrom 4.1 software. The following GC operating conditions were used: injection temperature, 250 °C; detector temperature, 170 °C; column PE-1 Perkin Elmer, 30-m long, 0.53-mm i.d.; carrier gas: helium at a flow rate of 3 μL.min^{-1}. The operating conditions were as follows: manual sample feed; split ratio 1:1; zero attenuation; initial oven temperature 70 °C, with a heating rate of +5 °C. min^{-1}. The flow rates of the flame gases for the FID were as follows: hydrogen, 45 μL.min^{-1}; synthetic air, 450 μL.min^{-1}.

Reagents

The feed in the distillation tests was prepared using 95% commercial-grade ethanol. The higher alcohols were propan-1-ol 99.5% (Vetec), propan-2-ol 99% (Synth), 2-methylpropan-1-ol 99% (Vetec) and 3-methyl-1-butanol 98.5% (Vetec). The internal standard was methanol 99% (Merck). The sample solutions used to generate the calibration curves contained 99.5% ethanol.

Procedures

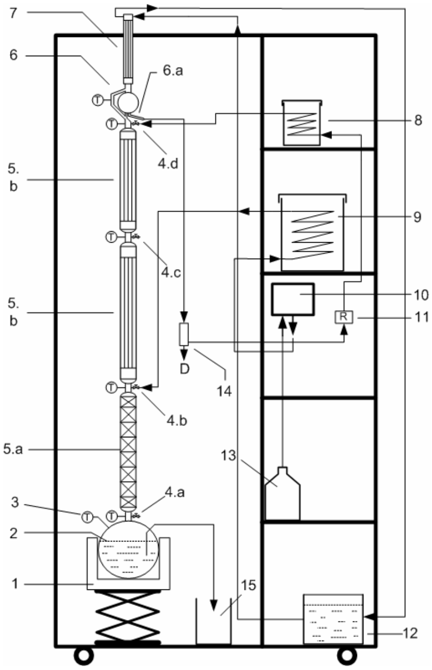
The analytical curves were obtained using triplicate injections of the higher alcohol solutions at concentrations of 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 % w/w with an internal standard of 5.0 % w/w methanol. All of the samples were made up in ethanol. The samples for the GC analyses consisted of 95% of the distillation sample and 5% of the internal standard (methanol). An injected sample volume of 1.0 μL was used in the GC analysis. The concentration of the higher alcohols was determined by measuring the area ratio of each analyte to that of methanol and comparing the ratio to that from the calibration curves (i.e., the area ratio analyte/standard was plotted *versus* the analyte concentration).

Distillation Procedure

The experiments were conducted by distilling solutions of ethanol + water + higher alcohol, whose compositions are shown in Table 3. The concentrations of higher alcohols were estimated using the data in Table 2. The concentration was overestimated to ensure that the experiments simulated conditions with the maximum concentration of fusel oil compounds found in fermented broth.

The experiments were performed using a continuous distillation bench column (Figure 1), which was located in the Laboratory of Process Engineering at Santa Maria Federal University. This bench column contained Vigreux and packing in the stripping and rectification sections, respectively. Each experiment was divided into two distinct stages. In the first step, distillation was performed under total reflux conditions to verify the maximum concentration obtained by the distiller. Five liters of feed, with the compositions given in Table 3, were introduced into the reboiler of the distillation apparatus to start the operation, which lasted until the temperature of the top vapor stabilized. Samples were collected at 10 minute intervals.

The second step consisted of continuous solution feeding (at the compositions shown in Table 3) at a rate of 3.206 kg.h^{-1}. The flow rates of the distillate and bottom products were 0.209 kg.h^{-1} and 2.997 kg.h^{-1}, respectively, to maintain a distillation performance of approximately 92%. The tests lasted three hours on average, with ninety minutes dedicated to equipment heating and stabilization. Samples were collected every 10 minutes after the top product concentration stabilized. More information on the features and operation of the distiller can be found in Mayer *et al*. (2013).



1. Heating mantle with adjustable height stand;
2. Reboiler;
3. Temperature transmitter;
4. Sample outlet tap (4.a, b, c, e, and d), feed input (4b) and reflux flow return (4.d);
5. a – Vigreux -type distillation column; 5) b - Distillation packing column (Raschig rings);
6. Distillation head with condenser; 6.a - 2-way valve;
7. Condenser;
8. Reflux pre-heating tank;
9. Feed pre-heating tank;
10. Peristaltic pump;
11. Reflux rate measurer;
12. Cooling bath of condensed recirculated water;
13. Feed reservoir;
14. Distillate output control valve;
15. Bottom product reservoir

Figure 1: Continuous distillation bench column diagram.

Table 3: Composition of six solutions with and without higher alcohols (% w/w).

Solution	Water	Ethanol	Higher alcohol (% w/w)			
			3-methyl-1-butanol	Propan-1-ol	2-Methylpropan-1-ol	Propan-2-ol
1	93.5	6.0	0.5	-	-	-
2	93.5	6.0	-	0.5	-	-
3	93.5	6.0	-	-	0.5	-
4	93.5	6.0	-	-	-	0.5
5	93.5	6.0	0.3	0.1	0.05	0.05
6	94.0	6.0	-	-	-	-

RESULTS AND DISCUSSION

The interference of fusel oil on the distillation of ethanol was assessed is two steps. The first was the assessment of the interference under ideal operating conditions, as represented by the total reflux condition. Under this situation, the distribution of the components was stable during the experiments. Stability was defined as the absence of the continuous accumulation of analytes (the higher alcohols) in certain regions of the distiller. The accumulation of fusel oil was visually observed in the region of the column corresponding to 75% w/w of ethanol. The top product concentrations in the six experiments under total reflux are presented in Table 4. The concentration of the higher alcohols in the top product depended directly on the alcohol boiling point, since the lower the boiling point of the higher alcohol, the higher will be the alcohol concentration in the top product. In addition, the experiments in which the minimum ethanol concentration for the top product was not attained suggest that they were more affected by the formation of an azeotrope between water and the higher alcohols than the experiments in which the minimum concentration was attained.

The experimental data show that the solutions 1, 2, 3, and even the solution 6, containing only ethanol and water, did not achieve the minimum concentration (92.5% w/w) required by ANP Resolution No. 07/2011, while solutions 4 and 5 had ethanol concentrations greater than the minimum. Experiments 4 and 5 also demonstrated that, when the number of separation stages was adequate, the minimum allowable limit could be attained in the presence of higher alcohols. Note that the concentrations of higher alcohols used in the experiments were overestimated to simulate an extreme situation because fermented broth concentrations can vary widely (see Table 2). The results obtained in total reflux suggest that the problem in achieving the ANP minimum concentration is more related to the number of separation stages than with the presence of higher alcohols.

Therefore, the effects of higher alcohols on the operation of a distillation column should be evaluated in continuous operation, to permit the assessent of cyclic flooding in small scale distillation. The data obtained for the average ethanol concentration and the reflux ratio for each of the six experiments in continuous operation are shown in Table 5. An ethanol concentration in the top product greater than 92.5% w/w was not obtained in any of the tests, indicating that there were an insufficient number of separation stages in the distillation column. A reflux ratio near 3.0 was measured in the experiments, which is the highest value obtained in a pre-flooding condition (i.e., at the loading point). Under total reflux operation, the concentration of higher alcohols in the top product was determined by the alcohols' boiling points, particularly that of propan-2-ol (4.95 % w/w). The propan-2-ol concentration increased the HEF enthalpy of combustion by approximately 6.0%, showing that the higher alcohols are favorable for the HEF energy content.

Figure 2 shows the top product concentration during distillation. The distillation of solution 6 was more stable in terms of the top product concentration (i.e., this solution exhibited the lowest standard deviation of all of the solutions – see Table 5). The stability of the operation using solution 6 was corroborated by the lower standard deviation observed for the reflux ratio. Other experiments showed that a larger time interval was required for the distillation process to reach steady state using solutions other than solution 6. This delay can be attributed to the stabilization of the compositions throughout the distiller. As Webb and Ingraham (1963) have discussed, water formed azeotropes with the alcohols in all of the experiments that were analyzed for water concentrations ranging from 4.0 to 49.6% w/w.

Table 4: Composition of samples under total reflux operation.

Solution	Ethanol (% w/w)	Higher alcohol (% w/w)			
		3-Methyl-1-butanol	Propan-1-ol	2-Methylpropan-1-ol	Propan-2-ol
1	89.46	0.63	-	-	-
2	91.40	-	1.39	-	-
3	89.98	-	-	0.64	-
4	92.98	-	-	-	5.00
5	92.67	0.00	0.04	0.14	1.01
6	92.10	-	-	-	-

Table 5: Mean concentration (% w/w) for six tests under continuous operation (top and bottom products).

Solution	Reflux ratio		Ethanol				3-Methyl-1-butanol		Propan-1-ol		2-Methylpropan-1-ol		Propan-2-ol	
	Average	Standard deviation	Top	Standard deviation	Bottom	Standard deviation	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
1	3.3	0.32	89.26	1.57	1.99	0.90	0.14	0.11	-	-	-	-	-	-
2	2.7	0.41	90.50	0.55	2.84	1.15	-	-	0.74	0.13	-	-	-	-
3	2.9	0.30	88.47	1.18	2.83	0.72	-	-	-	-	0.19	0.06	-	-
4	3.6	0.21	90.50	0.58	2.28	0.96	-	-	-	-	-	-	4.95	0.00
5	3.0	0.30	90.76	1.35	2.79	1.02	0.00	0.00	0.11	0.00	0.04	0.00	1.79	0.00
6	2.9	0.21	92.44	0.17	1.33	0.65	-	-	-	-	-	-	-	-

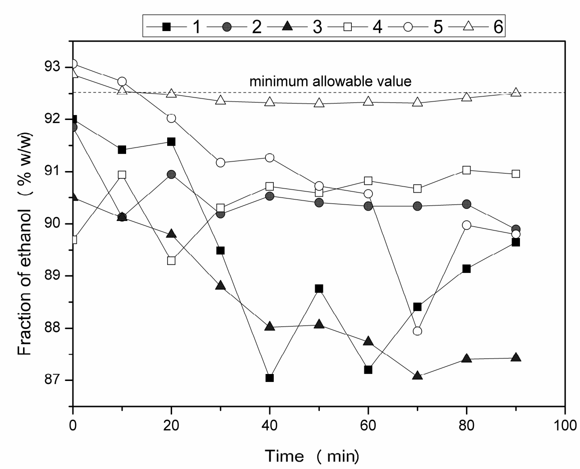


Figure 2: Top product concentration for continuous distillation.

The bottom product had a higher ethanol concentration than that recommended by Meirelles and Batista (2011) (0.02% w/w). Mayer *et al*. (2013) recommended that a maximum ethanol concentration of 0.5% w/w should be used because of the excessive loss of ethanol in the bottom product. The high concentration of ethanol in the bottom product could be attributed to the effects of the higher alcohols, as pointed out by Russel (2003). Note that solution 6 (ethanol + water) also resulted in a high ethanol concentration in the bottom product. This result can be explained by the fact that the tests were initially fed through the reboiler without sufficient time for stripping, as is shown in Figure 3. The ethanol concentration in the bottom product gradually decreased during distillation. Therefore, increasing the distillation processing time and/or the number of stripping stages could produce an ethanol concentration that is in compliance with the maximum allowable limit. Table 5 shows that the concentration of higher alcohols in the top product was greater than that in the bottom product, indicating that these alcohols tended to concentrate in the rectification section. A mass balance analysis showed that the higher alcohols may have accumulated in the column, thereby affecting the ethanol/water separation. Thus, longer duration experiments need to be performed.

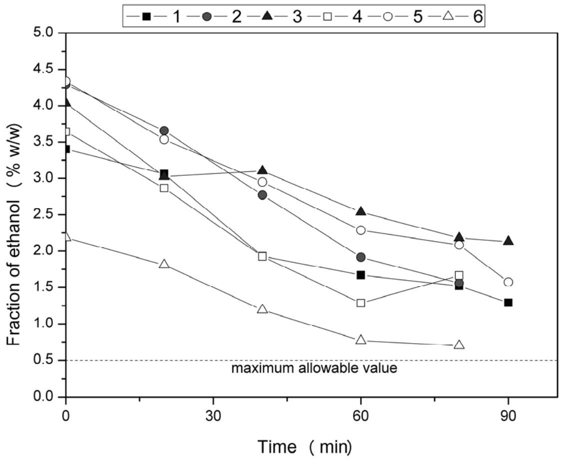


Figure 3: Bottom product concentration for continuous distillation.

These results show that the concentration of fusel oil in HEF should only be limited based on how fusel oil affects engine performance. However, the ANP Technical Notes 04- and 97-/2013/SBQ/CPT-101-DF state that fusel oil does not affect the performance of combustion engines. In this study, the fusel oil positively affected the HEF energy because fusel oil has a higher enthalpy of combustion than HEF, e.g., the enthalpy of combustion of 3-methyl-1-butanol is approximately 30% higher than that of ethanol (see Table 6).

Table 6: Properties of fusel oil components.

Component	Boiling point (ºC)^{a}	Density at 20 °C (g.cm^{-3})^{b}	Standard net enthalpy of combustion (MJ.kg^{-1})^{b}
Ethanol	78.4	0.7903	26.808
3-methyl-1-butanol	130.6	0.8108	34.737
Propan-1-ol	97.8	0.8038	30.685
Propan-2-ol	82.5	0.7867	30.518
2-methyl-1-propanol	108.0	0.8010^{c}	35.981^{c}

[a] Speight (2003)
[b] Calculated from Green and Perry (2008)
[c] BASF (2008)

CONCLUSION

The results of this study confirmed that the presence of higher alcohols during ethanol distillation can affect the concentration of both top and bottom products because of cyclic flooding. However, these alcohols did not prevent the production of HEF with an ethanol concentration in compliance with current legislation.

The primary challenge posed by these experiments is the high loss of ethanol in the bottom product. The results of this study suggest that this problem may have been caused by an insufficient number of separation stages and was not related to the fusel oil components, because similar results were obtained using the reference mixture (ethanol + water).

Note that the higher alcohol concentrations in the feed stream were overestimated; thus, the effect of these components in the distillation process should be lower in practice than observed in the experiments.

The data obtained showed that fusel oil does not need to be removed during the distillation process in small-scale fuel ethanol production. Eliminating this process could lower investment and operating costs. This statement is supported by the fact that the legislation regulating the commercialization of HEF does not impose limits on the content of higher alcohols. Thus, the presence of fusel oil in HEF only benefits engine performance because its increases the energy content of the fuel. The resulting constructive and operational simplification can facilitate the technical and economic viability of small-scale ethanol production.

NOMENCLATURE

ANP	National Agency of Oil, Natural Gas and Biofuels
HEF	Hydrous ethanol fuel
GC	Gas chromatograph

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