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Used Frying Oil: A Proper Feedstock for Biodiesel Production?

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Abstract Used frying oil seems to be an economically viable and environmentally attractive alternative for biodiesel production, but the acceptance and successful use of this and other biodiesels obtained from waste materials require careful evaluation of its fuel properties and impurities. Herein, we show that biodiesel made from used frying soybean oil display overall quality comparable to those obtained from the fresh oil as measured by standard parameters of fuel quality such as induction period, acid number, heat of combustion, and iodine value as well as at the molecular level via profiles of intact and oxidized fatty acid methyl esters. These profiles were obtained directly from the biodiesel samples by easy ambient sonic spray ionization mass spectrometry. An artificial antioxidant, N,N′-di-*sec*-butyl-*p*-phenylenediamine, was shown to significantly increase the oxidative stability of the used frying oil biodiesel at trace level.

Keywords Biodiesel · Fuel quality control · Ambient mass spectrometry · Soybean oil · Used frying soybean oil

Introduction

Increasing crude oil prices and diminishing supplies of fossil fuels have lead to the imperative necessity to develop alternative fuel sources. Renewable biofuels is currently one of the top priorities and biodiesel composed by fatty acid methyl esters seems to offer a viable alternative to petrodiesel. Biodiesel also exhibits several advantages over petrodiesel such as low toxicity, high biodegradation rates, and lower exhaust emissions and hence reduced impact on global warming. Biodiesel displays also lubricating properties superior to petrodiesel [1]. But a great obstacle for large-scale biodiesel production is the high prices of the feedstocks, and the controversial use of edible oils. The use of oil wastes has therefore the advantages of not competing with the food market while promoting its proper recycling and reducing production costs. Used frying oil has low market values currently of about one-fifth of that of the crude vegetable oil [2]. Used frying oils are generated in large quantities worldwide during food processing, and most of it goes to waste, creating ecological problems [3]. The use of used frying oil for biodiesel production seems therefore attractive but such a high variable-quality source of impure and oxidized raw material may not produce a fuel that meets the existing international specifications [4–9].

In this report, classical overall quality parameters has been compared for biodiesel produced from fresh and used frying soybean oil, herein referred simply as “frying” biodiesel. Soybean oil, due to its high unsaturation level, seems to offer one of the most critical to test the feasibility of frying biodiesel. An ambient mass spectrometric technique

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[10], easy ambient sonic-spray ionization mass spectrometry (EASI-MS) [11], was also used to access the chemical profiles of FAME or fatty acid ethyl esters (FAEE) as well as their corresponding oxidized molecules. The effectiveness of an artificial antioxidant [12] was also tested for frying biodiesel.

Materials and Methods

Chemical Reagents and Samples

High-performance liquid chromatography-grade methanol was purchase from Merck SA (Rio de Janeiro, Brazil) and used without further purification. Biodiesel was produced via transesterification of triacylgliderides (TAG), from fresh soybean and thermal oxidized soybean oil, with methanol in the presence of sodium methoxide as catalyst according to an improved procedure described in detail elsewhere [13]. Thermal oxidized soybean oil was obtained in a continuous heating of 8 h by 10 consecutive days (180 °C).

Frying biodiesel is a commercial biodiesel that came from production plant of Cooperativa de Processamento de Materiais Recicláveis in Campinas, Brazil. Used frying oil (which is known to result mostly from the use of soybean oil) was collected from households and restaurants in the surrounding communities. Frying biodiesel was produced via transesterification reaction using methanol or ethanol. The effect of different operating and processing variables such as the type of alcohol used, type of catalyst, reaction temperature, molar ratio of alcohol to oil, and reaction time have been studied [14]. The optimized parameters were: sodium methoxide as catalyst, reaction temperature of 45 °C, ratio of 1/10 alcohol/oil, and reaction time of 60 min.

Ambient Mass Spectrometry Analysis

EASI-MS was performed in the positive ion mode using a single quadrupole mass spectrometer (Shimadzu) equipped with a homemade EASI source, which is described in detail elsewhere [11]. A tiny droplet of the sample (2 μL) was dropped directly onto a paper surface (brown Kraft envelope paper). For EASI common parameters were used such as methanol flow rate of 20 $\mu L\ min^{-1}$, N_2 nebulizing gas 3 $L\ min^{-1}$, and paper entrance angle of ~30°. Mass spectra were accumulated over 30 s and scanned over the 50–1,000 *m/z* range.

Determination of Oxidative Stability

To evaluate the oxidation stability of the biodiesel samples, the oxidation induction period (IP) was measured with the use of Rancimat apparatus (Metrohm 873) as described by EN14112 [15]. Biodiesel samples (3 g) were heated to 110 °C, air was then passed through the samples at flow rate of 10 $L\ h^{-1}$, and then through a trap containing water. The kinetics of oxidation was followed by the sudden increase in conductivity of the water as a result of the formation of volatile organic acids. All determinations were performed in triplicate and the mean value is reported.

Determination of Acid Number and Iodine Value

The acid number is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specific end point. Acid number of oil or biodiesel samples was determined according to ASTM D664 and ABNT 14448 using a Titrino DMP 785 (Metrohm). Iodine value was determined following EN14111. Iodine value and acid number were performed in duplicate and quintuplicate, respectively, and the mean value is reported.

Determination of Heat of Combustion

Heat of combustion was determined according to ASTM D4809 and ASTM D240 using a 6400 Automatic Isoperibol Calorimeter (Parr Instruments Ltd). All determinations were performed in triplicate and the mean value is reported.

Results and Discussion

Table 1 summarizes the results for the overall quality parameters of the oil and biodiesel samples. All samples were tested initially for total acid number. Thermal oxidized soybean oil and used frying oil showed considerably high acid numbers, as expected. These results are consistent with the mechanism currently accepted for oil degradation [16] via initial peroxide formation leading to cleavage of C=C bonds and formation of lower molecular weight carboxylic acids or polymers. The specification limit of 0.5 mg KOH g^{-1} was exceeded for all biodiesel samples. The heat of combustion value remained relatively constant, indicating little or no influence of the oxidation process. Iodine value is a measure of total unsaturation measured via iodine consumption due to addition to C=C bonds given by g iodine/100 g of a sample. The iodine value therefore provides a

Table 1 Quality parameters for fresh soybean, thermal oxidized soybean and used frying oil and their respective biodiesels

	Induction period (h)	Acid number (mg KOH/g)	Heat of combustion (cal/g)	Iodine value (g/100 g)
Fresh soybean oil	7.88	0.863±0.010	9,316±13.43	133.0±0.33
Thermal oxidized soybean oil	1.49	4.092±0.057	9,006±1.10	98.3±1.42
Used frying oil	1.18	5.984±0.158	9,298±23.89	104.0±0.09
Biodiesel from fresh soybean oil	4.20	0.679±0.013	9,409±2.62	120.6±0.31
Biodiesel from thermal oxidized soybean oil	0.40	1.001±0.360	9,343±10.11	107.4±1.13
Biodiesel from used frying oil	0.17	1.119±0.029	9,341±20.82	89.2±0.88

measure of the tendency of the oil, fat, or biodiesel, to polymerize forming engine deposits. An upper limit of iodine value of 120 has been specified in EN14214, but this value would exclude the use of pure soybean and sunflower biodiesels. The iodine value has therefore not been included in biodiesel standards in the USA whereas the Brazilian standards require that it should only be reported. Table 1 shows lower iodine value for thermal oxidized soybean oil and used frying oil as well as for the respective biodiesels, when compared to the "fresh" biodiesel, indicating more stability towards polymerization of frying biodiesel. The value (89.2± 0.88) for frying biodiesel is around 30 units lower than that for the "fresh" biodiesel (120.6±0.31) indicating that frying reduces double bonds per mole likely due to oxidation. High value of iodine number may indicate the presence of methyl esters with two and three double bonds in the hydrocarbon chain characteristics to the linoleic and linolenic acids, where these esters show a higher tendency to oxidation. For used frying biodiesel, the thermal stress and oxidation has likely caused the breaking of the double bond decreasing substantially the iodine value of biodiesel. The frying biodiesel used in this work is a commercial product produced in Brazil and as such is attending all the quality parameters specified by the Brazilian Regulatory Body (Brazilian Agency of Petroleum, Gas and Biofuels - ANP) and ASTM. Viscosity, an important quality parameter for engine performance, is inside the range of 3–6 Mm^2/s at 40 °C measured by the Standards ABNT NBR 10441, ASTM D445, or EN ISO 3104 indicating a low concentration of polymers.

Recently, we have demonstrated the use of direct mass spectrometry analysis [17–19] most particularly via ambient MS [10, 20–23], as a direct, nearly undisturbed means to efficient single-shot characterization at the molecular level of both the oil [24] feedstock and their biodiesel [25–27] products via TAG and FAME profiles including impurities. For that purpose, we used mainly an desorption/ionization technique termed EASI-MS which allows the direct and fast MS analysis of samples in the open atmosphere with no sample preparation, pre-separation or derivatization procedures.

Figure 1 compares EASI(+)-MS profiles of the oil samples. Note the TAG are detected mainly as $[TAG + Na]^+$ ions: PLL of *m/z* 877, PLO of *m/z* 879, LLL or OLLn of *m/z* 901, OLL or OOLn of *m/z* 903, and OOL of *m/z* 905, with minor $[TAG + K]^+$ ions. These spectra are found to be quite distinct mainly due to the much higher abundances of ions associated with oxidation products in Figs. 1b and c [20]. The relatively high degree of unsaturation of soybean oil makes its quite susceptible to oxidation. During the frying process, oils are subjected to three agents: (a) water released by food (hydrolytic effect), (b) oxygen of the atmosphere (oxidative effect), and (c) high temperature (thermal effect). The EASI(+)-MS profiles in Fig. 1b and c show ions of *m/z* 933, 935, and 937 with greater abundances than those in Fig. 1a. Ions of *m/z* 965, 967, and 969 were also observed most particularly for thermal oxidized soybean oil (Fig. 1b). These ions probably correspond to oxidation products, as summarized in Table 2 [28]. Note that there is unfortunately a coincidence of *m/z* between [TAG + K]+ and [TAG + nO + Na]+ ions. For the $[TAG + nO + Na]^+$, it is possible that they are hydroperoxides, but they may coexist with more stable isomeric oxidation products such as epoxides and ketones. These species can be considered markers of used oil.

Thermal oxidized soybean oil and used frying oil also show more intense ions around *m/z* 600–700 which correspond to DAG ions, that is $[PL + Na]^+$ of *m/z* 615, $[LL + Na]^+$ of *m/z* 639 and $[OL + Na]^+$ of *m/z* 641 (Fig. 1b and c). As expected, the intermittent heating of oil as well as the frying process generates DAG and free fatty acids due to TAG hydrolysis. Hydrolysis also contributes therefore to higher acidic numbers. These species also can be considered markers of used oil.

Figure 2 compares the FAME profiles obtained by EASI (+)-MS of the biodiesel samples. As for TAG, the FAME are also detected mainly in their sodiated forms $[FAME + Na]^+$. FAME from linoleic acid of *m/z* 317 predominates with minor ions from methyl esters of oleic acid of *m/z* 319 and linolenic acid of *m/z* 315. Minor $[FAME + K]^+$ ions are also detected. As for the TAG, oxidation is clearly observed via

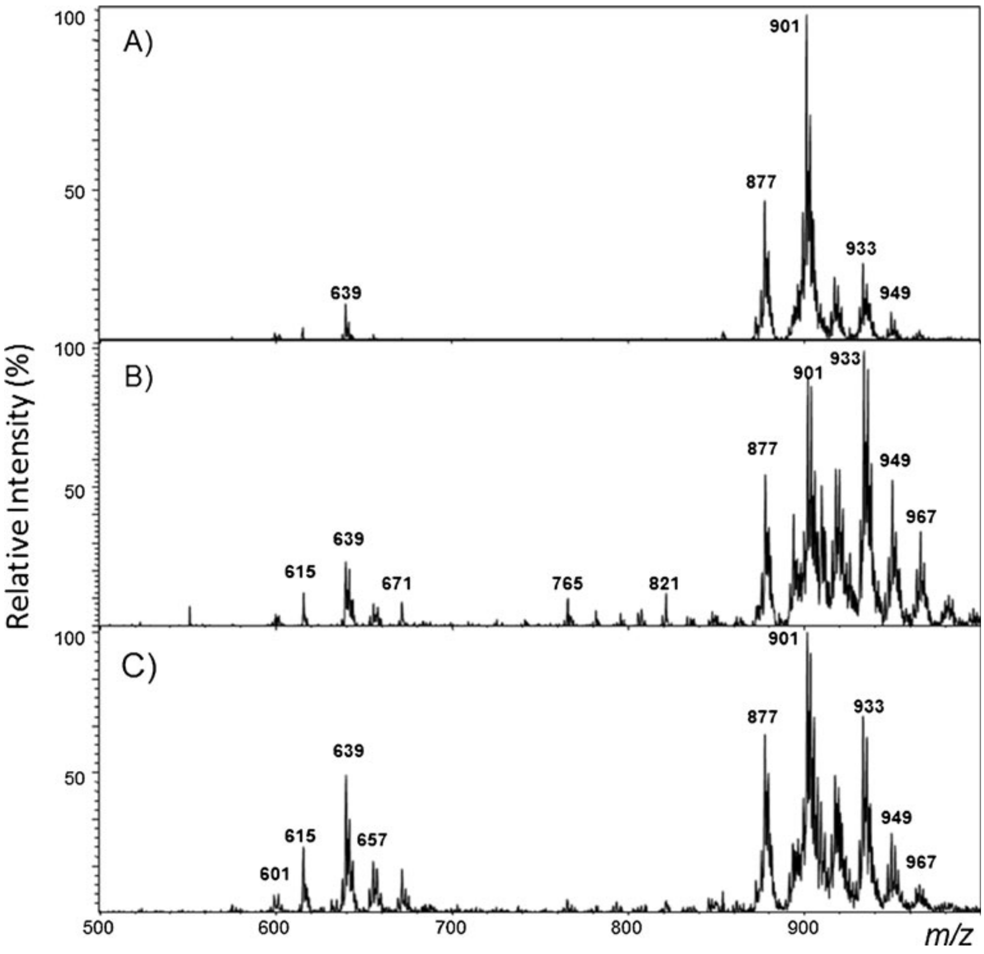

Fig. 1 EASI(+)-MS of **a** fresh soybean oil, **b** thermal oxidized soybean oil, and **c** used frying oil

the oxidation products ions of *m/z* 331, 333, 335, 347, 349, 351, 363, 365, 367, 379, 381, 383 with greater abundances for thermal oxidized oil and frying biodiesel. The EASI(+)-MS profiles for these two biodiesels are also unique as they show quite abundant intense ions around *m/z* 600–700 that probably correspond to dimers since de transesterification reaction has been completed. Otherwise, these ions can be associated with DAG that was not consumed. These species can be considered markers of biodiesel made from used oil. Table 3 summarizes FAME and their respective oxidation products detected by EASI(+)-MS.

Table 2 TAG and their oxidation products in fresh soybean, thermal oxidized soybean and used frying oil as detected by EASI(+)-MS

			Oxidation products							
Fatty acid composition	TAG (*m/z*)		[TAG + O] (*m/z*)		[TAG + 2O] (*m/z*)		[TAG + 3O] (*m/z*)		[TAG + 4O] (*m/z*)	
	Na^+	K^+	Na^+	K^+	Na^+	K^+	Na^+	K^+	Na^+	K^+
PLL	877	893	893	909	909	925	–	–	–	–
PLO	879	895	895	911	911	927	–	–	–	–
LLL or OLLn	901	917	917	933	933	949	949	965	965	981
OLL or OOLn	903	919	919	935	935	951	951	967	967	983
OOL	905	921	921	937	937	953	953	969	969	985

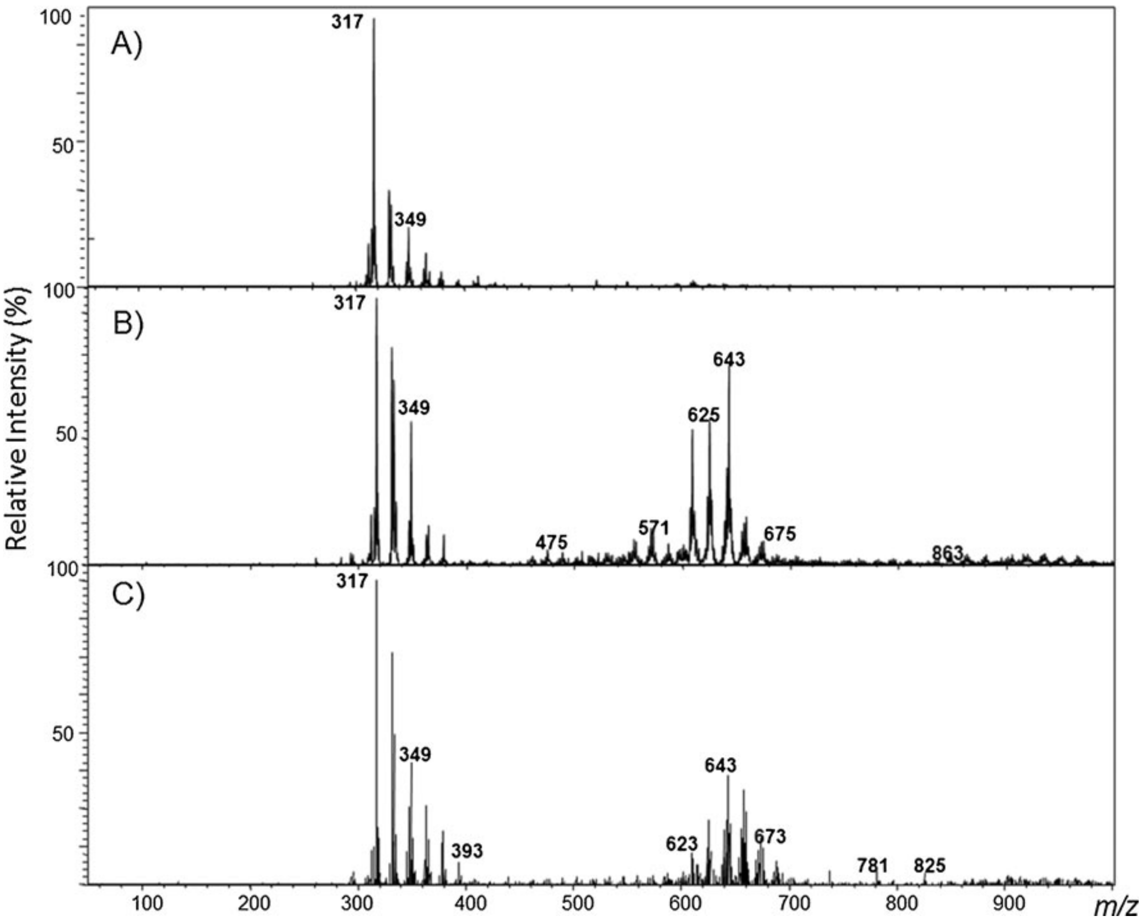

Fig. 2 EASI(+)-MS of biodiesel from **a** fresh soybean oil, **b** thermal oxidized soybean oil, and **c** used frying oil

In Brazil, owing to high availability and relatively low cost, transesterification using ethanol may be a viable alternative for biodiesel production. Figure 3 compares the EASI(+)-MS profiles for frying biodiesel produced via either methanol or ethanol transesterification. Note the +14 *m/z* shift for the $[\mathrm{FAEE} + \mathrm{Na}]^+$ profile in Fig. 3b as compared to the $[\mathrm{FAME} + \mathrm{Na}]^+$ profile in Fig. 3a due to ethanol versus methanol transesterification.

A main criterion for biodiesel quality is storage stability. Unsaturation of fatty acid methyl esters makes them susceptible to oxidation and polymerization, which may result in insoluble products that causes several problems within the fuel system, especially in the injection pump. Most of the natural antioxidants present in the fresh vegetable oils such as the tocopherols normally remain in the final biodiesel, but frying consumes such antioxidants which may lead to poor oxidative stability for frying biodiesels [6]. We have showed the effectiveness of the N,N′-di-*sec*-butyl-*p*-phenylenediamine as an artificial antioxidant for soybean, sunflower, and canola biodiesels [12]. The values for

Table 3 Biodiesel (FAME) and their oxidation products detected by EASI(+)-MS

			Oxidation products							
Fatty acid composition	FAME (*m/z*)		[FAME + O] (*m/z*)		[FAME + 2O] (*m/z*)		[FAME + 3O] (*m/z*)		[FAME + 4O] (*m/z*)	
	Na^+	K^+	Na^+	K^+	Na^+	K^+	Na^+	K^+	Na^+	K^+
Ln	315	331	331	347	347	363	363	379	379	395
L	317	333	333	349	349	365	365	381	381	397
O	319	335	335	351	351	367	367	383	383	399

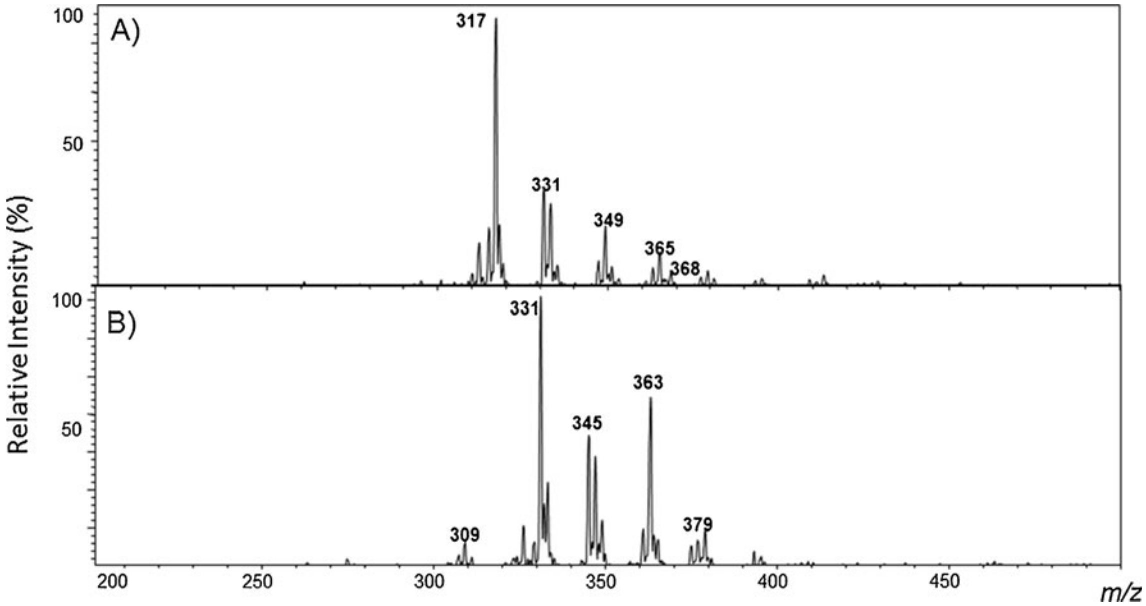

Fig. 3 EASI(+)-MS of frying biodiesel produced by transesterification using **a** methanol and **b** ethanol

the IP obtained by the Rancimat for frying biodiesel without and with artificial antioxidant indicated that this diamine also functions as an efficient antioxidant for frying biodiesel (Table 4). The addition of as little as 5 ppm of the diamine increase its oxidation stability the level of compliance with the European standard (EN 14214) [29] and of the National Petroleum Agency (ANP) [30] in Brazil (6 h at 110 °C).

Conclusion

Despite of using an impure and highly oxidized feedstock, the overall quality of the final frying biodiesel product is quite similar to that of standard biodiesel made from the more expensive (and controversial) fresh edible oil, as evaluated both in terms of overall fuel quality parameters and at the molecular level via EASI(+)-MS FAME profiles. The content of oxidized FAME is higher, but this seems not to effect considerably the overall quality for the frying biodiesel as a fuel as judged by normative parameters of fuel quality. Used frying oil seems therefore to be indeed a viable economic and environmentally advantageous alternative feedstock for biodiesel production. As shown here, in cases of too poor oxidative stability, trace amounts (ca. 5 ppm) of N,N′-di-*sec*-butyl-*p*-phenylenediamine could be added to frying biodiesel to bring its oxidation stability within acceptable values.

Table 4 Induction periods (h) determined by the Rancimat test for frying biodiesel doped with N,N′-di-*sec*-butyl-*p*-phenylenediamine [12]

[Diamine] (ppm)	IP (h)
0	0.17
2.0	0.94
5.0	8.73

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