Biodiesel production from high free fatty acid byproduct of bioethanol production process

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Abstract. Biodiesel is a reliable and promising replacement of fossil diesel. It is stable, less toxic and can be produced from sustainable resources, including a variety of raw materials. Currently, the most widely used are vegetable oils (edible and nonedible), due to their availability. The present paper considers the potential of obtaining fatty acid ethyl esters (FAEE) from corn oil, which is a byproduct of bioethanol production process. The ultimate outcome would definitely increase the profitability of the initial bioethanol production process. The biodiesel production process was implemented in two steps, due to the high content of free fatty acids of the obtained corn oil. The first step includes an acid-catalyzed esterification process and the second step comprises an alkali-catalyzed transesterification process to receive FAEE. Two different catalysts (sulfuric acid and p-toluene sulfonic acid) were utilized and compared each other in the esterification process, in order to cope with high acid number of the raw material. A comprehensive qualitative and quantitative analysis of both feedstock and biodiesel was performed using gas chromatography-mass spectrometry method. The obtained biodiesel was characterized by a significantly lower cloud point compared to the feedstock and high acid number.

1. Introduction

Climate change, increased energy demand and depletion of natural resources are ongoing concerns of the current century. Biofuels are considered as promising alternatives to fossil fuels in order to mitigate global greenhouse gasses (GHG) emissions. Among them, biodiesel is well established as the most suitable petroleum diesel substitute due to its lower toxicity, renewability, superior biodegradability, better lubricity and cleaner-burning in compression ignition engines [1].

Biodiesel consists of mono-alkyl esters of long chain fatty acids and it is mainly produced by catalytic transesterification of triglycerides with short chain alcohols under mild reaction conditions. Typical alkyl fatty acid chain ranges from C14 to C22 esters of methanol or ethanol. Obtained biodiesel's quality is totally associated with feedstock's origin and composition. In general, feedstocks for biodiesel production include edible and non-edible plant oils, waste oils as well as algae. Towards a more sustainable biodiesel synthesis, low cost and abundant materials, such as waste oils, can be utilized as feedstock [2, 3]. Nevertheless, due to high water and free fatty acids (FFAs) concentration, pre-treatment is crucial for these types of substrates. Undesirable side reactions, such as

saponification, occur and result in lower conversion rate of triglycerides and poorer product quality. Acid catalyzed pre-esterification process integrated with water separation reduces FFAs concentration and moisture levels prior to transesterification reaction [4, 5].

Regarding alcohols that are used during transesterification reaction, methanol and ethanol are the most common. Methanol presents higher reactivity and lower cost compared to other alcohols. On the other hand, ethanol improves cetane number and heat content of biodiesel and is less toxic. However, the price of biodiesel produced by ethanolysis is increased due to higher energy requirements and issues in ester and glycerol separation [6, 7]. In the current world market, bioethanol is one of the most prominent alcoholic biofuels and the second largest contributor in the transportation sector. Starch based feedstocks such as corn or wheat grains are the most utilized for bioethanol production through the fermentation process in North America and Europe [8].

In fact, corn to bioethanol conversion is the most mature technology. Two main conventional methods include wet-milling and dry grind. During last 25 years, commercial bioethanol production has expanded in the dry grind industry. Corn solid and fermentation efficiency affect bioethanol production. Fermented liquid is further processed to obtain pure bioethanol. Unfermented components (whole stillage) are recovered and used mainly as animal feed. After centrifugation the liquid fraction (thin stillage) that is produced is further concentrated into syrup [9].

Post-fermentation corn oil and thin stillage are by-products of dry grind corn bioethanol production. After centrifugation post-fermentation oil is separated from corn syrup and can be used for industrial purposes. Hence, valorization of by-products derived from first generation bioethanol refineries can serve as alternative feedstocks for biodiesel synthesis under the principles of circular economy [10].

The current research examined the possibility of obtaining fatty acid ethyl esters (FAEE) from corn oil, which is a by-product of bioethanol production process, and use it as a feedstock for biodiesel production. The ultimate outcome would definitely increase the profitability of the initial bioethanol production process.

2. Materials and methods

Corn oil was utilized as feedstock for biodiesel synthesis, which was a by-product of bioethanol production process. It was produced in the oil separation plant through a tricanter that separates the incoming syrup from the vacuum - evaporation by centrifugal forces. Three fractions were separated: liquid, solid and oily. The oily fraction delivered by the tricanter was then stored in a container and after passing through the corn oil cooler, it was pumped to storage.

The following reagents were used in the study: Ethanol (99.9% and 96%), p-toluene sulfonic acid (99%), Sodium (99.9%), Sulfuric acid (98%) and ortho-Phosphoric acid (85%).

2.1. Esterification method

The corn oil used in the study has a high acid number (above 22 mg KOH g^{-1}), which requires two-stage production method: the first stage is an acid-catalyzed esterification process and the second stage comprises an alkali-catalyzed transesterification process. In order to determine the appropriate parameters of the esterification, two catalysts were used, sulfuric acid and p-toluene sulfonic acid (p-TSA).

For the esterification, a three-neck round-bottom flask was used, equipped with a Dean-Stark apparatus, a thermometer, a separatory funnel and a magnetic stirrer. In the flask, the corn oil was mixed with the required amount of alcohol and the catalyst (sulfuric acid or p-TSA in amount 5% relative to the free fatty acids). A separatory funnel was placed in one neck of the flask, from which ethanol was added in portions during the reaction, which should compensate for the separated ethanol containing the reaction water. A thermometer immersed in the reaction mixture was placed in the other side of the neck. A Dean and Stark receiver was placed in the middle neck of the flask, in the reservoir of which the separated water-ethanol mixture was collected. A reflux condenser was installed on top of the extension, for condensing the vapors. After separating each 10 mL of the water-ethanol mixture

into the tank of the Dean and Stark burette, an equivalent amount of ethanol was added from the separatory funnel, ensuring that the rate of separation of the water-ethanol mixture was equal to that of ethanol addition. To follow the kinetics of the esterification reaction, samples were taken from the side neck of the reaction flask for measuring the acid number every hour after the commence of esterification. The esterification process took place under constant stirring at 1300 rpm and temperature of 120 °C.

The catalyst remained in the esterification product. Thus, the product was treated with sodium carbonate, in an amount equivalent to the double excess acid used, followed by filtration and washing with ethanol. Finally, the acid number of the sample, after solvent distillation, was determined.

2.2. Transesterification process

For the transesterification, a three-neck round-bottom flask was used, equipped with a reflux condenser, magnetic stirrer, thermometer and a separatory funnel. Reaction was performed using a 6:1 molar ratio of ethanol/oil and Na 1%w/w of the oil. A sodium ethoxide was freshly prepared in the laboratory by reaction of sodium metal with absolute ethanol. It was added in the flask to the esterified corn oil heated to 60 ºC, from the separatory funnel, drop by drop. The transesterification proceeded under continuous stirring at 900 rpm. The reaction continued for 2 hours, after the entire amount of sodium ethoxide had been fed. The resulting blend was transferred to a separatory funnel and separated into two layers (the upper layer contains ethyl esters, and the lower one - glycerol, catalyst, sodium soaps and ethyl esters). Both layers contain ethanol. A weak solution of phosphoric acid was added to the upper layer in order to neutralize the alkaline components and decompose the soaps.

If necessary, distilled water was used for esters washing until a neutral solution achieved. After the last wash, toluene was added to the ethyl esters in the separatory funnel for possible separation of an additional amount of water. The separation of toluene and other residues (water, ethanol, etc.) was held by distillation until a temperature of 140 °C was reached (at a residual pressure of 30 - 40 mm Hg).

2.3. Analytical method

The examined samples were analyzed by Gas Chromatography-Mass Spectroscopy (GC-MS) technique. The Agilent 6890N gas chromatograph system equipped with MSD5975B mass spectrometer detector and DB-XLB capillary column (30 m length, 0.25 mm internal diameter and 0.25 μm film thickness). Helium was used as a carrier gas at a flow rate of 1.3 mL/min. The samples were introduced by split mode with a 1:100 split ratio. Agilent 7683 auto injector was used to inject 2 μL of sample.

For the analysis of corn oil sample, the oven temperature was held isothermally at 50 °C for 5 min immediately after injection, then was increased from 50 °C to 340 °C at 10 °C/min and held at the final temperature for 10 min. For the analysis of the biodiesel sample, the oven temperature was kept at 170 °C for 2 min and then raised to 270 °C by 4 °C/min and held at the final temperature for 10 min. The mass spectrometer was operated in the electron impact (EI) mode at 70 eV in the scan range of 50 to 650 amu. The temperature of the transfer line and of the ion source was 270 and 280°C, respectively. Agilent's Chemstation software program was used for data acquisition and processing. Peak identification was based on their structural characteristics, with the help of the NIST MS Search V2.0 spectrum library and bibliographic data. Concentrations were based on relative area percentages.

2.4. Characterization of corn oil and biodiesel

The corn oil and synthesized corn oil biodiesel (COB) were fully characterized. Density, kinematic viscosities, cloud point, pour point, flash point, acid number, water content, sulphur content, oxidation stability, iodine value were measured using ASTM and EN ISO standard methods.

3. Results and discussion

3.1. Effect of reaction time on the acid number of the product

The preparation of fatty acid ethyl esters (FAEE) was carried out in two steps: esterification and transesterification.

In the course of the esterification with both acids (sulphuric or p-TSA), the change in the acid number of the intermediate products was monitored. Figure 1 and Figure 2 illustrate the trend of acid number in function with the esterification time for H_2SO_4 catalyst and p–TSA catalyst, respectively.

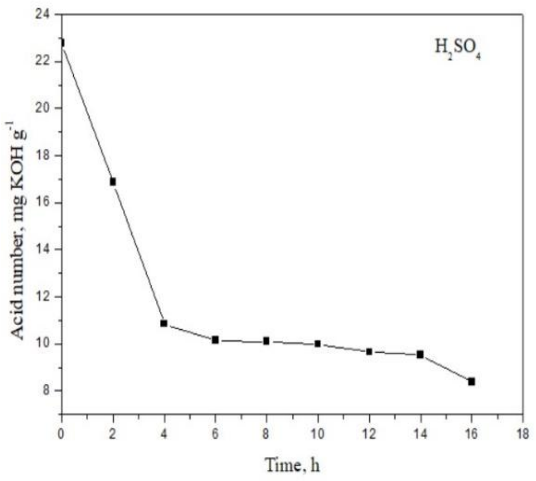

Figure 1. Dependence of the acid number on the esterification time using a sulphuric acid catalyst.

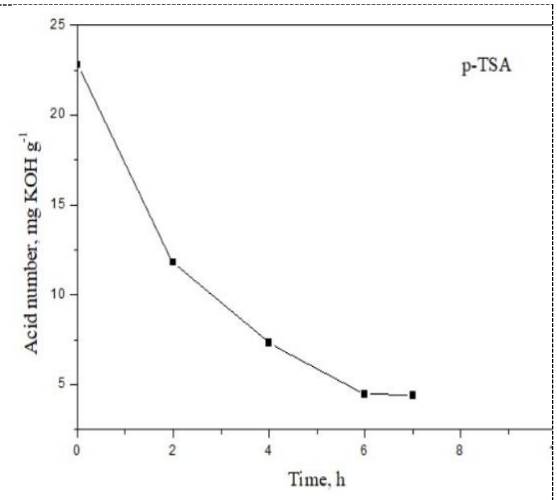

Figure 2. Dependence of the acid number on the esterification time using a p–TSA catalyst.

The obtained results revealed a significant reduction of the acid number during the first 4 hours, when using both catalysts. An increase in the duration of the process did not lead to a proportional decrease in the acid number values. The lowest acid number value was achieved using p-toluene sulfonic acid catalyst after 6 hours of esterification (4.47 mg KOH g^{-1}). The latter sample was transesterificated to produce the corn oil biodiesel.

3.2. *Physical and fuel properties of feedstock and corn oil biodiesel*

The corn oil was characterized for its physical and fuel properties. Table 1 showed that the corn oil had a very high acid number (AN). According to literature data [11, 12], in order for transesterification to proceed normally, the raw material must have an acid number no higher than 3-4 mg KOH g^{-1}. The water content was also very high, which further complicates the esterification process and leads to saponification [13].

Table 1. Feedstock (corn oil) properties.

Properties	Values	Test method
Density at 15 ºC, g cm^{-3}	0.9208	EN ISO 12185
Viscosity at 40 °C, mm^2 sec^{-1}	32.43	EN ISO 3104
Flash Point, °C	>190	EN ISO 3679
Cloud point, °C	6.2	EN ISO 3015

Pour point, °C	6.0	EN ISO 3016
Water, mg kg^{-1}	1604.60	EN ISO 12937
Acid number, mg KOH g^{-1}	22.78	EN ISO 14104

The results from the characterization of the obtained COB are given in Table 2 along with the EU specification standards for biodiesel according to EN 14214. The density of COB at 40 °C was 0.881 g cm^{-3} that was within the specified range of EN 14214 values for biodiesel (Table 2). The determined value of viscosity was 5.53 mm^2 sec^{-1}, slightly higher than the upper value of biodiesel specifications. Viscosity affects the operation of fuel injection equipment, while a high viscosity affects the fluidity of the fuel. The higher kinematic viscosity was due to the FAEE of the saturated fatty acids content [14]. This is in line with Table 4, where the palmitic and the stearic acid ethyl ester counts approximately 17%.

Table 2. Physical and fuel properties of corn oil biodiesel.

Properties	Value	Specs EN 14214	Test method
Density 15 °C, g cm^{-3}	0.881	0.86-0.90	EN ISO 12185
Viscosity 40 °C, mm^2 sec^{-1}	5.53	3.5-5.0	EN ISO 3104
Flash Point, °C	95	> 120	EN ISO 3679
Cloud point, °C	-0.5	NA[a]	EN ISO 3015
Pour point, °C	-3	NA[a]	EN ISO 3016
Sulphur, mg kg^{-1}	9.61	< 10	EN ISO 20846
Water, mg kg^{-1}	325.2	< 500	EN ISO 12937
Oxidation stability 110 °C, h	6.9	> 8	EN 14112
Acid number, mg KOH g^{-1}	2.07	< 0.5	EN ISO 14104
Iodine value, g I_2/100	117	< 120	EN 14111

[a] It is country specific and it has been replaced by CFPP value.

Flash point measurement is of great significance that has to be taken into consideration in the storage, handling and safety of fuels. Obtained flash point of COB was lower than the standard specifications. Flash point specification is used to certify the efficient purification of manufactured biodiesel by the removal of excess ethanol. Significant decrease in flash point can be observed even with the presence of small residual ethanol content in FAEE.

Behavior of fuels at low temperatures is described by characteristics such as pour point (PP), the lowest temperature at which the fuel can flow and cloud point (CP), the temperature at which wax first becomes visible when the fuel is cooled. Measured values of corn oil biodiesel were minus 3 °C (PP) and minus 0.5 °C (CP) that both of them were significantly lower than those of initial feedstock (6.0 and 6.2 °C, respectively on Table 1). The sulphur and water contents of the COB were found to be within the specified limits of biodiesel (Table 2).

Oxidation stability is another crucial parameter to examine; it is used to determine the degree of oxidation, potential reactivity with air, and the need for antioxidants [13]. The obtained COB is slightly less than the specifications.

The iodine value determines the number of double bonds of the fatty acids present in a fat or oil. The maximum specified value is 120 g I_2/100 g. The COB met the specifications with an iodine value of 117 g I_2/100 g.

The amount of acid number greater than 0.50 mg KOH g^{-1} can affect engine performance due to corrosion issues. The determined acid number of COB was 2.07 mg KOH g^{-1} that was significantly higher than the EN standards for biodiesel (Table 2).

3.3. *GC-MS Analysis*

The fatty acid composition is very important, as it determines the physical and fuel properties of biodiesel. Fatty acid ester profile is one of the main parameters for the suitability of any feedstock used in biodiesel production [15]. The GC-MS analysis can provide useful qualitative and quantitative information on biodiesel.

The chromatographic profile of the corn oil sample (Figure 3, Table 3) yielded a group of fatty acids, mainly palmitic acid, linoleic acid, and oleic acid, and their ethyl esters. Moreover, the linolenic acid ethyl ester and the stearic acid ethyl ester were identified as well as the plant sterol β-sitosterol and squalene.

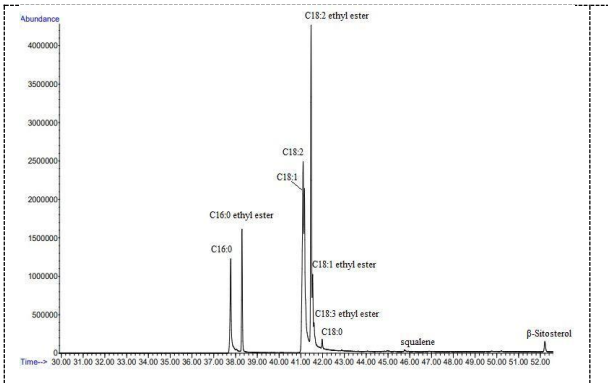

Figure 3. Total Ion Chromatogram (TIC) of corn oil sample.

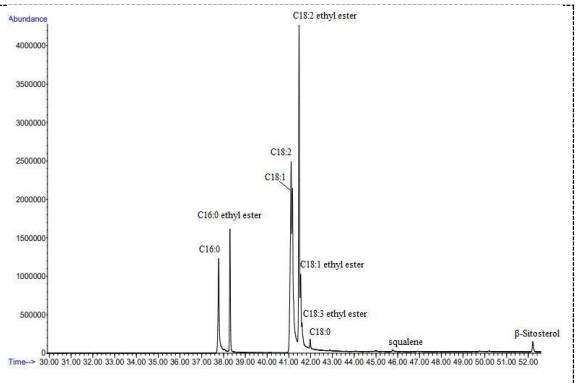

Figure 4. Total Ion Chromatogram (TIC) of biodiesel sample.

On the other hand, the GC-MS analysis of obtained biodiesel showed that the mixture was composed only of ethyl esters of fatty acids. The identified compounds illustrated in Figure 4 and the percentages of each component are listed in Table 4. Results indicated that the most abundant ester was the diunsaturated (C:2) linoleic acid ethyl ester with a percentage composition of 48.84%. The other main ethyl esters components in the sample were those of palmitic acid (C16:0), oleic acid (C18:1) and stearic acid (C18:0) ethyl esters amounted to 14.04, 33.41 and 2.79%, respectively. Other esters found in the biodiesel were ethyl esters of eicosenoic acid (C20:1), eicosanoic acid (C20:0) and docosanoic acid (C22:0), giving the percentages of 0.38, 0.42 and 0.11%. The only polyunsaturated (C:3) fatty acid ethyl ester detected in the sample was the linolenic acid ethyl ester in small amounts, which co-eluted under the experimental conditions with oleic acid ethyl ester.

Table 3. Composition of corn oil sample.

Retention Time (min)	Compound	Formula	Percentage
37.780	Palmitic acid	$C_{16}H_{32}O_2$	11.36
38.300	Palmitic acid ethyl ester	$C_{18}H_{36}O_2$	10.54
41.048	Linoleic acid	$C_{18}H_{32}O_2$	25.65
41.169	Oleic acid	$C_{18}H_{34}O_2$	21.09
41.473	Linoleic acid ethyl ester	$C_{20}H_{36}O_2$	26.18
41.545	Oleic acid ethyl ester	$C_{20}H_{38}O_2$	4.11[a]
41.606	Linolenic acid ethyl ester	$C_{20}H_{34}O_2$	
41.975	Stearic acid ethyl ester	$C_{20}H_{40}O_2$	0.55
45.810	Squalene	$C_{30}H_{50}$	0.10
52.201	β-Sitosterol	$C_{29}H_{50}O$	0.42

[a] co-eluted with C18:1.

The high content of free fatty acids (about 58 %, Table 3) determines the high acid number of corn oil. The conversion of free fatty acids and esters in corn oil into fatty acid ethyl esters was completely confirmed by Gas Chromatography-Mass Spectroscopy technique (Table 4).

Table 4. Composition of biodiesel sample.

Retention Time (min)	Compound	Formula	Percentage
10.176	Palmitic acid ethyl ester	$C_{18}H_{36}O_2$	14.04
13.727	Linoleic acid ethyl ester	$C_{20}H_{36}O_2$	48.84
13.818	Oleic acid ethyl ester	$C_{20}H_{38}O_2$	33.41 (co-eluted with C18:3)
14.278	Stearic acid ethyl ester	$C_{20}H_{40}O_2$	2.79
17.873	Eicosenoic acid ethyl ester	$C_{22}H_{42}O_2$	0.38
18.378	Eicosanoic acid ethyl ester	$C_{22}H_{44}O_2$	0.42
22.308	Docosanoic acid ethyl ester	$C_{26}H_{52}O_2$	0.11

Viscosity, iodine value and low-temperature properties depend primarily on the degree of unsaturation of fatty acids (esters). Oxidative stability is an important property for biodiesel and depends both on its chemical composition (or degree of unsaturation and type of complex bonds) and storage conditions [16, 17]. The oxidation stability of the obtained biodiesel COB was out of specifications, due to the content of unsaturated esters (Table 4).

Obtained biodiesel is not considered as suitable fuel, due to the high degree of unsaturation in free fatty acids. Peroxidation results in high polymerization tendency [15]. Fuel stability is an important characteristic, that is why the high double bond content such as linoleic acid (C18:2) in biodiesel is limited, although it exhibits excellent cold flow properties [18]. Nevertheless, the obtained COB was characterized by cloud and pour point, which were significantly lower to the feedstock.

4. Conclusions

Biodiesel was obtained from corn oil, which is a by-product of bioethanol production and is characterized by a high acid number. The biodiesel production process was implemented in two steps: i) acid-catalyzed esterification and ii) triglyceride alkali-catalyzed transesterification. A more efficient catalyst for the esterification process was found to be p-toluene sulfonic acid, compared to sulfuric acid. The conversion of free fatty acids and esters in corn oil into fatty acid ethyl esters was confirmed by gas chromatography-mass spectroscopy technique. Obtained biodiesel performed good cold flow properties, but high acid number.

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