A STUDY ON METHYL AND ETHYL ESTERS PRODUCTION - FROM SEED PREPARATION TO PRODUCT PURIFICATION

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For this work, a comprehensive analysis of the production of fatty acid esters with short-chained alcohols was carried out, starting from seed characterization of three types of indigenous species, to esters synthesis and purification. For the seeds containing the highest oil content, sunflower, and rapeseed, laboratory-scale experiments have also been carried out to synthesize ethyl esters in ultrasound (US)-assisted processes, which are potential green solvents for extracts in the food supplements industry.

Keywords: homogenous transesterification, fatty acid methyl and ethyl esters, indigenous seeds, ultrasound-assisted process

1. Introduction

Due to the increasing energy demand of a growing population and economic development, mainly represented by the increase in fuel consumption in the transport segment and petrochemical industry or heat and electricity generation, greenhouse gas emissions increased as a direct effect, threatening the stability of natural ecosystems, as well as coastline cities [1, 2 Society must consider replacing a significant fraction of their energy needs with renewable alternatives. The danger represented by climate change, forced the scientific community to identify renewable energy sources with reduced carbon footprint

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and a lower impact on the environment, which are sustainable from an economic point of view [3, 4].

Biodiesel, defined as a mixture of monoalkyl esters of triglycerides, is obtained by transesterification of vegetable oils or animal fats with alcohol, the most used being methanol and ethanol, with the mixture known as FAME (methyl esters of fatty acids), respectively FAEE (esters ethyl fatty acids), the schematic representation of the transesterification reaction can be seen in Fig. 1. For esters to be considered biodiesel they must also meet the quality demands of the standard EN 14214 [5]. The reasons why biodiesel has gained interest, as a viable alternative, are the reduction of dependence on fossil fuels, biodegradability, reduction of greenhouse gas emissions, excellent lubricity, and increased safety during transport and storage [2, 4].

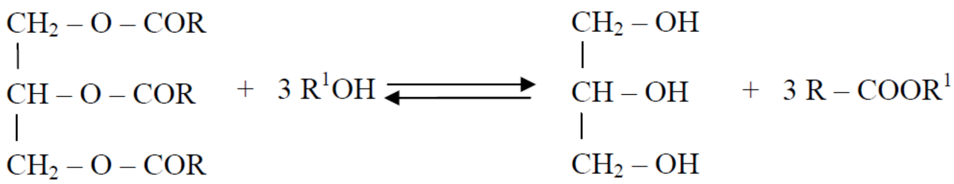

Fig. 1. Schematic representation of the transesterification of triglycerides with short-chained alcohols.

Some of the challenges and limitations associated with biodiesel as fuel are: higher production cost, less energy content compared to fossil diesel, and releasing nitrogen oxide emissions [2]. To reduce production costs, which is usually considered the main drawback, multiple paths have been studied: improving the production technologies using unconventional methods for better productivity/yield, reducing costs with raw material specifically feedstock cost, and reducing capital cost [6-8].

Although numerous studies have tackled the possibility of using alternative feedstocks [9], such as waste cooking oil, as well as the potential of using heterogeneous catalysts, no economically feasible alternative was able to replace the commonly used homogenous transesterification of vegetable oils with basic catalysts [10]. The high level of free fatty acids in waste cooking oils which are easily available from restaurants and household kitchens, result in undesirable side reactions during biodiesel production, therefore additional steps are required for treating waste cooking oil before being suitable for use as feedstock for transesterification [11]. While heterogeneous catalysts offer the advantages of separation and reusability, as well as being available from renewable sources, one of the more commonly studied being calcium oxide which can be obtained from shells, bones, and industrial waste, these types of catalysts generally require longer reaction times, and additional cost for conditioning or activating the catalyst, making it a less attractive option in the present [12].

The cavitation phenomenon, obtained both acoustically and hydrodynamically, is a topic of interest for researchers, covering a wide range of fields and chemical and physical processes. Starting from the first applications of sonar, ultrasound and cavity phenomenon has spread studied and applied in fields starting from the food industry, wastewater treatment, medical and pharmaceutical applications, to the concepts and models made on a laboratory scale of technologies that follow the implementation of the cavitation phenomenon in classical industrial processes. The cavitation phenomenon can allow better control over its effects and directing these effects until the development of chemical reactions and physical processes with increased efficiency, with lower energy consumption, being possible to restructure technologies limited by long reaction times and the degree of great complexity, around the cavitation phenomenon [13-17].

The subject of fatty acid methyl and ethyl esters, while covered in detail in existing literature, remains a topic of great interest [18-20]. This paper aims to establish a more comprehensive analysis of ester production from seed to the final product. Furthermore, this work also studied the potential of synthesizing ethyl esters from two types of oil, in US-assisted batch reactions, which have been less extensively studied but are of great importance for their potential uses as green solvents.

2. Materials and methods

Sunflower *(Helianthus annuus)*, rapeseed *(Brassica napus)*, and soybeans *(Glycine max)* are the most important crops used for the production of vegetable oil. According to the statistics of the Food and Agriculture Organization (FAO) - a specialized agency of the United Nations, in 2018, Romania recorded the highest production in the EU for sunflower - 3.06 million tons; for rapeseed oil, the production was 1.61 million tons and for soybeans, the production was 0.465 million tons [21]. For this study, the seeds were procured from local farmers from Calarasi district.

For the characterization of the seeds, the water, impurities, and oil contents are determined. Water and volatile compounds are determined by taking a sample of seeds, which is dried until constant mass between two successive measurements, according to the existing standard ISO 665 [22]. Impurities in seeds are considered to be all foreign bodies, organic or inorganic, being separated through the use of sieves or manual separation of weighing of the impurities, according to ISO 658 [23]. The resulting oils were characterized also by determining the phosphorus content [24], as well as the acid index and saponification value by established methods based on titration with potassium hydroxide solutions [25].

Biodiesel is analyzed to establish the methanol, free glycerol, and mono-, di-, triglycerides content, as well as ester content [26, 27]. By heating samples at 80°C methanol can pass into the gas phase and the residual methanol in the samples can be quantified by gas chromatography using as reference 3 calibration solutions of methanol in fatty acid methyl esters of known concentrations (0.01, 0.1, and 0.5% w/w methanol in biodiesel). For the determination of free glycerol and mono-, di-, triglycerides their transformation into more volatile silylated derivatives is required, which is carried out in the presence of pyridine and N-methyl-N-trimethylsilyl trifluoroacetamide. Analysis of silylated derivatives is accomplished by gas chromatography, the calculation is performed in the presence of 2 internal standard substances: 1,2,4 - butanetriol for the determination of free glycerol and tricaproylglycerol for the determination of glycerides (mono-, di- and tri-), commercially available at analytical grade. For the laboratory-scale experiments, analytical grade ethanol and sodium hydroxide, commercially available from Sigma Aldrich, were used.

3. Extraction and conditioning of oil from seeds

Following the separation of impurities from seeds, the oil is separated by mechanical crushing and just washing the seeds with hexane. The liquid phase consisting of oil and solvent are separated through filtering and distillation to obtain crude oil. The process is similar between the species of seeds, with small variations in the number of stages required to eliminate the shells during the crushing of the seeds and the fact that the lower oil content for soy, as seen in Table 1, leads to smaller amounts of oil being obtained by pressing alone, before adding the solvent.

Table 1

Characterization of 3 types of seed used for this study

Type of seed	Water content %	Impurities %	Oil content %
Sunflower	6.8 (6.1 - 7.3)	1.4 (1 - 1.9)	45.6 (44.9 - 46.2)
Soy	9.8 (9.4 - 10.2)	1.2 (0.9 - 1.5)	20.4 (19.4 - 21.3)
Rapeseed	8.5 (8 - 8.9)	1.9 (1.6 - 2.4)	42.4 (40.3 - 43.9)

The crude oil is analyzed and the average results are shown in Table 1, with significant higher acidity and phosphorus content being observed for the rapeseed crude oil. The average values of 10 sample readings, as well as the minimum and maximum values obtained for each parameter, are shown.

Table 2

Characterization of crude oil extracted

Type of oil	Acidity mg KOH/g	Impurities %	Phosphorus content mg/kg	Water content %
Sunflower	0.58 (0.47 - 0.65)	0.052 (0.04 - 0.07)	267.8 (256.7 - 281)	0.055 (0.03 - 0.1)
Soy	1.04 (0.79 - 1.3)	0.075 (0.05 - 0.1)	533.02 (500.1 - 554.1)	0.061 (0.05 - 0.08)
Rapeseed	1.5 (1.36 - 1.64)	0.06 (0.04 - 0.08)	770.93 (745.1 - 791)	0.091 (0.08 - 0.11)

The crude oil is filtered before being subjected to acid degumming, which is divided into three stages: acid conditioning, hydration, neutralization with sodium hydroxide, and washing of the oil. The crude oil is preheated to 80-90ºC, after which phosphoric acid is added to ensure that non-hydratable phosphatides which form stable complexes with metals such as Ca^{2+} and Mg^{2+}, are brought in a hydratable, water-soluble form to be easier to remove. To ensure good contact between the oil and phosphoric acid, it is necessary to mix the two phases, the acid forms precipitates with metals from complex combinations and the resulting phosphatides become more soluble in water. Dosing is done through a loop system, pressurized by a pump. The phosphoric acid flow is controlled by the automated system, the setpoint is automatically adjusted according to the incoming oil flow. From the mixers, the homogeneous oil/acid mixture is introduced into the multi-compartment reactor, where the non-hydratable phosphatides are transformed into their hydratable form. In this stirred reactor the acid/oil mixture is maintained for about 15 minutes. After acid conditioning, the pH of the mixture is adjusted with sodium hydroxide to a value of about 5. To complete the refining process, the mixture is passed through a centrifugal separator, where gums are separated from the oil which is then subjected to the washing stage to reduce the phosphorus and soap content of the oil which will be sent further in the drying step. A schematic representation of the main steps taken in the production of fatty acid esters with short-chained alcohols, starting from seeds, can be seen in Fig. 2.

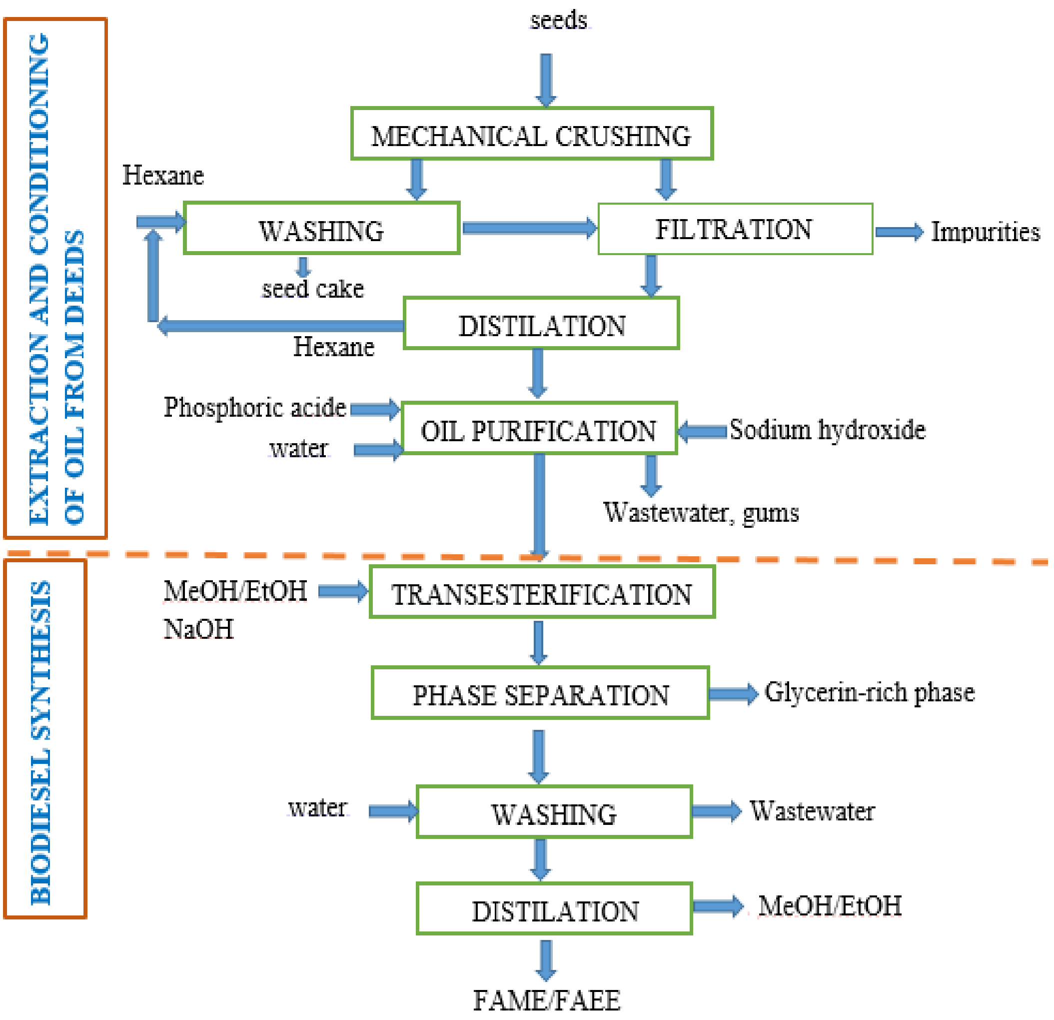

Fig. 2. Schematic flowchart of FAME/FAEE production from seeds

The refined oil is characterized by the analysis results shown in Table 3, where a significant reduction in phosphorus content can be observed between the crude and refined oils.

Table 3

Characterization of refined oil

Type of oil	Water content mg/kg	Acidity mg KOH/g	Saponification index mg KOH/g	Phosphorus content mg/kg
Sunflower	264.7 (230-291)	0.043 (0.04-0.046)	240.5 (193-293)	3.05 (2.8-3.5)
Soy	276.1 (255.4-299.9)	0.034 (0.03-0.039)	179.6 (143-201)	2.6 (2.3-2.9)
Rapeseed	304.5 (289.5-321)	0.042 (0.035-0.047)	260.9 (214-301)	3.43 (2.9-3.9)

4. Biodiesel synthesis and characterization

The transesterification process is carried out with sodium methylate as catalyst, with an excess of methanol and in mild conditions, the temperature of 55-60°C and pressure of maximum 0.3 bar. Excess methanol is recovered and reused to reduce production costs. The reaction takes place in 3 continuous reactors. Unlike the first two reactors, the third is equipped with a stirrer and has no recirculation system because the amount of unreacted oil is small, thus needing better stirring to ensure high conversions. The oil is fed to the first reaction loop, which consists of the recirculation pump, reactor, relevant pipes, and supplemented with a heater. Methanol and sodium methylate are dosed continuously in the recirculation pump suction. The first recirculation pump allows the required level of the mixture to be kept inside the reaction loop. The glycerin produced is deposited inside the vessel and discharged to the base of the reactor using a regulating valve, which allows the level established in the reactor to be maintained. The light phase (methyl ester) starts from the top of the reactor and is transferred to overflow to the second reaction loop which consists of the reactor, pump, and heater. The glycerin produces, which is relatively rich in the catalyst, can either be recirculated back to the first reactor to reduce catalyst consumption or sent to the glycerin treatment unit. The methyl ester stream contains traces of glycerin, soaps, and catalyst; these impurities are removed by washing with citric acid solution. The centrifugal separator separates the light phase consisting of pure methyl ester, containing traces of water and methanol from the heavy phase consisting of water and impurities (soaps, methanol, catalyst, and glycerin). The heavy phase is sent to the glycerin treatment unit to recover traces of glycerin and soaps. The light phase without glycerin, catalyst, and soaps, is then dried to remove the remaining moisture and methanol, by heating the biodiesel flux under vacuum. The purified biodiesel is then subjected to gas chromatography analysis [26, 27], with the results for each type of oil being presented in Table 4, with the best results in terms of FAME concentration being obtained for rapeseed oil.

Table 4

Comparison of obtained samples to standard biodiesel [5]

	Sunflower	Soy	Rapeseed	Biodiesel standard	Test method
FAME, %	98.43	98.79	98.99	>96.5	[27]
Methanol, %	0.10	0.11	0.15	<0.2	[28]
Monoglycerides, %	0.73	0.66	0.57	<0.8	[29]
Diglycerides, %	0.23	0.17	0.15	<0.2	[29]
Triglycerides, %	0.79	0.04	0.05	<0.2	[29]
Glycerol, %	0.01	0.01	0.01	<0.02	[29]

Water content, mg/kg	140.1	236.0	191.5	<500	[30]
Acidity, mg KOH/g	0.28	0.24	0.31	<0.5	[25]
CFPP, °C	-5.1	-8.5	-14.6	*depends on climate	[31]

When looking at the quality standard for biodiesel [5], we can observe that even though all samples meet the requirement of FAME content, the sunflower oil product has some parameters that don't meet the standard, such as di- and triglycerides content, as well as the highest CFPP temperature, which would be detrimental for use in cold weather. To remove free fatty acids that are present in the form of soap in both glycerin and the water from the heavy phase of the centrifugal separator, the glycerin is then sent with a pump to a recirculation circuit, where hydrochloric acid is introduced, to ensure a pH value of 3.5. The recirculation circuit consists of a pump, a static mixer, and a reactor, from which the mixture of glycerin and fatty acids flows through the overflow pipe into the glycerin/free fatty acid separator, where glycerin is separated at the base of the vessel. Following neutralization with sodium hydroxide to a pH value between 5-7, glycerin is purified in a distillation column to eliminate methanol and water present.

5. Fatty acid ethyl esters synthesis and characterization

Starting from the two types of seeds with the highest oil content, sunflower and rapeseed, experiments have also been carried out for the synthesis of ethyl esters, except that on a smaller laboratory-scale. For the comparative study of reactions to obtain US-assisted ethyl esters, using the equipment Vibracell VCX 750, starting from different types of oils, the experiments were carried out in a 70 mL glass reactor specially made for the ultrasonic probe, with a conical bottom to allow a better ultrasound dispersion in the reaction mass. The reactor as well as the equipment used to supply the ultrasonic energy, are shown in Fig. 3.

The reaction conditions used are: molar ratio oil to ethanol of 1:6, NaOH catalyst concentration 0.17% w/w to oil, reaction time 30 minutes. Due to the high ultrasonic energy supplied to the mixture, the reactor is immersed in an ice bath, the temperature being monitored in the reactor using a thermocouple with a digital display. The temperature is controlled with an ice bath to maintain the ethanol in liquid phase, as well as to favor the formation of the ultrasonic cavitation phenomena.

Fig. 3. Experimental setup for the US-assisted batch process for the synthesis of FAEE

Table 5

Reaction conditions and results for US-assisted FAEE synthesis

	Sunflower		Rapeseed	
US Power (W)	29	90	29	89
Amplitude (%)	30	70	30	70
Energy (J)	52313	162676	52739	160184
Time (min)	30	30	30	30
Maximum Temperature (°C)	30	45	30	48
FAEE content (%)	78.88	78.40	47.39	39.81

As seen in Table 5, in similar conditions, the reaction between sunflower oil and ethanol led to significantly higher results over the rapeseed oil, and in both cases, a higher amount of ultrasonic energy led to the heating of the reaction mixture to a point where the effect of the cavitation phenomena was diminished, leading to the thermal effect being the main driving force in the reaction, which in turn lead to lower reaction rates. For the ultrasonic cavitation phenomena to have a beneficial effect, the temperature control of the reaction medium becomes crucial. Due to the significant difference in FAEE content between the sunflower and rapeseed oils, further purification was carried out only for the ethyl esters produced from sunflower oil. The purification was accomplished, by subjecting the ester-rich phase, after washing, centrifugal separation, and drying, to distillation under vacuum, allowing the isolation of high purity FAEE (> 97%).

6. Conclusions

Sunflower, soybean, and rapeseed oil are widely used in the food industry, leading to a conflict over the use of raw materials between industries. Rapeseed and sunflower seeds have a much higher oil content (40-50%) than soybean seeds (~ 20%), making them more viable options from an economic viewpoint. Between rapeseed and sunflower, not only was the highest yield for biodiesel obtained for rapeseed oil, the Cold filter plugging point with the lowest temperature is found in biodiesel obtained from rapeseed oil, while sunflower oil had the CFPP with the highest temperature; therefore, rapeseed oil is the most suitable of the 3 for biodiesel production. On the other hand, for the synthesis of fatty acid ethyl esters, results obtained suggested that sunflower oil is the more suitable candidate as feedstock, with higher FAEE contents being obtained in similar conditions.

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