



and well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are some of its more obvious drawbacks [1, 11]. Today world production capacity of biodiesel is estimated at 1.3 million tons annually [12].

Low frequency ultrasonication is a useful tool for emulsification of immiscible liquids. Ultrasonic processing technology can be used, for example, for the reduction of particle size in minerals, powders and emulsions or for water treatment [9]. A truly unique method is the ultrasonic processing technology in the activation and acceleration of chemical, petrochemical and polymerisation processes [20]. Ultrasonication also has a general accelerating effect on heterogeneous reactions.

*In situ* transesterification differs from the conventional reaction in that the oil-bearing material contacts with acidified or alkalinized alcohol directly instead of reacting with pre-extracted oil and alcohol. That is, extraction and transesterification proceed in one step, the alcohol acting both as an extraction solvent and an esterification reagent. *In situ* transesterification of sunflower oil with acidified methanol produces fatty acid methyl esters in yields significantly greater than those obtained from the conventional reaction with pre-extracted seed oils [5].

The objective of the present work is to determine the effect of ultrasonication and catalyst type (acidic, alkaline) on the time and yield of the transesterification reaction of sunflower seed oil. It also compares commercial transesterification with *in situ* transesterification of pre-extracted sunflower seed oil.

## 2 Materials and Methods

### 2.1 Reagents and materials

Sodium hydroxide (>96%) was purchased from Merck (Darmstadt-Germany) and used after milling, to facilitate the dilution in methanol. Methanol of purity >95% and petroleum ether (pro analysis) employed were purchased from Fluka (Sigma-Aldrich, Germany). The sunflower oil seeds were provided by the Agricultural Cooperative of Kavala in Greece.

### 2.2 Procedures

**Solvent extraction.** Whole seeds (20g) were macerated in the extracting solvent, petroleum ether (50-100ml) in a home type blender, to give a product with a particle size of coarse sand. The solid material was transferred quantitatively to a Soxhlet thimble and extracted for various periods of time. Solvent was

removed from both the extracted oil and the solid residue via a vacuum rotary evaporator at 40 °C.

**Conventional oil transesterification.** Sunflower seed oils (80g, 0.102 mol), methanol (0.0395g, 0.0395mmol) and NaOH in various concentrations (1.0%, 1.5%, 2.0% wt/wt) were refluxed together in a 500 ml glass reactor equipped with a glass anchor-shaped mechanical stirrer, a water condenser and funnel. Heating was achieved by means of a heating mantle controlled by a proportional integral derivative (PID) temperature controller. The temperature was raised to 60 °C and the mixture was stirred either with the mechanical stirrer (600 rpm) (fig.1) or with the low frequency ultrasonicator (24 kHz) (fig.2). Ten ml samples were taken from the reaction mixture at regular intervals, neutralized and analyzed by TLC analysis. After the complete conversion of the vegetable oil, the reaction was stopped and the mixture was allowed to stand for phase separation: the ester mixture formed the upper layer and glycerine formed the lower layer [7]. The residual catalyst and non-reacted alcohol were distributed between the two phases. After phase separation, using a separatory funnel, the ester mixture was dried over anhydrous sodium sulfate and analyzed by Gas Chromatography.

***In situ* oil transesterification:** Whole seeds (20g) were macerated in methanol (50ml) as above and transferred to the previous described reaction flask. Methanol (150 ml) and concentrated sulfuric acid (10 ml) or 2% NaOH diluted in methanol (10 ml) were added and the mixture was refluxed at 60 °C and stirred either with the mechanical stirrer (600 rpm) or with the low frequency ultrasonicator (24 kHz). After the complete conversion of the vegetable oil, the reaction was stopped. The reaction mixture was filtered and washed with petroleum ether. After phase separation, the ester mixture was dried over anhydrous sodium sulfate and analyzed by Gas Chromatography [8].

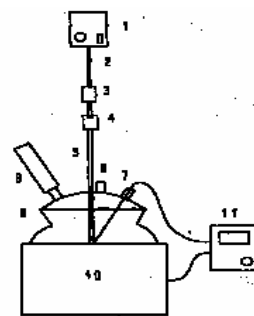


Fig 1. Scheme of the reactor used in the transesterification experiments. 1. Stirrer engine 2. stirrer steel bar 3. coupling device 4. Stirrer lubricant reservoir 5. Glass stirrer 6. Funnel 7. Thermocouple 8. water condenser 9. Glass tank reactor 10. heating mantle 11. PID temperature controller

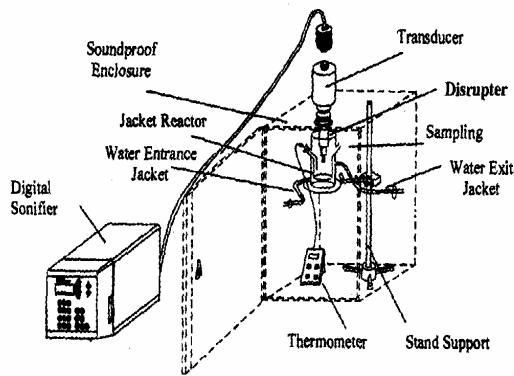


Fig. 2 Schematic diagram of the ultrasonic system

### 2.3. Sampling and analysis

The fatty acid composition of sunflower seed oil (Table 1) was determined by a well-established Gas Chromatographic procedure [8]. In brief, 0.1 ml of the biodiesel sample was dissolved in 5 ml of petroleum ether, and 3 µl of this solution were injected into a Varian 3700 GC for identification and quantification purposes. The standard mixture of the fatty acid methyl esters used was purchased from Sigma (stock No. 189-3).

Table 1: Principal fatty acid composition and molecular weight ( $M_r$ ) for Sunflower Seed Oil

Fatty acid	$M_r$	Content, %
Palmitic (16:0)	256	6.6
Stearic (18:0)	284	5.1
Oleic (18:1)	282	19.6
Linoleic (18:2)	280	68.7

The analysis of biodiesel by GC was carried out by dissolving 0.050 g of the biodiesel sample in 5 ml of petroleum ether, and injecting 3 µl of this solution into the GC, under the same conditions as above.

The content of biodiesel for each sample was quantified by comparing the FID response for each methyl ester of the GC sample of biodiesel with the FID response of each methyl ester in the standard mixture of FAME's.

The conversion of oil in each experiment was calculated from the content in methyl esters of biodiesel as analysed by GC, and the material balance of the experiment

$$\text{conversion}(\%) = \frac{\frac{\text{weight-biodiesel}}{MW_{\text{biodiesel}}} \cdot \text{biodiesel} \cdot \text{content}(\%)}{\frac{\text{weight-oil}}{MW_{\text{oil}} \times 3}}$$

$$MW = \sum MW_i \cdot \chi_i$$

where:

$MW$  is the mean molecular weight of biodiesel / oil. The mean molecular weight of biodiesel was

calculated averaging the individual molecular weights ( $MW_i$ ) of each constituent methyl ester, according to the biodiesel fatty acid methyl ester analysis ( $\chi_i$ ). The mean molecular weight of the oil was calculated averaging the individual molecular weights ( $MW_i$ ) of each constituent triglyceride according to the fatty acid oil analysis ( $\chi_i$ ). The factor 3 appears in this formula since each triglyceride molecule yields three methyl ester molecules.

## 3 Results and Discussion

A set of experiments was carried out to determine the effect of mechanical stirring and ultrasonication on the transesterification reaction. Yields of methyl esters isolated by conventional transesterification using mechanical stirring as a function of time and NaOH concentration are given in Table 2.

Table 2: The Yields of isolated methyl esters with mechanical stirring (600rpm)

1.0% NaOH		1.5% NaOH		2.0% NaOH	
Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
20	64	20	72	5	58
30	82	30	85	10	88
40	86	40	87	15	93

Based on the results in Table 2 it can be pointed out that the best yields were obtained when the catalyst was used at the highest concentration. To be more specific, by using 2.0 % NaOH wt/wt of oil the transesterification reaction was completed in 15 minutes. On the other hand, by using low concentrations of NaOH (1.0 or 1.5% wt/wt) the reaction was not completed even after a reaction time of 40 minutes. In conclusion, by increasing the amount of catalyst the yields of methyl esters also increase.

According to Stravarache et.al [7] by increasing the amount of catalyst, emulsions are formed in the washing step thus hindering the purification. During washing the soap present in the ester phase has the tendency to accumulate at the surface of the two liquids. The soap molecules, which are collected inside esters, and the water molecules form emulsions. Thus, the yields of isolated esters are very low. In the present study, this phenomenon did not occur and the increase of catalyst's concentration caused an increase in the yield of the isolated fatty acid methyl esters. However, a further increase of the catalyst's concentration (e.g 2.5% NaOH) led to soap formation and to a decrease in the yields of fatty acid methyl esters.

Yields of methyl esters isolated by conventional transesterification using ultrasonication as a function of time and NaOH concentration are given in Table 3.

Table 3: Yields of isolated methyl esters with ultrasonication (24 kHz)

1.0% NaOH		1.5% NaOH		2.0% NaOH	
Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
20	61	20	91	5	69
30	74	30	96	10	82
40	88	40	84	15	93

Based on the results in Table 3 it can be pointed out that the best yields were obtained when the catalyst was used at high concentration. To be more specific, by using 2.0 % NaOH wt/wt of oil the transesterification reaction was completed in 15 minutes. On the other hand, by using lower concentrations of NaOH (1.5% wt/wt) the reaction was completed in 30 minutes and by using 1.0% NaOH the reaction was not completed even after a reaction time of 40 minutes. In conclusion, by increasing the amount of catalyst the yields of methyl esters also increase. The yields of isolated products with ultrasonication are higher than with mechanical stirring, probably due to less soap formation through the use of ultrasonication. Indeed, after less than one minute of mixing with sonication the mixture became homogeneous. These results contradict to those of Stravarache et.al [7] according to which, by increasing the amount of catalyst the yields of isolated methyl esters decrease because of soap formation.

Yields of methyl esters isolated with *in situ* transesterification method using mechanical stirring as a function of time and H<sub>2</sub>SO<sub>4</sub> concentration are given in Table 4.

Table 4: Yields of isolated methyl esters with in situ transesterification using H<sub>2</sub>SO<sub>4</sub> as catalyst

Time (min)	Mechanical stirring (600rpm)	Ultrasonic irradiation (24kHz)
20	12	13
40	21	18
60	34	31
120	62	59
180	89	87
240	93	84

Based on the results in Table 4 can be concluded that acid-catalyzed *in situ* transesterification reaction is slow, requiring about 4 h to reach complete conversion

under mechanical stirring. In this case, ultrasonication does not accelerate the reaction. Even after 4h the yield of isolated fatty acid methyl esters was 84 %. Figure 3 illustrates the yields of fatty acid methyl esters as a function of time either with mechanical stirring or with ultrasonication. From this figure is obvious that with mechanical stirring the reaction is faster than this with ultrasonication. This phenomenon may be caused by the fact that ultrasonication produces more soap in the case of in situ transesterification. Thus the yield of the isolated fatty acid methyl esters is low.

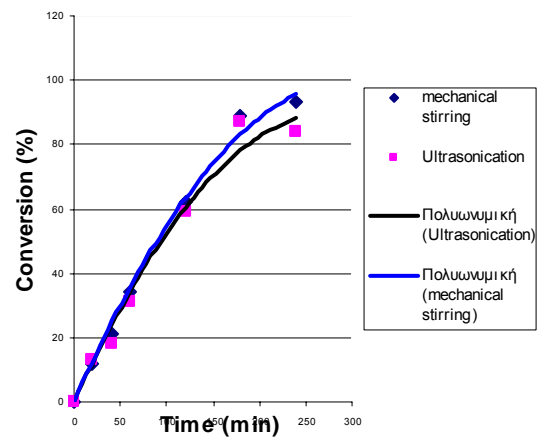


Fig.3 Yields of fatty acid methyl esters as a function of time either with mechanical stirring or with ultrasonication

Although transesterification by acid catalysis is much slower than that by alkali catalysis, according to Harrison et.al [3], acid-catalyzed transesterification is more suitable for oils that have relatively high free fatty acid content and more water. Akoy et.al [19] reported that it was necessary to perform transesterification under an acidic condition when the oil composition was a low grade material.

Yields of methyl esters isolated by *in situ* transesterification using ultrasonication as a function of time and NaOH concentration are given in Table 5.

Table 5: Yields of isolated methyl esters with in situ transesterification using NaOH as catalyst

Time (min)	Mechanical stirring (600rpm)	Ultrasonic irradiation (24kHz)
20	93	95
40	94	97
60	95	96
120	97	95
180	99	94
240	97	97

Based on the results in Table 5 it can be pointed out that the alkali-catalyzed *in situ* transesterification reaction is extremely fast, requiring only 20 min to reach complete conversion both under mechanical stirring and ultrasonication. Alkali-catalyzed transesterification proceeds approximately 4000 times faster than that catalyzed by the same amount of an acidic catalyst. Given this, along with the fact that alkaline catalysts are less corrosive than acidic catalysts, industrial processes usually favours the former.

#### 4 Conclusions

Biodiesel, is a new, clean renewable fuel and an attractive alternative to diesel fuel. Sunflower seed oil originating biodiesel production is the most popular and has found wide application in Europe. In this study the conventional and the *in situ* transesterification of sunflower seed oil with both mechanical stirring and ultrasonication was investigated. It can be concluded that ultrasonication is an efficient, time saving and economical process as compared to the conventional transesterification method. Regarding, *in situ* transesterification, mechanical stirring is more efficient offering a number of advantages as compared to ultrasonication. Furthermore, a considerable increase in the yield of esters is obtained in a remarkable short time span (the reaction is completed in 20 min) achieved by the use of alkali-catalysed *in situ* transesterification. On the other hand, acid-catalysed *in situ* transesterification is a rather time consuming method (the reaction is completed in 4 h).

#### References:

- [1] F. Ma, M.A. Hanna, *Bioresource Technology*, 70, 1999, 1.
- [2] S.J. Clark, L. Wagner, M.D. Schrock, P.G. Piennaar, *JAOCs*, 61, 1984, 1632.
- [3] B. Freedman, E.H. Pryde, T.L. Mounds, *JAOCs* 61, 1984, 1638.
- [4] K.J. Harrington, C. D' Arcy-Evans, *JAOCs*, 62, 1985, 1009.
- [5] J. A Colucci, E. E. Borrero, F. Alape, *JAOCs*, 82, 2005, 525.
- [6] T.J Mason, *Practical Sonochemistry* Ellis Horwood Ltd, 1991.
- [7] C. Stravarache, M. Vinatoru, R. Nishimura, Y. Maeda, *Ultrasonics Sonochemistry*, 12, 2005, 367.
- [8] K.J. Harrington, C. D' Arcy-Evans, *Industrial and Enginnering Chemistry Product Research and Development*, 24, 1985, 314.

- [9] R. Alcantara, J. Amores, L. Canoira, E. Fidalgo, M.J. Franco, A. Navarro, *Biomass and Bioenergy*, 18, 2000, 515.
- [10] P. Bondioli, A. Gasparoli, A. Lanzani, E. Fedeli, S. Veronese, M.Sala, *JAOCs*, 72, 1995, 669.
- [11] H. Fukuda, A. Kondo, H. Noda, *Journal of Bioscience and Bioengineering*, 92, 2001, 405.
- [12] M. Mittelbach, H. Enzelberger, *JAOCs*, 76, 1999, 545.
- [13] G. Kildiran, S. O. Yucel, S. Turkay, *JAOCs*, 73, 1996, 225.
- [14] G. Vicente, M. Martinez, J. Aracil, *Bioresource Technology*, 92, 2004, 297
- [15] J. Tickell, *From the fryer to the fuel tank*, New Media Productions, Third Edition, New Orleans, Louisiana, 2003
- [16] G. Pahl, *Biodiesel growing a new energy economy*, Chelsea green publishing company, White river junction, Vermont, 2003
- [17] T.J. Mason, *Sonochemistry*, Oxford University Press, New York, 1999
- [18] J. A. Colucci, E. e. Borrero, F. Alape *JAOCs* 82 (2005) 525.
- [19] H.A. Akoy, I. Kahraman, F. Karaosmanoglu, H. Civelekoglu *JAOCs* 60, 1983, 1596.
- [20] [www.telsonic.com](http://www.telsonic.com), telsonic Ultrasonics