

# Production of mono-, di-, and triglycerides from waste fatty acids through esterification with glycerol

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Received 10 July 2013; revised 10 August 2013; accepted 25 August 2013

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## ABSTRACT

Currently monoglyceride and diglyceride are representing important products, as they have numerous applications such as modifying agents in food and pharmaceutical industries. In this work, the production of these economically value added compounds by esterifying the fatty acids with the glycerol is presented. Effects of various reaction parameters were optimized to obtain high yield of mono, di- and triglycerids. The effects of temperature (180°C to 260°C), ZnCl<sub>2</sub> catalyst concentration (0.1%, 0.2%, 0.3%), glycerol to fatty acids molar ratio (1:1, 1:2, 1:3, 3:1), agitation speeds (200, 500, 1000 rpm), type of reaction system (opened and closed) and type of fatty acids including oleic and palmitic acids on esterification efficiency of fatty acids were investigated. The optimum conditions of esterification reaction were at temperature 195°C, molar ratio 1:1, amount of catalyst 0.3% ZnCl<sub>2</sub>, and agitation 500 rpm. Analysis of yield showed that at the optimum conditions mondi and triglycerids were produced in high purity, up to 99%. Infrared spectroscopy IR and thin layer chromatograph TLC proved that the final product contains mono, di- and triglycerides.

**Keywords:** Esterification; Fatty Acids; Glycerol; Monoglycerides; Diglycerides; Zinc chloride; Triglycerides

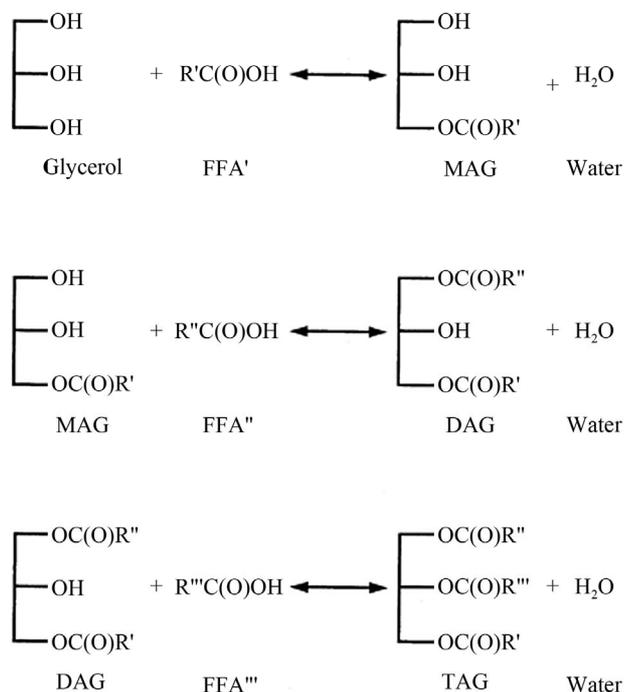
## 1. INTRODUCTION

Soapstock is a by product of the caustic refining of oils and fats. Fatty acids are the main component in the soapstock in the form of sodium salts. These fatty acids could be separated by soapstock acidulation to give waste oils.

Distilled fatty acids could be obtained from waste oils by two processes namely splitting and distillation. These free fatty acids could be used as a starting material for the production of very valuable products such as mono-, di- and triglycerides by esterification reaction with glycerol [1]. As consumers become more aware and concerned about the impact of the food they eat and the substances they commonly use on their health and general well-being, there is a growing interest in designer lipids. Among the lipid classes, surfactants, such as monoacylglycerols (monoglycerides, MAG), are desired by the food, cosmetic, pharmaceutical and chemical industries [2-5]. Production of tailor-made designer MAG with targeted fatty acids therefore offers promising industrial opportunities. The commercial synthesis of fatty acid esters of glycerol is carried out by two different routes: direct esterification of the fatty acid with the glycerol (Glycerolysis), catalyzed by a homogeneous acid, such as sulphuric or sulfonic acids, or by transesterification of triglycerides and polyalcohol catalyzed by alkaline hydroxides like NaOH, KOH or Ca(OH)<sub>2</sub> and sodium salts of low molecular weight alcohols, such as methanol. The esterification method is best suited for the production of designer MAG because the desired free fatty acid (FFA) can easily be selected prior to MAG formation [6]. It could be estimated that approximately 80% of manufacturing processes use acid catalysts [7]. The complete steps for esterification reaction are demonstrated in **Figure 1**. The major factors affecting the conversion efficiency of the esterification process are molar ratio of alcohol/oil, amount of catalyst, reaction temperature, catalyst type and stirring speed according to reaction duration [8,9].

Esterification of glycerol and fatty acids was studied under reduced pressure with and without the assistance of various metal chlorides and oxides as catalysts. Also super acids like sulphated zirconia and niobium acid were used as catalyst, for the reason that they could prevent

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**Figure 1.** Esterification reaction.

corrosion, their separation is easy, and also high *FFA* conversions could be achieved [10].

Recently, heterogeneous acid catalysts have been more widely favored over homogeneous ones since they are more separable and thus easier to recover. There have been only a few studies on non-catalytic esterification and/or transesterification reactions which lead to much simpler purification and environmentally friendly processes [11]. To avoid separation required in homogenous catalytic system, researches have explored the use of heterogeneous catalyst, such as glycerol esterification with lauric and oleic acid using solid cationic resins and zeolitic materials. More recently, mesoporous catalysts containing  $\text{SO}_3\text{H}$  groups have been reported to be efficient catalysts in the esterification of glycerol with fatty acids, where high yields of mono derivative could be obtained [7,12]. The synthesis of triglycerides by enzymatic esterification of polyunsaturated fatty acids (PUFA) with glycerol is well known by using Novozym 435 [13].

In the current work we demonstrate the feasibility of producing mono-, di- and triglycerides from waste fatty acids by direct esterification reaction with glycerol in a solvent free system.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Mixture of fatty acids Saturated and unsaturated were supplied from Al Manaar Company, Alexandria, Egypt. Palmitic acid, ethanol, methanol chloroform, sodium Hy-

droxide, potassium iodide, sodium thiosulfate and acetic acid were obtained from El-Nasr Company for chemicals, Cairo, Egypt. Sulfuric acid and phosphoric acid were provided by united company for chemicals, Cairo, Egypt. Distilled water was prepared in our department. Thin-Layer Chromatography paper (TLC), Kieselgel 60 f254 precoated plates, E. Merck, Darmstadt, Germany.

### 2.2. Equipment

Esterification reactions were carried out in a laboratory-built apparatus. An apparatus consists of laboratory conical flask 250 ml with 30 ml working volume. Esterification reaction was under atmospheric pressure (opened system), temperature of the reactor was controlled using hot plate (controlled with internal thermostat). All the reactants (fatty acids, glycerol and catalyst) were weighted and charged into the reactor. Then the temperature was increased through adjusting the thermostat. The magnetic stirrer was allowed to operate after 2 - 3 min (to heat up the mixture). After passing the desired reaction time, the reactor was removed from the hot plate. Samples were withdrawn from the reaction mixture for analysis. The reaction mixture was cooled to the ambient temperature by immersing it into a water bath. Also the esterification process in closed system was investigated, where all the reactors were isolated.

### 2.3. Optimum Conditions

Several reaction conditions were optimized including temperature, reaction time, type of catalyst, concentration of catalyst and molar ratio of glycerol to free fatty acids. The studied reaction temperatures were from  $180^\circ\text{C}$  to  $260^\circ\text{C}$ . The molar ratios of glycerol to fatty acids were 1:3, 1:2, 1:1 and 3:1. Concentrations of catalyst were 0.0%, 0.1%, 0.2%, and 0.3%. Effect of agitation speeds were in the range of 100 rpm to 1000 rpm.

### 2.4. Reversible Reaction

Three runs were conducted to study the effect of the reverse reaction of esterification. Reverse reaction experiments were run at  $195^\circ\text{C}$  for 60 min using 1:1 molar ratio without using a catalyst. To find out the best way of demolishing the effect of the reverse reaction on the overall yield of the esterification, the reaction mixture was rapidly cooled down by three different mechanism using refrigeration, water cooling, or air cooling. Then the yield of the esterification was measured in each case to investigate the conversion in each sample.

### 2.5. Analytical Methods

#### 2.5.1. Determination of the Fatty Acids Conversion

Titration method was selected for the determination of

the fatty acids conversion during the esterification reaction because it was simple and efficient analytical method that could be performed without the need for highly specialized equipment [14].

Five grams of the sample at time intervals was dissolved in ethanol and phenolphthalein indicator was used to determine the pH change during esterification reaction. The titration was carried out against aqueous solution of 0.1 N KOH. Acid value (*A.V*) was determined according to the equation given below:

$$A.V = \frac{56.1 * N * V}{M} \text{ mg KOH/g oil}$$

where:

*N*: normality of KOH solution

*V*: the volume of solution employed for titration, ml

*M*: weight of fatty acids sample, g

The conversion of *FFA* was calculated by the following equation:

$$F.F.A. \text{ conversion \%} = \frac{A_i - A_t}{A_i} * 100$$

Where *A<sub>i</sub>* is the initial acidity of the mixture and *A<sub>t</sub>* acidity at any time, *t*.

### 2.5.2. Thin-Layer Chromatography for the Produced Glycosides

TLC was used to identify the types of glycerides produced during the esterification reaction (*i.e* mono, di or triglycerides). TLC experiments were carried out by dissolving one drop of the esterification products into 0.5 ml mixture of chloroform and methanol (9:1). Then, a drop from the final mixture was applied over the TLC paper immersed into a 100 ml-beaker containing 10 ml of a mixture of chloroform and methanol (9:1) which allows a contact between the edges of the TLC paper with the solvent mixture. The TLC paper was allowed to stand until the solvent reach a level which must be just below the end line. Then, the TLC paper was dried and the bands of the different produced glycerides were detected under UV lamp. In some cases, the bands were not clearly appearing under the UV lamp. Accordingly, the TLC paper was exposed to an iodine vapor which allows a direct visualizing of the band by naked eye.

## 3. RESULTS AND DISCUSSION

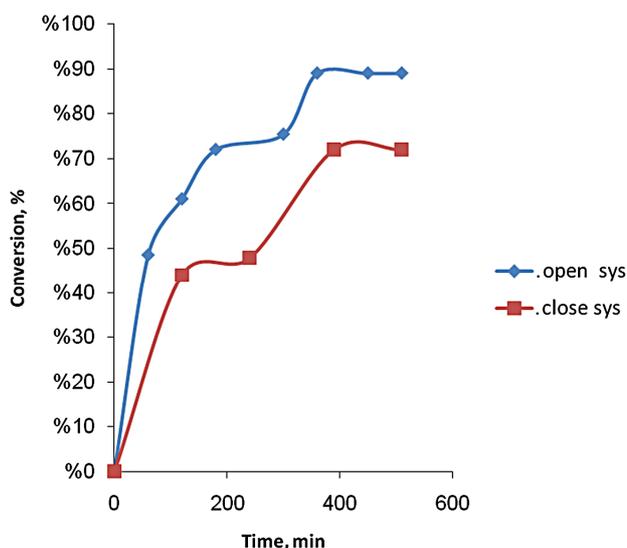
Monoglyceride, diglyceride and triglyceride were the major products obtained in this study. First, it was necessary to optimize the esterification conditions. To find out the optimum esterification conditions, the esterification process was carried out under different operating conditions at any time only one parameter was changing while the other parameters were kept constant.

### 3.1. Effect of Type of the System

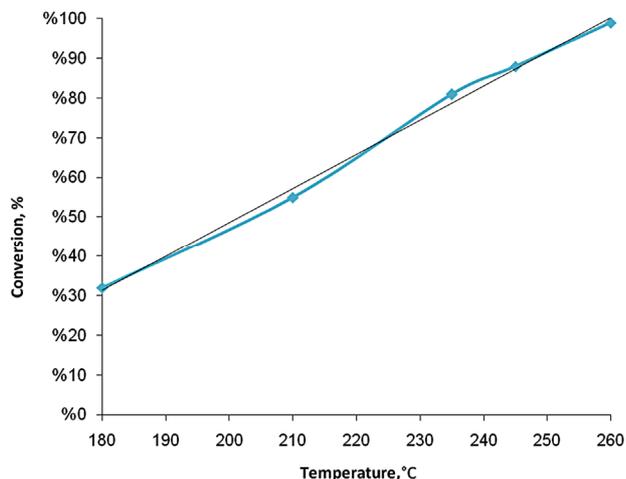
To investigate the effect of type of the system on the esterification yield, the same procedures described above were followed by applying both closed and opened systems (isolated and atmospheric systems). The esterification reactions were carried out using molar ratio of 3:1 (glycerol to fatty acids) at 180°C for 510 min. **Figure 2** shows the effect of both systems on the obtained esterification yield. The results indicated that the closed system and the opened system were come to equilibrium point at nearly the same time. However in the opened system the conversion (91%) was higher than that obtained by closed system (72%). Consequently it could be concluded that the opened system based process is more efficient than the closed one. This finding maybe due to the presence of the side reactions products in the esterification reactor inhibit the reaction to be proceed, therefore when these by products allowed to get out from the reactor, favorable products formation could be obtained.

### 3.2. Effect of Temperature and Time

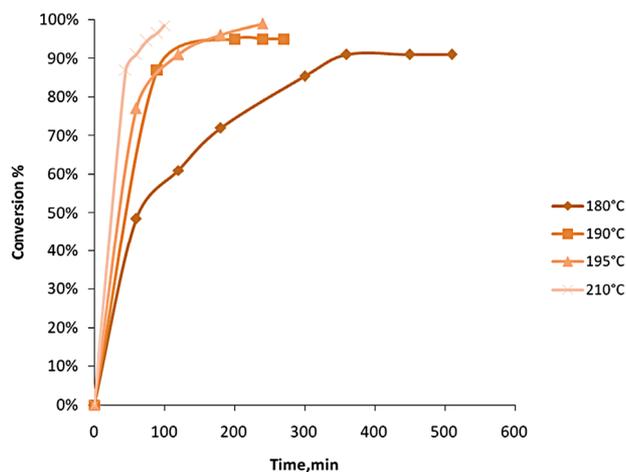
Both temperature and time are having major effects on the conversion of the esterification process. Accordingly, they were studied and optimized together. The obtained results showed that that by increasing the reaction temperature, the reaction conversion increases rapidly. **Figure 3** shows that after 20 min, the conversion reached 99%. However, the energy consumed was very high (260°C) which is not practical from the economic point of view. Therefore another esterification reaction was carried out within a temperature range of 180°C - 210°C as shown in **Figure 4**. The results revealed that by increasing the



**Figure 2.** Effect of the type of esterification system (opened system & closed system) at 180°C, 3:1 molar ratio and 510 min of the unsaturated fatty acid.



**Figure 3.** Effect of different temperatures on the esterification yield of saturated fatty acid after 40 min and 3:1 molar ratio (gly:fat).



**Figure 4.** Effect of temperature at 3:1 gly:fat molar ratio on the esterification of unsaturated fatty acid.

esterification time, the esterification yield increased up to a maximum conversion. To determine the optimum temperature of esterification process, not only the maximum yield of esterification should be considered but also the time required to reach the reaction temperature was taken into account. Heating time to reaction temperature was certainly longer and energy consumption was surely greater for higher reaction temperature. Consequently, a faster reaction at a lower temperature is desirable. From this economical point of view, the optimum temperature for the esterification was found to be 195°C at which the conversion reached up to 99%.

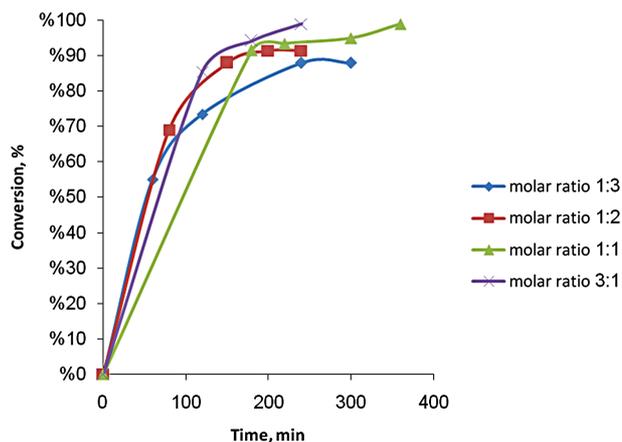
### 3.3. Effect of Molar Ratio on the Esterification Yield

The second studied parameter was the optimum esterification molar ratio (glycerol:fatty acids). In this part, all

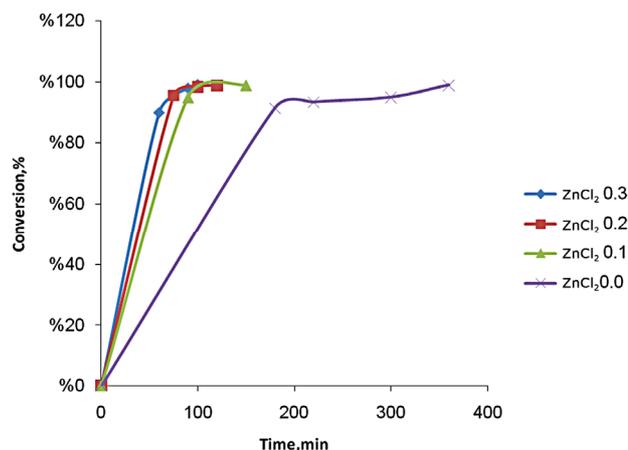
experiments were carried out at the optimum obtained temperature (195°C). The esterification process was carried out at 1:1, 1:2, 1:3 and 3:1 (glycerol to fatty acids). As shown in the **Figure 5**, it could be easily concluded that 1:1 molar ratio gave the maximum conversion under the required lower amount of raw material which in turn reduces the running cost of the process.

### 3.4. Effect of the Concentration of Catalyst on the Esterification Yield

After investigating the effect of temperature, time and molar ratio without catalyst, the effect of concentration of the catalyst (0.1%, 0.2%, and 0.3%) on the esterification yield under optimum temperature of 195°C and 1:1 molar ratio was investigated. **Figure 6** shows the effect of catalyst percentage on the esterification yield. As shown from the figure, by increasing the catalyst concentration, the time required to reach the maximum conversion decreases. So that 0.3% (by weight)  $ZnCl_2$  was considered to be the optimum dose, where the maximum yield of



**Figure 5.** Effect of glycerol:fatty acid molar ratio on the esterification of unsaturated fatty acid with glycerol at 195°C.



**Figure 6.** Effect of the concentration of catalyst on the esterification yield at optimum temperature (195°C).

99% could be obtained after 100 min. Further increasing in the catalyst concentration will make the downstream processes including catalyst separation more difficult.

### 3.5. Effect of Degree of Agitation (rpm)

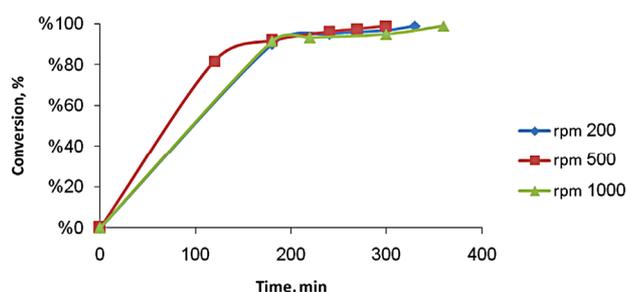
To investigate the effect of the degree of agitation (rpm), the esterification process was carried out at different agitating speeds (100, 500 and 1000 rpm) at 195°C, 1:1 fatty acids to glycerol and without catalyst. The results are presented in **Figure 7**. As shown from the figure the maximum conversion of 99% was obtained at 500 rpm.

### 3.6. Effect of the Reverse Reaction

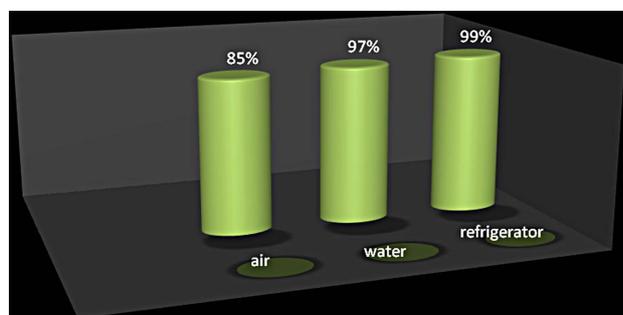
Reverse reaction effect was stopped using three different cooling mechanisms as described in the method part. The results were presented in **Figure 8**. As shown in the figure, the yield of esterification were 92%, 90%, and 88% for reactions cooled down by refrigerator, cooling water and air cooling, respectively. The rapid cooling of the reaction mixture prevents (through low temperature) the reversible reaction, which in turn keeping the conversion. Accordingly, by decreasing the cooling temperature the effect of reversible reaction is minimized.

### 3.7. Effect of the Type of Fatty Acids on the Esterification Yield

In this part of the study, all experiments were carried out at the optimum obtained conditions including temperature (195°C), molar ratio (1:1) and different types of fatty



**Figure 7.** Effect of the degree of agitation at 195°C, 1:1 (gly:fat) molar ratio.

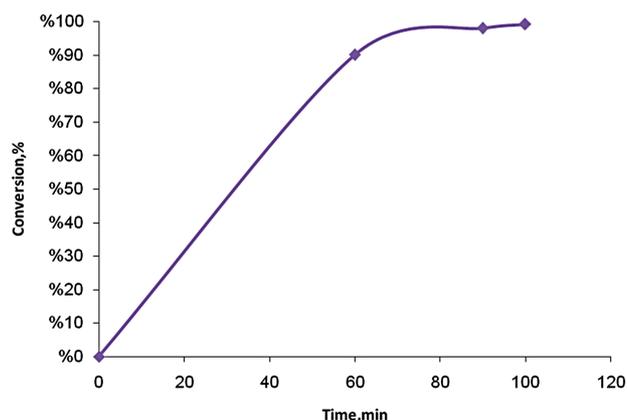


**Figure 8.** Effect of reversible reaction at optimum temperature.

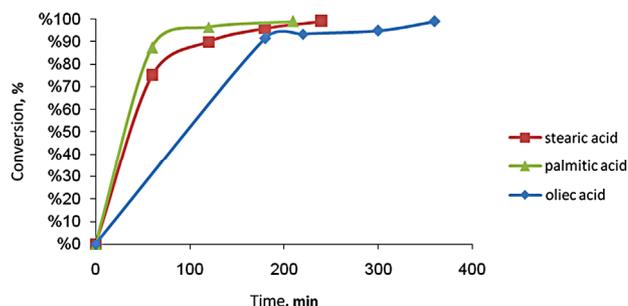
acids (oleic acid, stearic acid and palmitic acid **Figure 9** shows the effect of the type of fatty acids on the esterification yield. The results showed that the yield of esterification recorded a maximum conversion at time of 360, 240, 210 min in case of oleic acid, stearic acid and palmitic acid, respectively. From these results it could be concluded that the fatty acid chain length and the degree of unsaturation are having a considerable effect on the esterification reaction. Since long chain and unsaturated fatty acids need higher reaction time compared with the smaller chain and saturated fatty acids.

### 3.8. Esterification Reaction Using the Optimized Conditions

In this part, the esterification of free fatty acids was performed under the obtained optimum conditions. The time course of the esterification was measured and shown in **Figure 10**. The data showed that the maximum conversion (99%) was obtained after 100 min (instead of 180 min in the temperature effect experiments). Accordingly the esterification processes was achieved in a considerably short time and lower temperature. A sample was taken for IR and TLC analysis to prove the composition of the obtained esterification products. **Figure 11** shows



**Figure 9.** The esterification yield under the optimum condition (195°C, 100 min, 0.3% ZnCl<sub>2</sub>, 500 rpm).



**Figure 10.** Effect of degree of saturation and number of atoms of the fatty acids on the esterification reaction at optimum temperature.

the IR analysis, the results proved the existence of the carbonyl group (at wavenumber 1738.96 of the ester formation [15].

**Figure 12** shows the TLC paper plate of both esterified and free fatty acid. The results show the existence of the three main products of monoglyceride, diglyceride, and triglyceride.

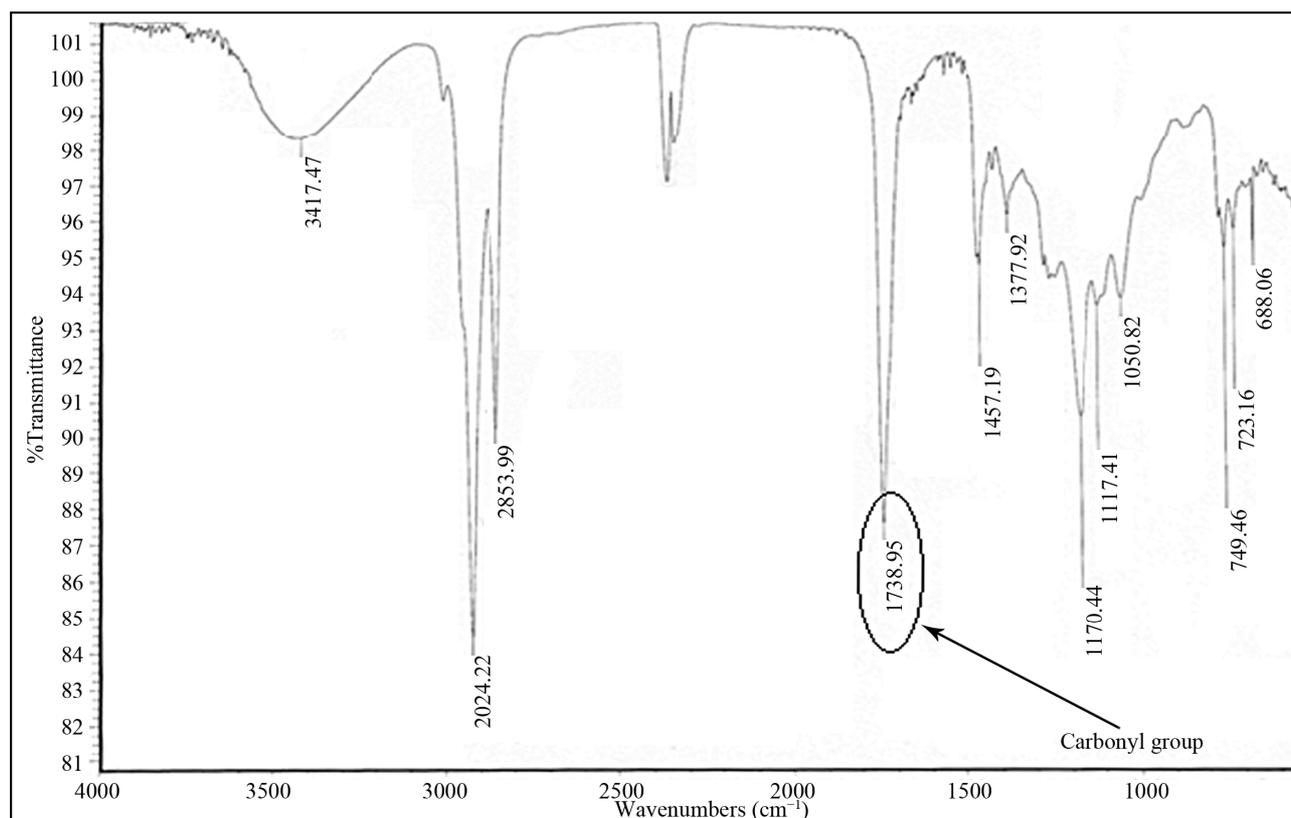
Now let us compare the results obtained in this study with others. Lilis Hermida [16] used a mesoporous catalyst in order to catalyzing the esterification reaction, the optimum conditions obtained were, 5% catalyst, 2:1 glycerol:fatty acid and 750 rpm which were higher than that obtained in this study. Furthermore the conversion obtained was 95% which was less than the 99% obtained in this study. Such a result indicated the effectiveness of the proposed route for production of mono-, di- and triglycerides.

Consequently, the esterification performed in the present work will make two major benefits; firstly, it will make the production of biodiesel more competitive with the existing diesel fuel market. Secondly, it will produce which is the most important emulsifier used in food industry.

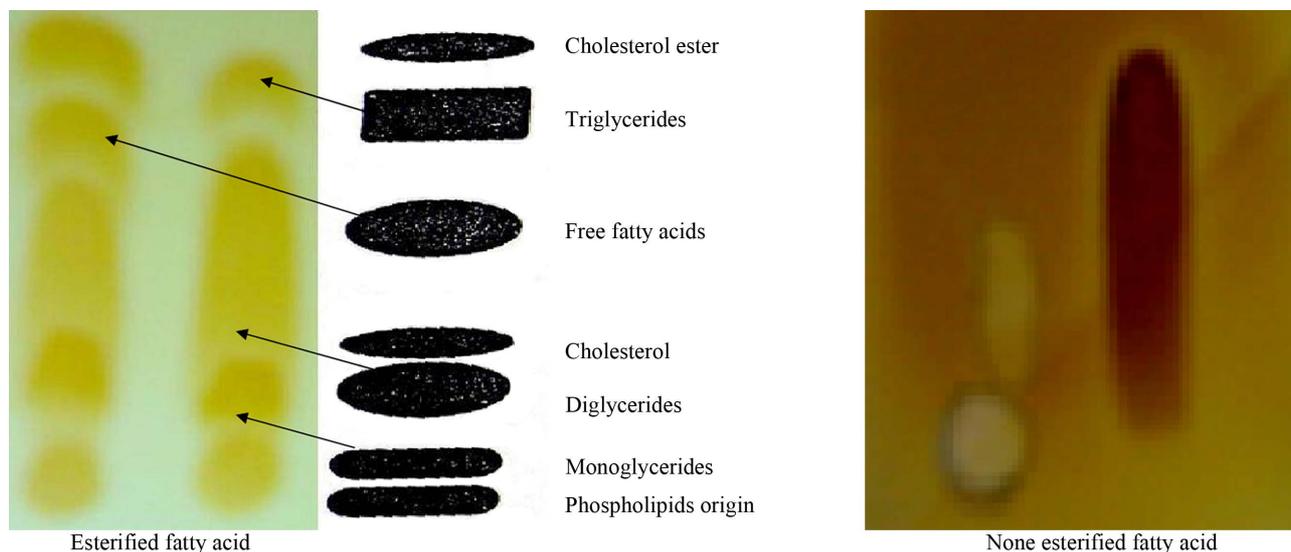
#### 4. PROCESS SIMULATION

The last step of this article was building an esterification

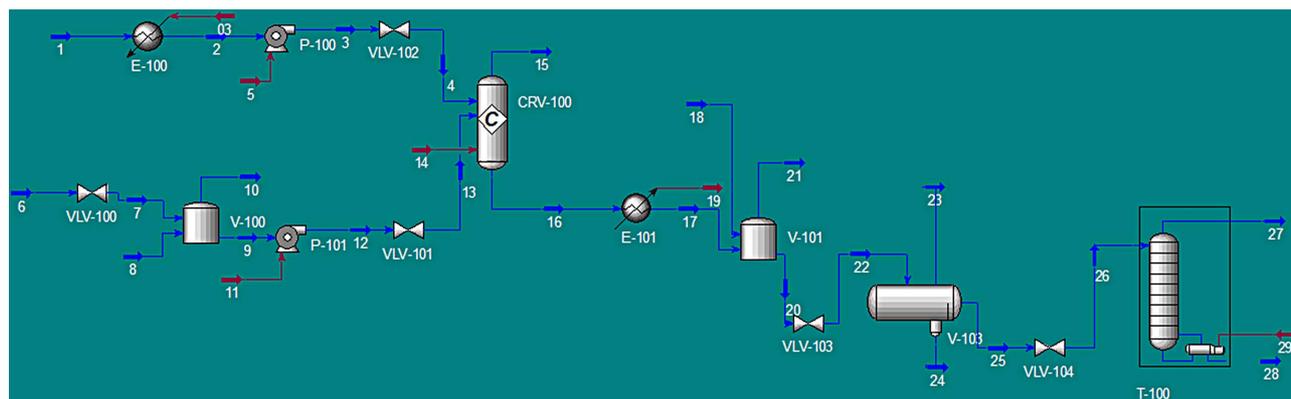
plant with a capacity of 100 ton of fatty acids/day using ASPEN HYSYS 2006 as shown in **Figure 13**. As demonstrated in the figure the process starts with a feeding pump (P-100) which was used for transferring the free fatty acids to the esterification reactor (converter type reactor, CRV-100) through a heat exchanger (E-100) equipped with control valve (VLV-102). Glycerol was transferred to mixing tank through control valve (VLV-100) and zinc chloride was mixed with glycerol in the same mixing tank (V-100). Then the mixture was pumped to reactor (CRV-100) through a transfer pump (P-101) equipped with a flow control (VLV-101). The product was cooled by the exchanger (E101). The resulting mixture was transferred to a washing tank (V-101). The washing was carried out using fresh water. Then, the washed mixture was transferred to a settling tank (V-102) using a control valve (VLV-103). The mixture inside the settling tank is divided into two phases. The first phase is composed mainly of esterified fatty acids and the second phase is composed mainly of catalyst, glycerol and water. The first phase was pumped through control (VLV-104) to a fractionation tower (T-100) equipped with ten stages fractionating the feed into glycerol from the top and esterified fatty acids from the bottom. The results of the simulation were summarized in **Table 1**. As shown in **Table 1** the yield of the final product was found to be



**Figure 11.** IR analysis of esterification unsaturated fatty acids.



**Figure 12.** TLC analysis of esterified and non esterified fatty acids.



**Figure 13.** Ester production plant from fatty acids and glycerol.

**Table 1.** Results of the simulation.

Feed		
Free fatty acid	M <sup>3</sup> /hr	4.9
	Mass%	99%
Glycerol make up	m <sup>3</sup> /hr	1.05
	Mass%	99
ZnCl <sub>2</sub>	kg/hr	16.5
	Mass%	99
Washing water	m <sup>3</sup> /hr	1
	Mass%	100
product		
Fatty acid ester	m <sup>3</sup> /hr	5.09
	Mass%	96
glycerol	m <sup>3</sup> /hr	0.4267
	Mass%	72.7

96% ester and 4% glycerol at the bottom of the distillation tower. On the other hand, at the top of the tower it was recovered for about 73% glycerol.

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