

## Synthesis of glycerol monooleate in presence of solid bed catalysts along with the analysis, detection and separation by GC-MS technique

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Manuscript received online 13 February 2014, revised 15 February 2014, accepted 24 February 2014

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**Abstract :** Glycerol oleates are non-ionic emulsifiers with low HLB. Two methods of synthesis of such compounds include esterification and trans-esterification. In this project, synthesis of glycerol oleates using new solid bed catalysts, Amberlyst 16 resin and silica-gel sulfuric acid 10%, esterification method was investigated. Separation, detection and measurement of glycerol mono-, di- and tri-oleates by GC-MS technique were determined. Optimized temperature and time for both catalysts were 70 °C and 8 h. Under these conditions, the efficiency of reaction for Amberlyst 16 resin and the silica-gel sulfuric acid catalyst was 84% and 68% for monooleate, 7% and 3% for dioleate, respectively.

**Keywords :** Emulsifier, HLB, Amberlyst 16, esterification, trans-esterification.

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### Introduction

Monoglycerides (MG) are fatty acid monoesters of glycerol of commercial significance. Due to the presence of specific hydrophilic and hydrophobic moieties in their structures, they act as important non-ionic surfactants of low HLB value, especially valuable as environmentally friendly “water in oil” emulsifiers<sup>1</sup>. Monoglycerides are widely used in a wide range of industries such as food and feed production<sup>2</sup>, cosmetics<sup>3</sup>, pharmaceutical formulations<sup>4</sup>, topical drug delivery systems<sup>5</sup>, oil well drilling<sup>6</sup>, textile<sup>7</sup>, packaging<sup>8</sup>, plastic processing<sup>9</sup> and construction materials<sup>10</sup>. They act as emulsifiers, emollients, lubricants and dispersants.

The MG are generally obtained from : (i) the glycerolysis of triglycerides, (ii) the hydrolysis of triglycerides and (iii) the direct esterification of glycerol<sup>11,12</sup>.

The industrial processes generally use homogeneous acid or basic catalyst, which lead to a mixture of mono-, di- and tri-glycerides in general (40 : 50 : 10) after direct esterifications. Before their application, a molecular distillation must be carried out to obtain a MG with a high purity (~90%)<sup>13</sup>.

In the industry, mineral acids (sulfuric acid), organic acids (paratoluene sulfonic acid) or mineral base (KOH

and Ca(OH)<sub>2</sub>) are the most often used catalysts<sup>14</sup>.

Besides the environmental problems, these catalysts show side-reaction from the degradation of the fatty acid (oxidation, dimerisation) or from the glycerol (polymerisation, dehydration into acrolein and oxidation). To minimize problems associated with the homogeneous catalytic processes, attempts have been made to develop heterogeneous catalyst systems. Solid base catalysts are promising to replace homogeneous catalysts, to minimize soap formation, separation, corrosion and to eliminate environmental problems<sup>15-17</sup>.

Various processes such as the esterification of fatty acid with glycerol<sup>18</sup>, glycidol<sup>19</sup>, (2,2-dimethyl-1,3-dioxolan-4-yl)methanol<sup>20</sup>, 4-(hydroxymethyl)-1,3-dioxolan-2-one<sup>21</sup> and trans-esterification of glycerol with fat or oil and fatty acid methyl ester (FAME)<sup>22</sup> have been reported for the production of monoglycerides (Fig. 1). For analysis, detection and separation of the synthesized products a chromatographic technique was then applied, including GC<sup>23</sup>, GC-MS<sup>24</sup> and HPLC<sup>25</sup> methods.

Variety of parameters can be effective in monoglycerides synthesis. In this study, temperature, molar ratio, catalyst and time were the parameters that were investigated in the monooleate synthesis.

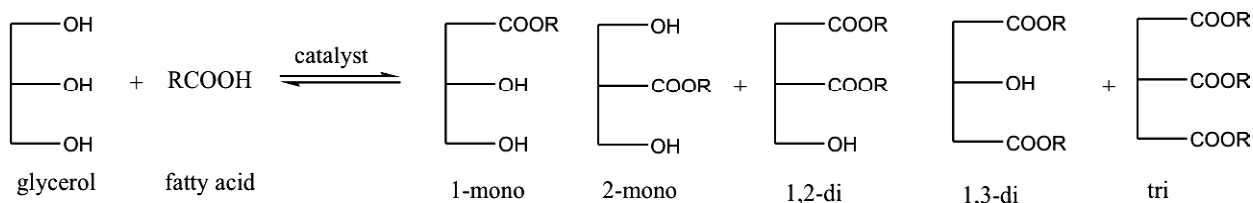


Fig. 1. Esterification reaction of glycerol with fatty acid.

In the present research, production of glycerol monooleate (GMO) by direct esterification reaction with a solid base catalysts and analysis of product by GC-MS chromatographic techniques will be discussed.

### Experimental

#### Materials :

Analytical were purchased from Merck; special-grade of oleic acid and glycerol silica gel 60G, sulfuric acid 98%, methanol 99% and *n*-heptan 99%.

Amberlyst 16 resin (Fluka, France) in particle size of about 700  $\mu\text{m}$  in the proton form was used as the cation-exchange resin catalyst.

#### Catalyst preparation :

**Amberlyst 16 resin :** The fresh resin initially contained color impurities, therefore it was rinsed with deionized water followed by ethanol. The resin was dried in oven at 80  $^{\circ}\text{C}$  for 24 h, to remove excess ethanol and water.

**Silica gel sulfuric acid 10% :** For the preparation of the 10% silica gel sulfuric acid, 10 g of the silica gel was in an oven at 200  $^{\circ}\text{C}$  for 24 h. Then 10 wt% sulfuric acid along with 20 ml of methanol was added to the mixture and stirred for 10 min until a homogeneous solution was obtained. The mixture was then transferred to a rotary evaporation to afford a dry sample.

#### Procedure :

Exactly 1.6 g of Amberlyst 16 resin or 1.0 g of silica gel sulfuric acid 10% was placed in a 100 ml three-neck flask fitted with a cooling system and mechanical stirrer. Then 16 mmol of oleic acid was added and the mixture was heated at 70  $^{\circ}\text{C}$  for 15 min to allow complete adsorption. At time 32 mmol of glycerol was added. The reaction mixture was kept at 70  $^{\circ}\text{C}$  on a thermostatic bath. The mixture was continuously stirred with a speed rate of 500 rpm for 8 h. The rate of the process was controlled by the chemical reaction, stirring was found not to be an

important factor. At the end of the reaction, the reaction mixture was analyzed by GC/MS.

#### GC/MS analysis :

GC-MS analysis was performed with a Varian, cp3800. The chromatographic separation was performed using a VF-5ms column of 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$  with helium as mobile phase 1 ml per min flow. The initial temperature was 50  $^{\circ}\text{C}$ , with an increase of 15  $^{\circ}\text{C}$  per min up to 180  $^{\circ}\text{C}$  (ramp1), 7  $^{\circ}\text{C}$  per min up to 280  $^{\circ}\text{C}$  (ramp2), and 10  $^{\circ}\text{C}$  per min up to 350  $^{\circ}\text{C}$ . The injection port temperature was 280  $^{\circ}\text{C}$ , the injection volume was 2  $\mu\text{L}$ , and *n*-heptan used as solvent.

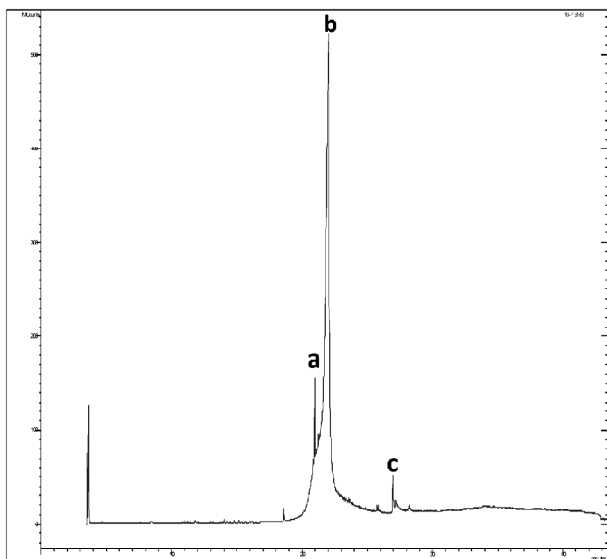
### Results and discussion

Results are illustrated as follows.

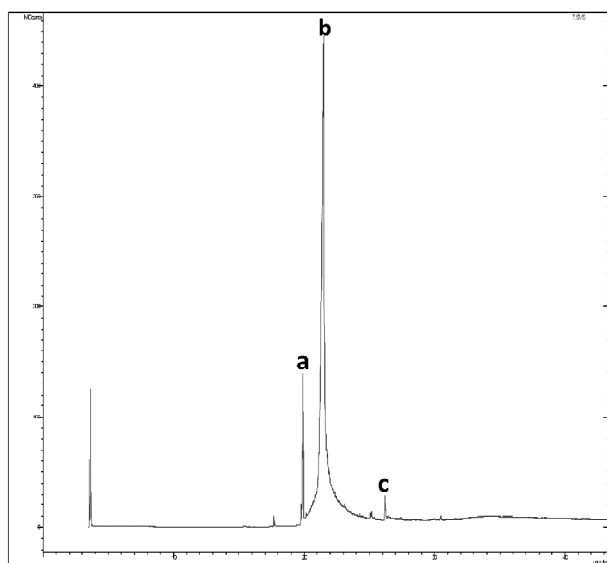
**Effect of temperature :** Temperature was found to be an important parameter. Heat was found to be favorable for the formation of 1-GMO. The investigations showed that in the 50–100  $^{\circ}\text{C}$  range, the optimum temperature for the synthesis of glycerol monooleate via use of both catalysts is 70  $^{\circ}\text{C}$ . In addition, observations showed that with the increase of temperature to higher than 70  $^{\circ}\text{C}$ , glycerol dioleate will increase and glycerol monooleate will decrease.

**Effect of the molar ratio :** The investigations showed that, Gly/OA molar ratio is an effective factor which can result in higher yields of glycerol monooleate. Obtained Gly/OA ratio of 1 : 1, 2 : 1, 3 : 1 and 4 : 1 were tried in order to obtain the optimum molar ratio this showed to be 2 : 1.

**Effect of time :** In such reactions, time was considered an effective feature. In order to determine the optimum reaction time, the reaction was examined during 24 h. The results showed that the optimum time for the highest yield of glycerol monooleate synthesis is 7 h.



**Fig. 2.** Representative GC chromatogram of the synthesized products at the temperature 70 °C, using an Amberlyst 16 resin as catalysts : (a)  $\alpha$ -glycerol monooleate, (b)  $\beta$ -glycerol monooleate, (c) glycerol dioleate.



**Fig. 3.** Representative GC chromatogram of the synthesized products at the temperature 70 °C, using a silica gel sulfuric acid 10% as catalysts : (a)  $\alpha$ -glycerol monooleate, (b)  $\beta$ -glycerol monooleate, (c) glycerol dioleate.

**Effect of catalysts :** Catalysts are a vital factor in monoglycerides synthesis. In the current study, the esterification reaction between glycerol and oleic acid with two solid catalyst beds, Amberlyst 16 resin and silica gel sulfuric acid 10%, were used for glycerol monooleate synthesis. This study showed that the required amount of

Amberlyst 16 resin and silica gel sulfuric acid 10%, were 1.6 g and 1.0 g per 10 mmol of oleic acid, respectively, for optimum yield.

GC-MS technique was then employed in the aim of detection, separation and analysis of the synthesized products.

Results showed that the glycerol monooleate yield in the presence of Amberlyst 16 resin and silica sulfuric acid 10%, at 70 °C, with a Gly/OA 2 : 1 molar ratio, and a reaction time of 8 h, resulted in 84% and 68%, respectively. The results are shown in Tables 1 and 2.

**Table 1.** The esterification results between glycerol and oleic acid in the presence of Amberlyst 16 resin

Sample	OA/Gly	Time (h)	Temp. (°C)	GMO (%)	GDO (%)
A	0.5	8	50	42	$\epsilon$
B	0.5	8	60	76	$\epsilon$
C	0.5	8	70	84	7
D	0.5	8	80	56	7
E	0.5	8	90	54	8
F	0.5	8	100	40	14

**Table 2.** The esterification results between glycerol with oleic acid in the presence of silica sulfuric acid 10% as catalyst

Sample	OA/Gly	Time (h)	Temp. (°C)	GMO (%)	GDO (%)
G	0.5	8	50	39	$\epsilon$
H	0.5	8	60	46	$\epsilon$
I	0.5	8	70	68	3
J	0.5	8	80	58	6
K	0.5	8	90	40	4
L	0.5	8	100	55	18

Solid bed catalysts have diverse advantages over homogeneous catalysts and showed more favorable results. Homogeneous catalyst contains acids and strong mineral bases. According to the previous reports, the yield of monoglyceride synthesis in the presence of homogeneous catalysts and in the temperature range between 210 °C and 230 °C was in the range of 60–40. The yield of the synthesized product supposed to be higher than 80% by means of molecular distillation, in order to be applicable in the food, cosmetic and pharmaceutical industries.

The effect of solid bed catalysts on reactions can result from the following factors : (i) particle interface aug-

mentation, (ii) presence of pores on the surface of the catalysts which can trap reactants and result in activation energy decrease<sup>26,27</sup>.

We recognized that by using solid bed catalysts as an alternative to homogenous catalysts in such reactions, higher yields and lower temperatures. Such replacement can lead to the elimination of problems that result from homogeneous catalysts usage, effects such as high toxicity, corrosion, pollution and difficulty of product work up and purification process. As a result, the mentioned reactions can be done under green chemistry condition which is environmentally friendly and have reduced health risks.

### Conclusion

Chromatography a method of choice for analysis of emulsifier samples, qualitatively and quantitatively, due its capability for separation and quantification of emulsifiers. The esterification reaction of glycerol and oleic acid in the presence of Amberlyst 16 resin catalyst and silica gel sulfuric acid 10%, as well as the detection, separation and analysis of the synthesized products using a GC-MS method, showed that such reactions can take place in the optimum conditions, namely lower temperature, favorable purification, more safety and higher yields.

### Acknowledgements

The authors acknowledgment the Department of Chemistry of North Tehran Branch Islamic Azad University for support of this research.

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