

Studying the Optimum Reaction Conditions for Organic Esterification of Glycerol to Benzoic Acid and Some Devices by Using Ecofriendly Media

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Abstract

The organic esterification reaction of some aromatic carboxylic acids and glycerol in the absence of organic solvents to obtain some α -mono aromate glycerol have been studied. The optimum reaction conditions were determined by esterification of glycerol and benzoic acid to produce α -mono benzoate glycerol (α -MBG). The optimal condition (catalysts and solvents) to get a high selective compounds and high yields have been studied. When use of heterogeneous catalyst (Amberlyst-15) and excess of glycerol (eight time) which plays as a reactive and solvent getting a required selectivity and high yield (about 70%) in comparison to the homogeneous catalysts (H_2SO_4 , CH_3SO_3H), in addition to the low selectivity of the final product. The reaction followed by using thin layer chromatography (T.L.C), the molecular structures have determinate by spectroscopy methods :FT-IR, 1H -NMR, ^{13}C -NMR.

Keywords: Glycerol, Benzoic Acid, Esterification Reaction, Amberlyst-15, Ecofriendly Media.

1. Introduction

Glycerol (also known as glycerin) is a polyol (1,2,3-propanetriol), naturally present in the structure of triglycerides, which are fatty acid esters of this alcohol [i]. Glycerol by production from biodiesel production process (10 kg of glycerol for each 100 kg of biodiesel) [ii,iii].

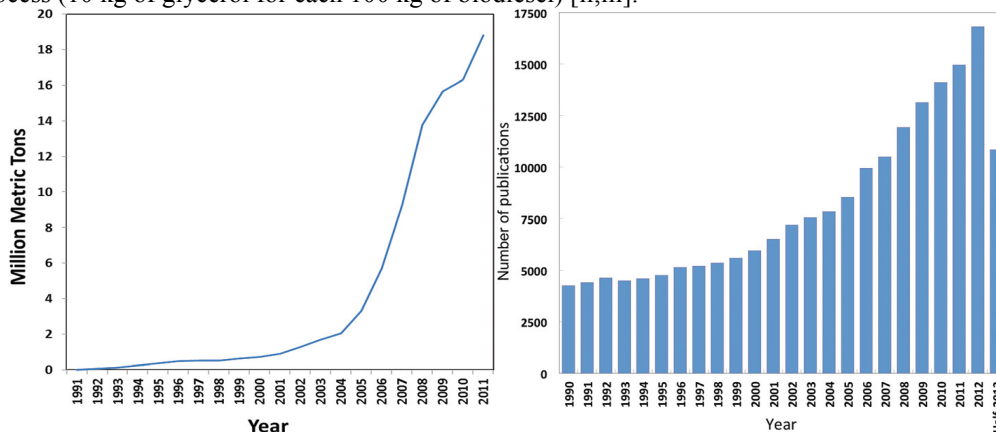
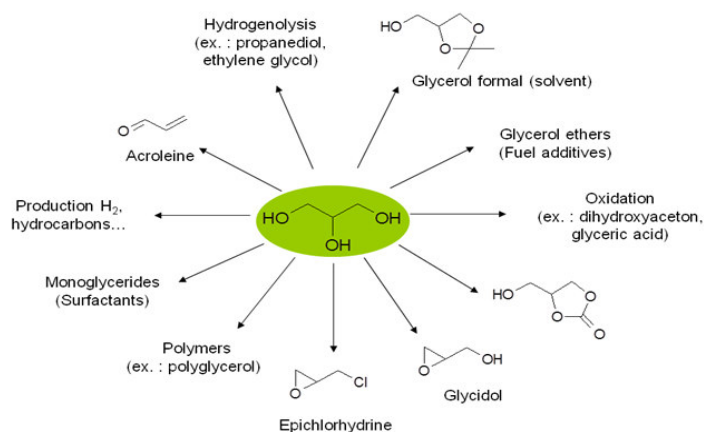


Figure 1. World biodiesel production, 1991–2011 and The number of publications containing “glycerol” as the topic, 1990–present (source: F. O. Licht; Worldwatch).

Thus, it is imperative that this aggravating glycerol be converted to higher value chemicals; otherwise the economic feasibility of biodiesel is jeopardized. In literature, the transference of this polyol into precious products has been reported [iv]. Glycerol can be converted to various chemicals through numerous routes such as etherification [v], hydrogenolysis [vi], oxidation [vii], transesterification [viii,ix].



Scheme 1. Roadmap of selected glycerol valorisation reactions.

There are currently a high number of applications found for this substance (more than 2000) in different fields such as the cosmetic, pharmaceutical [x] or food industry, where it is mainly employed as humectant, thickener, lubricant, sweetener or anti-freezer [xi]. Because of the high industrial demand of this substance. Esterification reactions are commonly catalyzed by bases (transesterification reactions) or acids (esterification reactions) [xii]. On the other hand, heterogeneous catalysts are outstanding catalysts in esterification reactions, due to their high activity and selectivity, even in solventless media.

In this context, solventless systems arise as an economic and environmentally friendly alternative for these syntheses. In such systems, various phases have to be considered because of the limited solubility of the mixture components, although this is not necessary [xiii,xiv]. Besides, as stated in a recent report, glycerol itself proves a nonaggressive, stabilizing medium for the enzyme, postulating the solvent-free system appear as a promising alternative for the synthesis of α -monoaromate of glycerol.

2. Experimental

2.1. Apparatus

spectrum NMR proton and carbon device 400 MHz model Bruker by Switzerland company, optical absorption spectrum infrared device model FT-IR-4100 from the Japanese company Jasco, rotary evaporator 4.91 model from the German company Normschiff, thin layer chromatographic of aluminum coated by Silica Gel 60F254 measuring 20 X 20 from the German company Merck, thin layer chromatographic of preparatory glass coated by Silica Gel 60F254 measuring 20 X 20 from the German company Merck.

2.2. Reagents and materials

glycerol (99.5% C Pure by Tekkim) Benzoic Acid, Salicylic Acid, and 2-Amino Benzoic Acid (Acros Organics, Belgium), and Amberlyst-15 (99% by sigma aldrech), Methan Selfonic Acid, Sulfuric Acid and some Solvents (99% by Merck).

3. Experimental Procedure

We added different molar ratios of glycerol to benzoic acid (4:1, 6:1, 8:1, 10:1, 14:1) and different solvents (toluene, dimethylsulfoxed) and solventless by excess of glycerol into a tow-necked flask equipped with a thermometer thorn fractionating column, using dean-stark trap (figure-2) and cooler reflex.

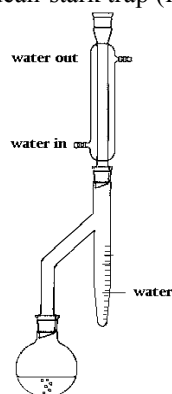
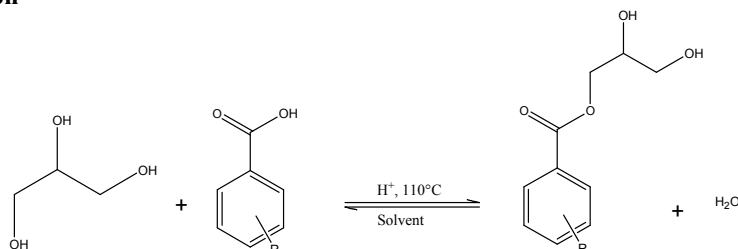


Figure 2. dean-stark trap using by fisher reterification reaction to remove of water.

Different kinds of catalysts (sulfonic acid, methane sulfonic acid, and amberlyst-15) were added, respectively, to a tow-necked flask equipped with athermo meter thorn fractionating column, using dean-stark trap and cooler reflex, we then added glycerol, benzoic acid and catalyst (the best molar ratio of glycerol to benzoic acid is 8:1, solventless and catalyst is amberlyst-15). All of these reactions were performed at about 110C° under stirring and reflowing. After the optimum conditions obtained, we used different aromatic carboxylic acids to synthesized α -mono aromate glycerol like salicylic acid, 2-aminobenzoic acid.

4. Results and Discussion



R: H, OH, NH₂.

Scheme 2. Synthesis route of the main reaction.

Table 1. different aromatic carboxylic acid to the Product.

Entry	Aromatic carboxylic acids	products
1	Benzoic acid	2,3-dihydroxypropylbenzoate
2	salicylic acid	2,3-dihydroxypropyl 2-hydroxybenzoate
3	2-aminobenzoic acid	2,3-dihydroxypropyl 2-aminobenzoate

The optimal conditions for preparations of α -Mono Aromate Glycerol, by esterification of glycerol and benzoic acid to produce α -mono benzoate glycerol (α -MBG). The catalytic effects of several catalytic systems were inspected in the esterification of glycerol with benzoic acid, these catalytic systems included sulfuric acid, methanesulfonic acid, and amberlyst-15 as shown in table(2), figure(3) sulfuric acid did a remarkably bad job on this reaction in reverse, while methanesulfonic acid and amberlyst-15 had good catalytic activities. However, it was easy to remove amberlyst-15 after the reaction, because it was a heterogeneous catalyst. There for, amberlyst-15 was determined to be optimal catalyst for the esterification of the aromatic acids. The several acidic catalysts homo and heterogeneous has used table (2):

Table 2. effect of different catalysts to the Product yield% (α -MBG).

Entry	H ₂ SO ₄	CH ₃ SO ₃ H	Amberlyst-15	Time (hour)
1	18.6	25.2	9.3	2
2	32.3	48.6	24.5	3
3	39.5	57.2	38.3	4
4	36.3	66.1	54.6	5
5	33.8	61.3	68.1	6
6	30.9	58.6	67.8	7
7	28.6	56.2	66.9	8

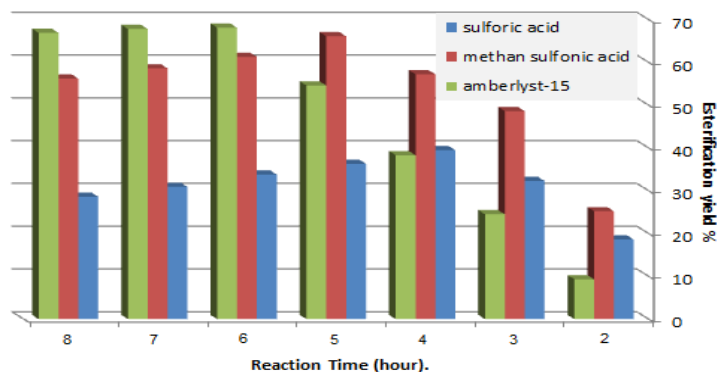


Figure 3. effect of different catalysts to produce (α -MBG).

The last figer shown that the best one has an Amberlyst-15 "acid heterogeneous catalyst" and the best time (6 hours), because after that Di and Tri glycereds was formed, so the yield of mono glycerol benzoate will be declining, as it shows when using other catalysts "H₂SO₄, CH₃SO₃H". besides an environmental perspective

It was found that the best acid catalyst is an Amberlyst-15, because it was an acidic heterogeneous catalyst figure(4): and it was easy to be used again after activated.

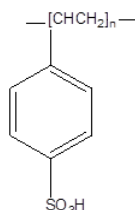


Figure 4. Catalytic formula (**amberlyst-15**).

The specific impacts of different molar amount of catalyst on the yield did not notice when increases the amount of catalyst table(3).

Table 3. effect of different amount of catalyst (amberlyst-15).

Entry	amount of catalyst %mol	% yield
1	-----	traces
2	5	69
3	10	69
4	20	69
5	40	69

So we conclude that when using large amounts of heterogeneous catalyst "Amberlyst-15" do not affect to the preparation α -MGB, so from an economic perspective preferred using the least possible result. After that the esterification reaction between glycerol and benzoic acid with different solvents had been studied as shown table (4).

Table 4. effect of different solvents.

Entry	solvent	% yield
1	toluene	45
2	dimethylsulfoxid	38
3	Excess of glycerol	69

Different solvents used to studying effects to the yield reaction. However, toluene was bad to the yield reaction, because it had a boiling point as a temperature reaction, and dimethylsulfoxid was bad to remove it after reaction. Beside using the excess of glycerol was the best choice (glycerol played a reactant and solvent simultaneously) because glycerol was an ecofriendly to use a solvent and it was a reactant in this reaction. So the effect of the different molar ratios (glycerol:benzoic acid) to the yield reaction had also been studied.

Table 5. effect of different molar ratios to the esterification yield.

Entry	Molar ratio (glycerol:acid)	% yield
1	4:1	55
2	6:1	61
3	8:1	69
4	10:1	66
5	14:1	65

The table (5) shown that the best molar ratio between glycerol and benzoic acid in entry:3.

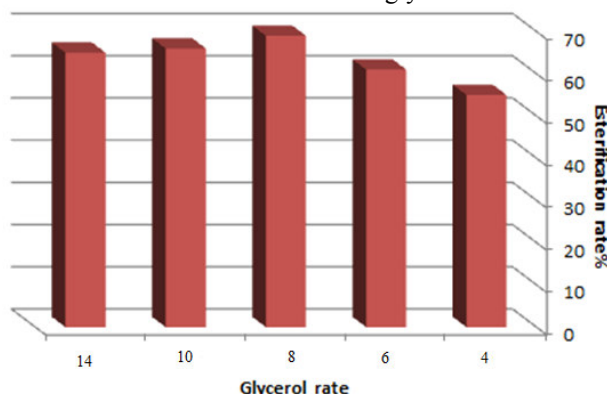


Figure 5. effect of different solvents to produce (α -MBG).

We found that when using a molar ratio (8:1) of glycerol to benzoic acid, the yield reaction was the best, it was noted that when using low percentage of glycerol, the yield reaction has decreased. The reaction was a secondary products was formed "Di and Tri glycereds", besides when using a very surplus of glycerol was also

the yield reaction decrease, because that a few amount of product (α -MBG) was formed, there fore we conclude depending previous studies that the best molar ratio of the esterification reaction was (8:1) (glycerol:acid) and when using an Amberlyst-15 (5%mol), time reaction 6 hours, yield was the formation of reaction product (α -MBG) about 69%.

FT-IR Results: α -MBG were further confirmed by IR spectroscopy, as shown in figure (6). Figure (6) shows the α -MBG spectra, an obvious absorption peak at 1713cm^{-1} belonged to carbonyl group. Also, there were two absorption peaks 1278 and 1118cm^{-1} , which were the characteristic absorption bands of the C-O-C stretching in α -MBG. The characteristic features near 2943 and 1453cm^{-1} belonged to methylene groups. At 3406cm^{-1} aweak absorption band of $-\text{OH}$ was also observed, there were several characteristic absorption bands of the benzene group near 1594 and 3069cm^{-1} , so the α -MBG was successfully synthesized.

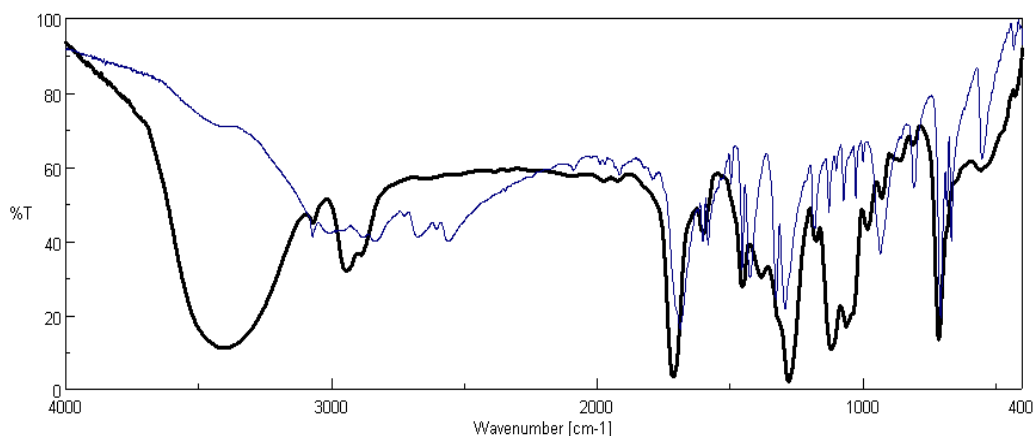


Figure 6. IR spectrum of benzoic acid (blue spectrum) and α -MBG (black spectrum).

$^1\text{H-NMR}$ Results: α -MBG were further confirmed by $^1\text{H-NMR}$ spectroscopy, as shown in figure (5).the spectrum corresponds to α -MBG in figure (7), the characteristic peaks around 3.5 and 4.5ppm belonged to α - and β -H, respectively in the glycerol. The peaks around 6 and 7ppm represented benzene group, and the other displacement of hydrogen was similar to that shown in figure (7). therefore, α -MBG was successfully synthesized.

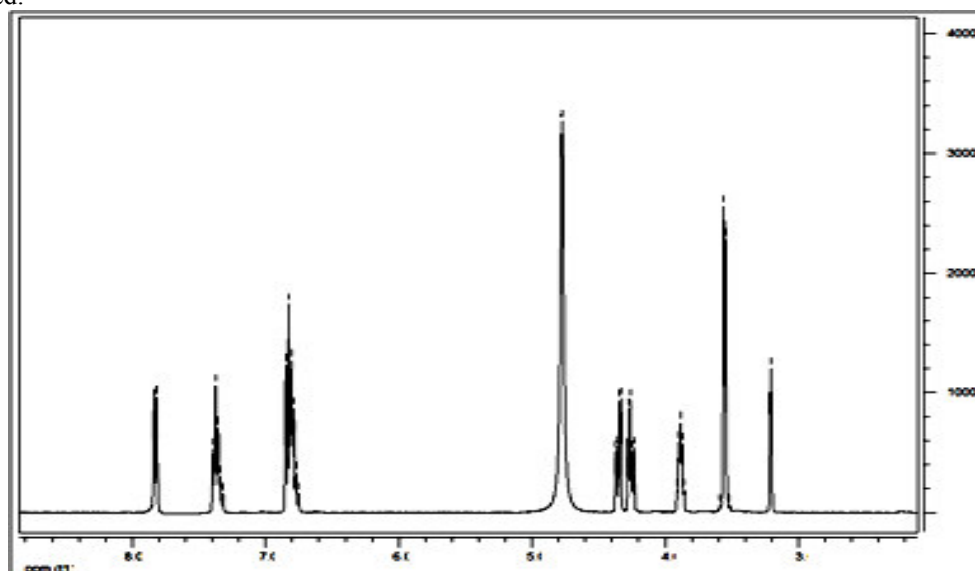
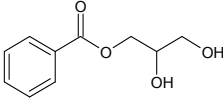
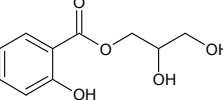
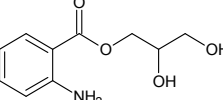


Figure 7. $^1\text{H-NMR}$ spectrum of α -MBG in CD_3OD .

Finally, when applying the previous conditions to prepare α -MBG on the reaction of preparing some mono aromatic esters of glycerol, we had synthesized successfully some of the mono aromatic esters which had used in the many applications in industry and food as shown in table(6).

Table 6. different products to the esterification.

Entry	product	amount of catalyst (5%mol)	amount of acid	temperature	Time reaction	% yield
1		0.026gr:0.000123mol	0.3gr:0.00246mol	110C°	6 hour	69
2		0.023gr:0.000108mol	0.3gr:0.00217mol	110C°	6 hour	68
4		0.0234gr:0.00011mol	0.3gr:0.0022mol	110C°	6 hour	66

5. Carecterization

product entry (1) gave yeild(69%), R_f 0.58 (ethyl acetate-n.hexane) (75:25).

IR spectrum (v, cm^{-1}): 1715 (C=O), 1600, 1585, 1500 (C=C), 3100-3600 (-OH).

1H -NMR (δ , ppm): 4.0 (2H, d, $J=4Hz$, CH_2OH , C-3), 4.13-4.49 (1H, m, $CHOH$, C-2), 4.64 (2H, d, $J=4Hz$, CH_2O-CO- , C-1), 6.1 (2H, s, OH), 7.20 (3H, d, $J=8Hz$, Ar).

^{13}C -NMR (δ , ppm): C-1 66.0 ($A\delta=+3.16$), C-2 70.0 (-2.2), C-3 63.0 (+0.16), aromatic. C (132.8, 129.9, 128. 1), -COO- (166.7).

product entry (2) gave yeild(68%), R_f 0.38 (ethyl acetate-n.hexane) (75:25).

IR spectrum (v, cm^{-1}): 1674 (C=O), 1299 (C-O), 3100-3600 (-OH).

1H -NMR (δ , ppm): 3.51-3.58 (m, 2H, $J^2=17.2$, $J^2=11.6$, C-1), 3.85-3.91 (m, 2H, $J^3=7.6$, $J^3=7.6$, $J^3=5.6$, C-2), 4.23-4.37 (qd, 2H, $J^2=39.2$, $J^3=11.4$, $J^4=6$, $J^4=6.4$, C-3), 7.73-7.83 (dd, 1H, $J^3=11.3$, $J^4=8$, Ar, C-4), 6.75-6.84 (m, 2H, $J^3=14.6$, $J^3=8.4$, $J^3=6.8$, $J^4=7.2$, Ar, C-5,7), 7.32-7.39 (m, 1H, $J^3=10.4$, $J^4=7.2$, Ar, C-6), 7.13 (S, 3H, OH).

^{13}C -NMR (δ , ppm): C-1 70.0 ($A\delta = +4.78$), C-2 65.8 (-9.12), C-3 63.4 (-1.82), aromatic. C (112.0, 161.6, 117.7, 136.1, 119.3, 129.9), -COO- (170.1).

product entry (3) gave yeild (66%), R_f 0.32 (ethyl acetate-n.hexane) (75:25).

IR spectrum (v, cm^{-1}): 1687 (C=O), 3000-3340 (-OH), 3371, 3464 (-NH₂), 1245 (C-O).

1H -NMR (δ , ppm): 3.49-3.58 (m, 2H, $J^2=9.84$, $J^2=10$, $J^3=8.6$, $J^3=6$, C-1), 3.82-3.87 (m, 2H, $J^3=8.2$, $J^3=8.2$, $J^3=6$, C-2), 4.13-4.26 (qd, 2H, $J^2=35.6$, $J^3=11.4$, $J^4=6$, $J^4=6.4$, C-3), 7.74-7.77 (dd, 1H, $J^3=8.2$, $J^4=1.2$, Ar, C-4), 6.44-6.48 (dd, 1H, $J^3=7.6$, $J^3=0.8$, Ar, C-5), 7.11-7.51 (dd, 1H, $J^3=7.8$, $J^3=1.2$, Ar, C-6), 6.62-6.64 (d, 1H, $J^3=8.4$, Ar, C-7), 7.13 (S, 2H, OH), 6.47 (S, 2H, NH₂).

^{13}C -NMR (δ , ppm): C-1 69.9 ($A\delta = +4.7$), C-2 64.8 (-10.1), C-3 62.8 (+2.4); aromatic. C (110.0, 151.3, 116.3, 133.7, 115.1, 130.8), -COO- (168.0).

6. Conclusion

In summary, the condition of organic esterification was successfully studied by synthesis of α -MGB. When the molar ratio of glycerol to benzoic acid was (8:1), amberlyst-15 worked as a green catalyst, excess of glycerol used as a solvent "eight times", using dean stark-trap figure(2), for the removal of water, and the reaction time was around 6 hours, the esterification yielded about (70%). Under these conditions most of products table(6) was successfully synthesized, With little difference in the yields of interaction. The results proved that the optimum conditions to obtain high selective compounds with high yields (mono esters glycerol) by studying the affect of different catalysts and solvents have been investigated.

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