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Esterification of Benzoic Acid with Propylene Glycol in an Experimental Bubble Column Reactor - Part II

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Abstract: Column type reactors play a particularly important role in the chemical industry and technology, being successfully used in various industrial processes. The esterification process, which takes place in a column type reactor, is very complex due to the intergrowth of two types of factors: those which usually influence the esterification process as a whole and those which are specific for the selected process. The inner stirring may be achieved by different mechanical means or by bubbling a gas. This study presents some aspects regarding the esterification, in different working conditions, of benzoic acid with 1,2-propylene glycol in an experimental bubble gas column reactor, establishing the optimal reaction conditions that result in the highest energetic efficiency.

Keywords: bubble column, reactor, esterification, energetic efficiency

1. Introduction

Due to the complexity of the reaction products of the esterification processes, the studies regarding the correlation between the molecular structure and the functional properties still exhibits interest.

Esters of aromatic acids were obtained using different catalysts. The catalytic system of SO_4^{2-}/Ti_3AlC_2 led to excellent results for the esterification reaction of benzoic acid with ethanol. This novel catalyst of SO_4^{2-} over Ti_3AlC_2 ceramic was prepared by an impregnation method. The resulting catalyst exhibited high catalytic activity and selectivity for the esterification of benzoic acid to ethyl benzoate. In this study, 80.4 % conversion of benzoic acid and > 99% selectivity for ethyl benzoate was obtained at 34 h reaction time and 120 ^{0}C [1].

The acidity index is most the frequently used parameter for monitoring the esterification reactions. In such a study, the conversion was calculated based on the acidity index of the esterification reaction of free fatty acids (FFA) in sunflower oil, coconut oil and concentrated FFA, with ethanol, methanol and ethanol 96 %, using homogeneous acid catalysts to produce biodiesel. The kinetic parameters were estimated with a simplified model, and then used to predict the reaction behavior. Reactions other than the reversible esterification were considered to explain the behavior that this system displays [2].

The direct esterification reaction of pure oleic acid with different alcohols: anhydrous ethanol, azeotropicethanol, 1-propanol, 2-propanol and n-butanol and catalysts such as solid resins, zeolite and enzymes, is another example in which the esterification reaction performance was monitored by the acidity index [3].

TG and DSC techniques are frequently used for characterization of various esters. The thermal stability and decomposition mechanism functions of 10 nitric esters including nitroglycerine, pentaerythritol tetranitrate, trimethylolethane trinitrate, dipentaerythritol hexanitrate, trimethylolpropane trinitrate, erythritol tetranitrate, xylitol pentanitrate, sorbitol hexanitrate, mannitol hexanitrate and nitroisobutylglycerol trinitrate were determined by means of non-isothermal TG and DSC techniques. The decomposition kinetics was described in terms of the Johnson-Mehl-Avrami and Sestak-Berggrenmodels. Two types of kinetic behavior were observed and most nitrate esters followed typical decomposition kinetics close to the first order reaction. Certain materials showed complex behavior caused by overlapping of more mechanisms/processes, which were represented either by simultaneous evaporation and decomposition or by different decomposition mechanisms originating from varying morphology and structure of the samples [4].

The reports about esterification processes performed in bubble gas column reactors, regarding the calculation of the energetic efficiency, are still inconsistent.

In the present study the total heat transfer coefficient has been determined for an esterification process performed in a bubble column type reactor, previously described by our group [5]. The effects of the catalyst concentration on the consumed energy and on the total heat transfer coefficient were analyzed.

2. Experimental

The esterification reactions were performed in a laboratory glass column reactor provided with heating jacket. The inner stirring was produced by bubbling an inert gas through a nozzle at the bottom of the column.

The raw materials were 1,2-propylene glycol >99.5% provided by Oltchim S.A., Romania, and benzoic acid 100% provided by Riedel de Haen AG, Seelze Hannover. The catalyst was p-toluenesulfonic acid monohydrate was provided by MerkKGaA, Germany.

The raw materials were introduced into the column, were they have been heated at the reaction temperature.

Samples were taken during the reaction process and the conversion was calculated based on the acidity index. At the end of the process, the reaction mass was cooled to the ambient temperature.

An ion trap mass spectrometer ITQ 1100 coupled with Gas Chromatograph Trace 1310 (Thermo Scientific) was used for qualitative analysis of benzoic acid and propylene glycol esters. MS parameters were set as following: transfer line temperature at 310 °C, source temperature at 170 °C and scan range between 50 and 700 amu. The reaction product structure was established based on the *m/z* ratio.

Separation was achieved on a capillary column 30 m x 0.25 mm ID, 0.25 µm (TG - 5MS, Thermo Scientific) the injection port temperature was set at 300°C. An automated sample delivery system (TriPlus RSH) with a split ratio of 1/30 for 1.5 min followed by splitless mode was used for sample injection. The oven program was set as following: 100 °C (held 1 min) raised to 300°C (held 3 min) with 10 °C/min.

The thermogravimetric (TG)/derivate thermogravimetric (DTG) and the differential scanning calorimetry (DSC) analyses were performed with a NETZSCH STA 449F1 STA449F1A-0220-M. Approximately 3÷7 mg of sample was heated in an Al_2O_3 crucible, with 5°C/min. in nitrogen atmosphere, in the temperature range of 20° ÷ 600°C.

3. Results and Discussions

In this study some aspects regarding the esterification process of the benzoic acid and 1,2-propylene glycol in an experimental bubble column type reactor are presented and discussed.

The reaction scheme and the possible reaction products are presented in Scheme 1.

The results previously reported by our group [6], were completed in this report by optimization of the reaction in terms of catalyst amount and pressure of the inlet gas, as well as the comprehensive characterization of the reaction products by mass-spectrometry and thermal analysis.

The catalyst concentration was studied at 6 levels, in the range of 0.5-3 %.The reactions were performed at 120 ^{0}C, as described in the experimental section.

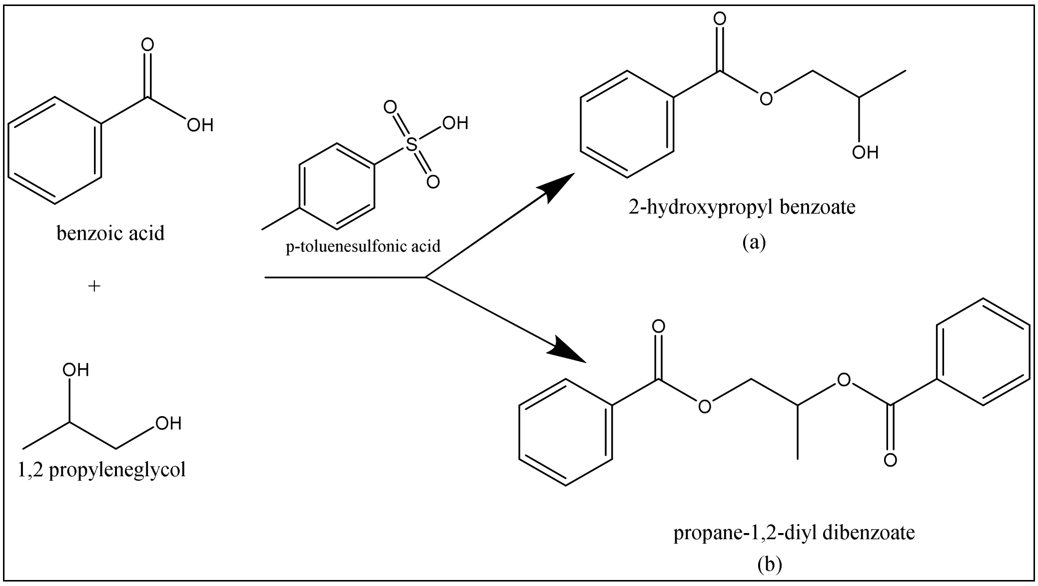
The results presented in Figure 1 as dependence of the conversion on time, indicate an increase of the conversion with the catalyst concentration up to 2 %. The increase of the catalyst concentration at higher values did not produce positive effect.

The best fit, based on the R^2 (R-squared) values obtained from regression equations for each curve, are higher than 0.98 (Table 1), excepting the experiment when 1.5 % of biocatalyst was used.

TABLE 1. Regression equations and R-squared values for the dependence of the total conversion of benzoic acid on time, at different catalyst concentrations and 120 ^{0}C

Catalyst concentrations %	Regression equations	R^2
0.5	$y = -0.1625x^2 + 7.3052x – 1.2012$	$R^2 = 0.9884$
1	$y = -0.3839x^2 + 11.077x + 2.3869$	$R^2 = 0.9891$
1.5	$y = -0.4241x^2 + 11.316x + 10.947$	$R^2 = 0.9338$
2	$y = -1.2069x^2 + 19.941x + 1.232$	$R^2 = 0.9972$
2.5	$y = -1.2494x^2 + 20.143x + 2.5023$	$R^2 = 0.9915$
3	$y = -1.1625x^2 + 19.546x + 0.7179$	$R^2 = 0.9986$

As we previously mentioned [10], the esterification process in the bubble column reactor occurs in three steps as concerns the energy balance: the first step (I) is the heating of the raw materials from the ambient temperature to the reaction temperature, the second step (II) is the chemical reaction and the third step (III) is the cooling the reaction mass from the reaction temperature to the ambient temperature.



Scheme 1. The esterification scheme of benzoic acid and 1,2 propylene glycol catalyzed by p-toluenesulfonic acid, yielding the mono-ester (a) as major compound and the di-ester (b)

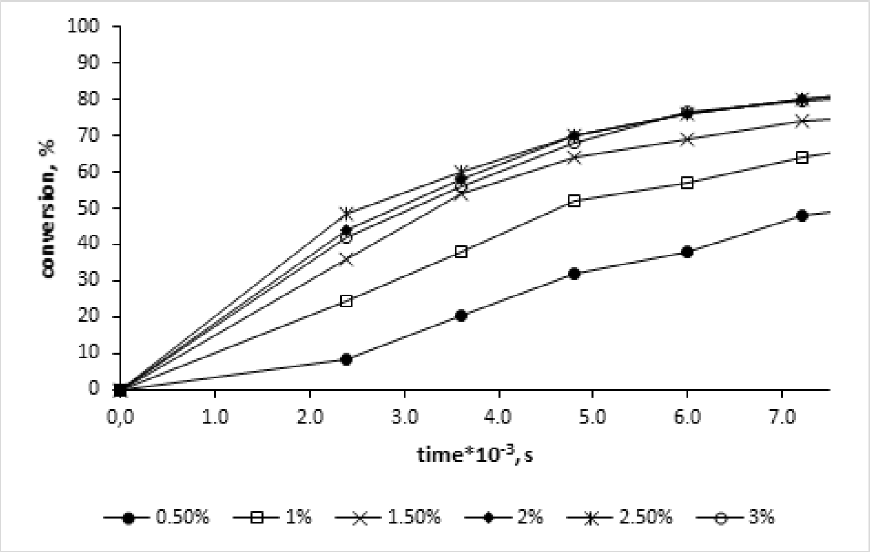
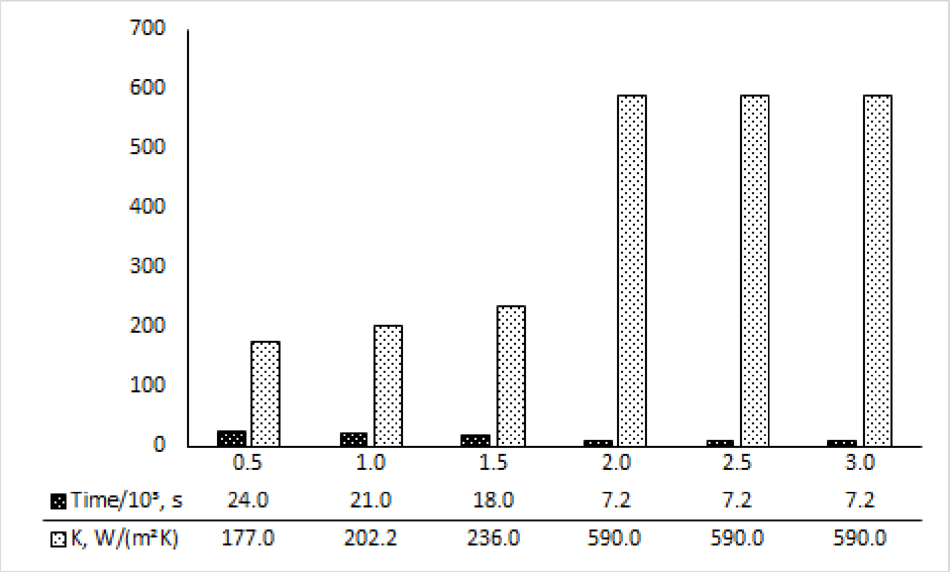


Figure 1. The dependence of the total conversion of benzoic acid on time at 120^{0}C, with different catalyst concentrations



	0.5	1.0	1.5	2.0	2.5	3.0
▩ Time/10^3, s	24.0	21.0	18.0	7.2	7.2	7.2
⚀ K, W/(m^{2}K)	177.0	202.2	236.0	590.0	590.0	590.0

Figure 2. Heat balance calculations for the esterification process performed at different catalyst concentrations and 120 ^{o}C

Using general energy balance equations [7, 8], the total heat transfer coefficient K was calculated for the processes performed with different catalyst concentrations, as it can be seen in Fig.2. When the catalyst concentration was increased up to 2% the total heat transfer coefficient K value increased significantly, while at higher catalyst concentration important differences were not observed. Thus, the heat balance calculations confirmed that the catalyst concentration should not exceed 2 %.

Characterization of the reaction product

The reaction products were purified by vacuum distillation, then were analyzed by GS-MS, TG/DTG and DSC/DDSC.

The GC-MS spectra revealed the presence of two reaction products. The mono-ester (compound (a) in Scheme 1) was the major compound, separated in the analysis conditions at 13.33 min retention time. The ion chromatogram of this product is presented in Fig. 3, confirming the presumed structure by the m/z values 51.3, 77.3, 105.1, 135.1, and 181.1. The di-esterproduct (compound (b) in Scheme 1) was eluted in the GC chromatogram at the retention time of 24.04 min (Fig. 4) and the structure was confirmed by the m/z values 77, 105, 163, and 207.

The thermal stability of the reaction products was established based on TG/DTG and DSC/DDSC analysis. The resulted curves are presented in Fig.5 and Fig. 6.

All the TG/DTG curves were collected in nitrogen atmosphere and the mass changes were recorded as follows: up to 100 $^{\circ}$C only 2.10 % loss of mass was measured, a major decomposition process starts at 189.8 $^{\circ}$C with 58.66 % loss of mass accompanied by an endothermic process (Fig. 6), a higher decomposition rate at 250 $^{\circ}$C with 96.43 % and a total mass loss at 350 $^{\circ}$C.

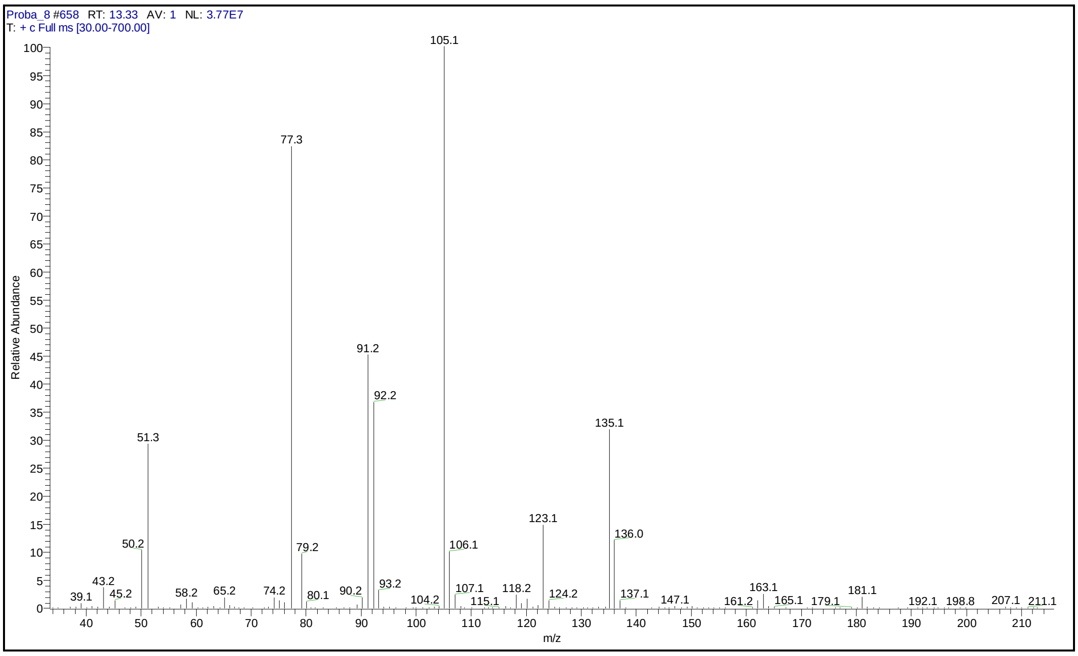


Figure 3. The mass spectrum of the 2-hydroxypropyl benzoatemonoester,corresponding to the peak separated on the GC column at 13.33 min retention time

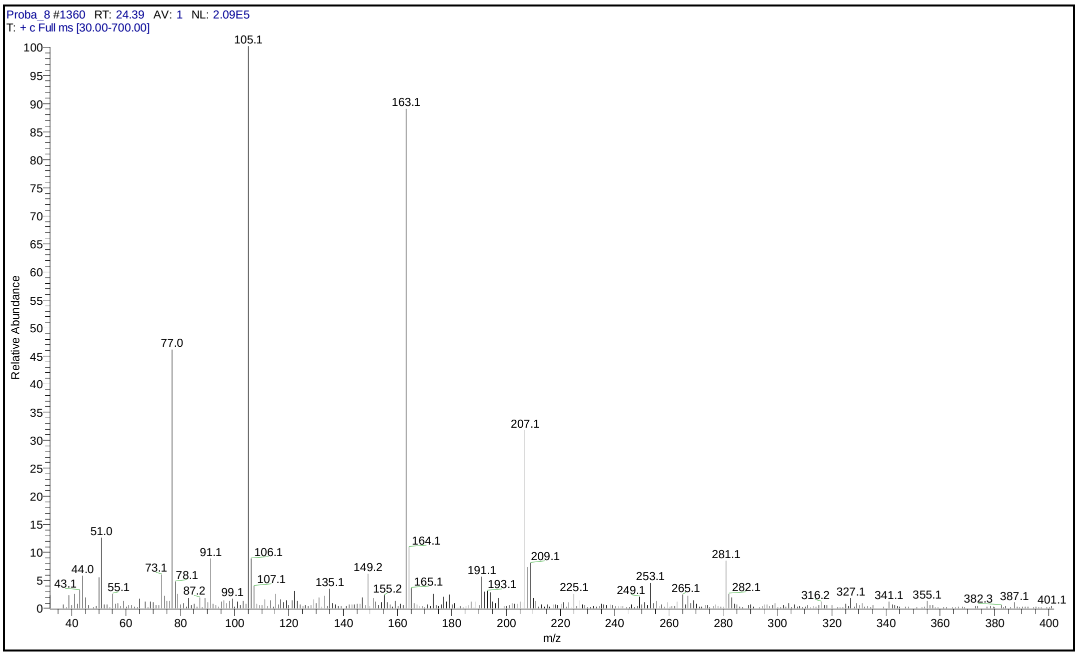


Figure 4. The mass spectrum of the propane-1,2-diyl dibenzoatediester,corresponding to the peak separated on the GC column at 24.39 min retention time

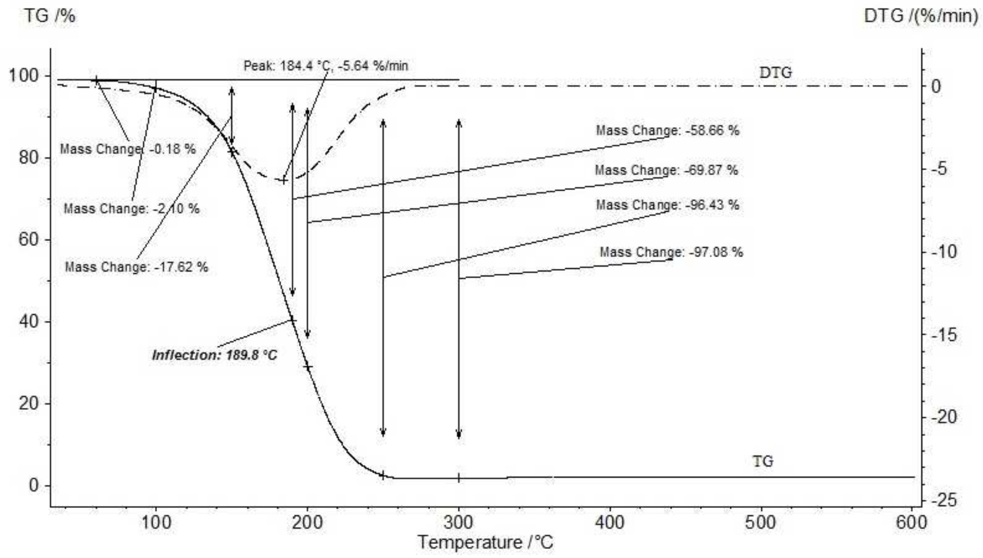


Figure 5. TG/DTG curves in nitrogen atmosphere

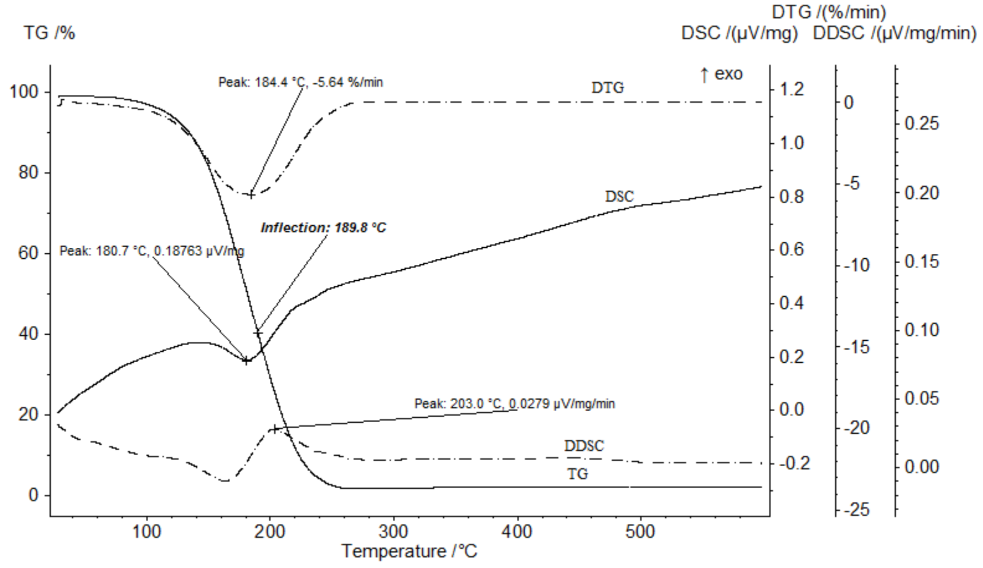


Figure 6. TG/DTG and DSC/DDSC curves in nitrogen atmosphere

4. Conclusions

The synthesis of benzoic acid and propylene glycol esters was performed by using different concentrations of the catalyst and the optimum value was determined to be 2 %, in terms of process efficiency. The reaction products were purified by distillation and characterized by different analytical techniques, including GC-MS, TG/DTG and DSC/DDSC methods.

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