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Esterification of Benzoic Acid with Propylene Glycol in an Experimental Bubble Column Reactor – Part I

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Abstract: The column type reactors play a particularly important role in the chemical industry and technology, because they are successfully used in most of the industrial processes. In this work, the esterification of benzoic acid with propylene glycol into a bubble gas reactor was investigated. The esterification process in a column type reactor is dependent on several factors such as: temperature, pressure, the diameters of the inlet nozzle, the inner stirring. The effect of these paramenters on the conversion and energetic efficiency were invetigated. The formation of the reaction product was proved based on the acidity index value, IR and ^{1}H-NMR spectra.

Keywords: bubble column reactor, esterification process, energetic efficiency

1. Introduction

The column type reactors have an important role in the chemical industry and technology, because up to now they were successfully used in several industrial processes that involve transfer processes, such as polymerization [1], hydrogenation, oxidation reactions. The potential advantages related to the sustainability of the column reactors include reduced energy requirments, flexibility of the raw materials. The inner stirring may be achieved by different mechanical means or by bubbling a gas.

Although the hydrodynamics and its effects on the performance of the columns have been reported in several works [2-5], the heat transfer characteristics were investigated only by few authors [6-16]. The results of an esterification process performed in a bubble gas column reactor, 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. Effects of the temperature and of the nozzle diameter of the inlet gas on the energy consumption and on the total heat transfer coefficient were analyzed.

2. Experimental

The esterification process was carried out in a laboratory glass column reactor provided with heating jacket. The inner stirring was produced by bubbling argon through a nozzle at the bottom of the column.

The materials used were 1,2-propylene glycol >99.5% provided by Oltchim S.A. (Romania) and benzoic acid 100% provided by Riedel de Haen AG (Germany)) using benzoic acid : 1,2-propylene glycol molar ratio of 1:2. The catalyst (0.2% in relation to the raw materials) was *p*-toluenesulfonic acid monohydrate provided by Merck KGaA (Germany).

The raw materials were solubilized into an usual reactor, heated at the reaction temperature, and then poured into the column reactor. Samples were provided during the reaction process in order to determine the conversion at previously setted times. At the end of the process, the reaction mass was cooled to the ambient temperature.
The conversion was calculated based on the acidity index of the reaction mixture.

The reaction product was purified and then was analised by FT-IR and ^{1}H-NMR. Fourier Transform Infrared (FT-IR) spectra of the samples were obtained in attenuated total reflectance (ATR) mode on a Bruker Vertex 70 (Bruker Daltonik GmbH, Germany) spectrometer equipped with a Platinum ATR, Bruker Diamond Type A225/Q. Spectra were collected in the range 4000-400 cm^{-1} with a resolution of 4 cm^{-1} and with 40 scans/min.

^{1}H-RMN şi ^{13}C-RMN spectra were registrated with Bruker de 200 MHz Spectrometer. $CDCl_3$ (99,8% atom. %D) + 0,05% TMS (v/v) or DMSO-d_6 (99,9% atom. %D).

3. Results and Discussion

3.1. The influence of temperature

This paper presents the preliminary results obtained for the esterification of benzoic acid by 1,2-propylene glycol in an experimental bubble column type reactor. The process was firstly performed in similar conditions previously used in the batch reactor [17], at 138^{o}C under reflux, but this temperature was too high and the reaction mass adhered on the reactor walls. Therefore, the temperature in the bubble column was reduced to 120^{o}C. The results are presented in Fig. 1 as conversion function of time, while the regression equations are shown in Table 1. The obtained data reveal that the acidity index decreased in a shorter period of time in the bubble column (approximately in 2 hours) compared to the batch reactor

(approximately in 6 hours [17]). Only a slight increase (less than 10%) of the conversion at higher temperature was observed during the esterification process and at the end of the reactions the conversions were similar (Fig.1), so there is no need for rising up the reaction temperature over 120^{o}C.

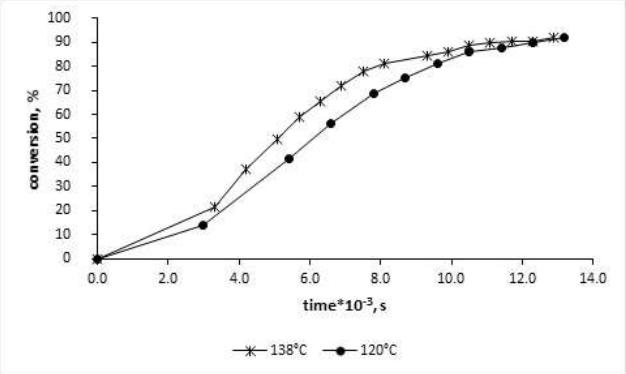

Figure 1. The dependence of the conversion on time when the process is performed at 138^{0}C and at 120^{0}C, respectively

TABLE 1. The regression equations for the dependence of the conversion on time when the process was performed at 138^{0}C and at 120^{0}C, respectively

Temperature, ^{o}C	Regression equations	R^2
120	$y = -0,2562x^2 + 11,163x - 6,4431$	$R^2 = 0,9747$
138	$y = -0,5085x^2 + 14,439x - 7,6154$	$R^2 = 0,9678$

3.2. The influence of the diameters of the inlet nozzle

The diameters of the inlet nozzle of the bubbling gas influence the inner stirring in the reactor. The results are presented in Fig. 2 as dependence of conversion on time. The regression equations for these curves (Table 2) indicate that the performance of the column is not affected by the increase of the diameter over 0.6 mm. The highest conversion value achieved in this case exceeded 90%. Based on these results, the nozzle diameter used in the following experiments was 0.6 mm.

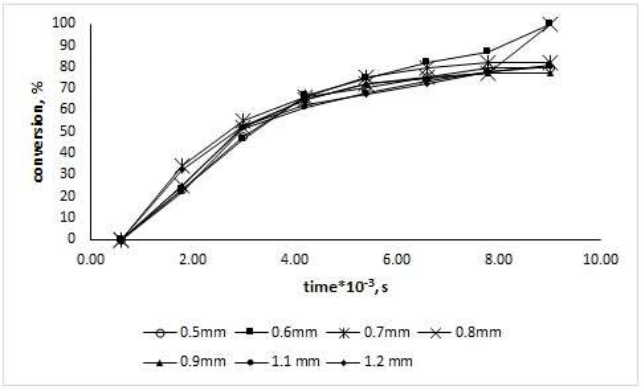

Figure 2. The dependence of the conversion on time at different diameters of the inlet nozzle

TABLE 2. Regression equations for the dependence of the conversion on time at different diameters of the inlet nozzle

Diameters of the inlet nozzle, mm	Regression equations	R^2
0.5	$y = -1,6164x^2 + 24,71x - 13,904$	$R^2 = 0,992$
0.6	$y = -1,1598x^2 + 22,381x - 11,903$	$R^2 = 0,990$
0.7	$y = -1,7339x^2 + 25,52x - 10,218$	$R^2 = 0,987$
0.8	$y = -1,101x^2 + 20,865x - 8,0733$	$R^2 = 0,953$
0.9	$y = -1,7517x^2 + 25,538x - 13,464$	$R^2 = 0,989$
1.1	$y = -1,467x^2 + 23,186x - 12,181$	$R^2 = 0,985$
1.2	$y = -1,4638x^2 + 22,483x - 7,5301$	$R^2 = 0,974$

3.3. Effect of the inlet gas pressure

Another tested parameter was the pressure of the inlet gas, which is proportional with the gas flow and also influences the inner stirring in the column reactor. For this reason, 3 levels (12.16 Pa, 36.5 Pa and 121.6 Pa) of presure were investigated. The dependence of the conversion on time at different pressures of the inlet gas is presented in Fig. 3. The regression equations for these curves are showed in Table 3. The results indicate a direct dependence of the conversion with the presure. The highest coversion value (about 90%) was obtained at 121.6 Pa. However, a 10 times increase of the value of the inlet gas presure did not lead to an increase of the conversion higher than 10%. It results that a higher flow of the inlet gas does not increase significantly the conversion, at least in the investigated range.

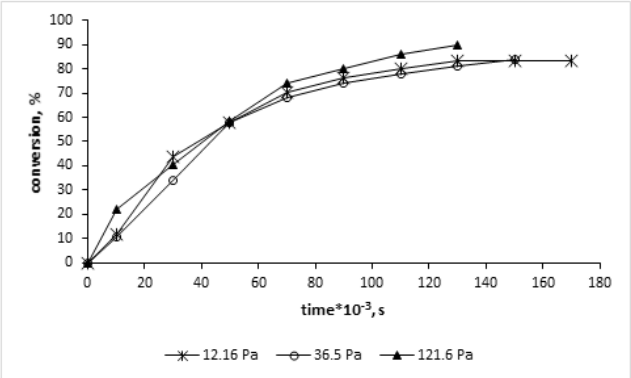

Figure 3. The dependence of the conversion on time when the process is performed at different pressures of the inlet gas

TABLE 3. Regression equations for the dependence of the conversion on time when the process was performed at different pressures of the inlet gas

Pressure, Pa	Regression equations	R^2
12.16	$y = -0,0048x^2 + 1,2646x + 3,2347$	$R^2 = 0,984$
36.50	$y = -0,0051x^2 + 1,3035x + 0,1156$	$R^2 = 0,991$
121.6	$y = -0,0055x^2 + 1,3634x + 4,1644$	$R^2 = 0,993$

3.4. The effect of the reaction paramenters on the total heat transfer coefficient

The esterification process in the bubble column reactor occurs in three steps, as regards 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. Using the general energy balance equations [18, 19] the total heat transfer coefficient K was calculated for the processes performed in different conditions and is presented in Fig. 4 to 6.

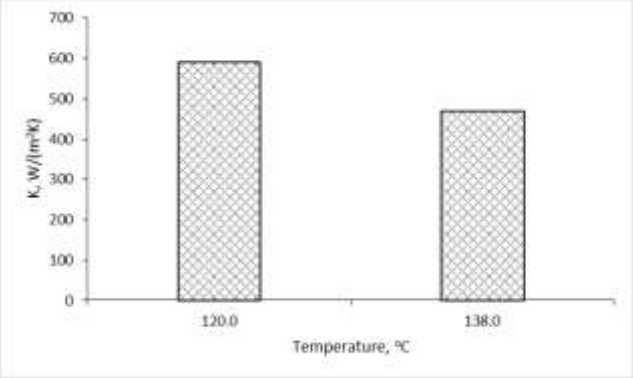

Figure 4. The total heat transfer coefficient K calculated for the processes performed at 120^0C and 138^0C, respectively

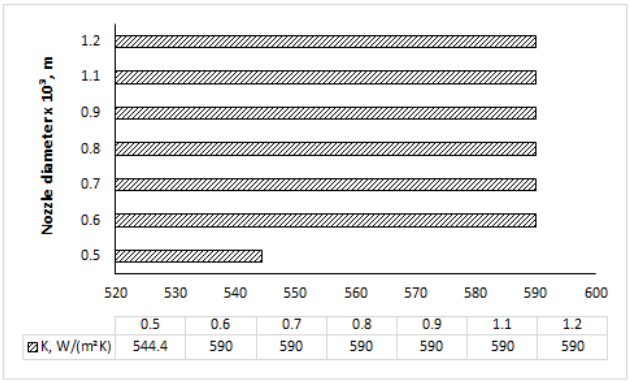

Figure 5. Heat balance calculations for the esterification process performed at different inlet nozzle diameters

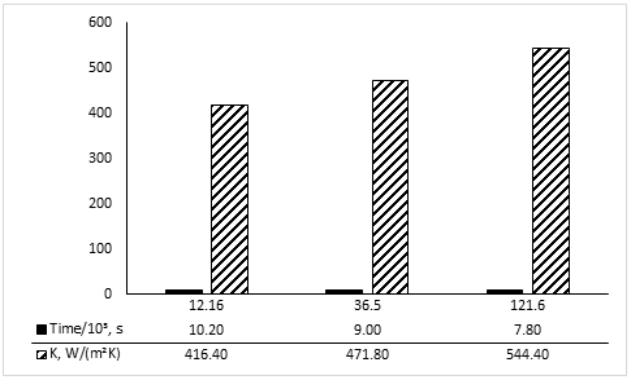

Figure 6. Heat balance calculations for the esterification process performed at different pressures of the inlet gas

It can be observed that using the pressure of the inlet gas of 121.6 Pa the reaction time needed to achive the maximal conversion was shorter and the total heat transfer coefficient K reached the highest value.

3.5. Purification and characterization of the product

The reaction products were purified by distillation, and then characterized by different techniques. They appear as relatively viscous homogeneous liquids, having acidity index (SR ISO 2114:2001) - 4 mg KOH/g, and refractive index n^{20} (STAS 145-67) in the range 1.5160-1.5168.

The FT-IR spectrum (Fig. 7) indicates the main characteristic absorbtion bands of the ester (cm^{-1}): 2979.68 for $\nu_{(CH)}$ corresponding to C-H aromatic; 1714.52 assigned to $\nu_{(C=O)}$ for ester group; 1267.09 $\nu_{(C=O)}$ester with an aromatic ring; 1026.01 assigned to monosubstitute of benzene nucleus; 707.79 $\nu(Sk_{ar})$ for the benzene ring.

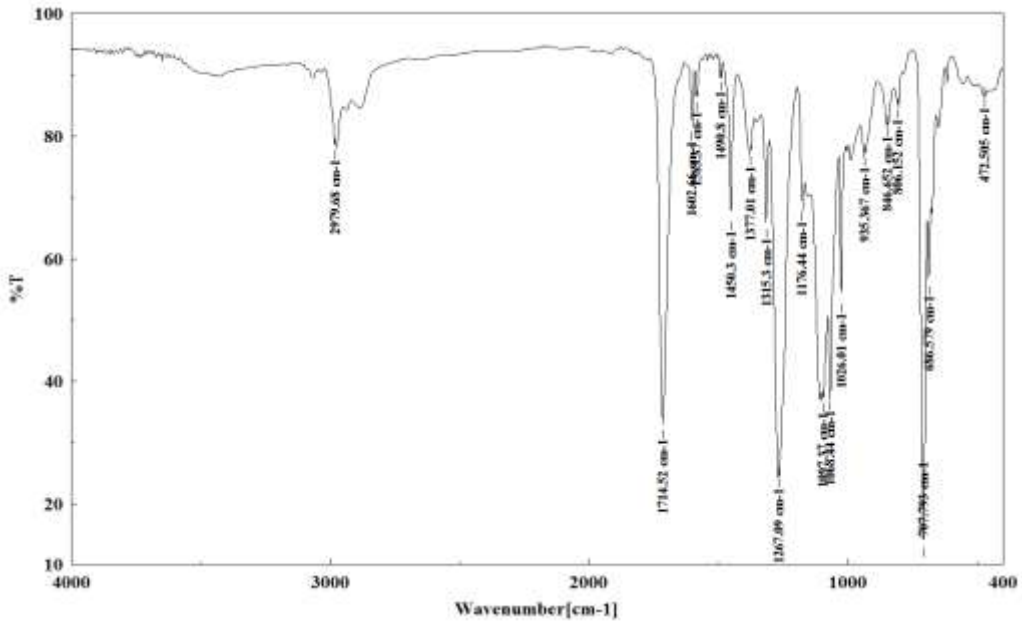

Figure 7. Infrared (FT-IR) spectrum of the esterification product

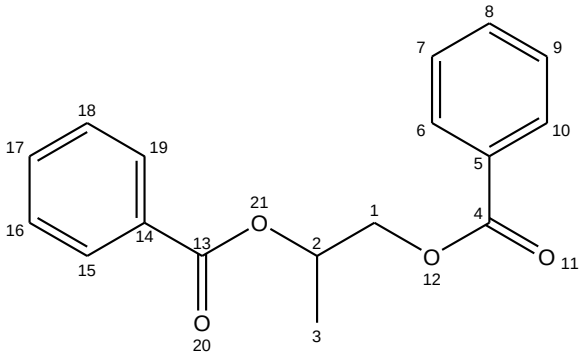

Figure 8. Chemical structure of the main reaction product

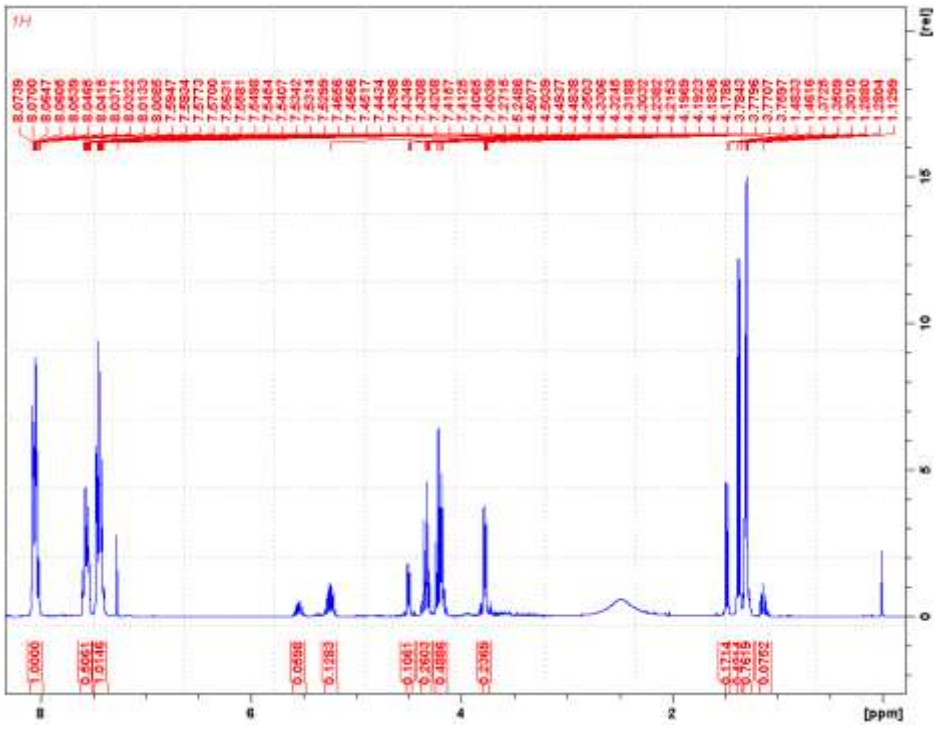

Figure 9. ^{1}H-RMN spectrum of the esterification product

The formation of the 1,2-propanediol dibenzoate (Fig. 8) as main reaction product was confirmed by the ^{1}H-NMR spectrum (Fig. 9) firstly based on the absence of the proton corresponding to aliphatic OH group in the range of ~2 ppm. The signals corresponding to the protons of the CH_2 group from the reaction product (protons corresponding to the C atoms no 1) in the region 4.5-4.2 ppm (multiplets) demonstrate the formation of the ester (the protons are shielded compared to the protons of the raw material). The presence of the aromatic ring is confirmed by the multiplets from 8.07-8.0 ppm (protons corresponding to the C atoms no. 6, 10, 15, 19) and 7.59-7.20 ppm (protons corresponding to the C atoms no. 7, 8, 9, 16, 17, 18). Moreover, the absence of the proton from the carboxyl group of benzoic acid (~11 ppm) confirms the efficiency of the purification step.

All these data confirm the formation of the targeted ester product.

4. Conclusions

The esterification process was performed in a bubble column reactor at the temperature previously set in the batch reactor (138^{o}C), and then at lower temperature (120^{o}C), with very good results regarding the total heat transfer coefficient K and the energy consumption.

Working with different inlet nozzle diameters, the total heat transfer coefficient was not influenced at diameters over 0.6 mm.

When the esterification process was performed at different pressures of the inlet gas, using the pressure of 121.6 Pa the reaction time was shorter and the total heat transfer coefficient K reached the maximum value.

The structure of the purified products was demonstrated by acidity index, refractive index, FT-IR spectrofotometry and ^{1}H-RMN spectrometry.

ACKNOWLEDGEMENTS

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