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THE STUDY OF LACTIC ACID ESTERIFICATION WITH METHANOL THROUGH REACTIVE DISTILLATION

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The reactive distillation is an inovative process representing a solution for the process intensification with the posibility of increasing the reactions selectivity with a preference to obtain certain products. In this work, it was studied the influence of the following factors on the esterification of the lactic acid with methanol through reactive distillation: the molar ratio of the reactants and the number of a theoretical plates performed by the column equipped with Raschig rings. The results showed that by using a column with packing equivalent with 4.9 theoretical plates, the yield of methyl lactate increases with the growth of the molar ratio methanol:lactic acid, up to 78.7% for a molar ratio of 3:1. Also, the yield increases with the increasing of theoretical plates number. A linear mathematical model was proposed correlating the methyl lactate yield with the reactants molar ratio and the number of theoretical plates. The model has a pretty good precision (correlation coefficient r^2=0.9754) and validated by analysis of variance (ANOVA); yields predicted with this model are close to the experimental ones.

Keywords: Reactive distillation; esterification; lactic acid; methanol; modeling

1. Introduction

The processes of diffusional separation including the distillation are huge energy consumers. In 2009, the European sector of Industrial Chemistry was responsible for almost 19% of the total electrical power consumption [1]. Almost 40% of the total energy consumption in this sector was used for the separation processes, especially for distillation [2].

The challenge of the globalization includes a continuous process of inovation, for improving the performances in chemical industry, as part of a sustainable economy. This can be made in two ways: by thermal integration and by process intensification [3].

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One of the most promising examples of concomitant intensification and thermal integration consists in the integrated reaction- separation process which combines a chemical reaction and a diffusional separation in a single apparatus. Compared to the traditional sequences of separation, the so called „integrated reactive separation process” allows a higher conversion of reactants and better selectivity and also savings of energy, water and solvent, all leading to mitigation of investment and operating costs [4]. In the last years, the integrated reactive separation processes gained a considerable interest for the scientific community and the industrial sector [5].

One important industrial application of the integrated reactive separation process is the reactive distillation, consisting in both reaction and distillation performed simultaneously in the same equipment. Harmsen [6] refered to reactive distillation as a very important process of industrial intensification, asserting that the application of the reactive distillation technology can lead to 80% reduction of the energy costs compared to the traditional sequences of separation-reaction. The first patents for the application of reactive distillation to esterification in homogeneous catalysis date from 1920’s [7,8]. The first process of heterogeneous catalysis was patented for the production of methyl-tert-butyl-ether, MTBE, in 1978 by the Chemical Research & Licensing Company [9]. The big number of recent works and patents clearly ilustrate that even though the reactive distillation seems to be a well known unit operation, it remains a research subject in attention of the science and industry specialists. The reactive distillation drew attention especially for reactions at chemical equilibrium in liquid phase which, in a traditional way, need an excess of one reactant.

The processes of reactive distillation can be homogeneously or heterogeneously catalysed. In general, the process of reactive distillation in homogeneous catalysis is more flexible because the concentration of the catalysts and the rate of reaction can vary in a large range. Moreover, the fresh catalyst can be continuously added in the column without being necessary to stop the process. But the homogeneous catalysis shows the disadvantage of an additional separation step for the recovering the catalyst. This step can be avoided in the heterogeneously catalysed reactive distillation process through special internal devices which secure the catalyst in the column [10].

The esterification is a reversible reaction in which a carboxylic acid reacts with an alcohol forming an ester. Lactic acid (2-hydroxy propionic acid, $CH_3CH(OH)COOH$) is a bifunctional compound with a hydroxyl group and an acid function which is reactive in numerous chemical conversions for obtaining commercial products. The lactic acid esters are biodegradable and can be used as synthetic additives in food industry, in farmaceutical, cosmetics and cleansers industry [11] or solvents with high boiling points for polishes, points, rubbers, oils, pigments, etc. [12]. The esterification of carboxyl group is also used for the separation of lactic acid from the solutions resulted in the lactic fermentation [13]. Lactic acid is difficult to separate from the reaction mass though distillation because it degradates at quite low temperatures [14]. As an adequate recovering method, it is recomended to be converted first into an ester and then separated by hydrolysis [15,16].

Methyl, ethyl, isopropyl and n-butyl esters of the lactic acid are usually obtained by esterification with the adequate alchool [17-20]. The esterification reactions are limited by the chemical equilibrium, and the reaction mass consisting in quaternary mixtures needs to be separated for obtaining pure lactates. The separation can be performed simultaneously with the reaction, in hybrid processes, in order to shift the chemical equilibrium towards esters formation. Some research works were made to selectively eliminate one or more species from the reaction mixture by pervaporation [21,22].

In this work, the reaction of methanol with lactic acid is performed in a reactive distillation process, in order to shift the chemical equilibrium by removing the alcohol excess during the reaction. The aim is to improve the methyl lactate yield. Also, a mathematical model will be proposed, to quantify the effect of the main factors identified as affecting the methyl lactate yield.

2. Experimental

2.1 Materials

In this experiment, reagents were supplied as follows: the lactic acid with a purity of 90% from Merck Company, absolute methanol from Carlo Erba Company, sulphuric acid 95% from Chemical Company and sodium hydroxide from Lachner.

2.2 Apparatus and procedure

The esterifications have been performed in a process of reactive distillation in batch, in a laboratory column made of glass with an internal diameter of 20 mm equipped with Raschig glass rings $\Phi 6$, in a packing bed with various heights between 100 and 400 mm. In a two-neck glass flask with a capacity of 500 mL, electrically heated, the reagents and catalyst are fill in from the beginning of experiment (Fig. 1). The distillation column is thermo-insulated.

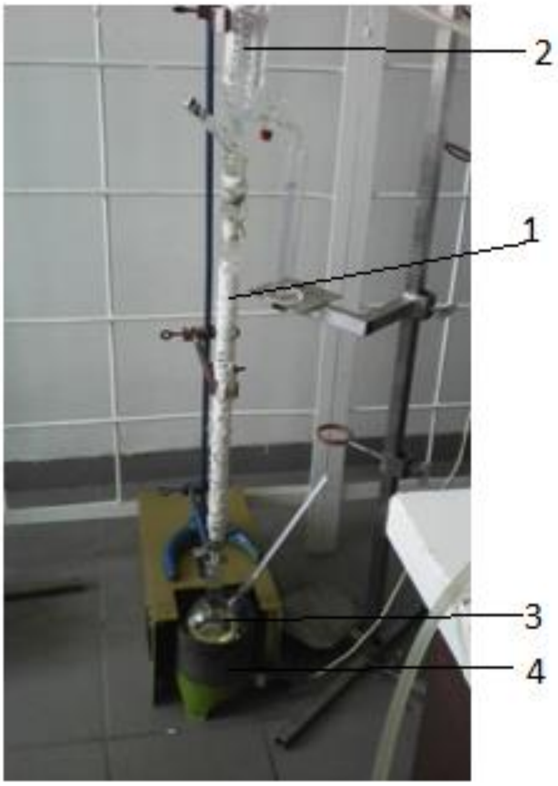

Fig.1. The experimental setting: 1- glass column with Raschig rings paking; 2- condenser; 3- bottom flask; 4- electrical heater

The esterification process was performed at different molar ratios alcohol:lactic acid (1:1, 2:1 and 3:1). The temperature in bottom has not out run 135 ^oC at any moment, to avoid thermal degradation of the products. The rectification was driven in batch with two overhead fractions and a bottom fraction. The first overhead fraction is pure methanol and the second fraction is a mixture of methanol, water and traces of ester; at the bottom of the plant was obtained methyl lactate. The temperature at the top of the column was between 64-66 ^oC during the distillation of methanol and rose up to 96 ^oC towards the end. A constant reflux was provided and the process ran enough time (40-60 minutes) to reach the maximum conversion. The reaction time was induced by trespassing of maximum temperature in the bottom as a result of complete methanol and water separation.

2.3. Analysis methods

2.3.1 Determining conversion

The lactic acid conversion during a test was determined by measuring the concentration of the acid in the reaction mass. It was analyzed through volumetric titration of samples with 1 N sodium hydroxide solution and phenolphtaleine as an indicator. The samples were collected every 15 minutes. In the mass reaction, apart from lactic acid there is sulphuric acid as a catalyst. The sodium hydroxide used of for H_2SO_4 neutralization is constant during the reaction so the conversion of the lactic acid can be calculated by difference, with Eq. (1):

$$C\% = \frac{n_0 - n_1}{n_0} * 100 \qquad (1)$$

where n_0 is the volume of 1 N NaOH solution used for titration at the initial moment of reaction (mL); n_1 - the volume of 1 N NaOH solution used for titration at the moment t (mL).

2.3.2 Determining methanol concentration

Methanol concentration in methanol-water mixtures was determined by refractive index, with the refractometer model ATAGO 3T. A calibration curve for binary mixture methanol–water was built. This curve is presented in Fig. 2. The curve served to identify the moment when methanol distillation ended and water distillation started and also served at determining the number of theoretical plates corresponding to different heights of packing bed.

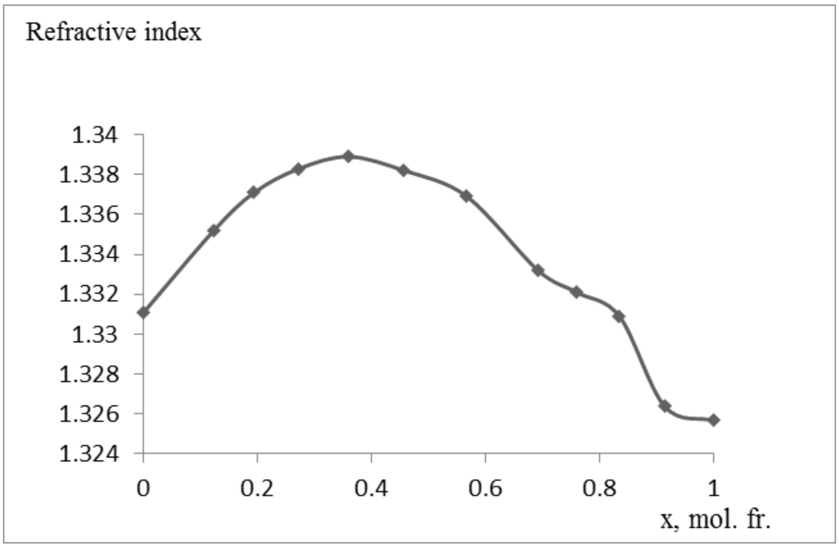

Fig. 2. Calibration curve to determine methanol concentration (as molar fraction) for methanol-water binary mixture

2.3.4 Determining the number of theoretical plates

The number of theoretical plates and the equivalent height of a theoretical plate for the laboratory column with package were calculated for the binary mixture methanol-water with a known concentration in the bottom and the measured concentration in distillate, at total reflux. The minimum number of theoretical plates was calculated with Fenske equation (Eq. (2)), and double-checked with Mc Cabe-Thiele graphical construction [24]. The results were very close, with a difference of max. 0.1 between the values determined by the two methods.

$$N_{min} = \frac{\log\frac{x_d}{1-x_d} - \log\frac{x_b}{1-x_b}}{\log \propto_m} \qquad (2)$$

where x_d is the methanol concentration in the overhead fraction (mole fraction); x_b - the methanol concentration in the bottom (mole fraction); α_m - the average relative volatility of methanol towards water.

The determinations were made on the same laboratory column used afterwards for esterification exepriments; the height of the packing bed varied from 400 mm to 200 mm and, finally, to 100 mm. The height of the equivalent theoretical plate (HETP) was calculated by dividing the height of the packing bed by the minimum number of theoretical plates (N_{min}). Results are presented in Table 1.

Table 1

Heights equivalent of a theoretical plate for the packing bed in the column

Sample	H_P [mm]	$t_{overhead}$ [°C]	t_{bottom} [°C]	N_{min}	H_{ETP} [mm]
1	400	64	88	4.9	81.6
2	200	65	88	2.4	83.3
3	100	66	88	1.8	55.5

2.3.5. Design of the experiment and data analysis

Experimental variables influencing the process are: the molar ratio methanol / lactic acid and the number of theoretical plates in the rectification zone. Considering 3 levels for each variable, a factorial experiment 3^2 was designed. The 3 levels for the molar ratio were: 1:1, 2:1 and 3:1; the 3 values for the number of theoretical plates were 4.9, 2.4 and 1.8 corresponding to the packing bed height of 400 mm, 200 mm and 100 mm, respectively. Microsoft Excel was applied for data analysis, regression, and statistics.

3. Results and discussions

3.1 Effect of molar ratio

Prior to the experiment designed for mathematical modeling, the effect of residence time on conversion was investigated. Tests were conducted in batch mode, at total reflux ratio. Molar ratio of methanol to lactic acid varied from 1 to 3 and the catalyst (H_2SO_4) had a concentration of 3wt% which is considered to be optimal [25]. The results of this investigation are shown in Fig. 3.

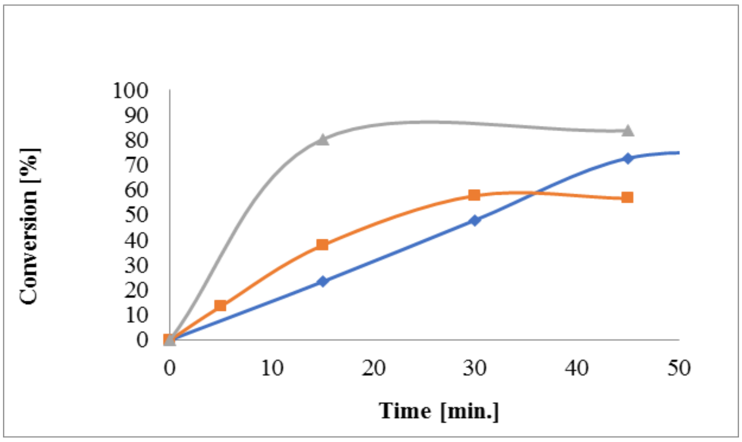

Fig. 3. The effect of methanol:lactic acid molar ratio on the esterification conversion. Legend: ■- conversion at molar ratio 1/1; ♦- conversion at molar ratio 2/1, ▲- conversion at molar ratio 3/1

From Fig. 3, one can observe that the conversion of lactic acid increases with the methanol:lactic acid molar ratio. Also, it can be observed that a maximum conversion is reached after maximum 40 minute from the start of reaction. It must comply with this residence time during the reactive distillation experiment, in order to obtain best yields of methanol lactate. The conversion of lactic acid increases from 57% to 80% when methanol:acid lactic molar ratio increases from 1:1 to 3:1.

3.2 The investigation of factors affecting the reactive distillation process

In order to determine the factors influence on the methyl lactate sythesis in a reactive distillation process, an experimental matrix with 2 factors and 3 variation levels was built, so it was necessary to perform a number of 3^2 tests. Tests were performed at three heights of the Raschig packing bed (400 mm, 200 mm and 100 mm) and at three initial molar ratios methanol/ lactic acid: 1:1, 2:1

and 3:1. The catalyst concentration (H_2SO_4) was 3wt% in the reaction mass in all the tests.

The methyl lactate yield was calculated based on lactic acid (LA) consumed in reaction, with Eq. (3):

$$\eta = \frac{mole\ of\ LA\ transformed\ in\ methyl\ lactate}{mole\ of\ LA\ in\ the\ feed} * 100 \qquad (3)$$

The results of tests are presented in Table 2.

Table 2

The methyl lactate yield depending on number of theoretical plates and initial molar ratio of reactants

No.	Height of the package [mm]	N_{min}	Molar ratio methanol: lactic acid	Methyl lactate yield [%]
1	400	4.9	3	76.7
2	400	4.9	2	70.1
3	400	4.9	1	57.0
4	200	2.4	3	75.3
5	200	2.4	2	63
6	200	2.4	1	48.7
7	100	1.8	3	72
8	100	1.8	2	60.8
9	100	1.8	1	50.0

The results show that for the same number of the theoretical plates, the yield of methyl lactate increases by increasing the molar ratio methanol:lactic acid. Also, it can be observed that increasing the number of theoretical plates at the same reactants molar ratio leads to increasing of the product yield. The highest yield was obtained at an initial molar ratio of 3:1 methanol:lactic acid, by using a 400 mm height of packing bed.

3.3 Mathematical model

A mathematical model is proposed for the prediction of methyl lactate (ML) yield as a function of reactants molar ratio and the number of theoretical plates (Eq. (4)):

$$y = A_0 + A_1 x_1 + A_2 x_2 \qquad (4)$$

where y is the yield of ML, %; x_1 - number of theoretical plates; x_2 - methanol:lactic acid molar ratio; A_0 , A_1, A_2 – coefficients.

The coefficients of the mathematical model were found by regression with the facilities provided by the Microsoft Excel. The following model resulted (Eq. (5)):

$$y = 34.22 + 2.36\, x_1 + 11.23\, x_2 \tag{5}$$

The regression statistics revealed the correlation coefficient: r^2=0.9754, the medium standard deviation of 1.88, and the following results of ANOVA test shown in Table 3.

Table 3

The results of ANOVA test

	Coeffi-cients	**Standard error**	**P-value**
Intercept	34.21907	2.184832	4.29E-06
x1	2.35635	0.467761	0.002363
x2	11.23333	0.769084	6.46E-06

As seen in Table 3, P-value is lower than 0.05 for every coefficient, so the model (Eq. 5)) has a statistical significance, at confidence level 95%.

The residuals output is presented in Table 4.

Table 4

The residuals output

y predicted	**y experimental**	**Residuals**
76.7	79.5	-2.8
70.1	68.2	1.9
57.9	57.0	0.9
75.3	73.6	1.7
63	62.3	0.7
48.7	51.1	-2.4
72	72.2	-0.2
60.8	60.9	-0.1
50	49.7	0.3

From the residuals analysis, one can see that the yields are predicted with acceptable tolerance by the model (Eq. (5)).

4. Conclusions

The esterification of the lactic acid with methanol in a process of reactive distillation was studied at the bench scale. The influence of the factors was quantified, in a factorial experiment. The tests have been performed by varying two factors at three levels. One factor was the molar ratio methanol: lactic acid which varied from 1:1 to 3:1 and the the other one was the number of theoretical plates which varied from 1.9 to 4.9 mm.

The results show that the yield in methyl lactate increases by increasing the methanol:lactic acid molar ratio and the height of packing bed. The highest yield (76.7%) was obtained at methanol:lactic acid molar ratio of 3:1 using a column with the height of packing of 400 mm, corresponding to 4.9 theoretical plates.

A mathematical model of linear type was proposed. Its coeficients were detemined by regression. The model has a good precision with a correlation coefficient r^2=0.9754 and a medium standard deviation of 1.88. The yield values predicted with this model are close to the experimental values, with a maximum residual of 2.8%. The model is valid in the following conditions: methanol:lactic acid molar ratio between 1:1 and 3:1 and a number of theoretical plates in range of 1.9 - 4.9, and serves to the prediction of methyl lactate yield in the reactive distillation process.

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