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Optimal conditions for depolymerisation of oligomers of butyl lactate in different types of reactors

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ABSTRACT

The process of producing L-Lactide from butyl lactate consists of two stages. In present work optimal conditions for the second stage-depolymerisation of oligomers of butyl lactate were found. Depolymerisation experiments were performed in three types of reactors, the influence of temperature and residual pressure on the yield of by-product - meso-lactide and on productivity of reactor was determined. According to the obtained results, the best type of reactor as well as the optimal conditions for the depolymerisation stage was chosen.

Keywords - Batch reactor, Depolymerisation, Lactide, Optimal conditions, Rotary film evaporator.

I. INTRODUCTION

In recent years, the problem of environmental contamination has become increasingly acute. Non-degradable petro-derived materials are produced worldwide on a large scale, introduced to the ecosystem and, being resistant to microbial attack, accumulated there as industrial waste. One of the possible solutions to this problem could be the development of methods of obtaining and industrial production of biodegradable polymers. Monomers for such materials are generally derived from renewable resources such as corn, potatoes and etc. Considering possible depletion of world oil and coal resources, development of methods of producing biodegradable polymers looks even more attractive.

One of the most promising and accessible biodegradable polymer is PLA (polylactic acid). PLA has such properties as good mechanical strength, thermal stability, transparency and after being used it can be easily degraded by microorganisms in environment to carbon dioxide and water. All these facts make PLA a good substitution to petroleum-based materials in the spheres of packaging, agriculture and medicine [1].

PLA is generally produced by ring-opening polymerization of cyclic dimer of lactic acid-lactide [2]. The process of L-lactide production consists of several stages: oligomerisation of lactic acid or its derivatives, depolymerization of obtained oligomer and further purification of L-lactide. In present work we used butyl ester of lactic acid-butyl lactate as a raw material for L-lactate. Using esters of lactic acid instead of lactic acid prolongs the duration of the whole process of production of L-lactide, but the stage of its purification, which is of extreme importance, simplifies greatly[3-7].

In our previous study the general approach for obtaining L-lactide was formulated and the catalyst was chosen [8]. The aim of this work was to find optimal conditions for the second stage of the whole process-depolymerisation of oligomers of butyl lactate. Depolymerisation experiments were performed in three types of reactors, the influence of temperature and residual pressure on the yield of by-product - meso-lactide and on productivity of reactor was determined. According to the obtained results, the best type of reactor as well as the optimal conditions for the depolymerisation stage was chosen.

II. EXPERIMENTAL PART

2.1. Materials

L-n-Butyl lactate was purchased from Alfa Aesar. According to the manufacturer, it contained of 97% of n-Butyl L-lactate and 3% of butanol. Catalyst tin chloride (IV) was also obtained from Alfa Aesar.

2.2. Oligomerisation

Oligomer of butyl lactate was obtained in batch reactor with continuous removal of butanol vapors and under gradual increase of temperature from 180 ^{o}C to 200 ^{o}C and under constant barbotage of N_2 through reaction mass. Concentration of catalyst in all experiments was 2.5×10^{-3} g-atom per kg of initial ester-butyl lactate. Average molecular mass of obtained oligomers was determined by GPC.

2.3. Depolymerisation

2.3.1. Batch reactor

Obtained oligomers (with average molecular mass 820-1000 g/mol) with catalyst remained after oligomerisation stage was placed into reactor with surface area of 0,025 m^2. Temperature was controlled with the help of electric range and thermometer. Process was carried out under vacuum 5 mm Hg. Lactide vapours from reaction zone were

condensed in condenser and collected in receiver. Concentration of lactide was measured by GLC.

2.3.2. Periodic process in rotary film evaporator

Obtained oligomers (MW = 820) containing catalyst in the reaction mass after oligomerisation stage were charged in round-bottom flask, which was connected to rotor-film evaporator. Flask was placed into an oil bath with oil temperature 220°C and process was carried out under vacuum 1-3 mm Hg and constant rotating at a speed of 60 RPM. The heated surface of the flask was 0.025 m^2. Formed in the film, lactide vapors left reaction zone of flask, condensed in condenser and were collected in receiver. Process was carried out till the completion of lactide formation in flask reactor.

***2*.3.3. Continuous process in rotary film evaporator**

Obtained oligomers (MW = 820) containing catalyst in the reaction mass after oligomerisation stage were charged into the heated dropping funnel. Dropping funnel was equipped with jacket filled with oil with temperature 120 °C. Then oligomer went to the film reactor where the film on the walls of reactor was created with the help of roller mixer rotating at a speed of 400 RPM. Feed rate of oligomer was controlled by valve. Process was carried out under vacuum 20 mm Hg. Resulting lactide evaporated from the film, condensed in the condenser and was collected in the receiver. Unreacted oligomer left in film melted and was collected in another receiver.

2.4. Measurements

Concentrations of all components were measured by GLC. "Kristall-2000m" chromatograph was used, which was equipped with flame ionization detector. The capillary column was 0.25 mm OD × 50 m long with liquid phase SE-54. Nitrogen was used as the carrier gas 2 mL/min. The columns temperature was held constant at 80 °C for 1 min, ramped at 20 °C /min to 200 °C, and held at 200 °C for 5 min. The injector temperature was maintained at 200 °C and the detector temperature was held at 210 °C.

Gel permeation chromatography (GPC) was carried out on liquid chromatography equipped with differential refractometer, binary pump, injector with a loop volume 50 mL and columns placed in an air thermostat. Columns Shodex 802.5 and Shodex 804 were calibrated by polystyrene standards. Chloroform was used as an eluent. Gauge dependence was approximated by polynomial of the third degree in the range 800-2000.

III. RESULTS AND DISCUSSIONS

In this study choice of optimal conditions and reactor was based on three main parameters of the process- the yield of L-lactide and by-product - meso-lactide, productivity of reactor, which were defined by Eqs (1)-(3):

$$W_L = m_L*100/m_{theor} \quad (1)$$

where W_L- percentage yield of lactide, m_L-actual mass of lactide, m_{theor}-theoretical mass of lactide;

$$m_{theor} = m_{ol} * n/2 * MM_L) / MM_{ol} \quad (2)$$

where m_{ol}-mass of oligomer taken for reaction, MM_L-molecular mass of lactide, MM_{ol}-molecular mass of oligomer, n – number of monomers in oligomer chain;

$$G = m_L /\tau*S \quad (3)$$

where G-productivity, τ -time of experiment , s, S-heated surface, m^2.

3.1. Temperature

Influence of temperature on the main parameters of the process was tested for three types of reactors. Range of temperatures from 210 °C to 230 °C was examined. Residual pressure was 5 mm Hg for batch reactor and periodic rotary film evaporator and 20 mm Hg for continuous rotary film evaporator. The results of experiments are listed in Fig.1-2.

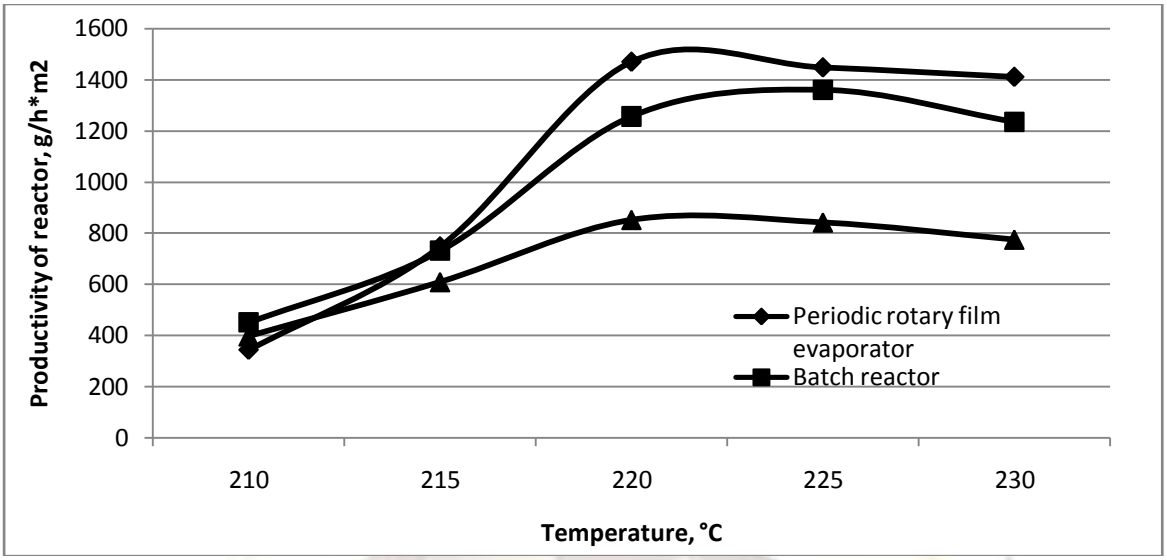

Fig.1. Productivity of reactor as a function of temperature.

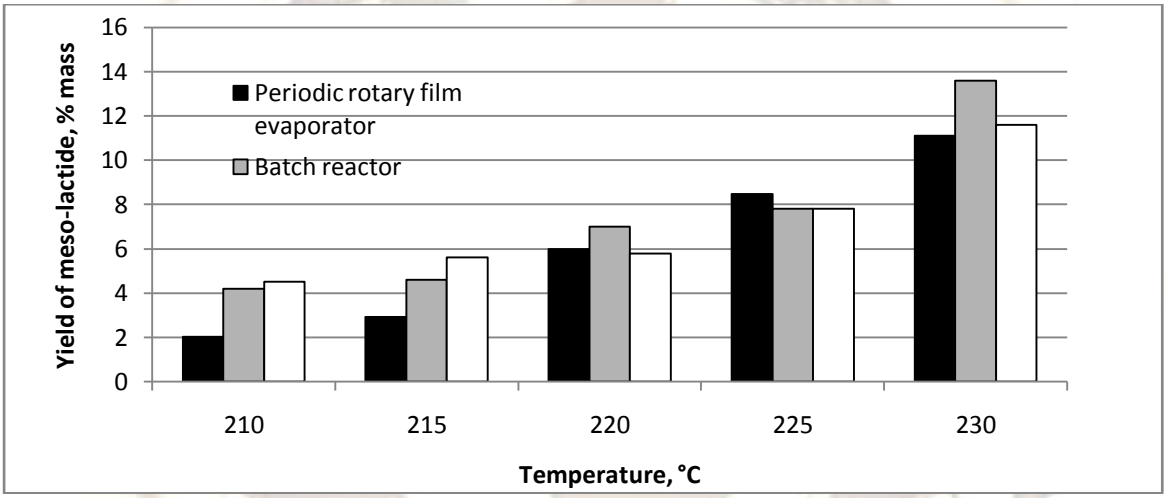

Fig.2. Yield of meso-lactide at different temperatures for three types of reactors.

According to the obtained results, optimal temperatures for every type of reactor are correspondently: 220 ^{o}C for periodic rotary film evaporator, 225-for batch reactor and 230-for continuous film evaporator. Best yield of L-lactide was obtained at periodic rotary film evaporator. It`s clear from the data that under the same residual pressure, productivity of batch reactor is lower than the one of rotary film evaporator. Such advantage of rotary film evaporator could be explained by the fact that the real heated surface in this type of reactor is much higher due to the fast rate of rotation and as oligomer is distributed on the surface as a film the process of removal of product from reaction zone simplifies greatly. Moreover the highest yields of by-product were also obtained in batch reactor.

3.2. Residual pressure.

Process was carried out according to described procedures (2.3.1.-2.3.3.) at optimal temperatures chosen for every type of reactor and under different residual pressure.

Results of experiments are presented in Fig.3-4.

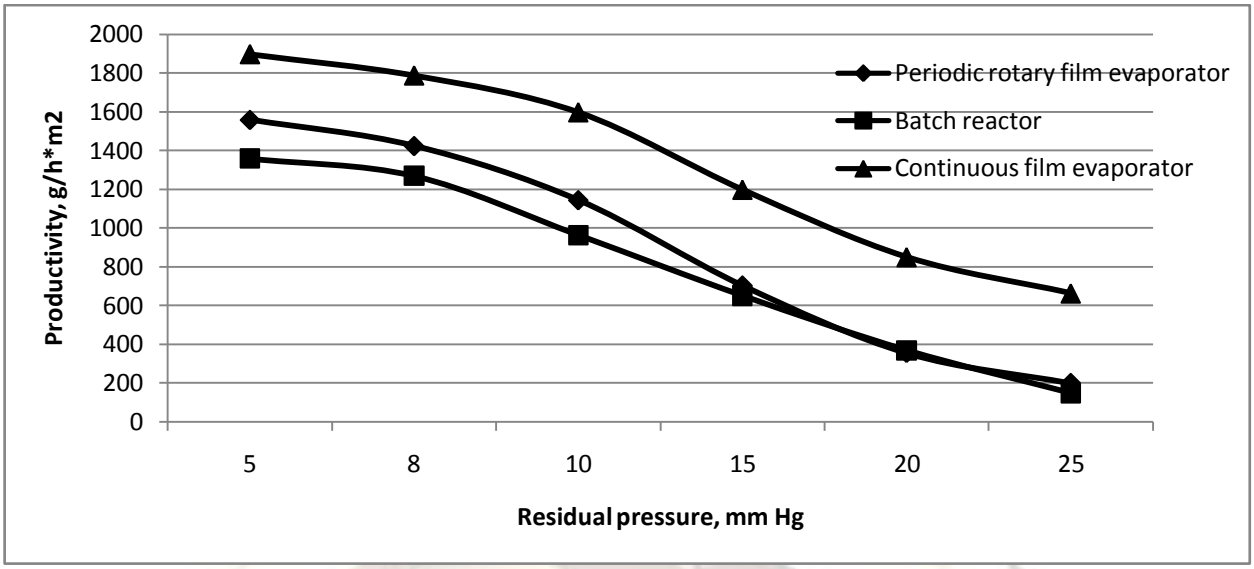

Fig.3. Productivity of reactor as a function of residual pressure.

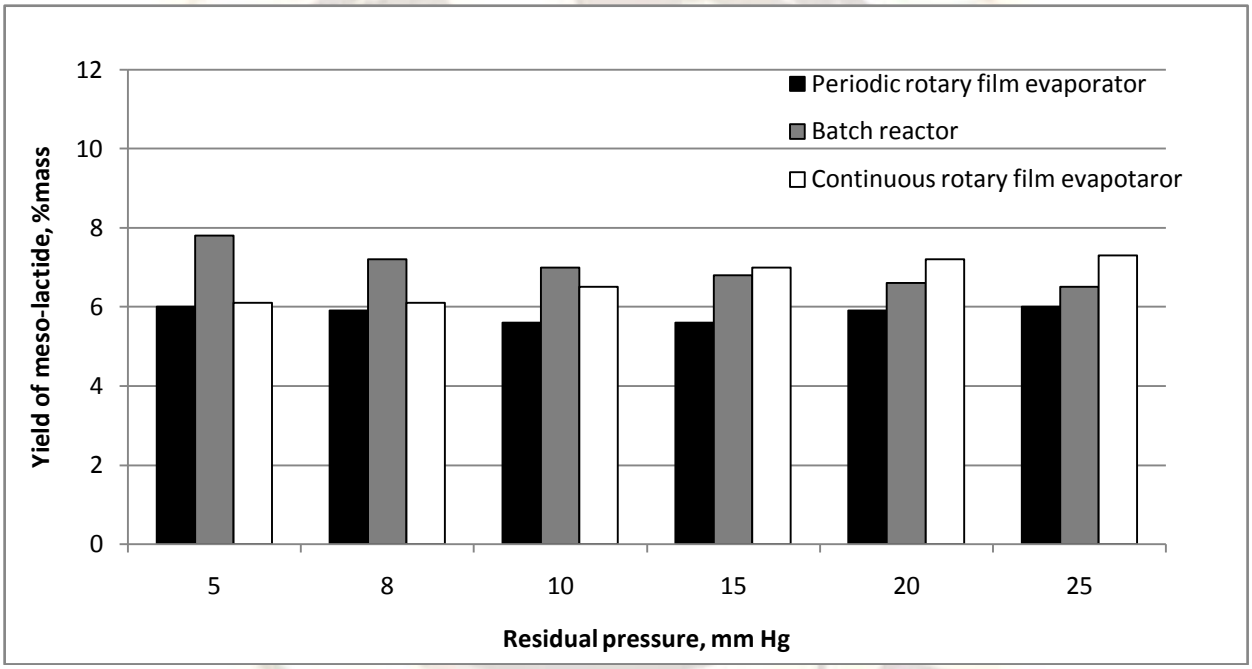

Fig.4. Yield of meso-lactide at different temperatures for three types of reactors.

Fig.3 shows the changes in productivity under different residual pressure. This data clearly indicates that the best productivity is obtained in continuous rotary film evaporator at temperature 230 under residual pressure 5 mm Hg.

IV. CONCLUSIONS

In present work, three different types of reactors for depolymerisation of oligomers of butyl lactate were tested. Optimal conditions of the process were found for each type of reactor. According to the obtained results, the best type of reactor was found to be continuous rotary film evaporator. It showed the highest productivity at 230^{o}C under residual pressure 5mm Hg. The worst results were shown by batch reactor.

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