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Purification of Crude Lactide to Polymerization Grade Purity by Molt Recrystallization Method

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Waste polymer materials are a greater threat to the environment, as a result it becomes necessary the development and production of biodegradable polymers. The process of purification of crude lactide by the method of melting impurities to polymerization grade L-lactide purity was investigated. Design and methodology for the process on a laboratory research installation was proposed. It is established that the yield and degree of purity of L-lactide are affected by two main parameters: the heating rate and nitrogen flow rate. It is found that under optimum conditions of purification of L-lactide from its major impurities is possible to obtain the product with polymerization grade purity with a yield of about 50 %. Optimal temperature profile of the process of the melting impurities were found. Wherein the total time of the stage of purification is reduced for 1.5 h with a sufficient reduction of energy consumption.

Keywords: Purification, Lactide, Melting of impurities, Biodegradable polymers, Esters of lactic acid.

INTRODUCTION

In recent times the actual area of chemistry and chemical engineering is finding efficient ways of synthesis of biodegradable polymers based on renewable vegetable raw materials. Research in this area contributes to two main factors *i.e.*, diversification of raw materials taking into account the depletion of reserves of fossil raw materials and global environmental situation [1]. The transition to biopolymers will solve the problem “plastic junk” [2,3], as entering the environment, they undergo biological and physico-chemical transformations to form carbon dioxide, water and other natural compounds, will make a significant contribution in reducing the “greenhouse effect” as grown for the production of vegetable raw material absorbs carbon dioxide [4-6].

Great interest among the biopolymers cause macromolecular compounds obtained on the basis of hydroxycarbonic acids, due to the fact that prices for fossil fuels, such as oil, gas, coal are costly compared to renewable biological resources. Moreover, most prospects expected from polylactic acid (polylactide), which is obtained by ring-opening polymerization of lactide (cyclic dimer of lactic acid) [7-9]. Possessing such important properties as thermal stability, transparency and mechanical strength, polylactide finds wide application in the field of production of packaging materials and biomedicine [10]. The basic qualities of polylactide is compatible with the human body, ease of processing, low barrier oxygen transmission,

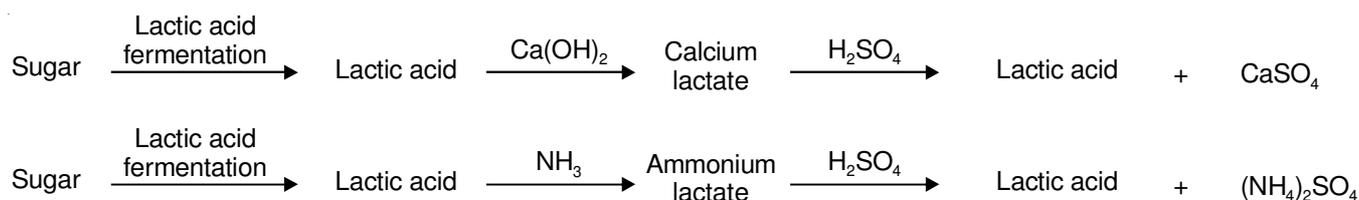
water vapour, resistance to degradation under normal conditions and ease with waste disposal [10].

Existing technologies of obtaining lactide used lactic acid as a raw material. However, the large number of process steps, their complexity and a large number of waste products, leads to an expensive product.

In addition, these technologies contain energy- and resource-intensive stages of purification of lactide from water and traces of lactic acid, which have strict criterion of purity of the lactide (lactic acid content not higher than 10⁻⁶ mol/g of water – not higher than 100 ppm) [8,11].

The formation of significant quantities of waste is connected with the industrial methods of production and isolation of lactic acid according to the following schemes of reactions (**Scheme-I**).

The main and general disadvantage of these two methods is that they both use a stage of acidification of the obtained salts of lactic acid with a strong mineral acid (usually sulfuric acid). All this leads ultimately to the formation of almost equimolar (relative to lactic acid produced) quantities of waste production of calcium sulfate (gypsum) or ammonium sulphate (more than 1 ton per ton of lactic acid), which is difficult to find qualified application due to their low purity. In this regard, the costs of isolation and cleaning of the lactic acid and waste disposal reach 50 % of the total cost of the product, making it economically unprofitable and its products cannot compete on price with products made of petrochemical plastics [12,13].



Scheme-I: Isolation of lactic acid

Recent studies have shown the possibility of direct conversion of the resulting aqueous solutions of ammonium lactate to the esters of lactic acid, which allows excluding from the process the stage of acidification of an aqueous solution of ammonium lactate and the formation of waste products [14,15]. Obtained according to this method, esters of lactic acid (alkyl lactates) can be used as a feedstock for the production of lactide. In this case, the synthesis of poly lactide can be carried out according to the following scheme [16,17] (Scheme-II).

The advantages of this method are as follows:

- Lactide obtained in this way contains a low level of concentration of lactic acid and water [16], which are very undesirable impurities during the process of polymerization to produce high-quality poly lactide (molecular weight over 100 kDa).
- Ammonia released at the stage of esterification is returned to the fermentation step.
- The alcohol released during the polycondensation of alkyl lactate is recycled to the stage of esterification.

In this work, we carried out the entire chain of synthesis of poly lactide from fermentation of glucose with obtaining ammonium lactate to lactide polymerization. This study is concerned to the optimization of the purification crude lactide to the polymerization grade of purity. As noted above, when using a technology for obtaining lactide from alkylation, impurities of lactic acid and water are virtually absent in the resulting crude lactide.

The major impurities during the synthesis of lactide are aliphatic alcohol, alkyl lactate, low molecular weight oligomers (mainly dimer) and meso-lactide. Aliphatic alcohol and alkyl lactate can be removed by simple vacuum distillation. However, the dimer and meso-lactide cannot be removed in such a way.

To remove the above impurities from the crude lactide a range of processes were offered: washing with cold water followed by vacuum evaporation, fractional vacuum distillation, extraction with solvent, recrystallization from solvents, crystallization from its own melt with subsequent melting (exudation) of impurities of solid crude lactide, as well as combinations of these methods [18-20].

Of the above methods, some are characterized by large losses of lactide (washing with water, solvent extraction, melting), the low efficiency of cleaning (vacuum distillation) and long duration of process – about 24 h (the solvent of recryst-

tallization). In addition, using the techniques of extraction and recrystallization from a solvent will require further organization of additional stages of purification of lactide from the extractant/solvent and recovery of the extractant/solvent.

The most promising, from our point of view, is a method of purifying crude lactide from impurities by melting them out of solid crude lactide. This method does not require the use of auxiliary substances (solvents). In addition, the product obtained at the stage of melting waste (containing mainly L-lactide and dimer and meso-lactide) can be recycled to the preceding stage of the technological chain. Therefore, the aim of this work is research aimed at finding optimal design of purification of lactide by controlled melting of impurities, the search of optimal regimes of its operation, providing the maximum yield of polymerization grade L-lactide.

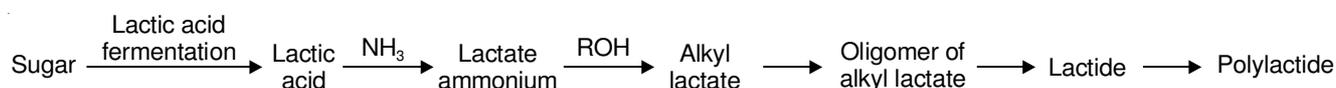
EXPERIMENTAL

Lactic acid (in the form of an aqueous solution of ammonium lactate with a concentration of 110 ± 10 g/L in terms of lactic acid) obtained by fermentation of glucose in laboratory membrane bioreactor using a strain of *Lactobacillus paracasei*. Culture liquid after fermentation was purified from the high molecular bio-impurities by the method of nanofiltration using membrane SPM-300PS on a flow-circulation of the membrane installation.

Butyl lactate was obtained by esterification of the purified culture liquid with butanol, followed by separation of butyl lactate (basic substance content not less than 98 % wt.) by rectification. Further, the synthesized oligomer was synthesized by polycondensation of butyl lactate in the presence of SnCl_4 as a catalyst. Crude lactide was obtained by depolymerization of the oligomer catalyzed by SnCl_4 . To remove the butanol and butyl lactate from the products of depolymerization vacuum distillation was used. The content of impurities in crude lactide ranged from 10 to 15 % by weight. A typical composition of the crude lactide was as follows: L-lactide – 87.6 %, meso-lactide – 4.42 %, dimer of butyl lactate – 8.51 %.

We used nitrogen gas as the noble gas (compressed, high purity 1-St grade of 99.999 %, GOST 9293-74).

Recrystallization from the melt was carried out on the installation shown in Fig. 1. A mold is a hollow tube having a jacket, through which thermostated water is circulated to regulate the temperature inside the crystallizer. In the crystallizer the perforated glass partition is soldered to prevent spontaneous lactide entrapment.



Scheme-II: Synthesis of poly lactide

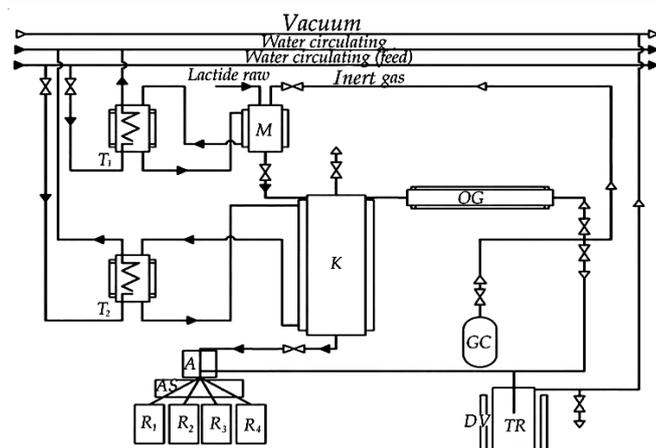


Fig. 1. Scheme of lactide cleaning process by the method of melting impurities: K – vertical heated apparatus of the type tube-in-tube, M – dosimeter, $T_{1,2}$ – thermostat, OG – oven gas, GC – gas cylinder, AS – adapter “spider”, A – the allonge, Tr – trap, $R_{1,4}$ – receiver (R), DV – Dewar vessel

Experimental procedure: Before starting the process, the installation is purged with nitrogen gas. Then, molten crude lactide was loaded in the measuring device M. The thermostat T_1 (mark VIS-T-02) create the necessary temperature in the measuring device M so that the crude lactide was in the form of a melt.

The thermostat T_2 (mark VIS-T-02) creating a temperature in the mold K, is equal to the temperature in the measuring device M. Open the valve and gravity fill the mold with molten crude lactide. After filling of the mold cooling of thermostat T_2 by cold or warm water through the cooling coil is switched on. Circulation of coolant through the jacket mold provides the crystallization of the melt of crude lactide in the mold.

Next, we create the necessary gas flow from the cylinder GC. We turn on furnace OG for heating gas stream and set the gas stream temperature to a predetermined rate. We turn on a vacuum pump (brand P. V. R. PHV-5) and create a vacuum. Dewar vessel (DV) is filled with a cooling medium (liquid nitrogen, dry ice, etc.) for cooling trap for light components Tr.

We start the temperature rise in the mold (with the help of thermostat T_2) and gas carrier (with the oven OG) for a given program. The temperature in the mold, indexed by the thermocouple should be equal to the temperature in the thermostat T_2 and temperature of the carrier gas. With the rise of temperature of the solid layer crude lactide viscoplastic impurities start vaporizing, which are collected successively in the receivers $R_{1,4}$, attached to the allonge “Spider” AS (GOST 25336-82).

After exudation of all low-melting fractions, the final product – clear lactide – is melted by raising the temperature in the mould up to 100 °C and collected in a receiver of pure lactide.

Analysis techniques: The composition of the obtained fractions is analyzed using gas-liquid chromatography (chromatograph brand Chromatek-Kristall 2000 m, capillary column 50 m long with an internal diameter of 0.23 mm, a stationary phase adsorbent SE-54), identifying the content of the target product (L-lactide) and organic impurities.

The water contents in the purified lactide is determined on the titrator coulometric Karl Fisher (Coulometer 831 KF brand).

The lactic acid contents in the purified lactide was determined using spectrophotometer (model Shimadzu UV 3600) and calculated according to the equation:

$$[\text{Lactic acid}] = C \times \frac{D_{515}^{\text{works}} - D_{515}^{\text{samples}}}{C_s} \quad (1)$$

where $D_{515}^{\text{works}} - D_{515}^{\text{samples}}$ – the difference between optical densities at a wave length of 515 nm of the rhodamine solution 6G, free of monomer and the dye solution containing the monomer in a concentration of C_s (g/L) (concentration of solution). $K = 1.77 \times 10^{-5}$ mol/L is a constant of proportionality.

RESULTS AND DISCUSSION

Selection of optimal operation mode of purification of lactide by the method of melting impurities was carried out by conducting single-factor experiments by varying two parameters *i.e.*, the speed of the temperature rise and flow rate of nitrogen. The experiments were carried out at a residual pressure in the range of 5-10 mm of mercury and in the temperature range from 60 to 100 °C. During the experiment several fractions were collected: in the range of 60-90 °C – 1 fraction (enriched dimer butyl lactate); in the range of 90-96 °C – 2 fraction (enriched meso-lactide) and in the range of 97-100 °C – 3 fraction (pure L-lactide).

Definition of optimal regime of the temperature rise:

In a series of experiments for determination of the optimal temperature rise the nitrogen flow rate was constant: 122.5 ± 2.5 mL/g. Preliminary experiments showed that in the range of heating rate from 0.1 to 0.2 °C/min there is the maximum yield of L-lactide. At higher heating rate, the yield of the target fraction rapidly decreases and at lower – the process time increases and the yield and composition of the target fraction remains almost unchanged. Therefore, it was conducted a more detailed series of experiments with the speed of temperature rise from 0.1 to 0.2 °C/min in order to clarify the optimum heating rate.

Table-1 shows the results of experiments with the speed of temperature rise from 0.1 to 0.2 °C/min. In this range of regulation of speed of temperature rise, the concentration of L-lactide and its optical purity is almost unchanged. Thus, the optimum heating rate is about 0.16 °C/min, in which there is the greatest yield about 44 %.

TABLE-1
RESULTS OF EXPERIMENTS WITH THE SPEED OF
TEMPERATURE RISE FROM 0.1 to 0.2 °C/min

Heating rate (°C/min)	Output (%)	Concentration (%)	Optical purity (%)
0.10	33.7	96.1	97.6
0.13	38.9	96.4	97.8
0.16	44.0	96.1	97.4
0.20	39.8	95.8	97.3
0.23	37.5	95.9	97.4

Table-2 presents the results of the experiment at a rate of temperature rise of 0.16 °C/min. Melting time amounted to 225 min. The water concentration in the target fraction is 60 ppm.

TABLE-2
RESULTS OF THE EXPERIMENT AT A RATE OF TEMPERATURE RISE OF 0.16 °C/min

Component	Composition of raw materials source		Fractions composition					
			Fraction 1 (60-90 °C)		Fraction 2 (90-96 °C)		Fraction 3 (100 °C)	
	g	%	g	%	g	%	g	%
L-Lactide	53.89	87.6	13.89	77.91	16.28	85.71	23.71	96.06
Meso-lactide	2.72	4.42	0.89	4.99	1.20	6.3	0.63	2.56
Dimer of butyl lactate	5.24	8.51	3.40	19.05	1.50	7.88	0.34	1.38
Σ	61.52	100	17.83	100	19	100	24.69	100

With the aim of reducing losses of L-lactide with the second fraction variable speed of temperature rise were investigated. The first fraction was collected at 0.16 °C/min and the second at 0.05 and 0.1 °C/min. Comparison of experimental results showed that the melting of the 2nd fraction is advantageously carried out at heating rate 0.1 °C/min. Table-3 presents the results when the speed of the temperature rise was in the range of 60-90 °C – 0.16 °C/min and in the range of 90-96 °C – 0.1 °C/min.

Under these conditions, the time of the melting were 248 min with the L-lactide yield about 48.2 %. The water concentration in the target fraction is 53 ppm. The purity of L-lactide was 98.25 %, optical purity was 98.9 %.

Determination of the optimal feed rate of noble gas:

Investigation of the effect of the feed rate of noble gas is carried out at optimal profile of temperature rise. Preliminary experiments showed that the increase in nitrogen flow rate leads not only to increase the purity of L-lactide (positive effect), but also to reduced yield of L-lactide by entrainment (negative effect). When the feed rate of nitrogen was below 20 mL/min the meso-lactide content in the target fraction exceeded allowable values. In addition, at feed rates of nitrogen above 40 mL/min low yield of L-lactide was observed. Therefore, for the optimal parameters of the nitrogen flow rate the range of variation from 20 to 40 mL/min was chosen.

Figs. 2-4 show the dependences of the yield of L-lactide, impurity concentration, the concentration of L-lactide in the target fraction and its optical purity from the feed rate of nitrogen, respectively.

These figures showed that the increase in nitrogen flow rate leads to increase the purity of L-lactide and at a cost of more than 40 mL/min it is possible to completely remove the dimer. At the same time increasing the gas flow through the crystallizer leads to the intensification of the ablation of L-lactide, which leads to lower output. In our opinion, the best value of the flow rate of nitrogen is 25 mL/min. At a value of the content of dimer of less than 1 % (a desirable feature during polymerization), there is a stock on the optical purity and the yield of lactide is at 50 %.

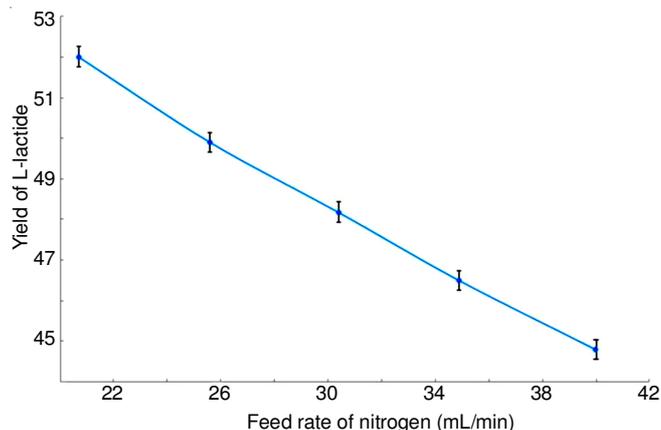


Fig. 2. Dependence of of L-lactide yield from the feed rate of nitrogen

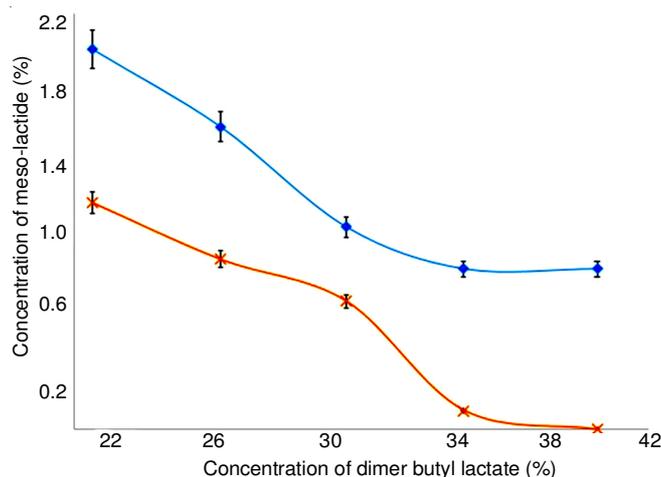


Fig. 3. Dependence of the impurities concentration of the meso-lactide and dimer of butyl lactate from the feed rate of nitrogen. Symbols: ◆ – the concentration of meso-lactide (%); × – the concentration of dimer butyl lactate (%)

Table-4 shows the experimental results when the feed rate of nitrogen is 25 mL/min. Total cleaning time amounted to 248 min, the yield of lactide, accounting for 49.9 %. The water concentration is 58 ppm, the concentration of lactic acid is 3×10^{-7} mol/kg.

TABLE-3
RESULTS OF THE EXPERIMENT WHEN THE RATE OF TEMPERATURE RISE WAS IN THE RANGE FROM 60 TO 90 °C – 0.16 °C/min AND IN THE RANGE OF FROM 90 TO 96 °C – 0.1 °C/min

Component	Composition of raw materials source		Fractions composition					
			Fraction 1 (60-90 °C)		Fraction 2 (90-96 °C)		Fraction 3 (100 °C)	
	Γ	%	Γ	%	Γ	%	Γ	%
L-Lactide	54.08	87.6	14.28	77.8	13.75	81.50	26.06	98.25
Meso-lactide	2.73	4.42	0.90	4.92	1.54	9.14	0.28	1.07
Dimer of butyl lactate	5.25	8.51	3.49	19.04	1.58	9.36	0.18	0.68
Σ	61.74	100	18.35	100	16.87	100	26.52	100

TABLE-4
RESULTS OF THE EXPERIMENT WITH THE FEED RATE OF NITROGEN 25 mL/min

Component	Composition of raw materials source		Fractions composition					
			Fraction 1 (60-90 °C)		Fraction 2 (90-96 °C)		Fraction 3 (100 °C)	
	g	%	g	%	g	%	g	%
L-Lactide	53.9	88	14.4	77.2	12.59	82.43	26.9	97.50
Meso-lactide	2.72	4.4	0.81	4.34	1.47	9.61	0.44	1.60
Dimer of butyl lactate	5.24	8.5	3.45	18.46	1.54	10.09	0.25	0.90
Σ	61.52	100	18.7	100	15.27	100	27.58	100

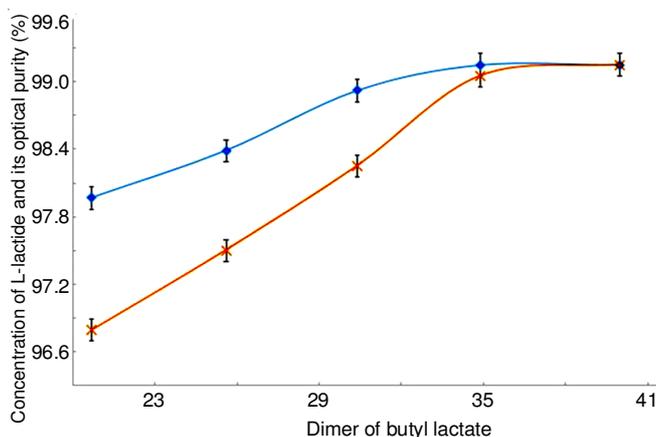


Fig. 6. Dependence of the concentration of L-lactide and its optical purity from the feed rate of nitrogen. Symbols: ◆ – optical purity, %; × – the concentration of L-lactide, %

Determination of the optimal temperature profile of the process of the melting impurities: With the aim of reducing the total time of the process of the melting impurities and reduce energy consumption additional experiments with different temperature profiles were carried out. The process of recrystallization from own melt consists of 4 stages *i.e.*, crystallization, partial melting of the first fraction, partial melting of the second fraction and the complete melting of the third fraction. The last three stages is already optimized so at this point the first stage of crystallization was optimized.

Fig. 5 shows the temperature profiles of the process of the melting impurities before and after the optimization.

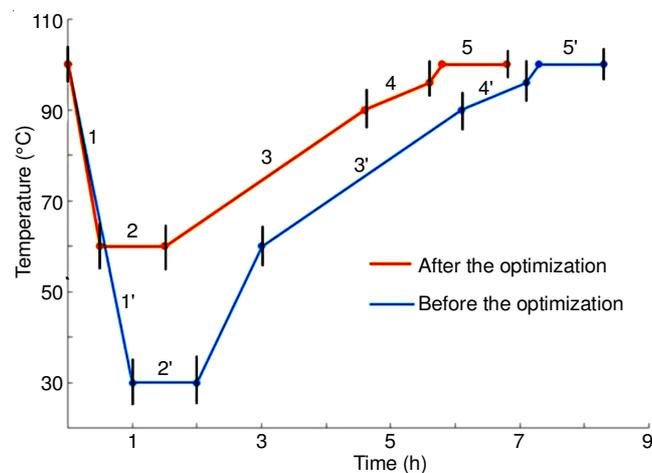


Fig. 5. Diagram "temperature-time" process of the melting impurities before and after the optimization. Symbols: 1,1' – crystallization, 2,2' – partial melting of the 1st fraction, 3,3' – partial melting of the 2nd fraction, 4,4' – full melting

As a result of the optimization is 1.5 h reduction of the total process time with maintaining the yield and purity of L-lactide, as well as a reduction of the energy consumption due to the less cooling of crude lactide on the crystallization stage and reduction of the amount of heat input at the stage of partial melting of the 1st fraction.

Conclusions

A method and design of the installation for the preparation of L-lactide polymerization were proposed. The optimal parameters of the mode of installation were experimentally determined, namely:

- The rate of temperature rise in the range from 60 to 90 °C is 0.16 °C/min and in the range of from 90 to 96 °C – 0.1 °C/min.
 - Nitrogen flow rate of 25 mL/min.
- The proposed method provides the lactide yield of about 50 % under the following quality indicators.
- The content of lactic acid in lactide is not higher than 10-6 mol/g.
 - The water content of lactide is not higher than 100 ppm.
 - The melting point of lactide is 90-100 °C.
 - The optical purity of lactide is not less than 97.5 %.

It is important to note that the sub-standard fraction (1-I 2-I) can be returned to the previous stage of the technological chain. Lactide, isolated and purified by the method of melting contains minimum amount of impurities and is suitable for further obtaining from it the polylactide with a high molecular weight (not less than 100 kDa).

The proposed optimal temperature profile of the process of the melting impurities make it possible to reduce the cleaning time for 1.5 h and to reduce the energy consumption.

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