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TRIALS ON UTILIZATION OF A LABORATORY SLOT-TYPE REACTOR TO THE OZONOLYSIS REACTION

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The possibility of utilization the laboratory slot-type reactor to the ozonolysis of erucic acid was examined. The influence of some parameters on the process yield was investigated.

INTRODUCTION

Rapeseed oil with about 50% of erucic acid is the main vegetable oil in Poland.

Ozonolysis of erucic acid gives one of the oportunities of its industrial application. Brassilic acid obtained by the ozonolysis, is a valuable raw material in manufacture of plasticizers, fibres, synthetic plastics and lubricants [1-3, 5].

Ozonolysis is an exotermic reaction, and the problem of cooling is very important here. A slot-type reactor assures heat exchange in an extremly effective way.

The slot-type reactor is an apparatus, which consists of cylinder fitted with a rotator — another cylinder rotating concentricaly. There is a narrow slot between this rotating plane and the stationary one. This slot forms the reaction zone where at an expansed surface the liquid and gas contact each other. The reactor construction ensures good mixing of the gas and the liquid phases in a relatively short time of the contact between two reagents. The inner and the outer surfaces of the slot-type reactor can be cooled or reated if necessary.

EXPERIMENTAL

In our studies a glass laboratory reactor was applied and its scheme is given in Figure 1.

In the bottom of the reactor, there is the outlet of reaction mixture and gas. The upper part of the reactor is widen and this protects

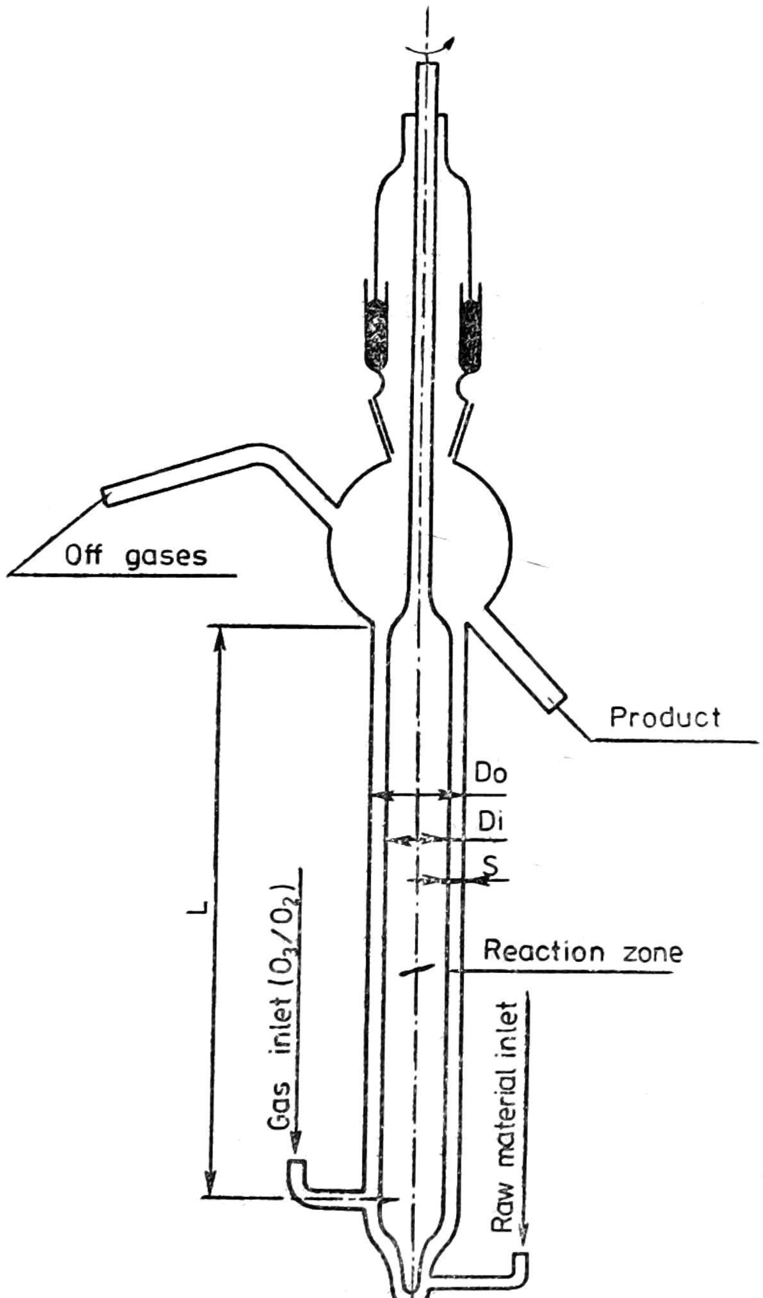

Fig. 1. Slot-type reactor

against foaming — and it is closed with a hydraulic seal. The proper reactor lead with raw material was visualized by a characteristic spiral track of the gases flowing through the slot-type reactor. Two reactors were applied to our investigations. Charateristics of these reactors are given in Table 1.

The reactors are of nearly the same dimensions reaction slot. The

Table 1

Characteristic sizes of laboratory slot-type reactors

Reactor	Outer diameter D_o (mm)	Inner diameter D_i (mm)	Slot width S (mm)	Length of reaction zone L (mm)
I	20.9	18.5	1.20	150
II	21.0	18.5	1.25	70

reaction zone of the first reactor was twice as large as the second one. Erucic acid of 94.6% purity was ozonolyzied. That acid was obtained from the technical erucic acid of 81.0% purity as the result of twofold crystalization from acetone. The crystalization yield was 70%.

The ozonolysis was carried out in pelargonic acid which is one of the product of erucic acid ozonolysis. All experiments on ozonolysis were carried out with a prototype ozone generator. That ozone generator gives 2.5% weight concentration of ozone in oxygen at the rate of oxygen flow equal 30 c/h.

Erucic acid ozonolysis was carried out in the apparatus presented at the scheme. Multiple circulation of the reaction mixture were warranted.

The slot reactor and a U-tube shaped heat exchanger were placed in thermostated baths. The ozone entered the reactor in the bottom above the reaction mixture. The gas as well as the product outlet is in the upper part of the reactor.

The experiments on the erucic acid ozonolysis were carried out to establish the optimum process parameters. First — the experiments were limited to the investigation of the effect of individual parameters on the ozonides formation.

The conditions of the second stage of the ozonolysis — oxydative decomposition of the ozonides — were constant. We tried to find process parameters giving the highest brassilic acid yield.

The ozonolysis was carried out at:

— different erucic acid concentration — c_E in the reaction mixture

$$c_E = 10 \div 50\%,$$

— changeable temperature of ozonides formation process

$$t = 25 \div 45°C,$$

— different flow rate of the reaction mixture

$$V_l = 20 \div 40 \text{ ml/min}.$$

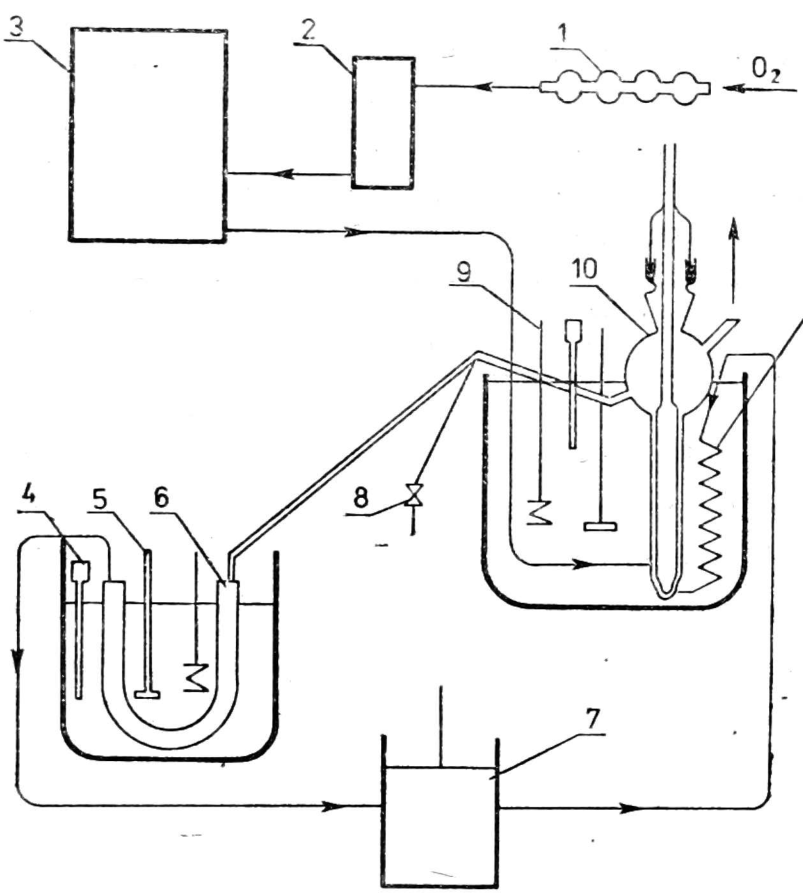

Fig. 2. Scheme of the apparatus set for ozonolysis: *1* — tube with calcium chloride, *2* — flow meter, *3* — ozone generator, *4* — contact thermometer, *5* — stirrer, *6* — heat exchanger, *7* — pump, *8* — sampling tube, *9* — electric heater, *10* — slot type reactor

Two following parameters were kept constant:

— 2.5% O_3/O_2 mixture at flow rate $V_g = 30$ l/h,

— the weight of the reaction mixture was equal 150 g.

The reactor rotator moved with the velocity of 1000 rotations/minute.

After reaching its desired temperature, the reaction mixture was pressed into the slot reactor, where in the reaction zone it met the gas mixture of ozon in oxygen. The ozonization was carried out until the decay of double bonds, what was proved by the bromine test [4]. Decomposition of ozonides in oxidizing conditions was the next stage of the ozonolysis. Oxygen was applied as the oxidizing agent.

The bath temperature was increased to 95°C and the circulation of the reaction mixture went on to get the decay of aldehyde groups what was determined by test with Fehling's solution [6].

The composition of erucic acids and of ozonolysis products were determined by gas chromatography of their methyl esters. The methode of inner standard was applied to the exact quantitive determinations of the acids. Sebacic acid was used as the standard.

The ozonolysis of samples with changeable contents of erucic acid

Table 2

The influence of erucic acid concentration in the reaction mixture on the product composition and the yield of brassilic acid

Initial concentration of erucic acid in the mixture C_E (%)	Yield of brassilic acid (%)	Composition of product (%)		
		Brassilic acid HOOC$(CH_2)_{11}$--COOH	Amount of dicarboxylic acids HOOC(CH_2)n--COOH n = 5÷13	Amount of all monocarboxylic and dicarboxylic acids up to n = 5
10	95.0	8.2	0.7	1.1
20	87.0	11.7	3.3	5.0
30	79.2	16.2	3.7	10.1
40	73.6	20.0	5.1	14.9
50	50.8	27.2	6.1	16.7

Conditions: Vg = 30 l/h; Vl = 40 ml/min; t = 40°C, reactor I.

were carried out to examine the effect of erucic acid concentration on the yield of brassilic acid.

Concentrations of erucic acid were: 10, 20, 30, 40 and 50%. It is seen from Table 2 that the increase of erucic acid concentration in the reaction mixture causes diminishing of the brassilic acid yield. This is caused by the formation of other mono — and dicarboxylic acids, probaly because of the double bond migration. The optimum erucic acid concentration was established as 30%. At that concentration the yield of brassilic acid is high and the amount of by-products is smaller, than at higher concentrations. Also, the mixture circulation is better at that concentration, than at higher ones. It seems however, that on commercial scale of production it would be more profitable to resign from obtaining the maximum yield to get better utilization of the equipment and smaller solvent consumption. The ozonolysis of erucic acid was carried out at five different temperatures.

The results are given in Table 3. The temperatures 25, 30, 35, 40 and 45° were applied.

40°C were found as the optimum temperature. The reactions carried out at lower temperatures are of lower yield. The cause of that situation lies in higher viscosity of reaction mixture at lower temperatures and because of that, there is a worse contact between gas and liquid.

This is especially important when an apparatus of slot-type is applied. At the temperature of 45°C the yield is lower than at 40°C. One can assume that above 40°C there is a higher intensification of various by-reactions which go parallel to the main reaction. This is ascertained

Table 3

The influence of the ozonization temperature on the product composition and the yield of brassilic acid

The ozonization temperature t (°C)	Yield of brassilic acid (%)	Composition of product (%)		
		Brassilic acid $HOOC(CH_2)_{11}$-$COOH$	Amount of dicarboxylic acids $HOOC(CH_2)_n$-$COOH$ $n = 6 \div 13$	Amount of all monocarboxylic and dicarboxylic acids up to $n = 6$
25	66.8	13.7	2.5	13.8
30	65.0	13.1	2.5	14.4
35	71.7	14.7	2.5	12.8
40	79.3	16.1	3.4	10.5
45	71.0	14.5	2.3	13.2

Conditions: $Vg = 30$ l/h; $Vl = 40$ ml/min, $C_E = 30\%$, reactor I.

by greater amounts of by-products. While the temperatures were increased the shortening of the time of ozonides formation was observed. When acetic acid was applied as the solvent the optimum temperature of ozonozation was 30°C.

Table 4

The influence of the reaction mixture flow rate on the product composition and the yield of brassilic acid

Flow rate of the reaction mixture V_l (ml/min)	Yield of brassilic acid (%)	Composition of product (%)		
		Brassilic acid $HOOC(CH_2)_{11}$-$COOH$	Amount of dicarboxylic acids $HOOC(CH_2)_n$-$COOH$ $n = 6 \div 13$	Amount of all monocarboxylic and dicarboxylic acids up to $n = 6$
20	55.6	11.3	15.2	3.5
30	65.3	13.9	13.3	2.8
40	79.2	16.2	10.7	3.1

Conditions: $Vg = 30$ l/h, $C_E = 30\%$, $t = 40$°C, reactor I.

The next examined parameter was the reaction mixture flow rate. The results are given in Table 4. Reaction mixture flow rates: 20, 30 and 40 ml/min. were applied. The optimum raw material flow rate was established to be 40 ml/min.

The highest brassilic acid yield and the lowest contents of by-products were reached at that flow rate. The ozonides formation time was shortest at that flow. Because of difficulties in liquid circulation

Table 5

The influence of the reaction zone dimension on the product composition and the yield of brassilic acid

Reactor	Length of reaction zone L (mm)	Yield of brassilic acid (%)	Composition of product (%)		
			Brassilic acid $HOOC(CH_2)_{11}$-$COOH$	Amount of dicarboxylic acids $HOOC(CH_2)_n$-$COOH$ $n = 5 \div 13$	Amount of all monocarboxylic and dicarboxylic acids up to $n = 5$
I	150	79.1	16.1	3.6	10.3
II	70	52.8	10.8	4.1	15.1

Conditions: V_g = 30 l/h; V_l = 40 ml/min; t = 40°C; C_E = 30%.

no higher flow rate was applied. To estimate the effect of the reaction space on the yield two reactors were applied, the dimensions of which presented earlier.

The distinctly higher yield was obtained at the first reactor. It is caused by twice longer reaction zone in that reactor. Besides of investigations in the slot-type reactor the ozonolysis was also carried out in a reaction flask by barbotage of the ozone through the liquid layer. The ozonolysis parameters were kept the same as they were in the slot reactor. By comparison of both ways of the process, it was ascertained that ozonides formation time in the slot reactor is distinctly shorter. The yields obtained in both apparatus were quite similar.

On the basis of our results it was ascertained that:

— total ozonolysis occurs in the slot-type reactor during multiple circulation of the reaction mixture. It can be assumed, that it is quite reasonable to use this apparatus to the fatty acids ozonolysis,

— the optimum yields of brassilic acid were obtained in the "I" reactor (the slot was 1.20 mm wide and the reaction zone was 150 mm long) at following ozonolysis parameters:

30% erucic acid concentration in the reaction mixture 40°C temperature,

40 ml/min, reaction mixture flow rate.

The results above discussed ensured about the usability of the slot-type reactor to the ozonolysis of unsaturated fatty acids.

Of course there are necessary further investigations on the effect of other parameters on the reaction course and yield.

REFERENCES

1. Green J. L.: J. Polymer Sci. 1967, 5, 391.
2. Nieschlag H. J.: Ind. Eng. Chem. Prod. Res. Develop. 1964, 3, 146.
3. Nieschlag H. J.: Ind. Eng. Chem. Prod. Res. Develop. 1967, 6, 201.
4. Pasero J., Naudet M.: Rev. fse Corps gras. 1960, 4, 192.
5. Shu-pei Chang, Miwa T. K.: J. Polymer Sci. 1967, 5, 2547.
6. Vogel A. J.: Preparatyka Organiczna WNT, Warszawa, 1964.

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PRÓBY WYKORZYSTANIA LABORATORYJNEGO SZKLANEGO REAKTORA SZCZELINOWEGO DO PROCESU OZONOLIZY

Streszczenie

Reaktor szczelinowy w wyjątkowo skuteczny sposób zabezpiecza wymianę ciepła. Zagadnienie tej wymiany odgrywa także dużą rolę w reakcji otrzymywania ozonków i ich rozkładu. Badano możliwość zastosowania reaktora szczelinowego do reakcji ozonolizy kwasu erukowego. Proces prowadzono w rozpuszczalniku (kwas pelargonowy) na zasadzie wielokrotnego obiegu. Zbadano wpływ następujących parametrów na wydajność reakcji: stężenia kwasu erukowego w mieszaninie reakcyjnej, temperatury ozonolizy, natężenia przepływu cieczy i wielkość przestrzeni reakcyjnej. Inne wielkości, mogące mieć wpływ na wydajność reakcji, jak natężenie przepływu mieszaniny ozonizującej-ozon w tlenie (O_3/O_2), stężenie ozonu oraz warunki utleniającego rozkładu ozonków były stałe.

Na podstawie uzyskanych wyników stwierdzono, że w reaktorze szczelinowym zachodzi proces całkowitej ozonolizy. Ponadto stwierdzono, że w badanych warunkach czas tworzenia ozonków jest krótszy w porównaniu z czasem takiego samego procesu prowadzonego w typowym reaktorze zbiornikowym.

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ПОПЫТКА ИСПОЛЬЗОВАНИЯ ЛАБОРАТОРНОГО СТЕКЛЯННОГО ЩЕЛЕВОГО РЕАКТОРА В ПРОЦЕССЕ ОЗОНОЛИЗА

Резюме

Щелевой реактор исключительно эффективно обеспечивает обмен тепла. Вопрос этого обмена играет также важную роль в реакции получения озонидов и их разложения. Исследовали возможность применения щелевого реактора в реакции озонолиза эруковой кислоты. Процесс проводился в растворителе (пеларгоновая кислота) по принципу многократного оборота. Исследовали влияние следующих параметров на производительность реакции: концентрация эруковой кислоты в реакционной смеси, температуры озонолиза, интенсивности протока жидкости и величины реакционного пространства. Другие величины,

которые могли вы влиять на производительность реакции, такие как интенсивность протока озонизирующей жидкости — озон в кислороде (O_3/A_2), концентрнция озона и условия окисляющего разложения озонидов, были постоянными.

На основании полученных результатов установлено, что в щелевом реакторе происходит процесс полного озонолиза. Сверх того установлено, что в исследуемых условияхпродолжительность образования озонидов была короче в сравнении с продолжительностью такого же процесса проводимого в типичном контейнерном реакторе.