Optimization of Process of Methacrylic Acid Obtaining by Aldol Condensation of Propionic Acid with Formaldehyde Using a Kinetic Model

Roman Nebesnyi, Volodymyr Ivasiv, Yulia Dmytruk, Nazar Lapychak

Technology of Organic Products Department, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandery street 12, E-mail: nebesnyi@ukr.net

Abstract* – *Methacrylic acid is widely used industrial monomer. An alternative method of its obtaining is aldol condensation of propionic acid with formaldehyde in the gas phase. It has been found that catalyst based on oxides of boron and phosphorus and promoted by oxide of tungsten is effective for this process. The purpose of this work is to find out optimal parameters of this process (temperature and contact time) using a kinetic model. The optimal parameters of this process have been found and technology basics of methacrylic acid obtaining have been developed.

Key words – kinetic model, methacrylic acid, propionic acid, formaldehyde, solid catalyst, optimization.

I. Introduction

Acrylic monomers are mass-production substances in basic organic synthesis, in particular the world production capacity of methacrylic acid (MAA) is estimated as 5 million tons per year, and the production of methyl methacrylate (MMA) is 4.5 million tons per year. Currently, the major industrial methods of acrylates production are acetone cyanohydrin method [1, 2] and method of oxidation of olefins [1, 3]. Also the method of acrylates obtaining from ethylene through an intermediate stage of unsaturated aldehydes formation (such as acrolein and methacrolein) is industrially implemented [1]. Due to the large scale of production, it is of high importance to improve existing and create new technologies of acrylic monomers producing.

Method of condensation by the carbonyl group has significant prospects of industrial application. This method allows acrylates obtaining from available materials using a small number of stages. In previous studies it was found that catalysts based on oxides of boron and phosphorus and promoted by oxides of zinc, vanadium, molybdenum or tungsten are highly effective for the condensation of propionic acid (PA) with formaldehyde (FA) to MAA [4, 5]; also the most effective promoter and its optimal content have been determined, and the effect of temperature on the process has been established [6]. The aim of this work is to find optimal parameters of the process (temperature and contact time) using a kinetic model.

II. Results and Discussion

To optimize the parameters of the process of condensation of PA with FA over a $B_2O_3 – P_2O_5 – WO_3$ / SiO_2 catalyst with atomic ratio B:P:W = 3:1:0.3, we used the following kinetic equations [7]:

$$W_{MAA} = \frac{k_1 \cdot K_1^{ef} \cdot C_{PA} \cdot C_{FA}}{1 + K_1^{ef} \cdot C_{FA} + K_2^{ef} \cdot C_{PA}} \quad (1)$$

$$W_{DEK} = \frac{k_1 \cdot K_2^{ef} \cdot C_{PA}^{\ 2}}{1 + K_1^{ef} \cdot C_{FA} + K_2^{ef} \cdot C_{PA}} \quad (2)$$

$$W_{PA} = k_1 \cdot \frac{K_1^{ef} \cdot C_{PA} \cdot C_{FA} + 2 \cdot K_2^{ef} \cdot C_{PA}^{\ 2}}{1 + K_1^{ef} \cdot C_{FA} + K_2^{ef} \cdot C_{PA}} \quad (3)$$

$$W_{FA} = \frac{k_1 \cdot K_1^{ef} \cdot C_{PA} \cdot C_{FA}}{1 + K_1^{ef} \cdot C_{FA} + K_2^{ef} \cdot C_{PA}} \quad (4)$$

W_{MAA} – MAA formation rate;

W_{DEK} – diethyl ketone (DEK) formation rate (by-product);

W_{PA} – PA consumption rate;

W_{FA} – FA consumption rate;

C_{PA}, C_{FA} – PA and FA molar concentrations respectively;

k_1, K_1^{ef}, K_2^{ef} – rate constants.

Rate constants and activation energies are calculated and are shown in Table 1.

TABLE 1

RATE CONSTANTS OF KINETIC EQUATIONS AND ACTIVATION ENERGIES

T, K	$k_1 \cdot 10^7$, $dm^3/m^2 \cdot sec$	$K^{ef}_1 \cdot 10^{-2}$, $dm^3/m^2 \cdot sec$	$K^{ef}_2 \cdot 10^{-2}$, $dm^3/m^2 \cdot sec$
563	2,44	1,96	0,072
593	2,83	3,05	0,241
623	3,24	4,54	0,716
653	3,66	6,52	1,93
E_a, kJ/mole	13,8	40,8	111,6

Formation rates of the reaction products (MAA and DEK) and consumption rates of the reagents (PA and FA) are well described by equations (1 – 4), as correlation coefficients between experimental and calculated data are in the range 0.95-0.99.

Optimization of the process was calculated at 573, 583, 593, 603 and 613 K by integration of equations (1 – 4) using the engineering calculation software Mathcad. The optimum conditions of the process (temperature 593 K, contact time 12 sec) were selected based on the array data. In these conditions the conversion of propionic acid per pass is 47.7%, the yield of methacrylic acid is 44.6% while selectivity is 93.5%, which was confirmed experimentally.

To assess the effectiveness of the proposed method of producing MAA using developed catalyst [4], cost of raw materials per unit of product was calculated (Table 2). The calculation was performed per unit of MMA, since MAA is mostly used for MMA production. Also, the cost of raw materials using the proposed method was compared with the cost of raw materials using industrial implemented method (MAA (MMA) production from ethylene through an intermediate stage of methacrolein formation).

Calculation of raw materials consumption in a particular method, is based on the values of the product yields at each stage:

$$C_2H_4 \xrightarrow{+CO+H_2} PAl \xrightarrow[B=98.1\ \%]{+\Phi A} MA \xrightarrow[B=78,7\ \%]{+O_2} MAA \xrightarrow[B=96,7\ \%]{+\text{methanol}} MMA$$

$$C_2H_4 \xrightarrow[B=99,0\ \%]{+CO+H_2O} PA \xrightarrow[B=93.5\ \%]{+\Phi A} MAA \xrightarrow[B=96,7\ \%]{+\text{methanol}} MMA$$

PAl – propionic aldehyde
MA – methacrolein

The total yield of MMA for the first method was 73.9 %, while the second – 89.5 %.

TABLE 2

RAW MATERIALS CONSUMPTION FOR METHYL METHACRYLATE PRODUCTION

Raw materials	Raw materials costs, €/t	Method of MMA obtaining from ethylene through propionic aldehyde, methacrolein and MAA formation stages		Method of MMA obtaining from ethylene through propionic acid and MAA formation stages	
		Kg/t of MMA	€/t of MMA	Kg/t of MMA	€/t of MMA
Ethylene	950	378,84	359,90	312,81	297,17
Synthesis gas	278 € per 1000 m^3	612,26	170,21	505,56	140,54
Methanol	255	330,92	84,38	330,92	84,38
Formalin	284	1116,22	317,01	921,68	261,76
Total			931,50		783,86

The effectiveness of the developed catalyst in the process of condensation of PA with FA to MAA is high enough [4] and the potential implementation of this method replaces the two stages of the industrial process – condensation of propionic aldehyde with FA to methacrolein and low-selective oxidation stages to MAA by one stage – aldol condensation of PA with FA to MAA, which has significantly higher selectivity (93.5 %). As shown in Table 2, raw material costs using the developed catalyst under optimal conditions is 15.85 % lower than its costs using the existing method.

Conclusion

Thus, the optimal conditions of the process are: temperature – 593 K, contact time – 12 sec. Under these conditions, the conversion of PA per pass is 47.7%, yield of MAA is 44.6% and selectivity is 93.5%. The effectiveness of the developed catalyst in optimal conditions is sufficient for implementation.

Acknowledgements

The studies have been performed in frames of Project GP/F49/149 (President of Ukraine Grant for Young Scientists).

References

[1] Koichi Nagai. New developments in the production of methyl methacrylate // Applied Catalysis A: General. – 30 November 2001. – Volume 221, Issue 1-2. – P. 367-377.

[2] C.I. Carlson Jr., M.S. Decourcy, J.J.J. Juliette, assignee: Rohm and Haas Company, "Process for production of methacrylic acid", U.S. Patent 7253307, August 07, 2007.

[3] US, S. Watanabe, M. Oh-kita, assignee: Mitsubishi Rayon Co., Ltd., "Process for producing methacrolein and methacrylic acid", U.S. Patent 6346646, February 12, 2002.

[4] R.V. Nebesnyi, V.V. Ivasiv, V.M. Zhyznevskyy, Z.G. Pikh, "Metakrylova kyslota. Oderzhannia kondensatsiyeyu propionovoyi kysloty z formaldehidom u gazoviy fazi" [Methacrylic acid. Obtaining by propionic acid condensation with formaldehyde in gas phase] Khimichna Promyslovist Ukrayiny, vol. 108, no. 1, pp. 3-6, 2012 (in Ukrainian).

[5] R. Nebesnyi, V. Ivasiv, V. Zhyznevskyy, Y. Dmytruk, "Kondensatsiya propionovoyi kysloty z formaldehidom na katalizatorakh kyslotnogo typu u gazoviy fazi" [Gas-phase condensation of propionic acid with formaldehyde on acid-type catalysts] in Chemistry and Chemical Technology – 2010: Proceedings of the 1st International Conference of Joung Scientists, CCT-2010, Lviv, Ukraine, November 25-27, 2010. pp. 34-35.

[6] Dmytruk Y.V., Nebesnyi R.V. Sintez metakrilovoi kisloty geterogenno-kataliticheskoi kondensatsiei propionovoi kisloty s formaldehidom [Methacrylic acid synthesis be heterogeneous catalytic condensation of propionic acid with formaldehyde] // Himiya v sovremennom mire – 2011: Materialy V Vserossiyskoi konferentsii studentov i aspirantov, Saint Petersburg, Russia, April 18 – 22, 2011. pp. 303-304 [In Russian].

[7] Roman Nebesnyi, Volodymyr Ivasis, Viacheslav Zhyznevskyi, Yuliia Dmytruk. Kinetychni zakonomirnosti reaktsii aldolnoyi kondensatsiyi propionovoyi kysloty z formaldehidom na B_2O_3 – P_2O_5 – WO_3/SiO_2 katalizatori v gazoviy fazi" [Kinetic regularities of the aldol condensation reaction of propionic acid with formaldehyde on the B_2O_3 – P_2O_5 – WO_3/SiO_2 catalyst in the gas phase] in Chemistry and Chemical Technology – 2011: Proceedings of the 2nd International Conference of Young Scientists, CCT-2011, Lviv, Ukraine, November 24-26, 2011. pp. 34-35.