KINETIC INVESTIGATIONS OF HETEROGENEOUS REACTOR PROCESSES – OPTIMIZATION OF EXPERIMENTS

Adrian Szałek, Mirosław Szukiewicz*, Elżbieta Chmiel-Szukiewicz

Rzeszów University of Technology, Faculty of Chemistry, al. Powstańców Warszawy 6,
35-959 Rzeszów, Poland

A series of steps taken to determine a kinetic equation that describes hydrogenation of propene on nickel catalyst is presented in this study. Mixed factorial design approach, belongs to designing of experiments methods was used to plane experiments. The investigations showed that the method applied makes possible determination of the kinetic equation in a relatively fast and cheap manner since only a few measurement points is required. The equation obtained was verified experimentally and statistically. Both tests showed satisfactory precision of anticipated values of the process rate.

Keywords: kinetic equation, hydrogenation of propene, designing of experiments

1. INTRODUCTION

The study of chemical kinetics is concerned with the measurement and interpretation of the rates of chemical reactions. In contrast to thermodynamics it tracks what happens between initial and final states of reaction, and how quickly, the transition from one to the other occurs. This know-how is necessary to commercialize any chemical process, e.g. for proper designing of chemical reactors. Kinetic studies often connect with determination of reaction mechanism, so they can give a deeper insight into process nature. Determination of kinetic relationship for heterogeneous chemical processes is expensive, or time-consuming, or both. Expenditure of money, time, and other resources can be treated as a cost of research. One technique for cost reduction as well as increasing the efficiency of investigations is that of the statistically designed experiment, usually called designing of experiments (DoE). To show how simple and efficient this manner of planning experiments is, we propose the application of factorial-design method. This systematic, economical technique speeds up the kinetic problem solution by permitting evaluations to be made before completing all experiments. Additionally, it also indicates the relative importance of process variables and possible interactions. And, finally, unfamiliar in statistics researchers can easily learn the fundamentals and apply them. However, a little experience with software of Excel type or, better, Statistica could be very helpful.

The DoE is a planned approach for determining cause and effect relationships. The purpose of statistically designing an experiment is to collect the maximum amount of relevant information with a minimum cost. There are many types of DoE strategies. The first were originated at the end of the first half of the twenty century. The most popular in technical appliances seems to be fractional factorials. Detailed description of them presents Montgomery (2017). These methods assume that higher order interactions (those between three or more process variables) are not significant. The 2^k factorials and 3^k factorials design are most

often applied. Since heterogeneous kinetics is usually non-linear process (as the majority of chemical engineering processes) the 3^k design predominates.

The DoEs methods were discussed in several articles that concern kinetics of processes. Özbay et al. (2013), investigated the removal of remazol yellow dye from aqueous solution by adsorption on activated carbon. They made the attempt to optimize the operating conditions for remazol yellow removal process. They applied a full factorial design method to investigate the effect of pH, adsorbent dosage and initial dye concentration. The method presented was employed to choice of an effective and low-cost adsorbent (as an alternative to commercial activated carbons). Sen (2016), applied full factorial experiment design 3^k to determine process window for the Knelson concentrator for chromite ore beneficiation. Three factors (feed rate, centrifugal force and water flow rate) at three levels were applied to develop an empirical model to predict the process responses. The result obtained showed the strongest impact of fluidization water flow. Esfe et al. (2017), used a three-level factorial design to evaluate the effect of temperature, volume fraction and nanoparticle on thermal conductivity od MgO/water nanofluids. Authors developed empirical model describing thermal conductivity on nanofluid based on experimental results. The statistical analysis made revealed that all three parameters influence thermal conductivity coefficient and enabled developing a new correlation with regression coefficient. It is easily to observe that full factorial methods are quite often applied to various problems. For investigations of chemical kinetics of heterogeneous processes the same attempts were made, as well. E.g., application of a three-level factorial design to evaluation of the kinetic model and thermodynamic parameters was presented by Pachulski et al. (2012). The results of the measurements the authors fitted on different kinetic models to obtain the best fit. Based on that, the performance of a bypass reactor, running in parallel to an industrial C2-tail end-selective hydrogenation reactor, was successfully calculated.

However, 3^k factorials design reduces cost of determination of kinetic equation comparing with full factorial design ("classic" method that look completely at all factors included in the experimentation) we show that application of factorials of mixed levels (factors at two and three levels) leads to further reduction of cost without precision loss. This is the first goal of the work. The mixed factorial design method will be applied for the process of hydrogenation of propene on nickel catalyst. This important heterogeneous process is applicable as a model or reference reaction. Based on this process, e.g. Carturan et al. (1990) studied intrinsic catalytic activity and activation energy of nickel catalysts; Aaserud et al. (2004), tested promoted and unpromoted cobalt Fisher–Tropsch catalysts supported on different types of supports; Schweitzer et al. (2014) presented similar topic with respect to silica-supported single-site Zn(II) catalysts; next Ahmadigoltapeh et al. (2015) studied the performance of catalytic reaction for structured and conventional catalyst beds. Brandao et al. (2004) studied the kinetics of propylene hydrogenation in an isothermal batch reactor under isothermal conditions using palladium nanosized clusters as catalyst, and they found that experimental rate data are coherent with a Langmuir-Hinshelwood rate equation that involves competitive adsorption between reactants for the catalyst surface, with dissociative adsorption of hydrogen. And finally Szukiewicz et al. (2019) investigated formation of dead zones in catalysts pellets. Determination of kinetic equation for the mentioned process is the second goal of this work.

2. EXPERIMENT

The propylene hydrogenation reaction was undertaken in a pressurized, stainless-steel, tubular reactor (Microactivity-Efficient Unit, manufacturer: Process Integral Development Eng&tech, Madrid, Spain). A 0.006 g of well-crushed catalyst (90 - 120 μm) was mixed with 0.544 g of silica beads of the same fraction size to give a homogenous mixture and loaded to the reactor. The system was purged of air with hydrogen before heating to activation temperature (723 K). Catalyst was reduced by 50 ml/min hydrogen for 2 hours. Next, the reactor system was cooled to reaction temperature. The outlet gas stream was analysed

using a CALIDUS™101 Gas Chromatograph (manufacturer: Falcon Analytical, Lewisburg, WV, USA) exactly every 10 minutes. The range of process variables changes is presented in Table 1 while a scheme of measurement system is presented in Fig. 1.

Table 1. Process window

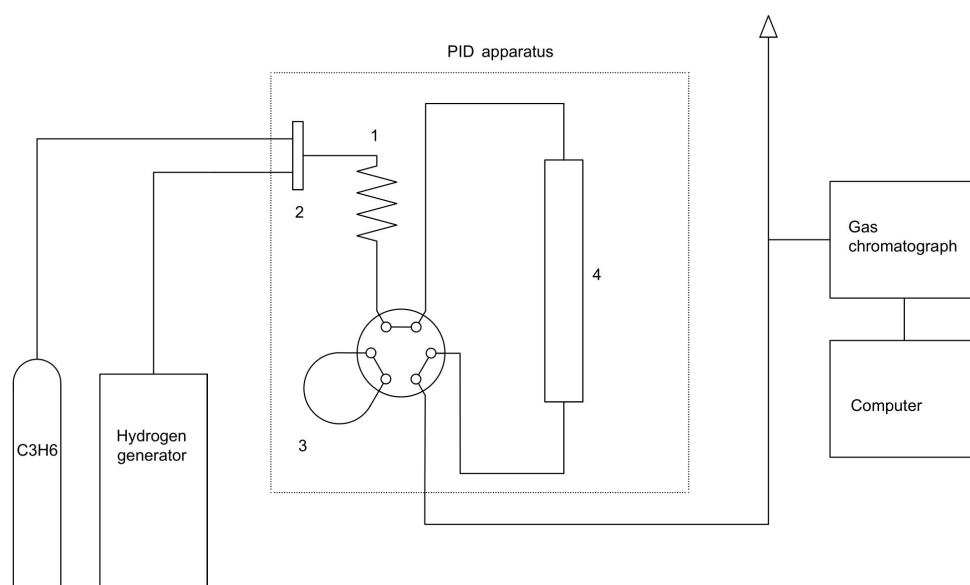| Parameters	Ranges
Pressure 10^{-5} [Pa]	1.2
Temperature [K]	320–350
Total flow 10^7 [m^3 s^{-1}]	5.4–6.1
Concentration of propene [%vol.]	8–20

Fig. 1. Scheme of the measurement system. 1 – pre-heater, 2 – mass flow controller, 3 – bypass loop, 4 – tubular reactor

3. RESULTS AND DISCUSSION

3.1. Mixed factorial design

All the presented below plans as well as analysis of results obtained were made using program Statistica 13.3. Functions predefined there makes solutions of the problem under consideration simpler and faster, and, in consequence, reasonably simplifies investigations. Obviously, application of the specialized software is not necessary, all tasks presented by Montgomery (2017), can be realized using a simple spreadsheet software or even without any software.

The process variables that affect propene hydrogenation process are as follows: temperature, total flow and propene concentration. The first variable, temperature, we accept as three level while the remaining as two levels variable. Taking into account the process window presented (Table 1) the designed plan of experiments is presented in the Table 2. In the last column the results of experimentally determined kinetic rate are included.

Table 2. Experimental determination of the process rate

No.	Total flow rate $\cdot 10^7$ [m^3/s]	Propene concentration [%]	Temperature [K]	Reaction rate [mol/(s·kg$_{cat}$)]
1	6.25	20	323	0.231
2	5.42	8	323	0.164
3	6.25	20	335	0.341
4	5.42	8	335	0.231
5	6.25	20	335	0.367
6	5.42	8	335	0.234
7	6.25	20	349	0.520
8	5.42	8	349	0.530

It is easily to observe that the designed plan of experiment is very simple. It includes only 8 points what shows that the number of necessary measurements is small comparing to full research plan (49 measurement points), or, even, comparing $3^k = 3$ full factorials design (27 measurement points). The small number of measurements points means considerable reduction costs included expenditure of money, time, and other resources.

The investigations made enables determination of kinetic equation for the process. A simple power-law equation that well fits experimental results has been used.

$$r_{C_3H_8} = k \cdot P_{C_3H_6}^n \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \tag{1}$$

The determined kinetic equation with confidence ranges of parameters is as follows

$$r_{C_3H_8} = (17.33 \pm 16.17) \cdot P_{C_3H_6}^{(0.55 \pm 0.09)} \cdot \exp\left(\frac{(-26320 \pm 3490)}{R \cdot T}\right) \tag{2}$$

In Table 3 the residuals obtained for Eq. (1) are presented.

Table 3. Residuals obtained for Eq. (1)

No.	$r_{C_3H_8}$ experimental	$r_{C_3H_8}$ predicted by Eq.(1)	Residuals for Eq.(1)
1	0.231	0.2447	–0.0132
2	0.164	0.1477	0.0159
3	0.341	0.3599	–0.0187
4	0.231	0.2173	0.0137
5	0.364	0.3599	0.0038
6	0.234	0.2173	0.0168
7	0.292	0.3104	–0.0185
8	0.530	0.5143	0.0157

In the next step the predictions of the Eq. (2) have been tested. If the predictions are correct, the points lie along a diagonal. It is easily to observe that the points anticipated lie near a diagonal. It indicates that the model described by Eq. (1) fits experimental results well.

Unfortunately, the frequency factor value uncertainties of are relatively large. It is an unpleasant consequence of reduction of the measurements points. For this reason we decided to verify predictions of Eq. (2).

3.2. Verification

To verify the kinetic equation obtained further experiments for selected values of process variables were made. Within the process window the additional measurement points were randomly chosen. The values of the process variables with determined kinetic rates are presented in Table 4.

Table 4. Experimental verification of Eq. (2) – data

No.	Reactant total flow rate $\cdot 10^7$ [m³/s]	Propene concentration [%]	Temperature [K]	Observed reaction rate [mol/(s·kg$_{cat}$)]	Predicted reaction rate [mol/(s·kg$_{cat}$)]	Residuals
1.	6.09	18	328	0.2721	0.2743	–0.0214
2.	5.81	14	322	0.2230	0.2000	0.0230
3.	6.25	12	349	0.3924	0.3855	0.0068
4.	6.25	10	343	0.3456	0.3000	0.0456

The residuals presented are of the same order of magnitude as those obtained in the model derivation step. It indicates that randomly chosen points within the process window reaction rate is predicted with high precision, despite the fact that the number of measurement points was small, more than 6 times less than those expected for a full research plan and more than 3 times less than those expected for a full factorial plan. Further proof of our method correctness is presented in Fig. 2.
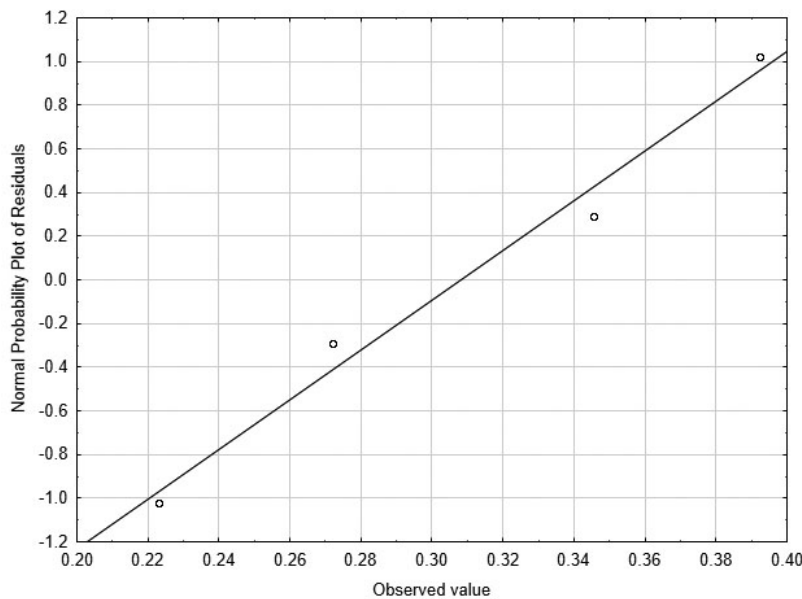

Fig. 2. Observed versus predicted values for Eq. (1)

In Fig. 3, the points lie along the straight line; it confirms that the model correctly describes the experiment. Both tests made confirmed that Eq. (2) anticipates real process rate well for some randomly selected points from the range of operating conditions, the deviations observed are acceptable.
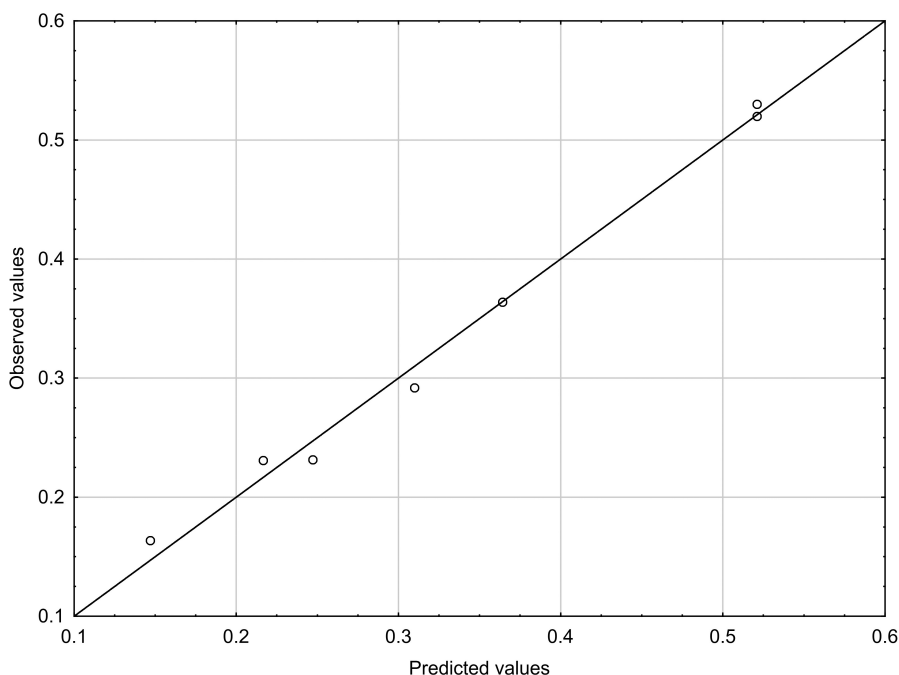

Fig. 3. Normal probability plot of residuals

To summarize investigations made the attention on the time of experiments conduction have to be considered. A simple comparison of time required to conduct the experiments is aware of DoE's usage profits. Estimated time required for experiments is about 3500 min., 1900 min., and, 570 min. for full research plan, for full factorial plan, and, for mixed factorial plan, respectively. Time of experiment was estimated taking into account the time necessary to obtain stationary conditions in the reactor and to conduct analysis; idle time was not included, however it should be rather obligatory in the first two cases. Large reduction of experiment duration will, obviously, reflect in money saving.

Investigations made will hereafter be used to obtain deeper insight into process nature and for better understanding the elementary surface processes.

4. CONCLUSION

The presented results unambiguously indicate that DoE methods can significantly reduce expenditure of money, time, and other resources at kinetic investigations. It is very important for heterogeneous processes since their complex nature: experiments are rather expensive and their conduction makes many troubles for investigators. So, any way to improve investigations is valuable. The mixed factorial design method makes possible further reduction of experiments number comparing the 3^k full factorial method without precision loss.

The determined kinetic equation for propene hydrogenation process on nickel catalyst indicates that the semi-empirical equation well describes the process rate and indicates of further studies are necessary for better understanding the process under consideration.

SYMBOLS

E_a activation energy, J mol^{-1}K^{-1}

k frequency factor, mol m^{-3} Pa^{-n} s^{-1}

$P_{C_3H_8}$ partial pressure, Pa

$r_{C_3H_8}$ reaction rate, mol/s

R gas constant, J mol^{-1}K^{-1}

T temperature, K

REFERENCES

Aaserud C., Hilmen A.-M., Bergene E.S.E., Schanke D., Holmena A., 2004. Hydrogenation of propene on cobalt Fischer–Tropsch catalysts. *Catal. Lett.*, 94, 171–176. DOI: 10.1023/B:CATL.0000020541.28174.c7.

Ahmadigoltapeh, S., Mehranbod, N., Halimejani, H.Z., 2015. Propylene hydrogenation through structured and conventional catalyst beds: Experiment and modelling. *J. Nat. Gas Sci. Eng.*, 27, 822–830. DOI: 10.1016/j.jngse.2015.09.030.

Brandao L., Fritsch D., Madeira LM., Mendes A.M., 2004. Kinetics of propylene hydrogenation on nanostructured palladium clusters. *Chem. Eng. J.*, 103, 89–97. DOI: 10.1016/j.cej.2004.07.008.

Carturan G., Enzo S., Ganzerla R., Lenarda M., Zanoni R., 1990. Role of solid-state structure in propene hydrogenation with nickel catalysts. *J. Chem. Soc. Faraday Trans.*, 86, 739–746. DOI: 10.1039/ft9908600739.

Esfe M.H.,. Rsotamian H, Shabani-Samghabadi A., Arani A.A.A., 2017. Application of three-level general factorial design approach for thermal conductivity of MgO/ water nanofluids. *Appl. Therm. Eng.*, 127, 1194–1199. DOI: 10.1016/j.applthermaleng.2017.07.211.

Montgomery D.C., 2017. *Design and analysis of experiments*. 9th ed., Wiley.

Özbay N., Yargıç A.Ş., Yarbay-Şahin R.Z., Önal E., 2013. Full factorial experimental design analysis of reactive dye removal by carbon adsorption. *J. Chem.*, 234904. DOI: 10.1155/2013/234904.

Pachulski A., Schödel R., Claus P., 2012. Kinetics and reactor modeling of a Pd-Ag/Al$_2$O$_3$ catalyst during selective hydrogenation of ethyne. *Appl. Catal., A*, 445–446, 107–120. DOI: 10.1016/j.apcata.2012.08.018.

Schweitzer NM., Hu B., Das U., Hacksung K., Greeley J., Curtiss L.A., Stair P.C., Miller J.T., Hock A.S., 2014. Propylene hydrogenation and propane dehydrogenation by a single-site Zn^{2+} on silica catalyst. *ACS Catal.*, 4, 1091–1098. DOI: 10.1021/cs401116p.

Sen G.A., 2016. Application of full factorial experimental design and response surface methodology for chromite beneficiation by Knelson concentrator. *Minerals*, 6, 5. DOI: 10.3390/min6010005.

Szukiewicz M., Chmiel-Szukiewicz E., Kaczmarski K., Szałek A., 2019. Dead zone for hydrogenation of propylene reaction carried out on commercial catalyst pellets. *Open Chem.*, 17, 295–301. DOI: 10.1515/chem-2019-0037.