

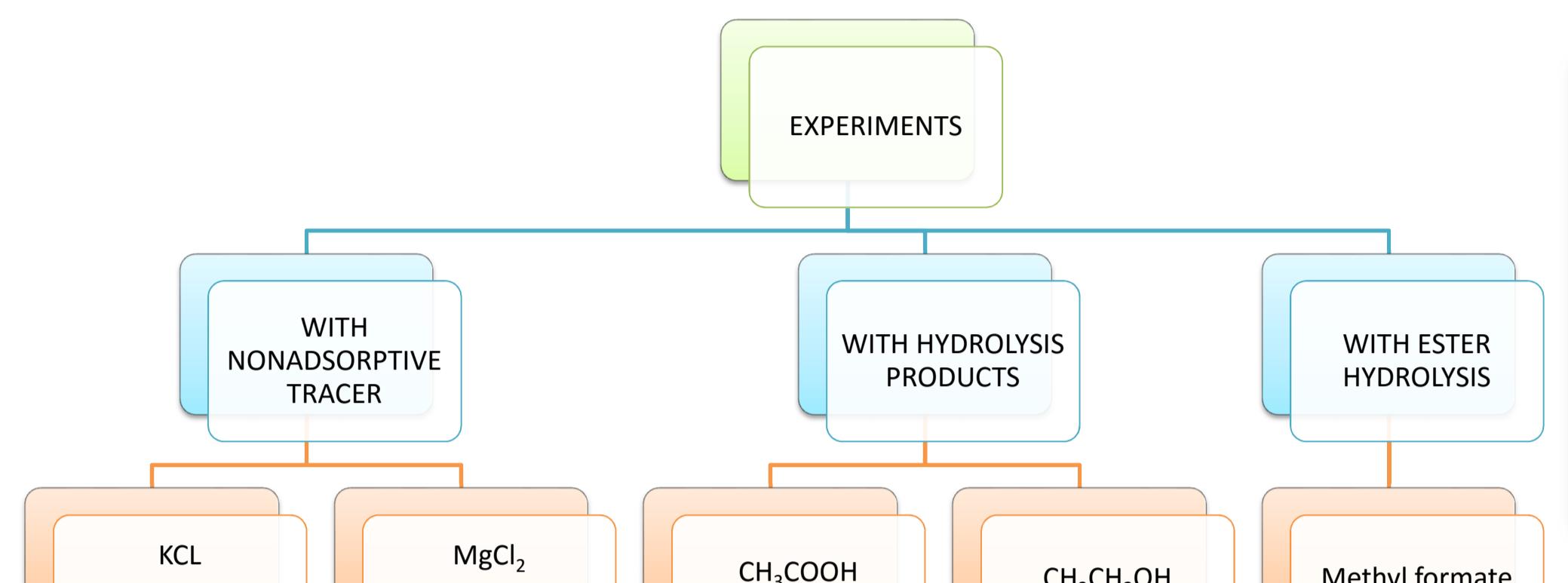
Anna Ostaniewicz - Cydzik, Krzysztof Wróblewski, Eugeniusz Molga

Methyl formate hydrolysis performed in chromatographic reactor. Simulation and experimental results.

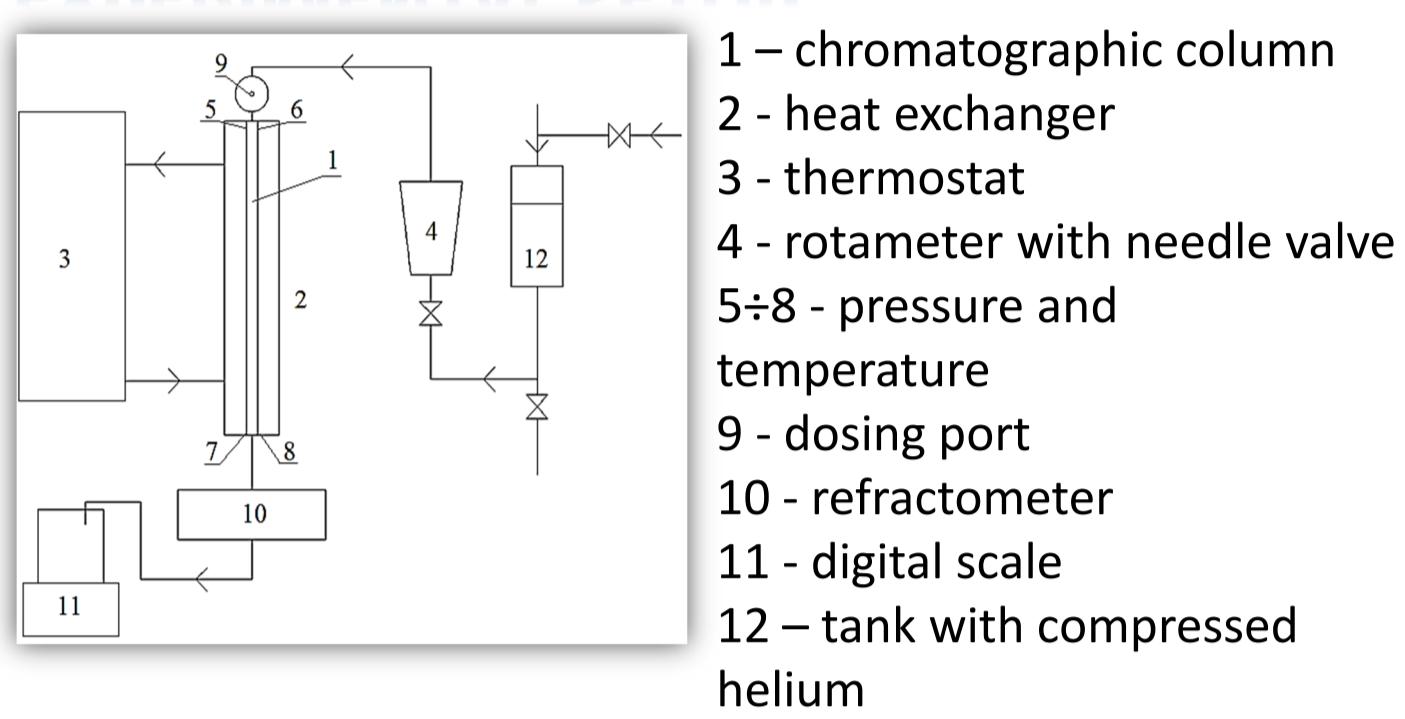
INTRODUCTION

Large part of goods manufactured today were at some point products of one of the variety of chemical reactions. These reactions run in very broad range of process parameters and proper reactor design is fundamental for achieving high yields and economy of processes. Number of high value substances are produced in reversible reactions as mixtures of substrates and products. Separation of this mixtures may account for the majority of manufacturing costs, especially when it comes to high purity products. Integration of chemical reaction with separation in one apparatus may bring noticeable benefits. Presented work is focused on modeling process of reactive chromatography, which combines chemical reaction with simultaneous chromatographic separation. In general, different affinity of reagents to fixed adsorptive bed is used to instantaneously separate products. Therefore, high yield is achieved and high purity products leave the chromatographic column one after another. This type of reactor is applied in petrochemical synthesis, pharmacy, optically active ingredients and esters industries, especially when standard separation techniques are inefficient or difficult to implement.

EXPERIMENTAL METHODOLOGY



EXPERIMENTAL SETUP



Outputs from temperature, pressure, weight and refractive index sensors were recorded with PC class computer with appropriate software. The reactor column was 400 mm high, and 10 mm in diameter.

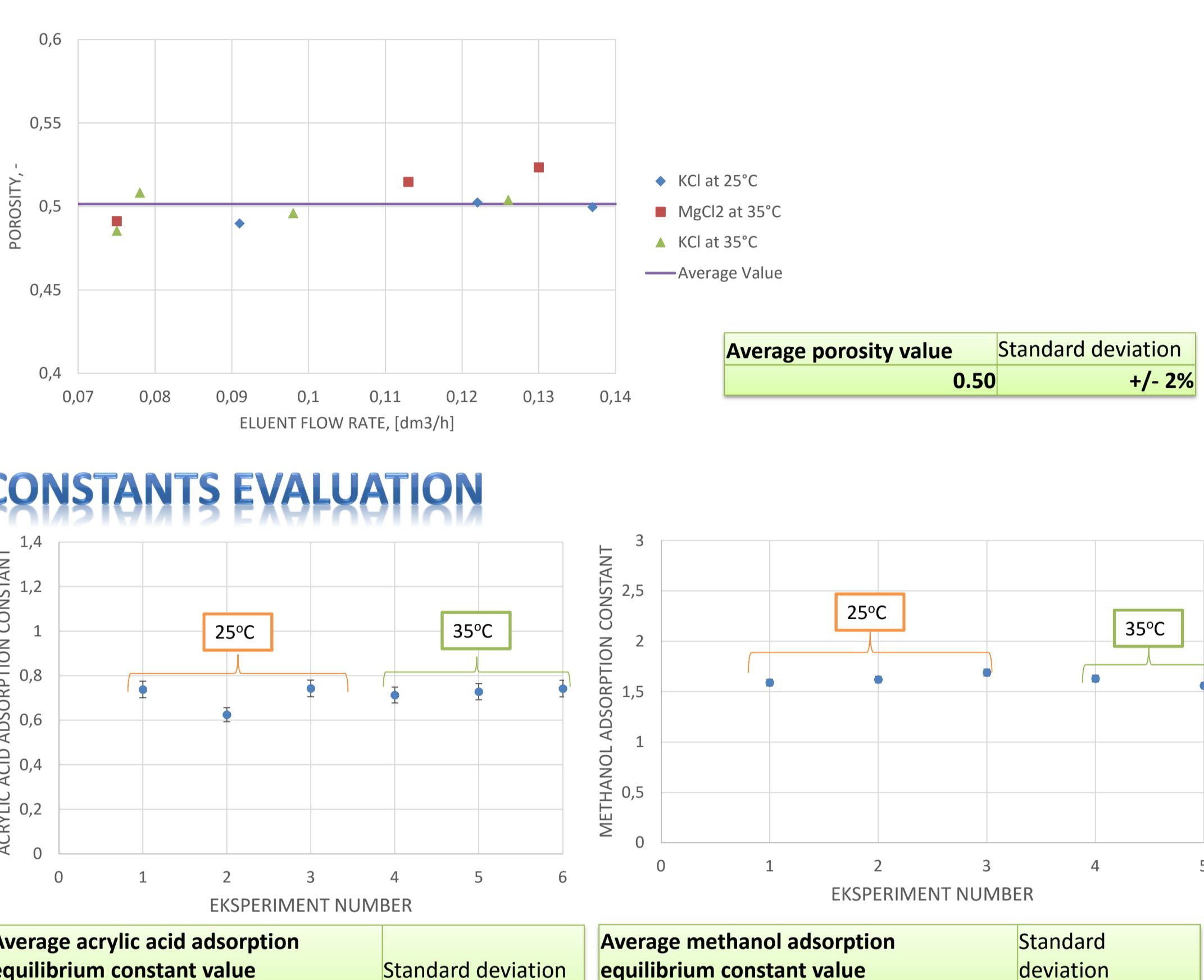
EXPERIMENTAL RESULTS

BED POROSITY EVALUATION

Run	Tracer	Q_e , dm ³ /h	T, °C	Retention time	Porosity
T1	KCl	0,137	25	411	0,50
T2	KCl	0,122	25	466	0,50
T3	KCl	0,091	25	607	0,49
T4	KCl	0,126	35	453	0,50
T5	KCl	0,098	35	575	0,49
T6	KCl	0,075	35	733	0,49
T7	MgCl ₂	0,075	35	740	0,49
T8	MgCl ₂	0,113	35	513	0,51
T9	MgCl ₂	0,130	35	457	0,52

THE ADSORPTION EQUILIBRIUM CONSTANTS EVALUATION

Run	Q_e , dm ³ /h	T, °C	Retention time	Adsorption equ. const. K_i
K1	0,092	25	1064	0,74
K2	0,112	25	754	0,63
K3	0,138	25	715	0,74
K4	0,086	35	1121	0,71
K5	0,109	35	892	0,73
K6	0,142	35	692	0,74
M1	0,092	25	1592	1,59
M2	0,122	25	1212	1,62
M3	0,138	25	1098	1,69
M4	0,110	35	1348	1,63
M5	0,138	35	1047	1,56



SIMULATION METHODOLOGY

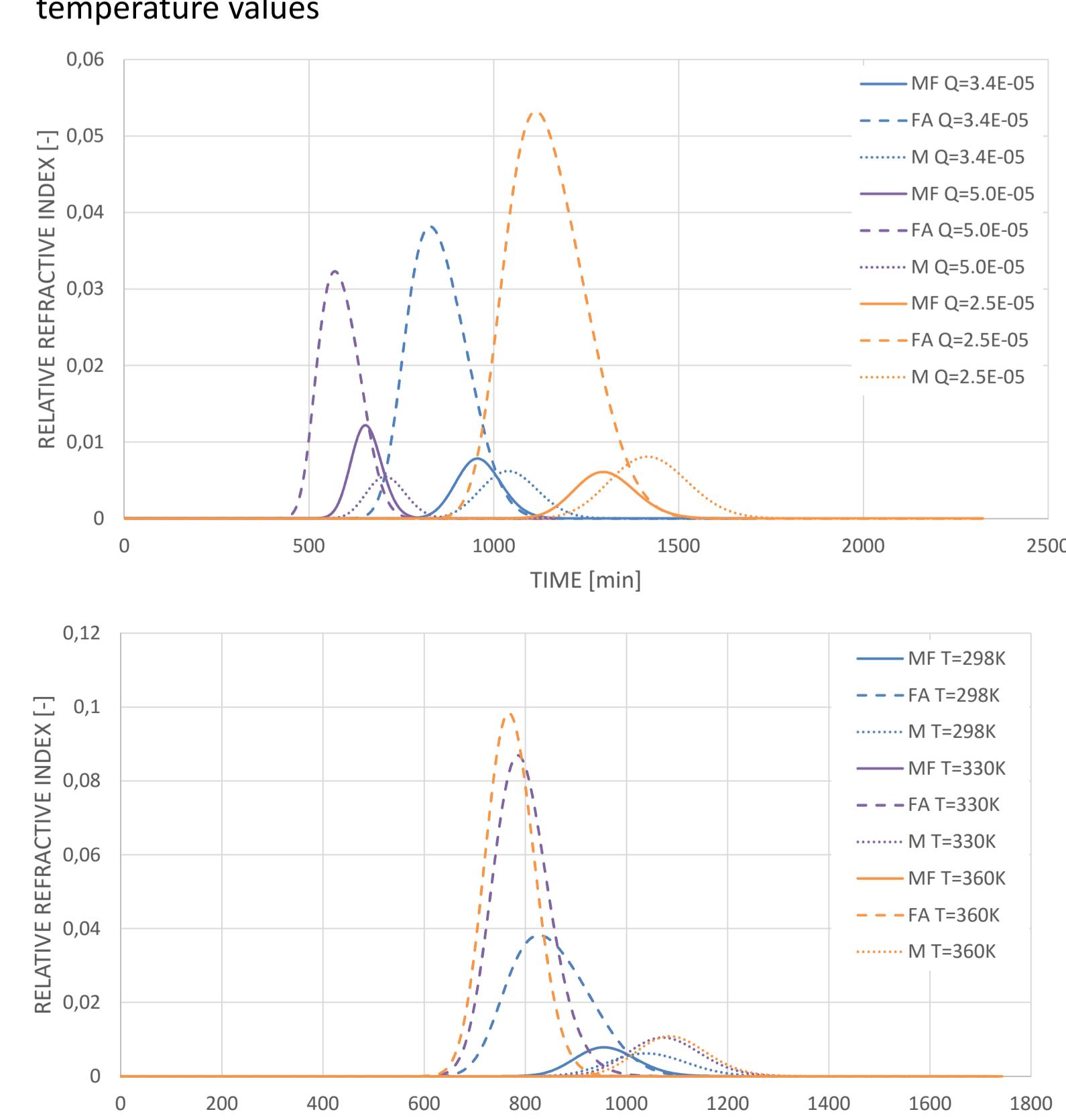


gPROMS Model Builder® version 4.0.0

Presented mathematical model of methyl formate hydrolysis performed in fixed bed chromatographic reactor was implemented with use of commercial software "general PROcess Modeling System (gPROMS®)", version 4.0.0 from Process System Enterprise. gPROMS Model Builder® gives wide range of possibilities of simulation such as simulated process performing, parameter estimation, schedule building and much more

SIMULATION RESULTS

Influence of two parameters: eluent flow rate Q and temperature T were investigated using the FBCR simulation. Simulations were performed for three different flow rate values and three different temperature values

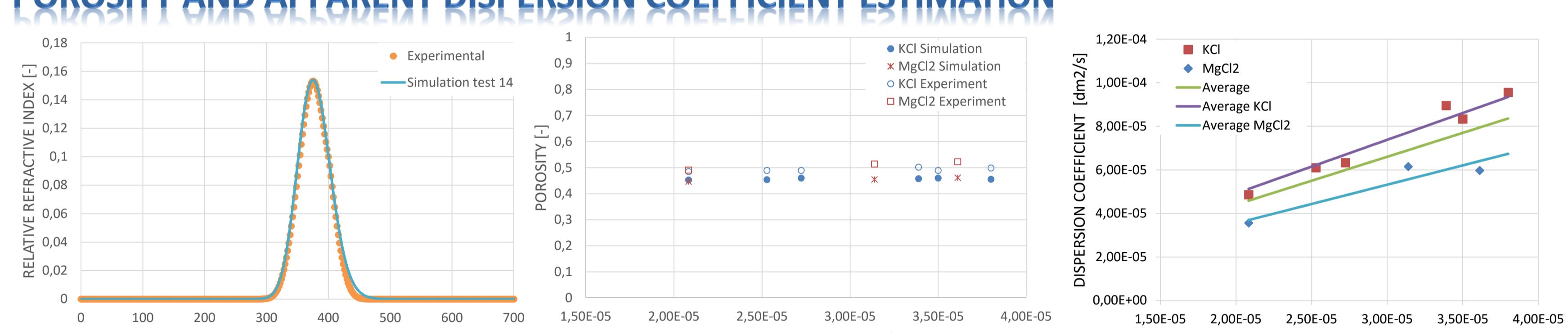


Flow rate changes

Temperature changes

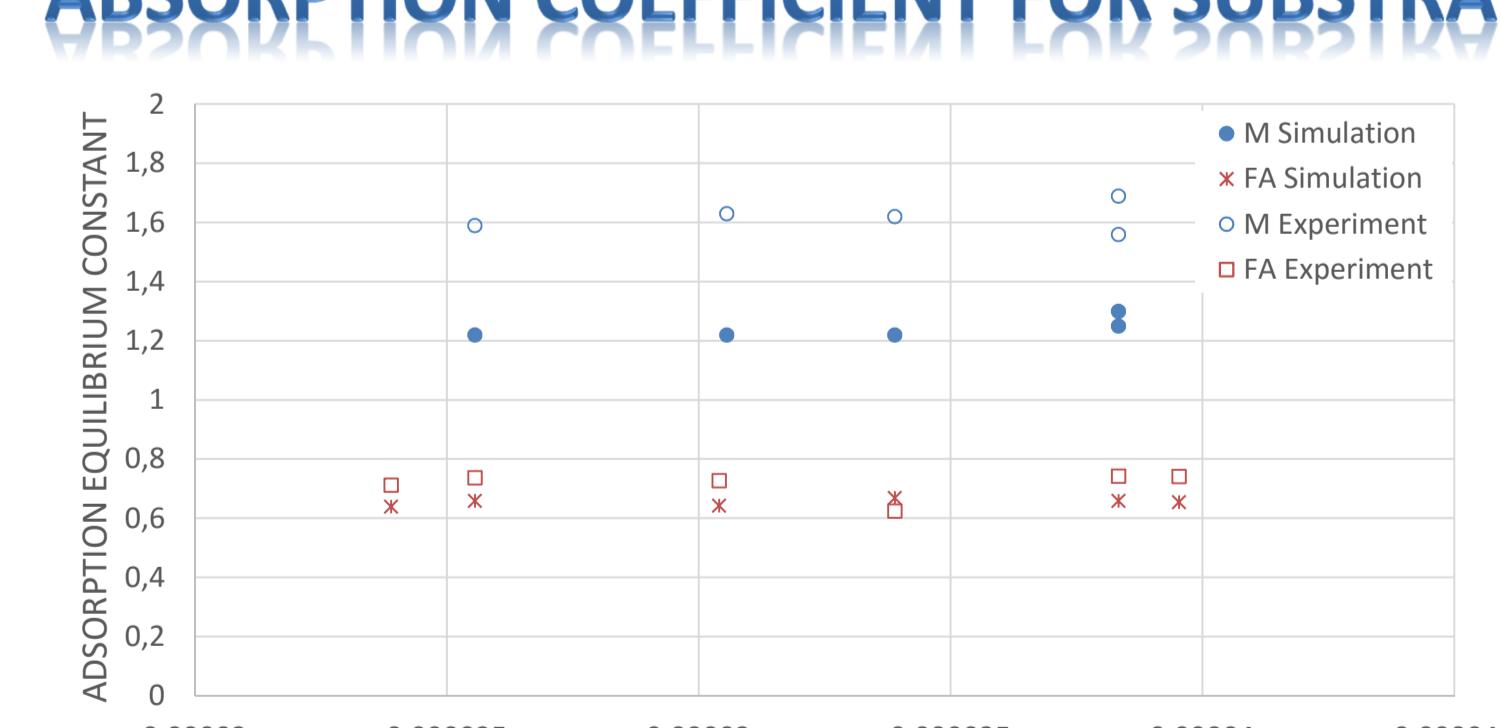
PARAMETER ESTIMATION RESULTS

POROSITY AND APPARENT DISPERSION COEFFICIENT ESTIMATION

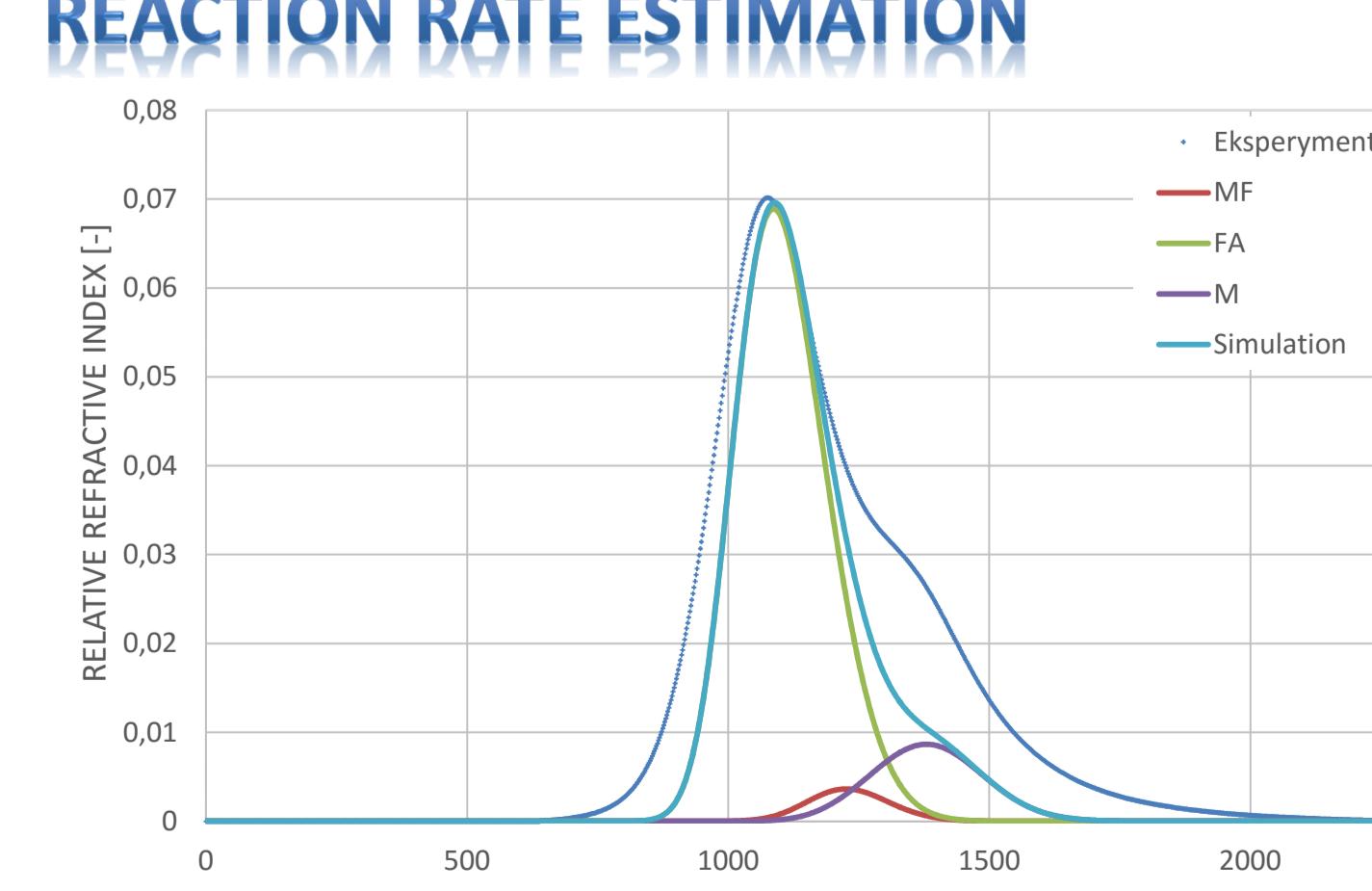


Based on experimental data calculated with statistical moment method, parameters estimation was performed. Simulated process was a tracer distribution in chromatographic column. Tracers were non-adsorbing and non-reacting substances, so only apparent dispersion and volume porosity effect appeared in simulations. In performed simulations the flow rate and temperature are in accordance with experimental parameters.

ABSORPTION COEFFICIENT FOR SUBSTRATES ESTIMATION



REACTION RATE ESTIMATION



Absorption coefficient for methanol and formic acid was estimated. Simulations were carried out in non-reactive setup, separately for methanol and formic acid. Based on previous simulations, average bed porosity and dispersion coefficient was implemented in the model. Methanol adsorption coefficient is slightly lower for simulation in comparison with experimental results. There is almost no difference between formic acid adsorption coefficients obtained from simulation and from experimental data.

Parameters	Estimated values	Standard deviation
Methanol experimental adsorption coefficient	1.62	+/- 2%
Methanol simulation adsorption coefficient	1.24	+/- 2%
Formic acid experimental adsorption coefficient	0.71	+/- 5%
Formic acid simulation adsorption coefficient	0.66	+/- 1%

Reaction rate for methyl formate hydrolysis is defined by several parameters: reaction kinetic constant, equilibrium constant and adsorption. From previous simulations adsorption coefficients for methanol and formic acid, bed porosity, apparent dispersion coefficient were estimated. Methyl formate hydrolysis in FBCR model was implemented and was used to estimate reaction parameters: k_0 - pre-exponential factor and E - reaction activation energy.

Parameters	Estimated values	Standard deviation	Literature values
Pre-exponential factor k_0	9500 [L/mol min]	+/- 1%	8516.7 [L/mol min]
Reaction activation energy	47733 [J/mol]	+/- 1%	62000 [J/mol]

* Vu T.D., Seidel-Morgenstern A., 2011, Quantifying temperature and flow rate effects on the performance of a fixed-bed chromatographic

Journal of Chromatography A, 1218, 8097-8109

CONCLUSION

A number of parameters were calculated with statistical moments method. Based on experiments with non-adsorbing, non-reactive tracers KCl and MgCl₂ bed porosity $\epsilon=0,500[-]$ was calculated. Experimental data for adsorption processes with methanol and formic acid were used to evaluate adsorption coefficients for both products of methyl formate hydrolysis $K_M=1,62[-]$ and $K_{FA}=0,71[-]$. Implemented model was used to estimate all unknown parameters in the process. Bed porosity obtained from simulations was $\epsilon=0,46[-]$ and it was slightly lower in comparison with experimental data. Apparent dispersion coefficient was estimated based on simulations with tracer and described as $Dax=2,46 \cdot Q$. Simulation carried out for pure methanol and pure formic acid resulted in acquiring adsorption coefficients $K_M=1,24[-]$ and $K_{FA}=0,66[-]$. Apart from chromatographic process characteristic, reaction parameters were estimated with implemented mathematical model. Arrhenius equation was chosen as model of temperature influence. Pre-exponential factor $k_0=9500$ [L/mol min] and reaction activation energy $E=47733$ [J/mol] were received and compared with values obtained from literature. Conclusion was that the presented mathematical model with good likelihood can simulate process of methyl formate hydrolysis in fixed-bed chromatographic reactor and can be recommended for obtaining process parameters.