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*Published in:*  
Chemical Engineering Journal

*DOI:*  
[10.1016/j.cej.2019.122811](https://doi.org/10.1016/j.cej.2019.122811)

Published: 15/02/2020

*Document Version*  
Accepted author manuscript

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*Please cite the original version:*

Murzin, D., Saleem, F., Wärnå, J., & Salmi, T. (2020). Kinetic modelling of heterogeneous catalytic oxidation of furfural with hydrogen peroxide to succinic acid. *Chemical Engineering Journal*, 382, –. Article 122811. <https://doi.org/10.1016/j.cej.2019.122811>

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**Kinetic modelling of heterogeneous catalytic oxidation of furfural with hydrogen peroxide  
to succinic acid**

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**Abstract**

Kinetic modelling of furfural oxidation with hydrogen peroxide over a fibrous polymer-supported sulphonic acid catalyst was performed. The proposed kinetic model describes the concentration profiles of the reactants, intermediates and products as a function of reaction time at different temperature. Parameter estimation has been performed followed by their statistical analysis showing that the kinetic parameters were statistically well identified.

**Keywords:** Furfural oxidation; hydrogen peroxide; Smopex-101; kinetics; modelling

## 1. Introduction

Lignocellulosic biomass originating from wood is an abundant non-food alternative feedstock for chemical and petrochemical industries. An important compound, which can be derived from lignocellulose is furfural, obtained by for example acid-catalyzed dehydration of xylose [1]. There are several possible options to valorize furfural including its transformation to succinic acid [2]. The latter was regarded as one of the platform chemicals [3] being considered as a starting compound for a number of industrially important chemicals including  $\gamma$ -butyrolactone, 1,4-butanediol and tetrahydrofuran [4].

Biobased succinic acid production comprising fermentation of sugars (i.e. hexoses and pentoses) has attracted a lot of attention as a viable alternative to fossil-based succinic acid [5]. Inhibition of microorganisms acting as a biocatalyst through accumulation of the final product [6], as well as high downstream processing costs are evident drawbacks even if the yields of the desired product are rather good.

While liquid phase aerobic oxidation of furfural with a homogenous catalyst gives maleic acid as the main product and oligomers of furfural as significant side-products [7], application of hydrogen peroxide in combination with a simple sulfonic acid based heterogeneous acid catalysts was reported to give succinic acid [8-11].

In [12] kinetic regularities in furfural oxidation with hydrogen peroxide over a fibrous polymer-supported sulphonic acid catalyst (Smopex-101) were reported focusing on the influence of reaction temperature, initial concentration of hydrogen peroxide and furfural and the contribution of hydrogen peroxide self-decomposition. The catalyst was Smopex-101, which is a fibrous non-porous material with sulphonic acid functional groups grafted on poly (ethylene-graft-polystyrene)

having the mean fiber diameter of ca. 0.01 mm , the average fiber length of 4 mm and the cation exchange capacity by dry weight between 2.1-3.6 (mm<sub>eq</sub>/g) [13]. A range of intermediates and products were formed. Kinetic analysis in [12] was limited to only modelling of furfural and hydrogen peroxide disappearance without description of concentration profiles for other compounds. In the current work, we would like to revisit the reaction kinetics and propose a model able to account also for concentration of intermediates and products.

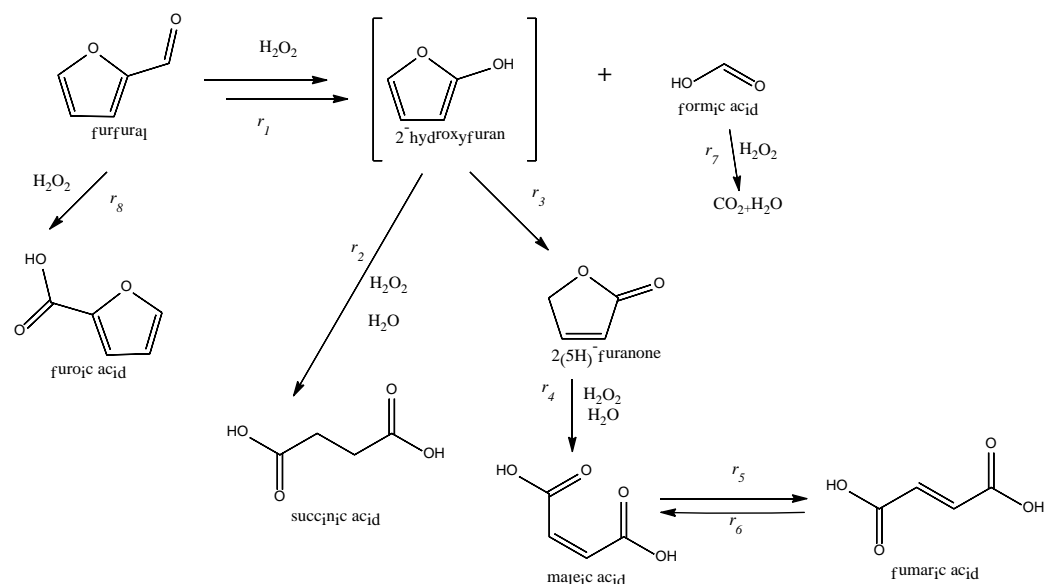
## 2. Experimental

The experimental work was described in the previous publication [12]. Here only the pertinent details will be given. The reactants - furfural ( $\geq 98$  wt%) was purchased from Sigma Aldrich. Potential products and intermediates were obtained from various suppliers and used as standards in GC analysis. Smopex-101 catalyst was supplied by Johnson Matthey.

Experiments were performed in a three neck isothermal glass reactor (100 ml), which was coupled to a reflux condenser, a mechanical agitator and a heating jacket. Stirring speed of 500 rpm as used to suppress external mass transfer limitations. As the reaction mixture reached the desired temperature, hydrogen peroxide was poured from the sampling line into the reactor. Gas and liquid phase samples from the reactor were withdrawn at regular intervals for quantitative analysis of the reaction mixture by off-line gas chromatography for gaseous products and off-line HPLC. Details of analytic procedure are available in [12]. The temperature range of 313-363K was investigated.

## 3. Reaction network

For kinetic modelling a reaction mechanism proposed in [11] was adapted (Figure 1).



**Figure 1.** A simplified reaction scheme I of furfural transformation to products [11].

Succinic acid was predominantly formed with a rather high selectivity. Side reactions, leading to formic acid and carbon dioxide, were accelerated when furfural conversion was exceeding ca. 75%. Formic acid was the first stable product obtained by the Baeyer-Villiger furfural oxidation. Such oxidation implies that the first step in oxidation is formation of furanol formate ester (not shown in Figure 1), which is then hydrolysed with formation of 2-hydroxyfuran (not experimentally observed) and formic acid (reaction  $r_1$ ). This former compound can be isomerized to 2(3H)-furanone (not observed) which is further oxidized to succinic acid (reaction  $r_2$ ). An alternative part is formation of 2(5H)-furanone (reaction  $r_3$ ) from of 2-hydroxyfuran with subsequent oxidation to maleic acid (reaction  $r_4$ ). The latter undergo reversible isomerization to fumaric acid (reactions  $r_5$  and  $r_6$ ). Formic acid can be further oxidized to carbon dioxide (reaction  $r_7$ ), while other compounds mentioned above can generate low carbon number components, including those compounds present in trace amounts in HPLC: lactic, hydroxyacetic, 4-oxopentanoic, oxalic, 3-hydroxypropanoic, glyceric, glutaric, L-threonic, 2,3,4-trihydroxybutyric,

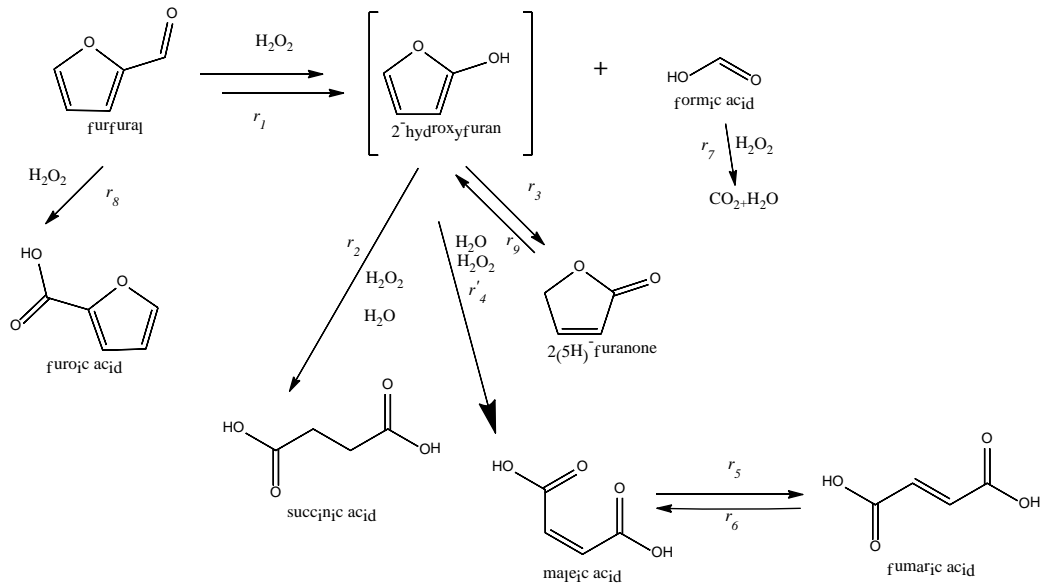
tartaric, 4,4-dihydroxybutenoic and 2-hydroxybut-2-enedioic acids. Furoic acid is formed from furfural (reaction  $r_8$ ) without further conversion to other products.

When the temperature was increasing the yields of 2(5H)-furanone and maleic acid started to decrease, concomitant with a decrease of carbon content in the liquid phase and an increase in the gas phase products. Higher temperatures can also give more profound decomposition of hydrogen peroxide.

In [12] the catalyst reuse was performed showing a minor difference between successive runs with the same catalyst. Therefore, catalyst deactivation can be excluded from modelling.

The reaction network in Figure 1 implies that initially furfural is oxidized with hydrogen peroxide and selectivity towards succinic acid is low in line with experimental observations. As the reaction progresses selectivity towards succinic acid is increasing. Previously [12] it was demonstrated that the contribution of the non-catalytic reaction in the presence of catalyst is minor and thus it can be discarded from the catalytic model.

A somewhat different approach for the reaction mechanism was considered in [12], where 2-(5H) furanone was not considered to be an intermediate in generation of maleic acid. The latter can be suggested to be formed from 2-hydroxyfuran or 2-(3H) furanone. The reaction scheme corresponding to this suggestion is shown in Figure 2.



**Figure 2.** A reaction scheme II of furfural transformation to products with direct formation of maleic acid [11].

### Kinetic model and parameter estimation

According to the reaction steps in Figure 1 the rate expressions of each step can be written in a following way for Scheme 1:

$$r_1 = k_1 C_F C_{H_2O_2} \rho_B \quad (1)$$

$$r_2 = k_2 C_{2HF} C_{H_2O_2}^{n_2} \rho_B \quad (2)$$

$$r_3 = k_3 C_{2HF} \rho_B \quad (3)$$

$$r_4 = k_4 C_{HFO} C_{H_2O_2}^{n_4} \rho_B \quad (4)$$

$$r_5 = k_5 C_{MA} \rho_B \quad (5)$$

$$r_6 = k_6 C_{FumA} \rho_B \quad (6)$$

$$r_7 = k_7 C_{FoA} C_{H_2O_2} \rho_B \quad (7)$$



$$r_8 = k_8 C_F C_{H_2O_2} \rho_B \quad (8)$$

Where  $\rho_B$  is the catalyst bulk density, and  $k_i$  are the respective reaction rate constants. The following notation was used above: furfural (F), formic acid (FoA), 2-hydroxyfuran (2HF), 2-(5H) furanone (HFO), fumaric acid (FumA) and maleic acid (MA). The equations for the reaction rates do not include adsorption of reactants on the surface of the catalyst assuming their low coverage in line with almost first order kinetics in line with experimental observation. Because samples (0.5 mL) were periodically taken out from the reactor, this resulted in an increase of the catalyst bulk density in the reactor. Such changes were taken into account in kinetic modelling. For the steps 2 and 4 reaction orders in hydrogen peroxide deviating from unity were considered in line the stoichiometric requirements. Mechanistic implications of such reaction orders will be discussed below.

For the Scheme 2 equations (1-3) and (5-8) are valid, while kinetic expressions for two other steps are

$$r'_4 = k'_4 C_{2HF} C_{H_2O_2}^{n_1} \rho_B \quad (9)$$

$$r_9 = k_4 C_{HFO} \rho_B \quad (10)$$

The generation equations for these and other compounds present in non negligible amounts, e.g. hydrogen peroxide, succinic acid (SA) and furoic acid (FurA), thus have the form for Scheme 1

$$\begin{aligned} -\frac{dC_F}{dt} &= r_8 + r_1; \quad \frac{dC_{FurA}}{dt} = r_8; \quad \frac{dC_{2HF}}{dt} = r_1 - r_2 - r_3; \quad \frac{dC_{SA}}{dt} = r_2; \quad \frac{dC_{HFO}}{dt} = r_3 - r_4; \quad \frac{dC_{MA}}{dt} = r_4 - r_5 + r_6; \\ \frac{dC_{FumA}}{dt} &= r_5 - r_6; \quad \frac{dC_{FoA}}{dt} = r_1 - r_7; \quad -\frac{dC_{H_2O_2}}{dt} = r_1 + r_2 + r_4 + r_7 + r_8 \end{aligned} \quad (11)$$

and Scheme 2

$$\begin{aligned}
-\frac{dC_F}{dt} &= r_8 + r_1; & \frac{dC_{FurA}}{dt} &= r_8; & \frac{dC_{2HF}}{dt} &= r_1 - r_2 - r_3 - r_4 + r_9; & \frac{dC_{SA}}{dt} &= r_2; & \frac{dC_{HFO}}{dt} &= r_3 - r_9; \\
\frac{dC_{MA}}{dt} &= r_4 - r_5 + r_6; & \frac{dC_{FumA}}{dt} &= r_5 - r_6; & \frac{dC_{FoA}}{dt} &= r_1 - r_7; & -\frac{dC_{H_2O_2}}{dt} &= r_1 + r_2 + r_4 + r_7 + r_8
\end{aligned} \quad (13)$$

The parameter estimation was carried out with a software ModEst [13]. The objective function  $\theta$

$$\theta = \sum_{i=1}^n (C_{\text{exp},i} - C_{\text{mod},i})^2 \quad (14)$$

where  $C_{\text{exp},i}$  and  $C_{\text{mod},i}$  are the experimental and calculated values, was minimized by using hybrid simplex and Levenberg-Marquardt algorithms, which resulted in a very good description of the experimental observations. The coefficient of determination  $R^2$  defined as follows

$$R = \left(1 - \frac{\sum_{i=1}^n (C_{\text{exp},i} - C_{\text{mod},i})^2}{\sum_{i=1}^n (C_{\text{exp},i} - C_{\text{mean}})^2}\right) * 100\% \quad (15)$$

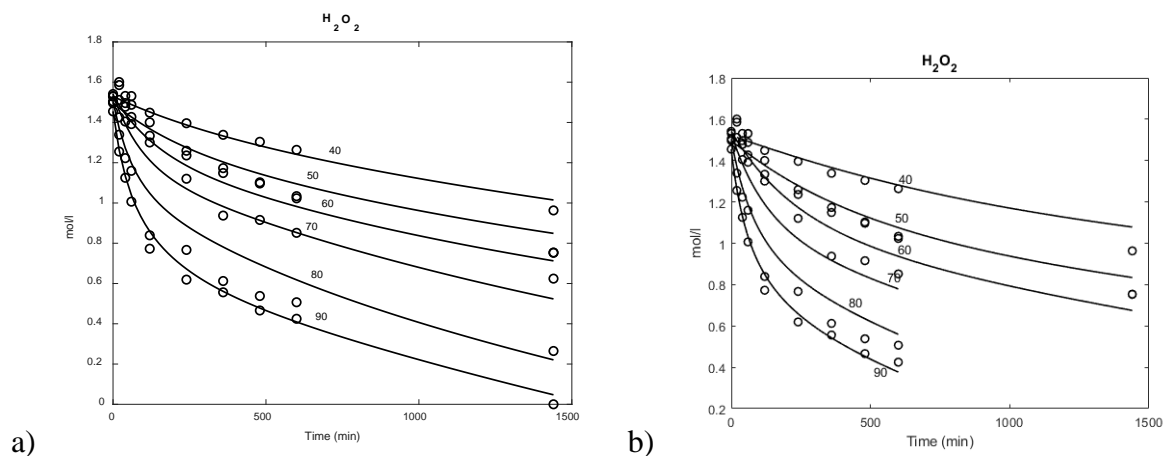
compares the model performance with respect to the variance of all experimental points. In eq. (15)  $C_{\text{mean}}$  denotes the mean value of all observations. A good deterministic model adequately describing the reaction kinetics should have a high value of coefficient of determination, typically exceeding 95%. In the current case this value was equal to 99.06% for Scheme 1 and 99.15% for Scheme 2.

The modified Arrhenius equation taking into account the influence of reaction temperature on the reaction rate constants was used

$$k = k_0 e^{-\frac{E_{\text{act}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ave}}}\right)} \quad (16)$$

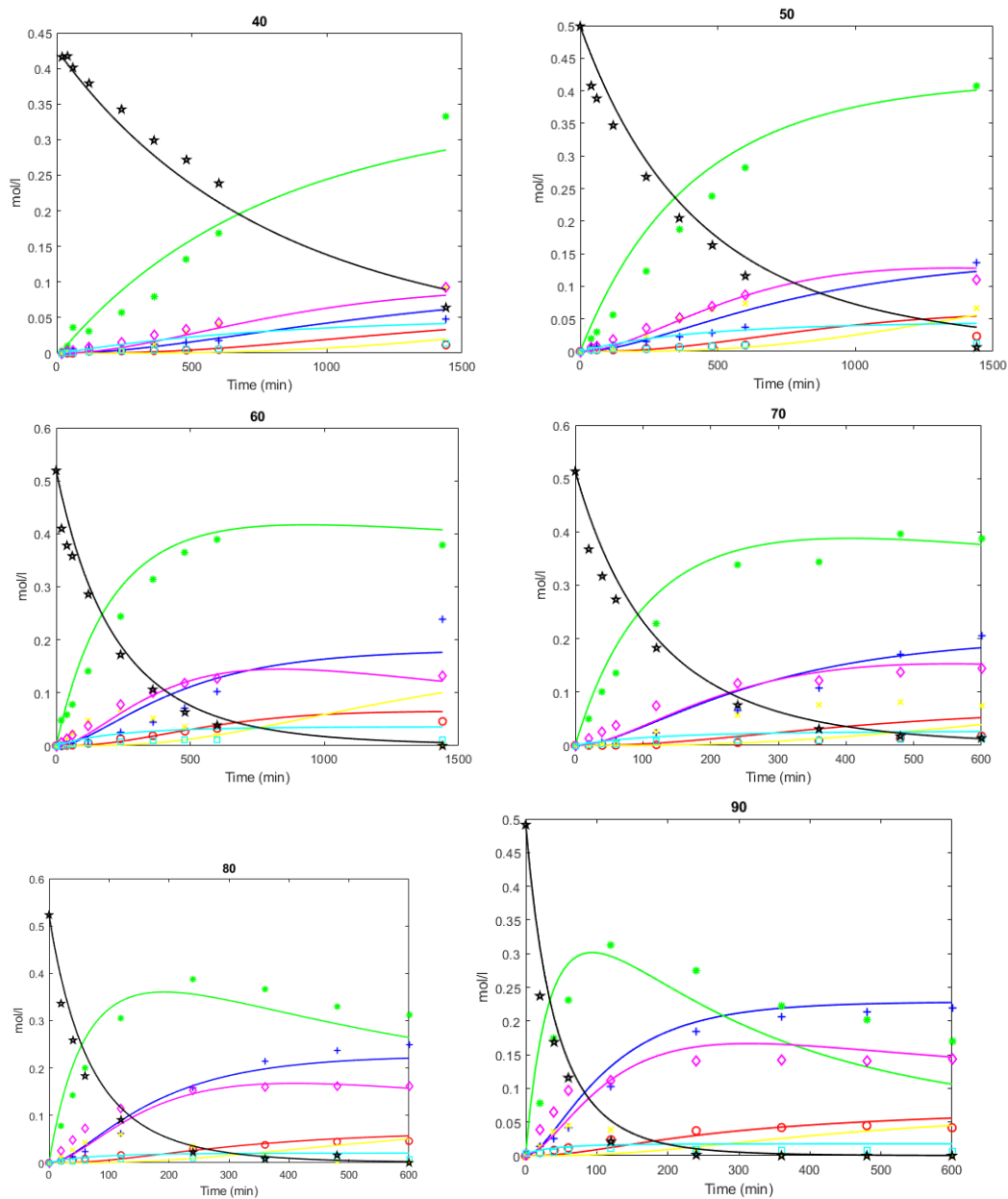
where  $T_{\text{ave}}$  is the average temperature (338K) and is the constant at the average temperature. Such approach is applied [14] to suppress correlations between the pre-exponential factor and activation

energy. The results of calculations are presented in Figures 3 – 5, illustrating a good description of experimental data for both Schemes and reasonably well identified parameters.

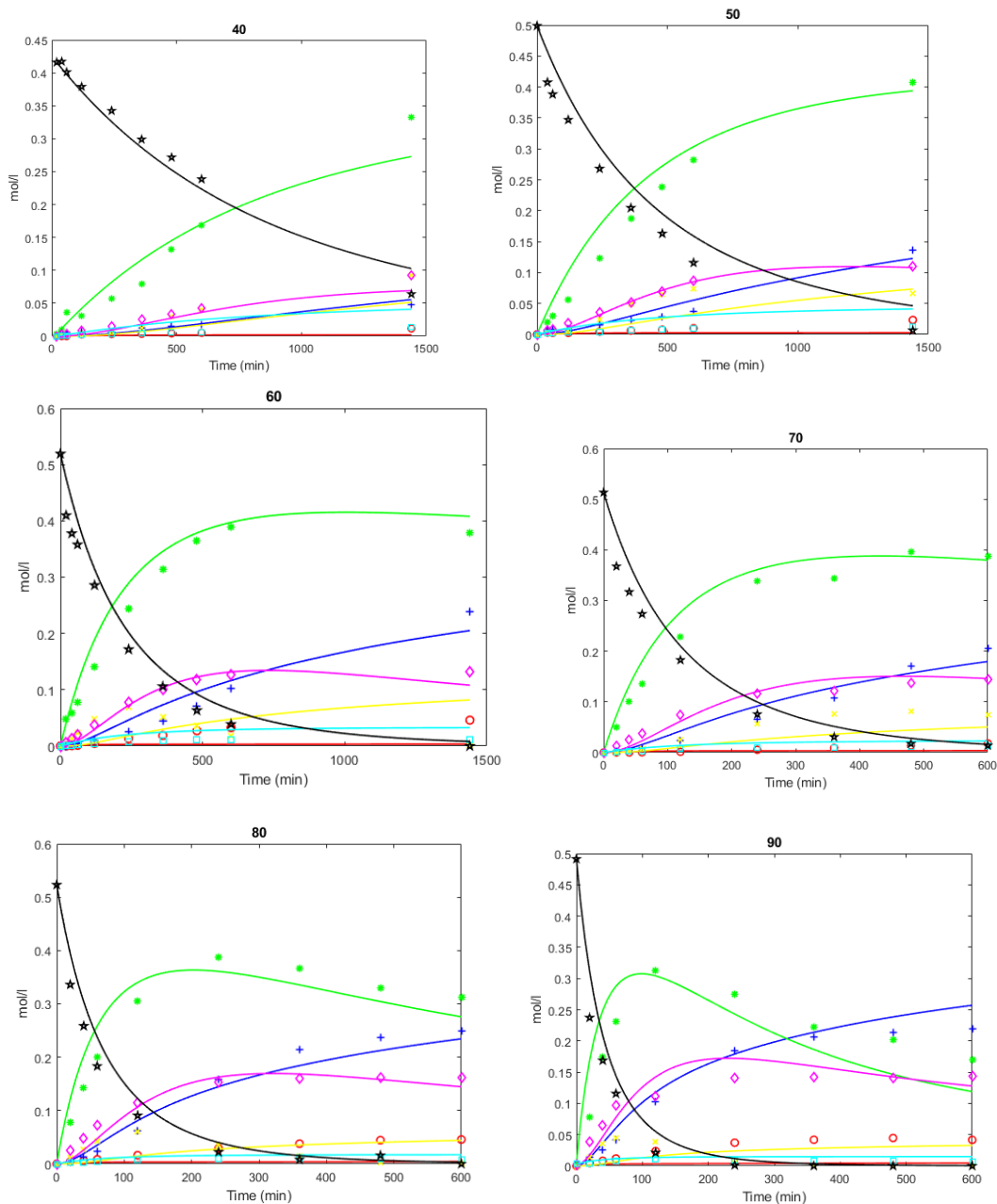


**Figure 3.** Comparison between experimental and calculated concentrations of hydrogen peroxide in oxidation of furfural [12]. Reaction conditions:  $[H_2O_2/Fal]_0 = 3$  (mol/mol),  $[Fal]_0 = 0.5$  (mol/L),  $[H_2O_2]_0 = 1.5$  (mol/L),  $[H^+]_0 = 0.02$  (mol<sub>cat</sub>/L). Numbers above each curve indicate reaction temperature in °C. Results correspond to a) Scheme 1, b) Scheme 2.

As follows from the Figures the fitting is able of simulating most of the reactants and products experimental points. The deviation of experimental points for hydrogen peroxide at 80°C can be explain that the experimental curve is rather close to the data generated at a higher temperature. For furfural conversion the description is very satisfactory. While formation of formic acid, 5-furanone and succinic acid show some deviations, overall the numerical fitting gave a good description taking into account that all data points in such a complex reaction network with many kinetic parameters were considered simultaneously.



**Figure 4.** Comparison between experimental data and calculations in oxidation of furfural with hydrogen peroxide for Scheme 1 [12]. Reaction conditions:  $[\text{H}_2\text{O}_2/\text{Fal}]_0 = 3$  (mol/mol),  $[\text{Fal}]_0 = 0.5$  (mol/L),  $[\text{H}_2\text{O}_2]_0 = 1.5$  (mol/L),  $[\text{H}^+]_0 = 0.02$  (mol<sub>cat</sub>/L). Number at the top of each graph indicates reaction temperature in °C. The following colour coding was used: maleic acid – red, succinic acid – blue; formic acid – green; fumaric acid – yellow; 2(5h)-furanone – magenta; furoic acid – cyan; furfural black.



**Figure 5.** Comparison between experimental data and calculations in oxidation of furfural with hydrogen peroxide for Scheme 2. Reaction conditions:  $[H_2O_2/Fal]_0 = 3$  (mol/mol),  $[Fal]_0 = 0.5$  (mol/L),  $[H_2O_2]_0 = 1.5$  (mol/L),  $[H^+]_0 = 0.02$  (mol<sub>cat</sub>/L). Number at the top of each graph indicates reaction temperature in °C. The following colour coding was used: maleic acid – red, succinic acid - blue; formic acid - green; fumaric acid – yellow; 2(5h)-furanone - magenta; furoic acid - cyan; furfural black.

The parameter estimation results are presented in Table 1 for Scheme 1 and in Table 2 for Scheme 2.

**Table 1. Results of parameter estimation for Scheme 1, giving degree of explanation 99.06%**

Parameter	$k_{0,1}\rho_B$	$k_{0,2}\rho_B$	$k_{0,3}\rho_B$	$k_{0,4}\rho_B$	$k_{0,5}\rho_B$	$k_{0,6}\rho_B$	$k_{0,7}\rho_B$	$k_{0,8}\rho_B$	$n_1$
Units	L/mol/s	(L/mol) <sup>m</sup> /s	s <sup>-1</sup>	(L/mol) <sup>n</sup> /s	s <sup>-1</sup>	s <sup>-1</sup>	L/mol/s	L/mol/s	-
Value	1.8 10 <sup>-3</sup>	0.76 10 <sup>-3</sup>	1.4 10 <sup>-3</sup>	0.5 10 <sup>-3</sup>	1.1 10 <sup>-3</sup>	0.4 10 <sup>-3</sup>	0.1 10 <sup>-3</sup>	0.13 10 <sup>-3</sup>	1.27
Error, %	3.1	19.4	14.4	14.1	38	>100	26	23	56
Parameter	$E_{act,1}$	$E_{act,2}$	$E_{act,3}$	$E_{act,4}$	$E_{act,5}$	$E_{act,6}$	$E_{act,7}$	$E_{act,8}$	$n_2$
Units	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	-
Value	61	53	30	25	24.6	79	116	22	1.1
Error, %	2.8	17.9	25.9	41.2	77	64.6	8.4	76	95

**Table 2. Results of parameter estimation for Scheme 2, giving degree of explanation 99.15%**

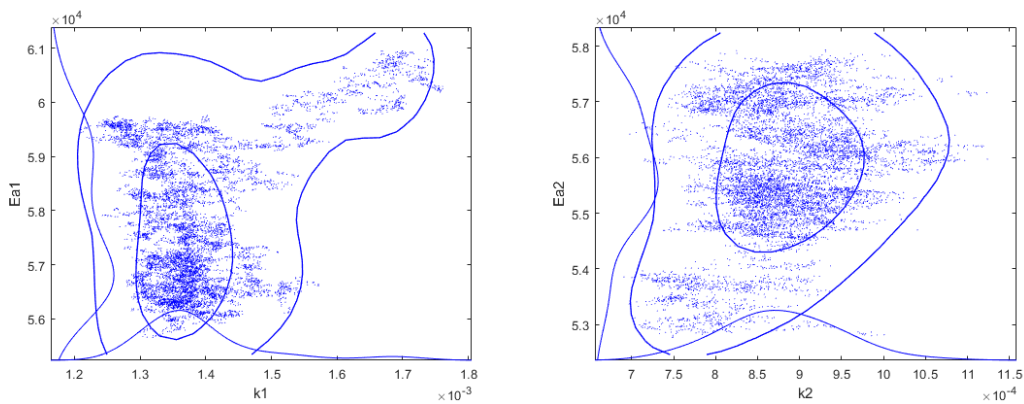
Parameter	$k_{0,1}\rho_B$	$k_{0,2}\rho_B$	$k_{0,3}\rho_B$	$k_{0,4}\rho_B$	$k_{0,5}\rho_B$	$k_{0,6}\rho_B$	$k_{0,7}\rho_B$	$k_{0,8}\rho_B$	$k_{0,9}\rho_B$	$n_1$
Units	L/mol/s	(L/mol) <sup>m</sup> /s	s <sup>-1</sup>	(L/mol) <sup>n</sup> /s	s <sup>-1</sup>	s <sup>-1</sup>	L/mol/s	L/mol/s	L/mol/s	-
Value	1.7 10 <sup>-3</sup>	0.77 10 <sup>-3</sup>	1.6 10 <sup>-3</sup>	0.38 10 <sup>-3</sup>	6.7 10 <sup>-3</sup>	0.8 10 <sup>-3</sup>	0.1 10 <sup>-3</sup>	0.9 10 <sup>-3</sup>	1 10 <sup>-3</sup>	1.36
Error, %	3.1	17.5	24.4	25.7	64.7	50.8	27	62	50	97
Parameter	$E_{act,1}$	$E_{act,2}$	$E_{act,3}$	$E_{act,4}$	$E_{act,5}$	$E_{act,6}$	$E_{act,7}$	$E_{act,8}$	$E_{act,9}$	$n_2$
Units	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	-
Value	61	53	33	21	20	91	113	22	23	0.97
Error, %	2.7	16.8	36.6	54.8	>100	30.9	9.0	71	98	71

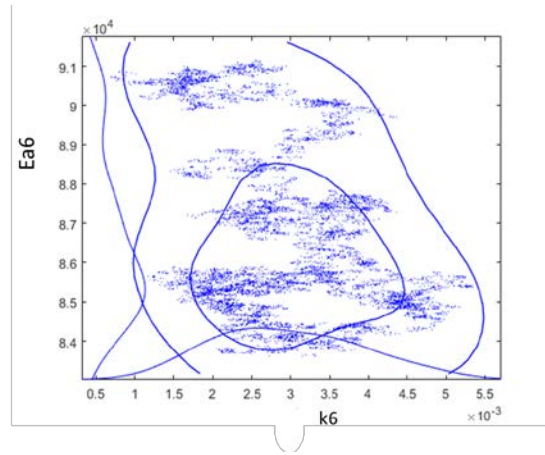
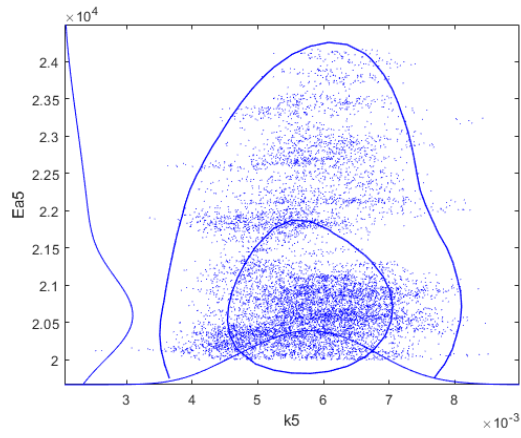
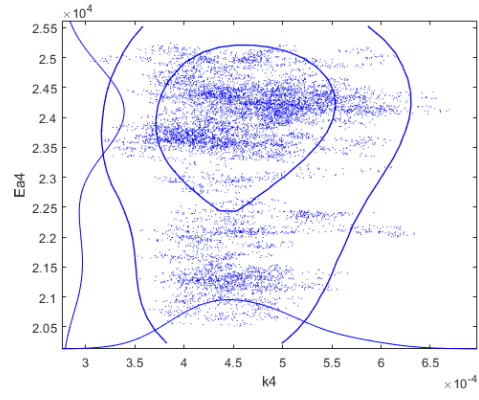
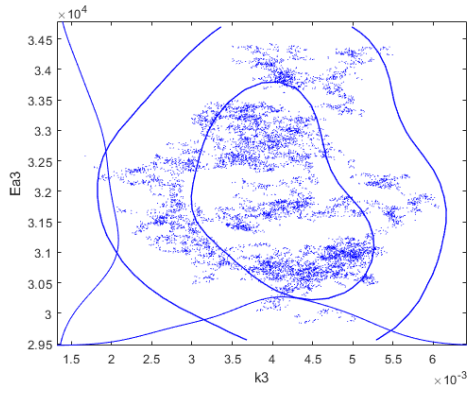
In general, the parameter estimation even for Scheme 1, which gave a slightly worse description, was satisfactory with mainly the rate constant of step 6 and the reaction orders in

hydrogen peroxide in steps 4 being poorly identified. Poor identifiability of  $k_{0,6}\rho_B$  can be related to a low concentration of fumaric acid. This parameter was better defined for **Figure 2**.

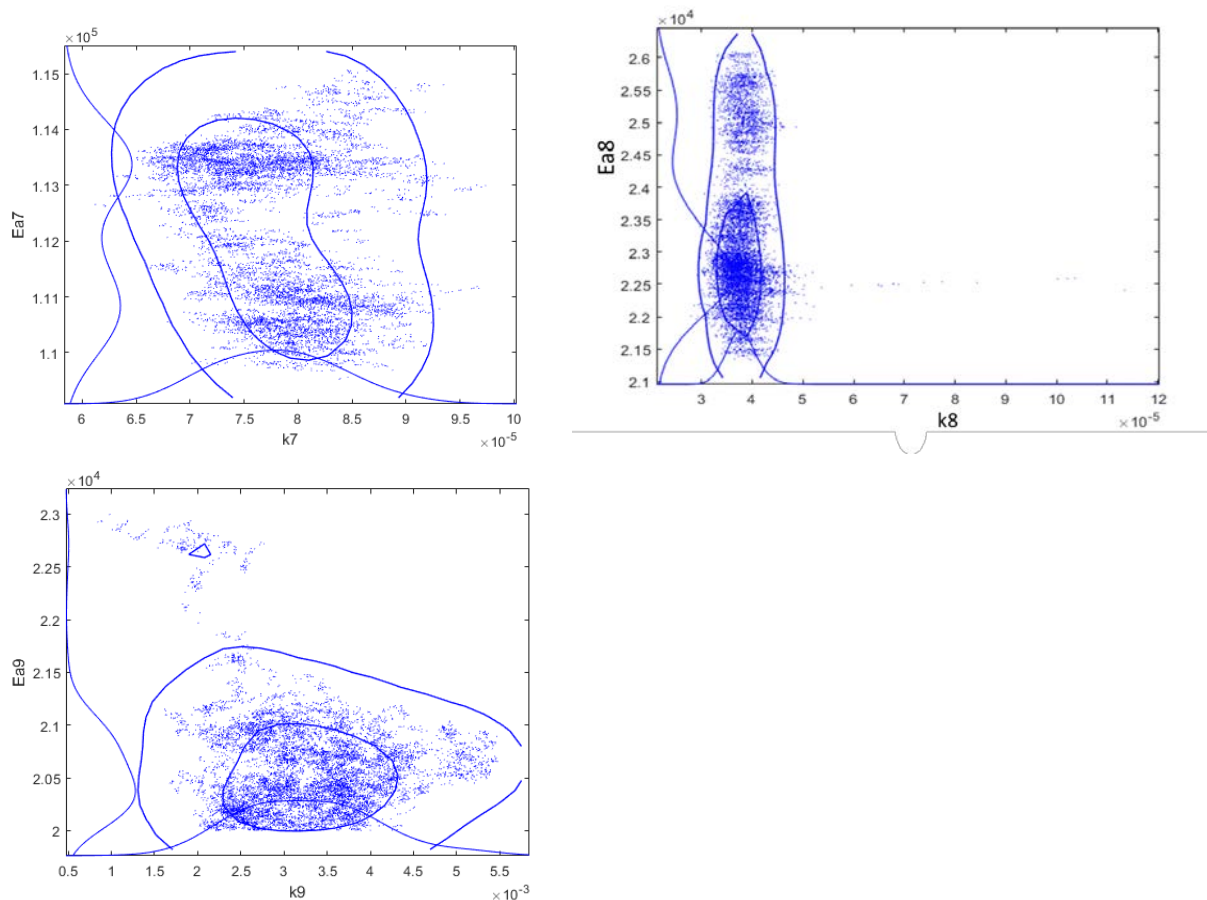
Errors of parameter values in Table 1 and 2 indicate that a certain parameter falls within an interval (value  $\pm$ error) with 95% confidence intervals. Such classical statistical analysis giving optimal parameter values and their error estimates is approximate being based on linearization. Reliability of the models and their parameters was investigated in this study using Markov chain Monte Carlo (MCMC) method implemented in [13]. This method based on Bayesian inference gives a probability distribution of solutions. For both Schemes in almost all cases low values of correlations were obtained.

A graphical representation of the correlations between pre-exponential factors and their corresponding activation energy is presented in **Figure 6** for Scheme 2, which gave a slightly better description.







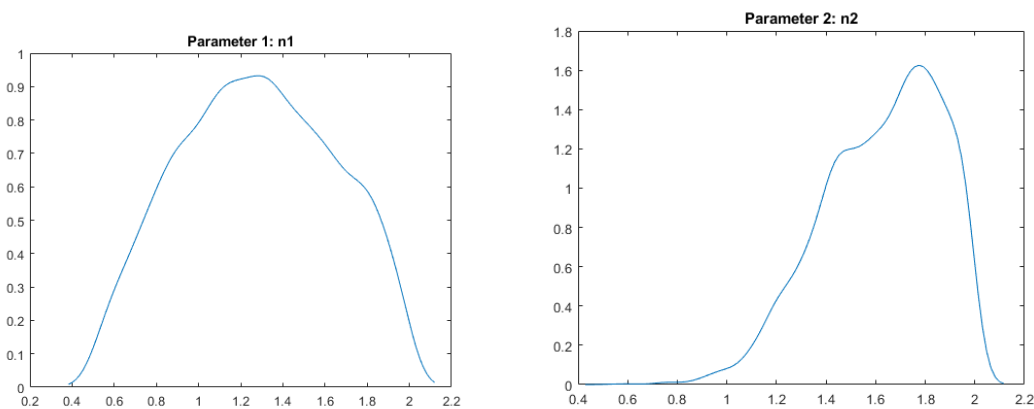


**Figure 6.** Correlations between pre-exponential factors and their corresponding activation energies obtained by MCMC method.

For steps 1 to 4 generating the organic compounds present in the reaction mixture in higher amounts (maleic, succinic and formic acids as well as 2(5h)-furanone) as well as for other steps (5, 6 and 9) cycle shapes confirm a low correlation level between the respective parameters for these steps. Some elongation of the probability distribution could be observed for step 8 giving furoic acid.

Finally, the sensitivity analysis of the estimated kinetic parameters was performed by calculating the objective function as a function of each estimated parameter, while keeping the other

parameters constants at the values corresponding to the minimum of the objective function. Sensitivity plots calculated in this way in the case of Scheme 2 and presented in Figure 7 for two parameters, namely the reaction orders in hydrogen peroxide, are confirming clear minima for the objective function for these parameters.



**Figure 7.** Sensitivity plots for kinetic parameters.

Such statistical analysis confirms that the values of the reaction orders in hydrogen peroxide for steps 2 and 4 determined in the current work clearly deviate from unity. Subsequently, some tentative mechanistic explanation could be proposed, even if an unequivocal mechanistic interpretation requires a detailed theoretical study. The reaction order in hydrogen peroxide higher than unity can be understood by suggesting that the reaction mechanism on a heterogeneous catalyst with sulphonic acid functional groups is similar to the mechanism with mineral acids. In the latter case, it was suggested [15] that after the initial protonation, two molecules of hydrogen peroxide are added in reversible steps, giving a peroxo complex, which undergoes oxidative cleavage. Such reaction mechanism with a stepwise addition of hydrogen peroxide to furanones can lead to the reaction order in hydrogen peroxide in the ultimate case approaching two.

## Conclusions

A detailed kinetic modelling was performed for furfural oxidation with hydrogen peroxide in a batch reactor with predominant formation of succinic acid over a catalyst representing non-porous poly (ethylene-graft-polystyrene) with sulfonic acid functional groups.

The reaction network comprised formation of formic acid along 2-hydroxyfuran in the initial stage of Baeyer-Villiger furfural oxidation. Isomerization of 2-hydroxyfuran to 2(3H)-furanone with subsequent oxidation resulted in succinic acid. In a parallel reaction route 2(5H)-furanone was generated from 2-hydroxyfuran and then oxidized to maleic acid. Other reactions in the overall network included isomerization of maleic to fumaric acid, oxidation of furfural and formic acid to furoic acid and carbon dioxide respectively. In an alternative variant of the reaction mechanism, 2-(5H) furanone was not considered to be an intermediate in generation of maleic acid, which was suggested to be formed from 2-hydroxyfuran or 2-(3H) furanone.

A set of differential equations representing concentration dependencies of reactants and products as a function of time was solved numerically for the experimental data set reported by the authors previously in the temperature range between 40 and 90°C. Parameter estimation was done for determination of the reaction orders in hydrogen peroxide, activation energies and rate constants. Kinetic modelling showed an adequate correspondence between the experimental data and calculations.

A detailed statistical analysis of the parameters was performed including calculations of correlations between the parameters. Such analysis confirmed reliability of determination of kinetic parameters.

## **Acknowledgement**

This work is a part of activities at the Åbo Akademi Process Chemistry Centre (PCC). Financial support from Tekes (Finnish National Agency for Technology and Innovation) and Magnus Ehrnrooth Foundation is gratefully acknowledged.

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