



Green Chemistry

Electronic Supplementary Information (ESI)

Acrolein production route from ethanol and methanol mixtures over FeMo-based catalysts

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ESI 1 – Additional information about DoE

In order to find the optimal conditions of methanol and ethanol coupling oxidation process, a Design of Experiments was performed. This method allows performing the optimization with the lowest possible number of experiments. It concentrates on parameters that influence the most the reaction performances, giving the information about their relative importance. In the case of the reaction considered herein, there are four independent main factors that can have an influence on the acrolein yield. All of them are presented below with the values range used during optimization:

Temperature: 225 – 350 °C;

Oxygen quantity: 7 - 12% molar in reactor feed;

Methanol/Ethanol molar ratio: 0.5 – 2;

GHSV: 3900 – 7700 h⁻¹

In the DoE experiments, the catalyst quantity was kept as a constant (200 mg). These studies were performed over industrial FeMo catalyst provided by Arkema. The influence

of GHSV was evaluated by changing the total flow rate. DoE is based on mathematical matrix and we decided to set up a standard centered composite matrix built of three parts: full factorial matrix, star matrix and central matrix. This type of approach enables obtaining responses surfaces to quickly get location of an optimum whether local or global. For the complete factorial design, the number of experiments is determined from the following equation (Eq. 1):

$$n = n_0 + 2k + 2^k \quad (1)$$

Here, n_0 represents the number of experiments in the center of the studied domain and k is the factors number. As a consequence, 27 experiments were performed with different operational conditions obtaining acrolein yields as a response^{1,2}. The results were treated with the Modde5.0 (UMETRI AB, Box 7960, S-90719 UMEA, Sweden, 2000) software, which, thanks to mathematical modelling, gave correlations between each factor. It was then possible to determine the optimal reaction conditions.

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Electronic Supplementary Information (ESI) available: 3D graphics obtained from DoE and supplementary information about DoE method. See DOI: 10.1039/x0xx00000x

¹ G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for experimenters, John Wiley and Sons, New York 1978 p.653

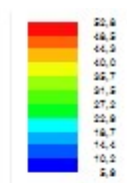
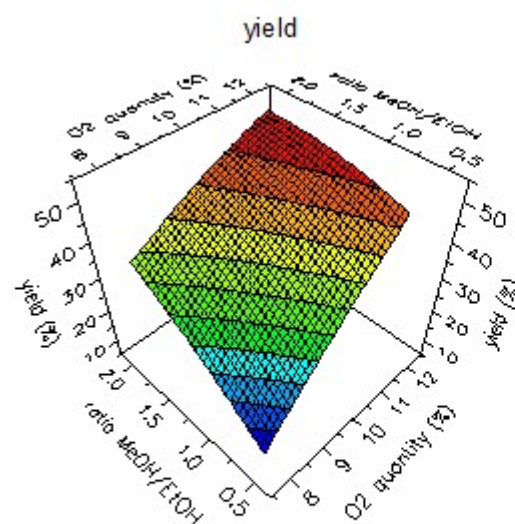
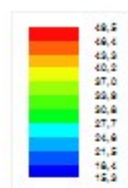
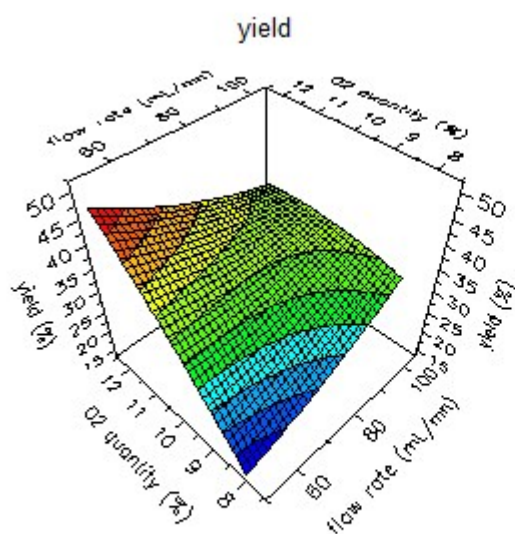
² J. Goupy, Plans d'expériences pour surface de reponses, Dunod, 1999, Paris

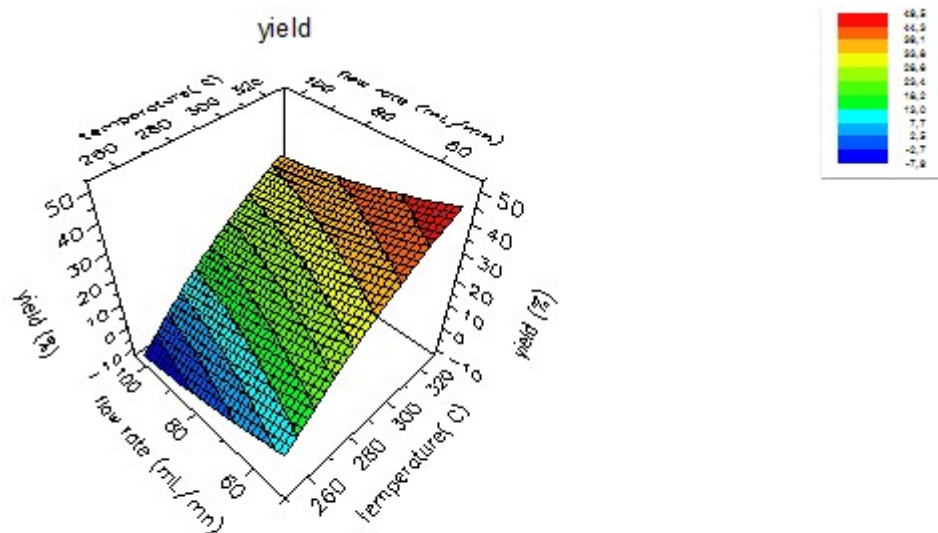
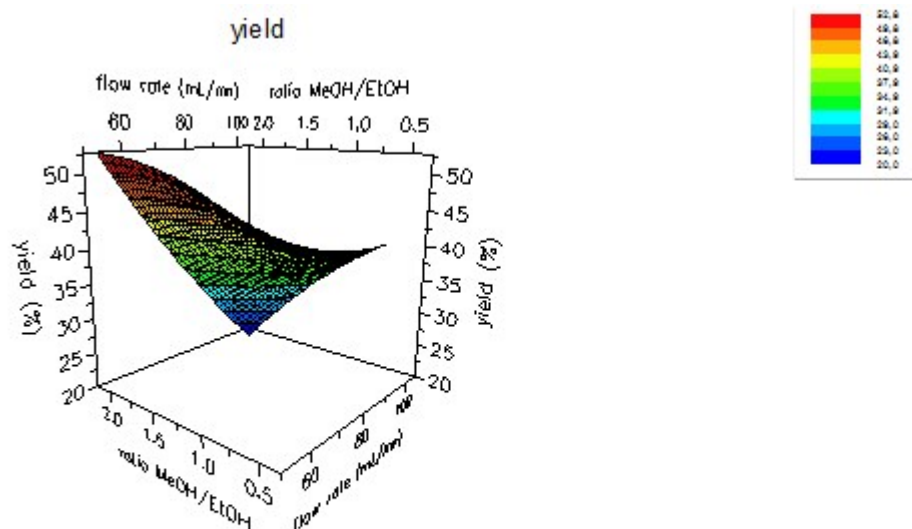
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ESI 2 – 3D figures obtained from DoE

Each graph represents the combined influences of two different factors on the acrolein yield. The red colour indicates the highest acrolein yield and the blue one the lowest one.





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