EFFECT of C3-ALCOHOLS IMPURITIES on ALUMINA CATALYZED DEHYDRATION of BIOETHANOL to ETHYLENE. EXPERIMENTAL STUDY and PROCESS MODELING

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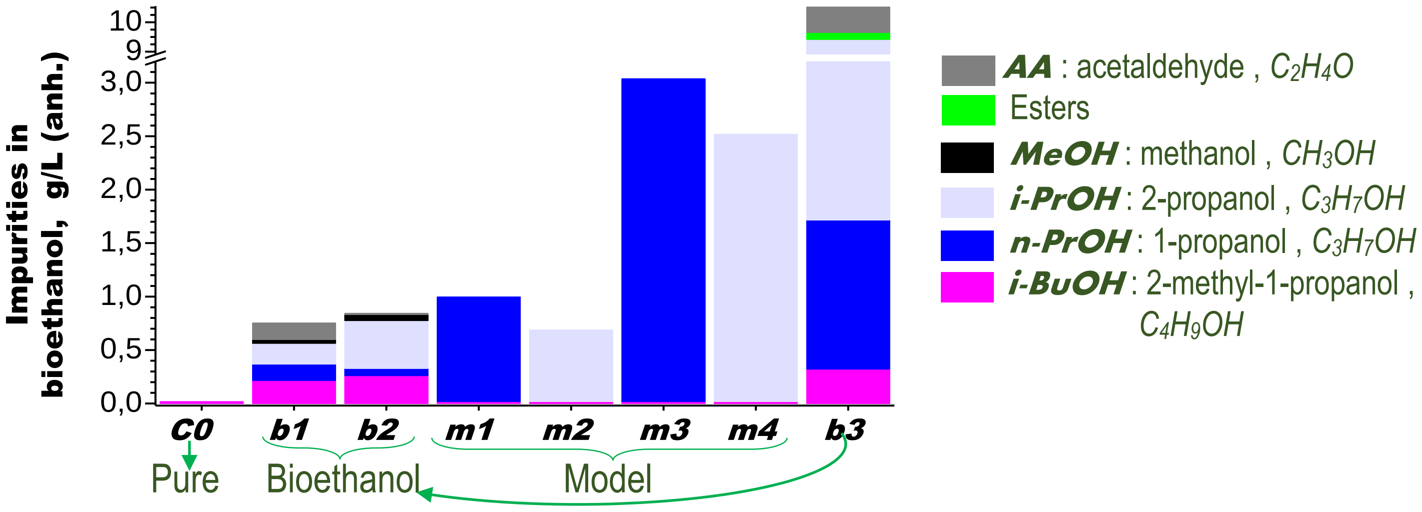
Bioethanol produced from non-food phytogenic feedstock can be used to produce ethylene as a platform product for a large number of downstream derivatives.

After distillation, bioethanol contains impurities of C_3-alcohols, which can have an adverse impact on its further processing.

Present work focused on the studies of the organic impurities influence on the dehydration of contaminated ethanol to ethylene and the catalytic activity of the proprietary alumina catalyst.



Catalyst: proprietary acid modified alumina[1-2]

Experiment:

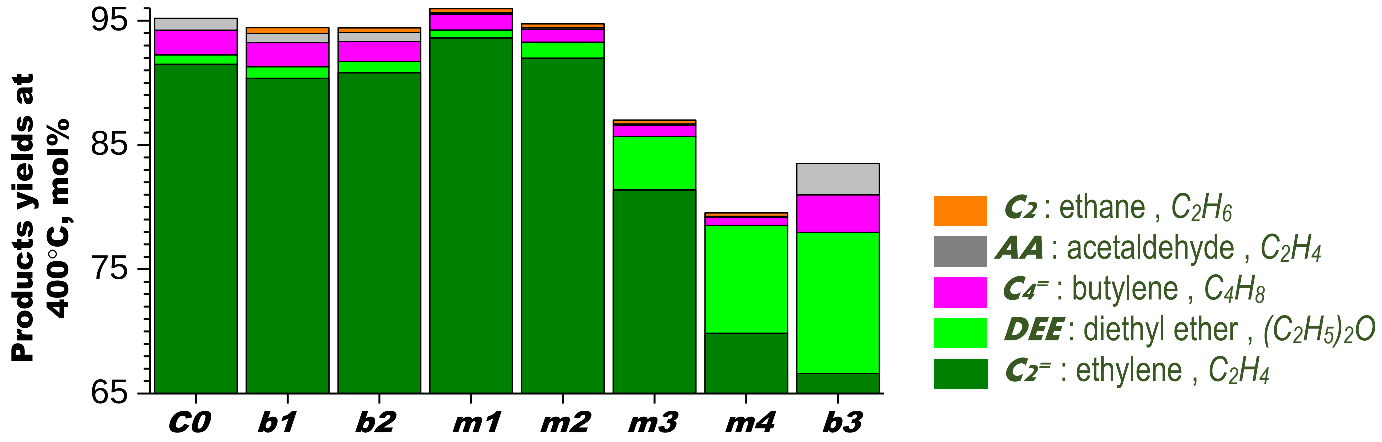
Catalyst loading: 1 ml, 6 mm ring crushed to 0.25-0.5 mm particles

Reactor: flow type

EtOH: 92%wt strength,

WHSV: 21 $g_{EtOH}\ g_{cat}^{-1}\ h^{-1}$

T: 350-400°C



(1) *Chem. Eng. J.* 374 (**2019**) 605–618; https://doi.org/10.1016/j.cej.2019.05.149

(2) *Russ. J. Appl. Chem.* 89 (**2016**) 683-689; https://doi.org/10.1134/S1070427216050013

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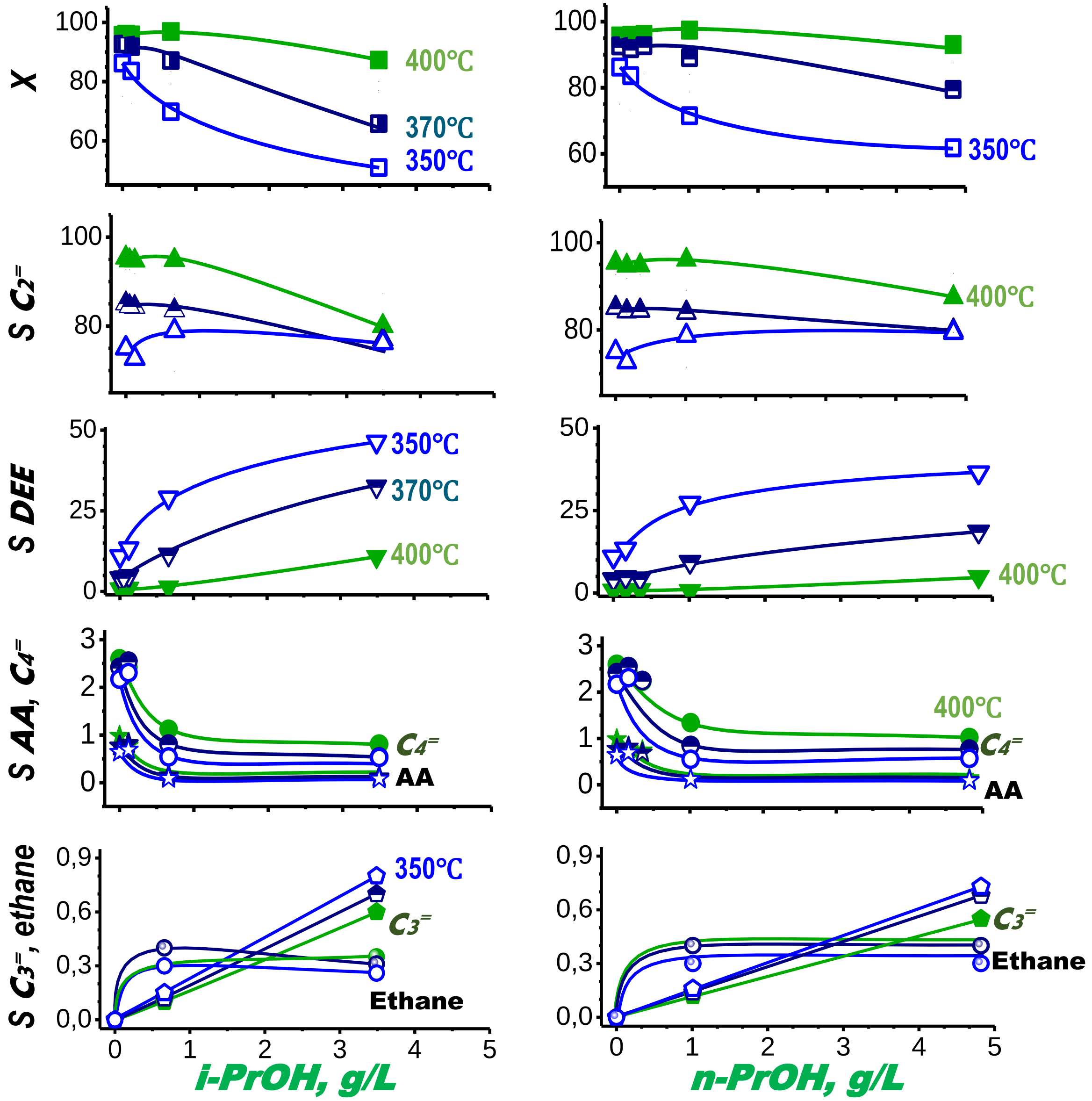
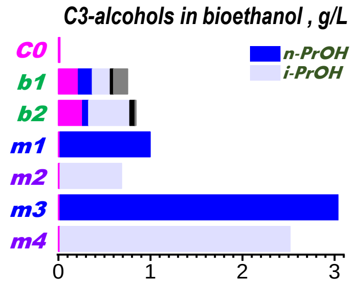
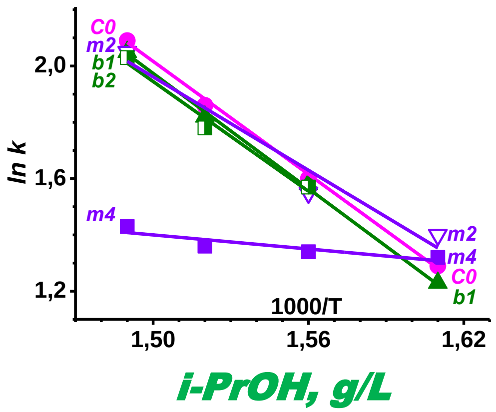


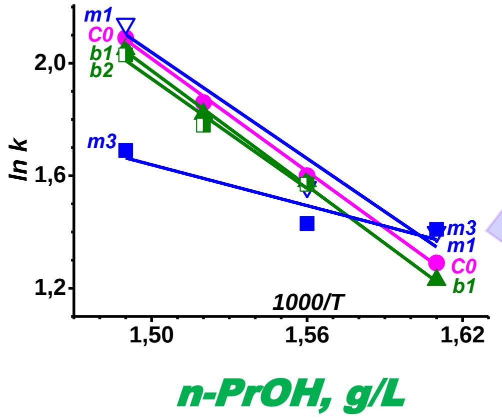
The effect of *C3*-alcohols on ethanol conversion (*X*) and products selectivity (*S*, mol%) in bioethanol dehydration at 350, 370 and 400°C

$C_2^=$ (ethylene)
DEE diethyl ether
AA acetaldehyde
$C_4^=$ butylene
$C_3^=$ propylene



Catalyst activity in dehydration of various bioethanol samples containing *C3*-alcohols





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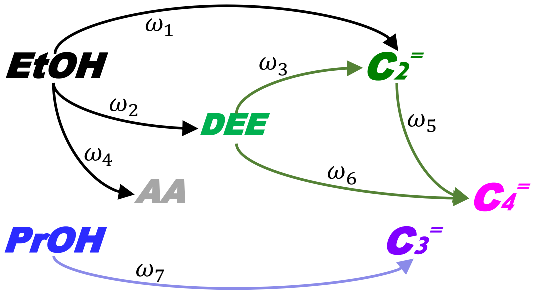
Kinetic model

Reaction network:



Kinetic equations:

$$\omega_1 = k_1 P_{EtOH}\frac{(1+k_8 P_{PrOH})}{(1+k_9 P_{PrOH})^2}$$

$$\omega_2 = k_2 P_{EtOH}^2\frac{(1+k_{10} P_{PrOH})}{(1+k_{11} P_{PrOH})^2}$$

$$\omega_3 = k_3 P_{DEE}\frac{1}{(1+k_{12} P_{PrOH})}$$

$$\omega_4 = k_4 P_{EtOH}\frac{1}{(1+k_{13} P_{PrOH})}$$

$$\omega_5 = k_5 P_{C_2^=}^2\frac{1}{(1+k_{14} P_{PrOH})}$$

$$\omega_6 = k_6 P_{DEE}\frac{1}{(1+k_{15} P_{PrOH})}$$

$$\omega_7 = k_7 P_{PrOH}$$

Model of the tubular fixed-bed reactor*

Chem. Eng. Res. Des.* 145 (2019**) 1-11; https://doi.org/10.1016/j.cherd.2019.02.041

Model of the pellet:

$$\frac{\partial}{\partial\rho}\left(D_{ri}^*\frac{\partial C_i}{\partial\rho}\right) - \frac{RT}{P}\frac{\partial}{\partial\rho}(V_i^* C_i) = \sum_{j=1}^{7}\gamma_{ij}\omega_j$$

Model of the tube:

Mass and heat balance equations:

$$\frac{P_0}{RT_0}\frac{\partial(\overline{u_l} y_i)}{\partial l} + \frac{1}{r}\frac{P_0}{RT_0}\frac{\partial}{\partial r}(r\overline{u_r} y_i) - \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{PD_r}{RT}\frac{\partial y_i}{\partial r}\right) = \sum_j (1-\varepsilon)\gamma_{ij}\varpi_j$$

$$\frac{P_0}{RT_0}\overline{u_l}c_p\frac{\partial T}{\partial l} + \frac{P_0}{RT_0}\overline{u_r}c_p\frac{\partial T}{\partial r} - \sum_i c_{pi}\left(\frac{\partial T}{\partial r}\right)\frac{P}{RT}D_r\frac{\partial y_i}{\partial r} - \frac{1}{r}\frac{\partial}{\partial r}\left(r\lambda_r\frac{\partial T}{\partial r}\right) = -(1-\varepsilon)\sum_j \Delta H_j\varpi_j$$

Boundary conditions:

$$0 \le r \le R_{tube}$$

$$l = 0;\quad \overline{u_l}(0,r) = \overline{u_0};\quad T(0,r) = T_{in}$$

$$y_i(0,r) = y_{in}$$

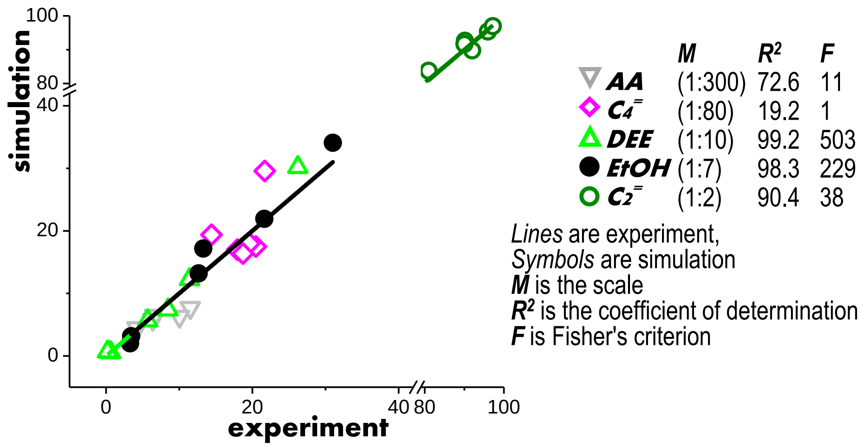
$$0 \le l \le L$$

$$r = 0;\quad \frac{\partial y_i(l,0)}{\partial r} = 0;\quad \frac{\partial T(l,0)}{\partial r} = 0$$

$$r = R_{tube};\quad \frac{\partial y_i(l,R_{tube})}{\partial r} = 0$$

$$\overline{u}_r(l,R_{tube}) = 0;\quad \lambda_r\frac{\partial T}{\partial r} = \alpha_w(T_w - T)$$

Correlation *btw* simulated and measured concentrations at the reactor outlet



Conclusions

- ✓ Effect of *C_3*-alcohols contaminated *EtOH* on the catalytic dehydration to *C_2H_4* was studied
- ✓ Simulation data of *EtOH* dehydration using a pseudo-homogeneous 2D reactor model and a draft kinetic model agreed satisfactorily with experimental results
- ✓ If the content of *C_3*-alcohols is less than 1.0 g/L, it affords a high yield of *C_2H_4* and improves *C_2H_4* quality due to a prohibited formation of by-products (*C_4=*, *AA*, *H_2*)
- ✓ To verify and confirm the preliminary results, a further in-depth study of the effect of impurities, with an expanded list and composition of components, is required.

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