ISOMERIZATION of n-BUTANE and C4 REFINERY FRACTIONS on Pd PROMOTED SULFATED ZIRCONIA. KINETIC ASPECTS and PROCESS MODELING

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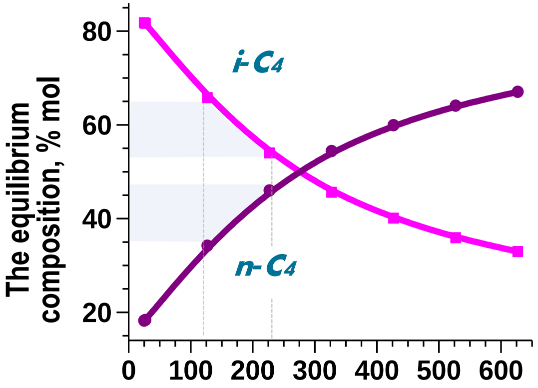
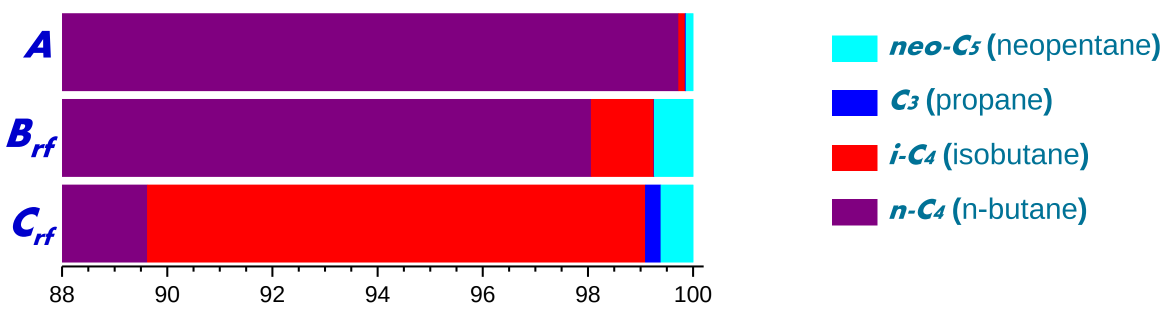


Catalyst [1-3]

Pd-SZ – Pd-modified sulfated zirconium

Composition (wt%):
0.5 *Pd*, 0.8 SO_4^{2-}, 98.7 ZrO_2
BET surface: 55.7 m²/g
V_{por} : 0.082 cm³/g
Mean pore diameter, D_{por}: 4.28 nm

Feedstock composition [3] , %wt.



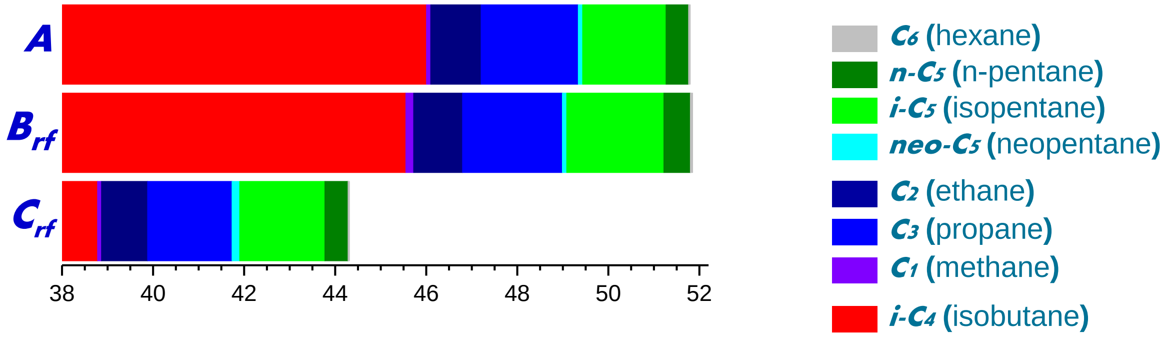
The ***n-C4*** isomerization catalyzed by sulfated zirconium is an alternative to the chlorinated alumina method.

Highly active and stable ***Pd-SZ*** catalysts [1-3] can significantly improve the ***n-C4*** (***A***) isomerization process and are promising for industrial implementation.

Studies of the kinetic aspects and the process when using real feedstocks, such as **C4** refinery fractions (***B_{rf}, C_{rf}***), were the goal of the present work.

Products yield [3] , %wt.

P: 2.4 MPa; ***T***: 140 °C; ***WHSV***: 1.5 h^{-1}; ***H_2/C_4***: 0.2; catalyst size 0.25-0.5 mm



(1) RU2693464C1 (**2018**) https://patents.google.com/patent/RU2693464C1/en
(2) *Chem. Eng. J.* 238 (**2014**) 148 https://doi.org/10.1016/j.cej.2013.08.092
(3) *Pet. Chem.* 59 (**2019**) S101 https://doi.org/10.1134/S0965544119130048

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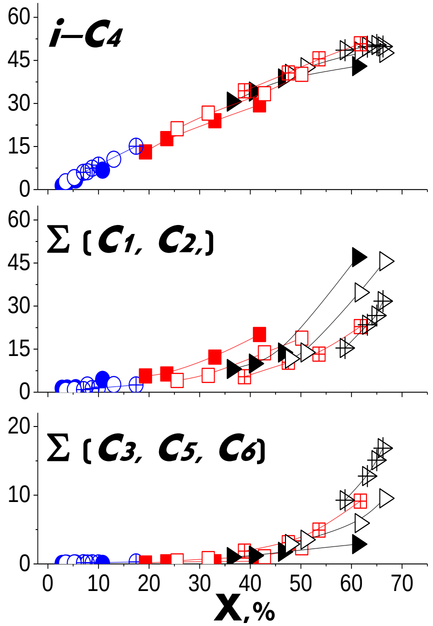
Isomerization of C4 refinery fraction B_{rf}: products yield with variations in WHSV, T , H_2/*n-C4*

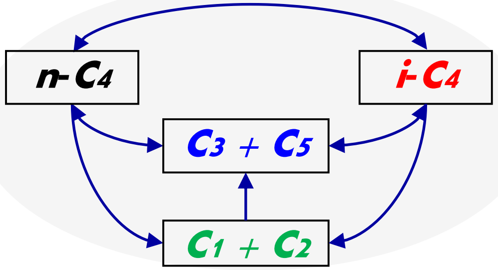


P: 2.4 MPa
WHSV: 1-2.5 h^{-1}
T: 120 °C, 140 °C, 160 °C
H2/C4: 0.1 (crossed symbols),
0.25 (open symbols),
0.5 (solid symbols)
Catalyst size 0.25-0.5 mm

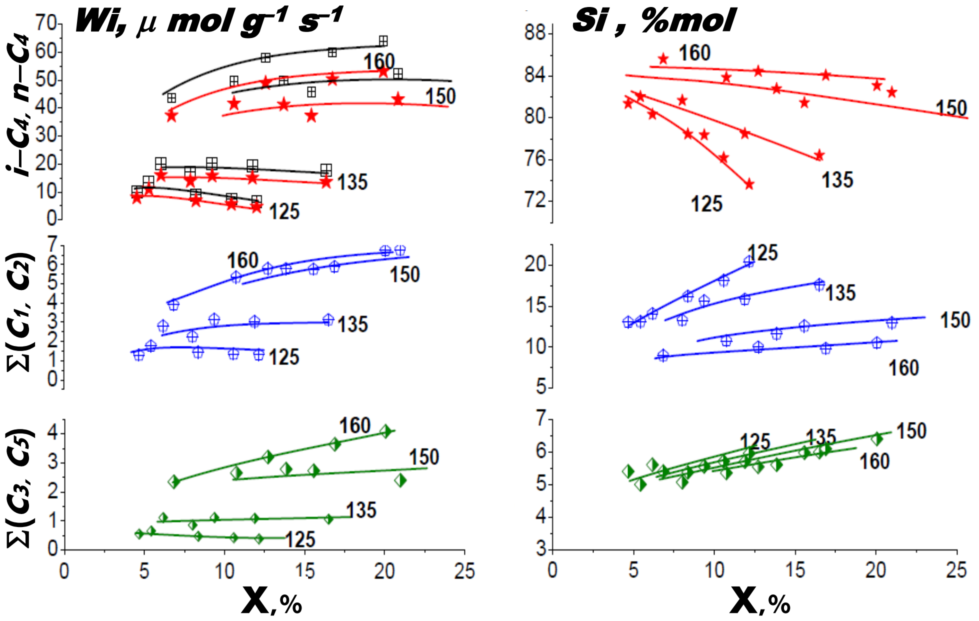
Simplified kinetic model

$$n\text{-}C_4H_{10} \Leftrightarrow i\text{-}C_4H_{10} \qquad R_1 = k_1\,[n\text{-}C_4]\,(1+1/Kp_1)^{(4)}$$
$$n\text{-}C_4H_{10} + H_2 \Rightarrow 2\,C_2H_6 \qquad R_2 = k_2\,[n\text{-}C_4]\,[H_2]$$
$$3\,n\text{-}C_4H_{10} + H_2 \Rightarrow 4\,C_3H_8 \qquad R_3 = k_3\,[n\text{-}C_4]\,[H_2]$$
$$5\,n\text{-}C_4H_{10} \Rightarrow 4\,C_5H_{12} + H_2 \qquad R_4 = k_4\,[n\text{-}C_4]$$
$$i\text{-}C_4H_{10} + H_2 \Rightarrow 2\,C_2H_6 \qquad R_5 = k_5\,[i\text{-}C_4]\,[H_2]$$
$$3\,i\text{-}C_4H_{10} + H_2 \Rightarrow 4\,C_3H_8 \qquad R_6 = k_6\,[i\text{-}C_4]\,[H_2]$$
$$5\,i\text{-}C_4H_{10} \Rightarrow 4\,C_5H_{12} + H_2 \qquad R_7 = k_7\,[i\text{-}C_4]$$
$$5\,C_2H_6 \Rightarrow 2\,C_5H_{12} + 3\,H_2 \qquad R_8 = k_8\,[C_2]$$
$$C_3H_8 + C_5H_{12} \Rightarrow i\text{-}C_4H_{10} + n\text{-}C_4H_{10} \qquad R_9 = k_9\,[C_3]\,[C_5] \quad (5)$$

$$W\,(n\text{-}C_4) = -(R_1 + R_2 + 3R_3 + 5R_4) + R_9$$
$$W\,(i\text{-}C_4) = R_1 - R_5 - 3R_6 - 5R_7 + R_9$$
$$W\,(C_2) = 2R_2 + 2R_5 - 5R_8$$
$$W\,(C_3) = 4R_3 - R_9$$
$$W\,(C_5) = 4R_4 + 4R_7 + 2R_8 - R_9$$



Reaction rates *W* and selectivity *S* as functions of conversion X in *n-C4* (A) isomerization



P: 2.4 MPa
WHSV: 1.5 – 11 h^{-1}
T: 125 – 160 °C
H2/C4: 0.2
Cat. size 0.25-0.5 mm

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(4) *Appl.Catal.A:Gen. 256 (**2003**) 243* https://doi.org/10.1016/S0926-860X(03)00404-6
(5) *Chem.Eng.Sci. 59 (**2004**) 4773* https://doi.org/10.1016/j.ces.2004.07.036

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Mathematical model (6)

Fixed-bed

$$\frac{u_0 P_0}{RT_0}\,\frac{dy_i}{dl} = \sum_j \gamma_{ij}\overline{\omega_j}\;, i = \overline{1,N}$$

$$\frac{u_0 P_0}{RT_0}\,c_p\,\frac{dT}{dl} = \sum_j \Delta H_j \overline{\omega_j}$$

$$l = 0:\; T(0,r) = T_{in}\,,\, y_i(0,r) = y_{i\,in}\,, i = \overline{1,N}$$

Cat.particle

$$\frac{\partial}{\partial\rho}\left(D^*_{ri}\frac{\partial C_i}{\partial\rho}\right) - \frac{RT}{P}\frac{\partial}{\partial\rho}\left(V_i^* C_i\right) = \sum_{j=1}\gamma_{ij}\overline{\omega_j}\quad i = \overline{1,N-1}$$

$$\overline{\omega_j} = \frac{1}{\rho_{grain}}\int_0^{\rho_{grain}}\omega_j(\rho)d\rho\;;\; \rho_{grain} = \frac{V_p}{A_p}$$

$$\rho = 0:\; \frac{\partial C_i}{\partial\rho} = 0\,;\; \rho = \rho_{grain}: C_i = C_i^s\,, i = \overline{1,N}$$

Hydrodynamics

$$\Delta P = \left(f_1\cdot u_{out} + f_2\cdot u_{out}^2\right)L$$

$$\begin{cases} u_l = u_{out}\cdot\varepsilon_{bed} + u_{hole}\left(\varepsilon_{hol}\cdot(1-\varepsilon_{bed})\right) \\ g_1\cdot u_{hole} + g_2\cdot u_{hole}^2 = \frac{\Delta P}{\langle\cos\alpha\rangle\cdot H} = f_1\cdot u_{out} + f_2\cdot u_{out}^2 \end{cases}$$

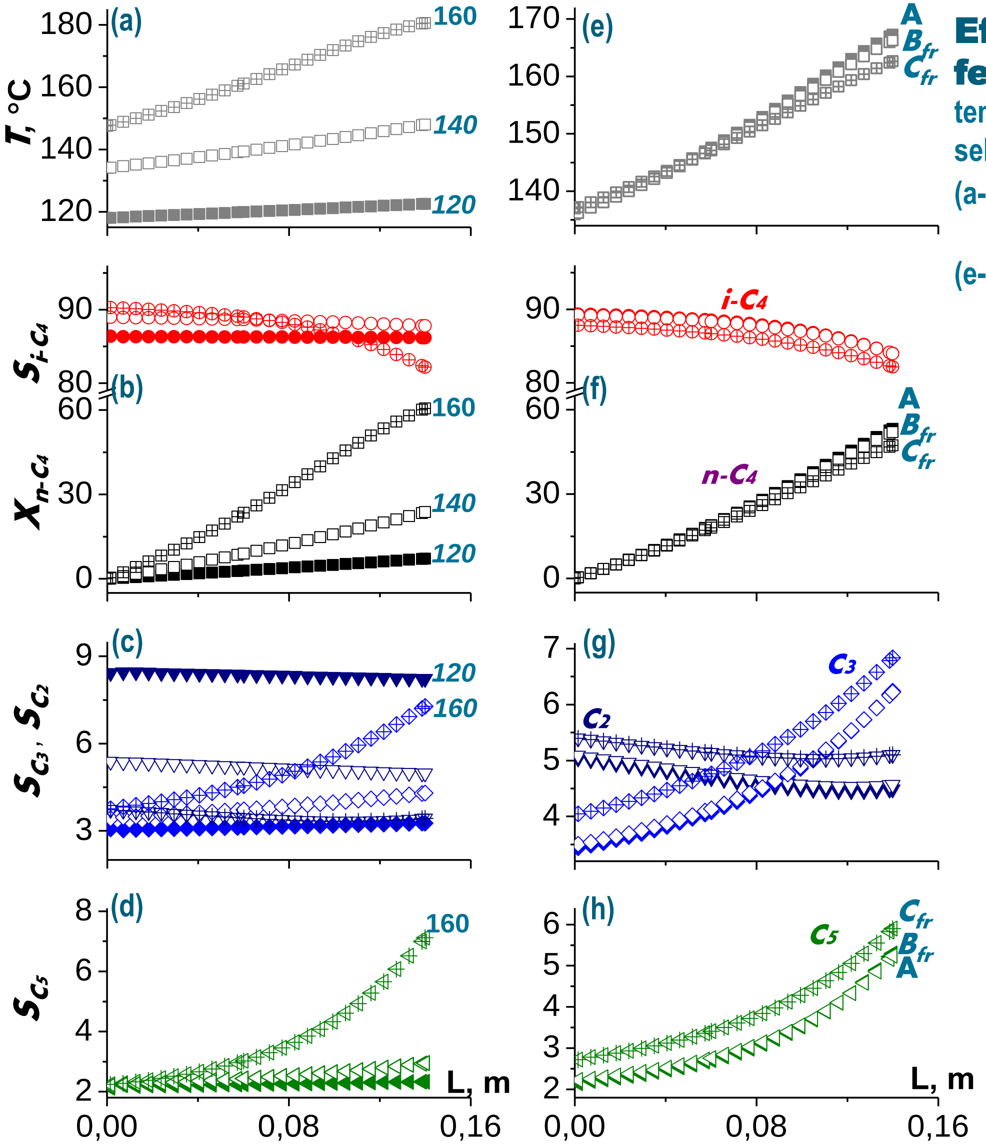
$$f_1 = \frac{150\cdot\mu}{d_p^2}\left(\frac{1-\varepsilon_{bed}}{\varepsilon_{bed}}\right)^2;\; f_2 = \frac{1.75\cdot\rho_f}{d_p}\,\frac{(1-\varepsilon_{bed})}{\varepsilon_{bed}}$$

$$g_1 = \frac{16\,\pi\mu}{d_{hydr}^2};\; g_2 = \frac{1.75\,\pi\cdot\rho_f}{4H}\left(1 - \frac{\varepsilon_{hole}}{N_{hole}}\right)$$

Conditions

Catalyst: ***Pd-SZ***, D_{por} = 4.28 nm
Shape: trilobe, *h* = 6 mm, d_{lob}= 1 mm,
circumcircle diameter *d* = 2 mm

Reactor: *ID* = 9.5 mm; *L* = 0.14 м
WHSV= 1.0-2.5 h^{-1}; *U*= 0.02–0.06 m/s
Molar ***H₂/n-C₄***: 0.1-0.4
P= 2.5 MPa; *T*= 120-160°C



Effect of temperature (a-d) and feedstock composition (e-h) on the temperature *T*, conversion $X_{n\text{-}C_4}$ and products selectivity S_i (wt%) profiles along catalyst bed *L*.

(a-d) : 120 (*solid*), 140 (*open*), 160°C (*crossed*),
WHSV= 2.5 h^{-1}; ***H₂/n-C₄*** = 0.1.

(e-h) : **A** (*solid*); B_{fr} (*open*), C_{fr} (*crossed*);
WHSV= 1.5 h^{-1}; ***H₂/n-C₄*** = 0.1; *T*= 150°C.

Conclusions

- The highest yield of ***i-C₄*** , Ymax= 52%, was obtained at **X**= 62%, *WHSV*= 1 h^{-1}, **H₂/*n-C₄*** = 0.1, *T*= 140°C.
- For ***C₄*** refinery fractions with ***n-C₄*** >98%, the process values are nearly the same, but for the feedstock with ***i-C₄*** >9%, there is a noticeable increase in the formation of by-products ***C₂***, ***C₃*** , ***C₅*** .
- To obtain high yield of ***i-C₄*** and to avoid excessive formation of alkanes ***C₁-C₃*** the process should be performed at 140-150°C and **H₂/*n-C₄*** = 0.1.

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(6) Reported by N.V. Vernikovskaya et al. in: Chem.Eng.J. 134 (**2007**) 228 https://doi.org/10.1016/j.cej.2007.03.035

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