

# Supporting Information for: Kinetics of Zeolite-Catalyzed Heptane Hydroisomerization and Hydrocracking with CBMC-Modeled Adsorption Terms: Zeolite Beta as a Large Pore Base Case

Umang Agarwal,<sup>a</sup> Marcello S. Rigutto,<sup>a,\*</sup> Erik Zuidema,<sup>a</sup> A.P.J. Jansen,<sup>b</sup> Ali Poursaeidesfahani,<sup>c</sup> Shrinjay Sharma,<sup>c</sup> David Dubbeldam<sup>d</sup> and Thijs J.H. Vlugt<sup>c</sup>

*a Shell Global Solutions International B.V., P.O. Box 38000, 1030 BN Amsterdam, The Netherlands.*

*b Shell India Markets Private Limited, Kundanahalli Main Road, Bangalore 560048, Karnataka, India*

*c Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical,*

*Maritime and Materials Engineering, Delft University of Technology, Leeghwaterstraat 39,*

*2628CB Delft, The Netherlands.*

*d Van 't Hoff Institute of Molecular Sciences, University of Amsterdam, Science Park 904, 1098XH, Amsterdam, The Netherlands*

(\*) Corresponding author: marcello.rigutto@shell.com

## 1. Comparison between Ideal Adsorbed Solution Theory and Mixed Langmuir isotherms

Understanding the adsorption selectivity of molecules in a mixture is important when designing a separator column or a catalyst for hydroisomerisation where selective adsorption plays a vital role [1]. The presence of a variety of molecules in a mixture leads to competitive adsorption inside the adsorbent. In a mixture, molecules with longer chain lengths have a

higher tendency to adsorb at low-pressure conditions. At higher pressure, since the adsorption strength of the molecules increases, there is a competition between different molecules for adsorption. The ones with shorter chain lengths will preferentially adsorb as they pack more efficiently [2]. This phenomenon is called length entropy [3]. Also, the position of branches in the chain plays an important role. For example, the presence of two methyl groups at the same position (2,2-dimethylpentane and 3,3-dimethylpentane) can sterically hinder the molecule from adsorbing. Selectivity of the molecules also depends on the shape and the structure of the adsorbent (zeolite) materials. The pore diameter or presence of any constrictions in the adsorbent structures will influence the adsorption of the molecules [4].

To understand adsorption phenomena, the calculation of adsorption isotherms becomes vital. This can be done in many ways. For pure components, experimental data for loadings can be fitted with isotherm equations like Langmuir, Langmuir-Freundlich, etc. to estimate the values of the parameters present in these equations. The isotherms can also be obtained using Monte Carlo simulations in the grand-canonical ensemble by calculating the average loading of the molecules inside the adsorbents [5]. This is valid for both pure components and mixtures. Calculating loadings of components in a mixture using grand-canonical Monte Carlo simulations can be computationally expensive [6]. Instead, equations like mixed Langmuir can be used to determine the equilibrium loadings of the components of the mixtures [7]. There are other alternatives like the Ideal Adsorbed Solution Theory (IAST) [6, 8]. The complexity and accuracy vary from method to method. Therefore, it becomes important to compare these different methods and determine the accuracy of their predictions.

Here, a comparative study has been presented to observe any deviation between mixed Langmuir and IAST, in the case of C7 isomers (n-heptane(C7), 2-methylhexane(C6m2), 3-methylhexane(C6m3), 2,2-dimethylpentane(C5m2m2), 2,3-dimethylpentane(C5m2m3), 2,4-dimethylpentane (C5m2m4), 2,3-dimethylpentane (C5m3m3), 3-ethylpentane(C5e3) and

2,2,3-trimethylbutane(C4m2m2m3)) and the cracked products (n-pentane(C5), 2-methylbutane(C4m2), n-butane(C4), 2-methylpropane(C3m2), propane(C3) and ethane(C2)). For this study we consider temperatures in the range of 481.29K to 606.48K and pressures in the range of  $10^2$  Pa to  $10^7$  Pa. The expression for the mixed Langmuir isotherm equals:

$$n_i = n_i^{\max} \cdot \frac{K_i P_i}{1 + \sum_{j=1}^{N_{\text{comp}}} K_j P_j} \quad (1)$$

in which  $n_i$  is the equilibrium loading for component  $i$ ,  $n_i^{\max}$  is the saturation loading for the component  $i$  in its pure state,  $K_i$  is the equilibrium constant for the component  $i$ .  $n_i^{\max}$  and  $K_i$  are obtained by fitting the Langmuir isotherms to the loadings for pure components calculated using grand-canonical Monte Carlo simulations.  $P_i$  is the partial pressure of component  $i$  and  $N_{\text{comp}}$  is the total number of components in the mixture. If all pure components in a mixture obey the Langmuir isotherm and all pure-component saturation loadings are identical, then IAST and mixed Langmuir are identical [6].

For comparison, we have considered mole fractions of C7 isomers and cracked products in the gas phase as obtained in the *n*-heptane conversion experiments of this study, at the outlet of the reactor, at various reactor temperatures covering a wide range of conversions, and thus covering the range of compositions relevant for the kinetic modeling. Pure component isotherms are obtained by fitting single site Langmuir isotherms to grand canonical Monte Carlo simulation data. The Langmuir parameters ( $n_i^{\max}$  and  $K_i$ ) for pure components are shown in Table S1. These parameters will be used as input in IAST and mixed Langmuir isotherms for calculating equilibrium loading of mixtures.

**Table S1.** Langmuir parameters at temperatures (481.29K, 506.35K, 556.48K, 606.62K) obtained by fitting single site Langmuir isotherms to grand canonical simulation data for pure

components (C7 isomers) in BEA zeolite.

	481.29K		506.35K	
Isomers	$n_i^{\max}$	$K_i$	$n_i^{\max}$	$K_i$
C7	1.25942	$3.89669 \cdot 10^{-04}$	1.23673	$1.79900 \cdot 10^{-04}$
C6m2	1.35446	$2.48738 \cdot 10^{-04}$	1.32906	$1.15900 \cdot 10^{-04}$
C6m3	1.39713	$1.63706 \cdot 10^{-04}$	1.36928	$7.64842 \cdot 10^{-05}$
C5m2m2	1.52663	$4.32642 \cdot 10^{-05}$	1.50584	$2.12831 \cdot 10^{-05}$
C5m2m3	1.57070	$1.19872 \cdot 10^{-04}$	1.56337	$5.23576 \cdot 10^{-05}$
C5m2m4	1.56124	$1.72081 \cdot 10^{-04}$	1.55169	$7.64582 \cdot 10^{-05}$
C5m3m3	1.58531	$2.83032 \cdot 10^{-05}$	1.57440	$1.37910 \cdot 10^{-05}$
C5e3	1.38781	$5.62990 \cdot 10^{-05}$	1.33093	$2.88460 \cdot 10^{-05}$
C4m2m2m3	1.68248	$2.32008 \cdot 10^{-05}$	1.67287	$1.15840 \cdot 10^{-05}$
C5	1.63160	$2.66465 \cdot 10^{-05}$	1.59854	$1.51628 \cdot 10^{-05}$
C4m2	1.82380	$1.92554 \cdot 10^{-05}$	1.77955	$1.11424 \cdot 10^{-05}$
C4	1.90913	$7.32633 \cdot 10^{-06}$	1.86763	$4.63765 \cdot 10^{-06}$
C3m2	2.08371	$7.06356 \cdot 10^{-06}$	2.06231	$4.30607 \cdot 10^{-06}$
C3	2.23507	$2.14496 \cdot 10^{-06}$	2.19258	$1.48173 \cdot 10^{-06}$
C2	2.62404	$5.48725 \cdot 10^{-07}$	2.58837	$4.13788 \cdot 10^{-07}$
	556.48K		606.62K	
Isomers	$n_i^{\max}$	$K_i$	$n_i^{\max}$	$K_i$
C7	1.18819	$4.83612 \cdot 10^{-05}$	1.14412	$1.63055 \cdot 10^{-05}$
C6m2	1.27906	$3.09263 \cdot 10^{-05}$	1.22724	$1.06776 \cdot 10^{-05}$
C6m3	1.30916	$2.08814 \cdot 10^{-05}$	1.24620	$7.31845 \cdot 10^{-06}$
C5m2m2	1.44990	$6.36152 \cdot 10^{-06}$	1.39028	$2.33563 \cdot 10^{-06}$
C5m2m3	1.53370	$1.26992 \cdot 10^{-05}$	1.47900	$4.14860 \cdot 10^{-06}$

C5m2m4	1.52322	$1.89062 \cdot 10^{-05}$	1.47444	$6.20346 \cdot 10^{-06}$
C5m3m3	1.55340	$3.93080 \cdot 10^{-06}$	1.51585	$1.39811 \cdot 10^{-06}$
C5e3	1.22609	$9.23319 \cdot 10^{-06}$	1.12441	$3.71571 \cdot 10^{-06}$
C4m2m2m3	1.67906	$3.13100 \cdot 10^{-06}$	1.74991	$9.81364 \cdot 10^{-07}$
C5	1.53589	$5.73663 \cdot 10^{-06}$	1.47936	$2.55703 \cdot 10^{-06}$
C4m2	1.71152	$4.21131 \cdot 10^{-06}$	1.66726	$1.82831 \cdot 10^{-06}$
C4	1.79270	$2.08632 \cdot 10^{-06}$	1.73560	$1.06477 \cdot 10^{-06}$
C3m2	2.01748	$1.83624 \cdot 10^{-06}$	1.96953	$9.17197 \cdot 10^{-07}$
C3	2.11997	$7.77496 \cdot 10^{-07}$	2.10503	$4.36134 \cdot 10^{-07}$
C2	2.59338	$2.44147 \cdot 10^{-07}$	2.61893	$1.56613 \cdot 10^{-07}$

The mole fractions in the gas phase are reported in Table S2. The corresponding loadings calculated using IAST and mixed Langmuir are shown in Table S3.

**Table S2.** Mole fractions of C7 isomers and the cracked products in the gas phase considered for comparison of loadings calculated at temperatures (481.29K, 506.35K, 556.48K, 606.62K) and 30 bar pressure using mixed Langmuir and IAST.

Isomers	Mole fractions			
	481.29K	506.35K	556.48K	606.62K
C7	0.039114	0.037573	0.008640	0.000032
C6m2	0.000174	0.000896	0.010096	0.000039
C6m3	0.000190	0.000904	0.010952	0.000041
C5m2m2	0.000000	0.000010	0.001859	0.000010

C5m2m3	0.000020	0.000033	0.002540	0.000013
C5m2m4	0.000000	0.000017	0.001847	0.000000
C5m3m3	0.000000	0.000004	0.001172	0.000000
C5e3	0.000027	0.000070	0.000865	0.000017
C4m2m2m3	0.000000	0.000000	0.000119	0.000000
C5	0.000000	0.000000	0.000029	0.000197
C4m2	0.000000	0.000000	0.000015	0.000376
C4	0.000000	0.000000	0.000129	0.005320
C3m2	0.000008	0.000040	0.002970	0.072020
C3	0.000000	0.000040	0.003100	0.077459
C2	0.000000	0.000000	0.000036	0.000473

**Table S3.** Loadings calculated for C7 isomers and cracked products inside BEA-type zeolite at 30 bar pressure and temperatures of (a) 481.29K, (b) 506.35K, (c) 556.48K and (d) 606.62K.

	481.29K			506.35K		
Isomers	Loadings/ [mol/kg framework]			Loadings/ [mol/kg framework]		
	IAST	Mixed Langmuir	Absolute difference	IAST	Mixed Langmuir	Absolute difference
C7	1.224466	1.226286	0.001821	1.143588	1.149674	0.006087
C6m2	0.004599	0.003755	0.000844	0.022016	0.018971	0.003045
C6m3	0.003693	0.002779	0.000914	0.016044	0.013021	0.003023
C5m2m2	0.000000	0.000000	0.000000	0.000067	0.000046	0.000022
C5m2m3	0.000421	0.000239	0.000182	0.000590	0.000376	0.000214
C5m2m4	0.000000	0.000000	0.000000	0.000425	0.000274	0.000150
C5m3m3	0.000000	0.000000	0.000000	0.000019	0.000012	0.000007
C5e3	0.000178	0.000136	0.000042	0.000428	0.000368	0.000060
C4m2m2m3	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C5	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C4m2	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C4	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C3m2	0.000023	0.000008	0.000016	0.000113	0.000049	0.000064
C3	0.000000	0.000000	0.000000	0.000044	0.000018	0.000026
C2	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
	556.48K			606.62K		
Isomers	Loadings/ [mol/kg framework]			Loadings/ [mol/kg framework]		
	IAST	Mixed Langmuir	Absolute difference	IAST	Mixed Langmuir	Absolute difference
C7	0.334759	0.356545	0.021786	0.001218	0.001359	0.000141
C6m2	0.288101	0.286821	0.001280	0.001058	0.001160	0.000102
C6m3	0.220373	0.215023	0.005350	0.000776	0.000847	0.000072

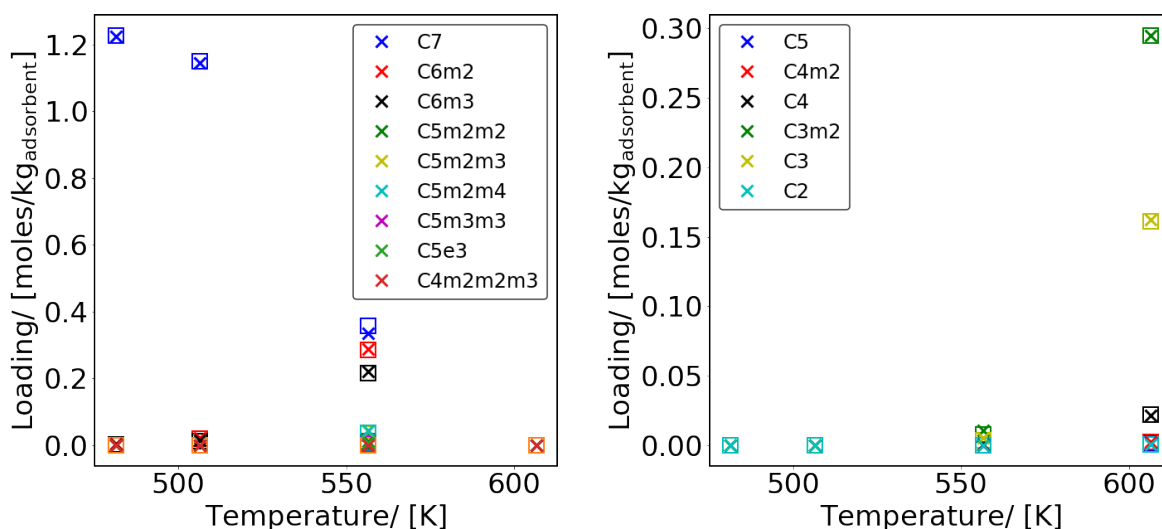
C5m2m2	0.013701	0.012314	0.001387	0.000068	0.000073	0.000004
C5m2m3	0.041190	0.035527	0.005663	0.000176	0.000186	0.000009
C5m2m4	0.044068	0.038195	0.005873	0.000000	0.000000	0.000000
C5m3m3	0.006010	0.005137	0.000873	0.000000	0.000000	0.000000
C5e3	0.006797	0.007029	0.000232	0.000141	0.000158	0.000017
C4m2m2m3	0.000552	0.000448	0.000104	0.000000	0.000000	0.000000
C5	0.000212	0.000182	0.000029	0.001601	0.001685	0.000083
C4m2	0.000095	0.000077	0.000019	0.002526	0.002599	0.000072
C4	0.000443	0.000345	0.000098	0.021800	0.022267	0.000468
C3m2	0.010826	0.007902	0.002925	0.294345	0.294688	0.000343
C3	0.005155	0.003669	0.001485	0.162433	0.161079	0.001354
C2	0.000025	0.000016	0.000009	0.000455	0.000439	0.000016

Figure S1. shows the plots for loading of C7 isomers and cracked products inside BEA-type zeolite. The comparison between mixed Langmuir and IAST is illustrated here. The plots are obtained using the mole fractions shown in Table S2 and the loading data shown in Table S3. The differences between the loadings calculated using the two methods are hardly distinguishable in the plot, and for each component always less than 11% of the maximum value for that component, corresponding to a maximum deviation of 0.5 kJ/mol in fitted activation energy. This is because partial pressures of the various components remain low enough to avoid significant competitive effects. Therefore, in this work, the use of mixed Langmuir for calculating the mixture loadings provide correct results for the modelling of the product distribution at the end of the reaction (see the main text on pages 27-29).

(a)

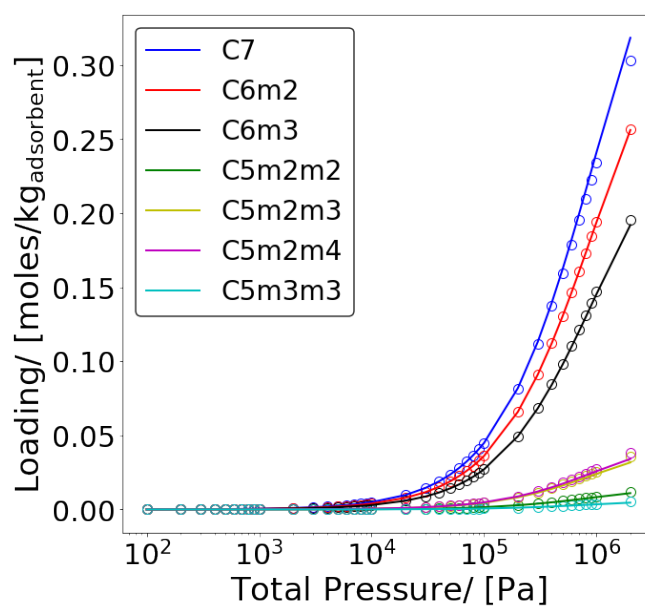
(b)





**Figure S1.** Loadings of (a) C7 isomers and (b) cracked products at temperatures (481.29K, 506.35K, 556.48K, 606.62K) inside BEA-type zeolite operated at 30 bar. Empty squares represent loadings calculated using mixed Langmuir and the cross marks represent loadings calculated using IAST.

For better clarity, adsorption isotherms are also plotted using the data for the mole fractions shown in Table S2. Figure S2 shows the adsorption isotherms calculated using mixed Langmuir and IAST at 556.48K.



**Figure S2.** Adsorption Isotherms of C7 isomers mixtures inside BEA zeolite at 556.48K and pressure range ( $10^2 - 3 \cdot 10^6$  Pa). Mole fractions of all the isomers in the gas phase are shown in Table S2. Solid lines represent loadings obtained from mixed Langmuir and empty circles represent loadings obtained from IAST.

If the concentrations of the components are very low, the difference between mixed Langmuir and IAST is negligible. One of the key assumptions of mixed Langmuir isotherms is that the adsorbed molecules do not interact with each other [7]. Such a condition is only valid when the number of adsorbed molecules is very low. In the limit of low concentration, the number of available sites for adsorption is much higher than the number of molecules for adsorption. In such a situation, the adsorbed molecules do not feel the competition from other co adsorbed molecules. The equivalence between IAST and mixed Langmuir at low loading can also be proven mathematically. The proof is shown below.

IAST:

In IAST, to account for the work done on the surrounding by the adsorbed molecule, a two-dimensional pressure called spreading pressure is introduced [6]. In this theory, it is assumed that the spreading pressure for the mixture is equal to the spreading pressure for adsorption of the pure components [6].

$$\bar{\pi} = \frac{\pi A}{RT} = \bar{\pi}_i = \frac{\pi_i(P_i^0)A}{RT} = \int_0^{P_i^0} \frac{n_i^0}{P} dP \quad (2)$$

In this equation,  $\pi$  is the spreading pressure of the mixture and  $\pi_i$  is the spreading pressure of the pure component  $i$ .  $A$  is the surface area,  $R$  is the universal gas constant and  $T$  is the temperature.  $n_i^0$  is the equilibrium loading for pure component  $i$ .  $P_i^0$  is the upper bound of the integral. Assuming Henry's law at low loading condition,  $n_i^0$  can be expressed as follows.

$$n_i^0 = n_i^{\max} K_i P \quad (3)$$

$n_i^{\max}$  is the saturation loading of component  $i$  and the equilibrium constant is represented by  $K_i$ . Substituting equation 3 for  $n_i^0$  in equation 2, we obtain

$$\bar{\pi}_i = \bar{\pi}_i = n_i^{\max} K_i P_i^0 \quad (4)$$

Analogous to the Raoult's law, for an adsorbed phase in equilibrium with a gas phase, the partial pressure of the component  $i$  in the mixture,  $P_i$  is a function of  $P_i^0$  and adsorbed mole fraction,  $x_i$ .

$$P_i = x_i P_i^0 \quad (5)$$

Since the sum of the adsorbed mole fractions is 1, we have

$$\sum_i^{N_{\text{comp}}} \frac{P_i}{P_i^0} = 1 \quad (6)$$

Substituting  $P_i^0$  in equation 6 using equation 4 and rearranging the terms, we obtain another expression for spreading pressure,  $\bar{\pi}$ .

$$\bar{\pi} = \sum_i^{N_{\text{comp}}} P_i n_i^{\max} K_i \quad (7)$$

Combining equations 4 and 7 leads to

$$P_i^0 = \frac{\sum_i^{N_{\text{comp}}} P_i n_i^{\max} K_i}{n_i^{\max} K_i} \quad (8)$$

Now,  $x_i$  can be expressed as a function of  $P_i$ ,  $n_i^{\max}$  and  $K_i$  by substituting  $P_i^0$  in equation 5 using equation 8.

$$x_i = \frac{P_i n_i^{\max} K_i}{\sum_i^{N_{\text{comp}}} P_i n_i^{\max} K_i} \quad (9)$$

The expression for total amount of loadings as a function of  $n_i^0$  and  $x_i$  is:

$$\frac{1}{n_T} = \sum_i^{N_{\text{comp}}} \frac{x_i}{n_i^0} \quad (10)$$

Replacing  $n_i^0$  using equation 3 and  $P_i^0$  using equation 8 in equation 10 leads to

$$\frac{1}{n_T} = \sum_i^{N_{\text{comp}}} \frac{x_i}{n_i^{\max} K_i P_i^0} = \sum_i^{N_{\text{comp}}} \frac{x_i n_i^{\max} K_i}{n_i^{\max} K_i \sum_i^{N_{\text{comp}}} P_i n_i^{\max} K_i} \quad (11)$$

Rearranging equation 11, we have,

$$\frac{\sum_i^{N_{\text{comp}}} P_i n_i^{\max} K_i}{n_T} = \sum_i^{N_{\text{comp}}} x_i = 1 \quad (12)$$

The total loading,  $n_T$  can be expressed as shown below.

$$n_T = \sum_i^{N_{\text{comp}}} P_i n_i^{\max} K_i \quad (13)$$

The adsorbed mole fractions can also be expressed as the ratio of the loading of individual component,  $n_i$  and the total adsorbed loading,  $n_T$ . Using equations 9 and 13, we obtain an expression for  $n_i$ .

$$n_i = n_i^{\max} K_i P_i \quad (14)$$

The expression for the loading of component  $i$  resembles Henry's law.

Mixed Langmuir:

The equilibrium loading for individual component in the mixture is expressed as follows.

$$n_i = n_i^{\max} \cdot \frac{K_i P_i}{1 + \sum_{j=1}^{N_{\text{comp}}} K_j P_j} \quad (15)$$

At very low loading,  $\sum_j^{N_{\text{comp}}} K_j P_j \ll 1$ . Therefore, equation 15 can be simplified as follows.

$$n_i \approx n_i^{\max} K_i P_i \quad (16)$$

Equations 14 and 16 are identical which proves the equivalence of IAST and mixed Langmuir at low loadings.

As mentioned earlier, if the pure components obey the Langmuir isotherm and have identical saturation loadings, then IAST and mixed Langmuir becomes identical in this case [6]. This can be proved mathematically as shown below.

$$\bar{\pi} = \frac{\pi A}{RT} = \bar{\pi}_i = \frac{\pi_i (P_i^0) A}{RT} = \int_0^{P_i^0} \frac{n_i^0}{P} dP \quad (17)$$

In this equation,  $\pi$  is the spreading pressure of the mixture and  $\pi_i$  is the spreading pressure of the pure component  $i$ .  $A$  is the surface area,  $R$  is the universal gas constant and  $T$  is the

temperature.  $n_i^0$  is the equilibrium loading for pure component  $i$ .  $P_i^0$  is the upper bound of the integral. Equilibrium loading for pure component using the Langmuir equation is shown below.

$$n_i^0 = \frac{n_i^{\max} K_i P}{1 + K_i P} \quad (18)$$

$n_i^{\max}$  is the saturation loading and  $K_i$  is the equilibrium constant for component  $i$ . Now, equating the spreading pressures of two components  $i$  and  $j$  ( $\bar{\pi}_i = \bar{\pi}_j$ ) and substituting  $n_i^0$  in equation 17 using equation 18, we obtain,

$$n_i^{\max} \ln(1 + K_i P_i^0) = n_j^{\max} \ln(1 + K_j P_j^0) \quad (19)$$

If the saturation loadings of the components are identical ( $n_i^{\max} = n_j^{\max}$ ), we have,

$$K_i P_i^0 = K_j P_j^0 \quad (20)$$

Analogous to Raoult's law we have,  $P_i = x_i P_i^0$  [6].  $P_i$  is the partial pressure of the component in the mixture.  $x_i$  is the adsorbed mole fraction of the component  $i$  and  $P_i^0$  is the pressure of the pure component. Considering the sum of the mole fractions of the adsorbed components, we have,

$$\sum_{j=1}^{N_{\text{comp}}} x_j = \sum_{j=1}^{N_{\text{comp}}} \frac{P_j}{P_j^0} = 1 \quad (21)$$

Substituting  $P_j^0$  in equation 21 using equation 20, we obtain,

$$\sum_{j=1}^{N_{\text{comp}}} K_j P_j = K_i P_i^0 \quad (22)$$

Replacing  $P_i^0$  in the equation  $P_i = x_i P_i^0$  using equation 22 and rearranging the terms, we have,

$$x_i = \frac{K_i P_i}{\sum_{j=1}^{N_{\text{comp}}} K_j P_j} \quad (23)$$

The total equilibrium loading of the mixture,  $n_T$  is determined by  $\frac{1}{n_T} = \sum_{j=1}^{N_{\text{comp}}} \frac{x_j}{n_j^0}$ . Replacing  $n_j^0$  using equation 18, we obtain,  $\frac{1}{n_T} = \sum_{j=1}^{N_{\text{comp}}} \frac{x_j(1+K_j P_j^0)}{n_j^{\text{max}} K_j P_j^0}$ . Using equation 20 and considering identical saturation loading ( $n^{\text{max}}$ ) for all the components,  $\frac{1}{n_T}$  can be expressed as follows.

$$\frac{1}{n_T} = \frac{1 + K_i P_i^0}{n^{\text{max}} K_i P_i^0} \left( \sum_{j=1}^{N_{\text{comp}}} x_j \right) = \frac{1 + K_i P_i^0}{n^{\text{max}} K_i P_i^0} \quad (24)$$

Substituting  $K_i P_i^0$  in equation 24 using equation 22, we have,

$$\frac{1}{n_T} = \frac{1 + K_i P_i^0}{n^{\text{max}} K_i P_i^0} = \frac{1 + \sum_{j=1}^{N_{\text{comp}}} K_j P_j}{n^{\text{max}} \sum_{j=1}^{N_{\text{comp}}} K_j P_j} \quad (25)$$

The loading for component  $i$  ( $n_i$ ) can be expressed as  $n_i = x_i n_T = x_i \frac{n^{\text{max}} \sum_{j=1}^{N_{\text{comp}}} K_j P_j}{1 + \sum_{j=1}^{N_{\text{comp}}} K_j P_j}$ .

Equating this expression with equation 23, we obtain,

$$n_i = \frac{n^{\text{max}} K_i P_i}{1 + \sum_{j=1}^{N_{\text{comp}}} K_j P_j} \quad (26)$$

This equation is identical to the expression for equilibrium loading obtained using the mixed

Langmuir equation. Thus, when the pure components obey the Langmuir isotherm and have identical saturation loading, the equilibrium loadings for components in the mixture obtained by IAST and mixed Langmuir are identical.

**Table S4.** Langmuir parameters at 576K obtained by fitting single site Langmuir isotherms to grand canonical simulation data for pure components (C7 isomers) in BEA zeolite.

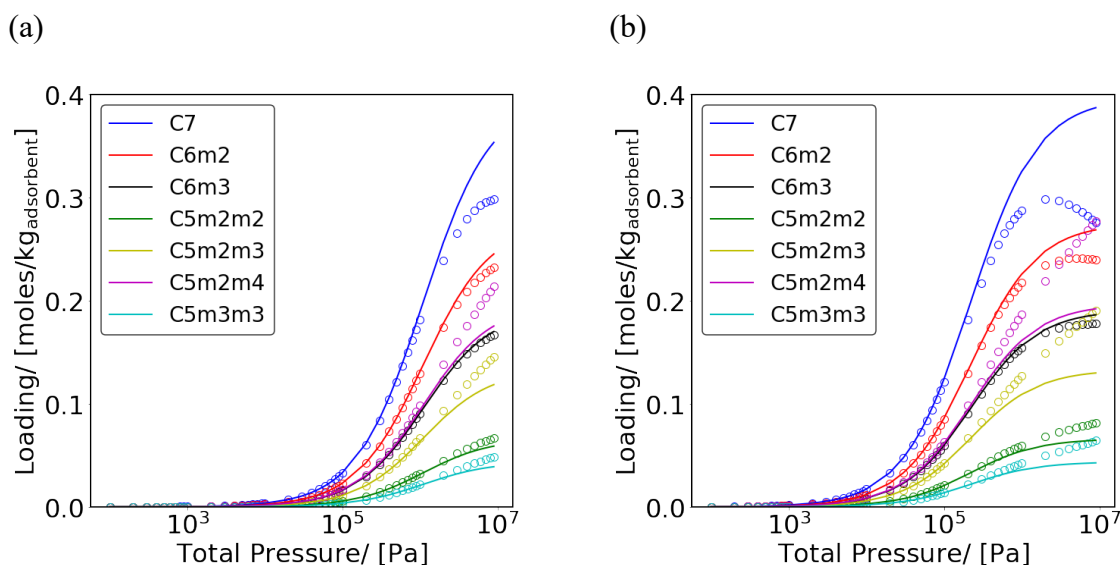
	576K	
Isomers	$n_i^{\max}$	$K_i$
C7	1.17037	$3.08884 \cdot 10^{-05}$
C6m2	1.25728	$1.99542 \cdot 10^{-05}$
C6m3	1.28626	$1.35240 \cdot 10^{-05}$
C5m2m2	1.42512	$4.22901 \cdot 10^{-06}$
C5m2m3	1.51397	$8.01073 \cdot 10^{-06}$
C5m2m4	1.50526	$1.19183 \cdot 10^{-05}$
C5m3m3	1.53214	$2.60179 \cdot 10^{-06}$

**Table S5.** Mole fractions of C7 isomers and the cracked products in the gas phase considered for comparison of loadings calculated at 576 K and 30 bar using mixed Langmuir and IAST.

Isomers	C7	C6m2	C6m3	C5m2m2	C5m2m3	C5m2m4	C5m3m3
Mole fractions	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	0.05	0.05	0.05	0.05	0.05	0.05	0.05

Considerable differences between the calculated loadings using the two methods can be observed at high loading conditions. This is well understood by observing the adsorption isotherms for mixtures obtained by both the methods.





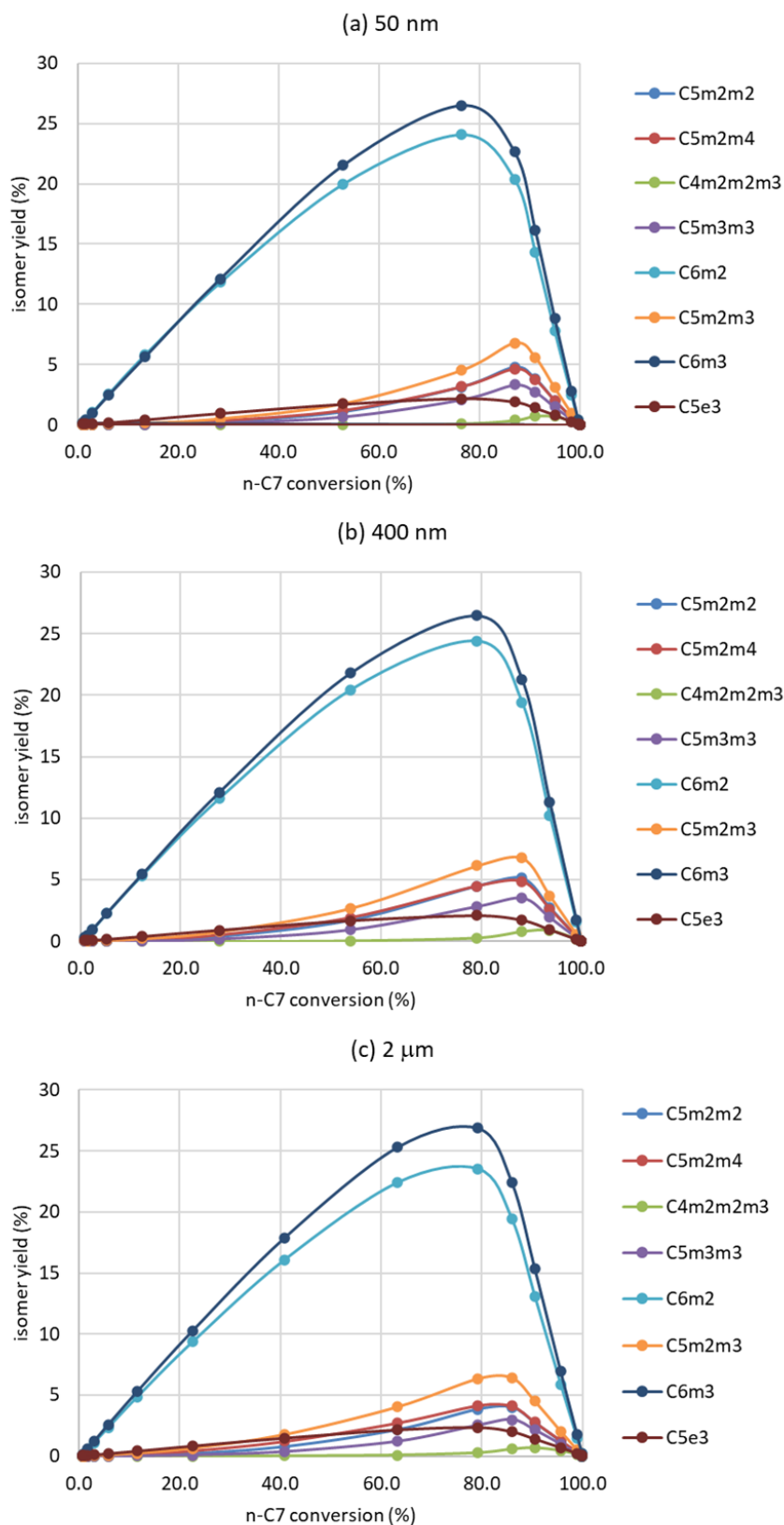
**Figure S3.** Adsorption Isotherms of a mixture of C7 isomers inside BEA zeolite at 576K and pressure range ( $10^2$  -  $10^7$  Pa). Mole fractions of all the isomers in the gas phase are kept at (a) 0.01 and (b) 0.05. Solid lines represent loadings obtained from mixed Langmuir and empty circles represent loadings obtained from IAST.

Figures. S3(a) and S3(b) show adsorption isotherms of mixtures obtained using mixed Langmuir and IAST for C7 isomers in BEA-type zeolite at different gas phase concentrations. Langmuir parameters for pure components are shown in Table S4. These values are used as input for calculating equilibrium loading of mixtures using IAST and mixed Langmuir isotherms. Mole fractions for the isomers in the gas phase used in the calculations are as shown in Table S5. Figure. S3(a) corresponds to mole fraction of 0.01 for all the C7 isomers whereas Figure S3(b) corresponds to mole fraction of 0.05 for all the C7 isomers. 576K was considered as the operating temperature for calculating the isotherms. At higher pressures, considerable differences in the loadings calculated using both the methods can be observed. The adsorption of molecules with lower chain lengths generally dominates at high pressure. This effect is called length entropy as mentioned before.

Increasing the degree of branching decreases the main chain length of the molecules which helps in efficient packing of the molecules inside the channels present in the adsorbent (BEA-type zeolite) [3]. Figure S3 shows that at higher pressure, adsorption of branched molecules surpasses the linear chains. C7 has the longest chain length out of all the isomers. At high pressure, its loading decreases compared to the other isomers. At such conditions, the adsorption of C5m2m4 and C5m2m3 starts becoming dominant. These effects are not well captured by the mixed Langmuir equation. This is because the interactions between the adjacent molecules are completely neglected in the case of the mixed Langmuir [7]. In sharp contrast, IAST considers an average strength of interaction between the molecules [6]. However, at low concentrations or loadings, there will be very few such interactions. This is because of the availability of large number of adsorption sites compared to the number of adsorbed molecules. In such a situation no significant differences will be witnessed in the loadings calculated using mixed Langmuir and IAST.

## 2. Crystal size effects in hydroisomerization of *n*-heptane over Pd-loaded zeolite Beta

In Figure S4, heptane isomer yields are plotted as a function of *n*-heptane conversion for three Pd-Beta catalysts with different zeolite primary crystal sizes of 50 nm (Si/Al=150 mol/mol), 400 nm (Si/Al=50 mol/mol) and 2  $\mu$ m (Si/Al=200 mol/mol), respectively. The 400 nm crystal material was the sample used in the main body of this study, and Pd loading and calcination was performed identically. The data show only very small differences in product profiles as a function of conversion, and hence do not indicate any signs of intracrystalline diffusion limitation.



**Figure S4.** Yields of *n*-heptane hydroisomerization products vs. *n*-heptane conversion over Pd-loaded zeolite beta with different primary crystal sizes: (a) 50 nm; (b) 400 nm and (c) 2  $\mu\text{m}$  (right).

## Nomenclature

### Abbreviation

IAST	ideal adsorbed solution theory
C7	n-heptane
C6m2	2-methylhexane
C6m3	3-methylhexane
C5m2m2	2,2-dimethylpentane
C5m2m3	2,3-dimethylpentane
C5m2m4	2,4-dimethylpentane
C5m3m3	3,3-dimethylpentane
C5e3	3-ethylpentane
C4m2m2m3	2,2,3-trimethylbutane
C5	n-pentane
C4m2	2-methylbutane
C4	n-butane
C3m2	2-methylpropane
C3	propane
C2	ethane

### Latin Symbols

$A$	surface area [ $m^2$ ]
$K$	equilibrium constant [ $1/Pa$ ]
$N_{\text{comp}}$	total number of components
$P$	partial pressure [ $Pa$ ]

$R$	universal gas constant [ $J/mol/K$ ]
$T$	temperature [ $K$ ]
$n$	equilibrium loading [ $mole/kg\ adsorbent$ ]
$x$	mole fraction

#### Greek symbols

$\pi$	spreading pressure [ $N/m$ ]
-------	------------------------------

#### Superscript

0	pure component
max	maximum or saturation
–	dimensionless

#### Subscript

T	total
$i, j$	components

#### References

- [1] B. Smit and T. L. M. Maesen, "Molecular simulations of zeolites: adsorption, diffusion, and shape selectivity," *Chemical reviews*, vol. 108, pp. 4125-4184, 2008.
- [2] T. J. H. Vlugt, R. Krishna and B. Smit, "Molecular simulations of adsorption isotherms for linear and branched alkanes and their mixtures in silicalite.," *The Journal of Physical Chemistry B*, vol. 103, pp. 1102-1118, 1999.
- [3] R. Krishna, B. Smit and S. Calero, " Entropy effects during sorption of alkanes in zeolites," *Chemical Society Reviews*, vol. 31, pp. 185-194, 2002.
- [4] D. Dubbeldam, S. Calero, T. Maesen and B. Smit, "Understanding the window effect in zeolite catalysis," *Angewandte Chemie International Edition*, vol. 42, pp. 3624-3626, 2003.
- [5] D. Frenkel and B. Smit, *Understanding molecular simulation: from algorithms to applications*, vol. 1, Elsevier, 2001.

- [6] C. Simon, B. Smit and M. Haranczyk, "pyIAST: Ideal adsorbed solution theory (IAST) Python package," *Computer Physics Communications*, vol. 200, pp. 364-380, 2016.
- [7] R. I. Masel, Principles of adsorption and reaction on solid surfaces, vol. 3, John Wiley & Sons, 1996.
- [8] A. Myers and J. Prausnitz, "Thermodynamics of mixed-gas adsorption," *AIChE Journal*, vol. 11, pp. 121-127, 1965.