

Gas-Solid Adsorption Parameters for Fischer-Tropsch Process

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The Fischer-Tropsch (FT) based Gas-to-Liquid technology presents an opportunity to obtain clean fuels from coal, natural gas and more recently from biomass. The process has been attracting more attention to meet future energy demands. In the FT process, synthesis gas (a mixture of hydrogen and carbon monoxide) is converted to a wide variety of valuable chemicals and the use of catalysts favoring the desired reactions is essential. The mechanism of the process involves the adsorption of the reagents on the surface (active sites) and desorption of the products. Information on the adsorption equilibrium is one of the most important parts in understanding the process, and it dictates how much of the component can be adsorbed by the solid adsorbent. In this work, we focus on the simulation of adsorption behaviour of CO₂ and alkanes in zeolite ZSM-5 at different temperatures using Monte Carlo technique. Additionally, the equation of Toth was used to fit the simulated data.

Keywords: Molecular Simulation, Grand Canonical Monte Carlo, Isotherm, Zeolite ZSM-5

1. Introduction

Bifunctional catalysts, composed of an active metal for the Fischer Tropsch (FT) synthesis and an acidic zeolite, have been the focus of many studies. The use of such system allows the direct production of desired products by coupling the activity toward FT synthesis with the cracking and/or isomerization properties of zeolite (Pour et al., 2008). The zeolite ZSM-5 presents acidic nature and shape selectivity ability, and for fuel hydrocarbons production show higher activity compared with other zeolites (Doluda et al., 2019).

According to Pour et al. (2008) the oligomerization of light olefins is catalyzed by acidic function (under ZSM-5), resulting in longer chains (the mole fraction C₅-C₁₁ hydrocarbons increased, while of light products decreased); followed by aromatization. Uykun Mangaloğlu et al. (2018) studied the effects of promoters on the performance of the bi-functional iron-low acidity ZSM-5 catalysts in the FT synthesis. As a result, those authors found an increase of 8.5 - 56% in the gasoline range and 20 - 743% in diesel range, respectively.

Yoneyama et al. (2005) employed Fe/HZSM-5 hybrid catalysts to obtain selective product of isoparaffins in a single step. According to Norval and Phillips (1990) the main products of the FT are aliphatic hydrocarbons, predominantly of n-alkanes. Marques and Guirardello (2018) analysed the thermodynamic equilibrium of a FT system, using constraints to take into account the effect of the catalyst. An important process to understand the mechanism involved in the catalytic conversion is the adsorption. An isotherm is an equation that relates the fraction of active sites in the catalyst occupied by a chemical specie as a function of the concentration or partial pressure (Do, 1998).

Data of equilibrium isotherms for the FT system, as well as experiments with catalysts, have been widely studied, but the literature is still scarce in this area. There are some experimental studies, such as Zhu et al. (1998), who measured adsorption isotherms of methane, ethane, propane and butane on silicalites-1. Furthermore, some computational studies, such as Granato and Vlught (2007), inspected the propane-propylene binary adsorption equilibrium in zeolite 13X through molecular simulation.

This work aims to use the computational simulation technique of Monte Carlo Method to obtain adsorption values for the main products of the FT synthesis on zeolite ZSM-5, and then fit these results to an adequate isotherm model (Toth equation).

2. Methods

2.1 Molecular Modelling

Adsorbent Structure

Bifunctional catalysts composed of an active metal for the Fischer Tropsch synthesis and an acidic zeolite have been the focus of many studies that seek to overcome the non-selective Anderson-Schulz-Flory product distribution. The use of bifunctional catalysts also favors the increase in octane number (Udaya et al., 1990). Thus, the adsorbent selected in this work was zeolite ZSM-5 (Marvast et al., 2005).

The X-ray characterizations obtained by Olson et al., (1981) were used to configure the crystallographic positions of the ZSM-5 zeolite atoms, the structure is orthorhombic with $Pnma$ groups of symmetry and cell parameters: $a = 20.07\text{Å}$, $b = 19.92\text{Å}$ and $c = 13.42\text{Å}$, and unit cell of $2 \times 2 \times 2$. Periodic boundary conditions with a size at least twice the cut-off radius were used. In the simulations, it is assumed that the zeolite is rigid. In this case, the positions of the atoms of the structure are fixed. For the adsorption of alkanes, the flexibility or not of the structure does not influence the results related to adsorption isotherms (Vlugt and Schenk, 2002). The pore volume in the structure was calculated using the Widom particle insertion method (Myers and Monson, 2002).

2.2 Simulation Details

The molecules were modelled using the united-atom model, where a group of atoms is represented by a unitary interaction site. The interactions with ZSM-5 zeolite were obtained from García-Pérez et al. (2007). The force field term refers to the functional form and the parameterization used to describe the energy of a system of interacting molecules. The simulations were performed using Monte Carlo (MC) Metropolis Method. The number of movements per cycle is equal to the number of particles present in the system. For a correct statistical description of the system, the number of cycles for the initialization was set to 2000 and the number of cycles for the production was 25000. Further details on the simulation technique can be found in the work of (Vlugt et al., 1999).

The adsorption isotherms were calculated in the Grand Canonic ensemble (GCMC), considering the number of particles (N), volume (V) and energy constants (E), both for the equilibrium/initialization phase and for the production phase. The number of movements per cycle is equal to the number of particles in the system (initialization: 2000; production: 25000 cycles). The points of adsorption were simulated through the RASPA computational packages version 2.0.8 (Dubbeldam et al., 2004). All Lennard-Jones (LJ) parameters and the initial atomic charges used in this work are listed in Table 1. The Lorentz-Berthelot mixing rules were used for the interaction with the zeolite structure.

Table 1: Lennard-Jones parameters used in this simulation.

Atom(s)	σ (Å)	g/k (K)	q (e)	Ref.
CH ₄	3.720	158.500		Dubbeldam et al. (2004)
CH ₃	3.760	108.000		Dubbeldam et al. (2004)
CH ₂	3.960	56.000		Dubbeldam et al. (2004)
C-CO ₂	2.757	28.129	0.651	Harris and Yung (1995)
O-CO ₂	3.033	80.507	-0.325	Harris and Yung (1995)
Si			2.050	Calero et al. (2004)
O _{zeolite}			-1.025	Calero et al. (2004)
CH ₄ – O _{zeolite}	3.470	115.00		Dubbeldam et al. (2004)
CH ₃ – O _{zeolite}	3.480	93.000		Dubbeldam et al. (2004)
CH ₂ – O _{zeolite}	3.580	60.500		Dubbeldam et al. (2004)
C-CO ₂ – O _{zeolite}	2.781	50.200		García-Pérez et al. (2007)
O-CO ₂ – O _{zeolite}	2.919	84.930		García-Pérez et al. (2007)

3. Results

3.1 Framework Characterization (ZSM-5)

The hollow fraction, which is the empty space of a structure divided by the total volume, was calculated by the Widom particle insertion method (Myers and Monson, 2002). The Rosenbluth weight using helium of the orthorhombic structure ZSM-5 (Olson et al., 1981) obtained is 0.2941 ± 0.00016 . The volume of the unit cell is $5,365.24\text{Å}^3$ with a molar mass of $5,768.09\text{g}\cdot\text{mol}^{-1}$. Calculation of the pore volumes using the Widom insertion technique leads to a value of $0.1647\text{cm}^3\cdot\text{g}^{-1}$ for the structure. Similar values were obtained by (Castillo et al., 2009). It is important to emphasize that the values depend on the cut-off radius and the displaced potential vs. truncated.

3.2 Prediction of Adsorption Isotherms

The adsorption of carbon dioxide on ZSM-5 zeolite is shown in Figure 1. The simulated data were compared with experimental data obtained from the literature. Figure 1b shows the simulated adsorption data at different temperatures (498.15 K, 598.15 K and 698.15 K).

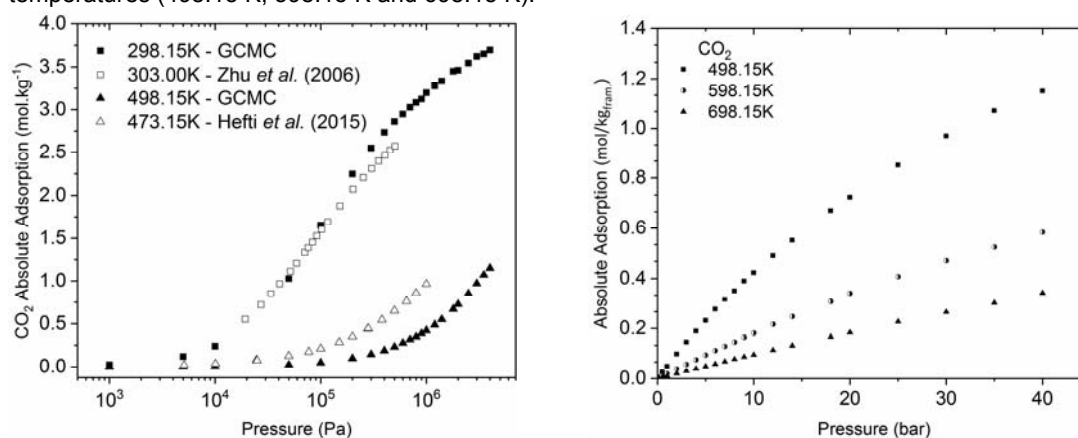


Figure 1: Carbon Dioxide adsorption isotherms in ZSM-5. (a) Comparison of the simulated data with the literature. Experimental: 303.0 K (Zhu et al., 2006) and 473.15 K (Hefti et al., 2015); Simulated: 298.15 K and 498.15 K. (b) Isotherms simulated at 498.15 K, 598.15 K and 698.15 K.

According to Figure 1a it is possible to verify that there is an excellent prediction of the adsorption values and, consequently, of the parameters used in the GCMC simulation. Absolute adsorption data of pure components on ZSM-5 were obtained at 498.15 K, 598.15 and 698.15 K. Figure 2 and 3 shows the isotherms for the studied hydrocarbons (C1 – C4) and (C5-C10), respectively. The simulated points follow a pattern, except for octane, nonane and decane at 498.15K. This behavior is due to the fact that the model simulates only molecules in the gas phase, and in those conditions the molecules have properties that are possibly close to saturation, thus generating that results (Lithoxoos et al., 2010).

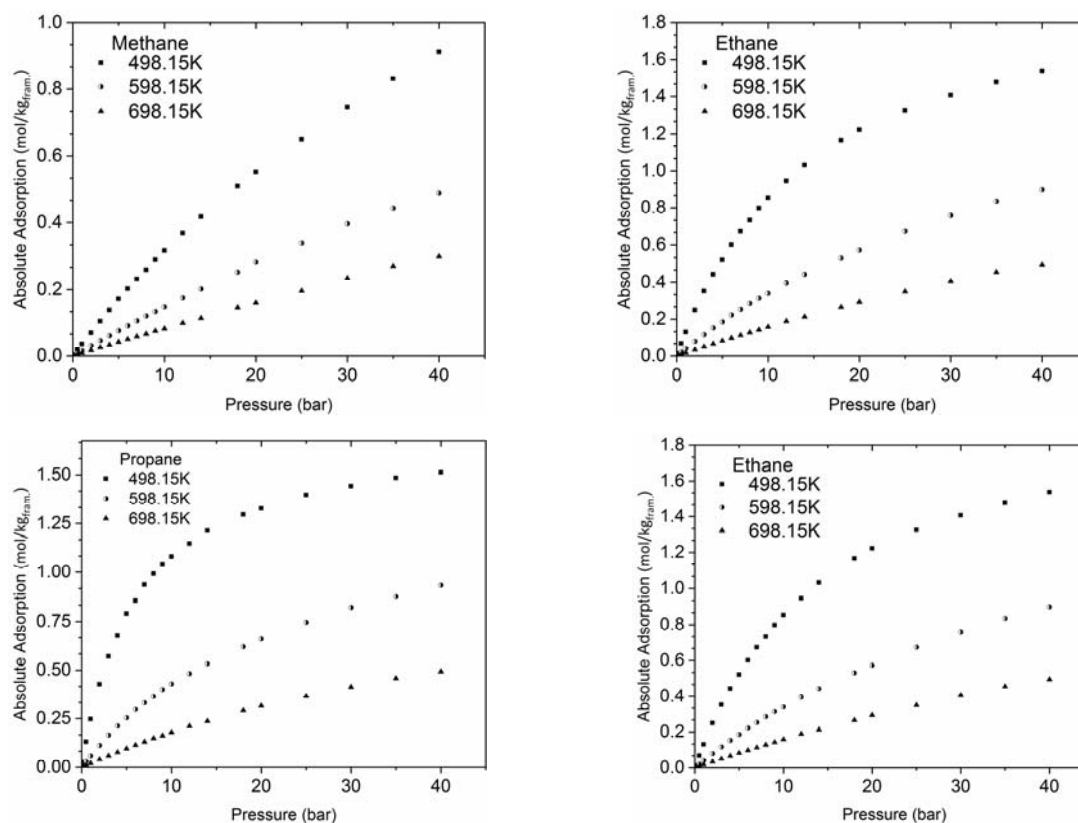


Figure 2: Equilibrium isotherms for the hydrocarbons (C1 – C4) under ZSM-5 at 498.15 K, 598.15 and 698.15K.

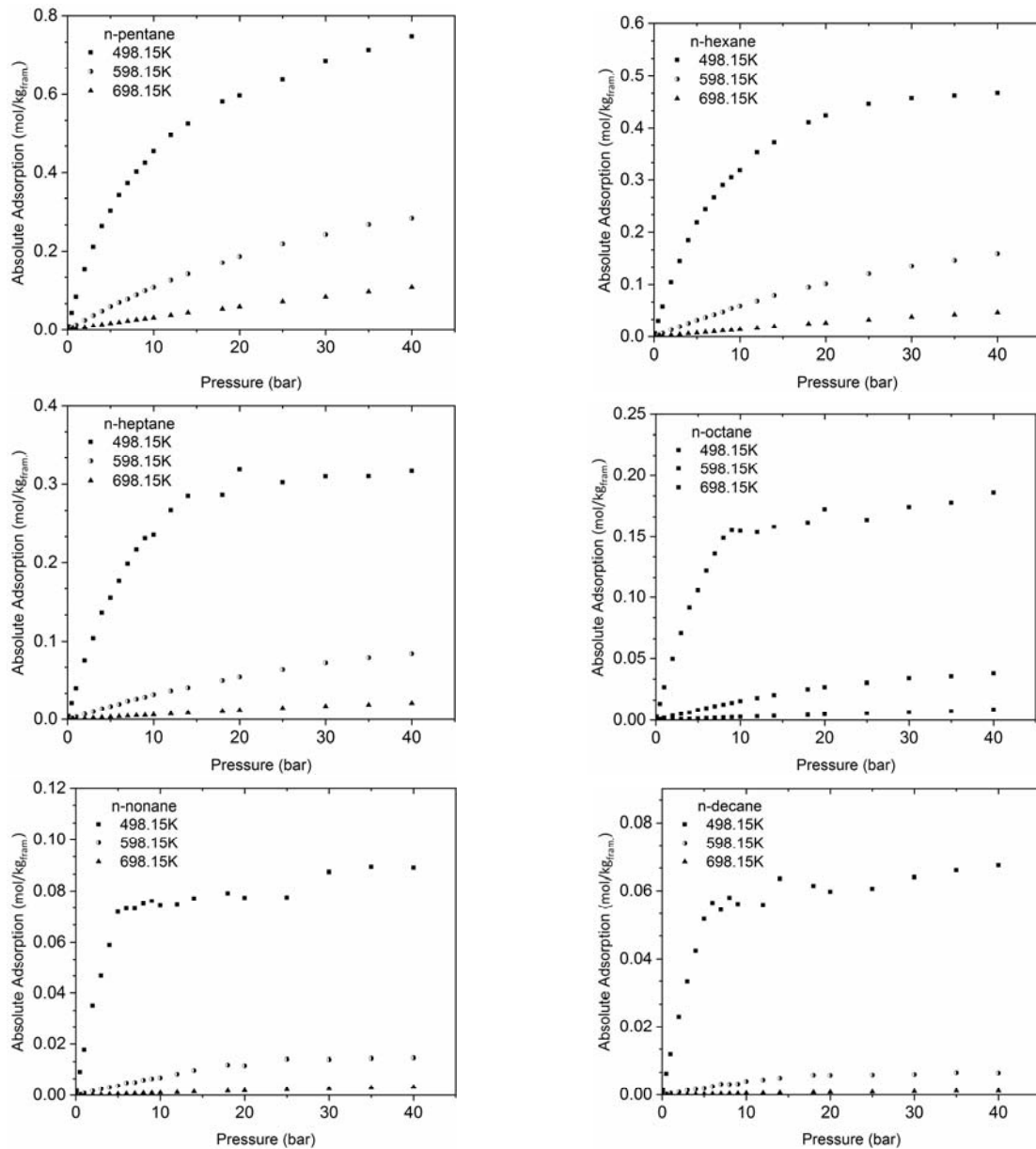


Figure 3: Equilibrium isotherms for the hydrocarbons (C5 - C10) under ZSM-5 at 498.15 K, 598.15 and 698.15K.

According to Tétényi (1994) the adsorption data derived from kinetic equations are different from those obtained by direct adsorption measurements. In this way, the data simulated by the GCMC method were fitted to an isotherm (e.g. Langmuir, Freundlich, Toth).

However, Freundlich equation is not valid at the low and high ends of the pressure range, and Sips equation is not valid at the low end, so both do not possess the correct Henry law type behaviour in those ranges (Do, 1998). Therefore, Toth equation is better to fit the data in all ranges of pressure.

In this work, the Toth isotherm was employed to fit the simulated data of hydrocarbons and carbon dioxide on zeolite, according to Equation 1.

$$q = q_{max} \frac{(K_{ads} \cdot P)^t}{[1 + (K_{ads} \cdot P)^t]^{1/t}} \quad (1)$$

The parameter t in Equation 1 is specific for adsorbate-adsorbent pairs species. It characterizes the heterogeneity of the system, which may result from the characteristic of the solid or the adsorbed specie, or a combination of both. When $t = 1$, the Toth isotherm reduces to the Langmuir equation.

The adjustment of the parameters $q_{\max}(T)$, $K_{\text{ads}}(T)$ and $t(T)$ of the Toth equation (Equation 1) with the data was performed using error minimization techniques. The parameters were obtained by adjusting the isotherms, following the procedure described by Do (1998).

Although there are several studies of adsorption of hydrocarbons in zeolites, few have the complete isotherms or at higher temperatures (>498.15 K). In this way this study presents a new and original contribution in the field of adsorption in zeolites. The values of the parameters of the Toth equation (see Equation 1) are presented in Table 2.

Table 2: Parameters of the Toth Equation.

Molecule	T = 498.15 K			T = 598.15 K			T = 698.15 K		
	q_{\max} (mol/kg)	K_{ads} (atm ⁻¹)	t	q_{\max} (mol/kg)	K_{ads} (atm ⁻¹)	t	q_{\max} (mol/kg)	K_{ads} (atm ⁻¹)	t
C1	3.91	0.0102	0.75	1.18	0.0132	1.44	1.17	0.0073	1.40
C2	2.01	0.0678	1.09	2.45	0.0179	0.85	1.24	0.0137	1.25
C3	1.74	0.1656	1.00	1.84	0.0371	0.81	1.02	0.0205	1.13
C4	1.40	0.1105	0.92	0.87	0.0312	1.08	0.70	0.0119	1.08
C5	1.42	0.1155	0.56	0.56	0.023	1.10	0.39	0.0084	1.22
C6	0.52	0.1091	1.38	0.29	0.0234	1.28	0.10	0.014	1.56
C7	0.32	0.1107	2.16	0.15	0.0233	1.30	0.05	0.0127	1.55
C8	0.18	0.1477	2.42	0.05	0.0368	1.93	0.05	0.0056	0.91
C9	0.08	0.2407	2.15	0.015	0.0503	3.32	0.013	0.0088	0.97
C10	0.06	0.1864	3.56	0.006	0.0633	3.31	0.002	0.0275	1.88
CO2	3.55	0.0152	0.83	1.58	0.0124	1.22	2.87	0.0036	0.91

The parameter t is a function of temperature, but it is not possible to observe a pattern for such parameter. The maximum adsorption capacity decreases with the increase in the number of carbons in the hydrocarbon chain, considering the same temperature. The exception is butane (C4). For example, at 598.15 K the maximum adsorption capacity for propane was 1.84 mol/kg, while for heptane it was 0.15 mol/kg.

The parameters presented in Table 2 can also be used in the thermodynamic modeling of the Fischer-Tropsch process in order to estimate the contribution of the adsorption phenomenon in the process.

4. Conclusions

The available literature relating adsorption data for the main FT synthesis products at operating temperatures is scarce, so molecular simulations are required. This work used the Grand Canonical Monte Carlo method to obtain the isotherms for hydrocarbons on zeolite and fit the data to Toth equation, so it presents a new contribution in the the FT and zeolite adsorption modelling fields. The method was robust to calculate the adsorbed quantities for the first ten linear alkanes. Adjusting the GCMC simulated data to an adsorption isotherm such as Langmuir, Freundlich or Toth allows to obtain adsorption parameters (adsorption constant and maximum capacity), in which the shape of the isotherm has great effect on mathematical modelling, therefore the correct selection of the isotherm model is important. In this work, the Toth isotherm was chosen.

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