



# Comparison of different molecular sieves for the liquid phase separation of linear and branched alkanes



Edith Meneses-Ruiz<sup>a,b,1</sup>, Georgina C. Laredo<sup>a,\*</sup>, Jesús Castillo<sup>a,1</sup>, Jesús O. Marroquin<sup>a,1</sup>

<sup>a</sup> Programa de Investigación de Procesos de Transformación, Instituto Mexicano del Petróleo, Lazaro Cardenas 152., Mexico D.F. 07730, Mexico

<sup>b</sup> CICATA, Instituto Politécnico Nacional, Legaria 694, México D.F. 11500, Mexico

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## ABSTRACT

A carbon molecular sieve adsorbent (CMS-IMP12) obtained from the pyrolysis of a poly(vinylidene chloride-co-vinyl chloride) (PVDC-PVC, Saran™) material was tested and compared with other molecular sieve materials for the separation of a multi-component hydrocarbon mixture. Liquid phase experimental adsorption curves at 303 K were obtained in a stirred tank using a model mixture composed by n-heptane, 2-methylheptane, 2,5-dimethylhexane and 2,2,4-trimethylpentane, considering the last one as a non-adsorbing solvent. Materials compared against the CMS-IMP12 were zeolites ZSM-5 (Si/Al = 15), ZSM-5 (Si/Al = 140), ZSM-22, ZSM-23, Silicalite-1 and Silicalite-2. The CMS-IMP12 adsorbed at least three times the amount adsorbed by the other material tested (i.e. 206 versus 79 mg/g<sub>ads</sub> for Silicalite-1) mainly because three components of the mixture (linear, methyl and non-geminal dimethyl alkanes) were adsorbed in higher proportions. None of the other tested materials adsorbed non-geminal dimethyl branched compounds. Regarding the kinetics of adsorption as represented by their second order rate constants, all the materials except the CMS-IMP12 adsorbed the methyl alkane molecule at the same rate as the n-alkane. The slower adsorption rate observed for 2-methylheptane as compared to n-heptane in the CMS-IMP12 may be due to the competition for adsorption sites between the two slow diffusing species: 2-methylheptane and 2,5-dimethylhexane.

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## 1. Introduction

Improving the quality of fuels is one of the most important topics nowadays. In the case of gasoline, it depends on a balance between octane number and environmental impact. The octane number for a gasoline-type fuel is measured by its anti-knocking capacity. A gasoline with a high octane number is usually preferred [1]. The environmental impact is related to the reactivity of hydrocarbons towards formation of ground-level ozone [2]. These factors are associated with the composition of the fuel. Gasoline is essentially a complex mixture of hydrocarbons that boils below 200 °C [1]. The hydrocarbon constituents in this boiling range are those that have 4–12 carbon atoms in their molecular structure. In this context, linear alkanes have the least desirable knocking characteristics (low octane numbers) and this became progressively worse as the molecular weight increases. Iso-alkanes have higher octane numbers than the corresponding linear isomers and the octane number increases as the degree of branching of the chain is increased [1]. Other compounds like aromatics and olefins may have high octane numbers; however they usually present also environmental

risks due to its reactivity on the formation of ground-level ozone [2]. A high octane number, low environmental impact gasoline can be obtained from a procedure involving the separation of branched alkanes usually associated with higher octane numbers, from linear alkanes with lower octane numbers from paraffinic naphtha. In an industrial procedure, the recovered linear alkanes are sent to an isomerization procedure, and then, back to the separation process [1]. This separation has been studied in gas and liquid phases with molecular sieves as adsorbents [3]. These adsorbents present capabilities for separation of the hydrocarbons by molecular size. Some data regarding octane numbers [4] and average molecular sizes [5] of this type of hydrocarbons are shown in Table 1. Interesting microporous molecular sieve materials are the carbons obtained from the pyrolysis and/or activation of poly(vinylidene chloride) copolymers (PVDC). PVDC based microporous carbons have been considered in separation technologies because of their adsorptive properties and molecular sieve discrimination capacities, i. e. separation between linear and branched alkanes [3, 6–14].

Usually, thermodynamic and kinetic studies of adsorption processes are carried out at low partial pressures in the gas phase, although most industrial separation processes require high hydrocarbon pressures or are performed in the liquid phase. Some relevant information regarding liquid phase hydrocarbon separation processes for linear and multi-branched alkanes can be found [3,15–23].

\* Corresponding author. Tel.: +55 9175 6615; fax: +55 9175 8429.

E-mail addresses: [emeneses@imp.mx](mailto:emeneses@imp.mx) (E. Meneses-Ruiz), [glaredo@imp.mx](mailto:glaredo@imp.mx) (G.C. Laredo), [jcastill@imp.mx](mailto:jcastill@imp.mx) (J. Castillo), [jmarroq@imp.mx](mailto:jmarroq@imp.mx) (J.O. Marroquin).

<sup>1</sup> Tel.: +55 9175 6615; fax: +55 9175 8429.

**Nomenclature**

$c$	Individual moles per unit volume of liquid
$C$	Total moles per unit volume of liquid
$n$	Individual number of moles within the system
$N$	Total number of moles within the system
$q$	Individual sorbed moles per unit mass of adsorbent
$\bar{q}$	Individual sorbed mass per unit mass of adsorbent
$Q$	Total sorbed moles per unit mass of adsorbent
$v$	Sample volume
$V$	Total liquid volume
$W$	Total mass

**Greek letters**

$\Delta$	Sample mass
$\omega$	Mass fraction in the liquid

**Subscripts**

$0$	About the liquid in its initial state
$A$	Adsorbent
$k$	The $k$ th sample has just been drawn
$k,i$	About the $i$ th compound when the $k$ th sample has just been drawn

Denayer et al. [15] observed that the strong dependence of the adsorption constants on the carbon number of *n*-alkanes, which is presented in the gas phase adsorption studies, is reduced to minor differences between short and long *n*-alkanes, or even disappears completely in liquid phase on Y zeolites, at complete saturation of the adsorbent with any type of alkane.

The sorption and diffusion in large silicalite crystals of  $C_6$ – $C_7$  single and double branched alkanes and cycloalkanes (*n*C7, 2MC7, 2MC5, 33DMC4, 22DMC4, 24DMC4, cyclohexane, cyclohexene, 2-methylhexene) with *n*-hexane as carrier was studied by Boulicaut et al. [16]. They concluded that both absolute values of the equilibrium constants and the exchange

energies obtained in the liquid phase were consistent with vapor phase data, though kinetic data yielded exchange diffusivities which were larger by several orders of magnitude relative to values derived from single component vapor phase measurements at low sorbate loadings.

Denayer et al. [17] observed that methyl branched  $C_5$ – $C_9$  alkanes in liquid phase were adsorbed on ZSM-22, but on ZSM-23 neither vapor nor liquid phase methyl alkanes were adsorbed, despite the small differences in pore size among both zeolites.

De Meyer et al. [18] studied the adsorption of  $C_5$ – $C_{22}$  linear alkanes in liquid phase in ZSM-5 and determined that packing density relies on the possibility for fitting into the pores (i.e. bending and crossing at the intersections) depending on the chain length of the hydrocarbon, as it was demonstrated by GCMC simulations.

Denayer et al. [19] stated that diffusion-limitations in the separation of *n*-alkane mixtures were observed in ZSM-22 which has small pores, while zeolites with larger pores (Na-USY and MCM-41) had a low selectivity. The most selective adsorbent was the ZSM-5 zeolite that presented differences in adsorption selectivity between short and long paraffins.

According to Yu et al. [20] for *n*C6/3MC5 mixtures, *n*C6 was adsorbed preferentially than 3MC5 in silicalite-1, even at concentrations as high as 74% of 3MC5 in the liquid. 22DMC4 was adsorbed so slowly on silicalite-1 that total saturation took over 1650 h at 294 K (Table 2).

By performing liquid phase adsorption at 298 K (batch technique) of linear and branched alkanes (tetradecane, 3MC5, 23DMC5 and 224TMC5) on several microporous adsorbents with different structures and Si/Al molar ratios: H-Beta (BEA), H-ZSM-5 and silicalite-1 (MFI) and SAPO-11 (AEL), Uguina et al. [21] found that MFI samples showed no adsorption of geminal alkanes due to molecular sieve effect, as well as a preferential adsorption of linear alkanes (Table 2). Geminal refers to two alkyl groups, in this case methyls, which are attached to the same carbon atom. A competitive adsorption between the mono- and dibranched alkanes was observed on MFI samples, showing an increase in adsorption capacity for 3MC5 at higher Si/Al molar ratios. AEL and BEA samples adsorbed significant amounts of all adsorbives.

From studies to evaluate the apparent diffusivity in silicalite at 458 K of  $C_6$ – $C_7$  monobranched alkane isomers in mixtures, Dubreuil et al. [22] concluded that the apparent diffusivity of monobranched isomers was reduced by the presence of slow-diffusing dibranched molecules in the silicalite network. The effect of 22DMC4 was even greater than the observed from 23DMC4. However, further adding of a fast-diffusing species such as *n*C7 in the adsorbent network can compensate for this effect.

Laredo et al. [23] studied the capabilities of a carbon molecular sieve derived from PCDV-PVC (CMS-IMP12) for adsorption of *n*C7, 2MC7 and 25DMC6, both: as single solute and in mixtures, using 224TMC5 as a non-adsorbing solvent in a liquid batch system at 303 K (Table 2). The equilibrium adsorption of the pure hydrocarbons ranged from 182 to 230 mg/g<sub>ads</sub>, following the order: 25DMC6 < 2MC7 < *n*C7. Total adsorption loadings of the hydrocarbons in the mixture at different concentrations at equilibrium (207–230 mg/g<sub>ads</sub>) were very similar to the values found in single hydrocarbon experiments. The treatment of the data according to the employed dual site Langmuir model showed that diffusion decreased with an increase in branching based on the size of the hydrocarbon.

The objective of this work was to prove the advantages of the CMS-IMP12 material on the separation of the same hydrocarbon mixture (*n*C7, 2MC7 and 25DMC6 in 224TMC5 as a non-adsorbing solvent), as compared to other molecular sieve materials usually used for this type of separation. In order to do so, liquid phase adsorption dynamics of a model multi-component mixture of linear and branched alkanes on CMS-IMP12 were compared to the following molecular sieves [24]: zeolites ZSM-5 (MFI) Si/Al = 15 and Si/Al = 140, ZSM-22 (TON) and ZSM-23 (MTT), and the following silicalites: silicalite-1 (MFI) and silicalite-2 (MEL) in a batch reactor at 303 K.

**Table 1**

Octane numbers and average molecular sizes from some  $C_6$ – $C_8$  linear and branched hydrocarbons.

Compound name	Abbreviation	Carbon number	Octane number [4]	Average molecular size [5]
<i>n</i> -Heptane	<i>n</i> C7	7	0	0.45
<i>n</i> -Octane	<i>n</i> C8	8	–17	0.45
<i>n</i> -Nonane	<i>n</i> C9	9	–19	0.45
2-Methylpentane	2MC5	6	44.4	0.59
2-Methylhexane	2MC6	7	44.4	0.59
2-Methylheptane	2MC7	8	21.8	0.59
3-Methylpentane	3MC5	6	74.4	0.59
3-Methylhexane	3MC6	7	53.9	0.59
3-Methylheptane	3MC7	8	30.9	0.59
2,2-Dimethylbutane	22DMC4	6	92.6	0.62
2,2-Dimethylpentane	22DMC5	7	94.2	0.62
2,2-Dimethylhexane	22DMC6	8	74.9	0.62
2,3-Dimethylpentane	23DMC5	7	89.8	0.62
2,3-Dimethylhexane	23DMC6	8	75.1	0.63
2,4-Dimethylpentane	24DMC5	7	83.5	0.59
2,4-Dimethylhexane	24DMC6	8	67.6	0.59
2,5-Dimethylhexane	25DMC6	8	55.5	0.65
2,2,4-Trimethylpentane	224TMC5	8	100	0.67
2,3,4-Trimethylpentane	234TMC5	8	99.2	0.62

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