Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Selective Separation of Normal Paraffins from Slack Wax Using the Molecular Sieve Adsorption Technique

F. Tomás-Alonso[a]; L. A. Angosto Olmos[b]; M. A. Muñecas Vidal[c]
[a] Departamento de Ingeniería Química, Facultad de Química, Campus de Espinardo, Universidad de Murcia, Murcia, Spain [b] Repsol YPF, Petroleum Refinery, Cartagena, Spain [c] Centro Tecnológico Repsol YPF, Mostoles-Madrid, Spain

To cite this Article Tomás-Alonso, F. , Olmos, L. A. Angosto and Vidal, M. A. Muñecas(2005) 'Selective Separation of Normal Paraffins from Slack Wax Using the Molecular Sieve Adsorption Technique', Separation Science and Technology, 39: 7, 1577 — 1593
To link to this Article: DOI: 10.1081/SS-120030787
URL: http://dx.doi.org/10.1081/SS-120030787

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 7, pp. 1577–1593, 2004

Selective Separation of Normal Paraffins from Slack Wax Using the Molecular Sieve Adsorption Technique

F. Tomás-Alonso,[1,*] L. A. Angosto Olmos,[2] and M. A. Muñecas Vidal[3]

[1]Departamento de Ingeniería Química, Facultad de Química,
Universidad de Murcia, Murcia, Spain
[2]Repsol YPF, Petroleum Refinery, Cartagena, Spain
[3]Centro Tecnológico Repsol YPF, Mostoles-Madrid, Spain

ABSTRACT

The selective separation of heavy *n*-paraffins (C_{20}–C_{30}) from refinery slack wax was performed by adsorption onto zeolite molecular sieves (5A). Sorbents were characterized by thermogravimetric analyses, N_2 adsorption, and mercury porosimetry. Three slack waxes: light, medium and heavy, were used, being analyzed by gas chromatography (GC) and simulated distillation. Several tests were carried out in a stirred batch reactor at high pressure and temperature for determining the system kinetics. Process variables were temperature (100–150°C), pressure (0.5, 1.5, and 2.5 MPa), and time (1–24 hr). Afterwards, adsorption

---

[*]Correspondence: F. Tomás-Alonso, Departamento de Ingeniería Química, Facultad de Química, Campus de Espinardo, Universidad de Murcia, 30071, Murcia, Spain; E-mail: ptomas@um.es.

DOI: 10.1081/SS-120030787
0149-6395 (Print); 1520-5754 (Online)
www.dekker.com

isotherms in the range of 60–170°C were obtained for each wax by being fitted to a Langmuir type equation. Results showed that adsorption equilibrium is controlled by internal diffusion due to the large length of the normal paraffin chains, which have a diameter very close to the size of the zeolite channels. The amount of paraffin retained in the sieve is strongly influenced by the feedstock: lighter products adsorb more, also producing a higher purity *n*-paraffin. The reverse trend is observed for the heavier feeds. However, adsorption of larger molecules ($>n$-C_{32}) is strongly hindered. For temperatures above 170°C, cracking reactions become more and more important.

Key Words: *n*-Paraffins; Wax; Zeolite; Adsorption; Molecular sieves.

INTRODUCTION

Paraffins and their derivatives are widely used as a raw material for the chemical industry, i.e., detergents, varnishes, solvents, wax for candles and many other uses. In the refining industry, paraffins are obtained as a minor product in the lube oil manufacturing process.[1] In a typical lube refinery, the atmospheric residue is vacuum distilled. Four main lube oil base cuts are obtained: spindle, light, medium, and heavy, according to the molecular weight. These base oils are dearomatizated (for increasing viscosity index) and deparaffinated (to improve cold properties, as paraffins freeze). The paraffin stream is further purified to remove oil. Slack wax is a semiliquid side stream obtained during this process. Its chemical composition is a mixture of *n*-paraffins, iso-paraffins, aromatics, and some oil (from 10 to 30 wt%). It is not a very valuable stream, and normally it is added to fuel oil for viscosity improvement.[2] However, it has some potential added value, if it would be possible to recover the *n*-paraffin it contains.

The separation techniques of *n*-paraffins from petroleum fractions using molecular sieves have a long commercial history. The key of the process is the A zeolite.[3] This crystalline silicate is synthesized in the sodium form: $Na_{12}(AlO_2)_{12}(SiO_2)_{12} \cdot xH2O$ (zeolite 4A). When Na is replaced with Ca, the zeolite 5A is obtained, with openings about 0.50 nm. This zeolite is capable of separating *n*-paraffins having molecular diameter near 0.48 nm, while selectively excluding the iso-paraffins. Major commercial processes developed are UOP Molex,[4] BP, and Union Carbide IsoSiv.[5] Most common treated petroleum fractions are kerosene, diesel, light naphtha, etc., the range of separation being from n-C_5 to n-C_{16}. This is a very suitable raw material, among others, for the detergent industries.[6,7]

However, not much work has been done for separating *n*-paraffins of higher molecular weight. Adsorption in the liquid phase, up to *n*-C_{20}, was studied by Alkandary et al.[8] Only Nwadinigwe and Nwobodo,[9] reached up to C_{42} in a petroleum crude. Here, the adsorption process becomes progressively complex due to increased diffusional effects. In fact, general belief is to use the alternative technique of adduct formation with urea.[9,10] This technique is based on the unique properties of the urea–paraffin system. In the presence of *n*-paraffins, urea forms hexagonal lattices with hollow channels of diameter between 0.50 and 0.60 nm, where *n*-paraffins can penetrate, being adsorbed by dispersion forces. Some inconveniences of this method are the difficulty for controlling the adduction rate, the lower purity of the *n*-paraffin recovered, and the major relative costs.

The objective of this work is to systematically study the separation process of long *n*-paraffins, in the range of C_{20}–C_{30}, using zeolite 5A. The study will review the effect of the process variables (temperature, pressure, concentration, and time) and the effect of the feedstock used on the amount and purity of *n*-paraffin recovered.

EXPERIMENTAL

Characterization of Materials

Commercial Zeolite 5A (fully exchanged CaA form) supplied for Zeolyst Inc., UK, was used as sorbent for the process. The physical shape was as a high-purity powder (>99%), with 8 μm of average diameter, BET surface area was 677 m^2/g, and calculated mesopore area (*t*-plot) of 12 m^2/g.

Three slack waxes supplied for Repsol-YPF were used, light, medium, and heavy. They were characterized by melting point (ASTM E-473), oil content (ASTM D-938), simulated distillation (ASTM D-2887), and gas chromatography (GC) analyses (ASTM D-5442) using an HP6890 chromatograph for measuring normal and iso-paraffin content. A summary of their properties is shown in Table 1.

Experimental Procedure

Adsorption tests were conducted in a stirred autoclave reactor of 500 mL volume, 50 bar maximum pressure, and 180°C maximum temperature, supplied by Sotelem, B.V. Tests were conducted in N_2 atmosphere at pressures between 5 and 25 bar, temperatures of 60–170°C, and adsorption time from 1 to 24 hr.

Table 1. Physical properties of the materials used.

	Light	Medium	Heavy
Melting point (°C)	46.0	46.0	41.0
Oil (%)	26.8	11.9	14.7
n-Paraffins (%)	31.7 (C_{12}–C_{32})	15.6 (C_{20}–C_{36})	8.4 (C_{20}–C_{47})
iso-Paraffins (%)	68.3 (C_{22}–C_{36})	84.4 (C_{23}–C_{44})	91.6 (C_{24}–C_{51})
		Simulated distillation	
5 vol.% (°C)	374	398	413
50 vol.% (°C)	410	470	505
95 vol.% (°C)	474	509	573

Due to its excessive high viscosity, in all tests the wax was diluted with a highly branched compound, such as iso-octane (2,2,4 tri-methyl-pentane). This allowed the work at lower stirring speeds and also an improvement in the external diffusion rate of *n*-paraffins through the liquid phase to the pore entrance. As iso-octane is so highly branched (molecular diameter near 0.70 nm), it is assumed that it will be not adsorbed in the 5 A zeolite micropores. This does not extend for adsorption in mesopores or micropores regions of the zeolite, but presence of this porosity is very small in the zeolite used. Finally, experimental evidence (blank tests) confirms, as a matter of fact, the validity of the assumptions taken. In the tests, weight of sieve was fixed to 10 g; iso-octane amount was 35 g and weight of wax varied from 2 to 12 g.

After activation to remove preadsorbed water of the zeolite at 350°C, in a muffle furnace for 5 hr in air, it was immediately put in contact (slurry phase) in the batch reactor with the diluted wax at the selected temperatures and pressures. Once the test finishes, the slurry is filtered for separating the solid and the liquid part of the mixture. The solid was thoroughly washed with iso-octane to avoid the nonadsorbed wax impregnating the zeolite. Zeolite was later dried in an oven at 80°C for removing iso-octane. A thermo-gravimetric analysis was done for calculating (after blank correction) the weight of adsorbed wax. The over-floating wax was distilled and separated from the iso-octane in a rota-vapor equipment. The GC analysis was then performed and material balance calculated.

The desorption of the *n*-paraffin previously adsorbed in the zeolite was performed by stripping the solid with steam.[11] Experimental conditions used were steam (150 mL/hr of water) at 0.2 MPa, during 4 hr in 1 cm diameter plug-flow reactor. The paraffin was collected in a receiver at 0°C; its purity was checked by GC.

DISCUSSION

Kinetics and Thermodynamics of the Adsorption Process

Sorbent Activation

Zeolite 5A, especially in the powder form, is a very hydrophilic sorbent. Water must be removed before the paraffin adsorption process. A thermogravimetric (TGA–TDA) study was conducted in order to determine the optimum conditions, by heating the zeolite in an air atmosphere at the rate of 4 K/min from room temperature to 500°C. It can be seen that the main weight loss takes place between 50 and 250°C. The TDA shows a strong endothermic peak at 150°C due to water desorption. This peak is absent when adsorbent had been previously calcined at 350°C for 5 hr. These conditions were chosen as standard for adsorbent treatment prior to the adsorption tests.

The effect of preadsorbed water on the paraffin adsorption process is shown in Table 2, by comparing the *n*-paraffin amount adsorbed by samples calcined and noncalcined in an adsorption test at 150°C, 5 hr, and 1.5 MPa. It is clear that the amount of paraffin is much higher if water was previously removed. In the noncalcined sample, paraffins and water move counter-current and the adsorption process of the paraffin speed is slowed.

Adsorption Kinetics from Light Slack Wax

The adsorption of *n*-paraffins in a sieve material such as 5 A zeolite is, certainly, a slow process. Thus, a minimum equilibrium time must be set before proceeding to obtain adsorption isotherms. This time is also dependent on the testing conditions used (pressure and temperature). For this purpose, some tests were carried out by contacting established quantities of wax and sieve and changing the contact time in the sorption experiment. Figure 1 shows the adsorption kinetics of light slack wax at two levels of temperature (100°C and 150°C), three levels of pressure (0.5, 1.5, and 2.5 MPa), and contact times up to 24 hr.

Table 2. Effect of the activation of the sorbent.

Sorbent	Water content wt%	*n*-Paraffin adsorbed wt%
Zeolite 5A activated (350°C, 5 hr)	0.91	7.5
Zeolite 5A fresh	15.6	3.4

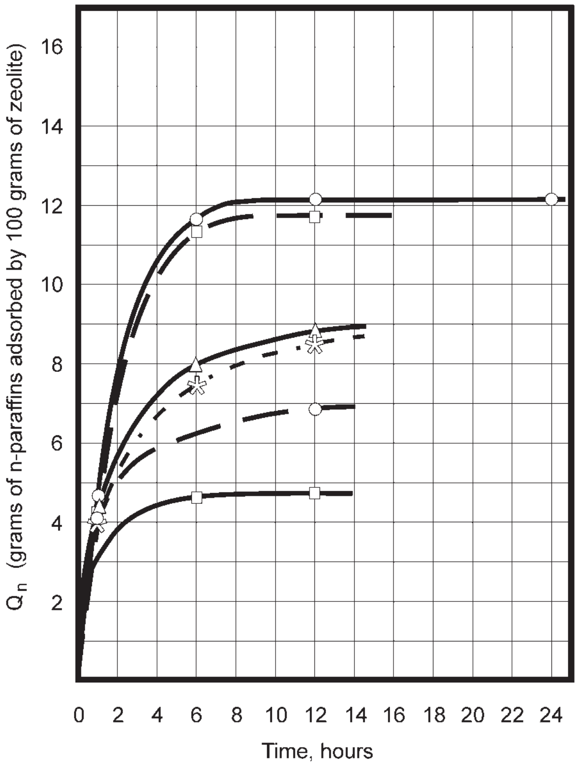

Figure 1. Adsorption kinetics for light slack wax. *Key:* —○—, P: 25 bar, T: 150 °C; —□—, P: 15 bar, T: 150 °C; —△—, P: 25 bar, T: 100 °C; —*—, P: 5 bar, T: 150 °C; —○—, P: 15 bar, T: 100 °C; —□—, P: 5 bar, T: 100 °C.

It is seen from the graph in Fig. 1 that the amount adsorbed in the first stages is very low, progressively increasing until a "plateau" is reached for every experimental condition. However, the amounts adsorbed widely differ, being higher as temperature or pressure are increased. The time required for stabilization is reached between 6 and 12 hr. The test conducted at 24 hr did not reveal revealed not any additional increase in the adsorbed amount.

As the shapes of the curves are so similar, it can be said that, from the kinetic point of view, the effect of pressure on the kinetics is negligible. On the other hand, the pressure has a strong effect on the adsorbed amounts, more important at 100°C. However, if the temperature is high enough (e.g., curves at 150°C for 1.5 and 2.5 MPa), the adsorbed amount is dependent on temperature and not on pressure. There is, certainly, no thermodynamic reason

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

that can explain this increase of adsorbed amount with pressure, as adsorption potential on a micropore surface does not depend on the liquid phase. This effect may be caused by the diluent: at lower pressures, some iso-octane may vaporize (but not the wax), and, accordingly, less iso-octane remains at the liquid phase, that will have a higher viscosity, with higher restrictions for the *n*-paraffins to diffuse.

The effect of temperature on kinetics is more easily seen, as the plateau is reached more rapidly (6–8 hr) at the higher temperatures (150°C), and more slowly (10–12 hr) at the lowest (100°C). This effect can be explained in terms of a strong diffusional control during the adsorption process. During the first one or two hours, the mass transfer is controlled by external diffusion from the bulk in the liquid phase to the pore entrance of the sorbent particle, which is basically related to the stirring speed. Once the normal paraffin molecules have reached the pore, they must diffuse through the pore channels, and the internal diffusion becomes progressively the limiting step of the adsorption process.

The process is slow because the length of the *n*-paraffin molecules is high. The molecules also have a molecular diameter very close to the size of the zeolite pores in which the diffusion process is taking place. When pressure increases, the adsorbed amount increases because, kinetically, *n*-paraffins can diffuse better in a less viscous fluid through the macropore region. Also, when temperature increases, the viscosity of the *n*-paraffins is lower. As they can diffuse more rapidly, the equilibrium time decreases; in addition, they can diffuse deeper inside the particle, allowing more room to new molecules for adsorption. Therefore, the amount adsorbed increases.

Adsorption Equilibrium from Light Slack Wax

The adsorption isotherms were determined for this slack wax at constant sorbent weight, constant time (12 hr), and constant pressure (25 bar); and by changing the initial product amount at chosen temperatures. Figure 2 shows the isotherm obtained, from 60°C to 170°C, in terms of *n*-paraffins remaining at the liquid phase at the equilibrium time vs. the grams of *n*-paraffins adsorbed by 100 g of zeolite (Q_n).

These isotherms clearly correspond to the type I of the BET classification,[12] being typical of the adsorption process in micropores, as it does correspond with the molecular sieve nature of the zeolite channels.

A number of models are available to mathematically treat the experimental data, such as Temkin, Freundlich, or Dubinin-Astakov.[13] However, one of the simplest ones is a Langmuir type equation, mainly applicable for adsorption on a localized monolayer, which may be the case of long *n*-paraffin

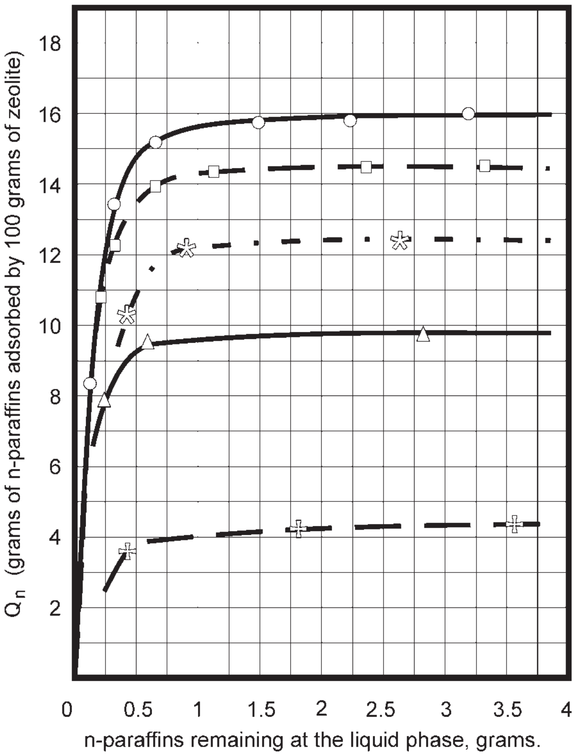

Figure 2. Adsorption isotherms of *n*-paraffin at different temperatures for light slack wax. *Key:* —○—, T: 170 °C; —□—, T: 150 °C; —*—, T: 130 °C; —△—,T: 100 °C; —+—, T: 60 °C.

molecules, physically interacting with the surface of the narrow zeolite channels. This equation, in linearized form, is given by:

$$\frac{1}{Q_n} = \frac{1}{Q_n^0} + \frac{1}{bQ_n^0 C_\mathrm{L}} \tag{1}$$

where Q_n is the adsorbed amount, Q_n^0, the maximum adsorbed amount in the equilibrium, C_L, the concentration of *n*-paraffin in the liquid phase, and b is a constant.

In effect, it can be found as a very fine correlation of the isotherms to the model ($r \approx 0.999$) for every temperature considered. The slope of the linearized plot is the same for all the temperatures, differing only in the Q_n^0 value, which increases with temperature.

However, it is well-known fact that adsorption is an exothermal process and, accordingly, the amount adsorbed should decrease with temperature. This is the normal trend observed, for example, in the adsorption of shorter alkane molecules (C_8–C_{15}), also in the liquid phase, at temperatures up to 50°C in the slightly wider channels of ZSM-5.[14] Nevertheless, in our case, the adsorption is activated, meaning that it increases with the temperature.

In molecular sieves in general or zeolites, when pore diameter is close to the molecular diameter of the adsorbate molecule, the diffusion may be restricted according to what is it called "Knudsen diffusion," expressed by Eq. (2):[15]

$$D_\mathrm{K} = \frac{2}{3} r \sqrt{\frac{8RT}{\pi M}} \qquad (2)$$

where R is the constant of the gases, T is temperature, r is the pore radius, and M is the molecular weight of the adsorbate. In this expression, the diffusivity, D_K, of the molecule depends on $T^{1/2}$.

Figure 3 plots the adsorption capacity of the sorbent, Q_n^0, according to Langmuir calculation vs. the square root of the temperature. An excellent linear plot ($r \equiv 0.9985$) is obtained, meaning that Knudsen diffusion may control the adsorption process. In other words, n-paraffins must overcome an energy barrier before being adsorbed. This diffusion control suggests that a part of the adsorption measurement taken may have been obtained in a stable, pseudo-equilibrium stage, which at the higher temperatures is easily reached (6–12 hr), rather than in true thermodynamical equilibrium, which only will be reached at infinite time.

An interesting question is to determine the point where the adsorption mechanism changes from "not activated" to "activated" diffusion (pseudo-equilibrium process). In the study[8] by Alkandary et al., using n-C_{12}, n-C_{16}, and n-C_{20}, they reported the decrease in the amount adsorbed with the temperature up to C_{16}, but for n-C_{20}, adsorption isotherms apparently coincide. They attributed these phenomena to increased viscosity in the n-alkanes causing decreased diffusivity. As our study extends much more than C_{20}, up to C_{30}, all the mentioned effects are dramatically increased. Accordingly, we can estimate the transition point to the activated adsorption just around n-C_{20}.

In addition, Fig. 3 suggests that temperatures over 170°C will further increase the n-paraffin adsorption. However, there is a limit of the adsorption capacity of any adsorbent. Two processes must occur here: on one hand, as adsorption is a well-known exothermic process, adsorbed amounts must decrease if the limiting adsorption step is thermodynamic, not kinetic and; on the other hand, there is a limit, reached after complete filling of the pore volume of the sorbent. Adsorption in micropores is a very special case; in

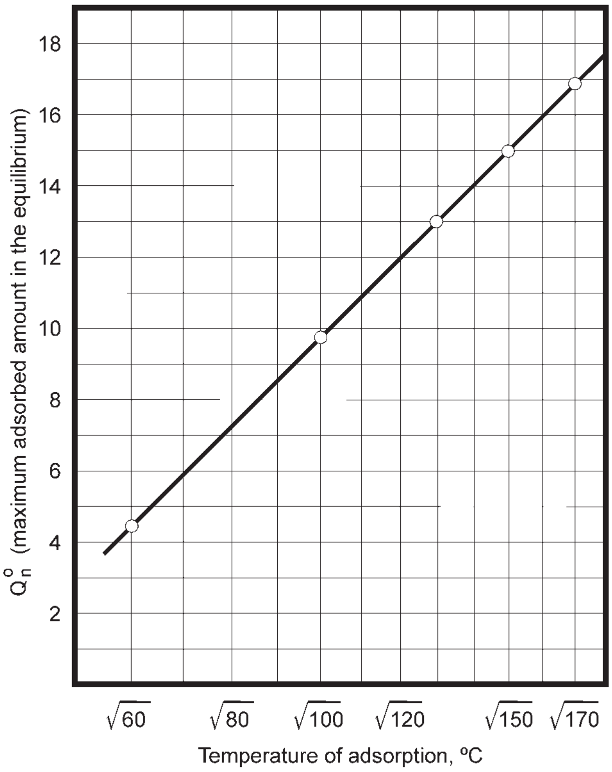

Figure 3. Knudsen plot for adsorption of light slack wax.

terms of the Polanyi theory,[12] the energy potential of a micropore is much higher than in an open surface, and we must apply the concept of micropore space filling as a volume, or as a fraction of the total available adsorption space. In this way, paraffin adsorbed amounts decrease (as density decrease with temperature), but always occupying the same space. All of our tests seem to be kinetically controlled, even at 170°C.

There are several methods for measuring the zeolite total pore volume. By N_2 adsorption at 77 K, this volume is 0.266 g/cm^3; some minor variation may take place with temperature. A similar value is obtained by *n*-hexane wetting (at 298 K), a paraffin as well, it is also very easily adsorbed by the 5 A zeolite due to its very short chain. To answer the question of how far we are from the maximum capacity of the sorbent, the amount adsorbed, in weight, shown in Fig. 3, must be converted in volume units divided by the average density of the adsorbed product. For a typical *n*-C_{25} molecule, density estimated by the Hankinson–Brost–Thomson method[16] is 0.700 g/cm^3 at 170°C. This gives a zeolite micropore volume filled of 0.243 g/cm^3, representing about a 90% of the total available. However, using adsorption temperatures as high as 200° would not be practical, due to the cracking phenomena, as it will be discussed later.

Properties of the *n*-Paraffin Obtained from Light Slack Wax

The *n*-paraffin recovered from the sieve by desorption with steam at 150°C may be characterized by its purity, melting point, and distribution of the *n*-paraffin chains.

The purity in *n*-paraffins of the product obtained is superior to 99.5% ($\pm$0.3%), while the original content was 31.7%. This high purity is independent of the adsorption temperature used, along the interval studied (60–170°C). No oil fraction was detected in this product. Accordingly, the melting point of the product increases from 46°C to 59°C, as measured by DTA.

The distribution of *n*-paraffin chains is shown in Fig. 4(a)–(c). It is observed that this distribution is, generally speaking, quite similar to that of the original material, also with a maximum in *n*-tetracosane (C_{24}). Some differences are found for *n*-paraffin chains above triacontane (C_{30}), practically are not present in the desorbed product. As well, some relatively short length *n*-paraffin chains ($<C_{14}$) are observed, while it did not appear originally, becoming more and more significant as adsorption temperature increases.

This fact is well explained in terms of a hydrocracking reaction of the adsorbed paraffins, catalyzed by the acid centers of the zeolite. In fact, extremely acid zeolites such as HY or ZSM-5 are quite common catalysts in industrial processes such as FCC or hydrocrackers. For comparison purposes, two additional tests were carried out. The first one was a blank using 10 g of wax, 35 g of solvent (iso-octane), and no sieve. In the second one, ZSM-5 zeolite (10 g), instead of 5A zeolite, was added to the previous mixture, in test conditions reported in Table 3. Zeolite ZSM-5 was chosen because it has very narrow channels of 5.4 nm × 5.6 nm, comparable in size to those of 5A zeolite, but of stronger acidity.[17] The ZSM-5 used was a high-purity powder, supplied by Zeolyst Inc., with a Si/Al framework ratio near 500.

The results obtained in these tests appear in Table 3. It is observed that thermal cracking in the absence of zeolite is negligible at these low temperatures. On the other hand, replacing 5A by ZSM-5 has a strong impact on the measured cracking. It is important to remark that no coke (less than 0.1 wt% of catalyst) was produced in the test using ZSM-5, and adsorption mass balance was not significantly affected. This agrees with the well-known fact in commercial experience in the FCC field that use of ZSM-5 additives (for increasing gasoline

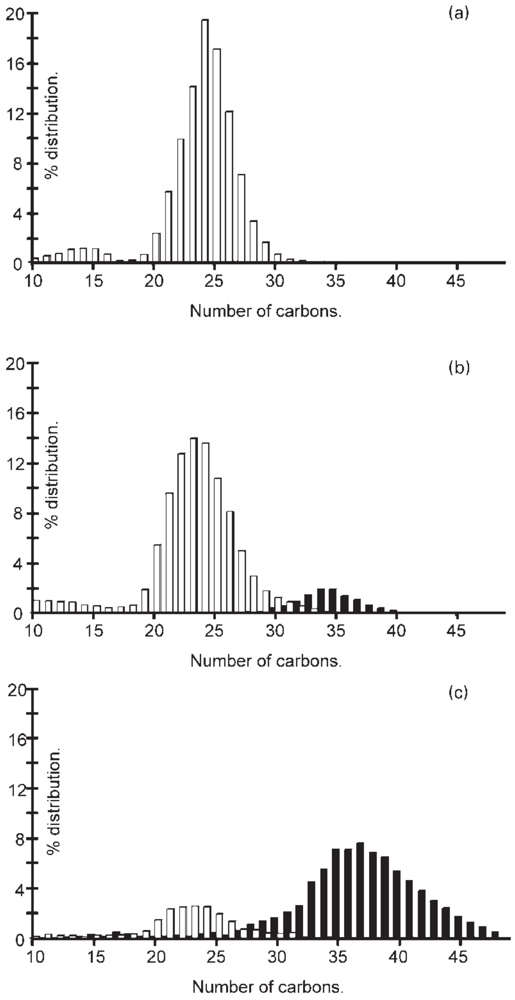

Figure 4. Iso- and *n*-paraffin distribution of chain lengths for: (a) light wax after adsorption at $T = 150°C$ and $P = 25$ bar; (b) medium wax after adsorption at $T = 150°C$ and $P = 25$ bar; and (c) heavy wax after adsorption at $T = 150°C$ and $P = 25$ bar. *Key:* □, *n*-paraffins; ■, iso-paraffins.

octane number MON) do not increase coke yield. As a consequence, it is clear that active centers of zeolites should be responsible of cracking reactions

It is also evident that cracking reactions using 5A zeolite are boosted at temperatures above 150°C. This is the negative counterpart of the one shown in Fig. 3 for increasing the adsorbed amounts with the temperature.

Table 3. Cracking to small paraffins (C_{10}–C_{16}) in the desorbed paraffin.

Sorbent	Cracking (%, C_{10}–C_{16})	Temperature (°C)	H_2 pressure (bar)	Contact time (hr)
5A powder	1.3	100	25	12
5A powder	3.8	130	25	12
5A powder	5.4	150	25	12
5A powder	11.8	170	25	12
BLANK	0.0	170	25	12
ZSM-5	32	170	25	6

Therefore, a temperature of compromise must be chosen for minimizing the cracking losses with the increase in adsorbed amount due to faster adsorption kinetic at high temperatures.

Effect of the Feedstock on the Adsorption Process

Adsorption Equilibrium

The properties of the three materials used were presented in Table 1, showing a progressive increase in molecular weight and paraffin distribution, which easily reveals the distillation curve. The total amount of *n*-paraffins existing in the slack significantly decrease from light to heavy, meaning that less valuable product can be recovered. In addition, in the heavier feeds the number of very long paraffins (more than C_{40}, up to C_{50}) becomes very important, which indicates that its recovery will be more and more difficult.

The operating variables of temperature (150°C), pressure (2.5 MPa), and contact time (12 hr) were set constants in order to perform a comparative study of the adsorption equilibrium of the three feedstocks. These conditions represent a good compromise between adsorbent capacity and low cracking degree. However, due to the fact that as the *n*-paraffin content in medium and heavy slack decreased, the amount of slack in the liquid media (slack with iso-octane) was increased in these feeds, in order to reach similar concentrations of *n*-paraffins in the adsorption tests. The adsorption isotherms obtained are shown in Fig. 4.

It is observed that the new adsorption isotherms for medium and heavy feeds still belong to type I (monolayer adsorption on micropore channels), although they become progressively less steep as feed is heavier. More significant than this, the amounts of *n*-paraffin adsorbed by the sieve are clearly decreasing from light to medium and to heavy. This is due to the increase of the diffusional resistances: first, in the liquid phase just at the pore entrance, where a lower concentration of *n*-paraffins must diffuse to the pore in a more viscosity media of other paraffins and oil molecules; second, for the increase in the length of the *n*-paraffins, up to C_{50}, which clearly diffuse very slowly through the pores, even blocking some of them.

Properties of the *n*-Paraffins Recovered

The purity of the *n*-paraffin product recovered decreases for the heavier feedstocks. The values obtained are 99.5+% for light wax, 90% for medium wax, and 15.5% for heavy wax. In the most extreme case, for heavy slack, the amount adsorbed, compared to light, is only a half, and the product recovered is, essentially, the original heavy slack wax (8.4% in *n*-paraffin according to Table 1), only slightly enriched with some *n*-paraffins up to the value measured of 15.5%. Diffusion of *n*-paraffins through the zeolite channels seems to be more and more hindered as feedstocks become heavier. Also, in tests for medium and heavy waxes, paraffin/iso-octane ratio was higher in the bulk phase (according to the experimental method used), producing a more viscous bulk phase, which induces further diffusional resistances.

In this way, the study of the distribution of chain length in the desorbed paraffins will further clarify this question. Figure 4(a)–(c) shows iso- and *n*-paraffin distribution of chain lengths, respectively, for light, medium, and heavy slack waxes.

In the case of medium slack wax, some iso-paraffinic chain appears in the range of C_{30}–C_{40}, with a maximum a C_{34}. For Heavy slack, iso-paraffins are a majority with a wider distribution between C_{26} and C_{48} but, according to the theory, these iso-paraffins should be rejected from the sieve. As an explanation, first, let us consider, first that the viscosity of iso-paraffins is lower than that of *n*-paraffins meaning higher diffusion rates and, second, that these extremely long chain iso-paraffins may be treated as mainly linear chains with some branching at one extreme. As their length is so high, their diffusivity is extremely low. It may happen that due to the higher diffusion rate, these molecules reach the pore entrance before the proper *n*-paraffins (in addition most of the molecules are iso-paraffins, not *n*-paraffins) and penetrate only partially inside the pore, thus blocking it. Therefore, the total amount of product retained by the zeolite will be low (Fig. 5) because normal paraffins cannot selectively diffuse through the 5 A sieve channels.

The *n*-paraffin distribution is, by the reverse, very similar for the three feedstocks considered, essentially limited to the range from C_{20} to C_{30}. Apparently, it seems C_{30}–C_{32} is the maximum linear chain length that can be accommodated into the cavities of the zeolite. Another unsolved question is how they get packed in the 5A zeolite structure, as adsorption probably involves forming bridges between at least two cages. In any case, this paraffin

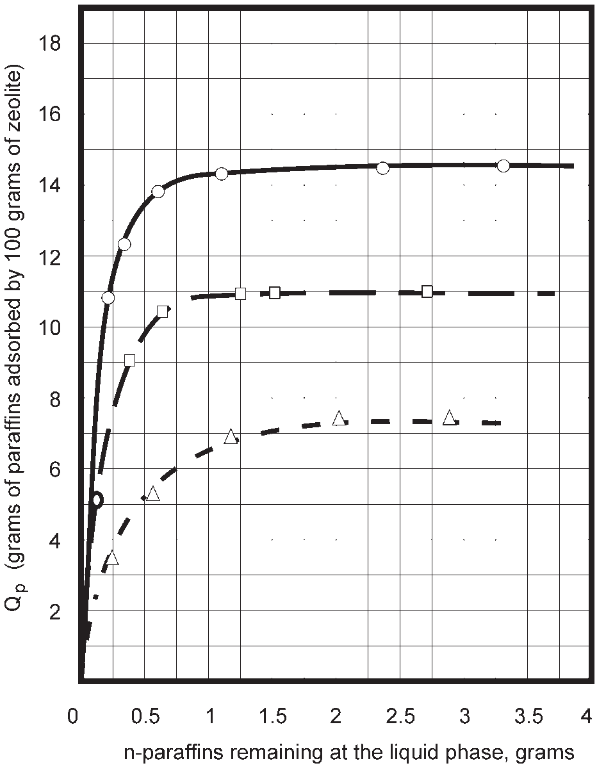

Figure 5. Adsorption isotherms of paraffin (*n*- and iso-) at 150°C for light, medium and heavy slack wax. *Key:* —○—, Light: >99.5% *n*-purity; —□—, Medium: ≈90% *n*-purity; —△—, Heavy: ≈15% *n*-purity.

range is maintained even in the case of heavy slack wax, which originally contains a high amount of *n*-paraffins, up to C_{47}. A similar effect was reported by Nwadinigwe et al.,[9] which found that most of the *n*-paraffins retained from crude oil lied in the range of n-C_{10}–n-C_{32} with a tail up to C_{42}. The reason becomes clearer if one compares the volume of an n-C_{32} paraffin vs. the known volume of the cavities of zeolite 5A, which is 0.770 nm^3.[18] Assuming that carbon chain length is given by:[14]

$$\text{Length (nm)} = 0.526 + 0.126(n - 2) \tag{3}$$

where n is number of carbon atoms, and that the critical diameter of *n*-alkanes is about 0.48 nm, the volume of a C_{30} *n*-paraffin is about.0.74 nm^3, in good agreement with our previous expectations.

CONCLUSIONS

Adsorption process of paraffins having very high molecular weight (up to C_{54}) in zeolite 5A molecular sieves has been systematically studied. The adsorption isotherms found are type I of BET classification, indicative of adsorption in microporous zeolite channels. Our results clearly support the idea of the existence of a strong diffusional control during the adsorption process. This is due to the huge length of the *n*-paraffin molecules having a molecular diameter very close to the zeolite pore size. The diffusion mechanism agrees well with the Knudsen diffusion process.

The amount of *n*-paraffin adsorbed (longer than C20 in our tests) increases with temperature (activated diffusion). Experimental data indicate that at temperatures near 170°C 10% of the zeolite pores are not yet filled. But the opposite, well-established data from the literature reports nonactivated diffusion for shorter *n*-paraffin chains (C5–C16). This suggests a change in the adsorption mechanism near C20. On the other hand, temperature boosts the role of acid-catalyzed cracking reactions, being significant, even though zeolite 5A is not too acid, for temperatures above 170°C.

The amount of paraffin retained by the sieve lowers as feedstock becomes heavier, indicating an increase of diffusional resistances. In addition, the purity of the *n*-paraffin recovered decreases from nearly 100% from the light slack wax to scarcely 15% for heavy material. In this case, the zeolite non-selectively retains the raw material. Apparently, there must be a limit lying near C_{30}–C_{32} for selective separation with zeolite 5A. From the point of view of the sieve, there is no distinction between iso- and *n*-paraffins for longer chains because they are bigger than zeolite cavities.

ACKNOWLEDGMENT

The authors are indebted to Repsol Petróleo Research Center in Cartagena (Spain) for allowing the use of their laboratories and equipment.

REFERENCES

1. Meyers, R.A. *Handbook of Petroleum Refining Processes*; McGraw-Hill: New York, 1997.
2. Le Page, J.F.; Chatila, S.G.; Davidson, M. Properties of pertroleum products. In *Resid and Heavy Oil Processing*; Technip: Paris, 1992.
3. Schweitzer, P.A. *Handbook of Separation Techniques for Chemical Engineers*, 2nd Ed.; Schweitzer, P.A., Ed.; McGraw-Hill: New York, 1998.

4. Humphrey, J.L.; Keller, G.E. UOP molex process for production of normal paraffins. In *Separation Process Technology*; McGraw-Hill: New York, 1997.
5. Rousseau, R.W. *Handbook of Separation Process Technology*; Wiley-Interscience: New York, 1982.
6. Hofmann, P.; Müller, W.H.E. Make surfactant feedstock by hydrocarboxymethylation. Hydroc. Proces. **1981**, *October*, 151–155.
7. Vora, B.V.; Pujado, P.R.; Imai, T.; Fritsch, A. Production of detergent olefins and linear alkylbenzenes. Chem. Ind. **1990**, *19* (March), 187–191.
8. Alkandary, J.A.M.; Al-Ammeri, R.; Salem, A.B. Adsorption equilibria of normal paraffins on 5A molecular sieve. Sep. Sci. Technol. **1995**, *30* (16), 3196–3209.
9. Nwadinigwe, C.; Nwobodo, I.O. Analysis of *n*-paraffins in light crudes: molecular sieve and urea adduction techniques revisited. Fuel **1994**, *73* (5), 779–782.
10. Hassan, N.M.; Al-Ameeri, R.S.; Oweysi, F. Separation of *n*-paraffins from kerosene-range feedstock by adsorption of fixed-urea. Sep. Sci. Technol. **1994**, *29* (3), 401–414.
11. Sinha, S.K.; Saraf, D.N.; Kunzru, D. Effect of steam desorption on adsorption of *n*-paraffins on molecular sieve 5-A. Zeolites **1982**, *2* (July), 175–178.
12. Gregg, S.J.; Sing, K.S.W. Gas phase adsorption. In *Adsorption, Surface Area and Porosity*; Academic Press: London, 1982.
13. Kai, L.; Kennedy, E.M.; Chen, S.Z. Adsorption of *n*-butane and *n*-heptane on 5A Zeolite. Sep. Sci. and Technol. **1998**, *33* (11), 1571–1584.
14. Jasra, R.V.; Choudary, N.V.; Bhat, S.G.T.; Patel, A.G.; Subrahmanyam, C. Liquid-phase sorption of higher alkanes and alkenes in zeolite NaZSM-5 at 10, 30 and 50°C. Sep. Sci. Technol. **1997**, *32* (9), 1571–1587.
15. Cybulshi, A.; Moulijn, J.A. Diffusion in molecular sieves. In *Structural Catalysis in Reactions*; Marcel Dekker: New York, 1998.
16. Reid, R.C.; Prausnitz, J.M.; Sherwood, T.K. Estimation methods for the density of fluids. In *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1987.
17. Chen, N.Y.; Garwood, W.E.; Dwyerd, F.G. Achieving molecular shape selectivity. In *Shape Selective Catalysis in Industrial Applications*; Marcel Dekker: California, 1989.
18. Rabo, J.A. *Zeolite Chemistry and Catalysis*; Rabo, J.A., Ed.; ACS Monograph, Amer. Chem. Soc: Washington, 1976; Vol. 171.

Received July 2003
Accepted November 2003

Downloaded At: 10:08 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/ Order Reprints" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Request Permission/Order Reprints

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS120030787