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Applied Catalysis A: General 315 (2006) 29–34

APPLIED CATALYSIS A: GENERAL

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Accessibility in alumina matrices of FCC catalysts

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Received 10 April 2006; received in revised form 11 August 2006; accepted 20 August 2006
Available online 11 October 2006

Abstract

The accessibility in aluminas considered to be representative of matrices used in FCC resid catalysts, with mean pore sizes between 64 and 201 Å, was characterized through a kinetic approach by means of the conversion of 1,3,5-tri-isopropylbenzene (TIPB) at 500 °C in a CREC Riser Simulator fluidized bed laboratory reactor. The product distribution was essentially the same as that observed on an equilibrium commercial FCC catalyst, but the activity of the aluminas was much lower. The main products (propylene, benzene, isopropylbenzene, di-isopropylbenzenes) showed that a series cracking mechanism prevailed in the conversion of TIPB. The apparent first order kinetic constants assessed and the conversion profiles allowed establishing a ranking of activities that could be associated directly to accessibilities and not to the number of acid sites (Lewis nature), which was proportional to the specific surface area of the alumina. The sequence of accessibilities followed the same trend as the mean pore size of the aluminas.

Keywords: Accessibility; Catalytic cracking; Matrix; Resid; Alumina

1. Introduction

The increasing demand to process heavier crudes and the maximization of the yields of petrochemical raw materials are the two main issues that impose new trends in the operation of modern refineries [1]. As a consequence, these facts impact significantly on the process of catalytic cracking of hydrocarbons (FCC), because it is one of the key processes in the petroleum refining industry. It is aimed at the conversion of low value, heavy hydrocarbon feedstocks into lighter, more valuable products such as liquefied petroleum gases (LPG), gasoline and diesel fuel. It is also a consequence that the catalysts used in FCC units are being shifted to high accessibility, resid or bottoms upgrading catalysts with active matrices and specific additives [2].

Among various functions, matrices in FCC catalysts provide the proper particle size and shape for the circulation of the catalyst particles in the unit [3,4], a heat sink to transport heat from the regenerator to the reactor, the best possible contact of reactant molecules with the zeolite component, and even a pre-cracking activity for very large molecules in the feedstock that can not diffuse into the zeolite's pores [5]. However, should the matrix be active, selectivity problems can arise, due to the formation of coke and gas products [6,7]. In order to improve the bottoms upgrading performance, many catalysts have high alumina matrices which are more resistant to the severe deactivation conditions of the commercial operation, with temperatures about 700 °C or higher and steam in the regenerator [8].

The problems in the mass transfer of large molecules through the catalyst pores and the higher content of contaminant metals like Ni, V and Fe, are inherent to the heavier feedstocks [9]. Thus, the need for specific resid catalysts with activity, selectivity and diffusion properties suitable to handle this type of feedstock, also makes new characterization techniques necessary. The pore systems of these materials, then, are to play a very important role in assisting mass transfer processes. The concept of "accessibility" was developed to have an indication of how the reactant molecules gain access to the catalyst active sites. While the

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0926-860X/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2006.08.028

Akzo Nobel Accessibility Index (AAI) test measures the diffusion of hydrocarbon molecules into commercial catalysts and can explain their performance, the experimental conditions used are far from those of the commercial process [10].

A different kinetic approach could be developed to assess accessibility, based on the conversion of a test reactant under appropriate conditions. In this way, the simultaneous diffusion, adsorption and reaction of large molecules would be considered. Among various candidates, the molecules of 1,3,5-tri-isopropylbenzene (TIPB) are bulky, with a kinetic diameter of 9.4 Å [11], and could be used as a test reactant over commercial FCC catalysts and active matrices. This hydrocarbon has been converted over acidic catalysts under different conditions. For example, Falabella et al. [12] studied the influence of the external surface area of rare-earth containing Y zeolites, Ross et al. [11] converted TIPB on mesoporous aluminosilicate MCM-41 and aluminophosphate Si-VPI-5, titanosilicate ETAS-10 and Y zeolite, and Al-Khattaf et al. [13] used two FCC catalysts in a wide temperature range, from 350 to 550 °C.

Is the objective of this work to study the catalytic cracking of TIPB over commercial aluminas with different pore size distributions and accessibilities, that can be considered representative of standard matrix components of FCC resid catalysts, and to compare their behavior with that of a reference equilibrium commercial catalyst.

2. Experimental

The catalysts used were three γ-aluminas derived from different commercial boehmite samples (Sasol) and an equilibrium commercial FCC catalyst (Vision V418, FCC S.A., Brazil; unit cell size, 24.23 Å; specific surface area, 139 m^2/g; AAI, 5.5; zeolite content, 16.9%; rare earth oxides, 1.26%). The spray-dried (nearly spherical particles) boehmites were calcined at 600 °C during 1 h to form the corresponding transition aluminas. Particle size distributions of the alumina powders were determined on a Malvern Master-Sizer 2000 instrument. The specific surface areas were determined by means of nitrogen adsorption isotherms (BET method), and the median pore diameters and pore volumes by mercury porosimetry. The AAIs were assessed following a standard procedure [10]. The textural properties of the catalysts are shown in Table 1. Acidity was characterized by means of FT-IR spectra of adsorbed pyridine. The powders were pressed to an auto-supported sample of approximately 10 mg and 14 mm diameter. Each sample was treated at 450 °C for 1 h under 70 mL/min O_2 flow, degassed at this temperature for 4 h, and then cooled to room temperature. Pyridine was dosed and equilibration was achieved at 150 °C/2 h until vacuum was nearly 10^{-6} mbar. Spectra of adsorbed pyridine were then recorded at room temperature in a Magna 760FT-IR Nicolet equipment, with resolution of 4 cm^{-1} and sweeping of 128 scans. The amount of acidic sites was expressed by the area under the 1452 cm^{-1} peak.

Table 1
Properties of the aluminas used

Properties	Catalyst		
	A	B	C
Specific surface area (m^2/g)	202	159	94
Median pore diameter (Å)	64	85	201
AAI	28.9	45.6	34.6
Particle size distribution			
D_{10} = 10% below (μm)	17	2	7
D_{50} = 50% below (μm)	54	11	37
D_{90} = 90% below (μm)	117	70	113
Pore volume (cm^3/g)			
30–1000 Å	0.44	0.45	0.67
1000–10,000 Å	0.02	0.28	0.09

The experiments of conversion of 1,3,5-tri-isopropylbenzene (Fluka, 97%), that was used without further purification, were performed in an internal recirculation, fluidized bed laboratory unit, the CREC Riser Simulator reactor [14], which was specifically designed for FCC studies. An impeller rotating at very high speed on top of the chamber that keeps the catalyst between two metal porous plates, induces the internal circulation of the reacting mixture in an upwards direction through the chamber, thus fluidizing the catalyst. When the reactor is at the desired experimental conditions the reactant is fed through an injection port, and immediately after the reaction time is attained, products are evacuated and analyzed by gas chromatography. The unit has been extensively and successfully used for catalyst evaluation, assessment of kinetic, diffusion and adsorption parameters, and studies about reaction mechanism; additional descriptive details of the reactor can be found elsewhere (e.g. [15,16]). The reaction conditions for the aluminas were: temperature, 500 °C, catalyst to reactant ratio of 2.34, and reaction times between 8 and 25 s. The mass of catalyst was 0.4 g in all the cases. The reaction conditions for the E-cat were: temperature, 350 and 450 °C, catalyst to reactant ratio of 3.80 with a mass of catalyst of 0.65 g, and reaction times between 3 and 12 s. The reaction products were analyzed by on-line standard capillary gas chromatography, using a 30 m length, 250 μm diameter and 0.25 μm film thickness, non-polar, dimethylpolysiloxane column. Product identification was performed with the help of standards and GC–MS analysis. The coke content was assessed by means of a method with temperature-programmed oxidation and further methanation [17]. The mass balances in the experiments closed to ±5%.

3. Results and discussion

Many factors have to be considered in the comparison of accessibility matters between an equilibrium commercial FCC catalyst (E-cat) and these aluminas. However, an actual E-cat would provide a genuine perspective of standard commercial catalytic performance, because even though many properties of the E-cats can be reproduced by laboratory deactivation methods, it has been shown that the pore structures and pore size distributions of laboratory steam deactivated catalysts do not match those in E-cats, leading to higher values of AAI [10].

The physical properties of the aluminas are crucial in terms of their role as catalyst matrices. In the case of the samples used, it can be seen in Table 1 that they show typical values that may represent matrices in FCC catalysts, particularly those present in resid catalysts. Based on empirical observations, it has been mentioned [18] that, in general terms, the ''optimum matrix properties'' in resid catalysts should be a specific surface area of approximately 100–120 m^2/g, with a mixture of meso- (about 60 Å mean pore size) and macropores (about 200–400 Å mean pore size).

The aluminas samples differ significantly in their physical properties. In effect, sample A has the smallest mean pore diameter, about 64 Å, sample B has an intermediate value of 85 Å and sample C shows the largest value of 201 Å. These differences in mean pore diameters reflect clearly the particular pore size distributions that are shown in Fig. 1. The distributions can be considered approximately sharp, with sample B showing contributions from some pores of very large size. Moreover, as expected, the larger the mean pore size, the smaller the specific surface area, that ranged from 94 to 202 m^2/g. In the case of the E-cat, two clearly distinct pore systems are present: that with micropores of 7.4 Å from the crystalline Y zeolite, and that from the matrix, with a mean pore diameter of about 90 Å.

The AAI test was developed specifically for compound FCC catalysts. It measures the liquid phase diffusion of large organic molecules (asphaltenes) into the catalyst by means of an UV spectrometer, by tracking the relative concentration of the molecules that adsorb at certain wavelength as a function of time [10]. The faster the evolution, the higher the index and the higher the accessibility in the catalyst. This constitutes an overall property, and the observed indexes range from 0 to 36. However, it has been observed that an AAI about 4 is ''critical'' for E-cats: even though this value varies from unit to unit, higher indexes will pertain to FCC catalysts with better performances from the point of view of accessibility [10], as evidenced by higher gasoline yields and conversions and lower slurry yields.

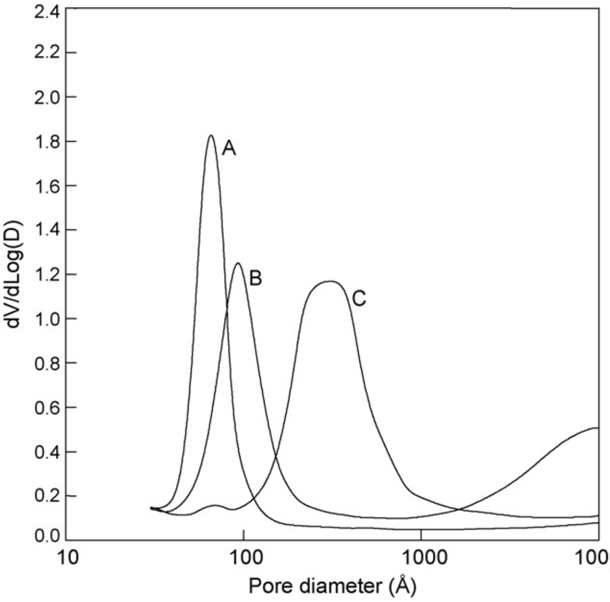

Fig. 1. Pore size distributions of alumina samples.

The AAI index of the E-cat in this work is 5.5, that is, a value slightly higher than the critical. As expected, the AAI indexes for the alumina samples are much higher. They locate in the upper limit of the method, or are even larger, like in the case of sample B. However, such a high value in sample B could be the consequence of the pore size distribution of this particular sample that showed contributions of pores in the macropore region above 1000 Å, while the other samples did not. These macropores, that could make AAI to increase, are not necessarily important concerning catalytic activity, because they would contribute moderately to the specific surface area of the catalyst.

The conversion of the bulky TIPB molecules had been used as a test reaction either to depict the behavior of heavy hydrocarbon feedstocks [19,20], or to inspect the diffusion properties of the Y zeolite in two FCC catalysts with different crystal sizes of 0.4 and 0.9 μm diameter [13]. In those works the reaction temperatures ranged from 350 to 550 °C. Due to the low activity of the aluminas, as compared to pure Y zeolite or compound FCC catalysts, the reaction temperature was chosen to be 500 °C in order to observe differences in the catalytic performances.

The conversions observed for each sample under those conditions are shown as a function of reaction time in Fig. 2. The conversions increase steadily as a function of time and indicate that the activities are different for each sample. The main products were propylene, benzene, isopropylbenzene, di-isopropylbenzene isomers, and two hydrocarbons with tetralin structure (cadine (1(10),6,8-triene) isomers).

Typical yield curves for the various products are shown in Fig. 3, where it can be seen that most of the products are stable. The cadine isomers show an unstable profile. Propylene, that is

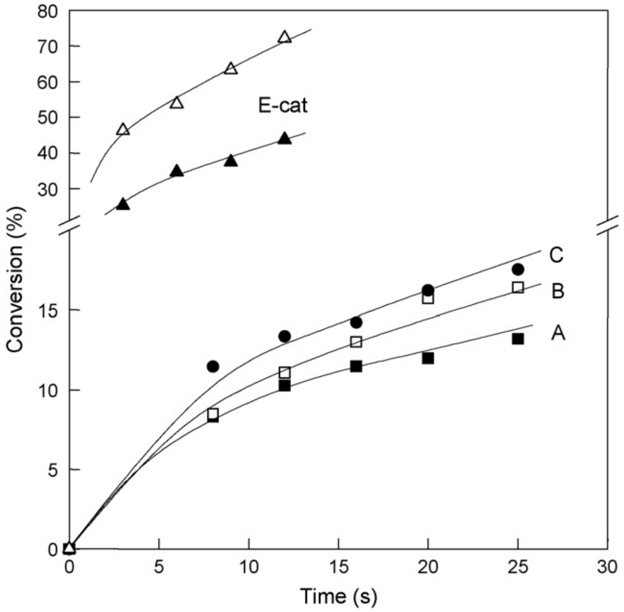

Fig. 2. Conversion as a function of reaction time for the various alumina samples; temperature: 500 °C. E-cat; temperatures: 350 °C (▲) and 450 °C (△).

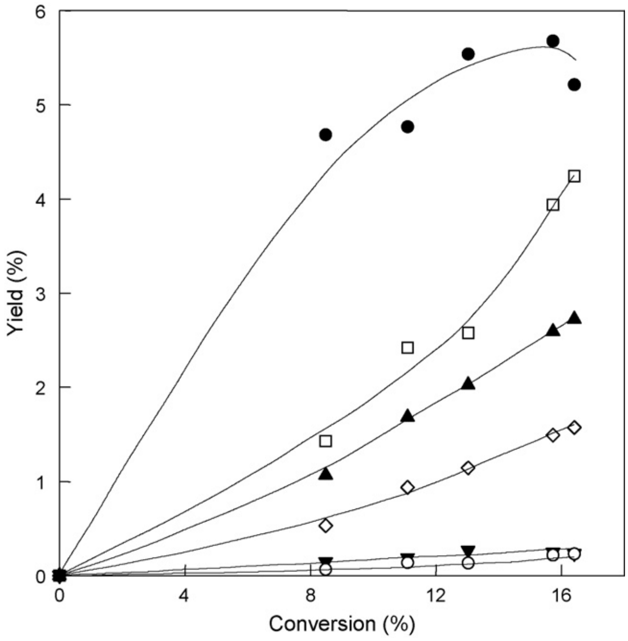

Fig. 3. Product distribution in the conversion of TIPB on sample B. Temperature 500 °C. (●) cadine; (□) 1,3-di-isopropylbenzene; (▲) propylene; (◇) isopropylbenzene; (▼) benzene; (○) 1,4-di-isopropylbenzene.

produced in each one of successive cracking steps yielding di-isopropylbenzene isomers, isopropylbenzene and benzene, was the most important cracking product in terms of molar yields. It is to be noted that propylene molar balances under this scheme close to more than 98%. The amount of coke on the catalysts was always very small, less than 0.15%. Considering the reactant and main products of this catalytic system, some molecules having aromatic and saturated rings, both alkylated, like cadine isomers, are feasible. However, it is to be noted that previous works with TIPB on acidic catalysts did not mention them. This bicyclic hydrocarbons can be formed by the cyclization of alkyl groups in the aromatic ring, following a mechanism similar to that of the formation of tetralin or indane from the reaction of polyalkyl-substituted aromatics over Ni/silica–alumina hydrocracking catalysts [21].

As confirmed by pyridine FT-IR analysis (see example of sample C in Fig. 4), the acidic sites on these aluminas are of Lewis nature [22,23]. However, according to the fact that the observed products were essentially the same as those in the E-cat, where zeolite Brönsted sites are responsible for the most important reactions, it can be inferred that passive Brönsted sites could be present in the alumina samples. Tung and Mcininch [24] showed that the activity of pure alumina at temperatures higher than 400 °C in reactions catalyzed by Brönsted sites can be based on the existence of passive protons trapped in cationic vacancies in the alumina lattice. Also, OH groups are observed in the 3600–3800 cm^{-1} region, that do not retain pyridine at 150 °C. Moreover, Sarbak [25] showed that pure aluminas, with only Lewis type sites, were able to dealkylate cumene at 400 °C (note that cumene is an intermediate product in TIPB conversion). Even a moderate contribution from thermal cracking could be considered at 500 °C.

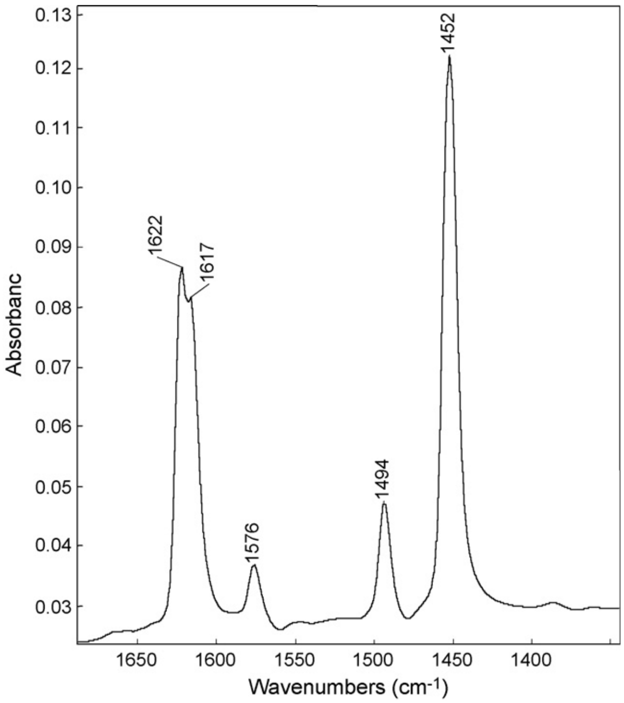

Fig. 4. FT-IR spectra from sample C after pyridine adsorption. Wavenumber range 1710–1350 cm^{-1}.

The characterization of acidity showed that the acidic surface sites in the different alumina samples are similar, since the chemical composition, source and nature of these catalysts are the same and, as it is shown in Fig. 5, the number of acidic sites per unit mass in the catalysts is proportional to their specific surface areas.

As expected, the conversions observed on the E-cat at 350 and 450 °C, that are also included in Fig. 2 for comparison, were significantly higher than those in the aluminas at 500 °C.

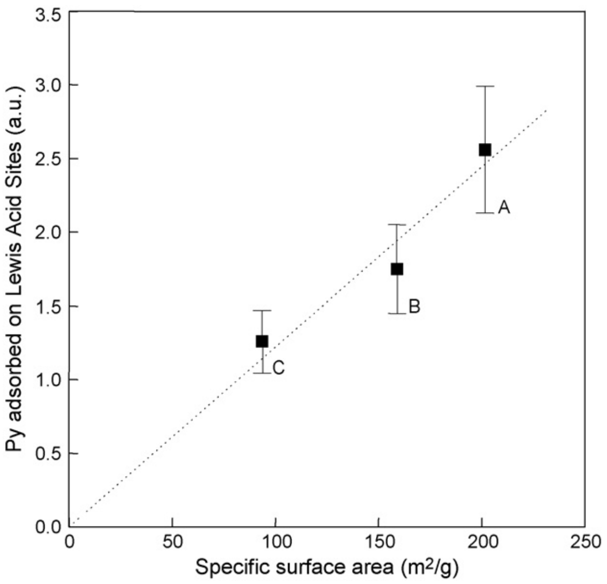

Fig. 5. Amount of Lewis acid sites (1452 cm^{-1} peak area) as a function of specific surface area.

As mentioned, the reaction products were essentially the same, with higher coke yields (about 0.6% coke on catalyst) but only one of the cadine isomers was observed.

The inspection of Fig. 2 reveals that at every time, the conversions observed on sample C are higher than those on sample B, in turn higher than those on sample A, thus determining catalyst activities. The activities could also be defined by means of the apparent first order kinetic constant in a simple model representing the direct conversion of the reactant to products, without catalyst deactivation. The apparent kinetic parameters were assessed through a conventional least-square optimization method, and the results on a mass basis are presented in Table 2, compared with those from the E-cat. As expected, the activity of the aluminas is much lower, even considering that the temperatures used in the case of the E-cat were lower. The differences are larger if the constants in the E-cat are referred to the amount of zeolite (16.9%), which is the most active component in the commercial catalysts, considering its matrix inactive. Again the ranking of observed activities between the aluminas, based on the apparent kinetic parameters, is in the order C > B > A.

The distinct activities observed can be rationalized considering the physical and chemical properties of the aluminas. Since these samples differ mainly in their pore systems, the results can be associated to, and considered representative of the different accessibility properties. Since the mass of catalyst used in each experiment was the same, according to the specific surface areas the number of active sites exposed to the reactant followed the same ordering (A > B > C). However, activities conform the opposite sequence ordering (C > B > A), thus reflecting increasing restrictions to access to the active sites. Thus, according to the observed activities, alumina C, with the largest mean pore size and lowest specific surface area would have the highest accessibility, followed by aluminas B and A, respectively.

A complete agreement between the activities and the AAI values is not observed (refer to Table 1). However, it has been discussed that the AAIs for these samples are in the upper limit, and possibly not reliable range, of the method for assessing AAI. Besides that, alumina B shows an important contribution to its pore volume from very large pores which might influence AAI, increasing it, but that are not expected to contribute significantly to the catalyst activity. AAI, then, seems not to be a good technique for screening FCC aluminas regarding their actual accessibility.

Table 2
Apparent kinetic constants corresponding to a first order conversion model

Catalyst	Reaction temperature (°C)	k ($\times 10^3$ cm^3/(g s))
A	500	0.80
B	500	0.97
C	500	1.08
E-cat	350	4.10
	450	9.20
Zeolite in E-cat	350	24.28
	450	54.45

This kinetic approach showed to be applicable to comparisons between the same type of catalysts (e.g. compound (zeolite plus matrix) FCC catalysts [26], or aluminas). Caution should be exerted if these results are extended directly to actual E-cat matrices, since strong interactions with the zeolite component may develop after the catalyst particles are subjected to so many reactor–regenerator cycles in the FCC units, from a reducing environment at 500–550 °C, to an oxidizing environment, with steam, at about 750 °C [27,28].

4. Conclusions

Aluminas that can be considered representative of matrices of commercial FCC catalysts converted 1,3,5-TIPB at 500 °C moderately. The product distributions showed a small number of products: propylene, benzene, isopropylbenzene, di-isopropylbenzenes and smaller amounts of tetralin-type hydrocarbons. The amount of coke formed was very low. The apparent first order kinetic parameters were one or two orders of magnitude lower than those observed on equilibrium commercial FCC catalysts or on the zeolite component, respectively, that were obtained even at milder conditions. Both the conversion profiles as a function of reaction time and the apparent, first order kinetic parameters define a ranking showing that the larger the mean pore size, the higher the catalyst activity. This can be associated to a higher accessibility in the alumina catalysts with larger mean pore size, since the samples differ only in their physical properties. This approach, based on the conversion of TIPB, proves to be simple and trustable to determine the true accessibility to the catalyst active sites, and could be very helpful in characterizing the properties of matrices of a given type in resid FCC catalysts.

Acknowledgements

This work was performed with the financial assistance of University of Litoral (Santa Fe, Argentina), Secretary of Science and Technology, Project CAID 2002 #20-144, CONICET, PIP 0630/98 and ANPCYT, PICT2000-2001 14-08990. The authors gratefully acknowledge the useful discussions with and contributions from Petrobras specialists Dr. Rosana L.P. Cardoso (GC–MS), and Denise Costa and Denise D. Filgueiras (FT-IR).

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