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USE OF MONTMORILLONITE (SMECTITE) AS CATALYST FOR OLEFIN POLYMERIZATION AND TRANSFORMATION OF SULFUR COMPOUNDS.

Rogério Gomes Rodrigues and Graziela Finger
Companhia Petroquímica do Sul - COPESUL
Pólo Petroquímico - CEP 95.853-000
Triunfo/RS, Brasil
and
Paulo César Pereira das Neves*
Museu de Ciências - Departamento de Química
Centro de Ciências Naturais e Exatas - CCNE
Universidade Luterana do Brasil - ULBRA
Rua Miguel Tostes, 101 - CEP 92420-280
Canoas/RS, Brasil.

ABSTRACT

Acid activated montmorillonite (smectite) clay was used to eliminate olefins and transform thiophenes and mercaptans present in aromatic BTX (benzene-toluene-xylene) streams from the aromatic extraction unit of COPESUL - Companhia Petroquímica do Sul.

The working temperature of the mineral clay was raised above normally specified values since difficulties were encountered to meet the specification for hydrogen sulfide in xylene and trimethylbenzene. The experimental results showed that montmorillonite (smectite) clay was suitable for olefin elimination and sulfur compounds transformation at higher reaction temperatures (200^{0}C), and that the useful life for catalytic operations could be prolonged by raising the temperature.

KEYWORDS: **Montmorillonite (Smectite); clay; olefin polymerization; desulfurization; BTX (benzene-toluene-xylene) streams.**

RESUMO

O composto montmorillonita (esmectita) ácido ativado, foi usado na eliminação de compostos olefínicos e transformação de compostos de enxofre, presentes numa corrente de extrato aromático, proveniente da Unidade de Extração de Aromáticos da Companhia Petroquímica do Sul.

*** Author to whom correspondence should addressed.**

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O argilo-mineral teve sua temperatura de operação elevada com objetivo de melhorar sua atividade catalítica, já que vinha apresentando dificuldade de manter o xileno e o trimetilbenzeno especificados em relação a presença de gás sulfídrico. Os resultados mostraram que a montmorillonita (esmectita) possui atividade catalítica para manter os produtos especificados, a temperatura de 200°C e que a vida útil do catalisador poderia ser prolongada elevando-se a temperatura de reação.

INTRODUCTION

The purpose of the present work was to study the properties and conditions under which the clay montmorillonite (smectite) acts in the elimination of unsaturated compounds and the removal of sulfur in the form of hydrogen sulfide from thiophenes and mercaptans. It is important to note that not all cations present in the clay have the same binding energy. The ease with which the cations can be exchanged is in accordance with the following order: Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++} and H_3O^+. The mineral clay is used in the Aromatics Fractionation Unit of COPESUL - Companhia Petroquímica do Sul. Its main function is to ensure that the aromatic products meet the bromine index and sulfur specifications. At the present, the unit is having difficulties in meeting the specifications for xylene and trimethylbenzene due to the presence of hydrogen sulfide.

Montmorillonite (smectite) $\{(Al_{1,5}Mg_{0,33})[Si_6O_{10}](OH)_2.nH_2O\}$ is a clay mineral of (t-o-t) smectic dioctaedric structure belonging to the smectic group. According to Klein and Hurbult[1] its principal characteristic is to absorb water molecules between the smectite layers or lamelae, leading to swelling and a pronounced expansion of the structure. The layers consist of tetrahedral SiO_4 units sharing corners with octahedral Al^{+++}, having coordinated oxygen and hydroxyl groups. The structural model of montmorillonite (smectite) in given in Figure 1.

In a slightly acidic solution, cation exchange with protons is possible and because of the layer structure swelling effects occur. The swelling is understandable in terms of ionic strength effects on double layer repulsion.

A typical montmorillonite (smectite) contains a variety of oxides in approximately the following composition: SiO_2 = 57,49%; Al_2O_3 = 20,27%; Fe_2O_3 = 2,92%; FeO = 0,19%; CaO = 0,23%; MgO = 3,18%; K_2O = 0,28%; Na_2O = 1,32%; TiO_2 = 0,12% and H_2O = 14%[3].

Its crystals are of reduced dimensions (average of about 0.15 μm) and their thickness is very small. Organic molecules can be absorbed between the smectite layers usually taking the place or coordinating with exchangeable cations [2-6]. The binding between the smectite layers involves van der Waals forces and considering the isomorphic substitution of the mineral can be used to explain the easy cleavage of montmorillonite (smectite) crystals in liquid medium[2]. Sheets of clay crystal can hold an equilibrium separation distance that may be as large as 100 A° and depends on the concentration of electrolyte in the interlayer aqueous phase.

The catalysis of many organic reactions by mineral clays has been known for a long time, it has been applied in many industrial processes and it has been described in detail in the literature[4,5,7].

The present paper will deal only with the use of montmorillonite (smectite) clay as a catalyst in olefin removal (polymerization olefins) and aromatics purification (desulfurization).

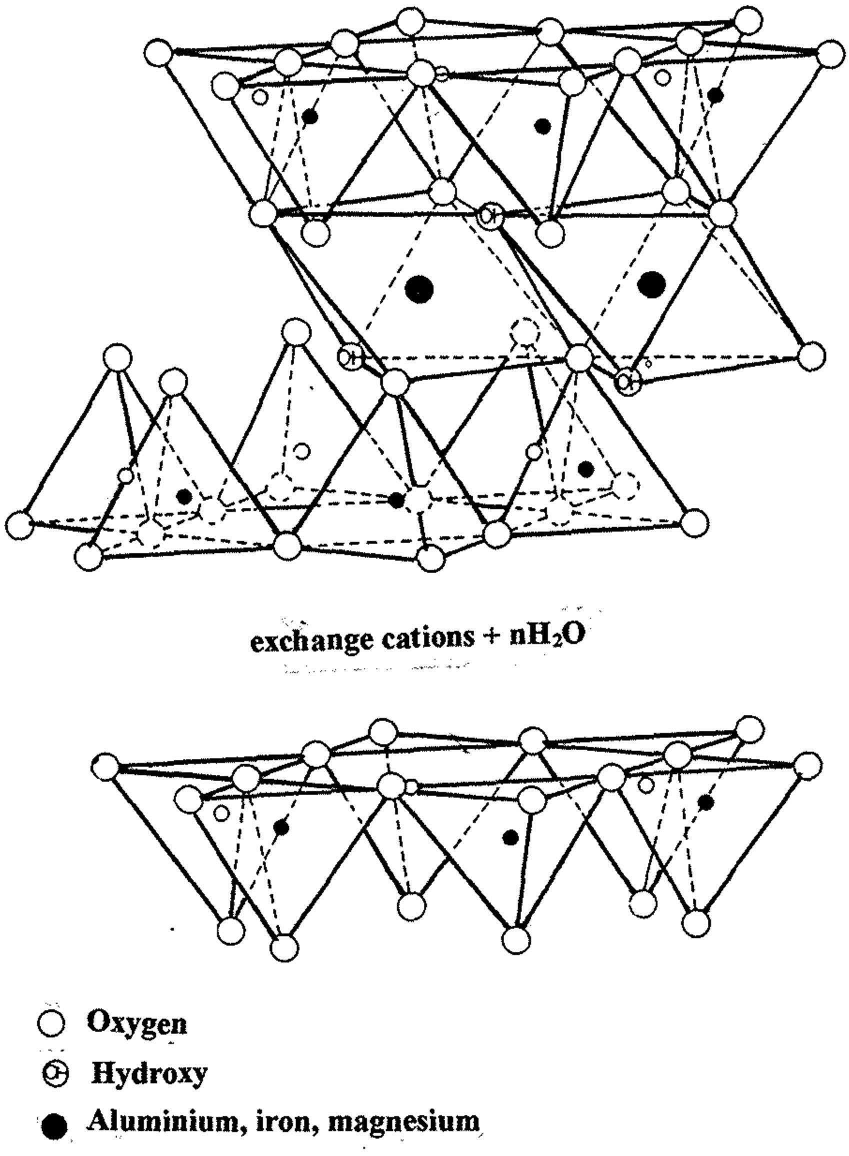


Figure 1. Structural model of montmorillonite (smectite)[2].

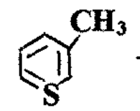
The catalytic properties of montmorillonite (smectite) are essentially related to its ability to absorb organic molecules on the internal surfaces (between the layers). The reactions generally occur at lower temperatures, when compared to clays such as kaolinite and pyrophyllite used in cracking and need time in order to orientate the molecules and introduce the different elements into structures at the correct junctions.

DESCRIPTION OF THE INDUSTRIAL PROCESS

The production of aromatics with high purity specifications involves several unit processes. A block diagram of the aromatics units of COPESUL - Companhia Petroquímica do Sul is given in Figure 2.

<u>U_{21} - Hydrogenation Unit of Pyrolysis Gasoline.</u> This unit was projected in order to hydrogenate in two steps the crude gasoline produced in the Olefins Unit. This gasoline contains an aromatics fraction. The first step involves selective hydrogenation of diolefinic and styrene derivatives. The second step involves the saturation of olefins and the desulfurization of sulfur compounds leading to the formation of hydrogen sulfide. The sulfur, mostly present in thiophenes and mercaptans is not totally removed in the hydrogenation unit and the presence of small amounts (less than 1.0 ppm) leads to failure to meet the required purity specifications. Montmorillonite (smectite) clay promotes this desulfurization process. The reactions under consideration are illustrated bellow:

$$Y^+ + H_2C = CH_2 \rightarrow Y - CH_2 - CH_2 + H_2C = CH_2 \rightarrow Y - CH_2 - CH_2 - CH_2 - CH_2^+$$

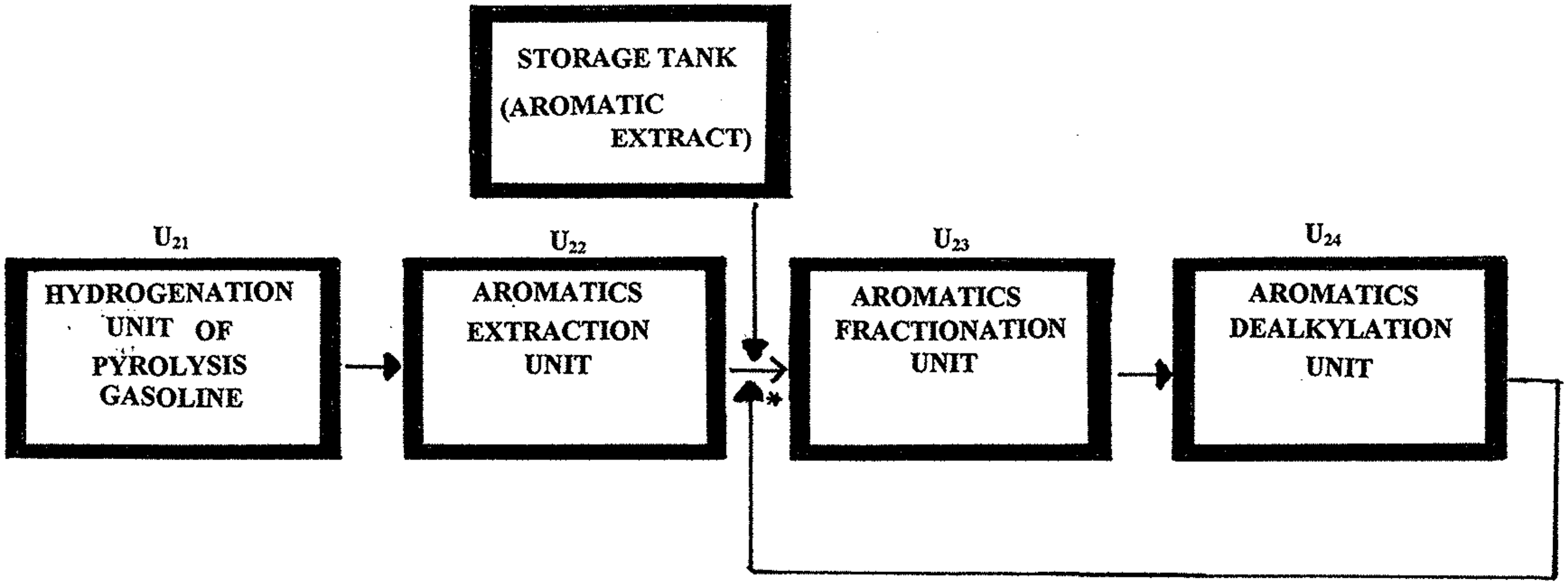


$$+ H^+ \xrightarrow{\text{high T}} CH_3 - CH_2 - CH - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}H_3}}} + H_2S$$

$$CH_3(CH_2)_2CH_2SH + H^+ \xrightarrow{\text{high T}} CH_3(CH_2)_2CH_3 + H_2S.$$

<u>U_{22} - Aromatics Extraction Unit.</u> The main function of this unit is to extract benzene, toluene and trimethylbenzene from pyrolysis gasoline produced in the Olefins Unit and hydrogenated in two steps in the Hydrogenation Unit (U_{21}) using sulfolane as a solvent. This extract contains undesirable contaminating traces of olefins that have not been hydrogenated in the Gasoline Hydrogenation Unit. Montmorillonite (smectite) clay promotes the polymerization of these defins and leads to acceptable bromine index values in the final product.

<u>U_{23} - Aromatics Fractionation Unit.</u> The purpose of this unit is to produce in high punty grade benzene, toluene, xylene and trimethylbenzene from a feed coming from three streams - the aromatic extract produced in the Aromatics Extraction Unit (U_{22}), aromatic extract from the storage tank and the benzene rich stream produced in the Aromatics Dealkylation Unit (U_{24}). Figure 3 shows a diagram of the BTX (banzene-toluene-xylene) Clay Treatment Towers. The treatment with montmorillonite (smectite) clay is done at the entrance of the Aromatics Fractionation Unit (U_{23}). As previously mentioned, the feed for this unit proceeds from three diferent streams. The first two streams combine and are preheated by the heat exchange with the stream that leaves the clay treatment and subsequently the three streams are heated to the desired operation temperature by using steam under medium or high pressure. The total or final stream is then treated with



* Montmorillonite (smectite) clay treatment.

Figure 2. Block diagram of the aromatic units[7].

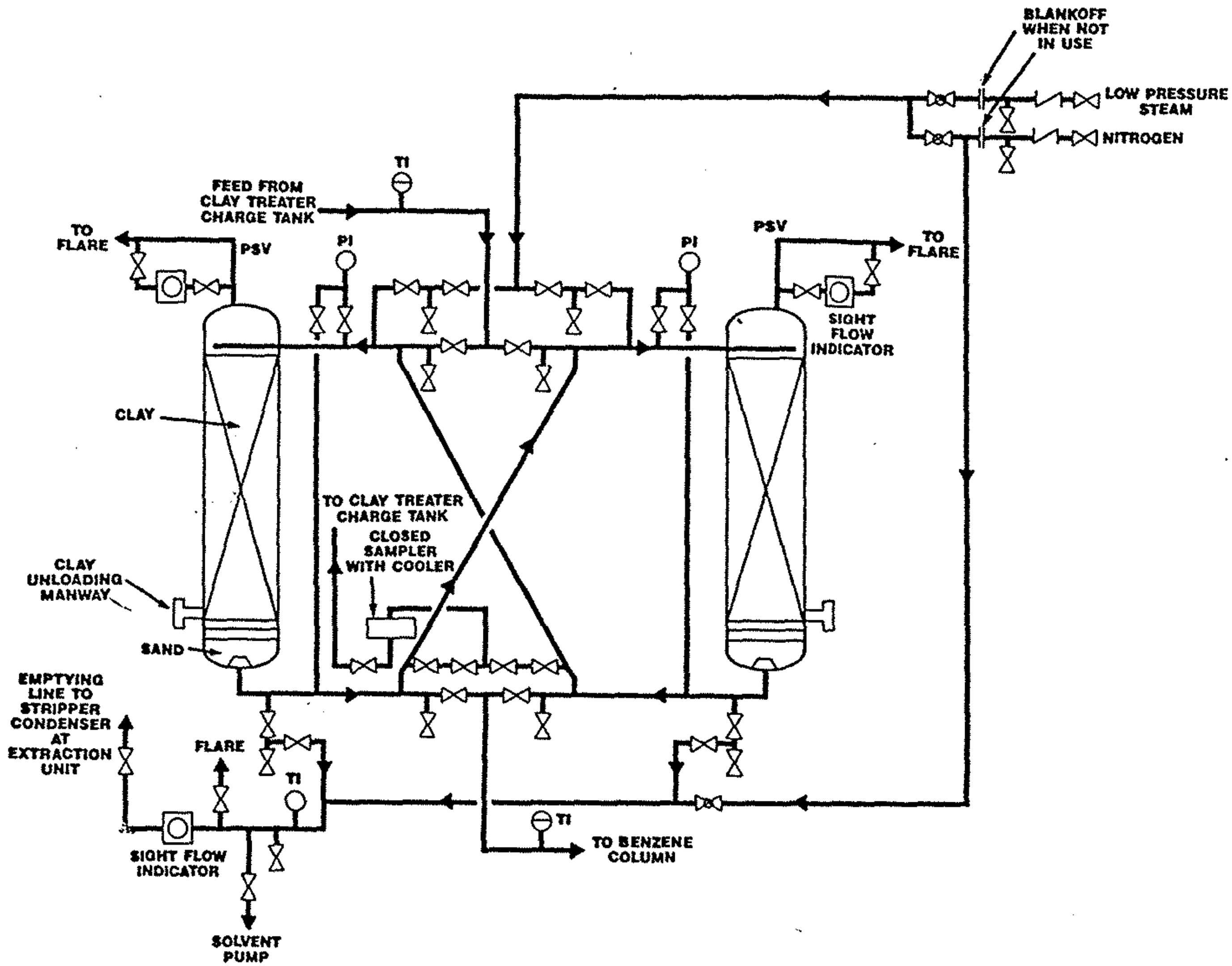


Figure 3. Diagram of the BTX (benzene-toluene-xylene) clay treatment towers[8].

montmorillonite (smectite) clay in one or two clay towers in order to remove the contaminants. The clean stream will then feed the benzene column. Two clay towers are necessary in order to avoid interruptions of the treatment when the clay in one of the towers is saturated. The benzene column also contains water and lighter products such as hydrogen sulfide and sulfur dioxide. The lighter products are removed from the top of the column and burned. Hydrogen sulfide results from reactions of sulfur compounds (thiophenes and mercaptans) from the feed in the presence of montmorillonite (smectite) and sulfur dioxide is the result of degradation of sulfolane used as solvent in the Aromatics Extraction Unit (U_{23}). The degradation of sulfolane, present in small concentration in the clay towers, usually takes place when the temperature reaches 200°C.

U_{24} - Aromatics Dealkylation Unit. The function of this unit is to produce benzene from toluene, xylene or trimethylbenzene streams coming from the Aromatics Fractionation Unit (U_{23}). This unit employs dimethyl disulfide as an eluent in the reaction section (650°C). Reaction of dimethyl disulfide with hydrogen present in the reactor may lead to the formation of hydrogen sulfide and eventual contamination of the product with thiophene.

EXPERIMENTAL PROCEDURE

The experimental work consisted essentially in elevating temperature in the clay towers for a period of operation that lasted over a month. The temperature used was varied from 150°C to 200°C and the pressure range employed was from 12.0 kgf/cm^2 to 15.0 kgf/cm^2. A detailed description of experimental procedure is given in Table I.

Table I. Variation of pressure and temperature in the clay towers.

Date (1995)	Temperature (°C)	Pressão (kgf/cm^2)
10.08	150	12.0
11.08	170	12.0
14.08	200	15.0
19.08	195	15.0
20.08	190	15.0
28.08	200	15.0
14.09	195	14.0

The montmorillonite (smectite) clay used was obtained from Engelhard Exceptional Technologies, Jackson, Mississippi, USA. It was an acid treated clay produced in granular form to facilitate its use in fixed bed applications. It was produced by ion exchange (of Mg, Ca, Na, K and Al ions) in specially selected montmorillonite (smectite) clay and it is characterized by high adsorptive capacity, high catalytic and high surface area. Some typical properties are illustrated in Table II.

The products obtained were analyzed using standard laboratory tests for bromine index in the case of benzene and the presence or absence of traces of H_2S/SO_2 in xylene and trimethylbenzene. The bromine tests verifies the degree of purity with respect to the presence of olefins and the bromine used per g of sample[10].

Table II. Some typical properties of the montmorillonite (smectite) clay used[9].

Moisture	
Free @ 105°C, wt. % loss	14
Residual Acidity	
mg. KOH/gm. At phenolphtalein end point	14
Particle size. Tyler Standard Sieve	
Passing 20 mesh, wt. %	75
Passing 60 mesh, wt. %	5
Apparent Bulk Density, Packed	
lbs./cu. ft.	50
gm./cc.	0.80
Surface Area	
B.E.T. Method , m^2/gm.	400

The presence of H_2S was tested using lead acetate indicator paper in the presence of vapors of the product. The presence of hydrogen sulfide leads to the formation of lead sulfide, characterized by its black color. The test of SO_2 consists of wetting filter paper with 5% starch solution followed by drying, impregnation with potassium iodate solution and placing in contact with vapors of the sample. The formation of a blue color indicates the presence of sulfur dioxide in the product[10].

EXPERIMENTAL RESULTS

The experimental results obtained are summarized in Table III.

The analysis of the experimental results shows that activity of the clay improved with relation to rise in temperature, as far as the removal of olefins is concerned. In fact the first elevation in the temperature of the catalyst from 150°C to 170°C significantly removed the olefins present in the benzene fraction (from 12 mg to 4 mg of bromine per g of benzene). However, operation of the clay towers at this temperature did not solve the problem of contamination of xylene and trimethylbenzene with hydrogen sulfide. The elevation of temperature to 200°C led to satisfactory results for both olefin and this removal.

Attempts to lower the operating temperature to 190°C lead to unsatisfactory for xylene and trimethylbenzene due to contamination by H_2S. Subsequent experiments showed that the best operating temperature in order to meet the required specifications for xylene and trimethylbenzene was 195°C. The rise in temperature from 150°C to 200°C had no effect on contamination of the aromatics fraction by sulfur dioxide. This may be due to fact that the feed was low in sulfolane content.

The pressure was raised from 12.0 kgf/cm^2 to 15.0 kgf/cm^2 in order to maintain the product in the clay towers in the liquid phase. The liquid promotes a cleansing or washing of the clay, diminishing the deposits of polymers at the acid sites and increasing the useful life of the catalyst. The lowering of the pressure from 15.0 kgf/cm^2 to 14.0 kgf/cm^2 had as a main purpose a reduction of the pressure of the system, alleviating the load on the feeding pump.

Table III. Experimental results obtained by variation of the temperature in the montmorillonite (smectite) clay tower during the period of August 10, 1995 to September 14, 1995.

Date (1995)	Temperature (^{0}C)	Pressure (Kgf/cm^2)	H_2O/SO_2 Xylene	H_2S/SO_2 Aromatics	Br in Benzene (mg/100 g)
10.08	150	12.0	+/-	+/-	12
10.08	150	12.0	+/-		
12.08	170	12.0	+/-	-/-	14*
13.08	170	12.0	+/-	-/-	4
14.08	200	15.0	+/-	-/-	6*
15.08	200	15.0	-/-	-/-	1
16.08	200	15.0	-/-	-/-	<1
17.08	200	15.0	-/-	-/-	<1
18.08	200	15.0	-/-	-/-	<1
19.08	195	15.0	-/-	-/-	<1
20.08	190	15.0	-/-	-/-	1
24.08	190	15.0	+/-	-/-	2
25.08	190	15.0	+/-	+/-	1
28.08	200	15.0	+/-	-/-	<1
29.08	200	15.0	-/-	-/-	2
14.09	195	14.0	-/-	-/-	<1

* These analyses were performed before raising the temperature.
+ Positive (indicates presence of traces amonts of H_2S or SO_2.
- Negative (indicates absence of contaminant).

The pressure differential of the clay towers (pressure at entry minus pressure at exit) was essentially constant with the rise in temperature indicating that there was no significant increase of polymer formation over the reaction bed, allowing free flow of the products.

The experimental results showed that the useful life of montmorillonite (smectite) clay for catalytic operations could be prolonged by raising the operating temperature of the clay towers from 150^{0}C to 200^{0}C.

The mechanism of olefin removal takes place by polymerization reactions at the acid centers of the clay. Montmorillonite (smectite) also catalyzes the transformation of thiophenes and mercaptans present in BTX (benzene-toluene-xylene) streams to hydrogen sulfide[7]. Apparently, the rise in temperature of the clay treating towers helps remove polymers and coke from the acid sites. The presence of sulfolane in small amounts (less than 500 ppm) in the feed has little effect on the catalytic activity since it is readily converted to SO_2. At higher concentrations, however, sulfolane in adsorbed on the clay affects catalytic efficiency.

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