KAOLIN AND COMMERCIAL FCC CATALYSTS IN THE CRACKING OF LOADS OF POLYPROPYLENE UNDER REFINARY CONDITIONS

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Abstract - The efficiency of Commercial FCC catalysts (low, medium and high activities) was evaluated by the catalytic cracking process of combined feeds of polypropylene (PP) and vaseline, using a microactivity test unit (M.A.T.) for the production of fuel fractions (gasoline, diesel and residue). The PP/vaseline loads, at 2.0% and 4.0% wt, were processed under refinery conditions (load/catalyst ratio and temperature of process). For the PP/vaseline load (4.0% wt), the production of the gasoline fraction was favored by all catalysts, while the diesel fraction was favored by PP/vaseline load (2.0% wt), showing a preferential contact of the zeolite external surface with the end of the polymer chains for the occurrence of the catalytic cracking. All the loads produced a bigger quantity of the gaseous products in the presence of highly active commercial FCC catalyst. The improvement in the activity of the commercial FCC catalyst decreased the production of the liquid fractions and increased the quantity of the solid fractions, independent of the concentration of the loads. These results can be related to the difficulty of the polymer chains to access the catalyst acid sites, occurring preferentially end-chain scission at the external surface of the catalyst.
Keywords: PP; Catalytic cracking; FCC catalyst; Gasoline fraction.

INTRODUCTION

Polymeric residues are the cause of increasing environmental concern in the developed world. In view of their non-biodegradability, most polymers are considered inappropriate for disposal. Because of these limitations, the tertiary or chemical recycling is growing in importance. Therefore, waste plastics are converted into monomers, fuels or valuable chemicals for the petrochemical industry (Lin & Yen, 2005; Cardona & Corma, 2000). The concept of recovery of valuable products from the waste plastics using various chemical reactions such as hydrolysis, alcoholysis, acidolysis, and pyrolysis is believed to be a promising approach. Pyrolysis or thermal cracking is

an important industrial process for obtaining basic raw materials of the petrochemical industry. Polyolefins such as polyethylene (PE), polypropylene (PP) and polystyrene (PS) can be converted into clean fuel by pyrolysis process. Therefore, many researchers have made efforts to make the pyrolysis process economically viable (Dawood & Miura, 2002).

Two main chemical recycling routes are the thermal and catalytic cracking of waste polymers. In thermal cracking, the process produces a wide range of products and requires high operating temperatures, typically over 500 ºC, even up to 900 ºC. These facts severely limit their applicability and increase the cost of raw materials originating from the treatment of plastic waste recycling.

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Hydrocracking and thermal cracking have been investigated in the laboratory, at the pilot plant level and in some semi-commercial plants that were constructed for the treatment of mixed plastic waste, even those containing chlorine. However, the yield of thermal cracking is low because it provides unstable hydrocarbons with a wide range of boiling points. Thus, catalytic degradation is a means used to solve these problems. The addition of the catalyst is expected to reduce the decomposition temperature, to promote faster decomposition and change products.

The description of cracking reactions during the degradation of plastics is quite difficult, because they are very complex. The method for determining the kinetics of the reaction depends on the technology of degradation of the plastic waste. For example, there are considerable differences in thermal degradation of plastic waste in the absence and presence of catalysts. The catalytic cracking of alkanes in the presence of acid catalyst generally occurs through a mechanism of the ionic type. According to this mechanism, the reactivity and selectivity differ from paraffins to olefins and branched to linear hydrocarbons. Supposing a similar mechanism for catalytic pyrolysis of polymers, it is reasonable to expect that a modification in the structure of the polymer before pyrolysis catalyst can lead to further improved activity and selectivity (Dawood & Miura, 2002; Cardona & Corma, 2000; Angyal et al., 2007; Lin & Yang, 2008).

There are different methods for carrying out the catalytic cracking of polymers: catalytic cracking of plastic wastes and liquid streams mixtures, thermal cracking plus catalytic upgrading, catalytic cracking of plastic wastes by direct contact with the catalyst, and hydrocracking. A simpler way of processing the plastics via catalytic cracking would consist in mixing the plastic wastes with a FCC feed, forming a slurry that is treated conventionally in the FCC unit of a refinery. The principal limitations to this solution are the transportation costs of the plastics from origin to the refinery, the need of important refining liquid streams necessary for taking into account the limited amount of plastics that can be mixed, and the restricted use of chlorine and other heteroatoms contained in the plastics that can negatively affect the FCC unit and catalyst (Cardona & Corma, 2000).

Furthermore, the commercial FCC catalysts contain two main components: a zeolite (3.0% to 40% by weight) and a matrix. These components include a wide variety of materials which serve for different purposes of the refinery. A catalyst particle is actually a composite. The presence of zeolite in the FCC catalyst promotes high concentrations of active sites, high thermal and hydrothermal stability and high selectivity. The matrix gives the FCC catalyst porosity, acidity, metal resistance, mechanical strength. The porosity allows the loading and product molecules to be released faster in the catalyst particle. The acidity of the matrix is an important factor in the efficiency of the cracking of heavy hydrocarbons (Baptista, 2005; Costa et al., 2004).

The effectiveness of the zeolite catalysis is due to some peculiar characteristics of these materials. Zeolites have high surface area and adsorption capacity. The structure of the zeolites enables the creation of active sites such as acid sites, whose strength and concentration can be controlled according to the desired application, and the size of the channels and wells are compatible with most of the molecules of the raw materials used in industry. Zeolites also have a complex network of channels, giving them different shape selectivity, i.e., of reactant, product, and selectivity of the transition state. The amount of the active component (zeolite) in the composition of the catalyst adjusts the activity to the level desired, as well as the selectivity. The alterations in the composition of zeolite Y, like the ratio SiO_2/Al_2O_3 (SAR = Silica Alumina Ratio), make possible the attainment of more convenient characteristics, depending of the situation and application (Maia, 2002).

Several authors have studied the application of these catalysts to the pyrolysis of plastic materials (Vasile et al., 1985 and 1988; Beltrame et al., 1989; Audisio et al., 1992; Lin & White, 1995; Ochoa et al., 1996; Serrano et al., 2001; Aguado et al., 2001; Marcilla et al., 2003; Seo et al., 2003; Ribeiro et al., 2006).

Therefore, the objective of this work was the evaluation of the performance of commercial FCC catalysts (low, medium and high activities). The specific objective was the evaluation of catalytic cracking of loads of polypropylene (PP) with vaseline (petroleum jelly), through a microactivity test unit (M.A.T.), for the production of combustible fractions (gasoline, diesel and residue).

MATERIALS AND METHODS

Materials

The materials used in this work were PP (ABCM Plásticos LTDA), vaseline (Resim Industria e Comércio LTDA/PETROBRAS/BR); kaolin - aluminosilicate (CADAM - Kaolin of Amazônia S.A.) and Fluid Catalytic Cracking (FCC) commercial catalysts (supplied by the Fábrica Carioca de Catalisadores - FCC S.A./RJ).

Vaseline (petroleum jelly), containing 95-99% paraffin, 0.4% aromatic compounds and 0.07% sulphur compounds, was used as solvent, and kaolin was used as an inert material. The catalysts were classified in accordance with the percentage of zeolite Y (active component) contained in the commercial composition as: Low Activity (L.A.), Medium Activity (M.A.) and High Activity (H.A.).

Samples Characterization

The global chemical compositions of the kaolin samples (inert material) and of the catalysts were determined through analyses by X-Ray Fluorescence (FRX). The samples were analyzed on a Philips, model PW 1407 X-ray spectrometer with a Cr generating pipe and a proportional flow detector, 50 KV radiation and 40 mA. The spectrometer was connected to a microcomputer running the software PHILIPS PW1492. This analysis supplied the percentage by weight (% wt) of the oxides of sodium, aluminum, silicon and metals that compose the inert material and the commercial FCC catalysts.

The surface characterization (adsorption of N_2 - Quant-Sorb) to obtain the values of the specific area and the micropore volume of the samples of catalysts (L.A., M.A. and H.A.) was determined by analyses with an ASAP (Accelerated Surface Area and Porosimetry) device, Micrometrics model 2400, through the isothermal adsorption and desorption of N_2 at -196 ºC, using the method of Brunauer-Emmet-Teller (B.E.T.). The volume of microspores was determined by the t-plot method, combined with the equation of Harkins and Jura (BARRETT *et al*., 1951; GREGG & SING, 1982).

Loads of PP/Vaseline

The solubility of the polymers was tested *versus* vaseline (paraffin mixture) under stirring, heating and refluxing, in order to obtain polymer loads PP/vaseline of 2.0 and 4.0% wt (by mass).

Catalytic Cracking Process

The process of catalytic cracking used in this work was based on the Standard Test Procedure - 20 ASTM D 3907 and on the test unit for microactivity evaluation (M.A.T.) existing in the Fábrica Carioca de Catalisadores S.A., which can be used to establish variations of space velocity, reaction time, temperature etc. (Ribeiro, 2004).

In this work, the loads of different concentrations of vaseline and PP/vaseline (2.0 and 4.0 % wt) were submitted to catalytic cracking test, in the real conditions used in the refinery (temperature, pressure and load/catalyst ratio, injection time of load). The samples of commercial FCC catalyst (L.A., M.A. and H.A.) were activated "*in situ*" for 20 min at 520 °C under a flow of nitrogen and at atmospheric pressure to eliminate any residual humidity. These loads were processed in the test unit (M.A.T.) *versus* kaolin and the commercial FCC catalysts. All cracking loads were performed in duplicate, in the microactivity test unit (M.A.T.), *versus* all of the FCC catalysts.

Conditions of Experimental Cracking

All samples were processed under the same experimental conditions (conditions for the refinery), considering the same standards adopted by the test microactivity unit existing at the Factory Carioca of Catalyst S.A. The experimental conditions used for the catalytic cracking were: furnace temperature of 520 °C, atmospheric pressure, injection time of 30 s, commercial FCC catalyst mass of 5.0 g, ratio between PP and vaseline of 2.0 and 4.0% wt, flow rate of feed (load) of 2.0 g/min, carrier gas flow rate (nitrogen) of 50 mL min^{-1} and purge time of 900 seconds. The total reaction time of cracking was 15 minutes and 30 seconds (injection time + bleed). The products of the catalytic cracking process were classified as liquids, solids and gaseous. Scheme 1 shows the diagram with the M.A.T. and the analyses of the products of the catalytic cracking of the propane.

The liquid fraction was collected in the test unit (M.A.T.) and weighed on an analytical balance. The gas chromatographic analysis provided only the composition of condensed fuel fractions.

The liquid fraction was analyzed on a Varian, Model 3300 Gas Chromatograph with flame ionization detector (FID), connected to a microcomputer. The solid product was analyzed by determination of the amount of coke. The gaseous product was calculated by the difference of liquid and solid products, its composition not being analyzed.

For the gas chromatography a Chrompack CP-SIL-5 CB silica column (length of 25 m and 0.25 mm internal diameter) was used. The initial temperature of the column was 60 °C, kept for 2 minutes, then heated at 10 ºC/min until 250 ºC, and at 12 ºC/min until 280 ºC and kept for 20 minutes. The samples of liquid products (0.5 μL) were injected in triplicate in order to test reproducibility and the separation of the products analyzed in accordance with standards used by the petrochemical industry.
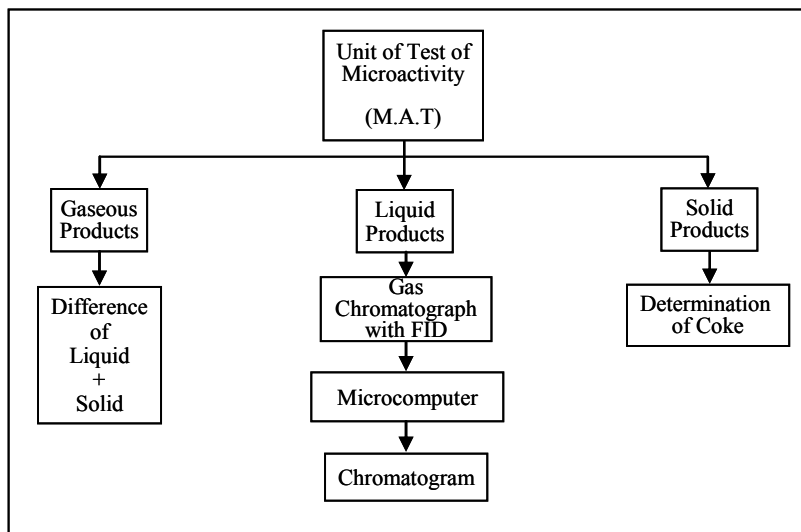
Scheme 1: Diagram of the M.A.T. and analyses of the products of the catalytic cracking of propane.

Analyses of the Products

The chromatograms were used to determine the retention times of the gasoline, diesel and residue limits, in accordance with the chromatograms of the components adopted as internal FCC standards, such as hexane (C_6H_{14}), used as minimum range limit (the lower molecular weight component) of the gasoline, dodecane ($C_{12}H_{26}$) as the maximum range limit (higher molecular weight component) of gasoline and range limit between gasoline and diesel, and icosane ($C_{20}H_{42}$) as the range limit between diesel and residue. These pure and mixed components were injected (0.5 μL) with the objective of getting the overlapping of the times of retention of the internal standards, establishing accurately the time of the start of retention and the end of each combustible band produced by the cracking. The chromatograms of the FCC standard with 50% gasoline (C_5-C_{12}); 30% Light Recycle Oils - LCO (C_{13}-C_{20}) containing the diesel fractions inside of this limit and 20% residue (above of C_{20}) are shown in Figure 1. The dotted lines in the chromatograms were used as baseline for calculating the areas of the curves. The chromatograms were edited in Photoshop CS6 program, with the acquisition of two areas: total area and dotted area. These areas were vectorized in Corel Draw, and values calculated in the CAD program. The area of each chromatogram was calculated by the difference between the total area and the dotted area.

The percentage in weight of gasoline, diesel and residue were calculated using the areas between 0 – 11.6 min., 11.6 - 23 min. and above 23 minutes, in each chromatogram. The percentage of liquid fraction was calculated by Equation (1).

$$\% \text{ liquid fraction} = \frac{m(g) \text{ liquid fraction}}{m(g) \text{ load}} * 100 \qquad (1)$$

where m (g) of the liquid fraction was obtained in the test unit (M.A.T.), m (g) of load = 1.0 g (for a load injection time of 30 s).
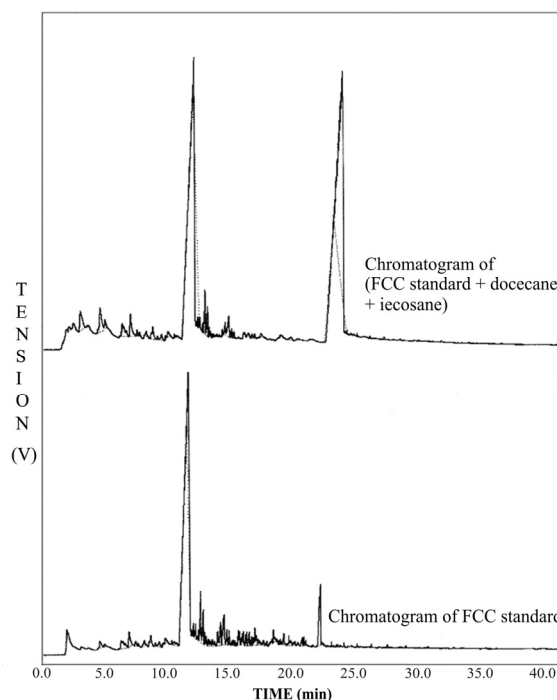
Figure 1: Chromatograms of FCC standard and mixture of FCC standard + dodecane + icosane.

The percentage of gasoline by load was calculated in accordance with Equation (2).

$$\% \, \text{Gasoline Load} = \frac{\begin{array}{c} \% \, \text{gasoline in the} \\ \text{chromatogram} * m(g) \\ \text{liquid fraction} \end{array}}{m(g) \, \text{load}} \quad (2)$$

where percentage of gasoline in the chromatogram was calculated from the area between 0 – 11.6 min., m (g) liquid fraction is obtained in the test unit (M.A.T.) and m (g) of load = 1.0 g (for a load injection time of 30 s).

The percentages of diesel fuel and residue per load were also calculated according to Equation (2), but using the areas between 11.6 – 23 min. and above 23 minutes.

The solid products were analyzed by the equipment LECO, model CS-125, for the determination of the amount of carbon (coke formation), on the surface of the catalyst, and in the interior of its pores, after the reaction. The percentage in weight of coke formed in the FCC catalyst, due to cracking, was calculated by Equation (3).

$$\% \, \text{Coke by Load} = \frac{\begin{array}{c} \% \, \text{coke LECO} * m(g) \\ \text{catalyst} \end{array}}{m(g) \, \text{load}} \quad (3)$$

where m (g) of catalyst = 5.0 g and m (g) of load = 1.0 g (for a load injection time of 30 s), % Coke by Load = % solid product.

The amount of gaseous products was determined by the difference between the liquid and solid products, without specification of its compositions.

RESULTS AND DISCUSSION

Characterization of the Catalysts and Kaolin

The average size of kaolin (inert material) and the commercial FCC catalysts, of low, medium and high activities by analysis of Distribution of Particle Size has proved that they had particle sizes similar to or within the same size range, all around 77 μm. The Table 1 shows the particle size distribution of the Commercial FCC catalysts.

The global chemical composition of the inert material and catalysts, using the FRX technique, provides the quantities of constituent oxides (Na, Si

and Al), in accordance with the program for the equipment used for the samples of kaolin (inert material) and FCC catalysts of low, medium and high activity (L.A., M.A. and H.A.) (Table 2).

Table 1: Particle Size Distribution of the Commercial FCC catalysts.

Samples	Particle Size Distribution					
	<149	**<105**	**<80**	**<40**	**<20**	**TMP**
Catalyst L.A.	95	80	56	16	1	74
Catalyst M.A.	90	73	51	14	1	78
Catalyst H.A.	90	72	49	12	1	80

L.A. – low activity, M.A. – medium activity, H.A. – high activity

Table 2: FRX analyses of the Commercial FCC catalysts and Kaolin.

Samples	SiO_2 (%)	Al_2O_3 (%)	SAR (%)	Na_2O (%)	Re_2O_3 (%)
Kaolin	53.0	42.7	2.11	0.15	-----
Catalyst L.A.	53.7	42.6	2.14	0.19	1.0
Catalyst M.A.	54.1	41.4	2.22	0.26	2.54
Catalyst H.A.	53.8	41.8	2.19	0.32	2.13

L.A. – low activity, M.A. – medium activity, H.A. – high activity

An important property of the zeolites is the possibility of the presence of Lewis and Brönsted acid sites. The Brönsted sites are found in the form of protons linked to oxygen atoms in the structure, and Lewis sites can be found in the form of charge compensation. The content of the active component (zeolite) in the formulation of the FCC catalyst adjusts the activity to the desired level, as well as selectivity. Changes in the composition of zeolite, like the ratio SiO_2/Al_2O_3 (SAR), allow obtaining more convenient features, depending on each situation and application. Furthermore, one can also employ the inclusion of other compounds, such as rare earths (RE), which give greater stability to deactivation (Maia, 2002; Macedo, 2007; Moreno & Rajagopal, 2009).

In this work, Table 2 shows that SiO_2/Al_2O_3 (SAR) values were slightly higher for medium and high catalysts, showing the acid strength of these catalysts. It can also be observed in Table 2 that the values of sodium and rhenium oxides increased for the catalysts of higher activity. The presence of the rhenium atoms can increase the stability of the FCC catalysts and accessibility of the load to be cracked to the acid sites existing.

The isotherms (Table 3) were used to calculate the areas and the microporous volume of the commercial FCC catalysts (L.A., M.A. and H.A.). The values of specific area and microporous volume of the catalysts showed that the catalyst of high activity had higher specific area and higher microporous volume values, as compared to the catalysts with medium and low activities. These results may indicate that the active sites (acid sites) may be more accessible to the loads, allowing the loads to remain longer times within this catalyst.

Table 3: Specific and external areas and microporous volume values for the Commercial FCC catalysts.

Samples	Specific Area (m²/g)	External Area (m²/g)	Microporous Volume (cm³/g)
Catalyst L.A.	266	57.52	0.088
Catalyst M.A.	276	58.70	0.092
Catalyst H.A.	422	47.39	0.118

L.A. – low activity, M.A. – medium activity, H.A. – high activity

Loads of PP/Vaseline

The polypropylene (PP) was dissolved in vaseline (petroleum jelly) to obtain loads of different concentrations (2.0 and 4.0% wt). The temperature of the complete solubilization of PP was below the flash point of the mineral oil, the base of the compound of the mixture of paraffin (188 °C). The resulting loads remained fluid at room temperature, and not just under heating, for periods greater than or equal to three days, depending of the load concentration.

Catalytic Cracking Process

The results obtained in the process with loads of PP/vaseline and the FCC commercial catalysts (of low, medium and high activity) allowed the determination of the efficiency of this process for the production of combustible fractions (Gasoline, Diesel and Residue).

Analyses of the Products

Table 4 shows the retention times of the chromatograms obtained from FCC standard with 50% Gasoline (C_5-C_{12}); 30% Light Recycle Oils - LCO (C_{13}-C_{20}), containing the Diesel fractions and 20% Residue (above C_{20}), used to calculate the percentages of gasoline, diesel and residue formed in the liquid products of the catalytic cracking of polypropylene.

Table 4: Limits of the liquid fractions in accordance with the retention time.

| Limit of the fractions	Retention Time (min.)
Gasoline (C_5-C_{12})	0 – 11.607
Diesel (C_{13}-C_{20})	11.607 – 23.030
Residue (> of C_{20})	> 23.030

The chromatograms of the liquid products of the cracking of vaseline and loads of PP/vaseline (2.0 and 4.0% wt), in the presence of the kaolin, L.A., M.A. and H.A. catalysts are shown in Figures 2 – 5, respectively.
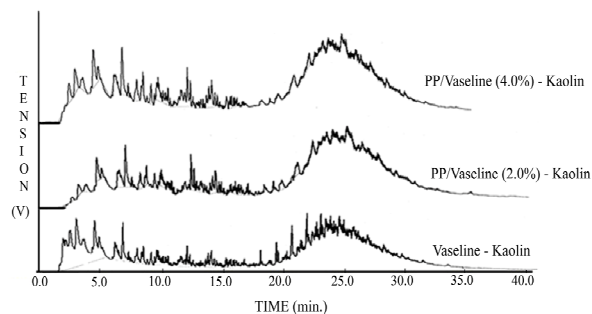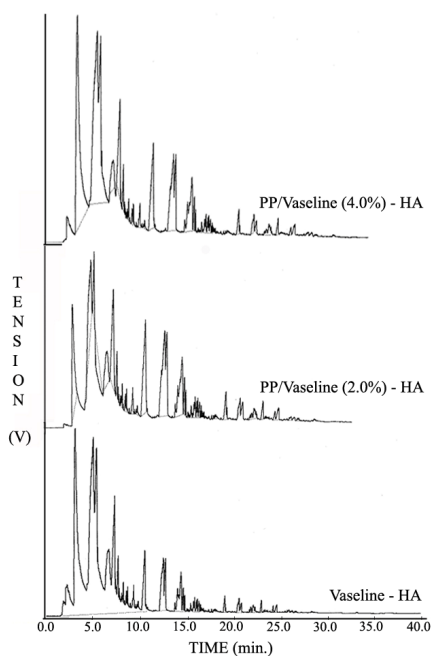

Figure 2: Chromatograms of liquid products of cracking of Vaseline and loads of PP/Vaseline (2.0 and 4.0% wt) in the presence of kaolin.
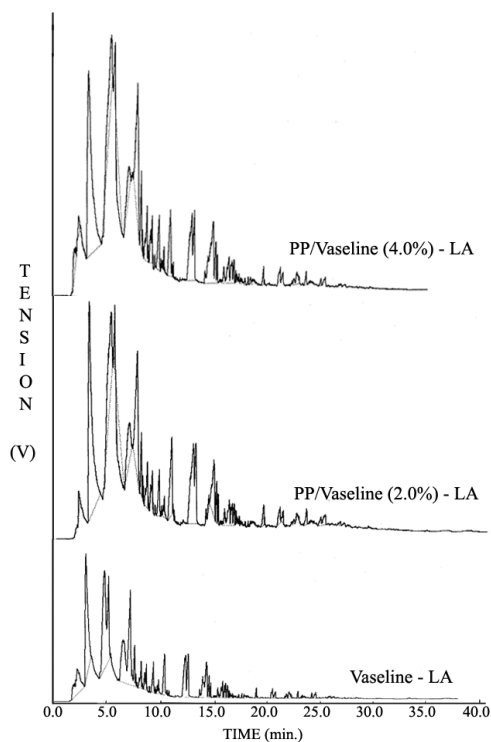
Figure 3: Chromatograms of liquid products of cracking of Vaseline and loads of PP/Vaseline (2.0 and 4.0% wt) in the presence of Commercial FCC catalyst – L.A. (low activity).
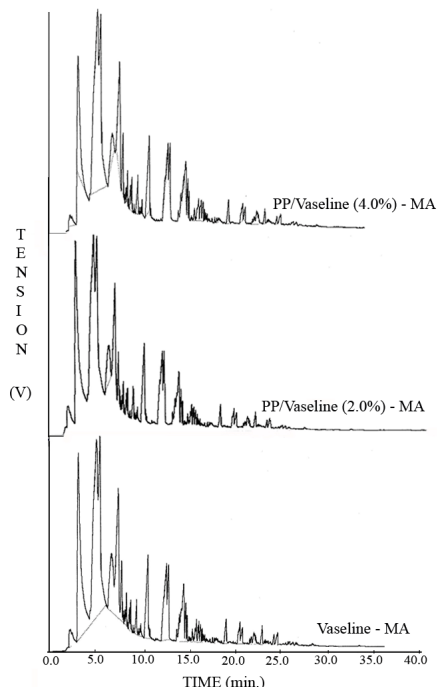
Figure 4: Chromatograms of liquid products of cracking of Vaseline and loads of PP/Vaseline (2.0 and 4.0% wt) in the presence of Commercial FCC catalyst – M.A. (medium activity).


Figure 5: Chromatograms of liquid products of cracking of Vaseline and loads of PP/Vaseline (2.0 and 4.0% wt) in the presence of Commercial FCC catalyst – H.A. (high activity)

These chromatograms were used to determine the retention time limits of gasoline, diesel and residue,

in accordance with the FCC standard chromatograms and the mixture FCC standard and pure hydrocarbons, and also used to calculate the percentage of gasoline, diesel and the liquid residue formed during the catalytic cracking of polypropylene

The chromatograms obtained in the presence of kaolin and the Commercial FCC catalysts showed the same behavior for all the loads. However, the chromatograms obtained in the presence of kaolin are very different from the chromatograms in the presence of catalysts. The amount of liquid fractions obtained by the cracking of polypropylene in the presence of Commercial FCC catalysts (L.A., M.A. and H.A.) varied with the use of kaolin. Figure 6 shows the behavior of the cracking of loads of vaseline and PP/vaseline (2.0 and 4.0% wt), in relationship to the gasoline, diesel and residue products.
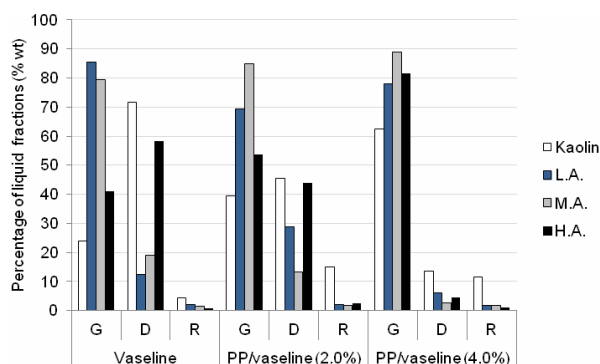
Figure 6: Liquid fractions of cracking of vaseline and PP/vaseline loads (2.0 and 4.0% wt) for production of gasoline (G), diesel (D) and residue (R).

Marcilla *et al.* (2006) reported in their work that zeolites show excellent properties as catalysts for the pyrolysis of plastic waste. They cause an important reduction in the decomposition temperature and allow more valuable gaseous products to be obtained. However, the pore size of the zeolites is limited to a maximum value of about 1.0 nm, which hinders the access of bulky molecules to the acid sites located inside the channels. On the other hand, Aguado *et al.* (2001) concluded in their work that the main components of the gasoline fraction (C_5-C_{12}) are formed predominantly via end-chain scission reactions. This fact is probably related to the strong acidity of the commercial FCC catalyst, although it might also be due to a preferential contact of the zeolite external surface with the end of the polymer chains.

In this work, the cracking of vaseline (solvent) showed a high percentage of the gasoline fraction

produced by all the catalysts, mainly for catalysts of low and medium activity, due to the smaller size of the molecules that are susceptible to cracking. The cracking of the PP/vaseline load showed high variation in the production of gasoline and diesel fractions, depending on the catalyst and the load composition. However, the high activity catalyst (H.A.) showed better efficiency in the production of gasoline compounds (C_5-C_{12}) for the load PP/vaseline (4.0% wt) relative to the load PP/vaseline (2.0% wt).

The introduction of polypropylene in the load, in general, leads to an increase in the production of the gasoline fraction. This fact can be attributed to the concentration of the hydrocarbon molecules with higher accessibility to the acid sites to be cracked in the gasoline range (C_5-C_{12}). Higher concentrations of polypropylene in the load of PP/vaseline can increase the access to the acid sites within the pores of the catalyst and, at the same time, increase the concentration of polymer chains which can undergo scission at the end of the chain when they come into contact with the external surface of the catalyst, as in the studies of Marcilla *et al.* (2006) and Aguado *et al.* (2001). Therefore, higher concentrations of PP in the load, in the presence of the high activity catalyst (H.A.), presented the expected behavior for the production of gasoline due to the greater mass of the macromolecule available for this range of cracking.

Table 5 shows the values of percentage/Load for the fractions: gasoline, diesel and residue.

Table 5: Percentages of gasoline, diesel and residue, in presence of Commercial FCC catalysts.

Loads	Catalyst	Fraction/Load (%)		
		Gasoline (G)	Diesel (D)	Residue (R)
Vaseline (paraffin mixtures)	Kaolin	13.71	41.20	2.59
	L.A.	26.54	3.84	0.62
	M.A.	24.21	5.84	0.46
	H.A.	11.51	16.29	0.2
PP/vaseline (2% wt)	Kaolin	19.12	22.11	7.28
	L.A.	19.75	8.18	0.57
	M.A.	22.49	3.53	0.48
	H.A.	13.16	10.76	0.59
PP/vaseline (4% wt)	Kaolin	32.77	13.59	6.14
	L.A.	23.77	6.15	0.58
	M.A.	24.42	2.61	0.47
	H.A.	20.8	4.39	0.31

PP – Polypropylene;
L.A. – low activity, M.A. – medium activity, H.A. – high activity

It can be observed that the L.A. and M.A. catalysts presented better results in the production of the gasoline fraction for all the loads and the load of PP/vaseline (4.0% wt) showed the highest production values of gasoline fraction for all catalysts, but for

acceptable percentage of gasoline and diesel, the load concentration of 2.0% is more appropriate, in the presence of low catalytic activity. The cracking of the PP/ vaseline (4.0% wt) load, in the presence of catalysts of different activities (L.A., M.A. and H.A.), produced an average of 29.0% of liquid fraction, and approximately 23.0% of this charge is transformed into gasoline. However, the load of PP/vaseline (2.0% wt), in the presence of the different catalysts, produced an average of 26.5% of liquid fraction, with the formation of 18.5% of gasoline, on average, showing that the presence of higher concentration of polymer in the load increases the proportion of production of gasoline fraction.

Determination of Coke in the Solid Product

The coke formation in the solid product is greatest for kaolin, as expected. The percentage of coke varied according to the catalyst activity and concentration of load, but in general is lower than that obtained with the use of kaolin, which shows that thermal cracking occurred preferentially with the load of PP/vaseline. The coke is deposited on the surface of the catalyst or inside its pores. Table 6 shows the percentage in weight of coke calculated on the surface of the FCC catalyst by the cracking process, in accordance with Equation (3)

Table 6: Quantity of coke formed and deposited on the surface of the kaolin or of the commercial FCC catalysts.

Loads	Catalysts	Coke (%)	Coke/load (%)
Vaseline (paraffin mixture)	Kaolin	0.77	3.85
	L.A.	0.82	4.10
	M.A.	1.37	6.85
	H.A.	1.39	6.95
2% wt PP	Kaolin	0.76	3.55
	L.A.	0.81	4.55
	M.A.	0.87	5.80
	H.A.	1.37	6.70
4% wt PP	Kaolin	0.52	2.60
	L.A.	0.89	4.45
	M.A.	1.04	5.20
	H.A.	1.47	7.35

PP – Polypropylene;
L.A. – low activity, M.A. – medium activity, H.A. – high activity

Determination of the Gaseous Products

The amounts of gaseous products were obtained by difference of (liquid + solid products). The results for gaseous product are shown in Table 7.

Table 7 shows that all the loads produced a bigger quantity of the gaseous products, mainly in the presence of the H.A. catalyst. The improvement in

the activity of the commercial FCC catalyst decreased the production of the liquid fractions and increased the quantity of the solid fractions, independent of the concentration of the loads. However, the 4.0% wt PP/vaseline load produced around 30% and 61% by wt of liquid and gaseous combustibles, respectively.

Table 7: Liquid, solid and gaseous products for the vaseline and PP/vaseline loads.

Loads	Catalysts	Products (%)		
		Liquid	Solid	Gaseous
Vaseline (Paraffin mixture)	Kaolin	57.50	3.85	34.65
	L.A.	31.00	4.10	60.90
	M.A.	30.50	6.85	61.35
	H.A.	28.00	6.95	62.05
2% PP	Kaolin	48.50	3.55	43.95
	L.A.	28.50	4.55	62.95
	M.A.	26.50	5.80	64.70
	H.A.	24.50	6.70	65.80
4% PP	Kaolin	52.50	2.60	40.90
	L.A.	30.50	4.45	61.05
	M.A.	27.50	5.20	63.90
	H.A.	25.50	7.35	64.60

PP – Polypropylene;
L.A. – low activity; M.A. – medium activity; H.A. – high activity

Marcilla *et al.* (2006) and Xie *et al.* (2008) mentioned that the catalytic cracking of polymers (specifically polypropylene) usually uses solid-acid catalysts. However, this process in the presence of zeolites is limited by strong steric hindrance, due to both the bulky nature of the polypropylene and the small size of the zeolite micropores, producing, at the end, higher yields of gases and liquids and higher concentrations of branched hydrocarbons. In this study, the higher percentage of the gaseous products can be related to the greater difficulty of the polymer chains to access the pores of the catalyst, occurring contact of the polymer chains with the external surface of the catalyst and end-polymer chains, thus increasing the amount of gaseous products and solid and decreasing the amount of the liquid.

Table 8 shows the results of the catalyst micro-activity evaluation test (M.A.T.) realized by the Fábrica Carioca de Catalisadores S.A. with the commercial FCC catalysts and refinery load.

The pyrolytic products can be divided into a gas fraction, a liquid fraction consisting of paraffins, olefins, naphthenes and aromatics, and solid residues. Comparing the results of Tables 7 and 8 indicates that the liquid and gaseous fractions obtained from catalytic cracking of the PP/vaseline loads (2 and 4% wt) may be composed of (naphtha+LCO+OCLA) and (H_2+CG+LPG), respectively. This comparison proves that the 2% and 4% wt PP/vaseline loads are very appropriate for producing liquid and gaseous fuels.

Table 8: Microactivity evaluation of the Commercial FCC catalysts and refinery load.

Samples	H_2	CG	LPG	Naphtha	LCO	OCLA	Coke
Catalyst L.A.	0.132	2.7	16.8	50.1	16.2	10.4	3.8
Catalyst M.A.	0.162	3.4	17.4	49.9	15.8	8.7	4.9
Catalyst H.A.	0.178	3.1	16.6	49.4	16.1	9.6	5.2

CG – fuel gas;
LPG – liquefied petroleum gas; LCO – light cycle oil; OCLA – residual oil

CONCLUSION

The catalytic cracking of loads of PP with petroleum jelly (vaseline), using commercial FCC catalysts of different activities (low, medium and high), provided good results for the production of combustible fractions, depending directly on the FCC catalysts and the PP/vaseline composition.

The production of expressive liquid (gasoline and diesel) and gaseous fractions from the catalytic cracking of polymers like polypropylene (PP) in the presence of Commercial FCC catalysts under refinery conditions makes this process a viable alternative for the development of new technologies for energy production.

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