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PYROLYSIS OF PETROLEUM FRACTIONS
Kinetic investigation by thermogravimetry

Maria Luisa A. Gonçalves[1*], *Deusa Angélica Pinto da Mota*[2], *Ana Maria R. F. Teixeira*[2] *and M. A. G. Teixeira*[3]

[1]Federal Fluminense University (UFF) –IQ/CNPq, Niterói, RJ, Brasil
[2]Federal Fluminense University (UFF) – IQ/Chemistry Pos-Graduation Program, Niterói, RJ, Brasil
[3]Petrobras Research Center (CENPES/Petrobras), Rio de Janeiro, RJ, Brasil

Dynamic kinetic analyses were performed on different Brazilian petroleum fractions by thermogravimetry. The data were treated by a multiple heating rate methodology. The apparent activation energies for the light and middle fractions within the range of 62–74 kJ mol^{-1} and for heavy distillation residues were within the range of 80–100 kJ mol^{-1} at lower conversions and 100–240 kJ mol^{-1} at higher conversions. The kinetic study can be a criterion for tells apart the main phenomena involved in the thermal behavior of the refinery feedstock.

Keywords: *kinetic analysis, petroleum fraction, thermogravimetry*

Introduction

Fluid catalytic cracking (FCC) is considered to be one of the most important refining processes, involving the conversion of heavy feedstock into gasoline and other products. Heavy feedstocks are the residues from the atmospheric (AR) and vacuum distillation (VR) of petroleum.

Processing high-density petroleum feeds that are nowadays very important in the scenario of fossil fuel supplies bring naturally the challenge of dealing with heavy ends in great abundance, i.e., AR and VR. On the other hand, the optimization of refining facilities to deal with such feeds brings economical competitiveness, since these oils have low prices in the international market. Studies on pyrolysis mechanisms are quite important in this aspect.

Heavy gas oils (HGO) – C_{13} to C_{60} with a boiling point between approximately 230–590°C – which come from the vacuum distillation of AR, are the traditional FCC feedstock. The challenge of introducing distillation residual in the feedstock demands better knowledge on the thermal generation of coke, a carbon-rich solid phase, which deactivates the catalysts of the FCC process. The FCC units may have their operation optimized with deeper knowledge on the feedstock pyrolysis mechanisms.

Thermal analysis has been used in the last thirty years to characterize the thermal behavior of petroleum and derivatives. For crude oils, the techniques were normally applied to study oil pyrolysis and combustion [1, 2]. Thermogravimetry (TG) has been used to study the effect of the oil composition on the pyrolysis and combustion kinetic of the crude [3–7]. This has recently been applied to study the influence of the asphaltenes on coke formation in the pyrolysis of atmospheric residues [8]. The classical Arrhenius model was used in thermogravimetric studies to get information on pyrolysis and combustion behavior of both crude oil and its alphaltenes [9].

TG cannot be used to elucidate the mechanism of pyrolysis of heavy oil residue, but it can be useful to give reliable information about activation energy of overall reaction. There are different methods to determine kinetic parameters by TG [10–12] and commercial software can be used for that purpose [13].

The determination of pyrolysis kinetic constants is based on the supposition that the mass losses observed in TG curve are not due to volatile species present in the residue sample. This is a major difficulty in the petroleum processing area. Petroleum is a mixture of a great number of compounds and, in the heavier fractions, the ones which cannot be directly separated into valuable products by distillation, are gathered together. Valuable information could be gathered with the possibility to demonstrate the distillation and pyrolysis phenomena apart, in such a way to determine, for refinery feedstock, the part of each one of them that is pyrolyzed and, therefore, undergoes coke formation.

In this work we decided to investigate the sensitivity of kinetic parameters calculated from thermo-

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* Author for correspondence: maleixo@infolink.com.br

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Table 1 Basic characteristic of 19°API Brazilian crude oil fractions

Test	Samples			
	LCO	HGO	AR	VR
Density (ASTM 4052) mL mg^{-1}	1.0652	0.936	0.9848	1.006
RCR (*p*/*p*/%)[(a)]	6.7	0.4	9.9	17.9
Asphaltenes (*p*/*p*/%)[(b)]	0	0.1	2.7	7.5

[(a)]Carbon residue determined by ASTM524 [16], [(b)]poly-aromatic compounds quantify by IP143 Methodology [17]

gravimetric measurements to distinguish these two phenomena. The data were treated by a multiple heating rate method developed by Ozawa–Flynn and Wall [14, 15]. Software customized for our purposes was used but the principles of the calculations are the ones established by the above authors. The aim of the study was to compare the activation energy of mass losses of Brazilian petroleum fractions to get information on the different events that happen during the heating of the same ones.

Experimental

Samples

Some different fractions from 19°API Brazilian oil were used in this study. The crude oil viscosity is 537.52cP at 20°C and the typical calorific value is about 45000 kJ kg^{-1}.

Heavy residues from atmospheric (AR) and vacuum (VR) of this oil distillation were selected. The heavy gas oil (HGO) from the same crude was selected as a reference sample, because it yields negligible amounts of coke. Light cycle oil (LCO), a product of the FCC process contained C_9 to C_{25} hydrocarbon mixture boiling from approximately 170 to 370°C, was also studied, because it is supposed to have chemical characteristics that guarantee that it will suffer no further conversion after it is produced. The basic characteristics of the materials provided by the manufacturer are summarized in Table 1. The distillation curve obtained by traditional methodology is presented in Table 2.

Thermogravimetry

TG experiments were performed on the Netzsch STA-Luxx 409 apparatus with platinum crucible (300 μL) from 35 up to 600°C. The experimental conditions employed at heating rates of 2.5, 5.0, 10.0 and 20.0 K min^{-1}, initial sample mass was 20 mg and dynamic atmosphere of N_2 at 50 mL min^{-1} in the temperature range of 35–600°C. Experiments were repeated twice becausee of the reproducibility. Temperature calibration was performed with $RbNO_3$, $KClO_4$ and CsCl.

Table 2 Distillation curve of 19°API Brazilian crude oil fractions obtained by distillation standard methodology

	LCO	HGO	AR	VR
Standard methodology	(a)	(b)	(b)	(b)
Distillation curve	*T*/°C			
Initial boiling point	200	239	242	386
2% (v/v)	242			
5% (v/v)	279	322	340	418
10% (v/v)	314	351	377	502
20% (v/v)	342			560
30% (v/v)	361	409	450	
40% (v/v)	379		513	
50% (v/v)	397	442	585	
90% (v/v)	495	524	660	
92% (v/v)	505			
95% (v/v)	526	543	684	
Final boiling point	595	591	715	569

[(a)]Simulated distillation ASTM D-2887 [18], [(b)]Simulated distillation at high temperatures HT750 [19]

Determination of apparent activation energies (E_a)

The kinetic of decomposition parameter was determined by Ozawa–Flynn–Wall method [12, 13], which requires three or more TG determinations at different linear heating rates, usually between 0.5 and 50°C min^{-1}. It is a non-isothermal methodology and is based on kinetic Eq. (1):

$$d\alpha/dt = A\exp(-E_a/RT)(1-\alpha)^n \qquad (1)$$

where α is the degree of conversion, *t* the time (seconds), *T* the temperature, *A* the pre-exponential factor (s^{-1}), E_a the activation energy (J mol^{-1}), *R* the gas constant (8.314 J mol^{-1} K^{-1}) and *n* is the reaction order (dimensionless). Ozawa–Flynn–Wall rearranged this equation considering β=d*T*/d*t* getting the Eq. (2):

$$E_a = \left(\frac{-R}{b}\right)\frac{d\ln\beta}{d\left(1/T\right)} \qquad (2)$$

where *b* is a constant assuming *n*=1, β is the heating rate (K min^{-1}) and *T* is the maximum temperature of mass loss (°C).

Using a point of equivalent mass loss, which is supposed to be beyond any initial mass loss due to volatiles evolution, a plot of lnβ *vs.* 1/*T* is constructed, according to the original methodology. The slope of this straight-line plot is then used to calculate activation energy (E_a). All TG curves are normalized and a part of the range of α= 0.10–0.98 is used for the calculations. In the present work, all mass losses were considered, including the ones that were well known to include volatilization.

Results and discussion

In a preliminary experiment, each sample was measured at a relatively high heating rate, e.g. 20 K min^{-1} in order to estimate quickly the initial and final temperatures as well as the heating rates for the following measurements to determine the kinetic parameters. TG and DTG curves on the samples pyrolysis are presented in Figs 1a and b. Besides the carbonaceous residue content – coke – formed during the pyrolysis, the TG curves give the initial and final temperatures (T_{onset} and T_{end}) of the lost mass and the content of volatile materials formed during the analysis. The DTG peak represents the maximum reaction rate temperature ($T_{\max}$).

Table 3 summarizes the results taken from the TG and DTG curves of the samples. It should be noted that the VR sample starts to lose mass in a temperature below the one which the volatilization of the HGO ends, indicating that some distillable fraction is lost in the refineries, due to the need for a careful distillation to avoid coke formation. The possible reason is the difficulty to determine exactly which fraction of the residue yields coke.

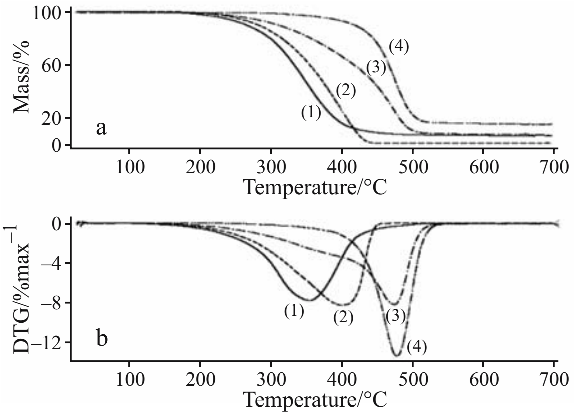

Fig. 1 a (——)– TG and b (- - -) – DTG curve of 1 – LCO, 2 – HGO, 3 – AR and 4 – VR: β=20 K min^{-1}; *m*=20 mg; N_2 flow rate=50 mL min^{-1}

TG curves of LCO, HGO and VR pyrolysis have similar shape with a one step of lost mass, but with different T_{onset} and T_{end}. The LCO and HGO mass loss took place at lower temperatures than the VR and AR samples. In the LCO and HGO samples the amount of the lost substances is rather due to the evaporation than to the thermal cracking of the sample, which is negligible in this case [7].

The results are consistent with each sample distillation curve (Table 2), where it can be seen that most of the LCO and of the HGO distilllate before 400°C. The DTG curves (Fig. 1b) show-increasing $T_{\max}$ from LCO to VR ($T_{\max1}<T_{\max2}<T_{\max3}<T_{\max4}$). However, the AR curve presents two well-defined steps, before and after approximately 420°C, which cannot be easily recognized in the TG curve (Fig. 1a). From the AR derivative curve it is also easy to see that the phenomena are superimposed, being the separation of volatilization and pyrolysis a very difficult task to be done by this technique. Lower heating rates could be supposed to provide a better separation of two phenomena. The samples were analyzed at 2.5 K min^{-1} (Fig. 2). LCO and HGO presented only one phenomenon. It can be seen by the AR sample – where the two phenomena are more clearly identified than the other samples – that even a heating rate of as low as 2.5°C min^{-1}, which yields a very time-consuming analytical procedure, will not be successful.

The next step was to analyze each sample at two more heating rates lower than 20 K min^{-1} (10.0, 5.0 K min^{-1}). TG and DTG curves are presented in Figs 3 and 4 respectively. Runs at all heating rates were repeated twice and were used for the E_a calculation.

Plots of lnβ *vs.* 1000/*T* to conversion levels of 0.02 to 0.98 at different heating rates for each sample pyrolysis were done and are presented in Fig. 5. The angular coefficients of straight lines are proportional to the E_a at different conversions. Although we have not accessed any physical meaning for the values of the distillated fractions – therefore it is called in this

Table 3 Data taken from the TG and DTG curves of refinery residues and middle fractions

Sample	T_{onset}/°C	T_{end}/°C	Volatile material 35– 400°C %$^{-1}$	Volatile material 35– 600°C %$^{-1}$	Residue at 600°C %$^{-1}$	DTG curve $T_{\max}$/°C
LCO	307	415	75	96	4	365
HGO	351	464	48	100	0	439
AR	420 (2$^{\mathrm{nd}}$)	499	25	92	8	482
VR	452	513	3	84	16	488

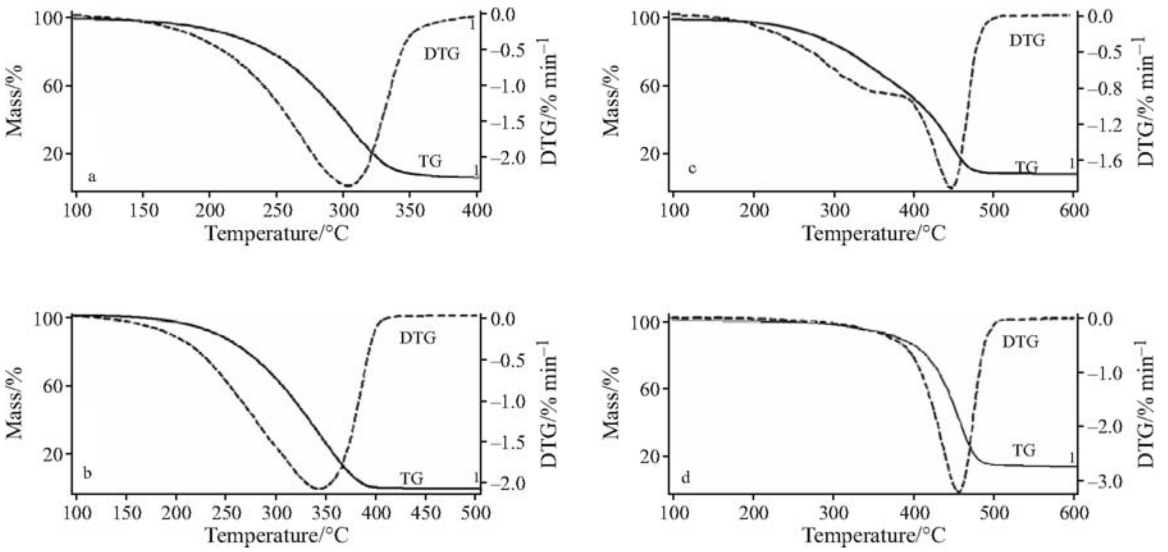

Fig. 2 TG and DTG curves of a – LCO, b – HGO, c – AR and d – VR at β=2.5 K min^{-1}; m=20 mg; N_2 flow rate=50 mL min^{-1}

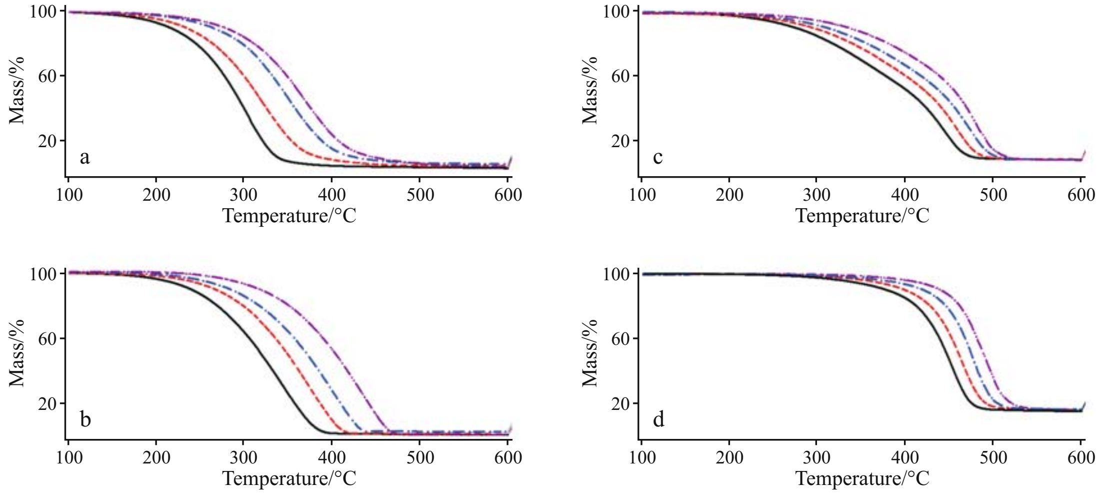

Fig. 3 TG curves of a – LCO, b – HGO, c – AR and d – VR at —– 2.5, - - - - – 5.0, -·-·- – 10.0 and -··- – 20.0 K min^{-1}, m=20 mg, N_2 flow rate=50 mL min^{-1}

paper apparent activation energy – it can be seen that there is a more considerable degree of parallelism for the lines obtained from the work with HGO and LCO (Figs 5a and b), than for the ones with the other samples. For AR and VR there is a noticeable change in the slope, as the conversion increases (Figs 5c and d). A good interpretation is that it means different phenomena are happening.

Table 4 presents the calculated apparent activation energies. The values are the mean of the two determination of E_a of each conversion values and were used to observe the tendency E_a *vs.* conversion level (Fig. 6).

Due to the fact that LCO and HGO are attributed to the distillation process, the apparent activation energies were within 62–74 kJ mol^{-1}. Nevertheless, for AR and VR the apparent activation energies were in the range of 80-100 kJ mol^{-1} at lower conversions and 100–240 kJ mol^{-1} at higher conversions.

The calculated values for the apparent activation energies were considered to be in a rather constant level for LCO and HGO. For VR there is a continuous variation, which is possible due to the differences in the tendencies of coke formation among the components of this heavy fraction. For AR, however, there is a clear inflection at about 50% mass loss. Therefore, the use of this E_a can be a consistent criterion for the determination of the fraction of the feedstock pyrolysis and, as a consequence, to undergo coke formation.

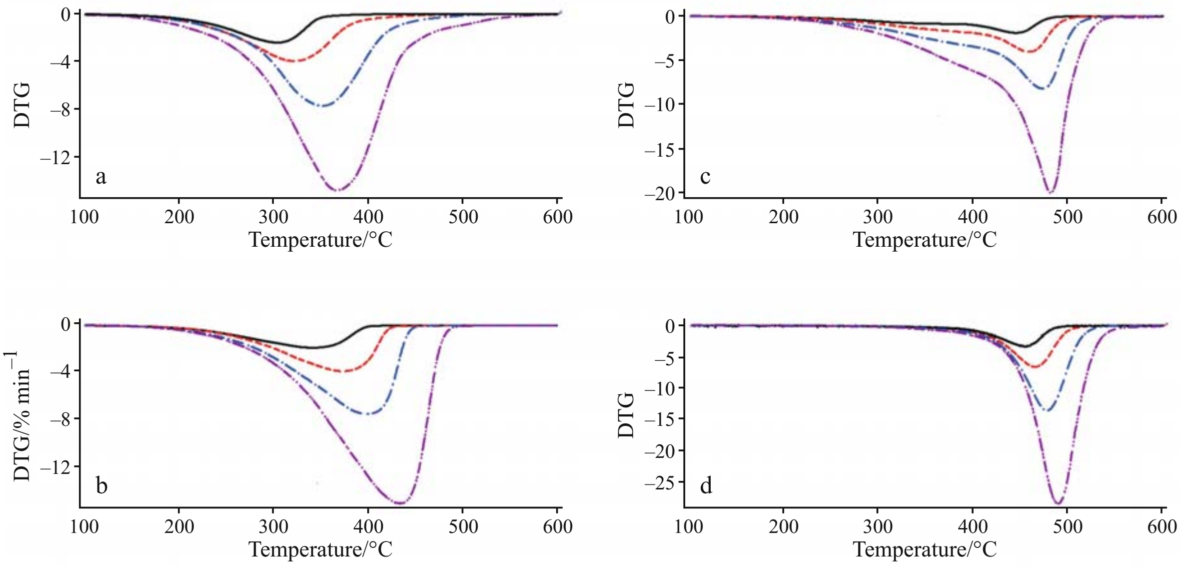

Fig. 4 DTG curves of a – LCO, b – HGO, c – AR and d – VR at —– 2.5, - - - - – 5.0, -·-·- – 10.0 and -··- – 20.0 K min^{-1}, m=20 mg, N_2 flow rate=50 mL min^{-1}

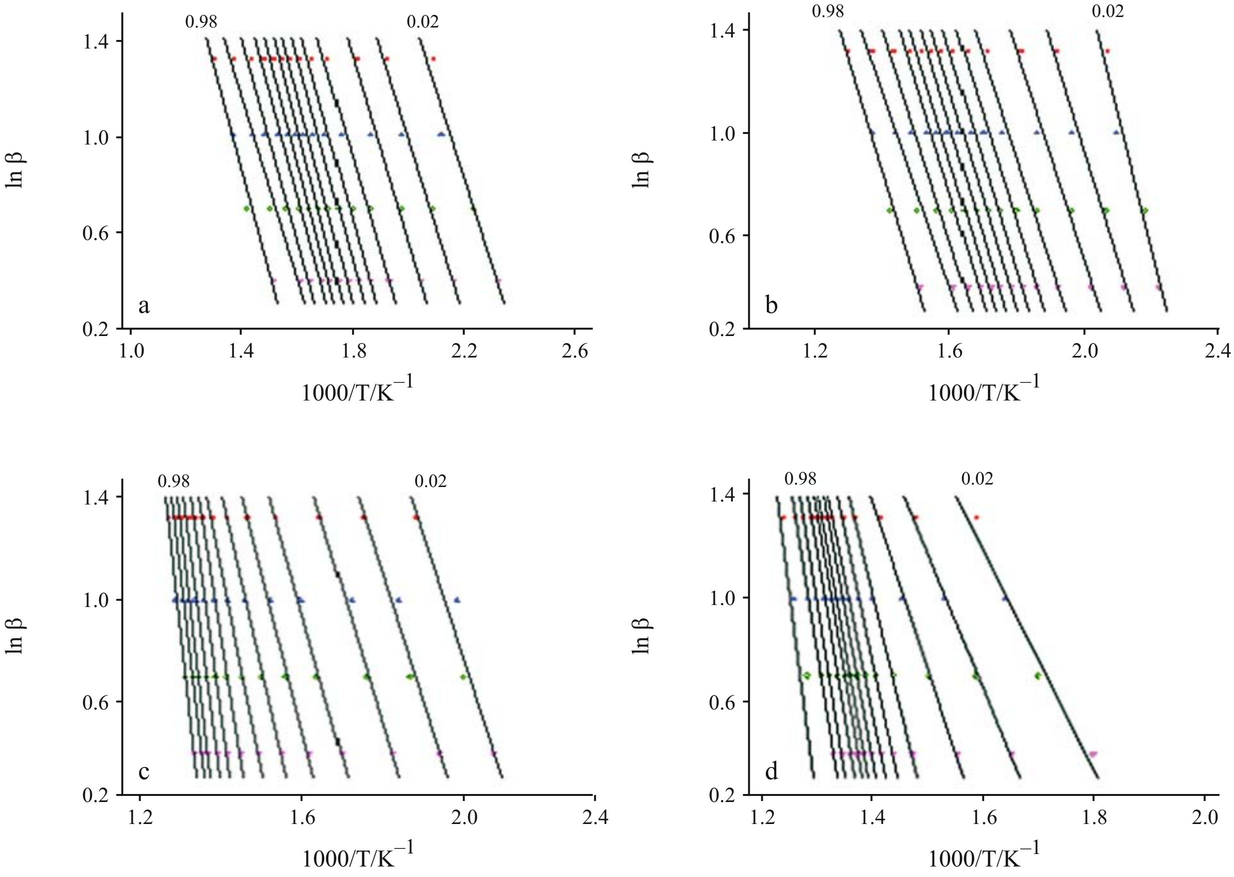

Fig. 5 lnβ plots *vs.* $1/T$ of a – LCO, b – HGO, c – AR and d – VR

Table 4 Apparent E_a of thermal decomposition of LCO, HGO, AR and VR samples at different conversion levels

Conversion	E_a^*/kJ mol^{-1}			
	LCO	HGO	AR	VR
0.02	62.2	56.6	75.2	63.3
0.05	62.8	63.6	82.8	84.9
0.1	64.7	66.1	90.2	110.6
0.2	67.6	68.8	99.9	155.8
0.3	70.8	71.7	107.8	180.2
0.4	73.3	75.4	119.9	186.3
0.5	74.8	77.1	142.8	212.2
0.6	75.7	80.7	172.7	222.6
0.7	74.8	83.9	198.3	231.2
0.8	74.6	87.5	222.0	240.4
0.9	70.9	93.6	244.2	243.3
0.95	68.6	98.6	248.0	240.5
0.98	44.6	106.9	258.4	260.8

*medium of two determinations

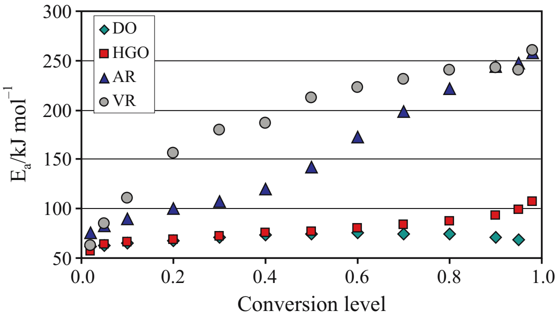

Fig. 6 E_a (KJ mol^{-1}) *vs.* conversion level

Conclusions

The apparent activation energies at different conversions of petroleum fractions used as feedstock in the Brazilian refinery units were determined by thermogravimetry. The E_a values were considered to be in a rather constant level for lighter fractions (LCO and HGO). For one heavy fraction, like vacuum residue, there is a continuous variation, which is possibly due to the differences in the tendencies of coke formation among the components of this heavy fraction. Already values of E_a for AR fraction, there is a clear inflection at about 50% mass loss (TG curve) indicating the occurrence of a different phenomena. Determination of the apparent activation energies can be a criterion to determine the main phenomena involved in the thermal behavior of the feedstocks that is distillation and pyrolysis.

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