

## Thermogravimetric analysis of an atmospheric residue and its SARA fractions

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### Abstract

Thermal analysis of SARA fractions from atmospheric residue of heavy crude oil (12°API) was carried out to understand the way in which each fraction decompose to form coke. It was observed that asphaltenes are very prone to form coke as determined by thermogravimetric analysis (TG/DTG). Amount of coke for each component was saturates (0.3 wt%), aromatics (4.2 wt%), resins (4.6 wt%), asphaltenes (41.3 wt%), atmospheric residue (37.3 wt%). Activation energy ( $E_A$ ) was also calculated for aromatics, resins, asphaltenes, and atmospheric residue by using an isoconversional method based on Friedman's procedure.

### Introduction

Thermal decomposition of petroleum asphaltenes has received attention primarily because of its tendency towards coke formation under thermal conditions which deactivates the catalysts. Since asphaltenes produce substantial amounts of catalyst-deactivating coke during hydrotreating, they make the refining processes less efficient and more expensive. For this reason a key parameter for understanding residue processing is to study the chemistry of coke formation at different temperatures. It has been reported that the yield of coke from asphaltenes and resins vary from almost 25 wt% to more than 60 wt%, but thermal studies have been focused mainly on asphaltene constituents, which produce thermal coke in the range of 35 to 65 wt% but not only coke is formed from asphaltenes but also produce high yields of volatile products that include condensable liquids to gases [1-3]. The aims of this study were (1) to compare the thermal behavior by TGA of an atmospheric residue from a heavy crude (12°API) with that obtained from its fractions (saturates, aromatics, resins, and asphaltenes) and (2) to obtain the coking kinetics of different fractions from an atmospheric residue.

### Experimental

SARA fractionation was carried in two chromatographic columns packed with clay and alumina. Previously, asphaltenes were separated from the atmospheric residue by adding pentane. During the test, 2 g of sample are mixed with 25 mL of pentane and the mixture is stirred for 24 h. Then, the mixture is filtered and asphaltenes are recovered. The filtrate (pentane+maltenes) is poured into the columns adapted in series and washed with 25 mL of heptane. Pentane is added with enough amount to complete 280±10 mL. After washing, columns are decoupled and washed again individually. The zone one packed with clay is washed with a toluene-acetone mixture (50%/50%) to recover the polar fraction (resins) whereas in column packed with alumina saturates are recovered with pentane and aromatics with toluene. Then, TG/DTG analyzes were carried out from room temperature to 800°C under nitrogen atmosphere at 50 mL/min by using ~10 mg of sample. Samples analyzed were saturates, aromatics, resins, asphaltenes, and atmospheric residue to evaluate its behavior to coke formation. In the case of saturates, only one heating rate (8°C/min) was used due to its propensity to ease thermal decomposition. Aromatics, resins, asphaltenes, and atmospheric residue were analyzed at three different temperatures, i.e., 8, 12, and 16°C/min to obtain kinetic parameters toward coke formation.

### Results and discussion

Figure 1 shows the tendency to coke formation of each fraction compared with the atmospheric residue. For comparison purposes, thermograms from all fractions and atmospheric residue were recorded

at heating rate of 8°C/min. Saturates are rapidly reacted with almost no coke formation followed by aromatics and resins. In spite of being one of the heaviest fractions, resins contribute with less than 5 wt% of coke whereas asphaltene thermolysis produces more than 40 wt% of coke. Atmospheric residue as such forms a similar amount of coke compared with asphaltenes which could indicate that is this fraction the main responsible for coke formation. It is also observed that asphaltenes do not undergo any significant change in their mass up to 300°C.

It is assumed that heterocyclic nitrogen plays an important role in thermolysis of resins and asphaltenes by which the first reactions involve breaking aromatic alkyl bonds. Secondary reactions are aromatization of naphthenic species and condensation of aromatic rings that triggers the coke formation. Thus, the initial step in the formation of coke from heavier fractions (resins and asphaltenes) is the formation of volatile hydrocarbons and nonvolatile heteroatom-containing systems. The coke yield for each component under experimental conditions is: saturates (0.3 wt%), aromatics (4.2 wt%), resins (4.6 wt%), asphaltenes (41.3 wt%), atmospheric residue (37.3 wt%).

In addition, an isoconversional method based on Friedman's procedure was used to calculate the reaction

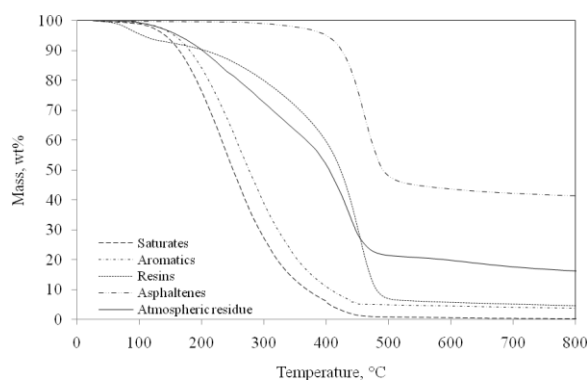


Fig. 1. Tendency of SARA fractions and AR toward coke formation

kinetic parameters from TGA for different components and a set of activation energies and pre-exponential factor was obtained as the reaction progresses. It was observed that asphaltene fraction is the most sensitive to the temperature due to its higher activation energies (40.9-52.7 kcal/mol), followed by resins, and finally by aromatics as shown in Table 1, where  $x$  is conversion,  $E_A$  is in kcal/mol, and  $k_o$  is in  $\text{min}^{-1}$ . The values of activation energies and pre-exponential factors reflect changes in the strength of bonds as volatilization of asphaltenes occurred.

Table 1. Activation energy and pre-exponential factors as function of conversion

$x$	Asphaltenes			Resins			Aromatics			Atmospheric residue		
	$E_A$	$k_o$	$r^2$	$E_A$	$k_o$	$r^2$	$E_A$	$k_o$	$r^2$	$E_A$	$k_o$	$r^2$
0.1	40.9	$5.6 \times 10^{13}$	0.995	10.8	$4.4 \times 10^4$	0.984	10.8	$6.7 \times 10^7$	0.982	10.7	$6.7 \times 10^4$	0.999
0.2	46.3	$2.6 \times 10^{15}$	0.995	14.8	$5.9 \times 10^5$	0.996	14.5	$7.8 \times 10^9$	0.994	15.3	$4.4 \times 10^6$	0.998
0.3	51.2	$6.1 \times 10^{16}$	0.996	21.1	$3.9 \times 10^7$	0.999	14.2	$1.7 \times 10^9$	0.982	12.4	$1.0 \times 10^5$	0.989
0.4	52.7	$1.3 \times 10^{17}$	0.998	35.8	$1.3 \times 10^{12}$	0.998	17.6	$4.6 \times 10^{10}$	0.985	15.9	$2.7 \times 10^6$	0.989
0.5	50.0	$1.5 \times 10^{16}$	0.995	45.9	$1.2 \times 10^{15}$	0.992	17.9	$1.3 \times 10^{10}$	0.981	17.7	$1.5 \times 10^7$	0.990
0.6	46.0	$4.6 \times 10^{14}$	0.996	47.5	$1.3 \times 10^{16}$	0.995	21.6	$1.1 \times 10^{11}$	0.984	24.8	$3.0 \times 10^8$	0.988
0.7	49.9	$4.9 \times 10^{15}$	0.997	38.9	$1.7 \times 10^{15}$	0.998	19.8	$8.9 \times 10^{10}$	0.989	24.0	$1.2 \times 10^8$	0.998
0.8	49.8	$1.2 \times 10^{15}$	0.992	37.5	$2.8 \times 10^{12}$	0.995	19.2	$1.2 \times 10^{10}$	0.989	22.3	$2.2 \times 10^7$	0.996

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