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# Thermogravimetric determination of coke from asphaltenes, resins and sediments and coking kinetics of heavy crude asphaltenes

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## ABSTRACT

Thermal analysis of asphaltenes and resins from heavy crude was carried out to understand the way in which they decompose to form coke. Sediments extracted from hydrotreated crude were also analyzed. It was found that asphaltenes produced 47 wt.% of coke, resins 9 wt.% of coke, and sediments decompose quickly toward coke giving the highest yield (66 wt.%). In the case of asphaltenes and resins a free radicals based mechanism is operating when labile points in alkyl chains are broken leading to condensation reactions. Thermal analysis of sediments obtained from hydrotreated crude revealed that they have high tendency to form coke. A non-isothermal technique using various heating rates was applied to study kinetics of asphaltene cracking toward coke formation. An iso-conversional method based on Friedman's procedure was used to calculate the reaction kinetic parameters from thermogravimetric analysis during asphaltene cracking and a set of activation energies and pre-exponential factor was obtained as the reaction progresses. Activation energy ranged from 29.2 to 52.4 kcal/mol.

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## 1. Introduction

Petroleum is a complex fluid containing many components ranging from low to high molecular weight. Most of them are kept soluble in the fluid under reservoir conditions but may precipitate as solid materials such as asphaltenes or sediments at some stage in storage, transportation, and refining of crude oil. During catalytic hydroprocessing, the formation and deposition of these solids on catalyst reduce its activity and eventually block the pores. In the case of heavy or extra heavy crude oils significant amount of these high molecular weight components is available that leads to high viscosity of petroleum. It is well recognized that these heavy components are the main cause for all the problems during petroleum handling. Thus, understanding the influence of heavy components on oil properties as well as on solid formation and deposition is of high concern.

Thermal decomposition of petroleum asphaltenes has gained attention primarily because of the asphaltene tendency to form coke, which is responsible for catalyst deactivation (Fig. 1). Usually, coke is formed from carbenes, which are insoluble in benzene or toluene but soluble in carbon disulfide; and carboids, which are

insoluble in any organic solvent. Carboids are condensed, cross-linked polymers in which the greatest part of the carbon atoms is aromatic. Experimental tests performed at 450 °C have indicated that dibenzyl produces 1% of carboids after 40 min while  $\alpha$ -methylnaphthalene requires 400 min. The conversion of condensed aromatics without side chains to advanced condensation products is even slower, e.g., naphthalene requires 670 000 min. These findings may be explained by the fact that hydrocarbons possessing alkyl chains or bridges form free radicals much more easily than those species lacking alkyl chains [1]. Pyrolysis of asphaltenes is considered as depolymerization in parallel with thermal decomposition of functional groups. When asphaltenes are heated prior to gasification, their volatile compounds are released leaving a residue [2]. Primary pyrolysis products include light hetero-atomic and hydrocarbon gases, alkanes, cycloalkanes and single-ring aromatics [3]. Apart from this, deactivation also depends on the nature as well as textural properties of the hydroprocessing catalysts [4,5].

In recent years, the application of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to study the pyrolysis behavior of fossil fuels has gained wide acceptance among researchers. For example, Abu-Khamsin et al. [6] investigated the spontaneous ignition potential of a light crude oil in an adiabatic packed bed reactor. Al-Saffar et al. [7] studied the behavior of a light crude oil and its SARA (Saturates, Aromatics,

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