



Pyrolysis kinetics of atmospheric residue and its SARA fractions

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ABSTRACT

Thermal analysis of atmospheric residue from heavy crude oil and its SARA fractions was carried out and the tendency of each fraction toward coke formation was determined. The coke yield was 16.3 wt.% for atmospheric residue, 43.1 wt.% for asphaltenes, 4.6 wt.% for resins, 3.8 wt.% for aromatics, and 0.3 wt.% for saturates. Pyrolysis kinetics of residue and its fractions, i.e., asphaltenes, resins and aromatics was also investigated. The TG experiments were conducted at three different heating rates of 8, 12, and 16 °C/min from room temperature up to 800 °C under nitrogen atmosphere to verify the weight variation with reaction temperature. Isoconversional analysis to fit data assuming first order kinetics was employed. Asphaltenes was the fraction that produces coke in higher amount having a range of activation energy of 41.0–58.6 kcal mol⁻¹ whereas activation energy for atmospheric residue ranged from 11.5 to 30.0 kcal mol⁻¹.

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1. Introduction

Thermal decomposition of petroleum asphaltenes has received attention primarily because of its tendency toward coke formation under thermal conditions which deactivates those catalysts used in hydroprocessing. 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 [1,2]. Various reaction pathways have been proposed for asphaltene thermal decomposition and it has been reported that the main products are alkanes ranging from C₁ to C₄₀ and polynuclear aromatics (from 1 to 4 aromatic rings) [3,4]. During pyrolysis of asphaltenes, C–S bonds are broken in the range of 350–400 °C whereas the cleavage of C–C bonds becomes dominant at temperatures higher than 400 °C [5]. The formation of methane and other normal alkanes during pyrolysis at mild conditions indicates that asphaltene contains thermally fragile alkyl groups on its outer surface [6]. Experimental tests by thermogravimetric analysis (TG) were carried out by Yoshida et al. [7] who studied thermal decomposition of coal-derived asphaltenes and concluded that weight loss is rapid from 300 to 500 °C where asphaltenes showed the greatest weight loss and then it reduced above 500 °C. When air is used in TG, three different reaction regions can be identified

and known as low-temperature oxidation, fuel deposition and high-temperature oxidation as reported by Kok [8]. Hauser et al. [9] studied the asphaltene pyrolysis at 412 °C and determined that the aromatic/aliphatic carbon ratio increased from ~1 to ~3 whereas the atomic H/C ratio decreased from ~1.1 to ~0.8.

On the other hand, reports on thermal analysis of petroleum fractions are more limited. Earlier studies [10] stated that pyrolysis of paraffinic, aromatic, polar, and asphaltene fractions from heavy oils can be interpreted in terms of a low-temperature phase involving the volatilization of paraffinic and aromatic fractions and a high-temperature phase in which polar and asphaltene fractions pyrolyzed producing a particulate carbon residue. Douda et al. [2] carried out the pyrolysis of asphaltenes from Maya crude obtaining maltenes (saturates, aromatics, and polar compounds), coke and gases as products. Maltenes were further separated by HPLC and it was found that saturate fraction is composed by tetracyclo-alkanes (18.2%), alkanes (15.9%), and hexacyclo-alkanes (10.9%), whereas aromatic fraction was distributed as follows: mono-aromatics (22.6%), di-aromatics (26.5%), thiophenoaromatics (19.5%), and penta-aromatics (1.3%). Douda et al. [11] also stated that maltenes from Maya crude oil are stable up to 215 °C but at higher temperatures a fast conversion is observed up to 550 °C and finally they are entirely decomposed at ~1000 °C. The coke yield from asphaltenes and resins varies 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 35–65 wt.%. Asphaltenes produce high yields of volatile products that include condensable liquids and gases as well

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