

Oxidative Cracking of Linear Hydrocarbons at Low Temperatures

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Abstract – Experiments of partial oxidations with molecular oxygen at low temperatures (below 473 K or 200 °C) were carried out using the linear hydrocarbons n-hexadecane, n-dodecane, n-decane and n-heptane. The analysis of the experimental data obtained showed an increase in the oxygen rate with the increase in the hydrocarbon size, being observed reactions of oxidative cracking with the formation of compounds with small molecular weight. The variation in the oxygen consumption was so small for hydrocarbons higher than C12 (n-dodecane). The reactions of partial oxidation showed autocatalytic behavior in which was observed an increase in the rate of oxidation with the progress of the reaction. From chromatographic analyses of the liquid samples were identified several types of oxygenated compounds and also small amounts of light hydrocarbons, with classes of compounds distributed principally according to the homologous series. The oxidative cracking mechanism can be applied in the recovery of heavy materials as the polymers and the residues of petroleum. Previous experiments with an atmospheric residue of a Brazilian light oil showed promising results related to the higher formation of liquid fraction.

The transformation of organic residues into liquid and gaseous products has been the subject of many researches [1]. The plastics and heavy fractions of petroleum represent a serious environmental challenge, since these materials are difficult to be degraded along time, requiring additional costs for their reuse or final disposal. On this way, it is necessary to find new technological alternatives to recovery economically these residues as raw materials to produce valuable substances.

The thermal treatment (pyrolysis) is the mostly used technique applied for the processing of organic residues for the production of liquid fuels. Improvements in the conventional thermal processes have been studied through the developments of new technologies as the utilization of new additives [2].

The utilization of oxygen in such processes is a new way to be followed due to the cracking evidences in the pyrolysis studies of polypropylene in the presence of oxygen [2]. From it was observed a great tendency to the formation of light oxygenated compounds from hydroperoxides compounds with a significant decrease on the activation energy of the polymer carbon-carbon bond cleavage when compared to the conventional thermal process (without oxygen). Values of conversion around 70% through photo and thermo decomposition of polypropylene hydroperoxides into gaseous products were obtained in the literature.

The experiments of partial oxidations of n-hexadecane, n-dodecane, n-decane and n-heptane at low temperatures (below 473 K or 200 °C) were performed being determined the consumption rates of oxygen for each paraffin (Fig. 1). The analysis of the experimental samples indicated mechanisms of oxidative cracking with the presence of homologous series. The Fig. 2 shows the GC-MS (Gas Chromatography Mass Spectrometer) mass fragmentogram (m/z 58) of the homologous series of linear aliphatic 2-ketones (from C5 to C9). The utilization of oxygen as an additive in the pyrolysis of an atmospheric residue of a Brazilian light oil showed promising results related to the higher formation of liquid fraction.

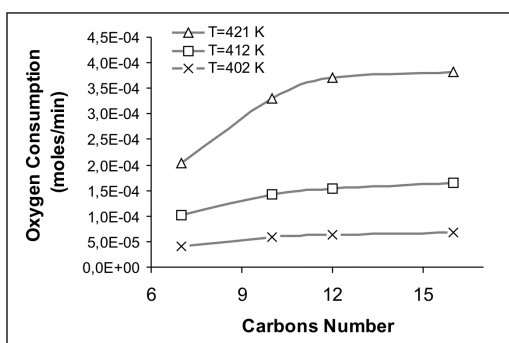


Figure 1: Consumption rate of oxygen according to the carbons number of the paraffin

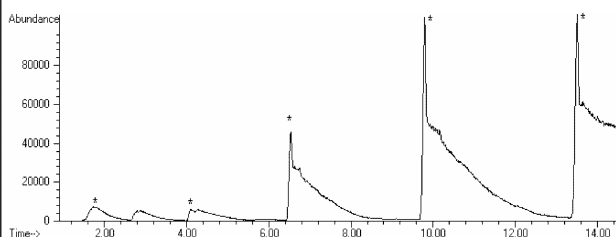


Figure 2: GC-MS mass fragmentogram (m/z 58) showing the presence of the homologous series of linear aliphatic 2-ketones (from C5 to C9).

References

[1] N.Özbay, *et al.* Fuel Processing Technology, 87, (2006) 1013.

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