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Effect of tetralin, decalin and naphthalene as hydrogen donors in the upgrading of heavy oils

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Abstract

Nowadays the upgrading of heavy crude oils is achieved by thermal cracking or hydrocracking, which are based on the carbon rejection and hydrogen addition routes. These processes have several problems yet to be solved, such as coke deposition both on the reactor walls and on the catalyst, low quality of products and low efficiency of usage of hydrogen. Thus, an efficient technology for the production of high quality distillates from heavy oils or residua has not been developed yet. An interesting alternative for improving the yield of valuable liquid products in the hydroprocessing of heavy feeds is the use of hydrogen donors (usually polycyclic naphthenic-aromatic or naphthenic compounds that can be reversibly hydrogenated-dehydrogenated in the reacting mixture). The molecules of the hydrogen donors are dehydrogenated, transferring hydrogen atoms to the heavy hydrocarbons in the oil, thus improving the quality of the cracked products and minimizing the polymerization of the heavier molecules via a free radicals mechanism. This work is focused on the effect of tetralin, decalin and naphthalene as hydrogen donors (H-donors) in the thermal cracking of a Mexican heavy crude oil (12.1 °API) in the presence of hydrogen or methane as reducing agents. Experiments were carried out in a batch reactor under relatively mild conditions, 1.1 MPa initial pressure and 693 K temperature. The results indicate that the combination of these H-donors and reducing agents leads to significant reductions in the yield of coke, compared to those obtained using only the reducing agents under the same conditions. The improvements in the API gravity, the viscosity and the distillates yield (as determined by GC-simulated distillation) upon treatment are nearly the same with or without H-donors, confirming that the primary cracking reactions depend mainly on the temperature of reaction and are not appreciably affected by the presence of reducing agents or hydrogen donors. The reduction in the yield of coke was similar for tetralin, decalin and naphthalene.

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1. Introduction

Nowadays the upgrading of heavy crude oils is mainly achieved by thermal cracking or hydrocracking, which are based on the carbon rejection and hydrogen addition routes [1-4]. These processes have several problems yet to be solved, such as coke deposition both on the reactor walls and on the catalyst, low quality of products and low efficiency of usage of hydrogen. Thus, an efficient technology for the production of high quality distillates from heavy oils or residua has not been developed yet.

An interesting alternative for improving the yield of valuable liquid products in the hydroprocessing of heavy feeds is the use of hydrogen donors (usually polycyclic naphthenic-aromatic or naphthenic compounds that can be reversibly hydrogenated-dehydrogenated in the reacting mixture). The hydroprocessing reactions in the upgrading of heavy oils are usually limited by the availability of hydrogen, which must be transferred from the gas to the liquid phase before the hydrogenation reactions can take place. In conventional hydroprocessing, the availability of hydrogen is increased by increasing the hydrogen partial pressure. When hydrogen donors are used, an additional amount of hydrogen is available for the hydrogenation reactions. The molecules of the hydrogen donors are dehydrogenated, transferring hydrogen atoms to the heavy hydrocarbons in the oil, thus improving the quality of the cracked products and minimizing the polymerization of the heavier molecules via a free radicals mechanism. In this way, the coke yield can be reduced and the yield of light and middle distillates can be markedly increased while achieving a more efficient usage of hydrogen compared with simple hydrocracking.

Nakamura et al [5] studied the thermal cracking of Kuwait crude oil atmospheric residue in the presence of hydrogen at 708-728 K and up to 7.5 MPa using supported nickel catalysts and found that Ni/active carbon and Ni/SiO_2-Al_2O_3 (an acidic support), unlike Ni/β''- Al_2O_3 (a basic support) or the non-catalyzed system, resulted in a liquid reaction product with low asphaltenes and aromatics contents and a high yield of coke and H_2S; these authors concluded that the Ni/active carbon and the Ni/ SiO_2-Al_2O_3 catalysts promoted the conversion of asphaltenes to coke and the reaction of hydrogen generated in the dehydrogenation of asphaltenes with sulfur, aromatic and olefin compounds in the oil.

Fujimoto et al [6] studied the liquid phase transfer hydrogenolysis of thiophene by decalin using metal-on-active carbon catalysts at 603-663 K and up to 1.1 MPa; the results of these experiments showed an excellent relationship between the degree of dehydrogenation of decalin and the degree of hydrogenolysis of thiophene. These authors concluded that decalin is adsorbed and dehydrogenated on the active carbon surface and that the hydrogen atoms migrate on the carbon surface to reach the metal sites (by a reverse spillover effect) and react with thiophene.

Carlson et al [7] evaluated the ability of six different pure hydrocarbons (n-heptane, cyclohexane, benzene, decalin, tetralin and naphthalene) to donate hydrogen and prevent coke formation during thermal (non-catalytic) cracking of a West Texas residuum without hydrogen addition, using about equal amounts of residuum and diluent, at 722 K for 2.5 hours; n-heptane, cyclohexane, benzene and naphthalene had little effect on the coke yield, while tetralin showed a significant reduction (from 17 to 2 wt. %) compared with the residuum-only test. Decalin was less effective than tetralin (coke yield 6 wt. %). The effectiveness of tetralin was attributed by these authors to the highly activated hydrogen atoms in the saturated ring adjacent to the aromatic ring, and the intermediate result with decalin was believed to be