

Fouling mechanisms of hydrocarbon streams containing conjugative olefins

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A number of mechanisms are known to contribute to fouling in hydrocarbon processing. In cracked streams, an important fouling mechanism can be free-radical polymerization of dienes to form polymeric gums. Polymerization rates can be expected to increase with temperature but, at higher temperatures, competing mechanisms can destroy formed polymer gums or can create new olefins by cracking. A better understanding of how these various mechanisms interact will improve management of fouling in process streams that contain olefins.

In this work, the fouling propensities of a coker gas oil (CGO) at different surface temperature were investigated by using a bench scale hot liquid process simulator (HLPS) Alcor units. The fouling mechanisms of CGO were also studied in a 5 liters stirred batch autoclave under inert atmosphere at different temperatures for 15~20 days. As well, the fouling deposits collected from the wall and stirrer were characterized by the means of elemental analysis, scanned electron microscope (SEM), thermogravimetric analysis (TGA), mid-Infrared photoacoustic spectroscopy (PAS-IR), etc.

The bench scale fouling tests indicates that the fouling propensity of CGO follows a bimodal distribution as a function of temperature (Figure 1). As the heating element surface temperature (carbon steel) increased up to 350°C, the fouling rate increased. Further increase of surface temperature resulted in a decline of the fouling and then increased again as temperatures raised to 400°C. Longer-term batch reaction results suggest, at temperatures of 270°C and 300°C, polymerization of unsaturated hydrocarbons is the main reason for the CGO fouling. However, at 350°C, CGO exhibits a unique reaction characteristic - diene values increase gradually in the first several days, and then increase dramatically with the time (Figure 2). Both density and viscosity increase at a much faster rate than at lower temperatures.

At low cracking temperatures (<350°C), it appears that new dienes contribute to gums formation and increased fouling. At higher temperatures (350 - 400°C), the cracking of gums may actually reduce fouling. When the temperature is above 400°C, fouling is increased again, presumably due to familiar coking reactions. The bimodal temperature dependence of fouling reactions provides clues for controlling fouling by subtle manipulation of temperatures. The change of dominant mechanism with temperature also

provides guidance for the selection of antifoulant additives.

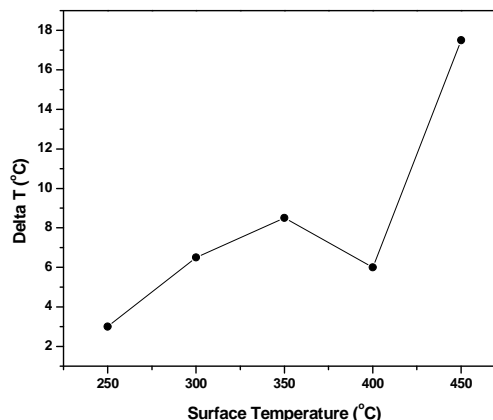


Fig.1. Fouling propensity of CGO at different temperatures

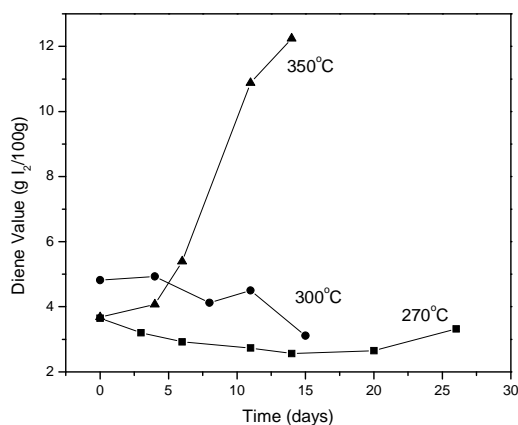


Fig. 2. Diene values of CGO change with reaction time at different temperatures