
Question 34: What has been the experience of refiners operating selective hydrotreating of FCC naphtha regarding gum formation potential of the low sulfur gasoline? Is gum inhibitor addition a recommended practice?

John Clower (Chevron)

Gum potential exists with unsaturated hydrocarbons (olefins or diolefins) stored in refinery operations with oxygen as a free radical. Organic sulfur and nitrogen compounds remaining in FCC gasoline product can form gums in the presence of olefins and oxygen.

Temperature, residence time, and oxygen ingress are key process variables in the formation of gums in gasoline component storage. Best practice requires antioxidant injection of all FCC gasoline tanks to tie up any oxygen that would otherwise play a role in the formation of gums.

Typical Gasoline Hydrotreating operations are mild, resulting in the following typical species conversions:

- 100 % diolefin saturation
- 90% organic sulfur reduction
- 20% olefin saturation
- 10 - 20% organic nitrogen reduction

Current best practice is to inject antioxidant into the product and measure both existent and potential gum in the component tank:

- Anti-oxidant is injected at 20 ppm on FCC gasoline product
- Target for existent gum via ASTM D381-04 < 4 mg/100 ml
- Target for potential gum via ASTM D 525 < 10 mg/100 ml

Greg Harbison (Marathon Petroleum)

Marathon has Axen's Prime G+ FCCU gasoline hydrotreaters at its Garyville, Louisiana and Robinson,

Illinois refineries. Both units utilize a selective hydrogenation process on the light naphtha streams (roughly 200-210 degrees endpoint). Prior to the installation of these two units, the gasoline streams were conventionally sweetened, and stability additives were used at both locations.

When the FCCU gasoline desulfurization units were commissioned, the stability additives were discontinued on the produced gasoline streams. There were no reports of gum problems associated with the products.

After initial startup of the units, projects were completed to allow the light portion of the naphtha to run down to tankage separately from the heavy naphtha. This facilitated additional blending flexibility as the light naphtha cut has different blend properties than similar refinery streams in use at the time.

The light naphtha products from our two desulfurization units are managed differently at each refinery. One plant routes the light naphtha product to storage after blending with isomerate, and the other blends with high octane reformat. Our refinery that blends the light naphtha product with high octane reformat has had experience with high gums. Following several gasoline blends outside of specification limits for gums in which tanks had to be treated for stability, a more comprehensive lab study was completed. Although the study was unable to predict the off specification finished product based on blend components and their ratios, tank circulation times, etc., we concluded that a field test was required.

The trial was conducted with the stability additive injected into the light naphtha product when it was segregated for gasoline blending. Following a successful trial, the program has since been made permanent, and all gasoline blends have met stability specifications when using the additive. The additive has been successful at moderately low dosages.

The other refinery stores the light naphtha combined with isomerate, and has had no incidents of high gums.

Gregg McAteer (Nalco Company)

Often, we see straight run naphtha hydrotreaters that traditionally did not have a fouling problem start to foul as FCC or coker naphtha is introduced to the feed. Gum studies are performed to determine if chemistry can reduce the fouling rate (gum formation/deposition rate). Gum inhibitor applications have been able to give the refiner the long run they were looking for.

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