
Question 27: What are the pros and cons of alkylating delayed coker butylenes (co-processed with FCC butylenes)? Does this require higher isobutane recycle? Should we consider processing them in a separate reactor? What are the economic alternatives to alkylation?

Brad Palmer (ConocoPhillips)

A more specific question is: "What is in Coker olefin that is problematic since a pure olefin is the same whether from a Coker or FCC unit?" A Coker derived olefin stream has more sulfur, diolefins and acetonitrile than FCC olefins. The presence of these contaminants will result in increased acid soluble oil (ASO) formation; therefore, coker olefins require more robust feed treatment. An increase in ASO formation can lower the acid strength so additional attention should be given to the acid regeneration operation. A Coker derived olefin stream also has higher amounts of normal butane than FCC olefins. Normal butane can lower the iC4 recycle purity if there aren't adequate means to remove it, which in turn would require a higher recycle rate to maintain the desired I/O ratio. Process variables needing additional attention when feeding Coker olefin include: ASO formation and acid strength, iC4 recycle purity and I/O ratio along with nC4 production. An alternative to processing Coker olefin on the Alky unit is to downgrade the olefins to butane sales. The economics for processing Coker olefin (operating costs of increased ASO) should be evaluated against alternate dispositions.

Contributing Comments Prepared by: Craig Meldrum – Alky Network Lead & Reformer/Isom Advisor, Nathan Cooledge – Alky / S Zorb™ Process Specialist

\Praveen Gunaseelan (Vantage Point Consulting)

Due to the differences in individual unit designs, type of catalyst (sulfuric or HF), and alky feedstock composition, etc., responses to the above questions could vary from site to site. It would, therefore, be prudent to discuss this matter with the alkylation process licensor or a qualified engineering contractor for a site-specific response.

Coker cracked gases typically contain more sulfur compounds, dienes, and normal alkanes compared to FCC cracked gases. Consequently, coker gases require more pre-treatment prior to alkylation, which typically involves caustic treating to remove mercaptans, and selective hydrogenation to remove dienes. If not adequately pre-treated, coker cracked gases hasten catalyst consumption in alky units.

In alky units that operate at higher isobutane ratios to maximize octane, the higher n-alkane content of coker butylenes will affect product fractionation, and theoretically call for higher isobutane recycle. In the US, however, mandated ethanol blending has eased octane demands on refineries, and thus the impact on isobutane recycle may not be as critical.

Randy Peterson (DuPont – STRATCO)

Coker butylenes typically contain more normal butane, more butadiene and less isobutane than FCC butylenes. Therefore, more makeup isobutane will be required with Coker butylenes to provide the required stoichiometric amount of isobutane to the reaction zone. The C4 olefins by themselves are not much different so expect similar alkylate quality and acid consumption, all else equal. Therefore, we see no reason to process in a separate reactor.

Since normal butane is a reaction zone diluent, slightly more recycle isobutane will be required to maintain the same alkylate quality with coker butylenes. Many refiners are maxed out on recycle isobutane rate and/or purity so a slightly lower octane and higher acid consumption may be the result.

Butadiene is an acid consumer for both HF and sulfuric acid alkylation units. Some refiners have a selective hydrogenation unit which removes the dienes before they get to the alkylation unit.

If no selective hydrogenation unit exists, expect a higher fresh acid requirement for sulfuric units. For HF units, more ASO (acid soluble oil) will be produced which may overload the HF regenerator and lead to lower maximum throughput.

Erik Myers (Valero)

Coker butylenes are high in mercaptans and diolefins, both are poisons to acid. Consideration for this must be included in the sizing of the upstream mercaptan extraction unit or increase the size of the acid regenerator / rerun system. An SHU can be utilized to address the diolefins.

Coker LPG streams are typically less olefinic than FCC generated LPG streams. If this increase in normal butanes and pentanes leads to alkylation unit fractionation issues and decreased isobutane recycle stream purity then a higher recycle rate may be required to achieve the same isobutane to olefin ratio (though an actual higher I:O ratio is not typically required).

Processing coker olefins in a separate reactor is not practical. Alternatives for alkylation of this material are to blend with coker naphtha into gasoline blending or hydrotreating the material.

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