

## PERP Program – New Report Alert

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Nexant's ChemSystems Process Evaluation/Research Planning program has published a new report, *Butadiene/Butylenes (01/02-3)*.

Mixed  $C_4$  streams, containing butadiene, butenes and butanes are co-produced in steam cracking processes. In the refinery too,  $C_4$  olefin and paraffin streams are also produced, mainly from the FCCU. These streams contain useful molecules that can be either processed in situ or extracted as pure components. The processing of  $C_4$  streams gives the petrochemical producer or refiner an opportunity to add value to either the cracker or the refinery depending on the level of  $C_4$  integration.

In Western Europe and East Asia, ethylene production tends to be based on the steam cracking of liquids, particularly naphtha, and as a consequence there is a considerable quantity of mixed  $C_4$  stream produced per ton of ethylene which has to be considered as a credit to the cost of ethylene production. In the United States, the Middle East and some other regions such as Canada and Mexico, ethylene is produced predominantly from gas cracking with little or no by-product  $C_4$  stream. Therefore those ethylene producers based on naphtha have an onus on them to add maximum value to their  $C_4$  co-product stream to minimize ethylene production costs.

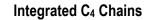
Maximizing the value of the steam cracker or refinery based  $C_4$  stream is a major objective for most companies. A variety of options exist to upgrade the  $C_4$  stream by separation of the pure  $C_4$  components and conversion of low value streams to higher value products.

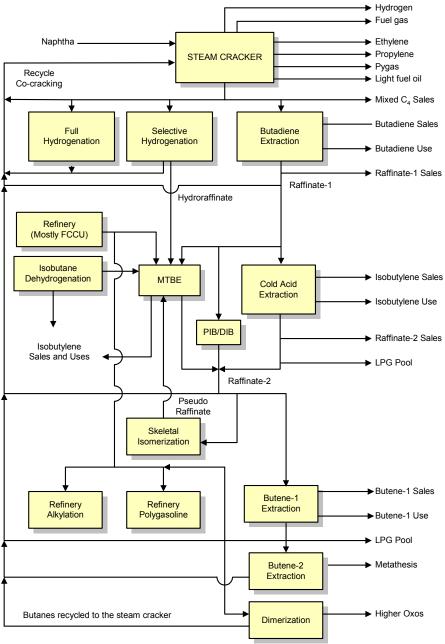
The process options available to upgrade the  $C_4$  stream are summarized in the figure below. An important factor is the interaction of the  $C_4$  chain with the cracker through the processing of recycle streams of various compositions.

For a naphtha based steam cracker the major use for the  $C_4$  stream is the extraction of butadiene. However, mixed  $C_{4s}$  can be fully or partially hydrotreated or recycled to the cracker without hydrotreatment. The  $C_4$  stream can also be exported to other companies for butadiene extraction. All these methods of  $C_4$  disposal are practiced and choices are made depending on downstream integration and relative economics.

Isobutylene-containing streams arise from butadiene extraction (co-product), mixed  $C_4$  selective hydrogenation and the refinery FCCU and dehydrogenation. Isobutylene can be extracted and consumed as a pure stream or consumed in a contained stream. The most common means of obtaining pure isobutylene from a contained mixed  $C_4$  olefin/paraffin stream is to first make MTBE, separate it and then crack it. Other technologies exist to remove isobutylene from contained streams, e.g. cold acid extraction, but its flexibility to handle very dilute isobutylene streams is limited.







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The co-product stream from isobutylene consumption is called raffinate-2. This contains normal butenes and mixed butanes. It has a limited number of chemical uses. It can be consumed in the refinery, fed to the LPG pool, or recycle co-cracked. Using technology such as skeletal isomerization, normal butenes can be converted into isobutylene and the stream recycled for chemical/MTBE use. Butene-1 can be extracted from raffinate-2 leaving a stream containing mainly butene-2 (raffinate-3). This stream can also be used in the refinery, the LPG pool and can be co-cracked. Residual olefin can be dimerized and used as a feedstock to produce higher oxo alcohols. However, butene-2 can be extracted and reacted with ethylene to produce propylene using metathesis.

Several producers have developed integrated production schemes for adding full value to the  $C_4$  stream involving a mix of the above processes. Additional optimization is obtained by exploiting the higher stream values obtained by integration across the refinery petrochemical interface.

This study is mainly concerned with certain technology elements that can be found in the figure. The major focus of the technoeconomic analysis covers recycle co-cracking options for the mixed  $C_4$  stream and the extraction of pure  $C_4$  components, namely, butadiene, isobutylene, and butene-1. Certain aspects of integrating  $C_4$  processing elements are also discussed to examine the value of simple and complex  $C_4$  integration.

Tri-regional supply/demand outlook for butene-1, isobutylene, and butadiene out to 2010 is also provided.

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