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Secure the best benefits from C_4 hydrocarbon processing–Part 1: Separation sequences

Crude C_4 streams from the steam cracker unit (SCU) or the fluidized catalytic cracker unit (FCCU) contain valuable hydrocarbons, such as butadiene and C_4 olefins. The upgrading of such streams can be carried out with different processing routes. The upgrading process of C_4 hydrocarbon streams is not standardized; a suitable route for each refinery must be studied individually. Both economic and environmental issues should be taken into account to achieve the best investment benefit.

Advanced petrochemical plant design requires flexibility to match different situations, e.g., variation in feedstock. A comprehensive understanding of C_4 hydrocarbon processing is prerequisite. This survey will discuss the characteristics of C_4 feedstocks, as well as the opportunities of the large variety of potential C_4 process routes from a practical engineering point of view. Some selected technologies will be compared and discussed in more detail.

Enhancing the process benefits. Spurred by the steady growth demand in light olefins (C_2 to C_4), the installation of SCUs and FCCUs—the latter operated with catalysts supporting light olefins formation—has been promoted in refineries during the last decades. The upgrading of C_4 hydrocarbons, one of the most important byproducts in cracker units, could enhance the benefits of the whole process. Many valuable products, such as gasoline additives (alkylate, tertiary butyl alcohol, methyl tertiary butyl ether and ethyl tertiary butyl ether), monomers for further polymerization (butadiene, isobutene, 1-butene) and commodities (methyl ethyl ketone, maleic anhydride), could be yielded from C_4 hydrocarbons. Furthermore, the C_4 fraction of field butane, such as oil-associated gas, natural gas and shale gas, is coming more and more into focus.[1]

Different from many conventional chemical processes, which use pure chemicals as feedstock, C_4 processing involves a complex mixture of hydrocarbons and other organic/inorganic compounds. This requires feasible solutions in petrochemistry that can only be realized by a tailor-made process design based on the individual feedstock to maximize productivity and process economics.

Besides butadiene and butenes, a considerable portion of butanes are included in the C_4 cuts from cracker units. Furthermore, according to the upstream process, the contaminations contained (e.g., traces of solvents, light/heavy hydrocarbons, C_3/C_4 acetylene and allenes) can also be different and must be taken into account during the process evaluation. Product purification and contaminant removal steps will strongly affect the final profit margin and increase the plant's complexity.

Feedstock. Crude oil is processed in petroleum refineries in different ways. In the field of light olefin production, FCCUs and/or SCUs are utilized.

An FCCU is used to convert the heavy oil (e.g., vacuum gasoil from crude oil vacuum distillation) to gasoline, and it can be operated in different modes to maximize middle distillate, gasoline or olefins yield. The product distribution from an FCCU depends on process conditions and catalyst.[2]

C_4 streams from FCCUs are isobutene-rich and contain less than 0.5 wt% butadiene. However, even a minute portion of butadiene could cause trouble for downstream processes, such as catalyst deactivation, because of the very active double-bonds or potential of polymerization. These small amounts of butadiene cannot be recovered economically. Selective hydrogenation is the best way to convert butadiene to n-butenes, another type of very valuable C_4 components.

Different from FCC, steam cracking is a thermal cracking method to break down the C-H bond in light hydrocarbon molecules to produce hydrogen and olefins. If naphtha and/or gasoil are used as feedstock, then the C_4 cut contains about 50% diolefines (mainly 1, 3-butadiene). High-purity 1, 3-butadiene can be yielded economically with a butadiene extractive distillation process. This opportunity is also the main source for 1, 3-butadiene, which is applied in the production of elastomers and co-polymer plastics, such as polybutadiene rubber or styrene-butadiene rubber.

Beside FCC and SC products, there exists a multitude of other C_4 feedstocks derived from blending within a refinery. Such blended C_4 feedstocks also require tailor-made processing.

Within this article, the nomenclatures of Raffinate 1 and 2 are used (**FIG. 1**). After the removal of 1, 3-butadiene from crude C_4, the residual stream is termed as Raffinate 1, which contains a certain portion of isobutene. Removal of the isobutene, usually by chemical conversion, leaves Raffinate 2. C_4 from field butane (oil carrier gas, natural gas or oil shale gas) is a further important source for C_4 processing. Typical feedstock compositions derived from an SCU, FCCU and field butane are depicted in **TABLE 1.**

Crude C_4 from an SCU could be more valuable compared with FCC C_4 because of a higher olefin content. However, the difficulty of separation should not be underestimated, and the final economic benefit has to be evaluated thoroughly with respect for the necessary intermediate steps.

Separation and purification. Upstream cracking processing generates certain undesired byproducts. The tailor-made design of C_4 upgrading processes welcomes

flexibilities to fit different feedstocks and operating cases. In some cases, C_4 mixture can be established directly as feedstock—e.g., FCC C_4 cut as feed for alkylation. However, in other cases, butanes-butenes separation is beneficial or inevitable as a process step. Product purification is mandatory to fulfill certain specifications of downstream chemical synthesis.

The complexity of a separation/purification process strongly depends on the properties of pure components, as well as the interactions between components in the mixture (vapor liquid equilibrium). The behavior of fluid mixtures can be calculated by using thermodynamic models, which allow the calculation of these properties from available binary experimental data.[3] The complexity of determining thermodynamic properties is enhanced significantly by increasing the number of components, and it is very important to gain the right thermodynamic knowledge as a function of temperature, pressure and composition.

Due to their better chemical reactivity, butenes are more valuable than butanes. The isolation of butenes from C_4 hydrocarbon streams is profitable, especially for further use in polymer production. Distillation with significant separation effort (stages, reflux ratio) for separating components with a very close boiling point is a traditional technology known as super fractionation, and it is used, for example, in C_2 and C_3 olefin/paraffin splitters. Due to the larger number of isomers in a C_4 stream, this system is more complex compared to C_2 and C_3 processes.

TABLE 1 shows the normal boiling points (NBP) of C_4 components, which are typically included in feedstock originating from cracking processes. Very close boiling points between singular components—e.g., 1-butene (–6.3°C) and isobutene (–6.9°C), and azeotrop formations (as in 1-, 3-butadiene and trans-2-butene with n-butane)—result in difficulties of separation. Those mixtures are not separable with conventional distillation methods, and additional measures are needed.

The available separation techniques can be mainly divided into adsorption, membrane processing and extractive distillation.

- Adsorption, known as molecular sieve technology, is a separation process based on the different physical interactions between olefins and adsorbent. It does not need an additional solvent, but it does require a significant amount of electrical energy (caused by high product circulation rates) and a sophisticated control system.
- The application of membrane processes is very sensible to feedstock composition, which contradicts with the diversity of the petrochemical process, including varying feedstocks, since a tight control of byproducts from an FCCU or SCU is difficult. The low tolerance of feed contaminants would be another limitation of membrane techniques for this industrial application.[4]
- The extractive distillation (ED) process comprises a simpler process setup. A solvent that takes advantage of molecular interaction, and creates or enhances the distinction in volatility between the components, will be used, allowing the paraffins/olefins molecules to be separated. Paraffins leave the column top and solvent with the less-volatile components (olefins) flow to the bottom of the distillation column, where the extracted components (olefins) are recovered by a subsequent distillation.[5] By adjusting the solvent-to-feed ratio, ED processes tolerate better fluctuation of olefin content in feedstock.

Many paraffin/olefin separation processes are based on ED processes, and the selection of the extractive agent is the core know-how of the process design. For instance, a morpholine-based solvent mixture is used in a butene concentration process. Such an ED process can be considered as a standalone butane/butene separation, as well as a pretreatment step in various synthesis processes for the concentration of reactive olefins in the feedstock. Pretreatment processes are suitable where the "one-through" conversion rate is limited by the concentration of reactive feed components, such as in the case of conversion of n-butenes and water to sec-butanol (SBA). With the implementation of an upstream feed concentration unit, the recycle stream is reduced (directly reflecting on CAPEX) and the operating expense (OPEX) is lowered.

Focus on potential C_4 processing routes. Butadiene as an intermediate product plays a special role in C_4 economy. The recovery of butadiene is accomplished by using selective solvent via extractive distillation. Some features, such as the contamination with acetylenes and allenes, and the risk of self-polymerization, have to be taken into account in the process design.

FIG. 2 shows a typical block flow diagram of the possible products yielded from C_4 hydrocarbons. However, the whole scheme would never be applied in its full range. The focus here is on potential opportunities to understand the C_4 hydrocarbon processing routes. Benchmark scenarios will be discussed in accordance with their different process complexities. First technical analysis will be outlined based on evaluation of three border cases. Economic evaluations, including the price development of feedstocks and products, and handling

TABLE 1. Typical composition of SC C_4, FCC C_4 and field butane feedstock

C_4 component	NBP, °C	SC C_4, wt%	FCC C_4, wt%	Field butane, wt%
1,3-butadiene	–4.4	35–50	0–0.5	–
Isobutene	–6.9	15–30	10–25	–
2-cis-butene	3.7	5–10	10–20	–
2-trans-butene	0.9	5–10	10–20	–
1-butene	–6.3	5–20	10–25	–
Isobutane	–11.7	1–5	20–40	100
N-butane	–0.5	1–10	10–20	

FIG. 1. C_4 process nomenclatures.

costs, will be carried out as Part 2 in an upcoming issue of *HP*.

Minimization of capital expenditure (Case 1).
Usually an olefin containing a C_4 stream is too valuable to be used as fuel (via total hydrogenation). In some cases, cutting the mixture into single components is not the goal, so CAPEX can be kept low due to minimized effort for separation and purification. As **FIG. 3** shows only isobutene conversion and further upgrading of Raffinate 2 to gasoline, an additive will be taken into account. Butadiene removal is only required if butadiene is a problem for downstream processes.

The upgrading of Raffinate 2 can be through alkylation, dimerization or oligomerization. The process that is best suited depends on the availability of the co-feedstock isobutane for alkylation, the requirements of the gasoline pool, and the local market demand, including transportation fuel specifications.

Maximization of product diversity (Case 2).
The main objective of this case is the maximization of the product diversity of C_4 intermediate products. By tailor-made configuration of the process
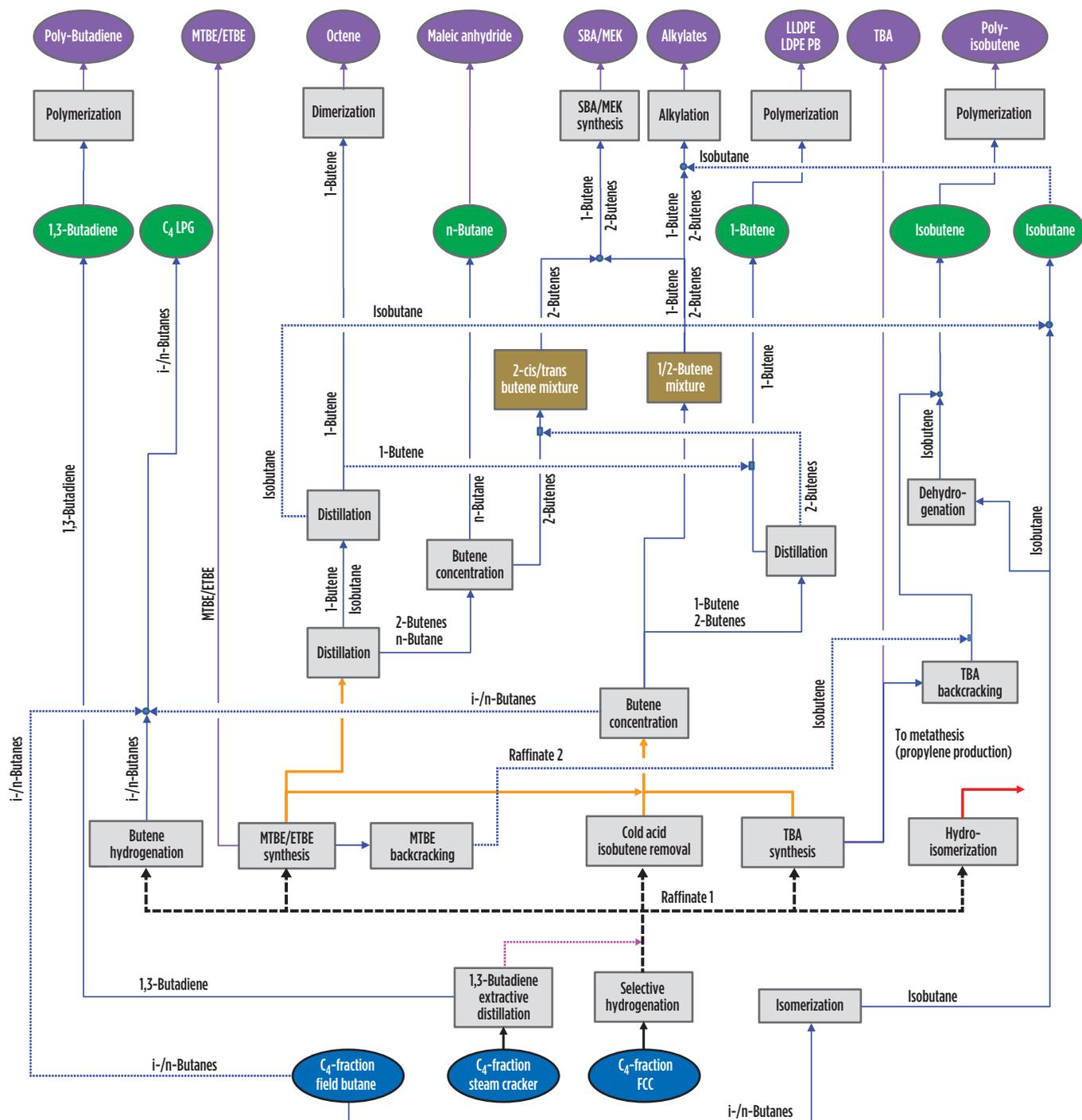
FIG. 2. Block flow diagram of process routes for the separation and conversion of C_4 hydrocarbons.

steps, it is possible to isolate almost all C_4 components derived from an SC/FCC stream. Only cis/trans-isomers of 2-butene will remain as a mixture. By applying polymerization, dimerization, metathesis, oxidation, alkylation, hydration and etherification, these components can be further processed to high-value products. **FIG. 4** represents the link between C_4 intermediates and high-value products.

With the removal of butadiene via extraction or selective hydrogenation, the cracker stream is converted to Raffinate 1. It is then routed to isobutene processing where isobutene is removed by chemical reaction from 1-butene (a nearly identical boiling point) and the other butene and butane components. Besides isobutene, four further products can be derived from Raffinate 1: 1-butene, 2-butene (cis/trans), isobutane and n-butane.

Isobutene is used for polymerization to polyisobutene or butyl rubber; for methyl tert-butyl ether (MTBE)/ethyl tert-butyl ether (ETBE) synthesis; and for tertiary butyl alcohol (TBA) synthesis. For isobutene isolation as an intermediate product with high purity, isobutene can be converted to ether (MTBE/ETBE) or to TBA via direct hydration. Crude TBA can be sold as TBA/water azeotrope or further treated to pure TBA (>99.9 wt%) by drying steps. Alternatively, the azeotropic mixture can be decomposed to high-purity isobutene (99.98 wt%) at temperatures below 150°C and moderate pressure with heterogeneous catalyst.[6] Etherification and TBA synthesis are highly selective to isobutene, due to the inert behavior of all other C_4 components at such mild reaction conditions.

By isobutene removal, Raffinate 1 is transferred into Raffinate 2 containing 1-/2-butenes and n-/iso butanes. The linear olefin 1-butene is a desired feedstock for the production of n-butene polyolefines, as co-monomer in the production of polyethylene—low-density polyethylene (LDPE) and high-density polyethylene (HDPE)—or as feedstock for propylene synthesis via metathesis of ethylene and butene.[6] The recovery of 1-butene from the cracker-mixed C_4 stream is difficult due to stringent limitations for isobutene and butadiene in 1-butene product (**TABLE 2**).[7]

Such separation can be accomplished by processing the Raffinate 2 stream in a two-step super fractionation. In the first distillation column, 2-cis/trans-butene and n-butane form the bottom product, whereas 1-butene and isobutane go overhead and are separated in the second column. Isobutane, along with some 1-butene, is recovered as overhead product and high-purity 1-butene forms the bottom product. Isobutane can be further used to produce alkylates via alkylation or tertiary butyl hydroperoxid via oxidation.

The bottom product of the first column of 1-butene separation consists mainly of n-butane and 2-cis/trans-butene. By using the butene concentration process, as shown **FIG. 4,** 2-butene can be separated from n-butane. The above mentioned process
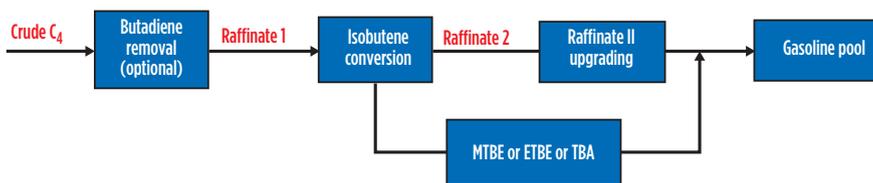
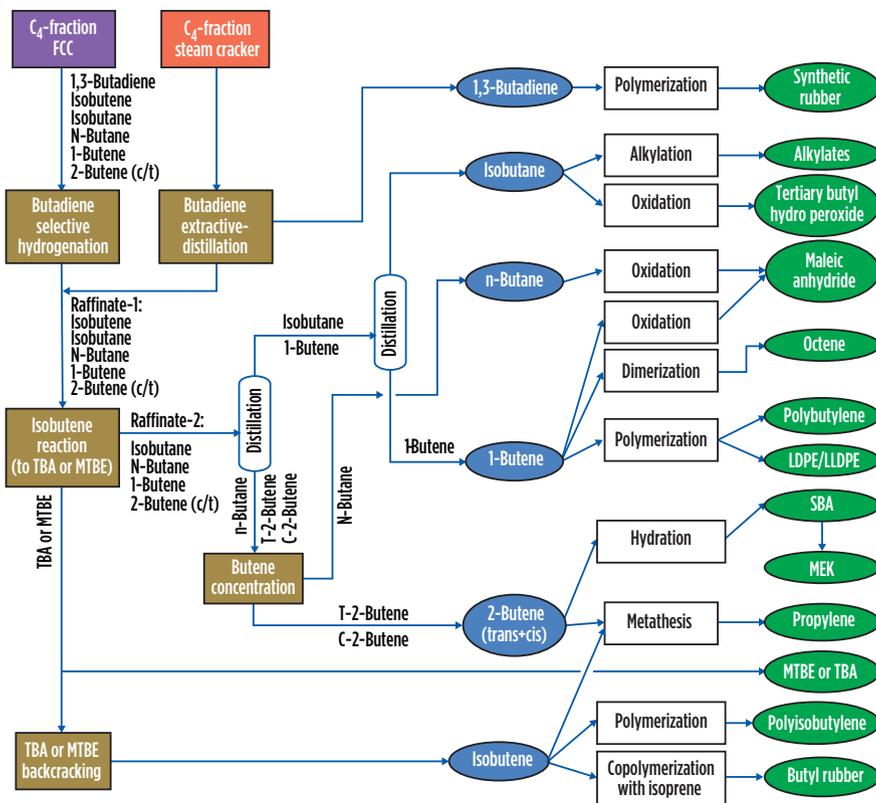**FIG. 3.** C_4 process route for minimized CAPEX for C_4 processing.

FIG. 4. C_4 intermediate products and corresponding final products.

TABLE 2. Composition of high-purity isobutene and 1-butene

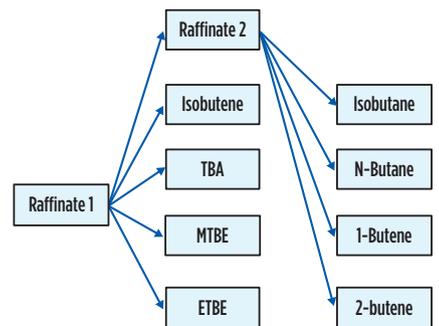| Component	Pure isobutene	Pure 1-butene
Isobutene	99.98 wt%	0.15
1-butene	0.005 wt%	99.7
2-butene	0.01 wt%	0.01
Butane	0.005 wt%	0.15
1, 3-butadiene	< 10 ppm	< 10 ppm
TBA	< 5 ppm	< 1 ppm
Water	< 30 ppm	< 10 ppm
Sulfur	< 1 ppm	< 1 ppm

FIG. 5. Raffinate 1 and Raffinate 2 secondary products.

route has an advantage compared to the conventional process route whereas 1- and 2-butenes are still in the feedstock. Due to the fact that 1-butene was already removed, the butene concentration unit can be operated more economically compared to using Raffinate 2 feedstock, including 1/2-butenes. N-butane can be further processed to maleic anhydride by oxidation with air. 2-butene (-cis/trans) is forwarded to SBA/methyl ethane ketone (MEK) synthesis, which will be outlined in the next section.

Within Case 2, five C_4 intermediate products and three final products can be processed, beginning with Raffinate 1 (**FIG. 5**).

Maximize single product yields (Case 3). In this case, the focus is on the maximization of one final product based on C_4 intermediates. As an example, MEK, which is derived from sec-butanol (SBA), is chosen (**FIG. 6**). The challenge is to minimize byproducts and to meet the feedstock specification for SBA/MEK synthesis (**TABLE 3**). A further objective of this processing route is to maximize the 1-butene/2-butene concentration of feedstock for SBA/MEK synthesis up to 97 wt%.

Technology used for the SBA synthesis is a direct hydration process of 1/2-butenes in the presence of sulfonic cation exchange resin in the water phase, and the subsequent C_4 gas separation from the raw SBA. Of the bulk of the SBA produced worldwide, over 90% is utilized as an intermediate for the manufacturing of MEK. MEK is mainly utilized as a solvent in paints, lacquers and printing inks, as well as an extraction solvent in several industrial sectors (e.g., lube oil, plastics and rubber).

With regards to byproducts, SC and FCC feedstocks have to be differentiated. Where an FCC feedstock is available, small contents of 1, 3-butadienes will be removed by selective hydrogenation. In the case of SC feedstock, it is recommended to extract 1, 3-butadienes due to a much higher concentration. A summary of this specification is given in **TABLE 3**. The limitation for isobutene is important to prevent formation of additional TBA during SBA synthesis.

A butene concentration unit (pretreatment) is able to provide a tailor-made feedstock, which can be used for

the production of SBA and/or MEK. A mixture of isobutane and n-butane derived from butene concentration can be sold as a liquefied petroleum gas (LPG) product. Within the SBA synthesis, all three species of butenes form SBA. The variation of feedstock with regard to ratio of 1-butene and 2-butenes (cis/trans) will have no significant impact on process design; hence, a separation of 1-butene is not considered. A block flow diagram for the SBA/MEK production is shown in **FIG. 7**.

Processing field butanes. The change in the availability of feedstocks over the years is driving the development of petrochemical technologies. In the last decades, ethylene plants/SCUs were often built as gas crackers

$(C_2–C_4)$, resulting in small amounts of propylene and C_4 byproducts. As compensation, propylene and butene on-purpose technologies have been developed.

Field C_4 that is separated from natural gas, oil associated gas or shale gas contains mainly butanes and no butenes. Butene yielded from such butane feedstock by dehydrogenation can also be applied in every butene upgrading processes discussed above, and is particularly suitable for a process with a high requirement on feedstock quality.

Dehydrogenation is an endothermic equilibrium reaction, usually operating in the vapor phase. The paraffin conversion increases with decreasing pressure and increasing temperature. Obviously, conversion is limited by the thermodynamic

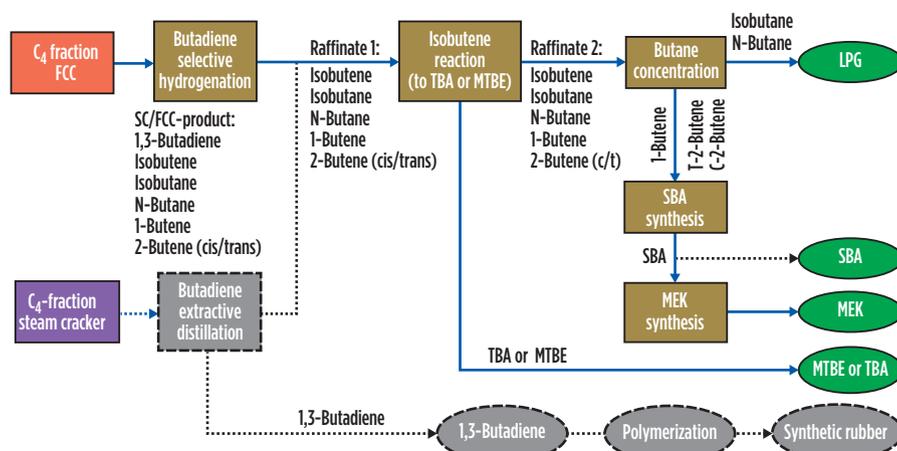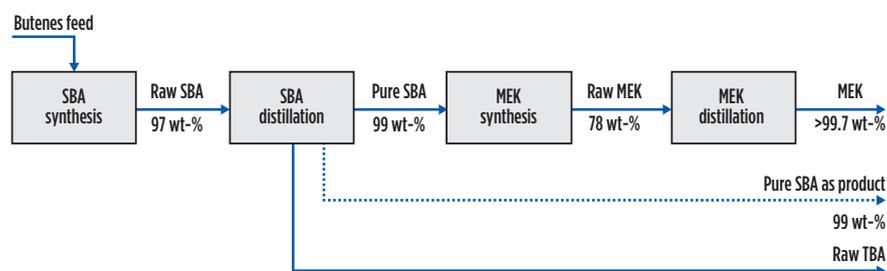> The upgrading process of C_4 hydrocarbon streams is not standardized; a suitable route for each refinery must be studied individually. Economic and environmental issues should be taken into account to achieve the best investment benefit.

FIG. 6. Processing route for the maximization of single-selected product MEK and minimum byproducts.

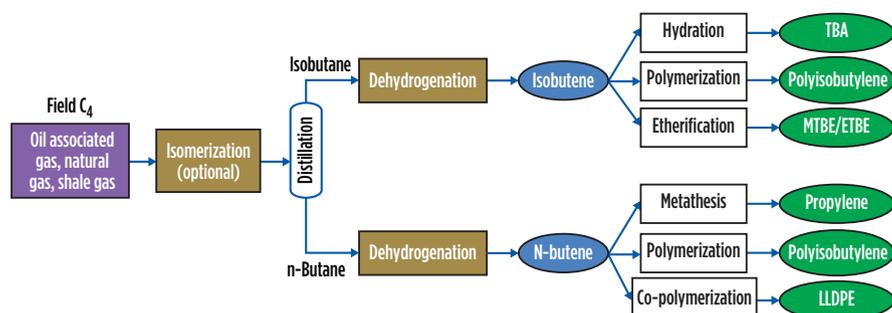**FIG. 7.** Block diagram of SBA/MEK synthesis and purification.

FIG. 8. Processing lines and corresponding products based on field butane.

TABLE 3. Typical specifications for n-butenes feed within SBA/MEK synthesis

Component	Composition
Isobutene	Max. 0.7 wt%
N-butane	Residual
Isobutane	
1-butene	Min. 97 wt%
2-cis-butene	
2-trans-butene	
1,3-butadiene	Max. 0.4 wt%
MTBE	Max. 0.2 wt%
MeOH	
H_2O	

equilibrium and requires a recycle of unreacted paraffins. Separation and purification yielding in high-purity butene is mandatory for the process. Generally, the hydrogen and light hydrocarbons that are the byproducts of dehydrogenation can be removed by distillation.

Either n-butene or isobutene could be produced with the butane dehydrogenation process. **FIG. 8** shows the product lines based on field butane. Owing to the high quality of butenes, polymerization would prove to be very beneficial to upgrading.

Overview and outlook. A comprehensive overview on C_4 olefin/paraffin-processing and the features of the crude C_4 feedstocks, as well as possible product lines, have been discussed. Engineering companies in petrochemical industries must steadily face the challenge that the available feedstock will somehow depart from the "desired" compositions and specifications. The reasons behind this indicate the wide diversities of product spectrum and the possibilities of blending inside of refineries. Meaningful economic evaluation is therefore based on the proper understanding and comparison of possible processing routes.

A simple way for upgrading C_4 hydrocarbons with minimized intermediate steps can result in high octane gasoline components. As a second extreme, the maximization of intermediate steps to separate the crude C_4 mixture into single components for further upgrading by chemical synthesis has been reviewed. There is a route with special reflection on one selected chemical synthesis, MEK. Butenes from field C_4 via dehydrogenation could cover the gap of high-purity butene requirements for certain special applications, e.g., polymerization.

Based on the technical possibilities discussed here, a full economic evaluation will be carried out in a follow-up part to this publication. Depending on the feed composition, a tailor-made process route should be chosen to get the best benefit from case to case.

Next month. Part 2 of this article will appear in July. **HP**

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