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From olefins to oxygenates: Fuel additives, solvents and more

Oxygenates are hydrocarbons containing oxygen atoms as part of their molecular structure. Some oxygenates are octane boosters that support the complete combustion of gasoline (anti-knocking) for reducing carbon monoxide (CO) emissions from vehicles.[1]

Methyl tertiary butyl ether (MTBE) is a widespread octane enhancer that was established in the 1970s. However, because of the considerable risk of contamination to groundwater due to its high solubility, MTBE was banned in the US in the early 2000s. Several alternatives to MTBE are available as anti-knock agents, such as ethanol, ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME) or tertiary amyl ethyl ether (TAEE). Nevertheless, MTBE is still used in Europe, Asia and the Middle East. Typical properties of common octane boosters are shown in **TABLE 1.**[2]

In addition to their application as an octane booster, oxygenates are utilized as solvents or chemical commodities—several ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone and diisobutyl ketone) are important chemicals in the automotive, pharmaceutical and chemical industries.

Oxygenates production routes. Four chemical species, and their respective processes, are commonly used as oxygen sources (**TABLE 2**).

Due to their reactivity and availability in high capacities, olefins up to C_5 are suitable as feedstock for large-scale commercial applications. Olefins higher than C_6 are not considered due to their high number of isomers. In this case, the oxygenate synthesis will form too many byproducts, requiring too much effort for further product purification. **TABLE 3** provides an overview of possible oxygenates products with different olefin feedstocks and compounds that contain oxygen atoms.

Primary formed oxygenates, such as alcohols, can be further processed into ketones via dehydrogenation, while aldehydes as intermediate oxygenates will form alcohols via hydrogenation.

From olefins to oxide (oxidation). Olefins can be oxidized directly into oxides by using an oxidation agent, such as hydrogen peroxide. Ethylene oxide (EO) and propylene oxide (PO) are of significant importance to the industry. EO has numerous industry applications for the production of ethanolamine, diethyl glycol, polyesters and plastics. PO is used for the production of polyester resins, propylene glycol, polyols and polyurethane.

A large number of additional products can also be produced by olefin oxidation (**FIG. 1**). However, several technologies, such as the industrial-scale productions of dimethyl ketone (DMK) and methyl ethyl ketone (MEK) via the oxidation of propylene (n-butene), are energy-intensive and no more appropriate to today's market situation. Innovative production routes are further discussed here.

From olefins to oxoaldehydes and derivatives (oxo synthesis). CO and hydrogen syngas reacts with olefins through oxo synthesis (hydroformulation) and builds aldehydes, which can be further hydrogenated into oxo alcohols. In addition to an oxygen atom, a carbon atom is added to the hydrocarbon structure.

Due to stability issues, aldehydes play practically no role as end products. However, aldehydes are important chemical

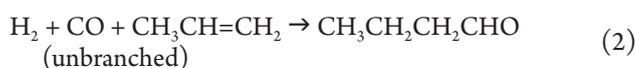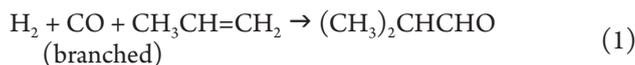**TABLE 1.** Typical properties of common octane boosters

Components	Chemical formula	NBP, °C	Oxygen content, wt%	RON	MON	RVP, kPa
Ethanol	CH_3CH_2OH	78.4	34.73	108	92	16
IPA	$CH_3CH(OH)CH_3$	82.6	26.63	118	98	13
SBA	$CH_3CH(OH)CH_2CH_3$	99	21.59	101	91	5
TBA	$(CH_3)_3COH$	83	21.59	104	91	12
MTBE	$CH_3OC(CH_3)_3$	55.2	18.15	117	101	55
ETBE	$CH_3CH_2OC(CH_3)_3$	72.5	15.66	118.5	99.5	28
TAME	$(CH_3)_2CCH_3CH_2OCH_3$	86.4	15.66	112	98	17
TAEE	$(CH_3)_2CCH_3CH_2OCH_2CH_3$	101.4	13.77	105	101	14

* Research octane number (RON)/motor octane number (MON)/Reid vapor pressure (RVP)

intermediates that can be converted into many derivative products, such as alcohols and carbonic acids (e.g., propionic aldehyde and butyraldehyde are precursors of the corresponding alcohols).

By using CO and H_2, this catalytic reaction entails the net addition of a formyl group (CHO) and an hydrogen atom to the carbon-carbon double bond of the olefin under certain temperature and pressures, depending on a chosen catalyst. Mild temperatures (< 100°C) and low pressures (< 20 bara), in the presence of a (homogeneous) rhodium-based catalyst with a phosphine ligand, are often used.

A key consideration of hydroformulation is the selectivity for branched or unbranched isomers. For example, the hydroformulation of propylene can afford two isomeric products: isobutyraldehyde or n-butyraldehyde, shown in Eq. 1 and Eq. 2:

$$H_2 + CO + CH_3CH=CH_2 \rightarrow (CH_3)_2CHCHO \quad \text{(branched)} \tag{1}$$

$$H_2 + CO + CH_3CH=CH_2 \rightarrow CH_3CH_2CH_2CHO \quad \text{(unbranched)} \tag{2}$$

Unbranched aldehydes, such as n-butyraldehyde, can be used to produce unbranched alcohol (n-butanol). The branched aldehyde isobutyraldehyde acts as a precursor for rubber antioxidants, or as an intermediate of drugs.

Catalysts used in hydroformulation have been improved to realize a higher reactivity with lower olefin consumption under mild reaction conditions, and a better control of linear and branched aldehyde selectivity for diverse applications.[3] **FIG. 2** shows the possible reaction network from olefins to aldehydes and its derivative products.

The hydrogenation of oxo aldehydes to alcohols occurs in a gas or liquid phase, in a pressure range of 2 bara–30 bara, and a temperature range of 50°C–160°C on nickel or copper-based catalysts. C_4 to C_6 oxo-alcohols are used as solvents in paint and in the polymer industry, or after esterification with carboxylic acid—n-butanol plays a significant role within C_4 oxo-alcohols.

Aldol condensation is the reaction of two molecules with the same oxoaldehyde, which reacts in the presence of alkaline catalysts to the corresponding intermediate aldol. Two potential reaction paths are then possible. Through hydrogenation, the aldol can be processed into the corresponding diol (e.g., the synthesis of 2-, 2-, 4-trimethylpentane to 1-, 3-diol, based on isobutyraldehyde). As an alternative, the aldol can be processed into higher primary alcohols with the elimination of the H_2O molecule and the subsequent hydrogenation. N-butyraldehyde, which is based on propylene, is processed into 2-ethyl-2-hexenal via aldol-condensation, and further processed to 2-ethyl-hexanol via hydrogenation (Eq. 3):

$$\text{Propylene} + CO + H_2 \rightarrow \text{n-butyraldehyde} \rightarrow \\ \text{2-ethyl-2-hexenal} + H_2 \rightarrow \text{2-ethyl-hexanol} \tag{3}$$
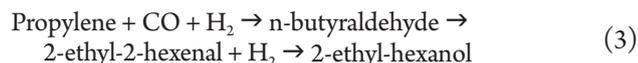
Of all higher alcohols, 2-ethyl-hexanol plays the most important role within the petrochemical industry. It is used to produce ester with di-carboxyl acids, such as phthalic acid and adipin acid. Together, 2-ethyl-hexanol and phthalic acid will form bis (2-ethylhexyl) phthalate (DEHP), which is the most common member of the class of phthalates and is used as a plasticizer.

From olefins to alcohols and derivative products (hydration).
Using direct hydration of olefins with H_2O, a corresponding secondary or tertiary alcohol-oxygenate can be produced. For example, propylene reacts with H_2O to form isopropyl alcohol (IPA), and n-butenes (1-butene and trans/cis-2-butene) react with H_2O to form sec-butyl alcohol (SBA). This direct hydration route is also applicable for the production of tert-butyl alcohol (TBA) based on isobutylene.

C_2 olefins.
Ethylene can form the basis for the production of high-purity ethanol, which can be used for certain applications (e.g. production of high-purity diethyl ether). Bioethanol is less suitable for such applications. The reaction (Eq. 4) is reversible
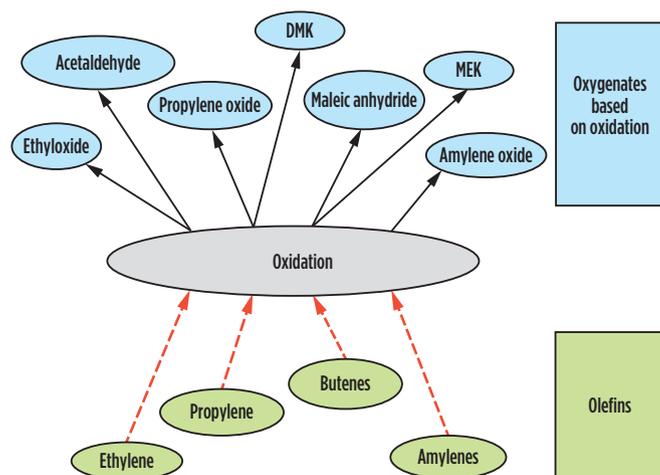

FIG. 1. Oxidation products from olefins.

TABLE 2. Oxygen sources and the corresponding processes for manufacturing oxygenate

Oxygen source	Process
Oxidation agent (O_2, hydrogen peroxide)	Oxidation
CO	Oxo synthesis (hydro-formulation)
H_2O	Hydration
Light alcohol (e.g., methanol and ethanol)	Etherification

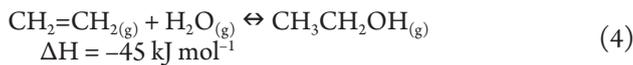**TABLE 3.** Formation of oxygenates based on olefins and oxygen carrier

Base components

Oxygen source	O_2/H_2O_2	H_2O	Alcohol	$CO + H_2$
C_2 olefin (ethylene)	EO/acetaldehyde	Ethanol	Methyl-ethyl-ether	Propion-aldehyde
C_3 olefin (propylene)	Propylene oxide	IPA	Methyl-propyl-ether	Butyr-aldehyde
C_4 olefin	Butylene oxide	SBA	MTBE/ETBE	C_5 aldehyde
C_5 olefin	Amylene oxide	Amyl-alcohols	TAME/TAEE	C_6 aldehyde

and exothermic :

$$CH_2=CH_{2(g)} + H_2O_{(g)} \leftrightarrow CH_3CH_2OH_{(g)}$$
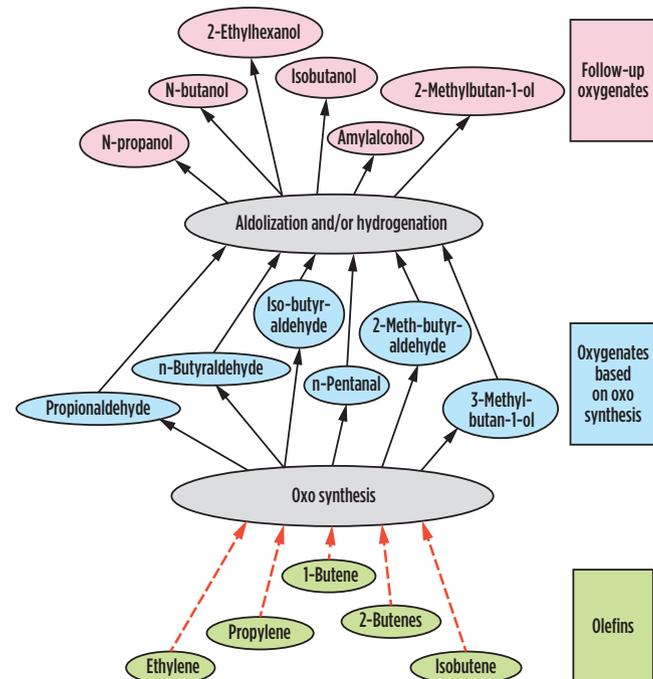$$\Delta H = -45 \text{ kJ mol}^{-1} \qquad (4)$$

Since ethylene conversion is very low (5%), a large internal reactor recycle is required for an acceptable overall yield.[4]

C$_3$ olefins. IPA is a C$_3$ olefin-based oxygenate. It can be used as a solvent, fuel additive, anti-icing additive or as raw material for derivatives. A major portion of global IPA production is used as a solvent or additive application, while a smaller portion is used as raw material for chemical derivatives, such as methyl isobutyl ketone (MIBK) or acetone.

Depending on the IPA production process, feedstocks with 90% propylene (with propane as the remainder) can be admitted directly to the reactor without additional preparation. Propylene and H$_2$O pass several catalyst beds of acidic resin in the trickle flow reactor, which is equipped with an H$_2$O quench for temperature control. About 75% of the propylene can be converted into IPA for each reaction pass. Two process designs are available: high-purity IPA and fuel-grade IPA product, which contains some on-purpose IPE as a byproduct.

C$_4$ olefins. The C$_4$ hydrocarbon cut from cracking units contains isomers such as isobutene, 1-butene, trans-2-butene, cis-2-butene, isobutane, n-butane and butadienes. Gasoline-grade tertiary-butanol (GTBA) can be produced by the reaction of isobutene with H$_2$O at a relatively low temperature. As n-butenes are not reactive at moderate temperatures, isobutene can be isolated from raffinate. N-butenes will react with H$_2$O under process conditions at higher pressures and temperatures to produce SBA. In the most modern process, SBA is produced via direct hydration of 1-, 2-butenes in the presence of a sulfonic ion exchange resin. This reaction is exothermic. Under

supercritical operation conditions (a pressure range of 50 bar–70 bar and a temperature range of 140°C–170°C), the reaction product is transported out of the reactor with the C$_4$ phase.[5]

SBA is an aliphatic alcohol in the medium boiling range with a characteristic odor, and partly miscibility with H$_2$O. While most of the SBA is used as a raw product for MEK production, approximately 10% is used directly as a solvent.

C$_5$ olefins. The hydration of pentene results in mixtures of amyl alcohols. The final product composition depends on the component composition in the feedstock stream. With feedstock consisting of primarily n-pentene, 2-pentanol can be produced by reaction with H$_2$O at an approximate temperature of 200°C and a pressure of 50 bar.

Derivatives from olefin-based alcohols. Secondary alcohols formed from olefins and H$_2$O can be further upgraded to more valuable products, such as ketones and higher alcohols, with different technologies. Technically relevant ketones are DMK (acetone), MIBK, diisobutyl ketone (DIBK) and MEK.

DMK is formed through IPA dehydrogenation. However, since DMK is available in large quantities as a coproduct of phenol from the cumene oxidation process, global IPA-based acetone production has decreased to less than 1%. The technology, originally developed for olefin-based acetone, is also applicable for acetone from other sources. Those processes are the one-step synthesis of MIBK and downstream dehydrogenation to methyl isobutyl carbinol (MIBC). More than 60% of MIBK is produced by aldol condensation of acetone and hydrogenation of the

FIG. 2. From olefins to oxo aldehydes and their derivative products.
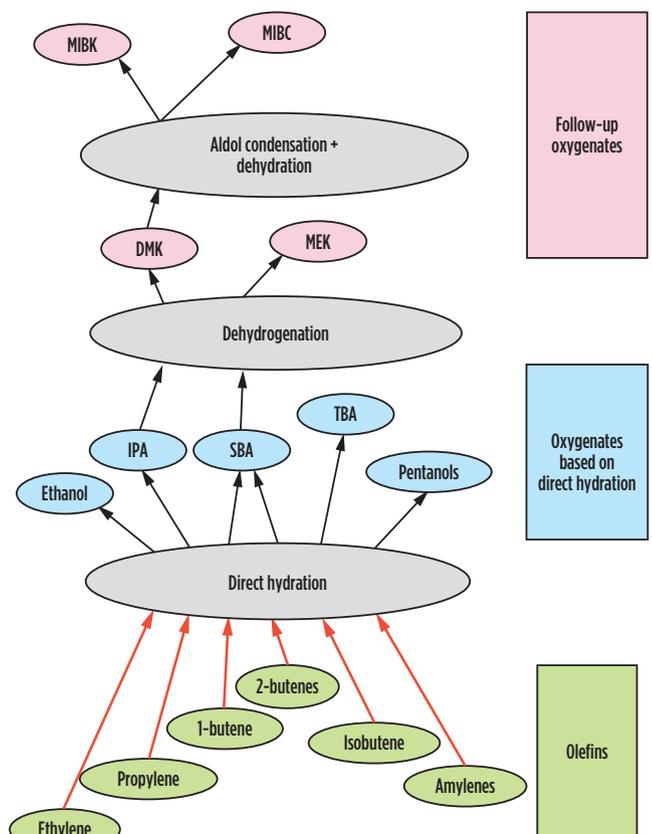
FIG. 3. Alcohols derived from olefins and their follow-up products.

intermediate mesityl oxide (**FIG. 3**). DIBK is a byproduct of MIBK synthesis, and can be applied as an extraction solvent or chemical intermediate for diisobutyl carbinol.

MIBK is primarily used as an alcohol denaturant, as solvent in cosmetic products and as an excipient in drugs. MIBC is applied in the production of lube oil additives, and for anti-wear and corrosion inhibitors. MIBC is also used as a flotation frother for treating copper ores, coal and tar sands mining.

MEK, which is formed via SBA dehydrogenation, is a colorless, stable and flammable liquid with an odor similar to that of acetone. Its exceptional solvency makes it a powerful and valuable solvent for many substances, particularly resinous materials.

From olefin to ether (etherification). Iso-olefins are used for etherification with light alcohols, such as methanol or (bio)ethanol, to produce ethers. Conventional synthesis routes exist for the production of MTBE, ETBE, TAME and TAEE, as well (**FIG. 4**).

The etherification of isobutene with alcohol is highly selective and results in high conversion rates for isobutene. The isobutene-free raffinate, containing butenes and butane, can be further processed through a butene concentration unit to get valuable feedstock for SBA synthesis.[6]

TAME and TAEE are higher analogues compared to MTBE and ETBE, which are produced by synthesis reactions of tertiary amylenes (C_5 iso-olefins) with methanol and ethanol, respectively. The corresponding ethers have slightly lower octane values, but better Reid vapor pressure (RVP) values than ethers synthesized from isobutene.[7]

> The oxygenates process value chain depends on the applied technology and feedstock availability, as well as on the market situation of the desired product, based on a balance of supply and consumption.

The synthesis section typically contains up to three reactors in plug flow mode. To avoid high temperatures in the first reactor due to exothermic reactions, a recycle is intended. High conversion rates are realized in the first two reactors. In the third reactor, a high equilibrium conversion is aimed at lower temperatures.

Etherification of higher hydrocarbons (primarily C_5 and C_6) becomes more interesting due to the high increase in ether demand, and the shortage of isobutene availability from C_4 streams. Contrary to C_4 etherification, the number of reactive olefins will increase with the carbon number during C_5 and C_6 etherification.[8]

Evaluation of the oxygenate value chain with olefin as a feedstock. Olefin-rich hydrocarbon fractions from crude oil processing are robust hydrocarbon sources for industrial application. Since these light products are often of low value for refiners, they are typically upgraded to gasoline components via alkylation or oligomerization. In contrast to these well-known classical refinery processes, the oxygenation route provides an advantageous method for the production of high-value chemicals.

The challenge for oxygenates process design is mainly the confrontation with an ever-changing market environment. **FIG. 5** shows the development of prices of several oxygenates. A clear trend can be observed due to steady market demand growth. However, the price developments of these chemicals are varied, and the final economy of the process should be studied individually.
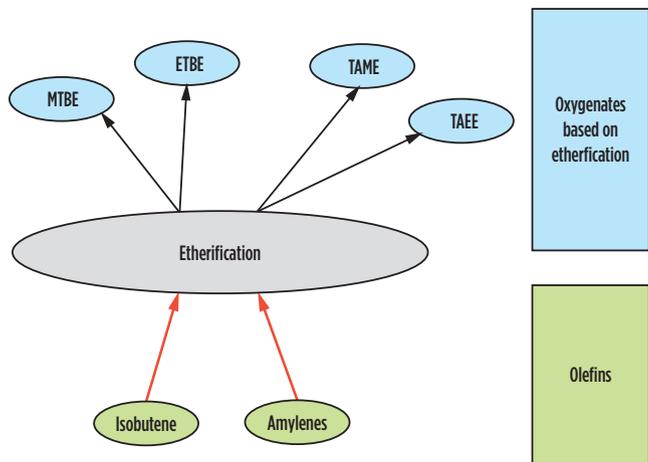

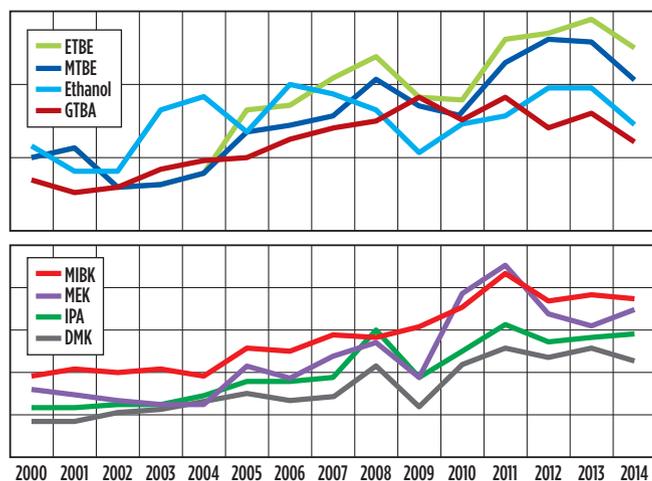**FIG. 4.** Ethers derived from olefins.

FIG. 5. Price history for selected oxygenates, 2000–2014. Source: ICIS.
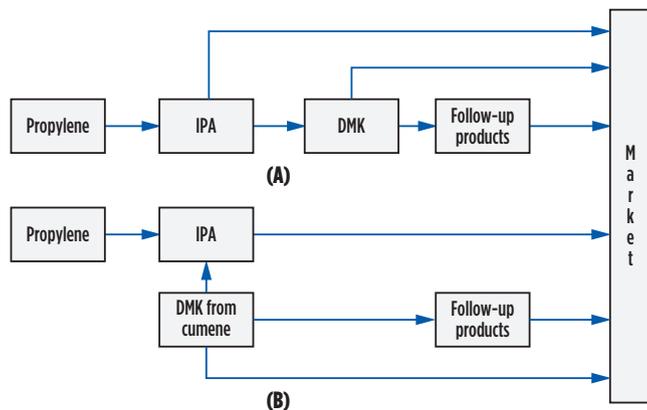

FIG. 6. Value chain of propylene-based oxygenates.

To get a sense of the volatile market and technology environment, a process route beginning with propylene will be discussed. In the past, more than 50% of DMK (acetone) was obtained via IPA dehydrogenation. A complete upgrading route of propylene-based oxygenates, including the dehydrogenation step, is shown in **FIG. 6A.**

The dehydrogenation step is now less attractive, as acetone is coproduced with phenol via the oxidation of cumene, which is produced from benzene and propylene. Due to a surplus in acetone, the route from IPA to acetone is no longer profitable as a standalone process. In contrast, IPA could be produced from acetone by hydrogenation (**FIG. 6B**).

Conversely, the relative stable price of acetone provides benefits to derivative products, such as MIBK via one-step synthesis from acetone, and MIBC as the derivative product of MIBK after dehydrogenation.

Takeaways. Oxygenates are obtained primarily by oxidation, hydration, hydroformulation (oxo synthesis) and etherification of reactive components (building blocks) derived from different feedstocks. The oxygenates process value chain depends on the applied technology and feedstock availability, as well as on the market situation of the desired product, based on a balance of supply and consumption. The oxygenate processing routes of propylene have been shown as an example of the volatility of the market, based on technology developments.

In terms of volume, the use as an octane booster in fuel is the main application of oxygenates, but it is not limited to only use as a fuel additive. Oxygenate products are widely applied in the automotive, pharmaceutical, chemical and agro industries as solvents, adhesives, plasticizers, detergents, etc.

The price of end products strongly depends on product quality and market location, as well as the overall economic situation. A deep understanding of the market and process is needed for a sensible investment decision and to maximize the overall profit. Technology licence providers must make their technology design as flexible as market requirements. HP

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