1
Olefins from Biomass

Alessandro Chieregato, Juliana Velasquez Ochoa, and Fabrizio Cavani

1.1
Introduction

The depletion of oil, the related environmental and economic concerns, together with the opportunities seen in renewable building blocks have paved the way for a significant reorganization of the chemical industry. Almost as a revival of the early twentieth century chemical industry, todays' oil refineries are in the process of being redesigned coupling petrochemical processes with bio-based productions and fermentation technologies. In this context, the invention of new (or reconsidered) processes for the synthesis of C_2–C_4 olefins from renewables is of crucial importance, since these molecules are fundamental building blocks for the chemical industry. Indeed, mainly due to a switch from naphtha to natural gas – primarily ethane – as a feedstock for steam crackers, there may be a shortage of C_3–C_5 olefins in the near future, making necessary the recourse to alternative feedstocks [1].

Light olefins are key building blocks for the production of strategic bulk chemical products; ethylene is used primarily to manufacture polyethylene, ethylene chloride, and ethylene oxide, which are used for packaging, plastic processing, construction, textiles, and so on. Propylene is used to make polypropylene, but it is also a basic product necessary for producing propylene oxide, acrylic acid, and many other derivatives; not only the plastic processing, packaging industry, and furnishing sector but the automotive industry too are users of propylene and its derivatives. Butenes, 1,3-butadiene (BD), isobutene, and isoprene are important monomers, comonomers, or intermediates for the production of synthetic rubber (mainly for tires and automobile components), lubricants, fuels, and fuel additives [2].

In this chapter the production of C_2–C_4 olefins from renewable sources is reviewed, highlighting the technologies involved, the best-performing catalysts, and the optimal engineering parameters but also discussing the reaction mechanisms. Among the viable options, particular focus is given to the more environmentally benign and sustainable routes, that is, the syntheses involving the least possible number of steps and relatively mild reaction conditions. Indeed,
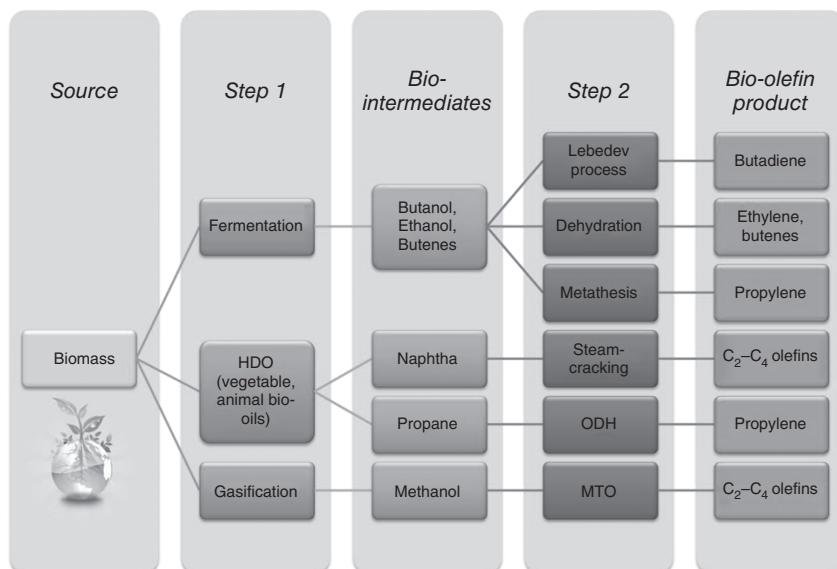
Figure 1.1 Routes from biomass to olefins.

processes such as oxidative dehydrogenation (ODH) or methanol to olefin (MTO) using methanol derived, for instance, from biosyngas produced by pyrolysis/gasification of biomass are of interest today [3]; however, they are energy-intensive processes and require several steps for the production of biochemicals.

The production of olefins from renewable sources can be carried out starting directly from the biofeedstock or certain intermediates (platform molecules) which are already available commercially, such as bioethanol and butanediols (BDOs) (Figure 1.1). In this chapter, the various routes starting from bioalcohols and that starting from bio-oils via hydrodeoxygenation (HDO) and cracking will be considered and described in detail.

1.2
Olefins from Bioalcohols

1.2.1
Ethanol to Ethylene

Bioethanol can be produced from biomass by fermentation processes; typically, engineered yeasts are used to transform C_5 and C_6 sugars into C_2 alcohol. Although this is a consolidated pathway that makes it possible to obtain high selectivity, low accumulation of by-products, high ethanol yield, and high fermentation rates [4], its economy is greatly affected by sugar production prices. A more attractive approach would be the direct use of chemically more complex biomass, such as cellulose and hemicellulose, or even lignocellulose, due to

their significantly higher availability and lower cost. Nevertheless, nowadays the technologies for the direct transformation of lignocellulosic biomass to ethanol present – with only a few reported exceptions – unsatisfactory performances for industrial applications [5]. For these reasons, so far it has been possible to put the synthesis of bioethylene from bioethanol into practice only in regions where the cost of sugars is very low, for example, in Brazil [6, 7]. In spite of these economic issues, this reaction has been the subject of a vast scientific production [8]. The ethylene market is growing continuously (US$ 1.3 billion market at 35% growth between 2006 and 2011), as is the demand for renewable polyethylene. It has been estimated that the demand for the bio-based olefin corresponds to 10% of the global polyethylene market, whereas its supply presently totals only <1% [7]. Nevertheless, the possibility of synthesizing ethylene from the steam cracking (or oxydehydrogenation (ODH)) of ethane, available at cheap prices from natural (shale) gas, might represent a significant economic obstacle for further developments of bioethylene production. A niche production of bioethylene, however, might be possible in those markets looking for small-scale volumes, that is, where full-scale crackers (using either naphtha or natural gas) would not be commercially viable. In order to meet this demand, several companies, such as BP, Total Petrochemicals, and Solvay, have been researching and have patented various technologies for the dehydration of ethanol into ethylene [9–11].

Despite the simple chemistry that one might expect from the dehydration of ethanol into ethylene, the careful tuning of the acid–base and redox properties of the catalysts used, as well as their time-on-stream stability, are mandatory requirements; however, these goals are not so straightforward to reach. Indeed, although a great number of acid catalysts can perform ethanol dehydration with selectivity and conversion >95%, only a few of them are able to resist coke deactivation for long periods of time, thus making the periodic regeneration of the catalyst compulsory [6, 8]. The problem might be solved using fluidized bed reactors that present a more uniform temperature profile (which limits the by-product formation) than fixed-bed technologies and that makes it possible to regenerate the spent catalyst under continuous conditions. Still, friction and collision problems between catalyst particles remain general issues with this kind of reactor to the advantage of the more conventional fixed-bed approach.

The first catalysts used industrially for this process were based on immobilized phosphoric acid used at temperatures as high as 500 °C; however, the significant coke formation and the high temperatures required encouraged the development of more efficient systems. Generally speaking, all the acid catalysts developed in the last decades have almost complete initial activity and ethylene selectivity [6]. For instance, in the 1980s, alumina-based catalysts were developed; among them, the SynDol® catalyst from Halcon/Scientific Design Company (Al_2O_3–MgO/SiO_2) was claimed to lead to conversion and selectivity >97% at 99% conversion, with regeneration intervals of 8–12 months [8]. This might be the catalyst currently used by India Glycols to produce bioethylene glycol through ethanol dehydration. Recently, BP has also developed new efficient catalysts based on modified tungsten-based heteropolyacids supported on
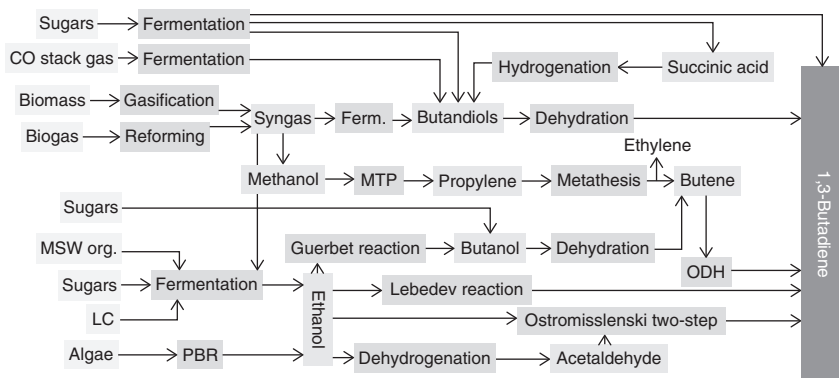
various substrates (e.g., porous silica), which operate at $180-250\,^{\circ}C$ and present very low selectivities into by-products (e.g., ethane) which are difficult to separate [11]. Many other acid catalysts, such as zeolites (e.g., ZSM-5) and SAPO, are active for ethanol dehydration at low temperature ($\sim$200 $^{\circ}C$); their relatively fast deactivation is generally considered to limit their applicability, although Solvay has recently patented the production of bioethylene using these kinds of materials as preferred catalysts [10].

As far as the reaction mechanism is concerned, ethanol dehydration is usually mentioned to be an acid–base concerted mechanism with the formation of intermediate ethoxy and hydroxy species on the catalyst surface, with consecutive water desorption as the rate-determining step (Scheme 1.1) [1, 6].

Scheme 1.1 Commonly accepted general mechanism for ethanol dehydration on solid catalysts.

However, as highlighted by the high number of papers recently published on this topic [12–17], the reaction mechanism seems to be more complicated than the general mechanism proposed with formation of intermediate ethoxide species; particularly, reaction temperature, nature of the acid–base sites, and ethanol partial pressure are fundamental variables that govern that phenomenon at the molecular level. New insights obtained into the reaction mechanism for ethanol transformation into 1-butanol (Guerbet reaction) and BD (Lebedev reaction) on oxide catalysts with basic features [18] (*vide infra*) might be extended to acid catalysts: Indeed, basic oxides such as MgO or CaO form ethylene and other by-products (e.g., acetaldehyde, hydrocarbons, methane, CO_x, H_2, etc.) that are also observed with acid systems [8]. Nevertheless, the final product distribution is clearly a function of the acid–base properties of the catalyst surface, which facilitate or hamper the different parallel and consecutive pathways that are thermodynamically possible.

1.2.2
Ethanol to Butadiene

Because of the forecasted decrease in BD production by means of the conventional naphtha cracking and extraction from C_4 fraction, as well as of the possible increase of the biosourced rubber requested by future legislation, several alternative routes are currently under investigation for the synthesis of bio-BD, starting from various renewable sources (Figure 1.2). Among these, the transformation of bioethanol into BD is the route raising the greatest expectations, also due to the fact that these technologies were already being practiced at an industrial level during the period 1930–1970s, before the advent of naphtha cracking, which made all the synthetic routes less economically convenient.

Figure 1.2 Several alternative routes investigated for the synthesis of biobutadiene.

Ethanol conversion into BD is a reaction with a very long history in the chemical industry and has encountered renewed interest within the biorefinery context today. The first accounts on this transformation date back to the beginning of the twentieth century, whereas it became an industrial process starting in the 1920–1930s [19]. From then up until the end of World War II, BD production from ethanol represented the main route for the manufacture of synthetic rubber, and the main players in this field were undoubtedly Russia (i.e., USSR) and the United States.

Although both the reaction mechanism and the catalysts' composition have always been a matter of debate since the very early stages of its history (*vide infra*), the ethanol upgrading into BD can be summarized as a dehydrogenation, dehydration, and condensation reaction (Scheme 1.2).

Scheme 1.2 Overall reaction stoichiometry from ethanol to butadiene.
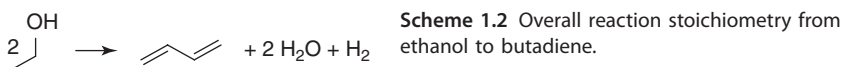
To carry out this transformation, the USSR opted for a single-step approach where ethanol was directly made to react on a multifunctional catalyst, whereas the United States found more convenience in a two-step synthesis, where the dehydrogenation step was separated from the condensation and dehydration ones. The two processes are also called the Lebedev (one-step) and Ostromisslenski (two-step) reactions, respectively, being named after their original inventors [19].

From the 1920–1940 period, the most abundant details on the kind of technology used at an industrial level can be found in the patent literature for the American two-step approach, which was operated by the Carbide and Carbon Chemicals Corporation [20]. A simplified flow sheet of the chemical plant is reported in Figure 1.3. Ethanol was dehydrogenated to acetaldehyde in a first reactor of the shell-and-tube type (R1 in Figure 1.3); the catalyst used in the first step contained copper, and the reaction was conducted at 280 °C with 10% water vapor in the inlet feed. Unconverted ethanol and reaction products such as hydrogen and acetaldehyde were sent to a preliminary separation zone 1 (SZ1) along with

some products (acetaldehyde, BD, diethyl ether, ethanol, mono-olefins, hydrogen, and saturated hydrocarbon gases) coming from the second reactor (R2). In SZ1, by means of in-series scrubbing towers, pure hydrogen was separated from all the other molecules. In the same zone of the chemical plant, a stream of light gases was vented (and likely used as industrial fuel); this stream, labeled as "gases" in Figure 1.3, was composed of a mixture of ethylene, propylene, saturated hydrocarbons, carbon dioxide, and carbon monoxide; no BD should be present in this stream since it was most likely all absorbed in the first scrubber and sent to separation zone 2 (SZ2). In the R2 of the shell-and-tube type, ethanol was made to react with acetaldehyde in a molar ratio of about 3 to 1 so as to produce BD. The catalyst used in this second step was claimed to be composed of 2.4% Ta_2O_5 on doped silica gel, operating between 300 and 350 °C, even if other kinds of silica-doped catalysts could have been applied [21, 22] (*vide infra*). The outstream from R2 was sent to SZ2 along with the BD-rich flow derived from the first scrubbing tower of the SZ1. SZ2 was composed of a distillation column and a scrubbing tower, both necessary to obtain a pure stream of BD. The bottom fractions from both rectification columns, containing water, acetaldehyde, diethyl ether, ethanol, and by-products, were collected and mixed with the bottom fractions coming from SZ1. The inlet feed of separation zone 3 (SZ3) was thus composed of a mixture containing approximately 15% acetaldehyde, 5% diethyl ether, 40% ethanol, 35% water, and 5% by-products. SZ3 was made of three distillation columns that had to separate both water and by-products from acetaldehyde and ethanol, which were recycled to both R1 and R2. The by-products withdrawn from SZ3 were composed of acetaldehyde, diethyl ether, ethyl acetate, butyraldehyde, methyl ethyl ketone (MEK), and other minor impurities. Importantly, both outstreams leaving SZ3 were not pure streams of ethanol and acetaldehyde, respectively: the acetaldehyde-rich stream was actually composed of 75% acetaldehyde, 20% diethyl ether, and 5% by-products, whereas the ethanol-rich stream was a mixture of 85% ethanol, 10% water, and 5% by-products.

It should be mentioned that during the same decade, the Carbide and Carbon Chemicals Corporation submitted other patents discussing alternative plant configurations with the aim of improving the overall process economy [20, 23]; thus, compared to the reaction scheme just discussed, some differences might have been used in the actual industrial plant. Nevertheless, these alternative configurations are only minor variations concerning the separation zones and the technology used for product recovery, which, in the end, do not alter significantly the general plant configuration as reported in Figure 1.3.

With regard to the Lebedev (one-step) process, details on the chemical plant configuration used in the USSR are more difficult to find, even if the general approach should be similar to the American technology. However, due to the lower BD purity known to be obtained through the one-step approach, one might expect a more complex separation procedure so as to finally gain the high-purity BD required for an efficient polymerization of the olefin. Nowadays, as previously mentioned, both the catalyst composition and the reaction mechanism are still an important subject of debate, whether talking about the one- or two-step

Figure 1.3 Schematic flow diagram of the two-step process for making butadiene from ethanol and acetaldehyde, as inferred from [20]. Symbols: R1: reactor to convert ethanol into acetaldehyde, R2: reactor to convert ethanol and acetaldehyde to butadiene, D: distillation column, S: scrubber, C: compressor, W: water, and V: vapor.

approach. In recent years, a number of papers and reviews have been published on ethanol transformation into BD, with particular attention to the Lebedev approach, due to the less demanding economic and engineering requirements theoretically needed by a one-pot synthesis. A very exhaustive review on both the catalyst and reaction mechanisms was published in 2014 by Sels and coworkers [24]. The catalysts for the Lebedev one-step process can be divided into three

main families: (i) doped alumina catalysts, (ii) magnesia–silica catalysts, and (iii) other catalysts. Some of the most interesting results obtained for catalysts belonging to each category are reported in Figure 1.4 and the associated Table 1.1. From there it is possible to see that most of them are in the 20–40% yield range, and only few of them overcome the 60% including the ones reported by Ohnishi *et al*. whose values were taken during the first 10 min of reaction and thus are not representative of the steady state.

As far as the Ostromisslenski two-step approach is concerned, the main difference to the Lebedev one is obviously the separation of the rate-determining dehydrogenation step (i.e., ethanol dehydrogenation into acetaldehyde) from an *in situ* reaction to a dedicated and separate unit. Provided this diversification, the remaining catalysts' features for both approaches stay the same. Acetaldehyde can be produced from ethanol with or without oxygen in the feed [19], leading to water or hydrogen as a coproduct, respectively. Some of the most efficient catalysts are summarized in Table 1.2.

The other hot topic in the conversion of ethanol into BD is undoubtedly the reaction mechanism. Although various routes have been proposed [24], the most generally accepted key step in the reaction mechanism is believed to be the aldol condensation of acetaldehyde. Remarkably, this was also supposed to be the key step for the synthesis of 1-butanol from ethanol, that is, the Guerbet synthesis. Nevertheless, since the downing of gas-phase Guerbet and Lebedev syntheses, the aldol route has often been criticized [20].

First of all, the intermediate acetaldol has never been detected among reaction products, but this detail is not sufficient for ruling out this route. Additionally, already in 1949, the engineers working for the Carbide and Carbon Chemicals Corporation published a paper in which they affirmed that if acetaldol was fed
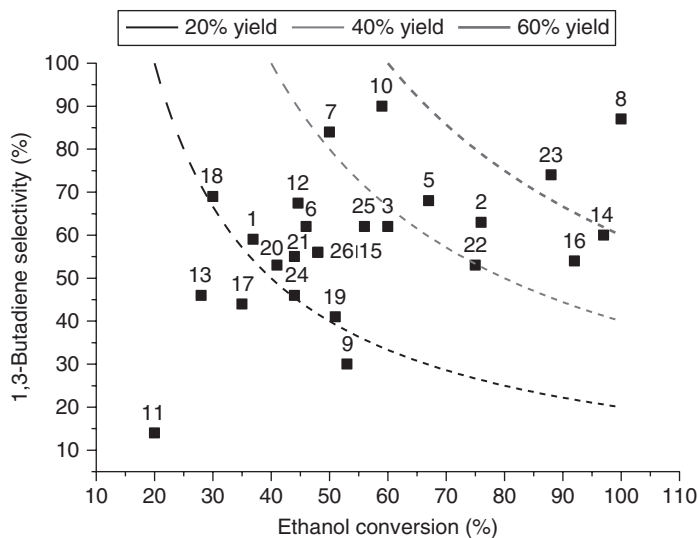
Figure 1.4 1,3-Butadiene selectivity versus ethanol conversion for representative catalysts.

Table 1.1 Active systems in the transformation of ethanol to 1,3-butadiene.

Number	Catalyst	T (°C)	Ethanol conversion (%)	1,3-BD selectivity (%)	1,3-BD yield (%)	References (year)
1	Mg/Si (2/3) wet kneading with acetic acid	380	36.9	59.0	21.8	[25] (1947)
2	$2\%Cr_2O_3 - 76\%MgO - 11\%SiO_2 - 11\%$ kaolin	435	76.0	63.0	47.9	[26] (1954)
3	$2\%Cr_2O_3 - 79\%MgO - 19\%SiO_2$	400	60.0	62.0	37.2	[27] (1960)
4	Al/Zn 6/4 (fluidized bed)	425	100.0	73.0	3.1	[28] (1963)
5	$ZnO - MgO - SiO_2 -$ kaolin	410	67.0	68.0	45.6	[29] (1966)
6	$Mg(OH)_2 +$ colloidal SiO_2	380	46.0	62.0	28.5	[30] (1972)
7	Mg/Si wet kneading 1/1	350	50.0	84.0	42.0	[31] (1985)
8	Mg/Si wet kneading 1/1 + 0.1% Na	350	100.0	87.0	87.0	[31] (1985)
9	MgO/SiO_2 (0.83:1)	350	53.0	30.0	15.9	[32] (1988)
10	$10\%NiO - 28\%MgO - 62\%SiO_2$	280	59.0	90.0	53.1	[33] (1996)
11	(Ca/P = 1.62) hydroxyapatite	350	20.0	14.0	2.8	[34] (2008)
12	$Cu(1\%)Zr(1\%)Zn(1\%)/SiO_2$	375	44.6	67.4	30.1	[35] (2011)
13	Mg/Si 2/1 mechanical mixing (with $Mg(OH)_2$)	350	28.0	46.0	12.9	[36] (2012)
14	Mg/Si 2/1 wet kneading + Cu 5%	350	97.0	60.0	58.2	[36] (2012)
15	Mg/Si 2/1 wet kneading + Cu 5%	350	46.6	56.0	26.1	[36] (2012)
16	$4\%Ag - 55\%MgO - 41\%SiO_2$	400	92.0	54.0	49.7	[36] (2012)
17	Mg/Si 3/1	325	35.0	44.0	15.4	[37] (2014)
18	Mg/Si 95/5 + Zr 1.5% + Zn 0.5%	325	30.0	69.0	20.7	[37] (2014)
19	Mg/Si 1/1 + Zr 1.5% + Zn 0.5%	325	51.0	41.0	20.9	[37] (2014)
20	Al and Zn nitrate impregnated on γ-Al_2O_3	400	41.0	53.0	21.7	[38] (2014)
21	Al and Zn nitrate impregnated on γ-Al_2O_3 + H_2O_2 in the feed	395	44.0	55.0	24.2	[38] (2014)
22	$CuO/SiO_2 - MgO$	425	75.0	53.0	39.8	[39] (2014)
23	$Ag/ZrO_2/SiO_2$	314	88.0	74.0	65.1	[40] (2014)
24	$1.0Ag/MgO - SiO_2$	400	44.0	46.0	20.2	[41] (2015)
25	$4\%ZnO/MgO - SiO_2(1:1)$	375	56.0	62.0	34.7	[42] (2015)
26	Ag/ZrBEA	327	48.0	56.0	26.9	[43] (2015)

Table 1.2 Catalysts for the conversion of ethanol into acetaldehyde.

Catalyst[a]	T (°C)	EtOH conversion (%)	C₂H₄O selectivity (%)	References
0.2%Au−0.2%Cu/SiO₂ (yes)	250	100	100	[44]
Au(6.7)/MCM-41 (yes)	200	20	90	[45]
5% WO₃−95% V₂O₅ (yes)	280	48	98	[46]
5.75 wt%Cu supported on rice husk ash (no)	275	80	100	[47]
Au(4.9)/SBA-15 and Au(5.8)/SBA-16 (no)	350	95	90−100	[45]

a) In parenthesis the presence or not of oxygen in the feed.

on the industrial catalyst to make BD, it was reversed to acetaldehyde and not dehydrated to crotonaldehyde, thus making clear that acetaldol cannot be the key intermediate for the production of BD from ethanol [48]. More recently, Meunier and coworkers [49] also definitively ruled out acetaldehyde self-aldolization as a main reaction pathway for the gas-phase transformation of ethanol into 1-butanol over hydroxyapatite, that is, the best catalysts so far reported in literature for this reaction. Therefore, neither the Lebedev nor the gas-phase Guerbet synthesis can have acetaldol as the key reaction intermediate, as summarized in Scheme 1.3.
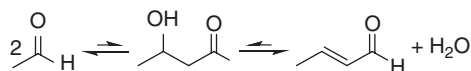
Scheme 1.3 Under the reaction conditions used for the gas-phase Lebedev and Guerbet processes, acetaldol is mainly reversed to acetaldehyde and not upgraded to crotonaldehyde.

Once the thermodynamically hampered aldol condensation is ruled out, the formation of C₄ compounds from ethanol in the gas phase must go through alternative pathways. Very recently an unconventional route has been proposed that avoids aldol condensation and does not require the Meerwein−Ponndorf−Verley (MPV) reaction to justify the formation of the aforementioned products, at least on basic oxide catalysts [18]. By means of a multifaceted approach using catalytic tests, DRIFTS analyses, and thermodynamic and Density Functional Theory (DFT) calculations, it was possible to assign a carbanionic species of ethanol as the common key intermediate for the formation of C₄ products (and ethylene [*vide supra*]). Once this species is formed, the carbanion can (i) dehydrate to form ethylene, (ii) react with another molecule of ethanol, or (iii) react with a molecule of acetaldehyde previously produced by ethanol dehydrogenation (either *in situ*, e.g., by reduced metals, or separately with a dedicated catalyst). In the first case, 1-butanol is directly produced from two molecules of ethanol as a primary product, without the need for acetaldehyde. In the latter case, the reaction of the C₂ carbanion with an adsorbed molecule of acetaldehyde determines the formation of an adsorbed intermediate similar

to 1,3-butandiol, which desorbs in the gas phase as crotyl alcohol. The latter can be finally dehydrated into BD, thanks to the high temperature of the Lebedev process (300–450 °C) and/or the acid sites always present in typical Lebedev catalysts. The overall reaction mechanism proposed is shown in Scheme 1.4.
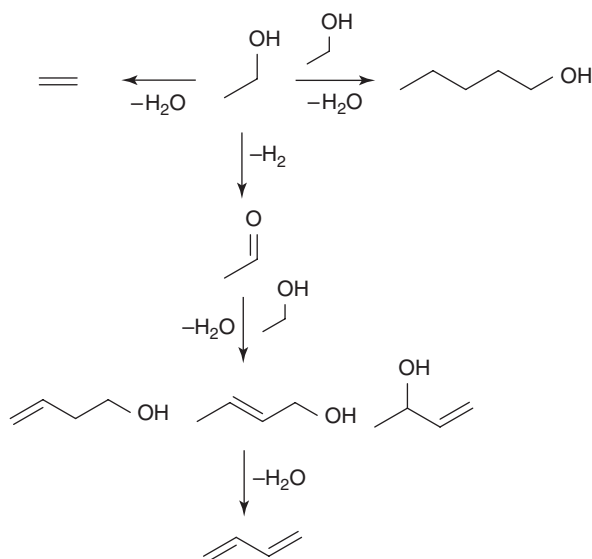
Scheme 1.4 General reaction network for the Lebedev and Guerbet processes in the gas phase on oxide catalysts with basic features. (Adapted from [18].)

Isobutene has also been recently demonstrated to be obtainable directly from ethanol [50, 51]. Nanosized Zn–Zr mixed oxides showed selectivity up to 83% at complete ethanol conversion (reaction temperature 450 °C).

Lastly, ethanol can be also converted into propylene on single multifunctional catalysts, mainly by the dimerization of intermediately formed ethylene (via acid-catalyzed dehydration) and subsequent metathesis of the resulting butenes with unreacted ethylene. Sc/In_2O_3 allowed obtaining propylene yields up to 62% at total ethanol conversion, if hydrogen and water were co-fed with ethanol at 550 °C [52].

1.2.3
C$_3$ Alcohols to Olefins

As far as the synthesis of C_3 olefins and particularly propylene is concerned, dehydration of C_3 alcohols might be an interesting option. Although in principle various alcohols could be used as raw materials, only a few of them are actually economically viable solutions. Indeed, at least so far, the prices of many C_3 alcohols are higher than or comparable to that of propylene. However, an attractive and sustainable route might be the transformation of glycerol to olefin (GTO) and, particularly, to propylene, in great demand. Indeed, glycerol is produced worldwide in massive amounts as a coproduct of biodiesel synthesis, and it is

currently more of a burden to treat as a waste than an economic opportunity enhancing the value of the whole biofuel production chain. Several chemicals and/or biological routes have been proposed in literature to upgrade glycerol into valuable molecules, although only few of them may be economically and technically viable for commercial application [5]. Nevertheless, the conversion of this polyol to olefins might both improve the supply for short-chain olefins and add economic value to biodiesel production.

GTO is a relatively new field of research, with only a few examples in literature and satisfactory catalytic results reported [53]. Indeed, the removal of three atoms of oxygen from such a highly hydrophilic molecule is a difficult task. One of the first reports published in literature on this topic [54] used a fluid catalytic cracking (FCC) approach, in which glycerol was made to react in a microdowner and in fixed microactivity test reactors using zeolites as catalysts. In spite of the high temperatures used ($290-720\,^{\circ}$C), C_3 and C_2 oxygenated species were always the main products, mainly as acrolein and acetaldehyde. Moreover, carbon monoxide also formed in large quantities at high temperatures (selectivity up to 51%), along with a wide range of by-products. Nevertheless, at temperatures higher than $500\,^{\circ}$C, C_2-C_4 olefins formed in considerable amounts along with methane, ethane, and higher hydrocarbons. At $700\,^{\circ}$C, ethylene selectivity was 21.8% whereas that of propylene was 7.8%. More recently, other groups have investigated metal-modified zeolites for analogous FCC–GTO [55, 56]; however the yields in light olefin have never reached 20%.

Recently, both in patent and open literatures, alternative processes to the direct cracking approach have been proposed in order to convert glycerol into light olefins. Schmidt and coworkers [57] reported a three-step conversion of glycerol into (i) acrolein, (ii) propanal, and (iii) propylene + ethylene. Both the first and last steps used zeolites (HZSM-5 and HBEA) as dehydration and deoxygenation (i.e., cracking) catalysts, respectively, whereas Pd/α-Al$_2$O$_3$ was used for the hydrogenation step.

In defiance of the direct cracking of glycerol previously discussed, the cracking of the intermediately formed propanal makes it possible to obtain much higher yields into light olefins at relatively low temperatures ($400-500\,^{\circ}$C); at 86% conversion of propanal, fed as pure compound in a preliminary catalytic test, some yields to ethylene and propylene as high as 70% were registered. However, the fast deactivation of the HBEA was observed. Another approach for the production of propylene from glycerol was also proposed by Cao and coworkers [58]; the polyol was first hydrodeoxygenated to *n*-propanol and finally dehydrated to propene. Working in a continuous flow reactor with two in-series catalytic beds, that is, Ir/ZrO$_2$ and HZSM-5-30, under optimized working conditions ($250\,^{\circ}$C, P H$_2$ = 1 MPa), propylene selectivity as high as 85% at total glycerol conversion was achieved.

Lastly, an interesting and original approach for the direct conversion of glycerol into propylene has recently been patented by Dow Global Technologies [59]. In this case, glycerol is made to react in a batch reactor with hydroiodic acid (HI) (HI-to-glycerol ratio $\sim$1:10) at $210\,^{\circ}$C under mild hydrogen pressure ($\sim$4 bar). Selectivity to propylene as high as 96% at 24% glycerol conversion is claimed after

a 6 h reaction. During the process, HI is oxidized to I_2, and in order to act as a catalyst, it must be reduced back to HI by the molecular hydrogen present in the reaction media.

Overall, the economic sense of such processes must be seriously evaluated not only in terms of viability of these multistep approaches but also in terms of product prices: added-value molecules such as acrolein, propanal, and 1-propanol are transformed into propylene which has a lower price. For instance, compared on molar bases, the price of 1-propanol is around 20 ctUSD/mol while that of propylene is still approximately 7 ctUSD/mol.

1.2.4
C$_4$ Alcohols to Olefins

A number of C_4 alcohols/diols can be used to produce olefins. Among alcohols, *n*-butanol is a valuable choice. It can be synthesized through both chemical and biotechnological processes. Among chemical processes, propene hydroformylation (also called *oxo-synthesis*) [60] is the preferred route today at an industrial level, and theoretically, it could also be applied to produce biobutanol from biopropylene and biosyngas. However, a less energy-intensive and more direct synthesis would be highly desirable, especially for small-size/on-purpose plants. Until the mid-1950s, *n*-butanol was synthesized by acetaldehyde aldol condensation followed by hydrogenation; thus this process could be used to produce biobutanol using the dehydrogenation of bioethanol as a route to bioacetaldehyde.

More conveniently, bioethanol could be directly transformed into *n*-butanol through the Guerbet process. The latter is an established chemical route mainly followed for the production of highly branched and saturated alcohols through the condensation of two primary alcohols. The higher alcohols produced are important intermediates for the synthesis of surfactants [61]; however, of great interest would also be the formation of short-chain C_4 alcohols, particularly *n*-butanol, to be used both as fuels and as chemical building blocks. Several catalysts have been reported in literature for the conversion of ethanol into butanol, and the most representative ones are listed in Table 1.3. MgO is generally recognized as a reference material for this reaction, mainly due to its simplicity and reproducibility; selectivity of about 30–35% can be obtained in the gas phase at low ethanol conversions (~10%) [18]. However, more efficient catalysts have been reported in the last decade; selectivities up to 75% and 85% can be reached for gas-phase [66] and liquid-phase processes [69], respectively. In the first case, basic oxides (e.g., MgO, hydroxyapatites, or hydrotalcites) may be used as catalysts to carry out the reaction, continuously, at atmospheric pressure and temperatures of 200–400 °C. Conversely, for the liquid process, Ru complexes make it possible to obtain much higher ethanol conversions (up to 45% vs. ~15% for the gas-phase route) with high *n*-butanol selectivities; the process, however, is discontinuous and requires long reaction times to achieve high conversions.

As previously discussed for the synthesis of BD from ethanol, the mechanism for the formation of the C–C bond in the gas-phase process is still controversial.

Table 1.3 Catalytic systems for the conversion of ethanol into *n*-butanol.

Catalyst[a]	T (°C)	EtOH conversion (%)	1-BuOH selectivity (%)	References
MgO	250	10	35	[18]
CuMgAlO (5:1:3)	260	9	80	[62]
MgAlO (3:1)	350	35	37	[63]
MgAlO (3:1)	350	23	17	[64]
MgFeO (2.9:1.1)	380	60	16	[65]
CaPO (1.64:1)	300	15	75	[66]
SrPO (1.7:1)	300	11	86	[67]
20.7% Ni/Al$_2$O$_3$[b]	250	25	80	[68]
trans-[RuCl$_2$(3)$_2$][b]	150	45	85	[69]

a) The atomic ratio between metals is shown in parenthesis.
b) Liquid-phase process.

Although aldol condensation is still generally mentioned as the key step, it is worthy of note that the best-performing catalyst, that is, hydroxyapatite, has significantly fewer dehydrogenation features than transition metal oxide-based catalysts. Indeed, Kozlowski and Davis [61] have stressed that the dehydrogenation rate of copper-containing material published by Gines and Iglesia [70] was about 370 times greater than that of hydroxyapatite with a Ca/P ratio of 1.67 [34]. Considering the fundamental role of acetaldehyde formation in the aldol scheme and the lower overall *n*-butanol formation on the Cu-containing oxide than on hydroxyapatite, it seems likely that acetaldehyde (and therefore aldol condensation) is not the key step for producing *n*-butanol from ethanol in the gas phase. This is a remarkable observation that supports the recent hypothesis that two molecules of ethanol react together directly through a carbanionic intermediate to form *n*-butanol as a primary product [18].

n-Butanol, as well as other valuable alcohols and diols, can also be produced directly by fermentation processes. One of the oldest technologies is the acetone/butanol/ethanol (ABE) process in which these molecules are produced using genetically modified bacteria for the fermentation of carbohydrates; however, due to low productivity and difficult product separation, its economy is not sustainable when compared to petrochemical routes, at least with current oil prices. The biological synthesis of C$_4$ diols seems to be more promising, and a number of companies such as LanzaTech, Versalis/Genomatica, Genecor/Goodyear, and Global Bioenergies are developing their own biochemical routes to BDOs [1].

Whether the bio-C$_4$ alcohols/diols are obtained from direct or indirect (bio-) chemical routes, they can be either used as such or finally dehydrated into olefins. *n*-Butanol can be easily and efficiently dehydrated into 1-butene, with a mechanism analogous to ethanol dehydration, by using low-to-medium-strength acid catalysts; however, it can also be upgraded to nonlinear C$_4$ olefins as a one-pot reaction. To do so, strong acid catalysts and higher reaction temperatures must be used so as to combine the dehydration step with skeletal isomerization. Zeolite catalysts such as Theta-1 and ZSM-23 gave high yields of isobutene (~60%)

and stable catalytic behavior [131]. In 2009, BP also filed a patent to skeletally isomerize *n*-butanol into linear and nonlinear hydrocarbons (mainly isobutene) on acid zeolite catalysts with unidirectional, nonintersecting channels [71].

The double dehydration of several BDOs can lead to the formation of BD, although its formation is often associated with several monodehydrated by-products, particularly unsaturated alcohols (alkenols). Among BDOs, 1,3-BDO is one of the most promising intermediates for the production of BD; for instance, on $SiO_2-Al_2O_3$ catalysts, BD is produced directly with selectivity up to 36%, but unsaturated alcohols are also major products (e.g., 3-buten-1-ol) [72, 73]. BD yields as high as 90% were claimed to be obtained in old patent literature through 1,3-BDO dehydration on doped phosphoric acid heterogeneous catalysts [24].

Theoretically, 1,4-BDO dehydration would be another option for producing BD; however, the monodehydration forms tetrahydrofuran (THF) – as the main reaction product, and the following deoxygenation of furan is very difficult. Nevertheless, the reaction is possible, and recycling the unreacted THF to the reactor has made it possible to obtain BD yields up to 95% [74]. Recent results show an easier and more promising BD formation if 2,3-BDO is used as the starting reagent [75], which can be produced via glucose fermentation. Scandium oxide (Sc_2O_3) calcined at high temperature (800 °C) showed BD yields as high as 88% at 411 °C, when H_2 was used as the carrier gas. Also, if a first catalytic bed of Sc_2O_3 was coupled with a consecutive bed of alumina (in the same reactor), a stable 94% BD selectivity was obtained; indeed, the intermediately formed 1-buten-3-ol was more efficiently dehydrated into BD. These results are a considerable step forward toward the direct double dehydration of 2,3-BDO, since in previous literature mainly monodehydration occurred and formed unsaturated alcohols or MEK [76, 77]. An alternative way to produce BD from BDOs is a two-step approach in which each hydroxyl group is eliminated using two different catalysts. For instance, various examples have been reported by Sato *et al.* [76] (and references therein) for the selective dehydration of BDOs into unsaturated alcohols. A summary of the best results obtained is shown in Table 1.4.

Table 1.4 Catalytic systems used for (butane)diol(s) dehydration.

Catalyst	BDO[a]	T (°C)	Conversion (%)	Selectivity (%)[a]	References
$SiO_2-Al_2O_3$	1.3	250	74	36 (BD); 28 (3B1OL)	[73]
Supported H_3PO_4	1.4	380	100	95 (BD)[b]	[74]
Sc_2O_3	2.3	411	100	88 (BD)	[75]
CeO_2	1.3	325	43.9	58.1 (3B2OL); 41.1 (2B1OL)	[78]
CeO_2	1.3	325	82.2	60.0 (3B2OL); 36.5 (2B1OL)	[79]
CeO_2	1.4	400	40.5	69.4 (3B1OL); 8.5 (2B1OL)	[80]
ZrO_2	1.4	350	86.4	48.0 (3B1OL); 44.9 (THF)	[81]
1.5 $Na-ZrO_2$	1.4	325	18.7	71.8 (3B1OL); 20.8 (THF)	[82]

a) BDO: butanediol; 3B2OL: 3-buten-2-ol; 2B1OL: 2-buten-1-ol; 3B1OL: 3-buten-1-ol; and THF: tetrahydrofuran.
b) Recycling the intermediately formed THF to the reactor.

Considering the efficient production of unsaturated alcohols from BDOs, the former can be dehydrated into BD on silica- and/or alumina-based catalysts.

Lastly, some patents have also been recently filed concerning the dehydration of BDOs for the production of olefins, particularly BD [83–85]. Rare earth (mixed) phosphate and hydroxyapatite–alumina catalysts are claimed to lead to high BD yields and diol conversions as well as to long-term stability.

1.3
Alternative Routes to Bio-Olefins

1.3.1
Catalytic Cracking

The catalytic cracking of low-value fats, greases, oils, and other renewable sources is one of the most potentially useful methods to obtain olefins from bio-oil upgrading. There are two types of process: Fluid catalytic cracking (FCC) and steam cracking. The former has already been studied for the transformation of vegetable oils (or their blend with vacuum gas oil) into a mixture of gasoline and cracking gas containing propylene [86]. However, the main products in FCC are liquid fuels. On the other hand, steam cracking might be more suitable for obtaining olefins. This process involves two separate steps: (i) Hydrodeoxygenation (HDO) to remove oxygen content from triglycerides and fatty acids in the feedstock – to obtain hydrocarbon chains in the diesel range and renewable naphtha and (ii) cracking of the naphtha to obtain olefins and some gasoline. The advantage of this approach is that existing conversion and production units can be used, thus eliminating the cost of building new "on-purpose" facilities [87]. A simplified diagram of the integrated process is presented in Figure 1.5.

Step 1: The first step of the process (HDO) is usually carried out using traditional hydrotreating catalysts such as $(Ni)Co-MoS_2/Al_2O_3$. This process includes the treatment of the feedstock at moderate temperatures (280–400 °C) and high hydrogen pressure (20–300 bar): this hydrogen should be preferentially produced with renewable energy sources (by steam reforming of ethanol, e.g., but preferably from water thermolysis and photolysis using solar energy) [88].

The problem of using transition metal sulfided catalysts for the HDO of bio-oils is that they might deactivate during a prolonged operation time due to sulfur stripping and surface oxidation caused by the low content of this heteroatom in the biofeedstock compared to fossil fuel oils. One suggested alternative for avoiding this problem is the co-feeding of H_2S to the system in order to regenerate the sulfide sites. The use of H_2S, however, also has some drawbacks, such as the formation of sulfur-containing products, and also the fact that H_2S could block the adsorption over active sites [89].

Alternative catalytic systems for this first step include noble metals like Pd, Pt, Ru, Rh, or even Ni and Co supported on C, ZrO_2, SiO_2, MgO, or zeolites (Al_2O_3 has been shown to catalyze coke deposition). Transition metal carbides, nitrides,
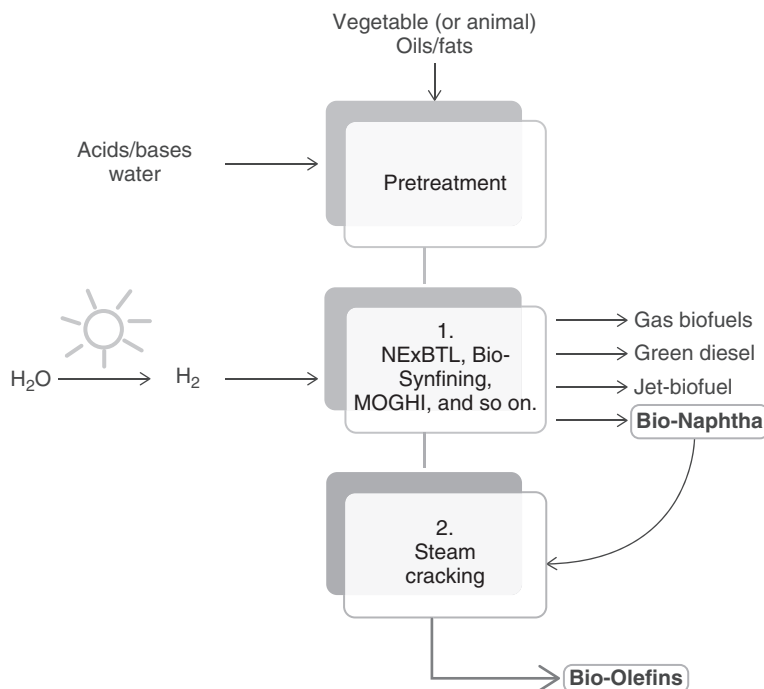
Figure 1.5 Two-step process for biomass/oil upgrading.

and phosphides have also shown promising performances in the HDO of bio-oils (or model compounds) [90]. All these catalytic systems feature advantages and challenges that require further investigation in order to develop more efficient processes. For instance, the know-how in sulfided catalyst synthesis and commercialization held by many large industries makes it worthwhile to continue investigating these materials. On the other hand, noble metal catalysts have the ability to activate H_2 under low-pressure conditions and, moreover, can operate in acidic or aqueous environments.

With regard to the mechanism involved, HDO of biomass entails a complex reaction network that includes decarbonylation, decarboxylation, hydrocracking, hydrogenolysis, and hydrogenation. When using transition metal sulfides, the pathway suggested resembles that for conventional oil HDO; oxygen from the biomolecule adsorbs on a vacancy of the MoS_2 matrix. Simultaneously, the H_2 from the feed dissociatively adsorbs on the catalyst surface, forming $S-H$ (and $Mo-H$) species. The addition of a proton to the adsorbed oxygenated molecule and the elimination of water produce the deoxygenated product [89]. In this type of catalyst, Mo serves as an active element, while Co and Ni act as promoters [91].

The HDO is a process with high carbon efficiency and therefore a high production potential [88]. There are industrial processes such as Bio-Synfining, property

of Syntroleum Corporation, currently available which are able to transform vegetable or animal oils, fats, and greases into renewable synthetic fuels that include diesel, naphtha, and propane. The renewable distillate produced from a plant could be separated into its components and then be used for more profitable applications such as olefin production. In fact, they have already patented the specific process aimed at maximizing naphtha production [92].
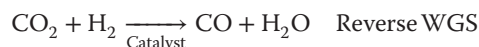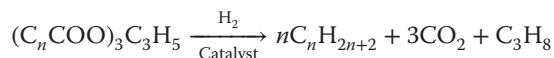
Another company having a similar technology is Neste Oil. Branded as NExBTL, this process uses tallow to produce fuels, mainly in the diesel range, but it produces also jet fuel, propane, and renewable naphtha which, as in the former case, could be hydrocracked to obtain olefins. Further competitors/producers of biofuels (including bio-naphtha) from biomass (or waste) include Total Petrochemicals [93], Biochemtex (MOGHI process), Eni/Honeywell UOP (Ecofining), Solena fuels (GreenSky), Rentech, the Energy and Environmental Research Center (EERC) in collaboration with the refiner Tesoro, Finland's UPM, and the Renewable Energy Group (REG) that recently acquired Syntroleum. On the other hand, Sasol and Shell have developed biomethane routes to obtain bionaphtha.

The three main reactions that occur during the first step are:

HDO:

$$(C_nCOO)_3C_3H_5 \xrightarrow[\text{Catalyst}]{H_2} nC_{n+1}H_{2n+4} + 6H_2O + C_3H_8$$

Decarboxylation:

$$(C_nCOO)_3C_3H_5 \xrightarrow[\text{Catalyst}]{H_2} nC_nH_{2n+2} + 3CO_2 + C_3H_8$$

$$CO_2 + H_2 \xrightarrow[\text{Catalyst}]{} CO + H_2O \quad \text{Reverse WGS}$$

Isomerization:

$$n\text{-}C_{n+1}H_{2n+4} + n\text{-}C_nH_{2n+2} \xrightarrow[\text{Catalyst}]{} i\text{-}C_{n+1}H_{2n+4} + i\text{-}C_nH_{2n+2}$$
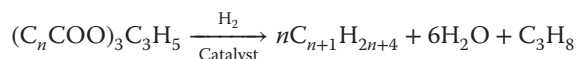
During this step, both the reaction temperature and the type of catalyst determine the products distribution. A severe hydrotreatment would lead to a high production of naphtha (C_5–C_{10}), whereas mild hydrotreatment conditions promote the production of green diesel.

Step 2: Once the renewable naphtha is obtained, the steam cracking step yields olefins and other compounds such as hydrogen, methane, ethylene, and aromatics (the latter in a lower content since the bionaphtha is expected to be highly paraffinic). However in this case, also, the exact composition of the outlet stream depends on several factors. Generally, propylene production is higher when using mild reaction conditions, whereas the yield to ethylene and aromatics increases at higher temperatures. In general, the process is carried out at atmospheric pressure and at temperatures of around 800 °C with approximately 0.2–1.0 kg of steam per kilogram of feedstock.

Studies on a pilot plant scale of the complete process (HDO and steam cracking) have already been performed using wood-derived tall oil [94] or a bio-oil blend (mainly fat and grease from prepared foods) [95], achieving olefin yields of over 50%; these yields were higher than those obtained by cracking fossil-based naphtha under similar conditions. Moreover, other advantages were the lower optimum temperature needed to maximize light olefins (entailing less energy input and fewer by-products such as pyrolysis fuel and gasoline) and lesser coke formation that occurs in longer length runs.

There are also related approaches such as the direct cracking of the bio-oil. For instance, Gong *et al*. [96] proposed the use of a modified La−HZSM-5 which, under optimized conditions (600 °C, 6%La, and weight hourly space velocity (WHSV) of $0.4\,h^{-1}$), produced $0.28\,kg_{olefins}\,kg_{bio-oil}^{-1}$. The same group also studied the production of olefins by mixing the catalyst (La−HZSM-5) and the dry biomass directly, thus obtaining $0.12\,kg_{olefins}\,kg_{dry\ biomass}^{-1}$ when using sugarcane [97].

In order to obtain higher yields of olefins by HDO + steam cracking, the key points which need further research and development are:

- Limiting the coke formation during the HDO step: the high amount of cyclic (and aromatic) products formed affects the catalyst lifetime considerably and make extremely high H_2 pressure necessary to attain better results. Up to now, lifetimes of much more than 200 h have not been achieved with any current catalyst due to carbon deposition [88].
- The control of the reaction heat in the HDO: this is extremely important since the highly exothermic nature of the reactions involved may cause unwanted side reactions, such as cracking, polymerization, ketonization, cyclization, aromatization, and coking of the catalyst.
- For steam cracking, there is a higher formation of CO_x, probably due to the absence of sulfur on the feedstock which, in the case of fossil fuel-based feedstock, is present and interacts with Ni in reactor walls, avoiding oxidation. Thus further studies of the interaction of S-free feedstock with industrial catalysts and the reactor are necessary.

In conclusion, the understanding of these mechanisms and the subsequent optimization of operating conditions and catalysts are still needed for the HDO and steam reforming of renewables, in order to bring them to an industrial-scale usage. Nevertheless, if this can be achieved, CO_2-neutral fuels can be produced via biomass transformation in a sustainable manner.

1.3.2
Metathesis

The metathesis reaction involves the exchange of a bond (or bonds) between similar species so that the bonding associations in products are similar to those in reactants. In the case of olefins, it can be used to produce propylene from more abundant (or cheaper) alkenes such as ethylene and butenes (see Scheme 1.5).
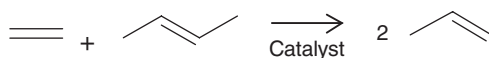
Scheme 1.5 Ethylene and 2-butene metathesis to produce propylene.

This kind of process is not new, but its "greener" version is still being researched. There are two approaches for carrying out such a process: (i) dimerization of the bioethylene produced by the dehydration of bioethanol and the reaction of the obtained butenes with the remaining ethylene and (ii) directly reacting biobutene (produced from biobutanol dehydration) and bioethylene.

The dimerization of ethylene is a technology that is already available. It is generally carried out under mild to moderate conditions ($0-100\,°C$ and $50-300\,$psig) [98]. Common metals in dimerization catalysts are Ti and Ni. Axens' *AlphaButol* is a commercial example of such a method.

Figure 1.6 shows a simplified flow diagram of the second type of process (similar to Lummus' Olefin Conversion Technology (*OCT*)). Here fresh and recycled biobutene streams are mixed with bioethylene and its recycled part. Reagents are sent first into a guard bed (GB) to remove all traces of impurities. Afterwards, the feed is heated before entering the reactor (R1), where the metathesis reaction occurs. Lastly comes the separation step (S) which is generally performed by distillation.

Catalytic systems for this process can be either homogeneous or heterogeneous. The homogeneous ones are usually in the form of organometallic complexes. However, heterogeneous systems are preferred due to their easier handling and low separation problems. Typical solid catalysts for olefin metathesis consist of a group VI A or VII A metal oxide (such as W, Mo, or Re oxides) supported on silica or alumina. Tungsten-based catalysts work at relative higher reaction temperature ($>300\,°C$) to obtain the equilibrium conversion [99–103]. The OCT process by
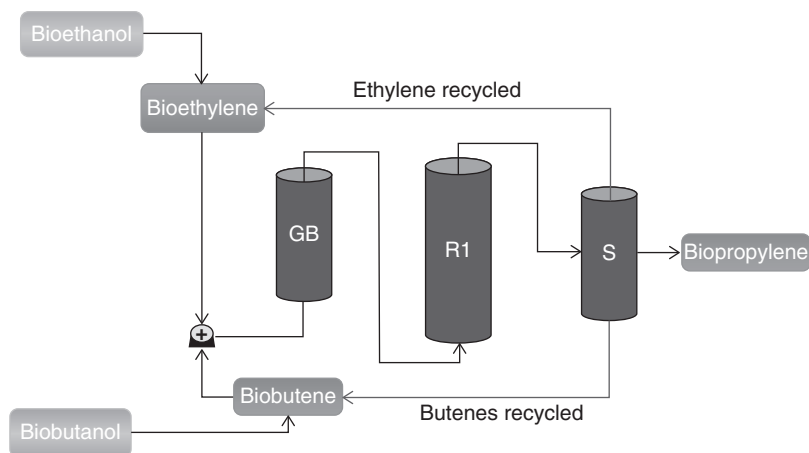

Figure 1.6 Bio-olefin metathesis flow diagram. GB: guard bed, R: isomerization/metathesis reactor, and S: separation unit.

ABB Lummus Global, for instance, is based on WO_3/SiO_2 as the metathesis catalyst and takes place in a fixed-bed reactor at T >260 °C and 30 – 35 bar. The conversion of butene is above 60% per pass, and the selectivity to propene is >90% [104]. However, the modification of the support (using zeolites) and thus the acidity and degree of reduction of W have been shown to promote the metathesis activity at lower reaction temperatures (~180 °C) for WO_3 catalysts [105]. Recently, W directly incorporated into mesoporous frameworks has shown a potential for this reaction, by making the isolation of the active sites possible [106, 107].

On the other hand, Re oxide catalysts operate at milder conditions and usually have a selectivity close to 100%; their drawback, however, is the fast deactivation (even by H_2O traces), which makes necessary an intensive feed pretreatment and constant catalyst regeneration [108]. Re_2O_7/Al_2O_3 was the catalyst chosen for the *Meta-4* process for propylene production which was developed by the Institut Français du Pétrole (IFP) and the Chinese Petroleum Corporation (Taiwan). However, due to the high cost of the catalyst and the deactivation issue, today this process is not being commercialized. A further disadvantage of Re-based catalysts is linked to the volatility of Re_2O_7 – which sublimates at 262 °C – which may lead to the loss of rhenium during the synthesis of the catalyst (calcination).

As for Mo oxide catalysts, they are recently receiving much attention [109 – 112], since they offer a good compromise between activity and robustness, while they are already used at an industrial scale in the Shell higher olefin process (*SHOP*) for the production of linear alpha olefins via ethylene oligomerization and olefin metathesis [113]. One advantage of the metathesis process is that it does not produce propane, thus making it unnecessary to install a P – P splitter (which is typically used in steam crackers and FCC units) and consequently reducing the investment cost.

Regarding the feed, it is generally observed that the reactions of isobutene or 1-butene with ethylene are nonproductive. Therefore it is common to use a double-bond isomerization catalyst (Mg, Ca, or Ba oxide) directly mixed with the metathesis catalyst in order to obtain the more reactive 2-butene [114]. However, if the available (bio-) source is rich in isobutene, the skeletal isomerization to obtain *n*-butene might require a separate step such as catalytic distillation (*CDIsis* technology, also licensed by ABB Lummus). The ethylene-to-butene ratio fed to the reactor must be controlled in order to minimize C_{5+} olefins and other by-products. Typical 2-butene conversions range between 60% and 75%, with a selectivity to propylene around 90% [104].

Another option that consists of the use of 1-butene (coming from biobutanol dehydration) alone as a feedstock is being investigated in order to overcome the dependence on the more costly ethylene [115 – 117]. This process is performed in the presence of an acidic cocatalyst via the isomerization to 2-butenes followed by cross metathesis between 1-butene and 2-butenes resulting in the formation of propylene and 2-pentenes [118]. The obtained 2-pentene can react further with 1-butene to produce more propylene and 3-hexene, and the cycle may continue until the C_4 conversion achieves around 65% and a propylene yield of 30% per

pass [119]. Table 1.5 summarizes the most recent results in heterogeneous systems dealing with the metathesis of ethylene and 2-butene. This general picture shows that there is still margin for improvement in this type of process, since alternative systems (different active metals, supports, feeds) and studies with real biofeedstock have received little attention.

Concerning the metathesis mechanism, the generally accepted one resembles that proposed by Chauvin, which is based on results for homogeneous systems [127]. It includes the initial formation of a metal-carbene species and its further propagation by a cyclic reaction with olefins (Scheme 1.6).

The initial carbene formation is believed to occur through a pseudo-Wittig reaction of the metal-oxo precursor with an olefin (Scheme 1.7). In the case of crossed metathesis of ethylene and 1-butene, the precursor is believed to react first with butene [128].

Many factors are reported to affect the structure−activity relationship, such as the degree of polymerization of surface MO_x species and the acidic properties of catalysts. For instance, for $Mo/Al_2O_3 − SiO_2$, Hahn *et al.* [129] suggested that polymerized octahedral MoO_x entities play a key role in directing the reactions toward propylene, since they hinder the isomerization of 2-butene to 1-butene, thus avoiding the further nonselective metathesis as compared to tetrahedral sites in which the production of 1-butene and its isomerization are faster than the reaction with ethylene. A recent review of Lwin and Wachs offers a comprehensive summary of the literature on this topic. They conclude, however, that there is still a need for more direct observation measurements (*in situ* and operando) which are able to confirm the catalytic active sites and intermediates proposed [130].

Today, in a related approach, the one-pot process from ethanol to propylene is being investigated as well and – while in the case of oxides such as Sc/In_2O_3 and $Y_2O_3 − CeO_2$, the pathway goes through the formation of acetaldehyde, acetone, and lastly propene – in the case of Ni/MCM-41 catalyst, according to them, the key step is the metathesis of the produced ethylene. In fact, ethylene is first dimerized on Ni sites to 1-butene, while the latter can be isomerized to 2-butene on acidic sites. Then the formed 2-butene is supposed to react via cross metathesis with unconverted ethylene. The mechanism claimed implies that Ni is able to perform a metathesis reaction by the formation of a nickel carbene intermediate. An exclusively acidic mechanism was ruled out because of the large pore size of MCM-41 [52, 123].

The metathesis reaction also finds application at an industrial level as a way to enhance the more abundant olefins. An example can be seen in the partnership of the companies Elevance and Versalis for the scale-up of a metathesis reaction of natural oil esters and olefins, particularly ethylene. Other important commercial processes include the SHOP for producing linear higher olefins from ethylene. Furthermore, the production of hexane and neohexene and many other polymers, agrochemicals, pheromones, and fragrances have reached the commercialization stage using the relatively new metathesis chemistry [119]. Therefore, the metathesis process, even if still under development, may become an important source of propylene.

Table 1.5 Recent results for propylene production by the metathesis of ethylene with butenes.

| Catalyst	Conditions[a]	1,3-Butadiene yield (or selectivity) (%)	Reference (year)
Molybdenum based (Mo)			
$MoO_3/SiO_2-Al_2O_3$ (one-pot aerosol)	Ethylene/2-butene = 1/1 $T = 40\,°C$	Propylene selectivity above 99%	[109] (2012)
$MoO_3/Al_2O_3-C+HNO_3$	Ethylene/2-butene = 1/1 $WHSV_{(C_2H_4+C_4H_{82})} = 1\,h^{-1}$ $T = 130\,°C$ and $P = 1.0\,MPa$	2-Butene conversion 69% Propylene yield (with respect to ethylene) 77.4%	[111] (2014)
$3.0Mo/(MCM\text{-}22\text{-}30\%Al_2O_3)$	Ethylene/2-butene = 4/1 $WHSV_{(C_2H_4+C_4H_{82})} = 0.5\text{--}2\,h^{-1}$ $T = 125\,°C$ and $P = 1.0\,MPa$	2-Butene conversion 86% Propylene selectivity 95%	[112] (2010)
Tungsten based (W)			
WO_3/SiO_2 calcined at 550 °C	Ethylene/2-butene = 2/1 $T = 400\,°C$ and $P = 0.1\,MPa$	2-Butene conversion 86% Propylene selectivity 81%	[100] (2012)
WH/Al_2O_3	Ethylene/2-butene = 0.35/1 Total flow rate = 20 ml min^{-1} $T = 150\,°C$ and $P = 1\,bar$	Total C conversion 43% 142.8 mmol$_{c3=g.cat\,h-1}$	[99] (2013)
$WO_3/SiO_2-(nano)TiO_2$	Ethylene/2-butene = 2/1 $WHSV = 2.34\,h^{-1}$ $T = 400\,°C$ and $P = 0.1\,MPa$	2-Butene conversion ~83% Propylene selectivity ~67%	[103] (2013)
$WO_3/SiO_2-Al_2O_3$ (nonhydrolytic sol–gel synthesis)	Ethylene/2-butene = 2/1 Total flow rate 20 cm^3 min^{-1} $T = 450\,°C$ and $P = 0.1\,MPa$	2-Butene conversion 92% Propylene selectivity 60%	[101] (2014)

(continued overleaf)

Table 1.5 (*Continued*)

Catalyst	Conditions[a)]	1,3-Butadiene yield (or selectivity) (%)	Reference (year)
$WO_3/SiO_2 - Al_2O_3$ (one-pot aerosol)	Ethylene/2-butene = 1/1 $T = 250\,^\circ C$	$(65\,mmol\,g^{-1}\,h^{-1})$ Propylene yield 39%	[102] (2014)
WO_3/SiO_2 (NaOH modified)	Ethylene/2-butene = 2/1 $T = 400\,^\circ C$ and $P = 0.1\,MPa$	2-Butene conversion 81% Propylene selectivity 77%	[120] (2014)
W-FDU-12 and MgO (doped vs. supported)	Ethylene/1-butene = 2 $T = 450\,^\circ C$ and $P = 0.1\,MPa$ $WHSV = 0.9\,h^{-1}$	1-Butene conversion: 79% Propylene selectivity 90%	[106] (2015)
W-KIT-6 (+MgO/Al_2O_3) One-pot hydrothermal synthesis (Si/W = 25)	Ethylene/1-butene = 2 $T = 350\,^\circ C$ and $P = 0.1\,MPa$ $WHSV = 0.9\,h^{-1}$	1-Butene conversion: 52% Propylene selectivity 74%	[107] (2013)
Rhenium based (Re)			
Re/$SiO_2 - Al_2O_3$ (nonhydrolytic sol–gel synthesis)	Ethylene/2-butene = 1/1 $T = 40\,^\circ C$ and atmospheric pressure	2-Butene conversion 60% Propylene selectivity 77%	[108] (2013)
10%Re/Al_2O_3 (high-throughput preparation and screening)	Ethylene/2-butene = 1/1 $T = 75\,^\circ C$ and atmospheric pressure WHSV $1.3\,h^{-1}$	Total C conversion: 61% Propylene selectivity 87% Propylene yield around 55–67%	[121] (2008)

Alternative systems

WO_3/MTS-9 (titanium silica sieve)	2-Butene $T = 320\,°C$ and $P = 0.8\,MPa$, $WHSV = 6.4\,h^{-1}$	2-Butene conversion around 42% Propylene selectivity 45–50%	[122] (2011)
Ni/MCM-41 The template-ion exchange (TIE) method	Ethylene 10% $T = 400\,°C$ and $P = 0.8\,MPa$, $WHSV = 6.4\,h^{-1}$	Ethylene conversion 57% Propylene selectivity 24%	[123] (2008)
Ni/Al-MCM-41	Ethylene 10% $T = 375–450\,°C$ and $P = 0.8\,MPa$, $WHSV = 1.4\,h^{-1}$	Maximum propylene selectivity 18–22% Maximum propylene yield 26%	[124] (2013)
$10WO_3/Al_2O_3$-70HY	1-Butene $T = 180\,°C$ and $P = 0.1\,MPa$, $WHSV = 1.5\,h^{-1}$	1-Butene conversion: 95% Propylene yield 21%	[117] (2009)
$Re/SiO_2 - Al_2O_3$	Ethylene/1-pentene = 3 GHSV of $500\,h^{-1}$ $T = 35\,°C$	Propylene yield of 88% 2-Pentene conversion 100% 455 min on stream	[125] (2012)
$MoO_x/\gamma-Al_2O_3$ one-dimensional support, synthesized via oleylamine-assisted hydrothermal method	1-Butene $T = 120\,°C$ and $P = 0.1\,MPa$, $WHSV = 2.4\,h^{-1}$	1-Butene conversion: 82% Propylene yield 30%	[115] (2014)
WO_3/SiO_2	Ethylene/decene = 15 $T = 360–400\,°C$	Decene conversion >90% Propylene selectivity 70–75%	[126] (2013)

a) Molar reagent ratio, WHSV: weight hourly space velocity (or GHSV: gas hourly space velocity), T: temperature, and P: pressure.
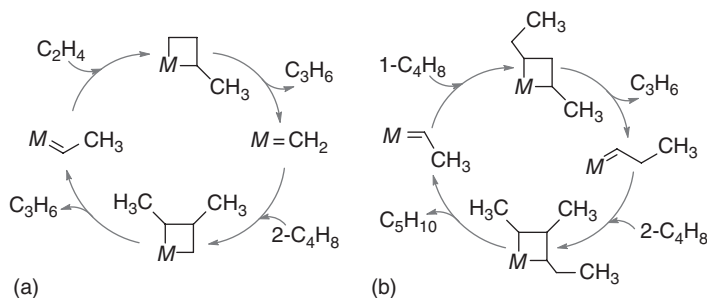
Scheme 1.6 Mechanism of the metathesis of ethylene with 2-butene (a) and 1-butene with 2-butene (b).
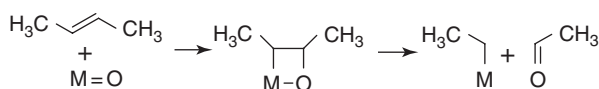
Scheme 1.7 Formation of the initial M-carbene species.

1.4
Conclusions

The field of bio-olefin production is growing extremely fast. Bioalcohol dehydration or chain-length increase routes (i.e. Lebedev and Guerbet reactions) are already practicable at an industrial level. Indeed, excellent yields and stable catalytic behavior have been demonstrated. Last but not least, the practicability of these processes is more likely compared to several other bioased productions proposed in literatre, showing better economic return. The most striking example is the synthesis of biobutadiene; several joint ventures and industrial alliances have been signed during the latest 10 years, and a possible future shortage of this olefin, coupled with the incentives deriving from the "green label" assigned to tires and other products obtained from biorubber, might lead to a quick construction of new plants in the next years.

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