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Review of Established and Emergent Methods for the Production of C$_4$ Olefins

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Abstract

Review of Established and Emergent Methods for the Production of C$_4$ Olefins

James Koval

Current production of C$_4$ olefins is dominated by naphtha cracking and butane dehydrogenation, but significant research interest is developing in alternate feedstocks due to an abundance of inexpensive natural gas and bioethanol. The current C$_4$ olefin production methods are costly, make use of already-depleted petroleum resources, and are often hazardous to workers, which forms the impetus for investigation into alternative methods and assessment of their viability as a future means of olefin production. Methods of natural gas conversion to higher order hydrocarbons are discussed, including Fischer-Tropsch synthesis and oxidative methane coupling, each of which could form the first step in a hypothetical natural gas-to-olefins process. The historically common Lebedev, Ostromislensky, and Fripiat methods for 1,3-butadiene production from ethanol feedstocks are described and analyzed, although these processes largely fell out of favor in the decades following World War II in favor of sources derived from naphtha cracking. Another well-known process involving C$_4$ olefins, olefin metathesis, is considered, although the reaction is more commonly used to produce propylene. Biological processes are discussed as well, including the well-known production of bioethanol from sugars and starches, and also more novel processes such as an effort to use genetically engineered microorganisms to produce specific intermediates for olefin production, and in some cases, direct olefin production from these organisms. Finally, several promising schemes are identified and analyzed, in an attempt to compare their potential viability in key areas. Two of the most promising emergent methods today identified in this review are the bio-catalyzed production of 1,4-butanediol and/or butadiene using *E. coli*, and a microwave radiation-assisted scheme in which methane is selectively dimerized twice to form 1-butene.

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Introduction

Olefins, or alkenes, are a highly important industrial chemical class consisting of an unsaturated hydrocarbon chain containing one or more double C=C bonds. Common olefins, such as ethylene and propylene, are precursors to polyethylene and polypropylene respectively, two highly important polymers used in a wide variety of commercial plastics. Although ethylene and propylene are among the two most massively produced olefins, and thus have attracted an abundance of research into different effective methods of synthesis, higher-order olefins (C_4 and above) have not been directly synthesized as readily. Instead, C_4+ olefins have historically been produced via the selective dehydrogenation of C_4+ alkanes or as a byproduct from other processes such as naphtha cracking. An estimated 95 percent of worldwide production of 1,3-butadiene, an important polyunsaturated olefin used in the production of rubber for automobile tires, was produced in one (or both) of these two ways as of 2018 [15]. These processes, which already rely on the use of C_4+ feedstocks, leave the price of the important C_4 olefins in flux due to inconsistent feedstock supply, and may be unsustainable regardless due to limited natural resources, creating the impetus for a well-established direct synthesis route to these important monomers [1,3,12-15].

Direct synthesis of C_4 olefins such as 1,3-BD is not without precedent, however. During World War II, a natural rubber shortage necessitated an investigation into synthetic routes of 1,3-butadiene monomer creation for use in rubber production for military vehicles. Around this time, two different processes were developed, both using ethanol as a feed source for butadiene synthesis: the one-step Lebedev process and the two-step Ostromislensky process [12,16]. Although these ethanol-as-feedstock routes were once popular for on-purpose 1,3-butadiene synthesis, particularly the Lebedev process, they were largely abandoned industrially in Europe

and the US by the 1960s in favor of butane/butene dehydrogenation schemes [3]. By 1990, only one stand-alone butadiene plant was operating in the United States [14]. To this day, the vast majority of 1,3-butadiene production takes place as a side unit in massive, preexisting ethylene plants. There, a mixed C_4 byproduct stream diverted from the main ethylene production unit is fractionally distilled into its main components [12]. This separation between these isomers and other chemically similar compounds can be rather costly, and much of the raffinate left over after removal of butadiene and isobutene has no established commercial significance. There is renewed interest in an efficient and less expensive pathway for butadiene synthesis from C_1 and C_2 sources, partially due to an abundance of inexpensive and more environmentally friendly potential feedstocks such as natural gas and bioethanol attracting attention. A review of these emergent techniques, and a comparison and contrast of their potential for the future in C_4 olefin production are proposed.

Use of Natural Gas as a Feedstock

In the years following the American shale gas boom of the early 2000s, much research attention has been focused towards getting value-added products out of a suddenly abundant and cheap supply of natural gas. Natural gas is mostly composed of methane and other low-order hydrocarbons, which can present a challenge when converting to heavier products. Methane, which comprises the vast majority of natural gas reserves, is particularly stable due to its tetragon structure consisting of four C-H, requiring a high temperature to break and form new bonds. There is an inherent concern of allowing too much combustion to occur when operating at high temperatures. Thus, at the heart of the improvement of natural gas is the concern for lowering the activation energy required to break these C-H bonds, via catalysis and other methods [11]. However, it is also important that the catalyst be able to discriminate between the strong C-H

bonds in methane and the relatively weak C-H bonds in higher order hydrocarbons [5]. Therein lies a key problem in synthesizing higher order olefins from natural gas rather than using conventional methods such as cracking: adding carbons to a growing chain becomes increasingly difficult with each elongation. However, many potential pathways for these valuable conversions have been demonstrated in the literature, even if they have not yet been commercialized to a great extent. This report seeks to catalog, describe, analyze, and evaluate the efficacy of these methods.

There are three main categories of pathways demonstrated thus far for the activation of methane to form higher order products: syngas production, oxidative methane coupling, and direct conversion to said value-added chemicals [5]. Syngas, a mixture primarily consisting of hydrogen and carbon monoxide, has long been a highly researched topic as an intermediate for natural gas conversion and can be derived from a variety of cheap and environmentally friendly sources including natural gas, biomass, and industrial waste. Fischer-Tropsch synthesis and similar methods have been well documented to convert syngas to liquid hydrocarbons, and depending on process conditions and catalysis, can be used to generate C_4 alkanes, alkenes, and alcohols from syngas. Oxidative methane coupling (OCM) is also of interest due to its ability to produce ethanol. Like syngas, ethanol is a highly researched molecule that is readily available from a variety of sources, and thus much is known about its potential for use to synthesize higher order chemicals. Finally, some methods for conversion of natural gas to higher order oxygenates have been discovered, although highly specialized catalysts are needed to achieve a viable selectivity and yield for the desired products.

There in an inherent challenge due to the disorder involved in combining relatively simple and stable C_1 reactants to form more complex C_4 products. Therefore, the control and

suppression of undesired side products is a key goal for any and all synthesis processes. This also means that there is unlikely to be any simple, elegant solution, and that any worthwhile strategy for producing high yields of a single C_4 olefin product will almost certainly employ a combination of the methods discussed herein. Although byproducts from intermediate reactions are likely to be unavoidable and may require additional equipment purchases, this may turn out to be a strength for a C_4 olefin production operation, as prices can vary widely over the course of several years [12]. The ability to process byproducts could lend to the flexibility of a hypothetical stand-alone butadiene plant in the event that there is a price drop for a previously desired product or value increase for a chemical not currently being produced in large quantities.

In summary, the methane conversion methods offer some promise as they are versatile and have abundant feed sources, but the reactions are usually difficult to control, and typical yields in most contemporary research are too low to attract more widespread attention from companies and investors. A review of literature has been conducted to evaluate the efficacy and viability of these methods for natural gas improvement, detailed in the following sub-sections.

Fischer-Tropsch Synthesis for Carbon Chain Elongation

One of the most common methods for conversion of methane and natural gas involves the production of synthesis gas ("syngas"), a moderately-energy dense mixture of hydrogen, carbon monoxide, and often carbon dioxide. Looking at natural gas as well as syngas from biomass and coal, Liu et al. formed mixed C_2+ alcohols using modified Fischer-Tropsch synthesis [8]. These reactions were primarily catalyzed with copper-doped cerium oxide and zinc oxide-based catalysts. Results were mixed, with the resulting catalyst mostly producing methanol from syngas and showing just under 40 percent selectivity for C_2+ alcohols. Somewhat unexpectedly, however, a large majority of the non-methanol product was found to be isobutanol, possibly due

to the low heat of enthalpy/Gibbs energy of isobutanol. This phenomenon occurred for both metals, and was particularly pronounced in the ceria catalyst [8].
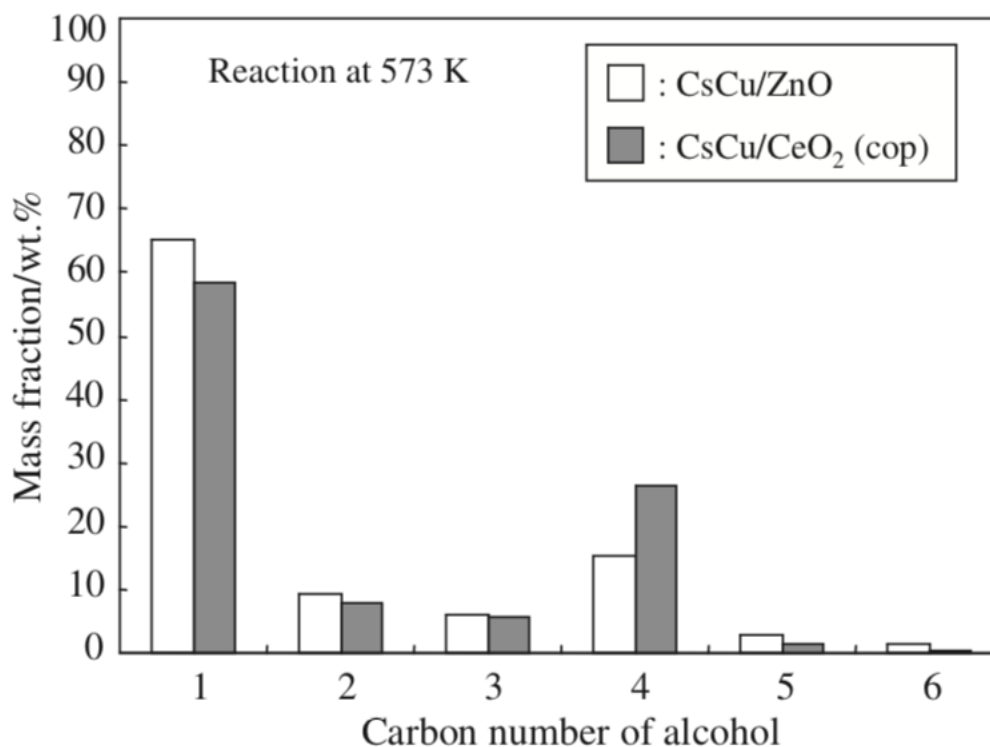
Figure 1: Proportions of carbon numbers of alcohols formed via the cesium-copper-doped catalysts, showing high relative abundance of C_1 alcohols followed curiously by C_4 (mostly isobutanol). The increased C_4 selectivity was especially prevalent in the ceria coprecipitated catalyst. From Liu et al. [8]

This effect of increased stability in C_4 isobutanol as opposed to lower-order alcohols could be worth consideration towards the goal of production of C_4 olefins. However, selectivity of isobutanol relative to methanol was poor, and with isobutanol being a branched molecule, C-C bonds would still need to break and reform to form straight-chain C_4 olefins such as 1,3-butadiene. Buniazet et al. demonstrated the potential of titanium/silicon oxide media to catalyze the dehydration of isobutanol. Although conversion was relatively low at 38 percent, more literature on this under-researched topic would be useful to determining whether this particular

modified Fischer-Tropsch method using ceria as a catalyst and isobutanol as a key intermediate could ever be viable industrially.

Other metal oxides have been studied and show potential for modified Fischer-Tropsch synthesis of higher-order alcohols. Surisetty et al. examined the catalytic potential for molybdenum/potassium oxides and also sulfides supported on multi-walled carbon nanotubes. Both CO hydrogenation rate and Fischer-Tropsch synthesis rate increased when these nanotubes were employed as catalyst support over traditional formation methods such as coprecipitation and impregnation, most likely due to improved dispersion of the metallic active sites [10]. The use of carbon nanotubes for catalyst support in more studies, and for additional metals which showed a predilection to catalyst C_4 alcohols would be a logical next step, such as cerium [8].

Another class of materials that have attracted interest as catalysts is metal carbides. Xiang et al. looked at molybdenum carbide catalysts with a variety of dopants and promoters. This particular catalyst showed high selectivity to methane, followed ethane and other alkanes; however, when potassium was added to the catalyst, selectivity of alcohols was "remarkably" increased, with ethanol becoming the most abundant product at a selectivity of around 40 percent [9]. Among many of the metal oxides and carbides, a small amount of nickel was found to increase selectivity for higher-order alcohols. Cobalt was also used in some instances as an effective promoter for this modified form of Fischer-Tropsch synthesis [8,10]. An addition of just 6 wt. percent cobalt to a Mo-K catalyst mounted on carbon nanotubes was found to increase CO conversion by half to 43.5 percent and more than doubled C_3+ alcohol selectivity to 23 percent. Future research should incorporate these effective Fischer-Tropsch promoting metals into the more effective bulk catalysts for the hydrogenation of CO. At any rate, these modified F-T methods would likely require a major breakthrough in the form of increased selectivity of

higher order products in order to be viable in comparison to more recent olefin production schemes discussed later in this review.

Oxidative Methane Coupling to C_2 Alkanes and Alcohols

Another common route of carbon chain elongation using methane as a feedstock is oxidative methane coupling (OCM), either using oxygen gas or carbon dioxide as the oxidant. This reaction is difficult to control due to the potential of overoxidation of the methane feed to CO or to CO_2 when oxygen is used as the sole oxidant. Cai and Hu demonstrated the use of CO_2 as a co-fed oxidant to limit the production of undesired products and thus produce more hydrocarbons [5].   In this CO_2-OCM process, an oxygen atom assists a C-H bond break in methane, creating methyl radicals which combine to form ethane or ethylene. Many different mono- and multi-component catalysts were tested, including rare earth metals and oxides of calcium, zinc, lanthanum, manganese, and other elements. The CO_2-OCM method had mixed results in this case, achieving high hydrocarbon selectivity above 80 percent, but with low yields no greater than 11 percent [5]. More conventional OCM methods using oxygen as the co-fed oxidant for methane (O_2-OCM) were found to have similarly high selectivity around 80 percent for C_2 hydrocarbons, and significantly higher yields of 25-30 percent. Undesired formation of combustion products such as CO and CO_2 are limited by performing O_2-OCM under conditions in which oxygen in clearly the limiting reactant [6].

In general, there are multiple reasons that oxidative methane coupling is considered difficult to effectively commercialize. Although selectivity of C_2 hydrocarbons is often high, yields are often below 10 percent due to the care taken to avoid over-oxidation at high temperatures to products of combustion [6]. The desired reaction is also thermodynamically difficult, due to the relative strength of the C-H bonds in methane compared to the slightly

weaker C-H bonds in ethane [5]. Some researchers noted that little economic data existed for the process existed in the literature. However, the method has some favorable qualities such as the avoidance of the production or use of syngas, which is often a costly process only viable at massive scales [6]. A key concern for any future research interest in CO_2-OCM would need to focus on effectively catalyzing the scission of the methane bonds without affecting the bonds in the desired C_2+ products.

Methane Conversion to Other C_2+ Intermediates

Although the main established methods for carbon chain elongation are the previously mentioned Fischer-Tropsch synthesis and OCM strategies, other studies have looked to establish a more direct link between lower-order hydrocarbon gases and higher order products than previous studies. One of these studies, conducted by Julian et al., used molybdenum-containing zeolite catalysts to convert methane. Instead of conventional heating, microwave plasma technology was employed to provide the necessary heats of fusion without combusting the methane and essentially wasting feed. Acetylene was noted as a primary product, with a significant amount of both ethylene and benzene forming as well [32]. While each valuable products in their own right, they each contain strong bonds that inhibit further selective conversion to olefins. Other researchers have employed microwave-assisted methane conversion with promising results. Lu et al. attempted to selectively synthesize butene from methane using a very similar experimental set-up, with some key improvements [1]. Hydrogen gas was co-fed with high-selectivity methane to prevent excessive dehydrogenation to triple-bonded acetylene, and nickel-molybdenum oxide mounted on a silica support served as the catalyst for the two-stage reactor. In the first stage, methane was coupled to form ethylene, with a maximum of 73.2

percent methane conversion observed. In the second stage, ethylene was in turn coupled to form 1-butene with 89.4 percent selectivity [1].

The microwave heating study appears promising for the synthesis of the important industrial monomer 1,3-butadiene, pending a successful dehydrogenation taking place on the 3rd carbon atom in the chain. In addition, the setup appears to be simple and employed a novel approach that has potential to be viable for the production of C_4 olefins, 1-butene and 1,3-butadiene, even on a relatively small scale. Unfortunately, Lu's study appears to be an anomaly and few, if any, further experiments to synthesize C_4 olefins directly from natural gas have been attempted. More information on how the microwave heating may assist carbon chain elongation could help legitimize a commercial approach, necessitating further study for this now-promising field.

Biological Methods of Obtaining Feedstocks for the Synthesis of C_4 Olefins

In addition to methane, other feedstocks have been considered by researchers for their potential in synthesizing C_4 olefins, particularly those which can be obtained in a sustainable fashion. Ethanol is of some interest due to the many potential sustainable sources of ethanol production, including corn or sugar crops, i.e. primary sources [3]. Secondary sources of bioethanol include cellulosic waste and algae, and could be particularly interesting as part of a sustainable C_4 olefin production operation. These secondary sources are beneficial as they do not divert as many natural resources or food crops that could otherwise be used to benefit society, and instead generate useful bioethanol from waste or otherwise inert material. Bioethanol can then, in turn, be converted to C_4 olefins like butadiene via the well-established Lebedev process and other similar syntheses, which will be covered in greater detail later.

Some start-up companies have begun to investigate new approaches for the synthesis of highly valuable chemicals such as C_4 olefins. Genomatica, a bioengineering company, selectively manufactures microorganisms which convert low-order organic feedstocks to specific value-added chemicals. Recently, a genetically-engineered strain of *Escherichia coli* was developed by Genomatica for the selective conversion of sugars to 1,4-butanediol in a test plant scenario, with the concept being proven to be effective on at least a 2000-ton scale [3]. This unique method of selective chemical production is achieved by evaluating many strains of genetically-modified microorganisms, then performing extensive fermentation experiments with only the best performing microorganism strains; in this case using *E. coli* to feed on and convert food sugars to 1,4-butanediol [7].

With so many successive reactions necessary to convert the sugar molecule to the butanediol product, many enzymes were needed for bio-catalysis, some existing endogenously or naturally in the bacteria and some needing to be added to the *E. coli* DNA through genetic modification and foreign species. Initially, naturally occurring enzymes in the bacteria were used to metabolize food sugars and amino acids such as alpha-ketoglutarate to the important biological molecule succinate, using the TCA cycle native to most organisms. Then, along the proprietary reaction pathway, the important biological molecule CoA plays a key role in converting the four-carbon succinate molecule to an olefin. CoA attaches to one of the carboxylic acid ends of the chain, and is protonated by a passing NADPH molecule to leave behind an aldehyde in its place. Next, the aldehyde end of the chain is protonated again to form a hydroxyl or alcoholic group. This process is repeated once more, eventually forming the established butadiene precursor, 1,4-butanediol, with alcohol groups on either end of the four carbon chain [30]. This pathway is presented in Figure 2 in full detail.
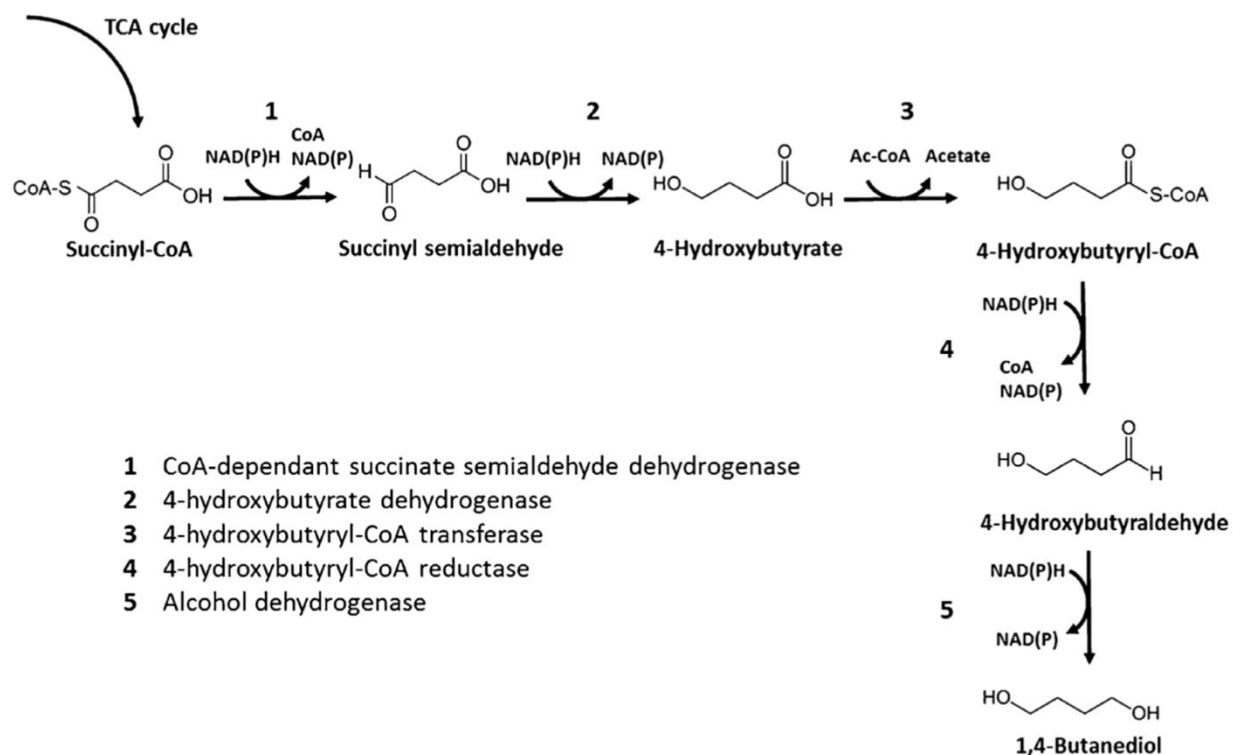
Figure 2: Main reaction network for the bio-based production of 1,4-butanediol in *E. coli*. Common metabolites such as succinate and alpha-ketoglutarate derived from the native TCA cycle are employed as the main reactants, and 4-hydroxybutarate forms a key intermediate. From Barton et al [7].

Although the technology is not yet at a globally viable stage, Genomatica has licensed the renewable 1,4-butanediol bioproduction process to larger companies for potential scale-up, and two commercial-scale plants: one with Novamont being a partner and another in conjunction with BASF, were scheduled in 2015 and 2017, respectively [3,27]. According to press releases from Genomatica, both plants have met early production goals and thus show great promise for the future of bio-butadiene production. Additionally, Genomatica has patented genetically modified *E. coli* to produce butadiene directly, using important biological molecules such as acetyl CoA and malonyl CoA in a fashion similar to their original 1,4-BDO production scheme [29]. A reaction schematic for this direct BD production route can be found in Figure 3 below.
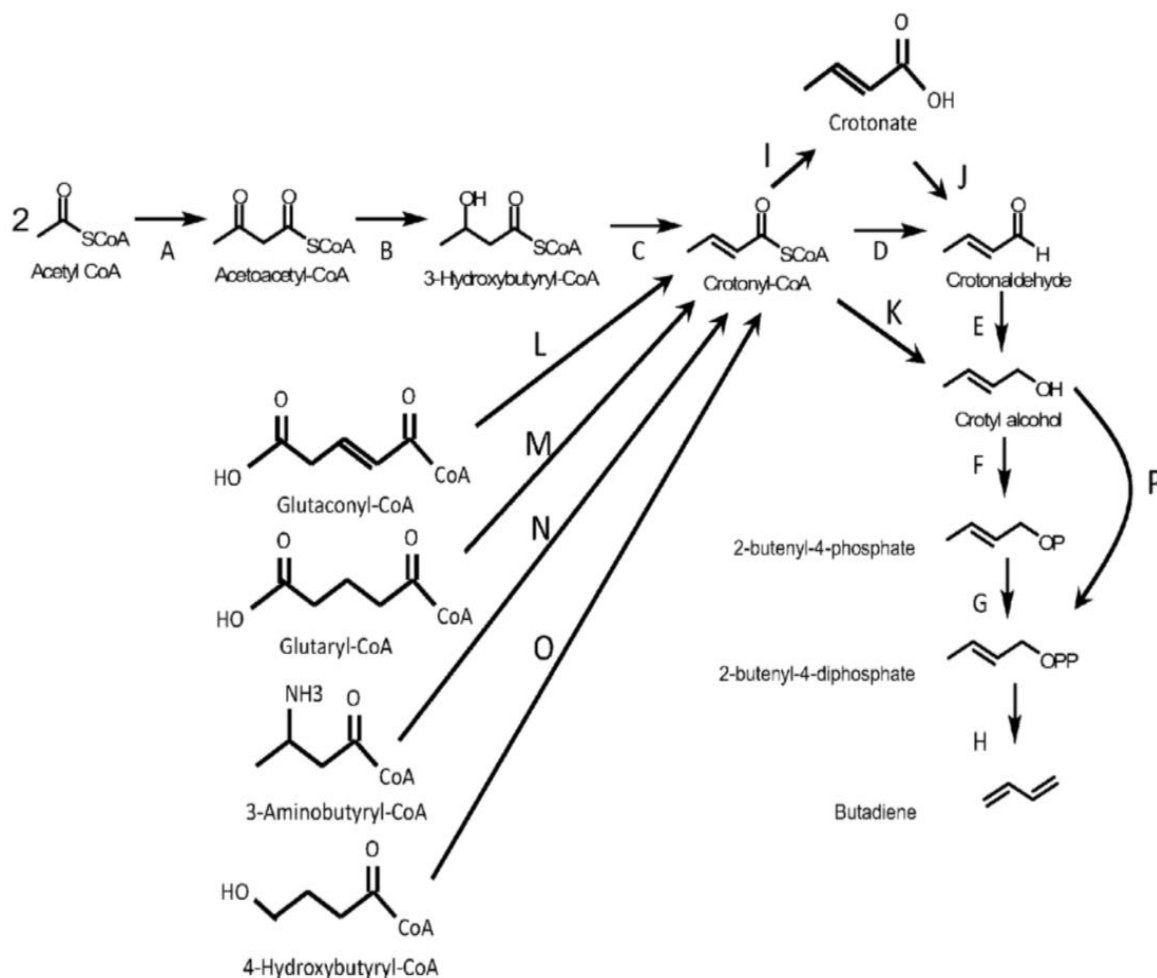
Figure 3: Genomatica's scheme for direct production of butadiene from various coenzymes in *E. coli*. Acetyl-CoA was primary reactant, but other molecules were used, with crotonaldehyde and croton alcohol forming key intermediates. From Burk et al [29].

As with the butanediol production scheme, a few of the necessary reactions early in the butadiene process could be catalyzed endogenously in the naturally-occuring *E. coli* organism. However, several genetic modifications were necessary in order to get the bacteria to diverge from its typical chemical pathway and produce butadiene gas [29]. Overall, the scheme is similar to that which is used for 1,4-butanediol production, with the main difference being a high-energy diphosphate ion added to the crotylalcohol (one internal double bond, one alcoholic group on the opposite end) in order to perform the final dehydration step to 1,3-butadiene. Research and commercial implementation of these exciting new processes is ongoing by

companies large and small. In late 2016, the Italian chemical company Novamont, the first licensee of this technology from Genomatica, opened the world's first industrial bio-butanediol plant. By mid-2017, the company reported that production goals were being met and that over 10,000 tonnes of bio-based 1,4-butanediol had been produced for use as a chemical intermediate [50]. Renewable, bio-based feedstocks should be instrumental in modernizing the butadiene production industry, representing a vast improvement over petroleum-based routes for BD which are energy-intensive, inefficient, and hazardous to human health.

Butanediol Conversion to Butadiene

Although the use of bacteria to convert simple sugars to butanediol represents a great opportunity for C_4 olefin production, 1,4-butanediol in and of itself is not a particularly useful product. With two successive dehydrations, 1,4-butanediol could potentially be converted to 1,3-butadiene, thus completing the production of highly valuable and sought after C_4 olefins from sugar with relatively little energy input. This potential reaction mechanism was proposed by Qi et al with 3-butene-1-ol as the key intermediate [15]. However, the use of conventional catalysts, both acidic and basic, can lead to problems, particularly the formation of cyclic compounds during dehydration rather than the straight chain butadiene [27,28]. Sato et al. used multiple metal oxides, including alumina, zirconia, silica, and ceria at varying temperatures and monitored product composition [28]. In order to maintain high butadiene selectivity, temperatures needed to remain below 300 °C, which resulted in very low conversion of the 1,4-butanediol feed. At temperatures exceeding 400 °C, conversion becomes much higher but the undesirable byproduct tetrahydrofuran dominates production. Of all the catalysts tested by Sato's team, ceria performed the best with an excellent BD selectivity over 85%, but with a particularly low conversion rate of 6.3% at 275 °C [28].

With the rising interest in selective biofermentation for the formation of butadiene and the relative ineffectiveness of traditional metal oxide catalysts on 1,4-butanediol, many researchers began looking at other ways to catalyze this important dehydration to butadiene. Ionic liquids have emerged a potential solution, particularly those involving the tetrabutylphosphonium (TBP) ion. Stalpaert, Cirujano, and de Vos examined the effectiveness of several TBP-halogenides as dehydration catalysts for diol conversion to desired dienes [27]. The study found that the compound TBPBr was extremely successful in forming both C_4 and C_6 dienes, and that none of the other halogenides tested (chloride or iodide) were nearly as effectively in catalyzing the successive dehydrations as bromide. A proposed reaction mechanism is included below in Figure 4. Using gas chromatography, the researchers were able to detect each of the proposed intermediates in limited quantities from the reaction effluent, supporting the validity of the proposed reaction network.

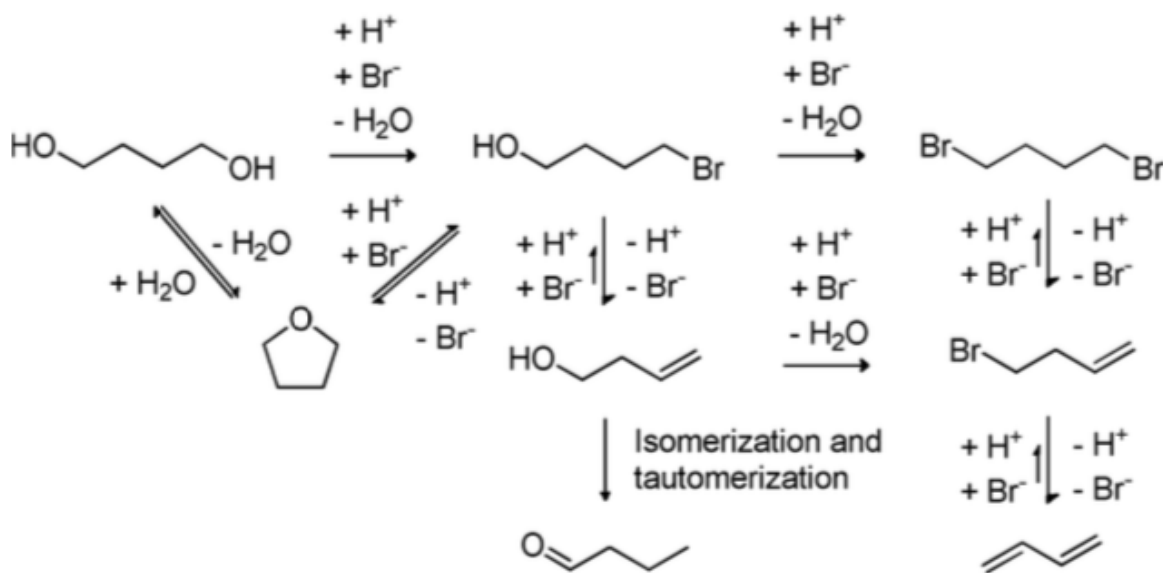Figure 4: Proposed reaction network for the double dehydration of 1,4-butanediol to form 1,3-butadiene using TBPBr. In this case, the dehydration is aided by the bromide ion acting as a base, which is left behind in place of the alcohol group. The two dehydrations as well as the two dehydrobrominations to reach the final product can occur in any order. From Stalpaert, Cirujano, and de Vos [27].

The experimental setup which produced the best results involved the use of TBP-bromide as the catalyst at 220 °C, with some THF added to suppress the formation of THF as an intermediate, and some HBr added to provide acidic active sites for the dehydrations to occur. After 120 minutes reacting under these highly idealized conditions, an extremely high yield of 94% 1,3-butadiene was reached [27]. In combination with promising bio-fermentation methods patented by companies like Genomatica, a fully "green" reaction mechanism for butadiene production from sugars or even waste such as cellulose could be a commercial possibility in the coming years.

C_4 Olefin Production from Ethanol

In several of the aforementioned methods, particularly bioethanol production, the desired product is merely an intermediate for C_4 olefin production. During World War II, a rubber shortage was the impetus for the development of at least two different methods of 1,3-butadiene production from ethanol: one-step Lebedev synthesis and two-step Ostromislensky synthesis. This 1,3-BD monomer was in turn used to synthesize polybutadiene and styrene-butadiene copolymers which are used as synthetic rubbers for automobile tires and the machines of war. Figure 5 contains a generalized reaction network for the coupling and conversion of ethanol to form 1,3-butadiene, showing that in addition to the coupling reaction, other reactions must occur to form the characteristic double bonds in 1,3-BD. Of course, many undesired side reactions and byproducts are possible and, in a sense, unavoidable due to the nature of a relatively complex one-step synthesis.
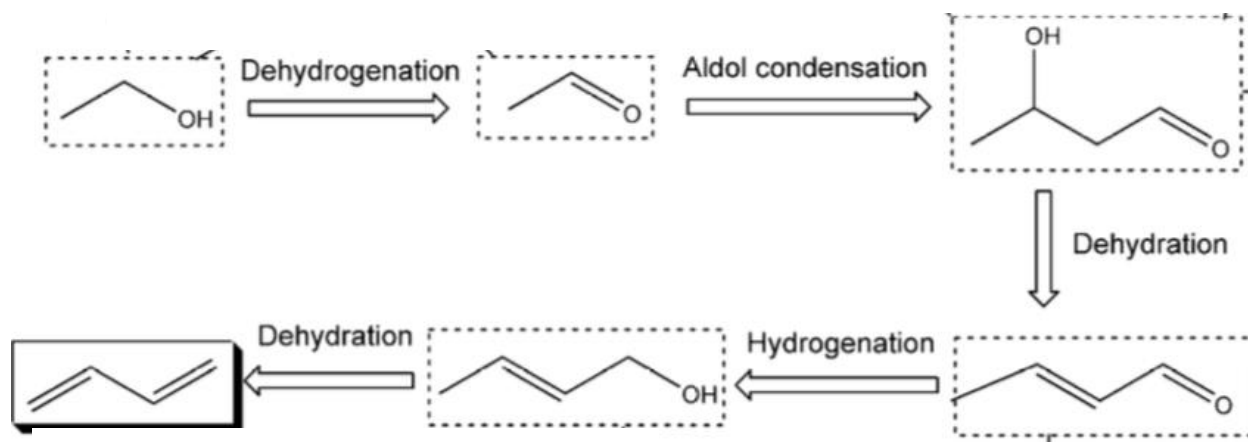
Figure 5: Generalized reaction network for 1,3-butadiene production from Qi et al. One ethanol molecule is dehydrogenated to form acetaldehyde, which then couples with another ethanol to form a four-carbon chain which then undergoes two dehydrations and a hydrogenation to form the final product, 1,3-butadiene [15].

Historic ethanol-to-BD production routes were proven to work in a somewhat limited fashion with up to 60 percent butadiene yield and 70 percent selectivity achieved by the German company I.G. Farben at atmospheric pressures [15]. These methods largely fell out of favor in industry by the 1960s as massive naphtha cracking operations in ethylene plants began to be able to produce cheaper 1,3-butadiene as a side product. Although naphtha cracking involves many side products and separation is an issue, the massive scale of these ethylene plants makes them able to make less expensive butadiene monomer than was possible using ethanol as a primary feedstock [14]. However, due to environmental and public health concerns with naphtha cracking as well as the relative abundance of inexpensive and potentially renewable ethanol in the US, research interest in butadiene production from ethanol is beginning to be renewed [21].

Lebedev Process and Other One-Step Methods

There are inherent challenges to performing the several intermediate reactions needed to convert ethanol to 1,3-butadiene with a commercially suitable selectivity. In 1910, Russian chemist Sergey Lebedev developed a process to do such, employing the following intermediate steps [16,22]:

- Hydrogenation of ethyl alcohol to form acetaldehyde

- Condensation of acetaldehyde with another ethanol to form crotonaldehyde

- Reduction of crotonaldehyde to form crotyl alcohol

- Dehydration of crotyl alcohol and rearrangement to form the final product, 1,3-butadiene
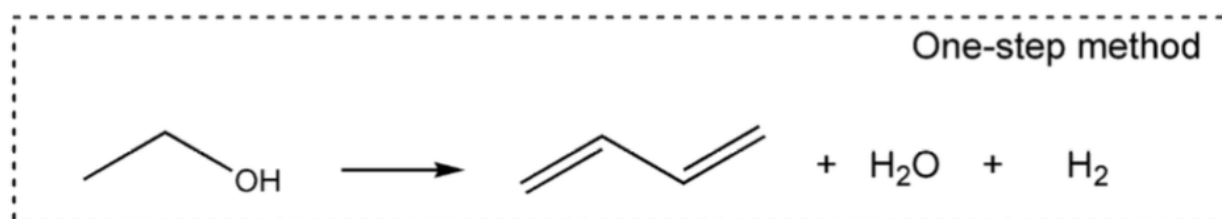

Figure 6: Simplified reaction model for the one-step (Lebedev) production of 1,3-butadiene from ethanol. Two ethanol molecules undergo all intermediate steps to form 1,3-butadiene in one reactor. From Qi et al [15].

Although Lebedev was able to use his process to demonstrate the potential for the creation of synthetic butadiene rubber sourced from ethanol, his results would be considered unacceptable by today's standards, with only 25 percent maximum butadiene selectivity and 10-13 percent yield of desired products [16]. However, many improvements were made to Lebedev's original process as scientists learned more about the reaction mechanism and demand continued to increase for practical, inexpensive synthetic rubber.

One of the key improvements made to the original Lebedev process has been in the more effective catalysis of the complicated main reaction path. Talc, or a magnesia-silicate (MgO/SiO_2) crystal, has been shown to be an effective catalytic medium for the ethanol-to-BD synthesis route [17-19, 22]. The conversion and selectivity for the desired product, 1,3-butadiene, has varied somewhat in the literature due to altered experimental conditions and the use of additional elements as promoters. Oxides of chromium, nickel, silver, zinc, and copper as well as metallic silver have been used as promoters for the Lebedev process with wildly varying success [17]. Tret'yakov et al. took likely the closest approach to the original Lebedev process, using γ-aluminum oxide with 25 percent by weight zinc nitrate catalyst. Despite high initial

activity, the catalyst showed a sharp decrease in yield over time across multiple different catalyst preparation methods. As a result, none of these γ-Al_2O_3-based catalysts eclipsed 24 percent yield of the desired product [16]. Angelici et al. had greater success using copper-promoted talc catalysts, achieving a maximum of 40 percent 1,3-butadiene yield. This Cu promoter was proposed to aid in the selectivity of the first step, acetaldehyde formation, by blocking acidic sites that would form the key undesired products ethylene and diethyl ether [17]. By blocking these "dead-end" byproducts early in the reaction network, that ethanol which is converted is hopefully maximized to form the most butadiene possible. Hayashi et al. also achieved some success using a magnesia-silica based catalyst to form butadiene from ethanol, this time using zinc as a promoter and employing density functional theory (DFT) to model the reaction. At lower ethanol conversion levels, selectivity was dominated by acetaldehyde, confirming its status as a key intermediate. 1,3-butadiene selectivity then steadily rises with conversion, until conversion reaches 60 percent or higher and butene begins to dominate the reactor effluent. Using DFT, zinc was found to aid in the initial step of acetaldehyde formation, but also weakened the basicity of the catalyst and thus hurt production of the subsequent steps of the reaction network [18]. Akiyama et al. employed a germanium-talc catalyst that exhibited remarkably high selectivity for 1,3-butadiene of 71 percent, but with only a 44 percent ethanol conversion rate [22].

Investigation into effective catalysis of the Lebedev process is ongoing. Key characteristics in a successful catalyst would be a high number of basic active sites, which aid in the formation of double bonds via reduction, as well as the ability to discriminate between the relatively weak C-C bonds in the final C_4 product and the stronger bonds found in the reactants. With so many possible side reactions, this problem is unlikely to have a simple solution.

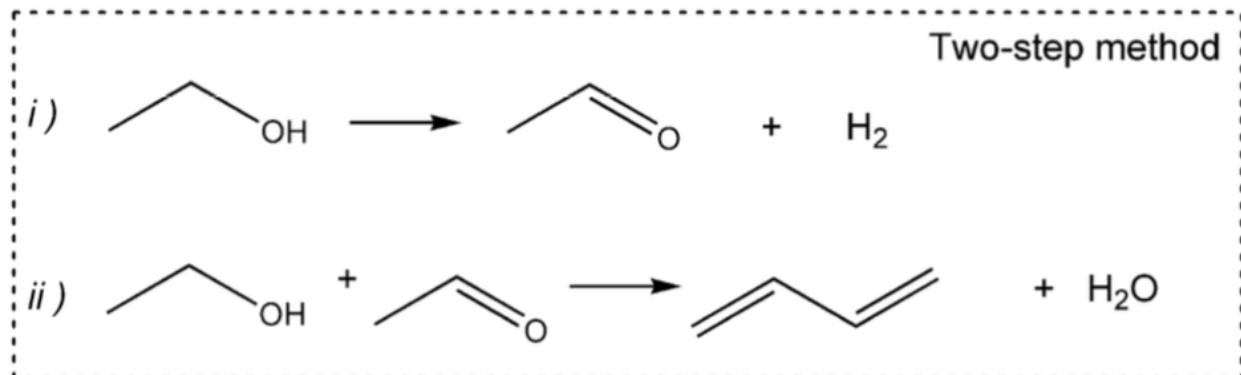**Ostromislensky Process and Other Two-Step Methods**

Figure 7: Simplified reaction model for the two-step production of 1,3-butadiene from ethanol. In contrast to the one step method, some ethanol is dehydrogenated to form acetaldehyde in a separate first step before coupling with ethanol in the second step and undergoing the necessary dehydrations to form the final product. From Qi et al [15].

Around the same time that the Lebedev synthesis process was highly popular for rubber production in the World War II-era Soviet Union, the Ostromislensky process was employed by American companies for their war effort [22]. The key difference between the Lebedev and Ostromislensky model was the separation of the highly important initial ethanol-to-acetaldehyde step from the subsequent reactions. Afterwards, a similar aldol condensation to the Lebedev method followed by rearrangements and dehydrations yielded 1,3-butadiene in a separate reactor, with reported yields reaching over 60 percent with very high purity in the final product. In the typical catalytic arrangement, the first step to form acetaldehyde was performed over a copper-doped silica catalyst, similar to the catalyst used in the Lebedev process. The subsequent conversion to butadiene was catalyzed by a tantalum-based metallic catalyst [24]. As in any chemical process, the suppression of side products, particularly ethylene which actually has a lower energy barrier of formation than acetaldehyde in this case, is of critical importance to attaining satisfactory yields [12]. Figure 8 contains a more detailed view of the Ostromislensky process and rearrangement, with key intermediates listed and named.
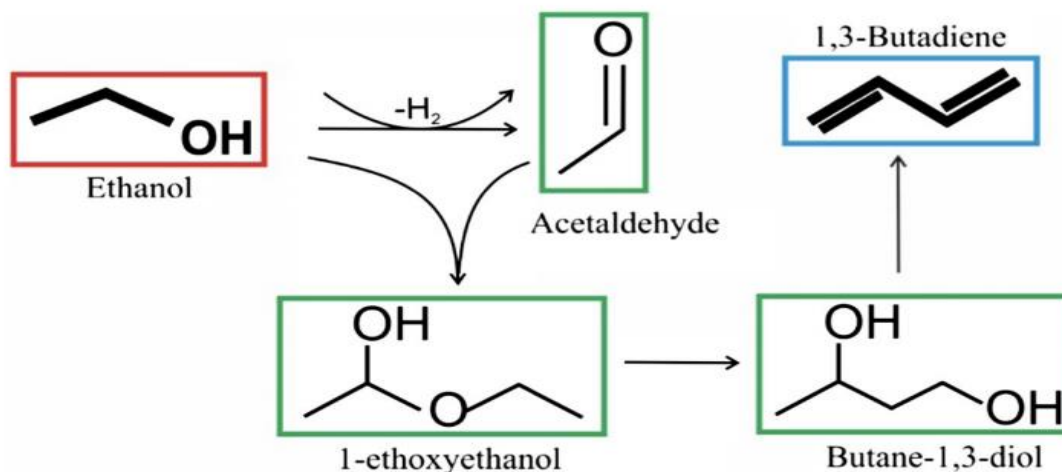
Figure 8: A detailed presentation of the Ostromislensky synthesis main reaction pathway. In an initial step, ethanol is dehydrated to form acetaldehyde, then in a separate reactor the two are combined and rearranged to form butane-1,3-diol. At this point the diol product undergoes two dehydrations to form the diene product. From Taifan et al. [24]

Although it was not widely commercially implemented as the Lebedev and Ostromislensky syntheses were, the Fripiat mechanism is a third proposed pathway for butadiene synthesis from ethanol feed. This method also employs two reaction steps, and also utilizes the nearly unavoidable ethylene side product as an intermediate. In the first step, some ethanol is dehydrogenated to form acetaldehyde, while an equal amount of ethanol is dehydrated to form ethylene. In the following stage, in what is called a Prins reaction, the ethylene is combined with the acetaldehyde to form a butenol, i.e. containing both a C=C double bond and an alcoholic group. This intermediate undergoes a dehydration to form the desired 1,3-butadiene product [12,24]. This reaction can be catalyzed similarly to other routes, with magnesia-silica having proven to be an effective catalyst for the Prins reaction. The magnesia is theorized to provide basic active sites, where the dehydrogenation and Prins steps are assisted, while the silica offers more acidic sites where dehydration of the butenol intermediate is likely to occur [12]. Figure 9 contains a detailed diagram of the Fripiat process with intermediates listed and named.
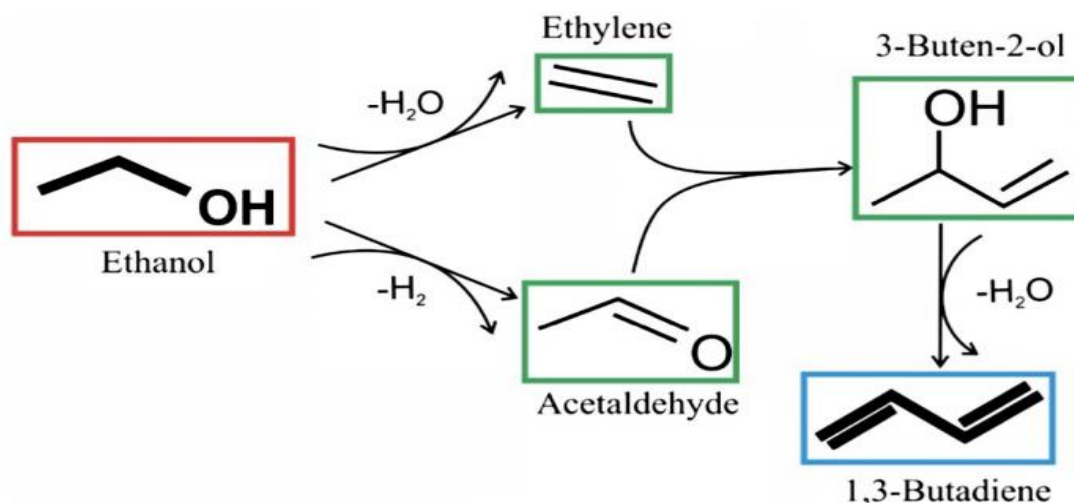
Figure 9: Detailed presentation of the main Fripiat reaction pathway. In two concurrent first steps, ethanol is dehydrated and dehydrogenated to ethylene and acetaldehyde, respectively. These two species are combined via the Prins reaction, then dehydrated to form the desired final butadiene product. From Taifan et al [24].

There are some reasons that Fripiat's Prins mechanism could be attractive relative to the more-established Lebedev and Ostromislensky routes. As alluded to previously, the energy barrier for ethanol dehydration to ethylene is lower than the barrier for ethanol dehydrogenation to acetaldehyde, as was confirmed via DFT calculations [24]. By utilizing this virtually unavoidable reaction as part of the main pathway, formation of undesired products could potentially be suppressed. This is supported by Fripiat's reported selectivity reaching 80 percent for 1,3-butadiene in some trials [12]. Unfortunately, since Fripiat's original work, relatively little research interest has been devoted to the Prins mechanism for ethanol-to-BD synthesis, although this could change in the coming years with such a large supply of ethanol available.

C_4 Olefin Production from C_4+ Sources

From the 1960s to the present, C_4 olefin production, and specifically butadiene production, has been dominated by C_4+ feedstocks rather than by synthesizing from lower-order hydrocarbons [3,12-14]. Prices for these olefins tend to fluctuate widely due to their status as a coproduct beholden to the supply and demand patterns of the more commercially important products ethylene and butane [12]. Indeed, historically speaking, very few stand-alone, on-

purpose butadiene plants have existed in the United States [14]. Naphtha cracking operations at

massive ethylene plants along the Gulf Coast produce large amounts of mixed C_4 streams that

would otherwise become waste. From this mixed butenes stream, some 1,3-butadiene and other

useful coproducts can be extracted, although these chemically similar species can be very costly

to separate [12,14]. After the butadiene is extracted, typically isobutylene is the next product

distilled off from the rest of the raffinate, followed by 1-butene, then *trans-* and *cis-*2-butenes.

These other, lesser-known C_4 olefins can be used as gasoline precursors or additives, but outside

of that industry they typically have little established commercial significance and are not in high

demand.

For other C_4 species, particularly butane and butene, the Houdry dehydrogenation process

is employed to convert the saturated butane into 1,3-butadiene. Zhang et al. noted that

degradation of catalysts was an issue for this process and used carbon nanotubes in an attempt to

increase catalyst durability and thus improve efficiency. Stability and conversion of these CNT

catalysts, particularly when oxidized in strong acid and doped with phosphorus, was very stable

over periods of 100 hours and beyond. However, maximum yield of C_4 olefins maxed out at

only 13.8 percent, with roughly even amounts of 1-butene, 2-butene, and 1,3-butadiene [13].

Although these processes can be costly and not particularly thermodynamically efficient due to

high separation costs, the sheer size of these ethylene plants and the economy of scale have

caused these C_4 extraction and dehydrogenation side units to dominate BD production for

decades.

Olefin Metathesis

Another major topic so far not discussed in this review is the field of olefin metathesis.

Olefin metathesis refers to the rearrangement of carbon chains by breaking a double bond,

changing the functional groups contained on either side, and reforming the double bond in the

new arrangement. For example, two propene molecules could be metathesized, via the scission

of a C=C bond in both molecules forming two C_1 radicals and two C_2 radicals. Via selective

dehydrogenation reactions, the like radicals combine together to form ethylene and 2-butene.

This process was inadvertently discovered by the Phillips company while attempting to alkylate

excess propylene to form high-octane gasoline. Using a supported molybdenum catalyst,

however, they found that the olefins tended to split rather than coagulate to form longer chains,

leading to the high yield of 2-butene and ethylene [31]. Today, however, due to high propylene

demand in the 21st century, the reverse reaction has become significantly more popular; with

excess ethylene being dimerized to form the 2-butene reactant, thus allowing for relatively

efficient conversion between ethylene and propylene based on demand and market trends

[26,31].

Multiple variations now exist on this method since its inception during the 1960s,

including the Phillips triolefin process to produce C_2 and C_4 olefin products from excess C_3

olefins, and the Shell Higher Olefin Process (SHOP) to produce larger C_6 and/or cyclic olefins

[26]. Interestingly, this makes olefin metathesis one of the few major fields in industrial

petrochemistry to primarily be developed and employed on an commercial scale in the last 50-60

years [31]. Multiple metal oxide catalysts have been shown to have both high selectivity and

high activity for olefin metathesis, with metals like rhenium showing an ability to bind propene

at high temperatures, facilitating the addition of an additional carbon from a passing propene

molecule [26]. Howell et al. noted an exceptionally high selectivity of 98% for the two desired

products, ethylene and 2-butene, using a tungsten oxide-based catalyst. Investigation of the

reaction using chromatography and other methods indicated that very little secondary metathesis

had occurred in the form of the desired products re-bonding to the metal, showing great promise

for tungsten oxide as a selective catalyst to activate propylene alone without disturbing the

desired ethylene or butylene molecules [25]. Lwin and Wachs noted that although rhenia-based

catalysts are more expensive, leading to less research on their potential usage, activity for olefin

metathesis using rhenia is typically quite high, and this effect increases with the size of the

reacting olefin [26].

Although olefin metathesis can be used to create C_4 olefins, the most commonly

produced via established OM methods is 2-butene. 2-butene is a relatively low-value product

with applications mostly in gasoline formulation. Little to no literature exists on the production

of higher value C_4 olefins from 2-butene, which could be for a variety of reasons. Structurally,

the dehydrogenation of 2-butene to form butadiene is difficult in comparison to other potential

BD precursors, such as 1,4-butanediol, 1-butene, or *n*-butane, for which literature on conversion

to dienes do exist [12-14, 27]. Additionally, the lone double bond in 2-butene would need to be

broken and reformed in order to form the 1,3-butadiene molecule, whereas this additional step

would not be required for the aforementioned molecules which mainly rely on simpler

dehydrations and/or dehydrogenations to be converted to BD. Thus, in order for an OM-related

scheme to compete with existing C_4 olefin production, a more direct route to highly valuable

product would be necessary.

Cost/Benefit Analysis for Selected Reaction Schemes

At this point in the review, several alternative schemes to produce C_4 olefins have been

identified, each being implemented to some degree in industrial chemistry past or present, or at

the very least having a significant amount of research and literature available on the topic. In

order to determine which of these schemes are more worthy of continued development than

others, the following sections represent an attempt to get these varied schemes on "equal footing," that is, try to compare each scheme on the basis of its pros and cons, what kind of energy inputs will be required, prices of raw materials and potential products, and other safety and economic considerations. Schemes that may be compared on this basis include but are not limited to:

- Ethylene cracking byproduct/mixed butene stream (most common method used in industry today)

- Butadiene synthesis from ethanol (multiple routes developed during WWII)

- Reverse reaction Phillips triolefin process (propylene to butadiene)

- Bio-based catalysis (the Genomatica method)

- Natural gas improvement (abundant and inexpensive feedstock)

  - Modified Fischer-Tropsch scheme (produce C_2+ alcohols)

  - Microwave-assisted synthesis (produce C_2+ hydrocarbons)

As some of these schemes undoubtedly show more promise for the production of C_4 olefins than other methods, Table 1 provides a simplified overview of the inputs required, desired products, major pros and cons, as well as information on current/historic usage of each scheme. Later, the known reaction networks and enthalpies of said reactions, as well as reported product yields from the literature, will be used to establish a rough quantitative comparison of the collected methods for C_4 olefin production.

Table 1: Major information on selected C$_4$ olefin production schemes

Scheme	Raw Materials	Main Products	Pros	Cons	Current Use?
Mixed butene distillation	Mixed C$_4$ stream (byproduct of naphtha cracking)	1,3-butadiene, isobutene, 1-butene, et al. depending on degree of separation	Makes use of potential waste, already used on massive scale	High energy demand to separate, use of non-renewables, health hazards	Comprises vast majority of C$_4$ olefin production in N. America
Ethanol-to-Butadiene	Ethanol, ideally from renewables (corn, sugar)	1,3-butadiene	Highly researched field, feed is abundant and potentially renewable	Large reaction network, many undesired products, relatively low yields	Popular during mid-20th century, still some usage in Asia
Olefin metathesis	Propylene	Ethylene and 2-butene	Highly researched field, feed is abundant	Relatively low-value products, difficulty converting/selling 2-butene	Reverse reaction is more common (high demand for polypropylene)
Bio-based catalysis	Bacteria, food, heat	1,3-butadiene, either directly or via 1,4-butanediol	Renewable, reduced danger to environment	Proprietary, limited data available, unproven on commercial scale	At least one industrial plant is operational, more in development
Microwave-assisted methane conversion	Methane (likely natural gas)	Higher order hydrocarbons (different results from other catalysts)	Avoids combustion of feed, high olefin yield in some instances	Very complex reaction network, limited data available	Mostly experimental use for hydrocarbon synthesis

With the exception of the mixed butene scheme, which relies almost entirely on distillation of the various chemically-similar C$_4$ components derived from naphtha cracking, each scheme listed above relies on some sort of reaction network, which contain some amount of undesired reactions and products, thus introducing selectivity and yield considerations for the remaining schemes. Additionally, the energy requirements for the reaction can be roughly

compared using enthalpies of reaction, most of which are obtainable through the literature. Of course, these calculations are mostly theoretical and each of the schemes besides the aforementioned mixed butene distillation likely requires additional research and development in order to compete commercially with the massive naphtha cracking operations in the economy of scale. Finally, thermodynamic data such as the heat of mixing for the various desired and side products can be used to roughly estimate the amount of energy that would be needed to distill and separate the main products from the rest of the effluent. Due to a lack of 100% efficiency, these calculations are likely to underestimate the total energy needed for distillation, but will provide an interesting data point when it comes to comparing the energy demands for these olefin production schemes.

Mixed Butenes Distillation Scheme Analysis

The mixed butenes distillation scheme is likely the simplest of the assembled methods, as the raw material already contains the desired products, C_4 olefins, in significant quantities and thus does not require any additional reaction steps. The raw material, mixed C_4 hydrocarbons, is sold by multiple companies as a byproduct from naphtha cracking. At least two successive distillations are performed to remove the most valuable products, which comprises the main operating costs for the scheme [49]. First, butadiene is extracted leaving behind "C4R1," or C_4 Raffinate-1. This raffinate itself is listed by some companies, including Dow and Royal Global Energy, as a product. Next, isobutylene is extracted, which has a variety of uses including polyisobutylene (PIB) production, a polymer used for sealing and insulation for plastic products [33]. This extraction leaves behind C4R2, or C_4 Raffinate-2, which is sold as a commodity similarly to C4R1. Additional extraction to obtain 1-butylene and other compounds present in the raffinate can be performed, but this is not as common due to lack of demand and difficulty of

separation. Other common uses for C4R2 if not further separated are methyl ethyl ketone (MEK) and fuel production. Both of these raffinate products are sold primarily in Europe and have little market fluidity due to lack of demand and the fact that most useful C_4 extractions are simply performed on-site by the company which cracked the naphtha to obtain the mixed C_4 stream in the first place [33]. For the purposes of this analysis, the sole raw material for this scheme is mixed C_4 and the products are 1,3-butadiene, isobutylene, and C_4 raffinate-2.

Table 2: Important data for mixed butene distillation scheme

Species	Commodity Price ($/kg)	Molar Mass (kg/mol)[35]	Heat of Formation (kJ/mol)[35]
Mixed C4* (feed)	$1.00[36]	55.50	26.13
1,3-butadiene (product)	$1.00[37]	54.09	110.83
Isobutylene (product)	$1.00[38]	56.11	-17.05
C4 Raffinate-2** (product)	Unknown	56.69	-42.43

*-Heat of formation and mass for the mixed C_4 determined using standard compositional data (wt. percent): 41% butadiene, 22% isobutylene, 15% 2-butene, 11% 1-butene, 7% n-butane, 4% isobutane [34]
**-Heat of formation and mass for C_4 raffinate-2 determined using standard compositional data (wt. percent): 39% 2-butene, 31% 1-butene, 18% n-butane, 11% isobutane, 1% butadiene/isobutylene [34]

As mentioned previously, due to a feed that is typically produced on-site as a cracking byproduct and a lack of necessary reactions to produce the desired olefin products, the main cost associated with this method is the massive distillation process needed to separate as many as a dozen different chemical compounds from one another. This problem is exacerbated by the chemical similarity in terms of boiling points and other physical properties of the various C_4 hydrocarbon species [49]. The most industrially important C_4 olefins tend to have very similar prices which fluctuate along with the demand for their respective derivatives. Thus, current market prices may dictate how much separation is employed by companies producing mixed C_4 as a byproduct from naphtha cracking. If butadiene and/or isobutylene prices are too low at any

given time to overcome the high energy costs associated with separation, a plant could opt not to undergo the separations and instead use or sell the mixed raffinate as is. This fluctuation in supply is a likely contributor to the unstable market price of butadiene, among other chemicals.

Due to the inherent complexity of the C_4 mixture thermodynamic properties, the exact costs associated with each distillation procedure to remove each individual product are difficult to determine. Empirical data would likely be required to determine the break-even prices for each purified C_4 olefin obtainable from the mixed butenes, although accurate process simulations provided by programs such as ChemCAD or Aspen could theoretically accomplish this task. Overall, this scheme dominates industrial production for C_4 olefins primarily due to the sheer amount of valuable products that are being formed. However, the amount of energy needed to separate the various components provides the impetus to search for a "greener" and less energy-intensive process to produce these valuable commodities.

Ethanol-to-Butadiene Scheme Analysis

The overall analysis of the ethanol-to-butadiene schemes via the Ostromislensky, Lebedev, or other similar synthesis is slightly more complex due to the reaction network. At least four distinct intermediate reactions are needed to create a four-carbon chain as well as dehydrate the alcoholic groups, leaving behind double-bonded butadiene. Additionally, the complexity of the reaction network practically guarantees the formation of other, less desired products such as ethylene or acetaldehyde. Yield data was determined from Hayashi et al, who were able to achieve about 47% single-pass ethanol conversion, with 63% of the product being the valuable chemical butadiene. The most significant side products formed were acetaldehyde (10% of product), diethyl ether (8% of product), and ethylene (6% of product) [18]. As acetaldehyde is actually an intermediate for the Lebedev mechanism, it can be recycled along

with unreacted ethanol and thus need not be counted as a "product" the same way that stable

ethylene would be. Table 3 contains important basic data for the reactants and major products in

the ethanol-to-butadiene Lebedev-based scheme.

Table 3: Important data for ethanol-to-butadiene distillation scheme

Species	Commodity Price ($/kg)	Molar Mass (kg/mol)[35]	Heat of Formation (kJ/mol)[35]
Ethanol (feed)	$0.20[39]	46.07	-235.02
1,3-butadiene (product)	$1.00[37]	54.09	110.83
Ethylene (side product)	$2.10[40]*	28.05	52.36
Diethyl ether (side product)	$2.00[41]*	74.12	-252.70

*-Prices for ethylene and diethyl ether from relatively mid-level quantities, likely lower in bulk

Using the heats of formation to roughly estimate energy demand, at least 480 kilojoules

would be required to produce one mole of 1,3-butadiene from two moles of ethanol, assuming

perfect conversion. However, this vastly underestimates the amount of energy required due to

the relatively low yields achieved under even the most ideal conditions. Using Hayashi's yield

of 63% as an adjusting factor, it is likely closer to 750-800 kilojoules of energy required to

produce just one mole of butadiene. Feed costs will also be considerably higher than the low

price of ethanol suggests; in addition to the 63% butadiene yield and 10% acetaldehyde yield

which is recyclable, some 27% of the effluent is dead-end byproducts, requiring the purchase of

additional feed to circumvent this lost product [18].

As with the mixed butenes distillation, these minor products complicate the extraction of

the useful butadiene from the rest of the reactor effluent. There are over a dozen species present

in quantities of a part per thousand or greater. This complexity makes calculation of energy

requirements to purify the butadiene and other valuable products more difficult. As this scheme

is not in wide industrial use, very little data exists about the operating costs associated butadiene production from ethanol. Advanced simulations such as ChemCAD could theoretically determine these energy demands, although empirical data from current or historical plants would be more accurate.

Olefin Metathesis Scheme Analysis

Olefin metathesis offers a relatively simple analysis due to the lack of multiple reaction steps, extremely high yields, and therefore, lack of undesired product formation. Historically, companies such as Phillips who patented the triolefin process have employed the reaction in both directions, depending on market trends in demand and price of ethylene and propylene [26]. Both ethylene and propylene are used extensively to create plastics in the form of polyethylene and polypropylene. 2-butene, however, is often sold as a mixture of *cis-* and *trans*-2-butene due to the two components having very similar chemical behaviors, thus making effective separation of the two challenging. In fact, many companies that employ the triolefin metathesis process opt to produce their butene feed on site by dimerizing excess ethylene [31]. As a result, fewer commercial processes which employ 2-butene as a feed or intermediate exist than for the high-demand C_2 and C_3 olefins. Additionally, this caused bulk quantities of 2-butene for sale to be difficult to find.   Table 4 contains relevant data to the tri-olefin metathesis scheme.

Table 4: Important data for olefin metathesis scheme

Species	Commodity Price ($/kg)	Molar Mass (kg/mol)[35]	Heat of Formation (kJ/mol)[35]
Propylene (feed)	$1.90[42]	42.08	19.93
Ethylene (intermediate)	$2.10[40]	28.05	52.36
2-butene (product)	$2.00*[43]	56.11	-9.13

*Large quantity prices for 2-butene could not be located, so the dollar value of 2-butene is almost certain to be less when sold in bulk.

Although the products ethylene and 2-butene are each currently slightly more valuable per kilogram than the propylene feed, multiple factors point to olefin metathesis being an inefficient way to product C_4 olefins. First, the lack of uses for 2-butene leads to bulk sales of the product being difficult or impossible to find, and price shown is based on a relatively small quantity of butene, just 10 kilograms. When selling 2-butene at a commercial scale, i.e. in terms of metric tons, it is reasonable to expect that there may be as much as a twofold or more drop in price per kilogram of 2-butene, based on how similar commodities are sold in bulk. Additionally, the forward reaction to produce ethylene and 2-butene is actually very slightly endothermic, with roughly over 3 kilojoules per mole of heat required to complete the reaction. This energy requirement, combined with the low (and fluctuating) profit margin achieved by consuming propylene, suggests that current market trends would need to change in order to make C_4 olefin production from propylene consistently profitable.

Biocatalysis Scheme Analysis

After nearly five years of identifying and evaluating potential reaction networks and metabolic processes for bacterial strains, the biochemistry company Genomatica patented a scheme to produce 1,4-butanediol endogenously in *Escherichia coli* bacteria [7]. Later, direct production of 1,3-butadiene using a similar scheme was patented, with both technologies reaching industrial implementation within the past several years [29]. Both schemes take advantage of the naturally-occurring TCA/citric acid cycle to metabolize simple sugars into important intermediates, then perform a series of non-naturally occurring reactions using foreign enzymes to reach the desired product. These schemes are relatively complex in comparison to others discussed in this review and require many intermediate reactions to reach completion. Table 5 contains relevant data on the chemical species associated with the bio-catalysis methods.

Table 5: Important data for biocatalysis schemes

Species	Commodity Price ($/kg)	Molar Mass (kg/mol)[35]	Heat of Formation (kJ/mol)[35]
Glucose (feed)	$0.33[44]	180.16	-1274
1,3-butadiene (product)	$1.00[37]	54.09	110.83
1,4-butanediol (product)	$1.10[45]	90.12	-426.00

Although the products butadiene and butanediol are much more valuable than the glucose feed, it should be noted that this unnatural metabolism is endothermic; thus, there is a high energy demand for these processes. Due to the extremely low heat of formation of glucose, nearly 1400 kilojoules of heat would be theoretically required to produce a single mole of butadiene under the Genomatica scheme. This high energy requirement for butadiene is mitigated somewhat when 1,4-butanediol is the desired product, with the lower heat of formation resulting in a theoretical energy savings of over 500 kilojoules per mole over the butadiene scheme, without sacrificing any production value due to the diol product's high value in its own right. As of 2017, one bio-butanediol plant was in operation in Italy by the company Novamont which had licensed Genomatica's Bio-BDO technology. In less than a year of operation, the plant had operated as promised, produced over 10,000 tons of product and was consistently producing at scale according to company press releases, although more specific economic data was not available [50].

Microwave-Assisted Methane Conversion Scheme Analysis

Methane conversion using microwaves to overcome energy barriers is another relatively new and under-researched field. Two main reactions are employed: first, methane is dimerized to form ethylene and hydrogen gas. Next, the ethylene is in turn dimerized to form 1-butene. Microwave heating is interesting as it appears to offer a way to impart high energy to reactive

systems such as flammable methane and ethylene gas causing them to react, without combusting

the raw materials. Additionally, methane is a highly abundant and relatively inexpensive raw

material, further generating interest in its potential as a hydrocarbon building block. Table 6

contains relevant information for the reactants and products of the microwave-assisted heating

scheme.

Table 6: Important data for microwave-assisted methane conversion scheme

Species	Commodity Price ($/kg)	Molar Mass (kg/mol)[35]	Heat of Formation (kJ/mol)[35]
Methane (feed)	$0.19*[46]	16.04	-74.53
Ethylene (intermediate)	$2.10[40]	28.05	52.36
1-butene (product)	$1.00[47]	56.11	0.05
Acetylene (side product)	$0.16**[48]	26.04	228.26

*Methane priced only by volume so ideal gas law was used to convert to mass/moles, using 200 bar product specifications and standard temperature of 290 K.
**-Assuming standard max tank capacity of 6.5 kg acetylene used by other vendors

Both dimerizations are extremely endothermic in nature, hence the use of high-energy

microwave radiation in order to provide sufficient energy for the reaction to occur. The

formation of ethylene from methane requires over 200 kilojoules per mole of ethylene, and the

formation of 1-butylene from ethylene requires over 100 kilojoules per mole. This high energy

demand is offset by the high values of butene and ethylene relative to methane. Care was taken

to avoid an additional dehydrogenation of the ethylene intermediate to form acetylene by

pumping excess hydrogen gas into the reactor, which resulted in very low yields of that relatively

inexpensive byproduct. Experimental data is mostly limited to the work done by Lu et al., who

reported relatively high selectivities of roughly 90% 1-butene from the second dimerization

reaction using a molybdenum-doped zeolite catalyst [1]. More studies should attempt to recreate

these promising results, which could provide another alternate pathway to efficiently producing C_4 olefins.

Discussion

Considering the mixed butenes distillation scheme which dominates current C_4 olefin production as the "control" method, there is some potential for improved outcomes using the various alternative schemes described herein. In particular, the bio-based catalysis scheme stood out as one of the more promising methods, due to a relatively simple setup with high yields and few waste products, an inexpensive and renewable feed, and potential for high profit margin. Similarly, the direct production of butenes from methane using microwave radiation could take advantage of an abundant feed in methane to produce high value products with little waste, although more research is needed into the microwave method in order to replicate the successful study by Lu et al. which produced 1-butene from methane with relatively high selectivity.

Thermodynamically speaking, all of the synthetic routes to major C_4 olefins are endothermic and will require large energy inputs. With just a few hundred theoretical kilojoules per mole, the microwave radiation reaction scheme has the lowest energy barriers, followed by the ethanol-to-butadiene scheme (adjusted for yield). The biocatalysis scheme requires the greatest theoretical energy input, but this cost is offset by the renewability of the feed and the lack of wastes. The ethanol-to-BD scheme, although it is by far the best understood synthetic pathway to produce C_4 olefins, suffers from low yields, difficult separation of byproducts/waste, as well as stagnation after being studied for nearly a century. Olefin metathesis is also a highly-researched field and boasts the highest proven yields (~99%) of any of the processes discussed herein, but the usefulness and industrial demand for the product 2-butene is low in relation to other C_4 olefins like butadiene or isobutylene, leading to the reverse reaction forming propylene

being more profitable. Comparing the schemes based on their post-reactor separation costs was a challenge, but the high yields from biocatalysis, followed by methane microwave radiation, suggest that their product purification costs would be relatively minimal compared to the much more complex ethanol-to-BD scheme or the mixed butene distillation.

Conclusion

This review as it stands is not an exhaustive survey of olefin production methods.   There are gaps that exist, particularly in the connections between the lower order C_1 to C_2 reactions and the higher order olefin productions. A vast amount of research exists for olefin production from C_4 hydrocarbons, as well as C_2+ alcohols such as ethanol, but very few studies have attempted to produce C_4 olefins from much lower feedstocks than ethanol. Some potential exists for connections between natural gas and these olefins, particularly the microwave-assisted radiation scheme which produced 1-butene from methane via successive dimerizations with relatively high selectivity. This scheme, along with green methods such as Genomatica's selective biocatalysis, show the greatest promise for a sustainable future of C_4 olefins which can replace the outdated and inefficient methods which dominate industry today.

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