

Mechanism-Based Thermodynamic Analysis for One-Step and Two-Step Ethanol-to-1,3-Butadiene Conversion Processes

Md Ziyaur Rahman, Abhishek R. Varma, Siddharth Gadkari, Atthasit Tawai, Malinee Sriariyanun, Vinod Kumar,* and Sunil K. Maity*



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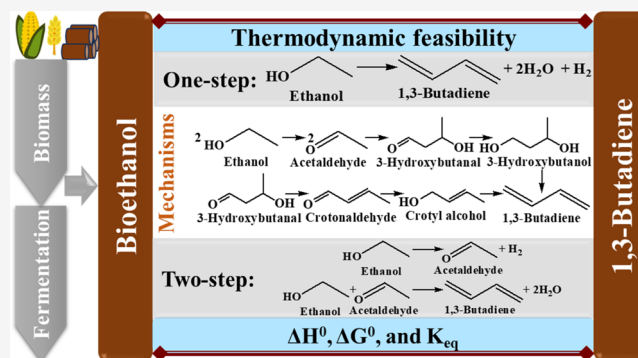
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ABSTRACT: Renewable 1,3-butadiene (BD) is essential for sustainability of the synthetic rubber sector. This work presents a comprehensive thermodynamic analysis for one- and two-step ethanol-to-BD conversion processes. The two-step process comprises ethanol dehydrogenation, followed by the condensation of acetaldehyde with another ethanol molecule into BD. The process involves a complex reaction network with a wide range of byproducts depending on the nature of the catalysts and operating conditions, lacking unique consensus on the C–C bond-forming mechanism. This study elucidates the temperature regime for the spontaneity of the reactions proposed in various mechanisms and side reactions based on the standard Gibbs free energy change. The equilibrium conversion and product selectivity were further calculated under a wide temperature and pressure range. The overall reaction in the one-step process is thermodynamically spontaneous above 417 K, while the first and second steps of the two-step process are spontaneous above 550 and 285 K, respectively. Excepting Prins condensation, other mechanisms lack the spontaneity of all reaction steps. The equilibrium BD selectivity is favorable at elevated temperatures and low pressures. The addition of acetaldehyde in the two-step process has a favorable impact with higher BD selectivity, the maximum being at a 1:1 molar ratio of ethanol/acetaldehyde. This study elucidates thermodynamic insights into existing mechanisms and drives the evolution of a feasible mechanism. This effort will eventually help design novel catalysts and optimized processes for sustainable biobased BD production using ethanol derived from renewable feedstocks, aligning with the global commitment to greener and resource-friendly chemical manufacturing.



INTRODUCTION

1,3-Butadiene (BD) is a vital building block chemical in the petrochemical industry. BD, a C₄-conjugated diene, is a versatile monomer/intermediate chemical in the manufacturing of synthetic rubbers (styrene-butadiene and polybutadiene), plastics, elastomers, and engineering plastics such as acrylonitrile-butadiene-styrene resin. The BD market is growing continuously due to the rising demand for end-user products in the building and construction, automotive, healthcare, and consumer durables sectors. The global BD market is more than 12 million metric tons with a market value of US\$34.99 billion in 2021 and is predicted to reach US\$ 55.77 billion by 2029 with a compound annual growth rate of 6%.¹ BD is mainly obtained as a coproduct while manufacturing ethylene and propylene by naphtha steam cracking at high temperatures (more than 1173 K). This BD production route is facing increasing uncertainty due to the rising use of lighter hydrocarbons from shale gas in the steam cracking process.² The gradual shifting of ethylene production away from naphtha creates a gap between BD supply and demand and soaring prices, suggesting a potential market for

biobased BD to meet the global demand.^{3,4} Besides, the dependence on nonrenewable and rapidly depleting petroleum feedstocks poses significant sustainability, carbon emission, and environmental challenges. Renewable carbon-based biomass feedstocks represent a sustainable solution for the continued production of essential petrochemicals through biorefinery approaches, aligning with the escalating demand for commodity products and contributing toward the global goal of a carbon-neutral society.

Bioethanol is one such successful biofuel in a biorefinery. It has also been placed in the revised list of platform chemicals prepared by the US Department of Energy.⁵ It is produced by the fermentation of carbohydrates derived from edible and inedible biomass such as sugar, maize, starch, and lignocellu-

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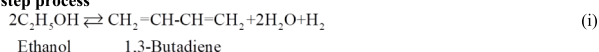


losic biomass. The global ethanol production was 28.22 billion gallons in 2022, with the US (15.36 billion gallons) and Brazil (7.4 billion gallons) as the major producers, contributing around 80% together.⁶ Brazil typically employs sugar cane, whereas the bulk of ethanol produced in the US comes from maize. Technological readiness is the most alluring attribute for the swift market penetration of bioethanol as a biofuel and platform chemical. Bioethanol provides diverse upgradation opportunities, such as ethylene, hydrogen/synthesis gas, propylene, aromatics, BD, etc.⁷ Researchers increasingly emphasize deriving BD from renewable sources, such as biobutanediols and bioethanol, underlining a shift from fossil-based synthesis toward more sustainable production methods.⁸ The current study investigates the possibility of catalytic upgrading of ethanol obtained by a fermentative route into BD. This study explicitly provides thermodynamic insights into the catalytic conversion of bioethanol into BD, exploring a viable approach to sustainable chemical synthesis.

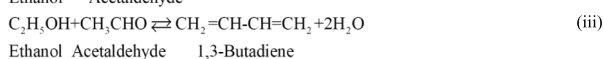
The development of synthetic routes of BD from bioethanol dates back to the early twentieth century, marked by the simultaneous emergence of two distinct technologies: the one-step and two-step processes (Scheme 1).⁹ The one-step

Scheme 1. Reaction Routes for Producing 1,3-Butadiene (BD) from Bioethanol

One-step process



Two-step process



process was developed by Russian scientist Sergey Lebedev, also known as the Lebedev process.^{10,11} This process involved BD production directly from ethanol in a single catalytic reactor by using a bifunctional catalyst comprising dehydration and dehydrogenation active sites. The two-step process was developed by American scientist Ivan Ostromislensky, where ethanol was dehydrogenated to acetaldehyde in the first stage, which was then combined with another ethanol molecule in the second stage to produce BD.¹² Despite the early success of these processes, the commercial ethanol-to-BD (ETB) technology waned post-1960s due to the advent of more cost-effective and selective petrochemical routes that leveraged inexpensive petroleum feedstock for BD production. However, the past two decades have witnessed a resurgence in the ETB reaction, spurred by the dwindling supply and price volatility of petroleum, escalating demand for commodity chemicals, and the imperative to mitigate the environmental impacts of nonrenewable petroleum-based resources. This renaissance has been reflected by a growing number of research articles on catalytic ETB reactions in recent times.

Numerous technological concepts have been researched in the recent past for sustainable BD production from biobased feedstocks. Butanediols are one such biobased platform molecule that can produce BD by dehydration of two alcohol groups.¹³ Double dehydration of 1,4-butanediol using acidic and amphoteric oxide catalysts yields BD at high temperatures.^{14,15} Bioethanol is another important biobased feedstock for BD production.¹⁶ The techno-economic and life cycle analysis of the one-step ETB process was recently performed

for an annual BD production capacity of 200 ktons.¹⁷ Their results demonstrated a marginally (1.13–1.26 times) higher minimum BD selling price than its market price for 10% internal rate of return. The life cycle analysis results showed around 8–26% reduction in CO₂ emissions compared to naphtha-based feedstock. These results emphasize the need to develop BD-selective catalysts to make the ETB process economically competitive with the petrochemical route.¹⁷ Therefore, numerous cutting-edge research articles have been published in the last two decades to develop robust BD selective catalysts and understand the fundamentals of the process, reaction mechanism, and kinetics.^{7,18,19}

The ETB process involves a complex reaction network with a diverse range of byproducts, rendering low BD yield and complexity of downstream separation processes. However, the ETB reaction mechanism is not fully understood due to the lack of evidence of intermediate molecular compounds and surface species, their kinetic and thermodynamic behavior, and exact C–C coupling reactions to obtain C₄ compound (BD) from C₂ reactants (ethanol and acetaldehyde). Although several mechanisms were proposed in the past, the researchers could not reach a unique consensus due to contrasting intermediates/products and kinetic behavior over different catalysts. Nevertheless, developing robust and BD-selective catalysts with minimal side reactions is critical to make the ETB process economically competitive against fossil-based production. The efficient catalyst design strongly depends on the fundamental understanding of mechanistic steps and the nature of active sites involved in each step. While the kinetic study provides insight into the reaction mechanism, thermodynamic analysis is an essential tool to demonstrate the feasibility of the reactions, identify the favorable reactions among the multiple competing reactions, and obtain suitable reaction conditions to enhance BD selectivity. The thermodynamic analysis also dictates possible options to shift the equilibrium of a reaction to favor desired products by manipulating reaction conditions, such as temperature, pressure, and reactant concentrations. Besides, the equilibrium constant (K_{eq}) calculated based on thermodynamic principles reveals information about the relative concentrations of reactants and products at equilibrium and how far the reaction will go before attaining equilibrium. Therefore, this work focuses on the thermodynamic understanding of overall reactions and main and side reactions involved in various proposed mechanisms of ETB processes.

Although the one-step process looks simple with a lesser number of reaction steps, ethanol dehydrogenation requires metal sites, while aldol condensation, dehydration, and Meerwein–Ponndorf–Verley (MPV) reduction reactions take place over basic or acid sites. Moreover, crotyl alcohol dehydration to BD requires relatively weak acid sites.¹⁹ Therefore, the one-step ETB process involves complex reaction networks with many possible side products, depending on the nature of catalysts and operating conditions. On the contrary, the chemistry of the two-step process is much simpler, with limited side reactions and a high yield of BD. However, only a few research articles have been published on the deeper thermodynamic understanding of the ETB processes so far. One of the earliest investigations on thermodynamic analyses reported the standard Gibbs free energy change (ΔG°) at 673 and 703 K of individual reactions involved in various possible mechanisms for the one-step conversion process.²⁰ Another earlier study also reported ΔG°

and K_{eq} at constant pressure for the overall reaction of the one-step process in the temperature range of 298–773 K.²¹ The same group also calculated ΔG° , ΔH° , and K_{eq} of each reaction of the one-step process via crotonaldehyde intermediate.²² Recently, Makshina et al. reported equilibrium product distribution for the one-step process based on the most accepted Toussaint-Kagan mechanism.²³ Garbarino et al. and Banu et al. also reported thermodynamic analysis of ETB processes in the temperature range of 373–773 K.^{24,25} Another study reported the K_{eq} for the formation of BD from acetaldehyde and ethanol mixture, ethylene from ethanol, and diethyl ether from ethanol.²⁶ These K_{eq} values were used to develop the reaction kinetics using their experimental data over the ZrO_2 – MgO – SiO_2 catalyst.²⁶ The reaction kinetics followed the Langmuir–Hinshelwood mechanism rather than the Eley–Rideal mechanism with aldol condensation as the rate-determining step. Recently, Angelici et al. reinvestigated the ΔG° changes for various reactions involved in ETB mechanisms proposed over the years and identified significant differences from the earlier reported data.⁷

The discussion presented above underscores the lack of a comprehensive thermodynamic assessment of the overall reactions, individual reactions involved in the several proposed mechanisms, and side reactions for ETB processes. This work thus aims to fill this gap by providing an extensive and in-depth thermodynamic analysis of the proposed reaction mechanisms and side reactions. The various thermodynamic parameters were calculated for each reaction under a wide temperature range, such as the standard heat of reaction (ΔH°), standard Gibbs free energy change (ΔG°), and K_{eq} . These parameters are essential in predicting the feasibility of the underlying reactions, the temperature regime for their feasibility, and the effect of temperature on their equilibrium, as per Le Chatelier's principle. The equilibrium product distribution was further calculated under a wide temperature and pressure range, considering the possible intermediates and byproducts for ETB processes. The thermodynamically favorable operating regime was then recognized based on equilibrium product distribution for maximum BD selectivity and minimum byproduct formation. This novel and comprehensive mechanism-based thermodynamic analysis will help arrive at a common consensus for the reaction mechanism that eventually facilitates the design of efficient catalysts and the choice of suitable operating conditions.

MATERIALS AND METHODS

Thermodynamic properties of the reactions, such as ΔH° , ΔG° , and K_{eq} , are calculated considering pure compounds in their gaseous states using the Aspen Plus V12.1 process simulation software package (Supporting Information for details). The ΔH° of the reactions is an important parameter for reactor design and understanding the effect of temperatures on the reaction equilibrium as per Le Chatelier's principle. According to this principle, the equilibrium of an exothermic reaction shifts in the backward direction at elevated temperatures, and vice versa. The ΔH° at any temperature, T , is related to ΔH°_{298K} by the following equation (eq 1). Le Chatelier's principle further suggests a negative impact of pressure on the equilibrium of the vapor phase reaction with a positive change in the number of moles (Δn = moles of products – moles of reactants) and vice versa.

$$\Delta H_T^0 = \Delta H_{298K}^0 + \int_{298K}^T \left(\sum_i \nu_i C_{p,i}^0 \right) dT \quad (1)$$

where ν_i is the stoichiometric coefficient of the component, i , involved in the reaction and $C_{p,i}^0$ is the heat capacity of the species at constant pressure. While ΔH° predicts a directional shift of reaction equilibrium qualitatively, it cannot provide quantitative information on the reaction equilibrium. Besides, ΔH° cannot predict the feasibility of a reaction. On the contrary, the ΔG° is the most important thermodynamic parameter for validating the spontaneity of a reaction, calculating K_{eq} , and determining equilibrium product composition at different temperatures and pressures. A chemical reaction is generally considered spontaneous if the ΔG° value is negative at a specific temperature and vice versa. The following thermodynamic equations show the relation of K_{eq} with ΔG° and the variation of ΔG° with temperatures (eqs 2–4).

$$\Delta G^0 = -RT \ln(K_{eq}) \quad (2)$$

$$\left[\frac{\partial \left(\frac{\Delta G^0}{T} \right)}{\partial T} \right]_p = -\frac{\Delta H^0}{T^2} \quad (3)$$

The integral form is as follows:

$$\Delta G^0 = \Delta G_{298K}^0 + \int_{298K}^T \Delta H^0 dT$$

For constant ΔH^0 ,

$$\ln(K_{eq_{T2}}) - \ln(K_{eq_{T1}}) = \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4)$$

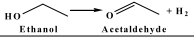
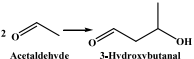
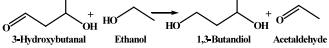
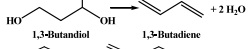
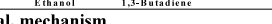
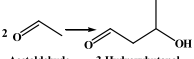
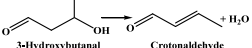
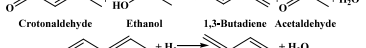
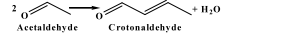
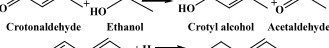
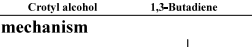
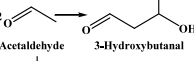
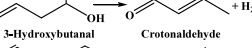
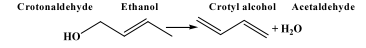
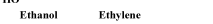
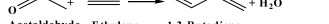
The equilibrium product composition is calculated using the RGibbs reactor model, which considers specified components as reactants and products. This model evaluates equilibrium product composition by minimizing the overall Gibbs free energy of the system; i.e., the composition with minimum Gibbs free energy is considered an equilibrium mixture. The thermodynamic parameters and equilibrium product composition are calculated in the temperature and pressure ranges of 273–873 K and 1–50 bar. The equilibrium product distribution is expressed by the conversion of ethanol or acetaldehyde and product selectivity. Ethanol (or acetaldehyde) conversion is calculated based on their inlet (F_{in}) and outlet (F_{out}) molar flow rates (eq 5).²⁷ However, the selectivity of a particular product is calculated based on the overall carbon balance, as shown by eq 6.

$$\begin{aligned} \text{Ethanol/Acetaldehyde conversion, \%} \\ = 100 \times \frac{(F_{in} - F_{out})}{F_{in}} \end{aligned} \quad (5)$$

$$\text{Selectivity of product (P), \%} = 100 \times \frac{nC_p \times F_p}{2 \times (F_{in} - F_{out})} \quad (6)$$

F_p and nC_p represent the mole flow rate of the product, p , and the number of carbon atoms present in p , respectively. The side reactions are inevitable in the ETB process depending on the nature of active centers in the catalyst and reaction conditions. These undesirable side reactions generate many

Table 1. ΔH° , ΔG° , and K_{eq} at Different Temperatures for Various Mechanisms of the One-Step Process

ΔH° , ΔG° , and K_{eq} at different temperatures for various mechanisms of the one-step process.						
Reactions	ΔH°_{298K} , kJ/mol	ΔG°_{298K} , kJ/mol	K_{eq}			
			573 K	673 K	773 K	
Common reaction						
1R1		63.9	30.0	1.7	14.4	69.5
Egloff and Hulla mechanism						
1R2		-16.5	4.6	5.3×10^{-5}	2.1×10^{-5}	1.1×10^{-5}
1R3		5.7	4.6	0.4	0.5	0.5
1R4		58.8	-15.6	6.8×10^7	4.9×10^8	2.1×10^9
Overall		47.8	14.2	2.68×10^3	7.36×10^4	8.94×10^5
Quattlebaum et al. mechanism						
1R2		-16.5	4.6	5.3×10^{-5}	2.1×10^{-5}	1.1×10^{-5}
1R5		27.3	-4.1	1.1×10^3	2.5×10^3	4.8×10^3
1R6		37.3	-6.8	2.7×10^4	9.4×10^4	2.4×10^5
1R7		-26.7	-36.9	1.5×10^4	6.6×10^3	3.4×10^3
Natta and Rigamonti mechanism						
1R2+1R5		-2.9	2.5	5.7×10^{-2}	5.5×10^{-2}	5.4×10^{-2}
1R8		19.7	12.6	0.3	0.5	0.8
1R9		-44.3	-17.5	1.6×10^{-1}	3.6×10^{-2}	1.2×10^{-2}
1R10		17.6	-19.4	9.5×10^4	1.8×10^5	2.9×10^5
Toussaint–Kagan mechanism						
1R2		-16.5	4.6	5.3×10^{-5}	2.1×10^{-5}	1.1×10^{-5}
1R5		27.3	-4.1	1.1×10^3	2.5×10^3	4.8×10^3
1R8		19.7	12.6	0.3	0.5	0.8
1R10		17.6	-19.4	9.5×10^4	1.8×10^5	2.9×10^5
Prins condensation						
1R11		45.6	7.7	3.5×10^2	1.5×10^3	4.5×10^3
1R12		-14.1	-9.5	4.4	3.4	2.9

byproducts, degrading the BD yield. In the present work, the equilibrium product distribution for the one-step process is estimated, considering all the compounds involved in the proposed mechanisms and products identified by several experimental studies reported in the literature.^{28,29} These compounds include ethanol, acetaldehyde, BD, 3-hydroxybutanal (acetaldo), 1,3-butanediol (BDO), crotonaldehyde, crotyl alcohol (2-buten-1-ol), *n*-butene, acetone, formaldehyde, methanol, ethylene, propylene, *n*-butanol, butanal, diethyl ether, ethyl acetate, acetic acid, methyl ethyl ketone, pentadiene, hexatriene, water, hydrogen, and carbon dioxide (Tables 1 and S1). Similarly, all compounds of the one-step process are considered in the equilibrium product analysis of the second stage of the two-step process, except BDO, acetic acid, and carbon dioxide, with new additions of methyl vinyl ketone, 3-buten-2-ol, and 2-butanol (Table S2). The selected compounds for thermodynamic analysis were based on the previously proposed byproduct formation scheme for the two-step process.^{27,30} Garbarino et al. and Banu et al. also

considered some of the above compounds for their equilibrium product analysis in the temperature range of 373–773 K.^{24,25}

RESULTS AND DISCUSSION

Different research groups proposed several reaction schemes for the one-step ETB process to explain the formation of BD from ethanol. The most popular reaction schemes include Egloff and Hulla mechanism, Quattlebaum et al. mechanism, Natta and Rigamonti mechanism, the Toussaint–Kagan mechanism, and the Prins condensation mechanism (Table 1). The Prins condensation mechanism proposed ethanol dehydration to ethylene as the initial reaction step. However, all other reaction schemes unequivocally advocated ethanol dehydrogenation to acetaldehyde as a preliminary reaction step, like the two-step process. However, all these reaction schemes diverge in their approaches in terms of the C–C bond-forming reactions and the subsequent reactions for converting the coupled intermediate into BD. In addition to the primary reactions, various other compounds generate inevitably from many unavoidable side reactions under the

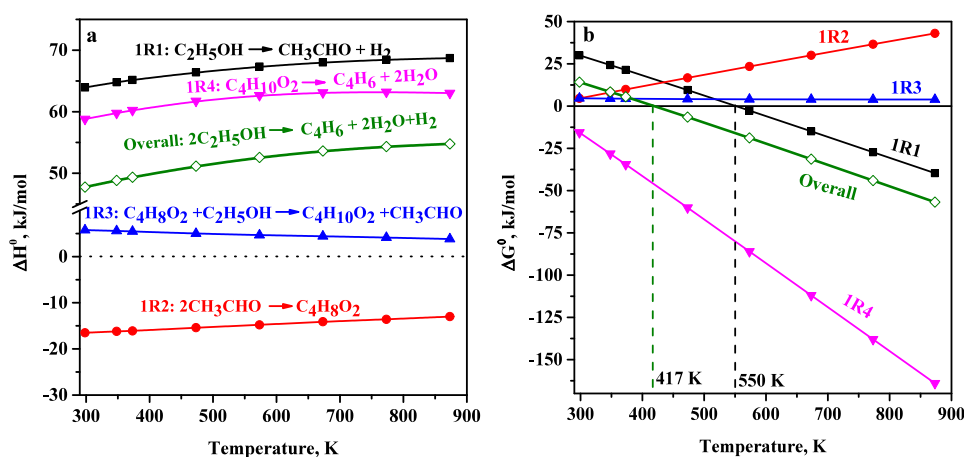


Figure 1. Standard (a) enthalpy (ΔH°) and (b) Gibbs free energy (ΔG°) changes with temperatures for the Egloff and Hulla mechanism at 1 bar.

given experimental conditions. This section presents the thermodynamic properties of these primary mechanisms and possible side reactions using their ΔG° , ΔH° , and K_{eq} values for a wide temperature range.

ΔG° and ΔH° of the Overall Reaction of the One-Step Process. The overall reaction for the one-step ETB process is endothermic for the entire temperature regime between 298 and 873 K (Figure 1). Besides, endothermicity increases slightly with an increasing temperature. The reaction equilibrium is thus favorable at elevated temperatures. However, the overall reaction is nonspontaneous at 298 K due to the positive ΔG° value. Nevertheless, the ΔG° of the overall reaction decreases linearly with temperatures, becomes zero at around 417 K, and tends to become negative beyond this temperature. The overall reaction is thus thermodynamically spontaneous above 417 K, whose reaction equilibrium progressively shifts toward the forward direction at elevated temperatures due to increased endothermicity and negative ΔG° values (Table 1). The experimental one-step ETB process was also typically studied in the temperature range of 623–773 K.^{21,31} The change in the number of moles is +2 for the overall reaction, implying unfavorable impact of pressure on the reaction equilibrium based on the Le Chatelier principle.

ΔG° and ΔH° of Ethanol Dehydrogenation Reaction. The ethanol dehydrogenation reaction into acetaldehyde is an undisputed initial reaction step in most of the one-step mechanisms and the first stage of the two-step process. The catalytic conversion of ethanol to acetaldehyde proceeds through oxidative or nonoxidative dehydrogenation reactions. The former reaction route uses molecular oxygen to activate ethanol, forming acetaldehyde and water simultaneously. A series of novel catalysts (V_2O_5/SiO_2 , $VO_x/\text{fume silica}$, V/Al_2O_3 , VO_x/Al_2O_3 , V/TiO_2 , and VO_x/TiO_2) have been developed for the oxidative ethanol dehydrogenation reaction.³² As in the present case, the nonoxidative ethanol dehydrogenation reaction employs ethanol as the solo reactant and produces an equimolar amount of acetaldehyde and hydrogen. The nonoxidative ethanol dehydrogenation is also a well-studied reaction in the literature using various catalysts, such as Al_2O_3 , $Cu-ZnAl_2O_4$, Au/SiO_2 , Au/MoO_3 , Au/TiO_2 , and $Au/MCM-41$.^{24,32,33} Gruver et al. studied the one-step ETB reaction using aluminated sepiolite and silver-exchanged aluminated sepiolite at 280 °C and 50 torr ethanol in helium.³⁴ The trends of acetaldehyde selectivity with ethanol conversion were opposite to that of BD selectivity, confirming

acetaldehyde as the BD precursor.³⁴ The participation of acetaldehyde in the BD formation reaction and the reversible nature of the ethanol dehydrogenation reaction was also confirmed by isotopic tracer experiments, in which ethanol was fed with deuterated and ^{14}C acetaldehyde.¹⁹

The nonoxidative ethanol dehydrogenation reaction (1R1) is highly endothermic, and its endothermicity increases slightly with temperature (Figure 1). The reaction equilibrium is thus favorable at high temperatures. The ΔG° of this reaction is positive at 298 K, making it thermodynamically nonspontaneous at this temperature. However, the ΔG° value decreases linearly with temperature, becomes zero at around 550 K, and tends to be negative above this temperature. The nonoxidative ethanol dehydrogenation reaction is thus thermodynamically spontaneous above 550 K. The negative ΔG° value further increases progressively with temperatures. The reaction equilibrium is thus increasingly favorable at higher temperatures (Table 1). Under the reaction conditions, all of the components involved in this reaction are in the vapor phase. The Δn of this reaction is +1, implying that the high pressure is unfavorable for the equilibrium of the ethanol dehydrogenation reaction for such a vapor phase reaction. Similar equilibrium data for nonoxidative ethanol dehydrogenation to acetaldehyde have also been reported by previous research group.²³ The experimental findings also evidenced that the ethanol conversion to acetaldehyde was significant only above 550 K, which was in line with our thermodynamic analysis results.³⁵ However, a few experimental studies exhibited a significant ethanol conversion well below 550 K.^{36–39} However, the exact reasons for such contradictory results are not clear to us and need further investigation.

ΔG° and ΔH° of the One-Step Process. Egloff and Hulla Mechanism. Egloff and Hulla proposed a mechanism using four series reactions via the BDO intermediate (Table 1).³³ The self-aldol condensation of acetaldehyde was proposed as the C–C coupling reaction to form a C4 intermediate from the C2 compound. The aldol condensation product, 3-hydroxybutanal, is then reduced to BDO by hydrogen transfer from ethanol, known as the MPV reaction, which itself oxidizes to acetaldehyde. BDO is finally dehydrated to BD. Except for acetaldehyde aldol condensation (1R2), all other reactions involved in this mechanism are endothermic, with the highest being for ethanol dehydrogenation (1R1), followed by BDO dehydration (1R4) and MPV reduction (1R3) (Figure 1). While the heat of the reaction

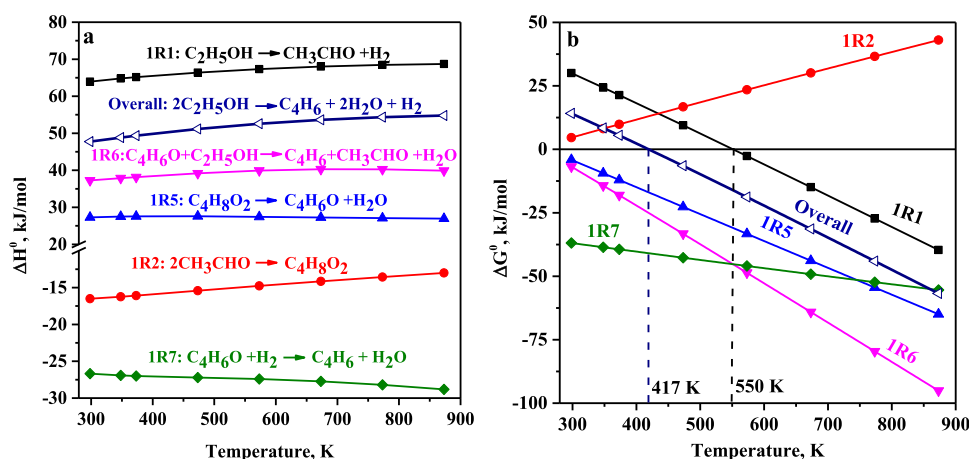


Figure 2. Standard (a) enthalpy (ΔH°) and (b) Gibbs free energy (ΔG°) changes with temperatures for the mechanism of Quattlebaum et al. at 1 bar.

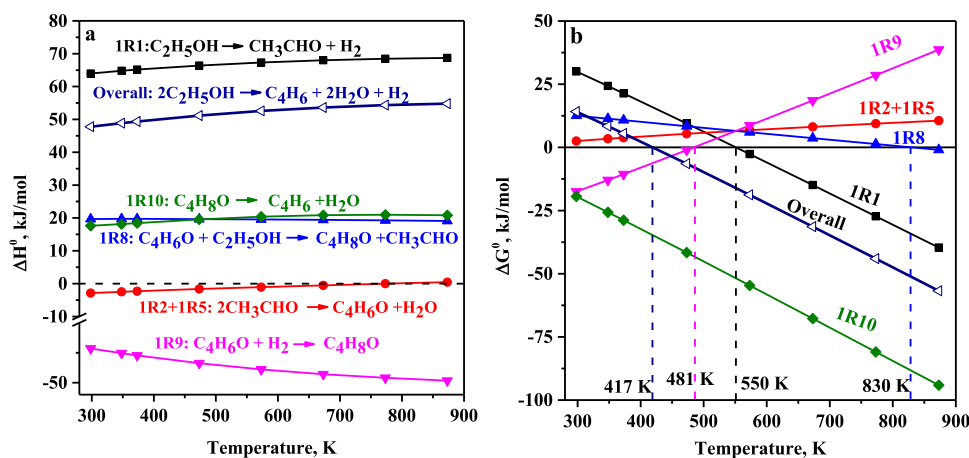


Figure 3. Standard (a) enthalpy (ΔH°) and (b) Gibbs free energy (ΔG°) changes with temperatures for the Natta and Rigamonti mechanism at 1 bar.

marginally declines with the temperature for 1R3, all other reactions exhibit an increasing trend of ΔH° with temperatures. Therefore, high temperatures favor the 1R1, 1R3, and 1R4 reaction equilibrium. However, the reaction equilibrium of 1R2 is unfavorable at high temperatures.

The ΔG° value of the acetaldehyde self-aldol condensation reaction is slightly positive at 298 K and rises sharply with temperatures. Therefore, this reaction is perhaps spontaneous only at lower reaction temperatures. This result is inexplicable, as aldol condensation is a well-studied reaction. To resolve this fallacy, the ΔG° of this reaction was further calculated considering all the components in the liquid phase, and ΔG° was found to be negative at 298 K. Earlier thermodynamic analysis also reported a positive ΔG° value for the acetaldehyde self-aldol condensation reaction.²³ Recently, pure 3-hydroxybutanal conversion was studied using the basic MgO catalyst at 523 and 673 K with a short residence time.⁴⁰ Their experimental results showed that 3-hydroxybutanal dehydration was the minor reaction with only trivial amounts of crotonaldehyde, and the reverse aldol condensation was the major reaction with significant amounts of acetaldehyde. All of these results corroborate that the self-aldol condensation of acetaldehyde is not thermodynamically spontaneous at high reaction temperatures.

The MPV reaction exhibits a small positive ΔG° value over the entire temperature range. However, the BDO dehydration reaction is thermodynamically spontaneous over the whole temperature range and becomes more and more spontaneous at higher temperatures. However, despite being spontaneous, the BDO dehydration experiments showed contrasting results. The experimental study using pure BDO showed ethanol and acetaldehyde as major products over the MgO catalyst at 673 K, with minor amounts of BDO dehydration products, methyl vinyl ketone and methyl ethyl ketone.⁴⁰ Based on these results, the authors concluded that the reverse addition reaction of BDO was dominant over the catalyst rather than the BDO dehydration reaction. Although all reactions are not spontaneous, the thermodynamic feasibility of this mechanism hinges strongly on subsequent series reactions, whose combination makes this mechanism feasible at higher reaction temperatures. Recently, Liu et al. successfully developed and validated a kinetic model based on this mechanism, considering aldol condensation as the rate-determining step over the $\text{ZrO}_2\text{-MgO-SiO}_2$ catalyst.²⁶

Quattlebaum et al. Mechanism. Quattlebaum et al. performed experimental studies using potential intermediates and their combination over various catalysts to elucidate the ETB reaction mechanism.⁴¹ Their study showed that BD formed rapidly when the crotonaldehyde-ethanol (rather than

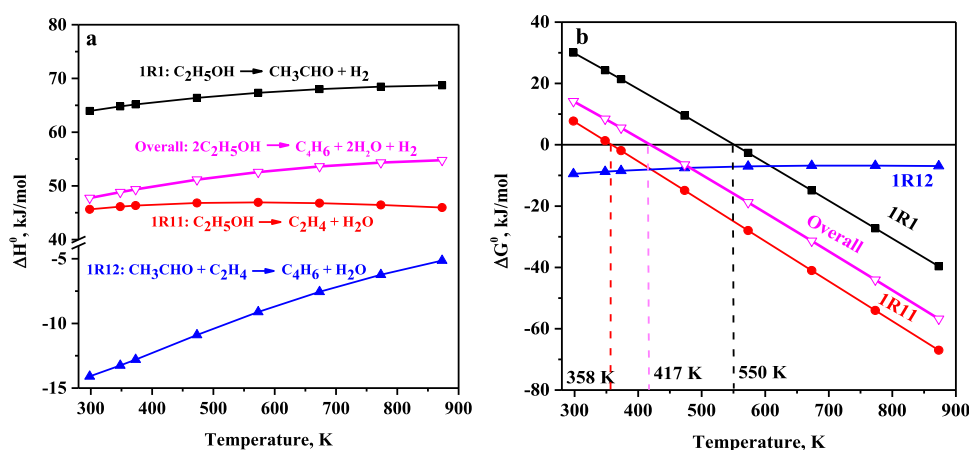


Figure 4. Standard (a) enthalpy (ΔH°) and (b) Gibbs free energy (ΔG°) changes with temperatures for the Prins condensation mechanism at 1 bar.

acetaldehyde) mixture was passed over the alumina catalyst, with the coproduction of acetaldehyde. Besides, crotonaldehyde was readily formed from acetaldehyde, but it was insignificant during the conversion of the ethanol-acetaldehyde mixture to BD over the tantalum-oxide-promoted silica gel catalyst. Therefore, their study undoubtedly confirmed crotonaldehyde as the main intermediate in both the one- and two-step ETB processes. Crotonaldehyde is formed via the dehydration of 3-hydroxybutanal (1R5). This reaction is endothermic and thermodynamically spontaneous, and its equilibrium is favored at higher temperatures (Figure 2). The crotonaldehyde is then converted into BD by hydrogen transfer from ethanol (1R6) or direct hydrogenation reaction (1R7). While the conversion of crotonaldehyde into BD by hydrogen transfer from ethanol is endothermic, direct hydrogenation of crotonaldehyde is exothermic. Nonetheless, both crotonaldehyde reduction reactions are exergonic over the specified temperature range, as supported by Natta et al.²⁰ and Bhattacharyya et al.²² The reaction equilibrium of 1R6 is thus favored at higher temperatures, while high temperatures negatively impact the reaction equilibrium of 1R7 (Table 1). Bhattacharyya and Sanyal have also reported ΔG° and K_{eq} at 298 K, 653 K, and 733 K for the reactions involved in the Quattlebaum et al. mechanism during their kinetic studies.²²

Natta and Rigamonti Mechanism. The ΔG° of the acetaldehyde self-aldol condensation reaction (1R2) is positive and increases with temperature, whereas 3-hydroxybutanal dehydration reaction (1R5) is spontaneous in the entire temperature range (Figure 2). These facts led Natta and Rigamonti to combine these two reactions to produce crotonaldehyde directly from acetaldehyde instead of via 3-hydroxybutanal intermediate.²⁰ The merged reaction was reported to be feasible with negative ΔG° values under the ETB reaction temperature range.²⁰ However, our calculation shows that the ΔG° value of the combined reaction is positive in the entire temperature range and increases slightly with temperature (Figure 3). Therefore, this combination is not thermodynamically spontaneous under the reaction temperature. Contrary to the Quattlebaum et al. mechanism, Natta and Rigamonti proposed an intermediate reaction step for crotonaldehyde reduction to crotyl alcohol. Crotonaldehyde is reduced to crotyl alcohol by an endothermic hydrogen transfer reaction from ethanol (1R8) or an exothermic reaction using molecular hydrogen (1R9) (Table 1). However, the reactions

display a positive ΔG° below 830 K for 1R8 and above 481 K for 1R9. Previous studies showed that crotonaldehyde reduction by ethanol was thermodynamically more favorable than molecular hydrogen.^{7,23} Recently, ethanol-to-BD conversion was studied over basic MgO catalysts at 523 and 673 K to identify intermediate compounds in a short residence time.⁴⁰ Acetaldehyde with traces of *i*-butanol was detected for less than 0.4 s of residence time, with the formation of *i*-butanol, crotyl alcohol, and 3-buten-1-ol at longer residence times. However, 3-hydroxybutanal and crotonaldehyde were not detected during their study. Their catalytic test using pure crotyl alcohol further showed the formation of BD along with *i*-butanol and acetaldehyde.⁴⁰ The crotyl alcohol finally undergoes an endothermic dehydration reaction to give BD (1R10), which is exergonic throughout the reported temperature range. Natta et al. and Bhattacharyya et al. also reported that the crotonaldehyde reduction to crotyl alcohol was more favorable by ethanol than hydrogen.^{20,22}

Toussaint–Kagan Mechanism. The reactions proposed in the Toussaint–Kagan mechanism are analogous to previous schemes, especially the Natta–Rigamonti mechanism. Quattlebaum et al. experimentally demonstrated that crotonaldehyde was the undisputed intermediate in both Lebedev and Ostromyslensky processes.⁴¹ Quattlebaum et al. considered the direct reduction of crotonaldehyde into BD by the MPV reaction or using molecular hydrogen. However, the Toussaint–Kagan mechanism introduced an intermediate crotonaldehyde reduction step, like the Natta and Rigamonti mechanism. The variation of ΔG° and ΔH° with temperatures for each of these reactions can be found in Figures 2, 3, and S1.

Prins Condensation Mechanism. Gruver et al. studied the one-step ETB process using Lewis acidic (aluminated sepiolite) and bifunctional (silver-exchanged aluminated sepiolite) catalysts at 553 K with 50 Torr of ethanol in helium and observed acetaldehyde, ethylene, diethyl ether, and BD.³⁴ Their results revealed a linear rise in ethylene and BD yields with ethanol conversion. Based on these results, they proposed the Prins condensation of acetaldehyde with ethylene for the formation of BD. According to this mechanism, ethanol is first dehydrated to ethylene (1R11), which subsequently condenses with acetaldehyde to form BD (1R12). Interestingly, except for ethanol dehydrogenation, the other reactions, especially the C–C coupling reaction, are unique and distinct from the previously proposed mechanisms. The ethanol dehydration

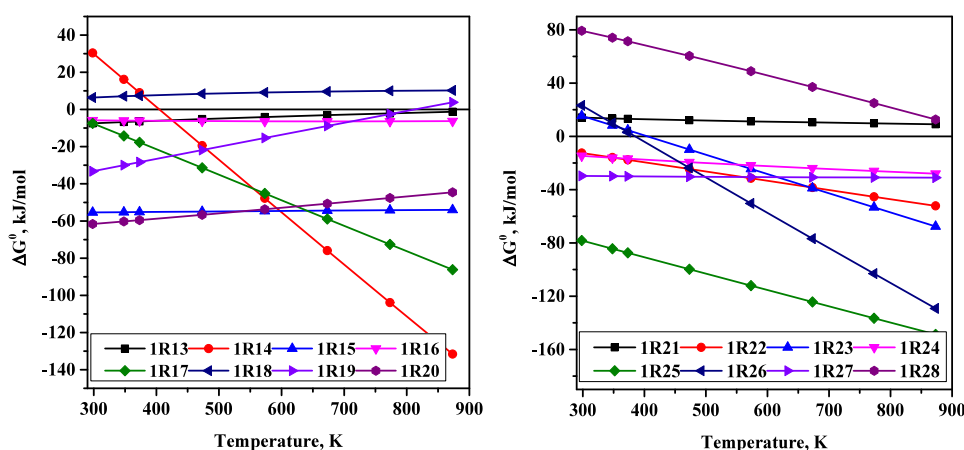


Figure 5. Standard Gibbs free energy (ΔG°) changes with the temperature for the side reactions of the one-step process at 1 bar.

reaction is endothermic, while 1R12 is exothermic (Figure 4). The ΔG° of ethanol dehydration (1R11) exhibits a positive value at 298 K, decreases with increasing temperature, becomes zero at 358 K, and tends to negative values beyond this temperature. This reaction is thus spontaneous above 358 K. The Prins condensation reaction (1R12) displays small negative ΔG° values over the entire temperature range, making it energetically feasible. However, the K_{eq} of 1R12 is relatively low compared to 1R11 and decreases with temperature. Therefore, a proper selection of the reaction temperature above 358 K is important for sufficient equilibrium conversion for both reactions. All individual reactions of this mechanism are spontaneous in the temperature range of the ETB process. However, the ability of the catalyst to accelerate the different reactions will determine the temperature range needed for the formation of BD from ethanol.

ΔG° of Side Reactions for the One-Step Process.

Besides the primary pathway leading to BD, many byproducts have been reported in the literature with numerous side reactions. However, most of the experimental studies have been mainly focused on understanding the main pathway for BD formation, overseeing the identification/quantification of byproducts or their formation mechanism. Nevertheless, byproducts and their quantity depend strongly on the type of catalyst and nature of active centers. The present work enlisted a few potential side reactions (1R13 to 1R28) based on reported data in the literature and proposed byproduct formation schemes by Da Ros and Dussol^{27,30} (Table S1). Several research groups identified a range of byproducts during their experimental studies, such as acetaldehyde, ethylene, diethyl ether, butanes,^{42–44} propylene,^{45–47} ethyl acetate,⁴⁸ *n*-butanol,^{49,50} crotonaldehyde,^{51,52} and crotyl alcohol.^{53,54} Carbon monoxide and carbon dioxide were also detected in small quantities.^{55,56} The formations of diethyl ether, butanal, *n*-butanol, 1-butene, ethyl acetate, acetone, carbon dioxide, propylene, formaldehyde, and methanol are thermodynamically feasible, with a negative ΔG° value for the corresponding reactions (Figure 5). However, ΔG° is positive for the BD formation reaction directly from ethylene (1R18) throughout the temperature range.²⁵ Diethyl ether dehydration (1R14) is favorable above 405 K, adding more ethylene. The K_{eq} value is very low for 1R21 and 1R28, implying that ethyl acetate hydrolysis to acetic acid and butene dehydrogenation to butadiene are unfavorable in the stated temperature range. However, Yan et al. reported a high BD selectivity during

oxidative dehydrogenation of 1-butene under the CO_2 atmosphere over alumina-supported iron-based catalyst.⁵⁷

ΔG° and ΔH° of the Overall Reactions of the Two-Step Process. Both steps of the two-step process are endothermic, and their endothermicity further increases with temperature, implying a favorable effect of temperature on the reaction equilibrium (Figure 6). The ΔG° values show that the

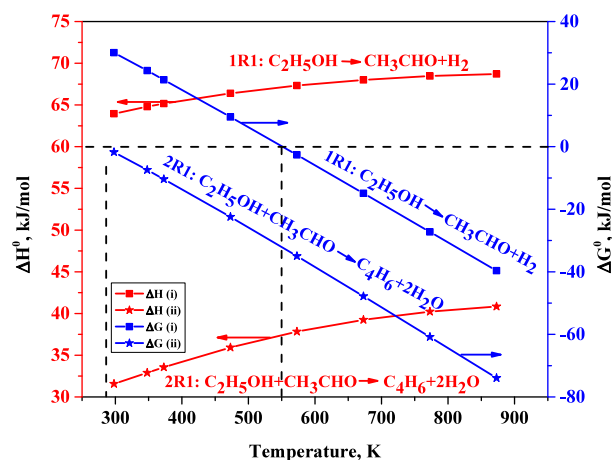


Figure 6. Standard enthalpy (ΔH°) and Gibbs free energy (ΔG°) change with temperature for overall reactions in the two-step process at 1 bar.

first stage is spontaneous above 550 K, while the second stage is spontaneous in the entire temperature range. Quattlebaum et al., Dussol et al., Jones et al., and Toussaint et al. investigated the second stage of the two-step ETB process using different catalysts.^{29,30,41,58,59} The experimental temperature range for BD production from ethanol and acetaldehyde is 633–733 K.³³ Dussol et al. proposed a reaction scheme for converting ethanol and acetaldehyde mixture into BD.³⁰ The Δn value of both stages of the two-step process is +1, implying a negative impact of pressure in both stages. However, experimental results over tantalum-silica catalyst showed that BD production could be increased 2-fold and 4-fold by operating at 50 and 200 psig, respectively, compared to atmospheric pressure.⁹

ΔG° and ΔH° of Side Reactions of the Second Stage of the Two-Step Process. The second stage of the two-step process is equally complex, like the one-step process, and involves the formation of various byproducts accompanied by

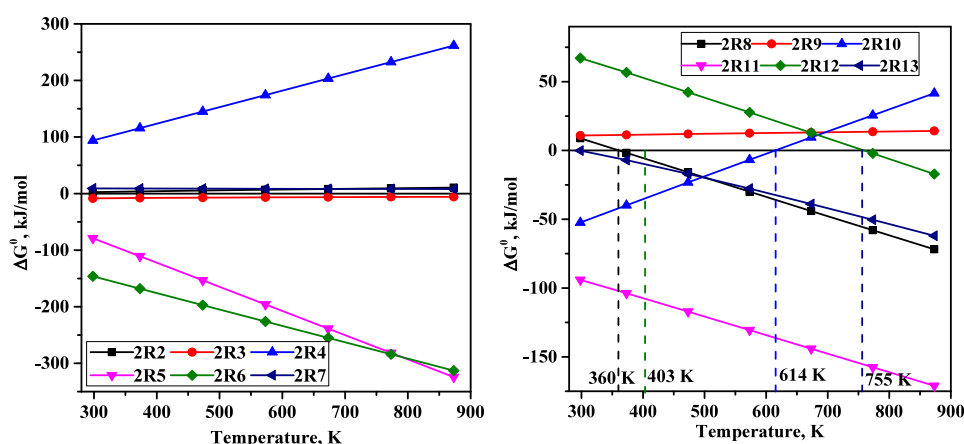


Figure 7. Standard Gibbs free energy (ΔG°) changes with temperature for the side reactions in the second stage of the two-step process at 1 bar.

many side reactions. Toussaint et al. demonstrated the two-step ETB process with an overall BD yield of 65–70% and ethyl ether, ethylene, hexenes, hexadienes, ethyl acetate, pentenes, pentadiene, acetic acid, and *n*-butanol as major byproducts.⁵⁸ In their study, ethanol dehydrogenation was performed using the copper catalyst, and the reaction of acetaldehyde with ethanol was investigated over 2% tantalum oxide silica gel catalyst at 598 K with an ethanol/acetaldehyde molar ratio of 3.0.⁵⁸ Corson et al. investigated the reaction of acetaldehyde with ethanol using 2% tantalum pentoxide on silica gel catalyst and reported the following optimal conditions based on laboratory and pilot plant studies: 0.6 h⁻¹ liquid hourly space velocity, 623 K, and 2.75:1 ethanol/acetaldehyde mole ratio.⁹ Quattlebaum et al. also studied this reaction using the same catalyst and observed the following byproducts: ethylene, propylene, butene, ethyl ether, acetic acid, ethyl acetal, ethyl acetate, methyl ethyl ether, crotonaldehyde, crotyl alcohol, *n*-butanol, butanal, methyl ethyl ketone, pentadiene, pentenes, hexaldehyde, hexadienes, and hexenes.⁴¹ Kim et al. reported the formation of ethylene, propylene, butene, ethoxy ethane, ethyl acetate, crotonaldehyde, and acetic acid over the spherical silica-supported tantalum oxide catalyst.⁶⁰ Kyriienko et al. obtained 80–90% BD selectivity at a total conversion of 45–30% over tantalum-silica-based zeolite catalysts with ethylene, diethyl ether, and crotonaldehyde byproducts.⁶¹ The reaction was studied using Ta₂O₅-SiO₂ catalysts at 613 K and 3.6:1 ethanol/acetaldehyde molar ratio.³⁰ Small quantities of crotonaldehyde, methyl vinyl ketone, crotyl alcohol, 3-buten-2-ol, butanal, methyl ethyl ketone, and 2-butanol were observed as the byproducts, and their yield decreased with space-time, implying their conversion to other products. However, the yield of ethylene, diethyl ether, and ethyl acetate was increased with residence time.⁴⁰ Da Ross et al. and Dussol et al. proposed the reaction schemes for forming these byproducts, as shown in Table S2.^{27,30}

The 2R4-5, 2R7-9, and 2R12-14 reactions are endothermic at 298 K, while the remaining side reactions are exothermic. The ΔG° for the reduction of methyl vinyl ketone with ethanol (2R4) is highly positive and increases with the temperature (Figure 7). Thus, this reaction is not spontaneous in the reported temperature range. The ΔG° shows small positive values for 2R2 and 2R7, with negligible changes with temperatures. The K_{eq} slightly decreases for 2R2 and increases for 2R7 with increasing temperatures. Similarly, the conversion of acetaldehyde to acetone and formaldehyde (2R9) is not

spontaneous, with positive ΔG° values in the entire temperature range. The ΔG° of ethyl acetate formation from acetaldehyde (2R10) is negative at lower temperatures and becomes nonspontaneous above 614 K. On the other hand, ΔG° values of 2R8, 2R12, and 2R13 are positive at lower temperatures, decrease with temperature, and become negative at 323, 403, and 755 K, respectively. All other side reactions are thermodynamically feasible in the entire temperature range.

Equilibrium Product Composition for the One-Step Process. Figures 8 and S2 present the effect of temperature and pressure on ethanol conversion and product selectivity. The equilibrium ethanol conversion is nearly complete (>99.9%) over the entire temperature range, especially at 1 bar pressure. However, the ethanol conversion falls slightly with increasing pressure due to the positive Δn value of the overall ETB and ethanol dehydrogenation reactions (1R1). Ethanol dehydrogenation (1R1) and overall one-step ETB reactions are endothermic and spontaneous above 550 and 417 K, respectively, at atmospheric pressure. Therefore, the ethanol conversion improves with temperatures above 473 K for atmospheric pressure. The BD is the desired end product. However, the equilibrium BD selectivity remains very low in the entire temperature and pressure range due to the formation of more stable products, and it is prominent only above 573 K at 1 bar. The BD selectivity proliferates by increasing temperatures and reducing pressures. The overall one-step ETB reaction is endothermic with $\Delta n = 2$ and thermodynamically spontaneous above 417 K, resulting in rising trends of BD selectivity at elevated temperatures and reduced pressures.

Ethanol dehydrogenation (1R1) is an undisputed initiation reaction step in the one-step process and is the primary source of acetaldehyde. Acetaldehyde also forms from MPV reactions, where ethanol acts as a hydrogen source, such as 1R6, 1R8, 1R16, 1R23, 1R25, and 1R27, of which 1R8 is not thermodynamically spontaneous. Among the acetaldehyde-forming reactions, only 1R1, 1R6, and 1R23 are endothermic. However, 1R25 and 1R27 are not significant reactions, as reflected by the low selectivity of methyl ethyl ketone and methanol. On the other hand, acetaldehyde is consumed by exothermic 1R2, 1R2 + 1R5, and 1R12 reactions. Therefore, higher acetaldehyde selectivity at elevated temperatures is due to enhanced acetaldehyde formation with reduced consumption. Besides, the low acetaldehyde selectivity indicates the dominance of consumption reactions compared to its formation. The Δn values of the acetaldehyde forming/

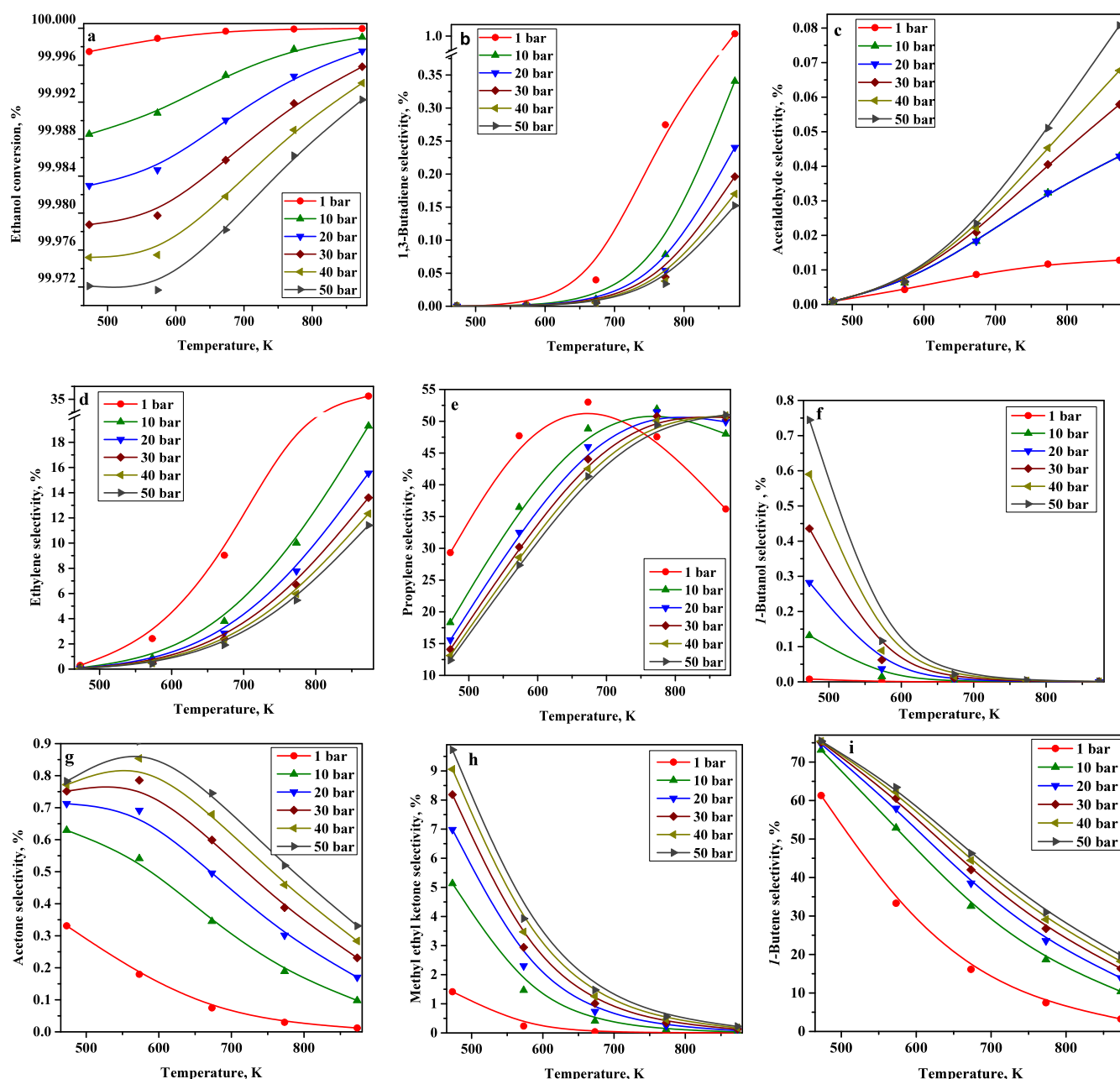


Figure 8. Effect of temperature and pressure on (a) ethanol conversion and (b–i) product selectivity for the one-step process. Selectivity of (b) 1,3-butadiene, (c) acetaldehyde, (d) ethylene, (e) propylene, (f) *n*-butanol, (g) acetone, (h) methyl ethyl ketone, and (i) 1-butene.

consuming reactions are + 1 for 1R1, 1R6, and 1R23, −1 for 1R2, and 0 for 1R16, 1R2 + 1R5, and 1R12. The acetaldehyde-consuming reactions might be favorable at elevated pressure due to negative Δn , with enhanced acetaldehyde selectivity.

3-Hydroxybutanal, crotonaldehyde, and crotyl alcohol are the intermediates in most reported mechanisms except for Prins condensation. However, their selectivity is extremely low in the entire temperature and pressure range (Figure S2) and increases slightly with temperature and pressure. The Egloff and Hulla mechanism proposed BD formation through BDO. It is formed from 3-hydroxybutanal via endothermic MPV reduction by ethanol (1R3, $\Delta n = 0$) and converted to BD by the endothermic dehydration reaction (1R4, $\Delta n = 2$) (Table 1 and Figure S2). While reaction 1R4 is thermodynamically feasible, 1R3 is not spontaneous in the entire temperature range, justifying the extremely low equilibrium BDO

selectivity. These factors also account for a slightly rising trend of BDO selectivity with pressures and temperatures up to around 650 K. However, the endothermic BDO decomposition reaction (1R26) becomes spontaneous only above 390 K, resulting in a slight downhill in BDO selectivity at elevated temperatures. The Prins condensation mechanism proposed BD formation through the ethylene intermediate. Ethylene is formed by an endothermic ethanol dehydration reaction (1R11 and $\Delta n = 1$), which is thermodynamically spontaneous above 358 K. The ethylene is then condensed with acetaldehyde to form BD by an exothermic reaction (1R12, $\Delta n = 0$). However, the ΔG° value of the ethylene-consuming reaction is much less negative than that of 1R11 in the entire temperature range. Therefore, ethylene is observed as a prominent product, contrary to the intermediates in other reported reaction mechanisms. Besides, the ethylene selectivity

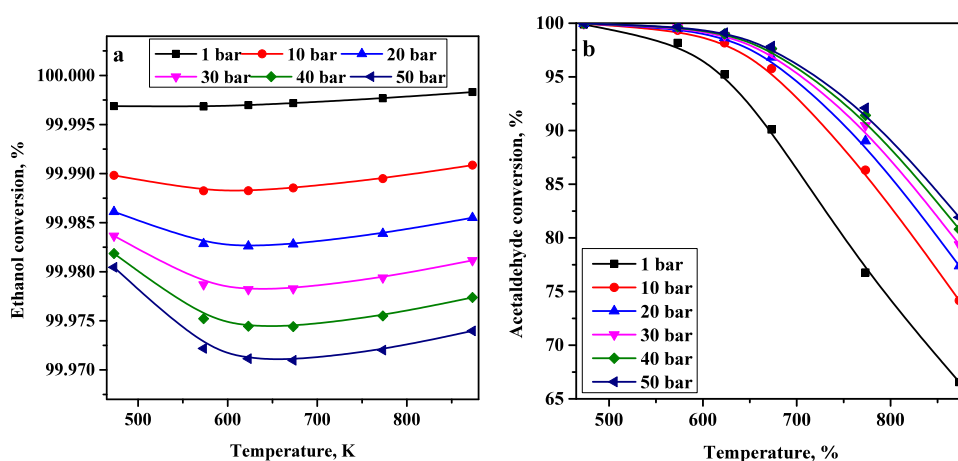


Figure 9. Effect of temperature and pressure on (a) ethanol and (b) acetaldehyde conversion at 3:1 ethanol/acetaldehyde mole ratio for the second stage of the two-step process.

is high at elevated temperatures and low pressures (Table 1 and Figure 8).

Propylene is another prominent equilibrium product and is formed by 1R23-24 and 1R26. 1R23 ($\Delta n = 1$) and 1R26 ($\Delta n = 2$) are spontaneous above 405 and 387 K, respectively, and their K_{eq} increases drastically with temperature (Table S1 and Figure 8). However, the K_{eq} of 1R24 ($\Delta n = 0$) is relatively low and decreases with temperature. The propylene selectivity thus increases with temperature and decreases with pressure. *I*-Butanol is formed via exothermic MPV reduction of butanal by ethanol (1R16, $\Delta n = 0$), which latter converts to *I*-butene by the endothermic dehydration reaction (1R17, $\Delta n = 1$). While both reactions are spontaneous, the K_{eq} of 1R16 is relatively lower than that of 1R17 and decreases with temperature. On the contrary, the K_{eq} of 1R17 increases with temperature. The *I*-butanol selectivity is thus higher at lower temperatures and higher pressures due to greater consumption of *I*-butanol than the formation.

Acetone is formed by the endothermic 1R22 ($\Delta n = 1$) and consumed by endothermic 1R23 ($\Delta n = 2$) and exothermic 1R24 ($\Delta n = 0$) reactions (Table S1 and Figure 8). The reaction 1R23 is spontaneous only above 405 K, while the other two reactions are spontaneous over the entire temperature range. However, the K_{eq} value of 1R22 is significantly higher than 1R23 and 1R24 and increases with temperature. Therefore, acetone selectivity increases with increasing temperatures and shows a downhill trend beyond a certain temperature when acetone consumption by 1R23 becomes prominent. However, the high pressure favors equilibrium acetone selectivity due to more unfavorable consumption by 1R23 ($\Delta n = 2$) than formation by 1R22 ($\Delta n = 1$) at elevated pressures. Methyl ethyl ketone is formed by exothermic and thermodynamically feasible 1R25 ($\Delta n = 1$) and 2R6 ($\Delta n = 0$) reactions, with low K_{eq} at elevated temperatures. Although these reactions can explain the methyl ethyl ketone selectivity drops at high temperatures based on the reaction parameters described above, they cannot explain the positive impact of pressure on the equilibrium selectivity.

I-Butene is the major equilibrium byproduct, especially at lower temperatures. It is formed by endothermic butanol dehydration (1R17 and 2R8) and exothermic ethylene dimerization (1R19) reactions. While former reactions are progressively spontaneous at higher temperatures, the K_{eq} of 1R19 gradually decreases with temperature and becomes

nonspontaneous above 811 K (Tables S1 and S2, Figure 8). However, the proposed *I*-butene consumption reaction (1R28) is not thermodynamically spontaneous. These parameters suggest the roles of both reactions in the trends of *I*-butene selectivity. While ethylene dimerization is prominent at low temperatures, *I*-butene forms by butanol dehydration at high temperatures, especially above > 811 K. This statement is supported by the increasing trend of ethylene selectivity and decreasing trend of butanol selectivity with temperature. The increase in *I*-butene selectivity with pressure is due to the negative Δn value for the ethylene dimerization reaction. On the contrary, the experimental study showed BD formation by oxidative dehydrogenation of *I*-butene using CO_2 as a soft oxidizing agent over the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst.⁶² The selectivities of butanal, diethyl ether, ethyl acetate, acetic acid, methanol, formaldehyde, *n*-pentadiene, and hexatriene are negligibly small, and their trends with temperature and pressure are graphically presented in Figure S2. Carbon dioxide is a thermodynamic stable compound, with high selectivity at low pressure and high temperature.

Equilibrium Product Composition for the Second Stage of the Two-Step Process. The equilibrium ethanol conversion is almost 100% in the second stage of the two-step process despite using more than stoichiometric moles of ethanol and favorable at low pressures like the one-step process (Figure 9). These results signify the direct conversion of ethanol to some other products besides the reaction with acetaldehyde. However, contrary to the one-step process, the ethanol conversion initially decreases with temperature and then shows a slightly increasing trend. In contrast, the acetaldehyde conversion is favorable at low temperatures and high pressures. The most prominent thermodynamically feasible acetaldehyde-consuming reactions (1R12, 2R3, and 2R10) are exothermic, resulting in a drop in acetaldehyde conversion at elevated temperatures. The equilibrium product distribution is shown in Figures 10 and S3. Although the trends of BD selectivity are analogous to the one-step process, the second stage of the two-step process shows BD as a prominent product with high selectivity in the entire temperature and pressure range. These results signify that the external addition of acetaldehyde is thermodynamically favorable for BD formation. These trends of results are due to the endothermic nature of the overall BD formation reaction (2R1) with $\Delta n = +1$ (Table S2).

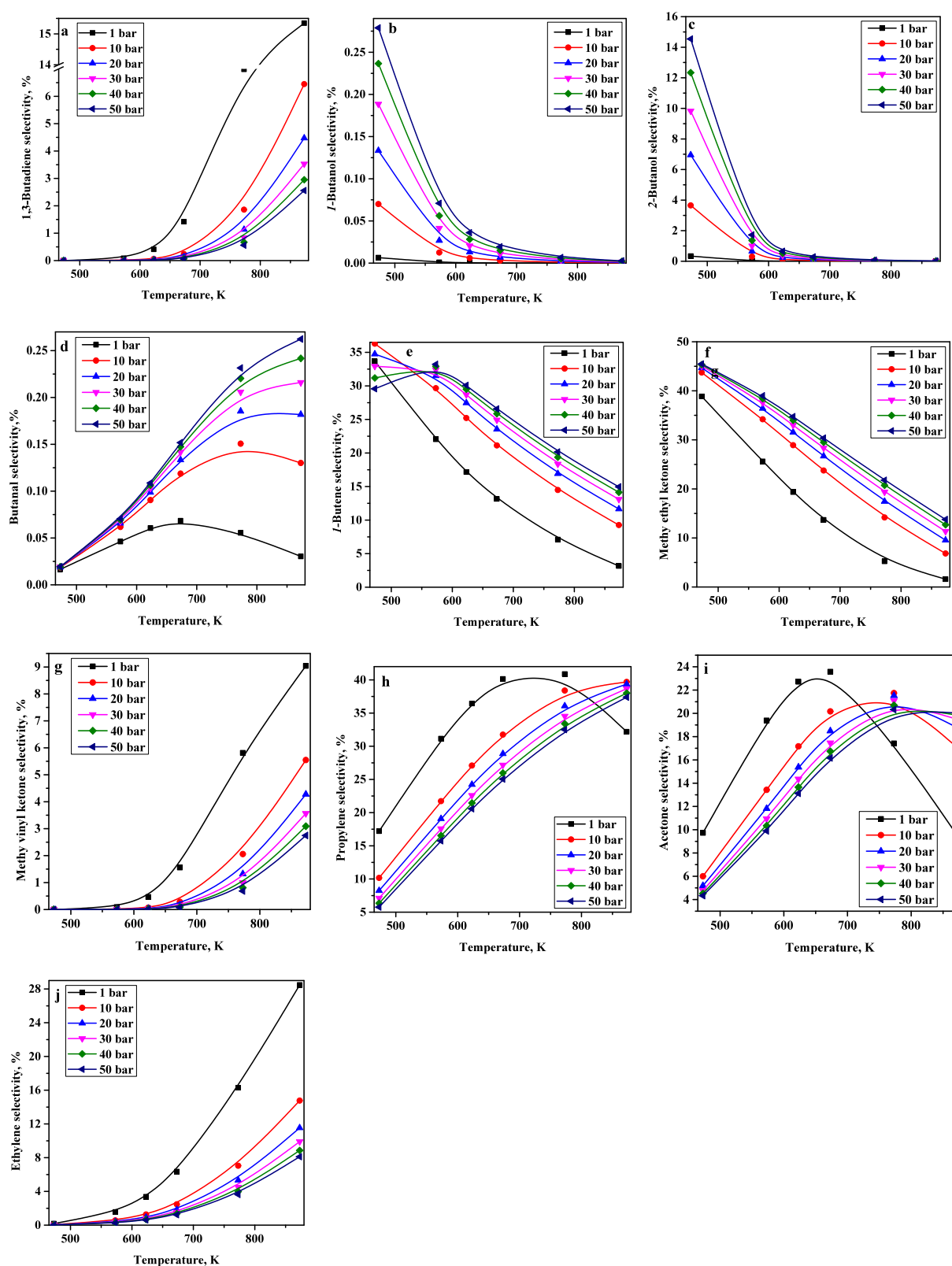


Figure 10. Effect of the temperature on product selectivity at different pressures for the second stage of the two-step process. Selectivity of (a) 1,3-butadiene, (b) 1-butanol, (c) 2-butanol, (d) butanal, (e) 1-butene, (f) methyl ethyl ketone, (g) methyl vinyl ketone, (h) propylene, (i) acetone, and (j) ethylene. Ethanol/acetaldehyde mole ratio=3:1.

The methyl vinyl ketone, 2-butanol, and 3-buten-2-ol are additional products in the two-step process. The methyl vinyl ketone formation reaction (2R3, $\Delta n = 0$) is exothermic and thermodynamically feasible in the reported temperature range.

However, the proposed methyl vinyl ketone consumption, as described in reaction (2R4), is not viable. The ΔH° and ΔG° of these reactions can explain the increasing trend of methyl vinyl ketone selectivity with temperature. However, these

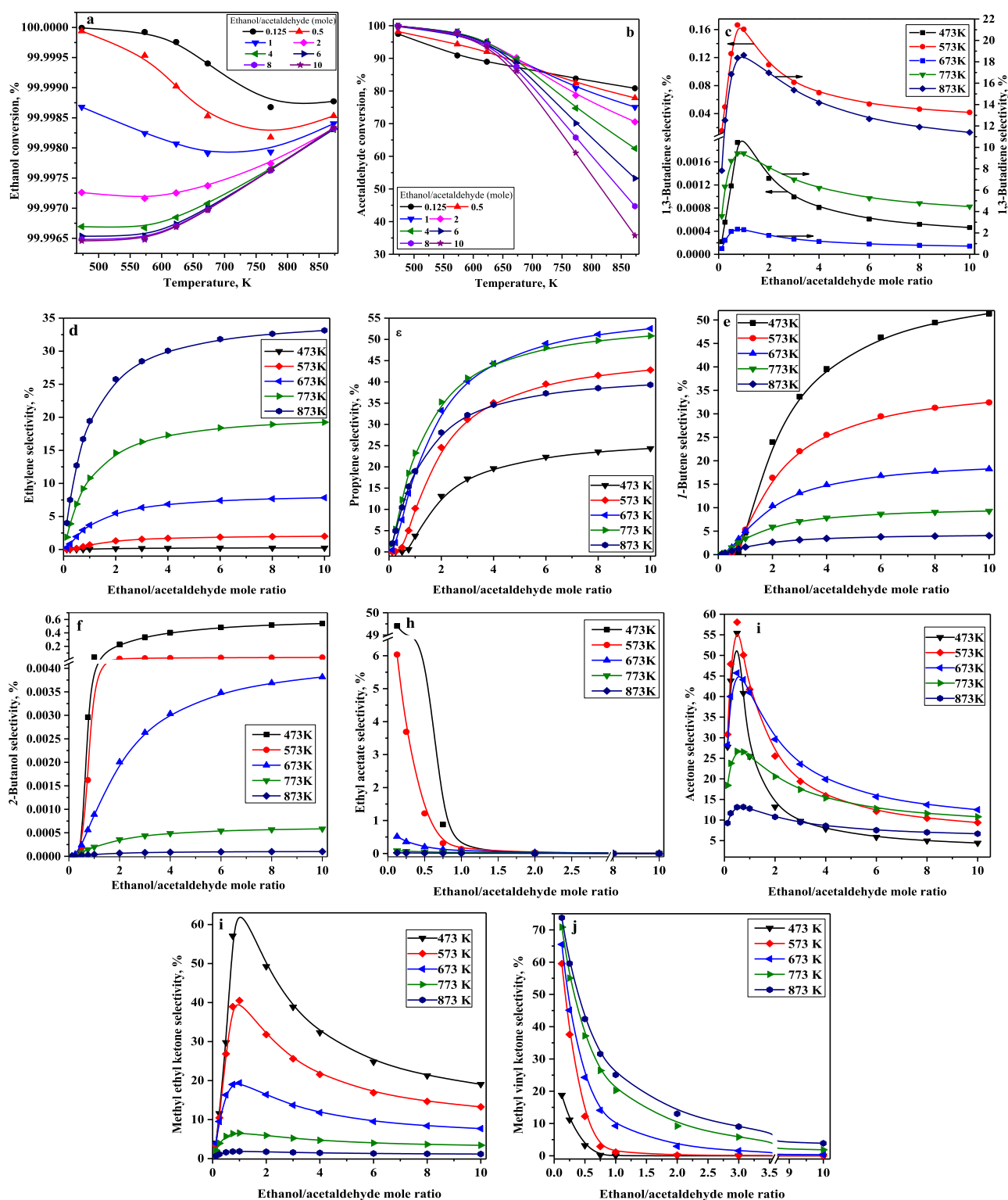


Figure 11. Effect of the ethanol/acetaldehyde mole ratio on (a) ethanol and (b) acetaldehyde conversion and product selectivity. Selectivity of (c) 1,3-butadiene, (d) ethylene, (e) propylene, (f) 1-butene, (g) 2-butanol, (h) ethyl acetate, (i) acetone, (j) methyl ethyl ketone, and (k) methyl vinyl ketone at various temperatures and 1 bar pressure for the second stage of the two-step process.

reactions alone cannot elucidate the negative impact of pressure on methyl vinyl ketone selectivity, indicating the possibility of some other reactions for its formation or consumption. The proposed 2-butanol formation reaction (2R7) is not spontaneous; however, its consumption reaction (2R8) is viable and endothermic. However, the equilibrium

analysis results show a significant amount of 2-butanol, especially at low temperatures and high pressures. These results indicate the possible involvement of some other feasible reactions in forming 2-butanol. The two-step process proposes a nonspontaneous 2R4 reaction for 3-buten-2-ol formation and highly spontaneous (2R5 and 2R6) reactions for its

consumption, with extremely low selectivity in the whole temperature and pressure range.

The trend and quantum of 1-butanol, ethylene, and propylene are comparable with those of the one-step process. Although trends are practically similar to the one-step process, the butanol is the prominent product in the two-step process. Identical arguments can be used to explain the trends of these results. The selectivity to methyl ethyl ketone is relatively higher in the two-step process, but the selectivity trends remain almost the same as in the one-step process. It is proposed to form via exothermic reactions from 3-butan-2-ol (2R6, $\Delta n = 0$) in the two-step process and 3-hydroxybutanal (1R25, $\Delta n = 1$) in the one-step process. The acetone selectivity is relatively higher than that of the one-step process. Like the one-step process, the acetone selectivity initially increases and falls below a certain temperature. However, in this mechanism, the pressure has a negative impact on the acetone selectivity. The two-step process proposes 1-butene formation from 2-butanol (2R8) by the thermodynamically viable endothermic reaction. However, the 1-butene selectivity is relatively lower in the two-step process.

Effect of Ethanol/Acetaldehyde Mole Ratio on Product Composition for the Second Stage of the Two-Step Process. The effect of the ethanol/acetaldehyde mole ratio on ethanol and acetaldehyde conversion and selectivity to major products is shown in Figure 11. The ethanol conversion is higher at lower ethanol/acetaldehyde mole ratios. For the ethanol/acetaldehyde mole ratios of 1:1 and lower, the ethanol conversion is almost 99.99% at low temperatures, dips slowly with temperatures, and increases again beyond a specific temperature. However, the ethanol conversion shows an increasing trend with temperature for an ethanol/acetaldehyde mole ratio of 2:1 and higher. Xu et al. studied the effect of ethanol/acetaldehyde mole ratio (2.5–4.5) experimentally using 0.5 wt% ZnO doped $\text{ZrO}_2\text{--SiO}_2$ catalyst at 1.8 h^{-1} WHSV and 583 K and observed a drop in ethanol conversion at an elevated ethanol/acetaldehyde mole ratio, with high selectivity to ethanol dehydration products (ethylene and diethyl ether).⁵⁰ The equilibrium ethylene selectivity also increases with the ethanol/acetaldehyde molar ratio due to the higher ethanol quantity. The acetaldehyde conversion is close to 100% at low ethanol/acetaldehyde mole ratio and decreases with temperature. The drop in acetaldehyde conversion may be due to its formation from ethanol.

The selectivity to BD, acetone, and methyl ethyl ketone initially increases with the ethanol/acetaldehyde mole ratio, attains a maximum at a certain mole ratio, and then decreases beyond that mole ratio. The maximum equilibrium BD and methyl ethyl ketone selectivity is observed at the stoichiometric ethanol/acetaldehyde mole ratio of 1:1 for the entire temperature range. However, acetone selectivity peaked at a 0.5:1 ethanol/acetaldehyde mole ratio. At a fixed temperature, a low ethanol/acetaldehyde mole ratio, i.e., high acetaldehyde concentration, favors reverse MVP reduction of crotonaldehyde (1R8) and methyl vinyl ketone (2R5), with low BD selectivity. Similarly, above the 1:1 ethanol/acetaldehyde mole ratio, the acetaldehyde quantity is less than the stoichiometric requirement with low BD selectivity. However, the experimental optimal ethanol/acetaldehyde mole ratio was reported to be a function of temperature, for example, 2:1 at 648 K, 2.75:1 at 623 K, and 3:1 at 608 K.⁹ With the increase in

ethanol content, more acetone and formaldehyde are hydrogenated (1R23 and 2R11), increasing the propylene selectivity.

The ethanol/acetaldehyde mole ratio has a favorable influence on 1-butene selectivity, especially at low temperatures. The experimental result over 2% Zr/SiO_2 catalyst at 593 K and 1.2 h^{-1} WHSV showed that selectivity to 1-butene was higher than that to BD for high acetaldehyde content. The Guerbet condensation of ethanol is another potential reaction to produce 1-butanol from ethanol, which further dehydrates to 1-butene.⁶³ The oligomerization of ethylene further adds 1-butene (1R19). The ethyl acetate selectivity is very high at a low ethanol/acetaldehyde mole ratio, especially at low temperatures. It may be due to the fact that the ethyl acetate forming reaction 2R10 is favorable at high acetaldehyde concentrations. Methyl vinyl ketone is formed from acetaldehyde by 2R3, with high selectivity at a low ethanol/acetaldehyde mole ratio. The variation of selectivity to 1-butanol, butanal, crotonaldehyde, and hexatriene with an ethanol/acetaldehyde mole ratio is shown in the Supporting Information (Figure S4). A lower acetaldehyde concentration (higher mole ratio) leads to the more selective formation of ethylene and diethyl ether, whereas a higher acetaldehyde concentration (low mole ratio) leads to more 1-butanol, hexatriene, and others (mainly C6 compounds). Other literature has reported a similar result for the two-step process.^{50,60,61,64}

CONCLUSIONS

This study scrutinized the thermodynamic feasibility of the available mechanisms and accompanying side reactions of ETB processes, assessing the equilibrium product composition at various temperatures, pressures, and ethanol/acetaldehyde mole ratios. The overall reactions in both processes are spontaneous at the experimental process temperatures. However, the exact sequence of intermediate reactions leading to BD is not fully understood. Except for the Prins condensation, the thermodynamic viability of other mechanisms is dubious, pointing to the necessity for further investigations to establish a universally accepted reaction scheme grounded on experimental evidence. The C–C coupling reaction is critical to obtaining the C4 product (BD) from the C2 reactant (ethanol). However, the exact C–C coupling reaction is still debatable, as acetaldehyde aldol condensation, which is considered in most of the mechanisms, is spontaneous only at low temperatures. Although Prins condensation of acetaldehyde with ethylene to BD shows small negative ΔG° values, it needs to be validated experimentally. Despite almost 100% ethanol conversion, equilibrium BD selectivity remains low in the one-step process and is enhanced at high temperatures and low pressures. However, BD is the prominent product in the two-step process, with the maximum being at a 1:1 ethanol/acetaldehyde mole ratio, signifying the positive impact of acetaldehyde addition. Butene is the most dominating equilibrium product in both processes, especially at low temperatures and high pressures. Ethylene and propylene are other prominent equilibrium products at elevated temperatures and low pressures. However, the selectivity to key intermediates in most reported mechanisms, such as 3-hydroxybutanal, crotonaldehyde, and crotyl alcohol, remains extremely low over the entire temperature and pressure range. Future experimental studies should be directed to understand the exact C–C coupling reaction to unravel the thermodynamically feasible reaction network for the ETB processes.

Knowledge of active catalytic sites will eventually help design novel BD selective catalysts with minimum byproducts to develop commercial ETB processes successfully.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.4c02681>.

Methodology used in Aspen Plus, ΔH° and ΔG° change with temperatures for the Toussaint–Kagan mechanism, ΔH° , ΔG° , and K_{eq} at different temperatures for side reactions of the one-step and two-step processes, and effect of temperature, pressure, and ethanol/acetaldehyde mole ratio on the selectivity of selected products for one-step and two-step processes (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Vinod Kumar – Faculty of Engineering and Applied Sciences, Cranfield University, Cranfield MK43 0AL, U.K.; Department of Biosciences and Bioengineering, Indian Institute of Technology Roorkee, Roorkee 247667 Uttarakhand, India; orcid.org/0000-0001-8967-6119; Phone: +44 (0) 1234754786; Email: vinod.kumar@cranfield.ac.uk

Sunil K. Maity – Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Sangareddy 502284 Telangana, India; orcid.org/0000-0002-1832-5060; Phone: +91-40-23016202; Email: sunil_maity@che.iith.ac.in

Authors

Md Ziaur Rahman – Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Sangareddy 502284 Telangana, India; Advanced Centre for Energetic Material (ACEM), DRDO, Nasik 422007 Maharashtra, India

Abhishek R. Varma – Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Sangareddy 502284 Telangana, India

Siddharth Gadkari – School of Chemistry and Chemical Engineering, University of Surrey, Guildford GU2 7XH, U.K.; orcid.org/0000-0001-5228-8534

Attasit Tawai – The Sirindhorn International Thai-German Graduate School of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand; orcid.org/0000-0001-7363-781X

Malinee Sriariyanun – The Sirindhorn International Thai-German Graduate School of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.iecr.4c02681>

Notes

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M.Z.R.: Investigation; Writing—original draft. A.R.V.: Data Curation; Writing—review and editing. S.G., A.T., and M.S.: Writing—review and editing. V.K.: Conceptualization; Writ-

ing—review and editing. S.K.M.: Conceptualization; Supervision; Funding acquisition; Writing—review and editing.

■ ABBREVIATIONS

ΔH_T° : standard enthalpy change at temperature T
 ν_i : stoichiometric coefficient of the component, i
 BDO: 1,3-butanediol
 $C_{p,i}^\circ$: heat capacity of the species, i , at constant pressure
 ETB: ethanol-to-1,3-butadiene
 ΔG° : standard Gibbs free energy change
 ΔH° : standard heat of reaction
 MPV Meerwein–Ponndorf–Verley R: ideal gas constant
 T : temperature
 K_{eq} : equilibrium constant

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Mechanism-based thermodynamic analysis for one-step and two-step ethanol-to-1,3-butadiene conversion processes

Rahman, Md Ziyaur; Varma, Abhishek R.; Gadkari, Siddharth; Tawai, Atthasit; Sriariyanun, Malinee ...

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