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Article

Determination of Thermodynamic Properties for the Esterification of Levulinic Acid with 1-Butene

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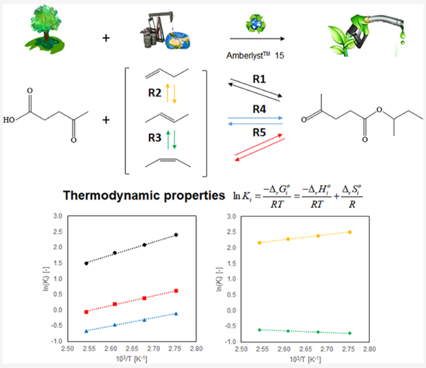
ABSTRACT: The thermodynamic equilibrium of the liquid phase esterification of levulinic acid (LA) with 1-butene (1B) to obtain *sec*-butyl levulinate (SBL) was studied. Equilibrium experiments were performed in a batch reactor at 2.5 MPa in the temperature range of 363−393 K using Amberlyst-15 as the catalyst. The thermodynamic equilibrium for the side reactions (i.e., isomerization of 1B to *trans*-2-butene, isomerization of *trans*-2-butene to *cis*-2-butene, and esterification of LA with these isomers) was also studied. The thermodynamic properties of the reaction were determined experimentally and compared to theoretical estimations and reported literature values. The enthalpy and entropy changes of the esterification reaction with 1B at 298.15 K were estimated to be −(32.9 ± 1.6) kJ/mol and −(70 ± 4) J/(mol·K), respectively. As for the SBL thermodynamic properties, it was found that the liquid phase enthalpy change of formation and entropy at 298.15 K were −(737.1 ± 0.3) kJ/mol and (423 ± 3) J/(mol·K), respectively.



1. INTRODUCTION

In recent years, the energy demand has been increasing, as fossil fuel resources have been decaying, leading to the need to speed up the search for alternative fuels.[1] This energy pattern requires a transition to more sustainable and cleaner resources to accomplish the goals set by the Paris Agreement 2015, such as limiting global warming to 2 °C or lower, as well as reaching net zero emissions by the second half of the twenty-first century.[2,3] A suitable alternative to the conventional fuels relies on the use of the biomass-derived fuels since biomass is considered a renewable energy source.[4]

Nowadays, biofuels can be classified into four different types: first-generation biofuels are obtained from food crops, second-generation are made of lignocellulosic materials, those in the third generation are based on algae biomass production, and fourth-generation biofuels use synthetic biotechnology.[5] At present, the most suitable choice leans toward the second generation of biofuels, because, on one hand, the first generation of biofuels must compete with food crops, which would be unethical, and, on the other hand, the third and fourth generation of biofuels are not yet cost-competitive when compared to the first two categories due to lack of development.[5]

Levulinic acid (LA), also known as 4-oxopentanoic acid, is a water-soluble organic compound that possesses a ketone and a carboxylic group, giving it a wide range of functionality as well as reactivity.[6] LA is considered one of the most promising platform chemicals from lignocellulosic biomass and can be produced by the Biofine Process.[7] Many value-added compounds can be prepared from LA, such as fertilizers, pesticides, or fuel additives, among others.[7,8] Among these LA derivatives, alkyl levulinates have received significant attention because they are potential substitutes of current chemicals coming from petrochemical routes. In fact, alkyl levulinates can be considered effective in reducing harmful emissions.[9] Furthermore, alkyl levulinates present outstanding properties to be blended with diesel fuel, such as high lubricity or low toxicity, resulting in a better engine performance.[10]

Typically, alkyl levulinates are obtained by esterification of LA with an alcohol, employing either a homogeneous or a heterogeneous catalyst.[11] Alternatively, the catalytic esterification of LA with an olefin, such 1-butene (1B), instead of an alcohol has been proven to be more efficient in terms of minimizing byproduct formation (e.g., water and dialkyl ether) and boosting atom economy, which, therefore, increases the yield to the desired product.[11,12] In addition, this chemical route would allow revalorization of unused olefinic streams, which are frequently burned when the demand for polybutene is low.[13] If 1B is used as the esterifying agent, *sec*-butyl levulinate (SBL) is produced.

As the first step toward the large-scale industrialization of alkyl levulinate production, thermodynamic information on

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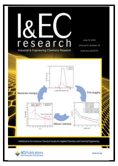

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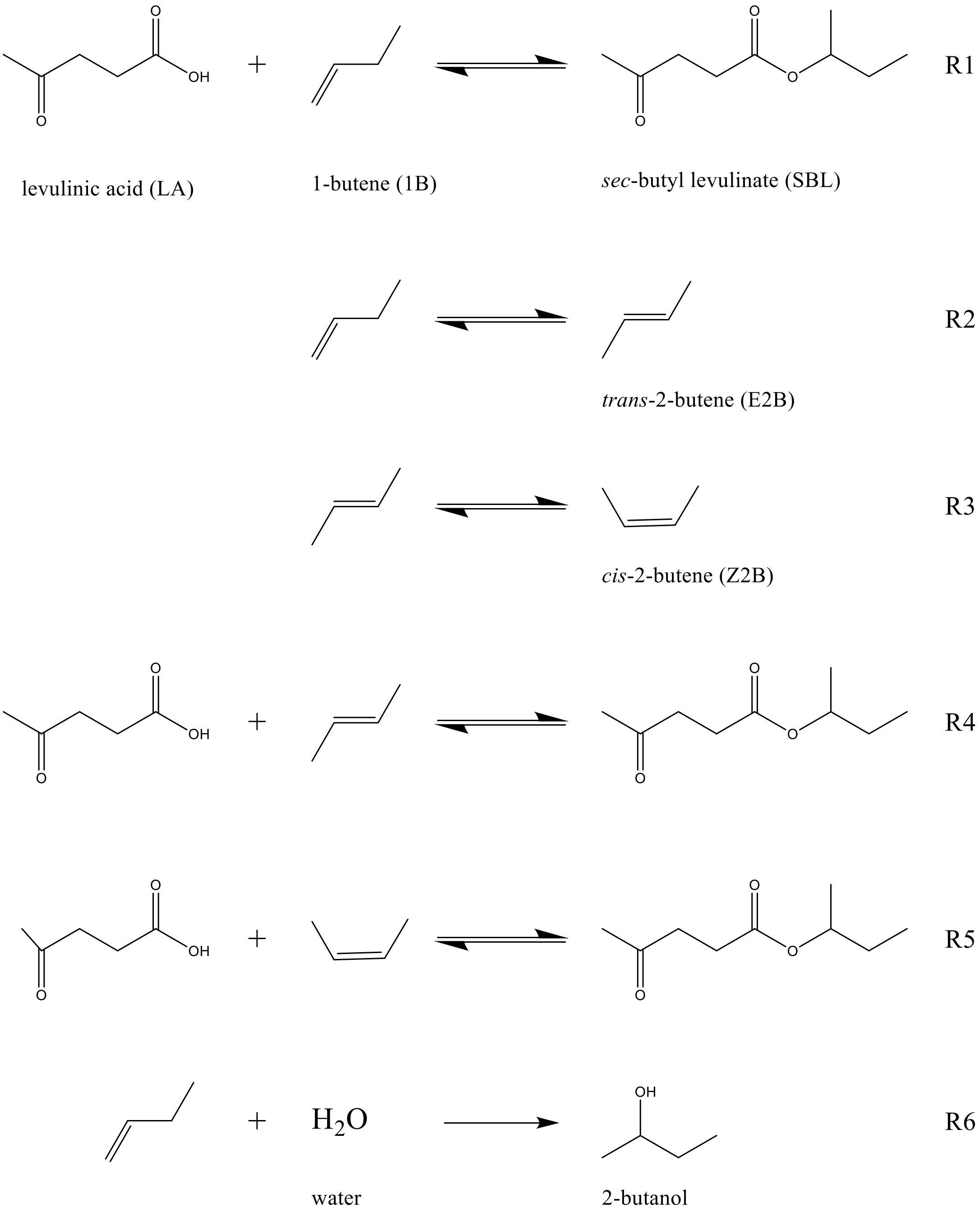
Scheme 1. Studied Reaction Network



these systems must be obtained and assessed. However, thermodynamic studies of reaction systems involving the presence of olefins, organic acids, and esters are very scarce in the literature. Therefore, the aim of the present work is to fill this lack of information, by determining experimentally the thermodynamic properties of the SBL synthesis by esterification of LA with 1B in the liquid phase.

2. MATERIALS AND METHODS

2.1. Materials. The reactants used were levulinic acid (LA, 98% GC; Across Organics) and 1-butene (1B, > 99.9% GC; Air Liquide). As chemical standards for chromatographic analyses, 2-butanol (99% GC; Panreac) and butyl levulinate (98% GC; Sigma-Aldrich) were used. Due to the unavailability of commercial *sec*-butyl levulinate (SBL), butyl levulinate (BL) was used instead. As found in previous works, BL has a similar chromatographic response to SBL.[11,12,14]

A commercial, sulfonic styrene-divinylbenzene resin, Amberlyst 15 (A15, DuPont), was used as the catalyst. It is a macroreticular ion-exchange resin with an acid capacity of 4.81 mequiv H^+/g and divinylbenzene content of 20%. The average bead diameter in the dry state is 0.74 mm.

2.2. Experimental Setup and Analytical System. Experimental runs were carried out in a batch reactor, which consisted of a 200 cm^3 stainless-steel jacketed batch reactor equipped with a magnetic stirrer containing a six-blade turbine (Autoclave Engineers, Pennsylvania, US). The reactor temperature was controlled within ±0.1 K by a 1,2-propanediol—water thermostatic mixture. GC-MS analyses of samples of the reaction medium allowed for quantifying the reactant and product concentrations during the runs. To this end, a sampling valve (Valco A2CI4WE.2, VICI AG International, Schenkon, Switzerland) was connected to the reactor vessel to inject 0.2 μL of pressurized liquid into an Agilent 7890B gas chromatograph coupled to a mass selective detector Agilent 5977B (GC-MS). The GC was equipped with a capillary column (HP-PONA 19091S-001, J&W Scientific, Santa Clara, US; 100% dimethylpolysiloxane, 50 m × 0.20 mm × 0.50 μm). The electron source of the mass detector was set to 503 K and the quadrupole to 423 K. Helium, with a flow of 0.5 mL/min, was used as the carrier gas. GC oven temperature was set as follows: an initial hold of 5 min at 313 K, followed by a 35 K/min ramp to 473 K, and a final hold of 9 min.

2.3. Experimental Protocol. All experiments were carried out isothermally in the range of 363−393 K and at 2.5 MPa, with a stirring speed of 500 rpm. The initial molar ratio between levulinic acid and 1-butene ($R^{\circ}_{\mathrm{LA/1B}}$) was set at 0.5 or 1.5, while the initial mass of reactants was set to fill a total volume of 200 mL, which corresponds to about 2 mol. Before every experimental run, the catalyst was pretreated to reduce its water content. First, by drying at room temperature for 48 h, then in an atmospheric oven at 383 K for 2.5 h and, finally, in a vacuum oven at 0.001 MPa and 373 K for at least 12 h, until the experiment started. This procedure ensures a 3−5 wt % maximum final water content in the resin beads.[15]

In every experiment, a weighed amount of levulinic acid (81 or 142 g) was introduced into the reactor vessel. Afterward, the heating and stirring were switched on. The corresponding amount of liquid 1-butene was loaded into a pressurized buret by weight (45−78 g, approximately) at 0.5−1 MPa and, then introduced into the reactor by pressure difference, impelled by nitrogen. Once the reactant mixture reached the desired temperature, the catalyst was injected into the reactor by pressure difference with a catalyst injector attached to the reactor. The operating pressure was set, and kept constant, at 2.5 MPa. Such pressure in the reactor allows samples to be impelled from the reactor to the GC and ensures that the reaction mixture remains in the liquid phase. The injection of the catalyst marked the initial time of the experiment. Each run lasted for about 8−10 h, which was considered enough time to ensure that the chemical equilibrium conditions had been met. To verify this, repeated GC-MS analyses of reaction medium samples were taken until no composition changes were detected.

2.4. Calculations. The equilibrium constant in an ideal system can be calculated by employing the mass-action ratio (Γ_x), which corresponds to the product of the molar fractions (x) of all species involved in the studied reaction, each raised to the corresponding stoichiometric coefficient (ν_j). In nonideal systems, activity coefficients (γ_j) must be taken into account to calculate the mass-action ratio in terms of activities (a_j), as shown below:

$$\Gamma_a = \prod_{j=1}^{s} (a_j)^{\nu_j} = \prod_{j=1}^{s} (\gamma_j)^{\nu_j} \cdot \prod_{j=1}^{s} (x_j)^{\nu_j} = \Gamma_\gamma \cdot \Gamma_x \tag{1}$$

where S are the species involved. Γ_a and Γ_γ are, respectively, mass-action ratios in terms of activities and activity coefficients. Activity coefficients have been calculated by means of the modified UNIFAC-Dortmund method.[16]

When the reaction reaches equilibrium, the medium composition remains constant with time. Then, the mass-action ratio equals the chemical equilibrium constant, that is, $\Gamma_x = K_x$, $\Gamma_\gamma = K_\gamma$, and $\Gamma_a = K$, with K being the thermodynamic equilibrium constant.

The Poynting factor allows for checking if the pressure influences the equilibrium constant values significantly. It takes into account the deviation in the K values due to the difference between the actual pressure of the mixture and the pressure at the standard state, usually 101.325 kPa.[17−19] The Poynting factor (K_Γ) can be estimated as follows:

$$K_{\Gamma_i} = \exp\left(\frac{P-1}{RT} \sum_{j=1}^{S} \nu_{ij} V_j \right) \tag{2}$$

where V_j is the liquid molar volume of compound j, P is the pressure in atm, R is the gas constant, and T is the temperature in K. If the pressure affects the equilibrium constant, K values need to be corrected, namely, $K = K_x \cdot K_\gamma \cdot K_\Gamma$. Liquid molar volumes were calculated by the HBT method.[20]

3. RESULTS AND DISCUSSION

3.1. Reaction System. Besides LA esterification with 1B to produce SBL (R1), the side reactions detected were the isomerization of 1B to *trans*-2-butene (E2B) (R2) and the double-bond isomerization reaction between E2B and *cis*-2-butene (Z2B) (R3). Since both E2B and Z2B can produce SBL by esterification of LA, these two reactions (R4 and R5) were also considered in the present work (Scheme 1). Other possible side reactions, such as 1B hydration with remaining water from reactants or the resin to produce 2-butanol (R6), were kept low (i.e., 2-butanol formation ranged between 0.17 and 1.5 wt % throughout the experimental work), and consequently, their influence on present results can be disregarded.

3.2. Theoretical Estimation of the Thermodynamic Properties of Reaction. The thermodynamic equilibrium constant of a given reaction can be related to its thermodynamic properties by the Van't Hoff equation, which measures the changes in the equilibrium constant with variations of temperature, as follows:[21]

$$\ln K_i = \frac{-\Delta_r G_i^{\circ}}{RT} = \frac{-\Delta_r H_i^{\circ}}{RT} + \frac{\Delta_r S_i^{\circ}}{R} \tag{3}$$

where $\Delta_r H^{\circ}_i$, $\Delta_r S^{\circ}_i$, and $\Delta_r G^{\circ}_i$ are the standard enthalpy, entropy, and Gibbs free energy changes of reaction i, respectively; K_i is the equilibrium constant of reaction i; and R is the gas constant.

Thermodynamic properties of reaction can be estimated from the formation properties of the involved compounds by employing the following expressions:

$$\Delta_r H_i^{\circ}(T) = \sum_{j=1}^{S} \upsilon_{ij} \Delta_f H_j^{\circ} \tag{4}$$

$$\Delta_r S_i^{\circ}(T) = \sum_{j=1}^{S} \upsilon_{ij} S_j^{\circ} \tag{5}$$

$$\Delta_r G_i^{\circ}(T) = \Delta_r H_i^{\circ} - T \Delta_r S_i^{\circ} \tag{6}$$

where ν_{ij} is the stoichiometric coefficient of the component j in the reaction i.

To estimate the thermodynamic properties of every reaction, thermochemical data of the compounds involved are needed.

Table 1. Liquid Phase Enthalpy Change ($\Delta_f H°$) and Entropy ($S°$) of Formation of the Involved Compounds at 298.15 K[a]

	$\Delta_f H°$ [kJ/mol]			$S°$ [J/(mol·K)]	
Compound	Literature value	Modified Benson's method[22]	Joback method[20]	Literature value	Modified Benson's method[22]
SBL	—	−736.0	−731.9	—	441.52
LA	−683.8[23]	−676.5 (1.0%)	−682.1 (0.2%)	268.6[23]	267.85 (0.3%)
1B	−20.8[24]	−20.54 (1.3%)	−23.8 (14.4%)	227[24] 229.1[25]	229.74 (0.7%)
E2B	−33.3[24]	−33.12 (0.3%)	−33.0 (0.9%)	205.3[24]	223.76 (9.0%)
Z2B	−29.8[24]	−33.12 (11.1%)	−33.0 (10.7%)	219.9[24]	223.76 (1.8%)

[a] Relative differences between estimated and literature values (or averaged) are shown in parentheses.

In this regard, the low number of literature references, if any, that have been detected referring to compounds in the present system is noticeable (for instance, no references to SBL thermochemical data have been found), which indicates that thermodynamic studies in this field are needed. When possible, literature values were compared and selected to choose reliable databases. When unavailable, two different group contribution methods, namely, the Joback method and the modified Benson method, were employed instead.[20,22] Table 1 shows a comparison between literature values of enthalpy changes of formation and liquid entropies at 298.15 K of the different species involved in the reaction system and those obtained with the modified Benson and Joback group-contribution methods.

As seen in Table 1, both methods coincide remarkably well with the reported literature values of enthalpy changes of formation, except for Z2B, which can be explained by the inability of the method to distinguish among the two 2-butene isomers. Between the two methods, the modified Benson's method was considered more appropriate for the present system, since no significant deviation from literature values can be detected for LA, 1B, and E2B. The same method was used to estimate liquid molar entropies of involved compounds, as also shown in Table 1.

Theoretical values of the liquid phase enthalpy, entropy, and Gibbs free energy changes of reaction at 298.15 K as estimated by eqs 4−6 with thermochemical data from Table 1 are shown in Table 2. From values in Table 2, it can be seen that all the reactions are exothermic except the isomerization of E2B to Z2B. In addition, the formation of SBL from 1B is the most favored reaction.

Table 2. Theoretical Values of the Liquid Phase Enthalpy, Entropy, and Gibbs Free Energy Changes of Reaction at 298.15 K

Reaction	$\Delta_r H°$ (kJ/mol)	$\Delta_r S°$ (J/(mol·K))	$\Delta_r G°$ (kJ/mol)
R1	−31.4	−55.1	−15.0
R2	−12.5	−22.8	−5.7
R3	3.50	14.6	−0.9
R4	−18.9	−32.4	−9.2
R5	−22.4	−47.0	−8.4

3.3. Experimental Equilibrium Constants Determination.

The thermodynamic equilibrium constants for the studied reactions were determined in batch runs. Values obtained with eqs 1 and 2 for each experiment are listed in Table 3. Since no further reaction progress was observed, it was considered that the chemical equilibrium had been met by the end of every experiment, and the equilibrium constants were calculated.

The values of the equilibrium constants for R1 and R2 are far greater than those of R3, R4, and R5, showing that SBL formation from 1B (R1) and isomerization of 1B to E2B (R2) are clearly thermodynamically favored. On the contrary, isomerization of E2B to Z2B (R3) and SBL formation by LA esterification with E2B (R4) and Z2B (R5) take place to a much lesser extent. Thus, reactivity of 1B to synthesize SBL is higher than reactivity of E2B and Z2B because K_1 values are larger than K_4 and K_5 at the same temperature. On the other hand, as seen in Table 3, the equilibrium constant of all reactions, except the isomerization of E2B to Z2B (R3), decreases as temperature increases. Consequently, they are exothermic, as expected from Table 2 values.

As can be seen in Table 3, the values of the equilibrium constant at different initial molar ratios of LA to 1B are similar. Furthermore, possible deviations of experimental K due to pressure effects can be neglected, since the Poynting correction factor, K_Γ, was always close to unity for all assayed conditions (that is, between 0.97 and 1.00). Therefore, K is only a function of the temperature. On the other hand, K_γ values were far from unity, except for the isomerization reactions R2 and R3; consequently, the reaction system is clearly nonideal. All the K_γ values for R1, R4, and R5 are less than unity because activity coefficients of LA are much larger than 1.

By comparing the equilibrium constant values of the isomerization reactions, namely, R2 and R3, to those quoted in the literature, it can be observed that values in Table 3 are reliable. For instance, Meyer and Stroz reported values for the isomerization equilibrium constants at 360.4 K from 1B to E2B (R2) of 10.6 ± 0.7, and from Z2B to E2B (R3) of 0.424 ± 0.066.[26] They are quite close to the values listed in Table 3 at 363.15 K (i.e., 11.84 ± 0.04 and 0.4850 ± 0.0011, respectively). In addition, from the equilibrium constants for the butene hydration system at 403.15 K found by Petrus et al., equilibrium constants of 6.92 and 0.68 for R2 and R3, respectively, can be estimated.[27] They are consistent with Table 2 values because R2 is exothermic, so that K values decrease with increasing temperature. Conversely, R3 is endothermic, and K values increase with temperature. K values found experimentally are thus reliable.

Figure 1 depicts the van't Hoff plot of the equilibrium constants found experimentally. For comparison purposes, equilibrium constant values estimated by eq 3 from enthalpy, entropy, and Gibbs free energy changes of reaction listed in Table 2 are plotted too as solid straight lines. It can be seen that in all cases, experimental K values fit a straight line well (shown as dashed lines in the figure). On the other hand, while the slopes of both solid and dashed lines are almost identical, K values predicted by eq 3 are noticeably larger than those obtained in this work, except for R2, where predicted values are smaller.

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Table 3. Experimental Values of the Chemical Equilibrium Constant for Every Studied Reaction

	T [K]	$R^{\circ}_{LA/1B}$ [-]	K_x [-]	K_γ [-]	K [-]
R1	363.15	0.5	54 ± 4	0.204 ± 0.010	11.0 ± 0.3
		1.5	31.0 ± 1.3	0.3350 ± 0.003	10.9 ± 0.4
	373.15	0.5	46.6 ± 1.1	0.1711 ± 0.0007	8.05 ± 0.17
		1.5	24.0 ± 0.4	0.3342 ± 0.0007	8.00 ± 0.06
	383.15	0.5	34.9 ± 0.7	0.1678 ± 0.0009	5.91 ± 0.14
		1.5	19.9 ± 0.2	0.332 ± 0.002	6.57 ± 0.03
	393.15	0.5	25.7 ± 0.4	0.1614 ± 0.0012	4.17 ± 0.08
		1.5	15.0 ± 0.2	0.319 ± 0.002	4.73 ± 0.06
R2	363.15	0.5	11.26 ± 0.04	1.0193 ± 0.0010	11.84 ± 0.04
		1.5	12.5 ± 0.2	1.0318 ± 0.0002	13.1 ± 0.2
	373.15	0.5	10.04 ± 0.03	1.01495 ± 0.00007	10.52 ± 0.03
		1.5	10.97 ± 0.06	1.02569 ± 0.00005	11.43 ± 0.06
	383.15	0.5	9.11 ± 0.06	1.01361 ± 0.00012	9.52 ± 0.06
		1.5	9.83 ± 0.11	1.0215343 ± 0.0000014	10.19 ± 0.12
	393.15	0.5	8.02 ± 0.02	1.01180 ± 0.00012	8.35 ± 0.03
		1.5	8.71 ± 0.02	1.0175 ± 0.00006	9.00 ± 0.02
R3	363.15	0.5	0.4935 ± 0.0013	1	0.4850 ± 0.0011
		1.5	0.493 ± 0.002	1	0.489 ± 0.002
	373.15	0.5	0.5132 ± 0.0007	1	0.5043 ± 0.0007
		1.5	0.5076 ± 0.0008	1	0.5033 ± 0.0008
	383.15	0.5	0.5280 ± 0.0005	1	0.5195 ± 0.0005
		1.5	0.528 ± 0.004	1	0.524 ± 0.004
	393.15	0.5	0.5447 ± 0.0004	1	0.5366 ± 0.0004
		1.5	0.5494 ± 0.0002	1	0.5451 ± 0.0002
R4	363.15	0.5	4.8 ± 0.3	0.200 ± 0.010	0.93 ± 0.03
		1.5	2.48 ± 0.14	0.343 ± 0.002	0.83 ± 0.04
	373.15	0.5	4.64 ± 0.10	0.1686 ± 0.0007	0.77 ± 0.02
		1.5	2.19 ± 0.03	0.3258 ± 0.0006	0.700 ± 0.010
	383.15	0.5	3.83 ± 0.06	0.1655 ± 0.0009	0.621 ± 0.013
		1.5	2.03 ± 0.04	0.3249 ± 0.0015	0.645 ± 0.010
	393.15	0.5	3.21 ± 0.04	0.1595 ± 0.0011	0.499 ± 0.009
		1.5	1.72 ± 0.02	0.314 ± 0.002	0.526 ± 0.007
R5	363.15	0.5	9.7 ± 0.6	0.200 ± 0.010	1.92 ± 0.05
		1.5	5.0 ± 0.3	0.343 ± 0.002	1.70 ± 0.08
	373.15	0.5	9.0 ± 0.2	0.1686 ± 0.0007	1.52 ± 0.03
		1.5	4.32 ± 0.05	0.3258 ± 0.0006	1.39 ± 0.02
	383.15	0.5	7.26 ± 0.12	0.1655 ± 0.0009	1.19 ± 0.03
		1.5	3.84 ± 0.04	0.3249 ± 0.0015	1.231 ± 0.008
	393.15	0.5	5.89 ± 0.08	0.1595 ± 0.0011	0.93 ± 0.02
		1.5	3.13 ± 0.04	0.314 ± 0.002	1.0 ± 0.2

By least-squares regression, the following fitted equations were obtained to compute K for every reaction, in the temperature range of 363.15 to 393.15 K:

$$\ln K_1 = \frac{(4216 \pm 197)}{T} - (9.2 \pm 0.5) \tag{7}$$

$$\ln K_2 = \frac{(1617 \pm 68)}{T} - (1.94 \pm 0.18) \tag{8}$$

$$\ln K_3 = \frac{-(502 \pm 12)}{T} + (0.66 \pm 0.03) \tag{9}$$

$$\ln K_4 = \frac{(2599 \pm 130)}{T} - (7.3 \pm 0.3) \tag{10}$$

$$\ln K_5 = \frac{(3102 \pm 138)}{T} - (7.9 \pm 0.4) \tag{11}$$

where the uncertainty of every fitted parameter is referred to the standard deviation.

3.4. Thermodynamic Properties Determination. As indicated, experimental results in Figure 1 fit well to straight lines, and consequently, enthalpy and entropy changes of reaction can be estimated from eqs 7−11. According to eq 3, enthalpy changes of reaction can be inferred from the slopes of the straight dashed lines in Figure 1 and entropy changes of reaction from their intercepts. Average values of thermodynamic properties of the studied reactions in the temperature range of 363.15−393.15 K are listed, together with literature values, in Table 4, along with their uncertainty corresponding to the standard deviation.

As Table 4 shows, mean thermodynamic functions of the 1B isomerization to E2B agree within the limits of the experimental error with those reported by Pérez-Maciá et al. in the study of the 1-butanol dehydration to di-*n*-butyl ether at 413−463 K.[28] It should be noted that mean thermodynamic functions for 1B isomerization to E2B found from the data of Petrus et al. in the temperature range 348.15−403.15 K for the hydration of butenes also agree well with present results. As for

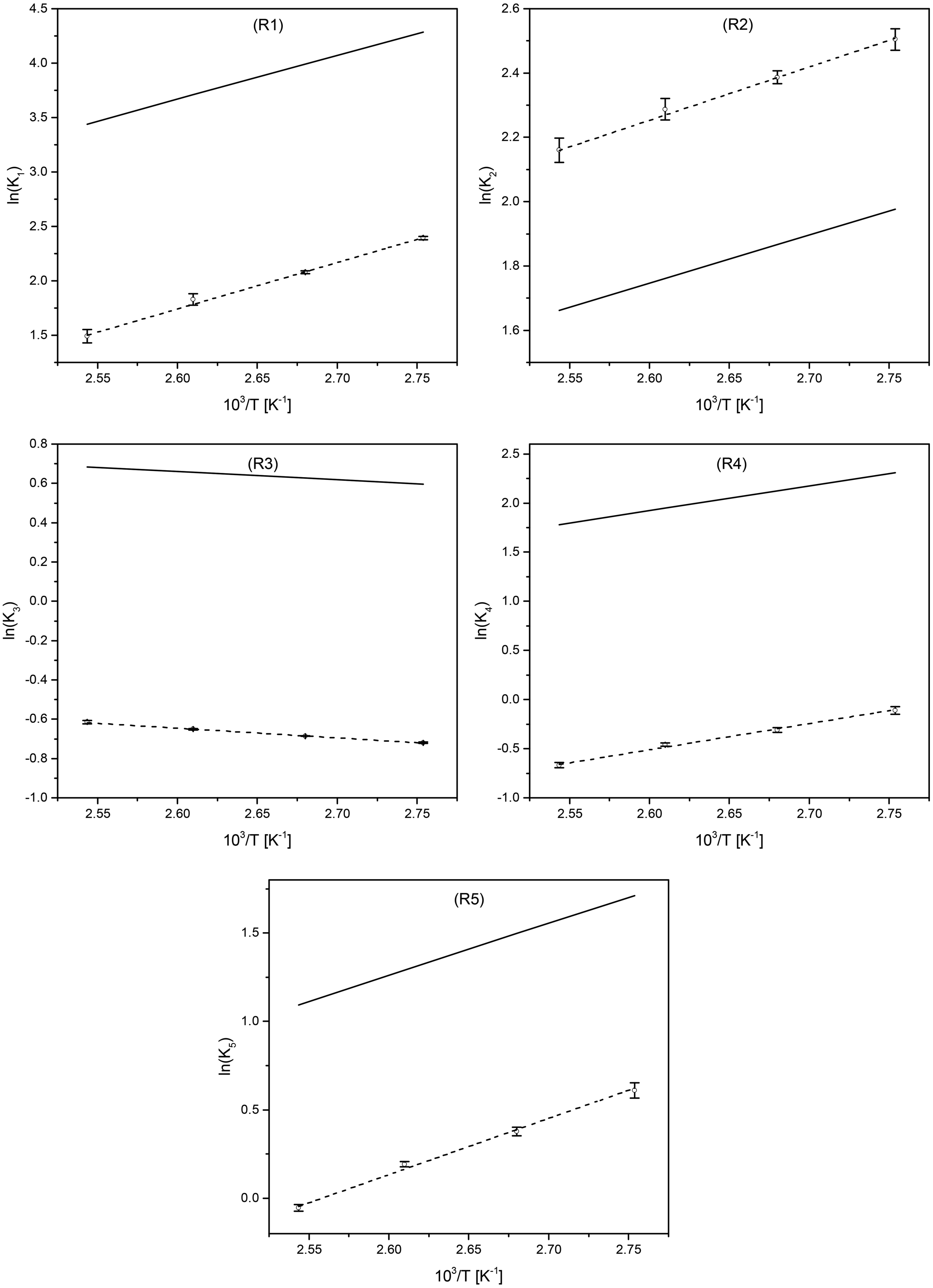

Figure 1. Van't Hoff plots for the reactions involved in the reaction system. Dashed lines are linear fits of experimental data. The solid straight line corresponds to the theoretical equilibrium constant estimated by eq 3 with Table 2 values. Error bars correspond to standard deviation for replicated experiments.

E2B isomerization to Z2B, the mean values of the thermodynamic functions of reaction are of the same order as those found in the literature. By comparing experimentally determined thermodynamic properties in Table 4 with

Table 4. Mean Enthalpy, Entropy, and Gibbs Free Energy Changes of Reactions in the Temperature Range 363.15−393.15 K

	$\Delta_r H^\circ$ (kJ/mol)		$\Delta_r S^\circ$ (J/ (mol·K))		$\Delta_r G^\circ$ (kJ/mol)	
Reaction	This work	Literature	This work	Literature	This work	Literature
R1	-(35 ± 2)	—	-(77 ± 4)	—	-(12 ± 3)	—
R2	-(13.4 ± 0.6)	-(13.0 ± 2.4)[a]	-(16 ± 1)	-(15.1 ± 5.4)[a]	-(8.6 ± 1.0)	-(8.5 ± 4.0)[a]
		−12[b]		−13.51[b]		−6.9[b]
R3	4.18 ± 0.09	3.2 ± 0.2[a]	5.5 ± 0.3	2.6 ± 0.4[a]	2.5 ± 0.9	2.4 ± 0.3[a]
		2.1[b]		1.95[b]		0.7[b]
R4	-(21.6 ± 1.1)	—	-(60 ± 3)	—	-(4 ± 2)	—
R5	-(25.8 ± 1.1)	—	-(66 ± 3)	—	-(6 ± 2)	—

[a] Temperature range 413−463 K.[28] [b] Temperature range 348.15−403.15K.[27]

Table 5. Molar Heat Capacity Coefficients and Molar Heat Capacities

	Molar heat coefficients			C_P [J/(mol·K)][a]	
Component	a_j [J/(mol·K)]	$b_j \times 10$ [J/(mol·K^2)]	$c_j \times 10^4$ [J/(mol·K^3)]	Estimated values	Literature values
1B	117.424	−1.400	2.6965	121.9	118[29]
					128.5[25]
E2B	131.700	−2.350	6.8012	122.1	—
				119.2[b]	124.4[b][29]
				117.8[c]	122.3[c][30]
Z2B	131.700	−2.350	6.8012	122.1	127[29]
LA	202.023	−1.041	6.7014	230.6	—
				256.4[d]	264.3[d][31]
SBL	348.590	−4.526	13.237	331.3	—

[a] Unless indicated, values are referred to 298.15 K. [b] 280 K. [c] 270 K. [d] 373.15 K.

theoretical values in Table 2, the following can be seen: (i) on one hand, enthalpy changes of reactions are very similar, yet some discrepancies are observed within the margin of experimental error; and (ii) on the other hand, entropy changes of reactions are very different, which, consequently, also implies divergences in Gibbs free energy changes. It can be assumed that the main cause for the observed discrepancy is related to the estimation of standard entropies of formation of involved compounds, which in turn greatly affect the theoretical entropy changes of reaction.

Alternatively, the enthalpy, entropy, and Gibbs free energy changes of reactions at 298.15 K can be computed from experimental data by considering $\Delta_r H^\circ$ dependent on temperature. The dependence of the enthalpy change of a reaction with temperature is expressed by the Kirchoff equation

$$\frac{d\Delta_r H_i^\circ}{dT} = \sum_{j=1}^{s} \nu_{ij} C^\circ{}_{pj} \tag{12}$$

where $C_{p,j}$ is the molar heat capacity in the liquid phase of the compound j involved in the reaction i. Usually, heat capacity is expressed as a polynomial of temperature, for example, a second order one, as follows:

$$C_{P_j} = a_j + b_j T + c_j T^2 \tag{13}$$

Molar heat capacities were estimated by the group-contribution method of Rùzicka and Domalski.[20,22] The parameters a_j, b_j, and c_j for each compound are listed in Table 5, along with a comparison of estimated values of molar heat capacity with available literature data.

Divergence of estimated capacities with respect to available literature values was about 4%. Consequently, the estimation method used can be considered reliable, and the proposed polynomials can be used to compute the variation of heat capacities with temperature.

The variation of the enthalpy change of the reaction i with temperature is obtained from the integrated form of the Kirchoff equation (eq 12)

$$\Delta_r H_i^\circ = I_K + a_i T + \frac{b_i}{2} T^2 + \frac{c_i}{3} T^3 \tag{14}$$

with

$$a_i = \sum_j \nu_{i,j} a_j \qquad b_i = \sum_j \nu_{i,j} b_j \qquad c_i = \sum_j \nu_{i,j} c_j \tag{15}$$

On the other hand, as described by the Van't Hoff equation, the dependence of the equilibrium constant on the temperature is

$$\frac{d \ln K_i}{d\, T} = \frac{-\Delta_r H_i^\circ}{RT^2} \tag{16}$$

At this point, eq 16 must be combined with eq 14, and after integration, the following expression is obtained for the variation of the equilibrium constant of the reaction i with temperature

$$\ln K_i = I_H - \frac{I_K}{RT} + \frac{a_i}{R} \ln T + \frac{b_i}{2R} T + \frac{c_i}{6R} T^2 \tag{17}$$

where I_H and I_K are integration constants. Moreover, from eq 17, and considering eq 3, the Gibbs free energy change of the reaction i as a function of temperature is given by

$$\Delta_r G_i^\circ = I_K - R \cdot I_H \cdot T + a_i \cdot T \cdot \ln T - \frac{b_i}{2} T^2 + \frac{d_i}{6} T^3 \tag{18}$$

Finally, the entropy change of the reaction i as a function of temperature can be found by combining eqs 3, 14, and 17

$$\Delta_r S_i^\circ = R\cdot I_H + a_i + a_i\cdot\ln T + b_i T + \frac{d_i}{2}T^2 \tag{19}$$

The integration constants I_H and I_K can be estimated from eq 17 through the linear fitting of experimental equilibrium constant data to the reverse of temperature according to

$$\ln K_i + f(T) = \ln K_i - \left(\frac{a_i}{R}\ln T + \frac{b_i}{2R}T + \frac{c_i}{6R}T^2\right) = I_H - \frac{I_K}{RT} \tag{20}$$

Figure 2 shows the plots of ln K_i + $f(T)$ against the reverse temperature for the five studied reactions. As can be seen, the linearity is good, and reliable values of I_H and I_K can be found. These values are shown in Table 6, as well as the enthalpy, entropy, and Gibbs free energy changes of reactions at 298.15 K obtained considering that the three thermodynamic quantities are temperature functions. For comparison purposes, Table 6 also shows literature values found for the enthalpy and entropy changes of reactions R2 and R3.

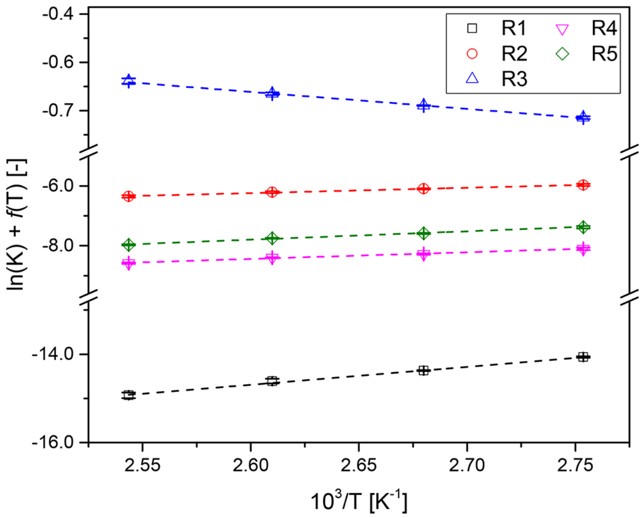

Figure 2. Plot of ln K + $f(T)$ against $1/T$ for the studied reactions. Dashed lines are linear fits of experimental data. Error bars correspond to standard deviation for replicated experiments.

Thermodynamic properties for the butene isomerization reactions in the liquid phase agree well with those estimated from the isomerization of linear butenes in the gas phase.[26,32,33] As for LA esterification reactions, little difference is observed between theoretical values of enthalpy change of reaction at 298.15 K (Table 2) and those listed in Table 6. In addition, obtained values are similar to those reported in Table 4 (i.e., mean value in the temperature range 363.15−393.15 K), showing that dependence on temperature of $\Delta_r H^\circ$ is small and, consequently, that the enthalpy change values in Table 4 can be used for technical calculations with accurate results, e.g., heat to remove in an industrial reactor. As for the entropy changes of reactions, a strong discrepancy between the theoretical values and those obtained from experimental results is observed at 298.15 K and, consequently, in the Gibbs free energy changes of reactions. Given the exponential relationship between equilibrium constant and temperature (eq 3), a small difference in the entropy of reaction can lead to a notable effect on the equilibrium constant, as Figure 1 shows.

Finally, liquid-phase standard-state thermochemical data concerning SBL, which cannot be found in the literature, has been estimated from the enthalpy and entropy changes of reactions in Table 6 to obtain reliable values. From enthalpy changes of reactions R1, R4, and R5, and enthalpies of formation of LA and butenes, a mean value for the SBL enthalpy change of formation at 298.15 of −(737.1 ± 0.3) kJ/mol has been obtained. Similarly, a mean value for the liquid entropy of SBL at 298.15 K of (423 ± 3) J/(mol·K) has been found. It is noteworthy the extremely good SBL estimation for the SBL enthalpy change of formation calculated by means of the modified Benson's method, −736 kJ/mol, which practically coincides with the value found in this work. However, the value found for the liquid entropy at 298.15 K is smaller than that estimated by the modified Benson's method by 4.2% (the values being 423 and 441.52, respectively). This discrepancy might explain the notable deviation between the equilibrium constants determined experimentally and those estimated theoretically (Figure 1).

4. CONCLUSIONS

The equilibrium constants for the liquid-phase esterification of LA with 1B to produce SBL have been determined experimentally as well as those of the side reactions that take place simultaneously in the reaction system, i.e., linear butene isomerization. The equilibrium constants in the temperature range 363.15−393.15 K show that the equilibrium of the esterification of LA with 1B is clearly shifted toward product formation. From the dependence of chemical equilibrium constants with temperature it follows that all the reactions are

Table 6. Coefficients I_K and I_H and Standard Molar Enthalpy ($\Delta_r H^\circ$), Entropy ($\Delta_r S^\circ$), and Gibbs Free Energy ($\Delta_r G^\circ$) Changes of Reaction at 298.15 K Considering $\Delta_r H^\circ$ = $f(T)$[a]

			$\Delta_r H^\circ$ (kJ/mol)		$\Delta_r S^\circ$ (J/(mol·K))		
Reaction	I_K (J/mol)	I_H (−)	This work	Literature	This work	Literature	$\Delta_r G^\circ$ (kJ/mol)
R1	-(33510 ± 1576)	-(25.2 ± 0.5)	-(32.9 ± 1.6)	—	-(70 ± 4)	—	-(12 ± 3)
R2	-(14894 ± 1539)	-(10.9 ± 0.5)	-(13.4 ± 1.5)	-(13.2 ± 0.5)[b26] -(12.2)[c32]	-(16 ± 4)	−17.74[b26] −13.40[c32]	-(9 ± 3)
R3	4170 ± 177	0.66 ± 0.06	4.2 ± 0.2	3.28 ± 0.12[b26] 3.11[c32] 3.53[c33]	5.5 ± 0.5	1.4[b26] 1.95[c32] 11.78[c33]	2.5 ± 0.3
R4	-(18623 ± 1722)	-(14.3 ± 0.6)	-(19.5 ± 1.7)	—	-(54 ± 5)	—	-(3 ± 3)
R5	-(22788 ± 1717)	-(14.9 ± 0.6)	-(23.6 ± 1.7)	—	-(60 ± 5)	—	-(6 ± 3)

[a] Uncertainty of every fitted parameter corresponds to the standard deviation. [b] Calculated from gas phase at 300 K with vaporization values. [c] Calculated from gas phase at 298.15 K with vaporization values.

exothermic except for E2B isomerization to Z2B, which is endothermic. The determination of these properties has been carried out at first considering total independence from temperature and at last considering its dependence on temperature. The mean enthalpy changes of reaction in the explored temperature range are −(35 ± 2) kJ/mol for the esterification of LA with 1B (R1), −(13.4 ± 0.6) kJ/mol for 1B isomerization to E2B (R2), (4.18 ± 0.09) kJ/mol for E2B isomerization to Z2B (R3), −(21.6 ± 1.1) kJ/mol for the LA esterification with E2B, and −(25.8 ± 1.1) kJ/mol for esterification with Z2B. As for the entropy change of reaction, mean values are −(77 ± 4), −(16 ± 1), (5.5 ± 0.3), −(60 ± 3), and −(66 ± 3) J/(mol·K), respectively.

If the enthalpy and entropy changes of reaction are considered as a function of temperature, their estimated values at 298.15 K are −(32.9 ± 1.6) (R1), −(13.4 ± 1.5) (R2), (4.2 ± 0.2) (R3), −(19.5 ± 1.7) (R4), and −(23.6 ± 1.7) (R5) kJ/mol for enthalpy; and −(70 ± 4) (R1), −(16 ± 4) (R2), (5.5 ± 0.5) (R3), −(54 ± 5) (R4), and −(60 ± 5) (R5) J/(mol·K) for entropy. Finally, the SBL formation enthalpy change and liquid entropy at 298.15 K were estimated to be −(737.1 ± 0.3) kJ/mol and (423 ± 3) J/(mol·K), respectively. The formation enthalpy practically coincides with the estimate by the modified Benson's method, while liquid entropy is smaller by 4.2%. This discrepancy accounts for the high deviation observed between equilibrium constants determined experimentally and those estimated theoretically in the temperature range explored.

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Notes

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REFERENCES

(1) Dogan, B.; Erol, D. The Future of Fossil and Alternative Fuels Used in Automotive Industry. In *Proceedings of the 2019 3rd International Symposium on Multidisciplinary Studies and Innovative Technologies (ISMSIT)*; October 2019; pp 1−8. DOI: 10.1109/ISMSIT.2019.8932925.

(2) Skjærseth, J. B.; Andresen, S.; Bang, G.; Heggelund, G. M. The Paris Agreement and Key Actors' Domestic Climate Policy Mixes: Comparative Patterns. *Int. Environ. Agreements Polit. Law Econ.* **2021**, *21*, 59−73.

(3) Van Soest, H. L.; den Elzen, M. G. J.; van Vuuren, D. P. Net-Zero Emission Targets for Major Emitting Countries Consistent with the Paris Agreement. *Nat. Commun.* **2021**, *12*, 2140.

(4) Demirbas, M. F.; Balat, M.; Balat, H. Potential Contribution of Biomass to the Sustainable Energy Development. *Energy Convers. Manag.* **2009**, *50*, 1746−1760.

(5) Aro, E.-M. From First Generation Biofuels to Advanced Solar Biofuels. *Ambio* **2016**, *45*, 24−31.

(6) Rackemann, D. W.; Doherty, W. O. The Conversion of Lignocellulosics to Levulinic Acid. *Biofuels, Bioprod. Biorefining* **2011**, *5*, 198−214.

(7) Yan, K.; Jarvis, C.; Gu, J.; Yan, Y. Production and Catalytic Transformation of Levulinic Acid: A Platform for Speciality Chemicals and Fuels. *Renew. Sustain. Energy Rev.* **2015**, *51*, 986−997.

(8) Hayes, G. C.; Becer, C. R. Levulinic Acid: A Sustainable Platform Chemical for Novel Polymer Architectures. *Polym. Chem.* **2020**, *11*, 4068−4077.

(9) Démolis, A.; Essayem, N.; Rataboul, F. Synthesis and Applications of Alkyl Levulinates. *ACS Sustain. Chem. Eng.* **2014**, *2*, 1338−1352.

(10) Climent, M. J.; Corma, A.; Iborra, S. Conversion of Biomass Platform Molecules into Fuel Additives and Liquid Hydrocarbon Fuels. *Green Chem.* **2014**, *16*, 516.

(11) Démolis, A.; Eternot, M.; Essayem, N.; Rataboul, F. New Insights into the Reactivity of Biomass with Butenes for the Synthesis of Butyl Levulinates. *ChemSusChem* **2017**, *10*, 2612−2617.

(12) Badia, J. H.; Ramírez, E.; Soto, R.; Bringué, R.; Tejero, J.; Cunill, F. Optimization and Green Metrics Analysis of the Liquid-Phase Synthesis of Sec-Butyl Levulinate by Esterification of Levulinic Acid with 1-Butene over Ion-Exchange Resins. *Fuel Process. Technol.* **2021**, *220*, 106893.

(13) Seok Kim, M.; Sup Park, M.; Jae Seo, H.; Hyun Lee, S. Method for Preparing Polybutene. US Patent US 9683060 B2, 2017.

(14) Tejero, M. A.; Ramírez, E.; Fité, C.; Tejero, J.; Cunill, F. Esterification of Levulinic Acid with Butanol over Ion Exchange Resins. *Appl. Catal. A Gen.* **2016**, *517*, 56−66.

(15) Iborra, M.; Tejero, J.; Cunill, F.; Izquierdo, J. F.; Fite, C. Drying of Acidic Macroporous Styrene−Divinylbenzene Resins with 12−20 Cross-Linking Degree. *Ind. Eng. Chem. Res.* **2000**, *39*, 1416−1422.

(16) Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178−193.

(17) Bringué, R.; Tejero, J.; Iborra, M.; Fité, C.; Izquierdo, J. F.; Cunill, F. Study of the Chemical Equilibrium of the Liquid-Phase Dehydration of 1-Hexanol to Dihexyl Ether. *J. Chem. Eng. Data* **2008**, *53*, 2854−2860.

(18) Badia, J. H.; Fité, C.; Bringué, R.; Ramírez, E.; Cunill, F. Thermodynamic Analysis of the Experimental Equilibria for the Liquid-Phase Etherification of Isobutene with C 1 to C 4 Linear Primary Alcohols. *J. Chem. Eng. Data* **2016**, *61*, 1054−1064.

(19) Smith, J. M. Introduction to Chemical Engineering Thermodynamics. *J. Chem. Educ.* **1950**, *27*, 584.

(20) Poling, B. E.; Prausnitz, J. M.; John Paul, O.; Reid, R. C. *The Properties of Gases and Liquids*; McGraw-Hill New York, 2001; 5th ed.

(21) Lima, E. C.; Hosseini-Bandegharaei, A.; Moreno-Piraján, J. C.; Anastopoulos, I. A Critical Review of the Estimation of the Thermodynamic Parameters on Adsorption Equilibria. Wrong Use of Equilibrium Constant in the Van't Hoof Equation for Calculation

of Thermodynamic Parameters of Adsorption. *J. Mol. Liq.* **2019**, *273*, 425−434.
(22) Domalski, E. S.; Hearing, E. D. Estimation of the Thermodynamic Properties of C-H-N-O-S-Halogen Compounds at 298.15 K. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805−1159.
(23) Verevkin, S. P.; Emel'yanenko, V. N. Renewable Platform-Chemicals and Materials: Thermochemical Study of Levulinic Acid. *J. Chem. Thermodyn.* **2012**, *46*, 94−98.
(24) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*; Internet Version 2005; CRC Press: Boca Raton, FL, 2005. http://www.hbcpnetbase.com.
(25) Takeda, K.; Yamamuro, O.; Suga, H. Thermodynamic Study of 1-Butene. Exothermic and Endothermic Enthalpy Relaxations near the Glass Transition. *J. Phys. Chem. Solids* **1991**, *52*, 607−615.
(26) Meyer, E. F.; Stroz, D. G. Thermodynamics of N-Butene Isomerization. *J. Am. Chem. Soc.* **1972**, *94*, 6344−6347.
(27) Petrus, L.; De Roo, R. W.; Stamhuis, E. J.; Joosten, G. E. H. Kinetics and Equilibria of the Hydration of Linear Butenes over a Strong Acid Ion-Exchange Resin as Catalyst. *Chem. Eng. Sci.* **1986**, *41*, 217−226.
(28) Pérez-Maciá, M. A.; Bringué, R.; Iborra, M.; Tejero, J.; Cunill, F. Thermodynamic Equilibrium for the Dehydration of 1-Butanol to Di-n-Butyl Ether. *Chem. Eng. Res. Des.* **2015**, *102*, 186−195.
(29) Chao, J.; Hall, K. R.; Yao, J.-M. Thermodynamic Properties of Simple Alkenes. *Thermochim. Acta* **1983**, *64*, 285−303.
(30) Guttman, L.; Pitzer, K. S. Trans-2-Butene. The Heat Capacity, Heats of Fusion and Vaporization, and Vapor Pressure. The Entropy and Barrier to Internal Rotation. *J. Am. Chem. Soc.* **1945**, *67*, 324−327.
(31) Nikitin, E. D.; Popov, A. P.; Bogatishcheva, N. S.; Faizullin, M. Z. Critical Temperatures and Pressures, Heat Capacities, and Thermal Diffusivities of Levulinic Acid and Four n-Alkyl Levulinates. *J. Chem. Thermodyn.* **2019**, *135*, 233−240.
(32) Voge, H. H.; May, N. C. Isomerization Equilibria among the N-Butenes. *J. Am. Chem. Soc.* **1946**, *68*, 550−553.
(33) Scott, B. R. B.; Ferguson, W. J.; Brickwedde, F. G. Thermodynamic Properties of Cis-2-Butene from 15° to 1,500 K. *J. Res. Natl. Bur. Stand.* **1944**, *33*, 1−20.

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