Tutor/s

Dr. Jordi H. Badia i Córcoles
Chemical Engineering & Analytical Chemistry Department

Dra. Eliana Ramírez Rangel
Chemical Engineering & Analytical Chemistry Department

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Biomass transformation to biofuels: determination of thermodynamics properties of reaction and selection of optimal catalyst for the esterification of levulinic acid with 1-butene.

Eloi Canadell i Soler

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> *La veritable saviesa està en reconèixer la pròpia ignorància.*
>
> Sòcrates

Primer de tot m'agradaria agrair als meus tutors d'aquest projecte, Dr. Jordi H. Badia i Dra. Eliana Ramírez, per la confiança i la oportunitat de poder realitzar aquest projecte i sobretot, per l'ajuda que m'han proporcionat i els coneixements que m'han transmès durant aquest any.

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També m'agradaria agrair tots els professors que han aportat el seu gra de sorra en la meva formació.

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SUMMARY

The present project is related to the study of butyl levulinates syntheses, which are products of great interest that, among other applications, can be used as fuel additives for both diesel and gasoline, due to some of their properties.

More specifically, the present work is focused on the synthesis of *sec*-butyl levulinate (SBL), which has been identified as an effective antiknocking agent for gasoline formulations. SBL is considered a biofuel because it is produced from levulinic acid (LA), which is a renewable source of biomass—since it is a platform molecule originated from lignocellulose—, and 1-butene, a low value-added olefin. SBL synthesis pathway proposed in this work is esterification of LA with 1-butene (1B) over an acidic ion-exchange resin as the catalyst. A more traditional, hence more studied, approach to carry out this synthesis is the esterification of LA with 1-butanol, which also leads to water formation and is affected by side reactions in a greater extension than the proposed pathway using an olefin as the esterifying agent.

Prior to implementing the studied synthesis at industrial scale, optimal operation conditions, best catalyst, and thermodynamics of the reaction need to be determined. Previous studies concluded that temperatures between 80 and 100 ºC, and 1B excess were the most favorable conditions, and that the optimal catalyst was the ion-exchange resins Amberlyst-15, due to the high yield towards SBL achieved and low extension of side reactions.

Therefore, the aim of the present work is to experimentally determine the equilibrium constants of the reaction in the temperature range 90-120 ºC and to determine the thermodynamic properties thereof. Determined values of enthalpy and entropy changes of reaction have been compared to theoretical values, and different estimation methods have been employed.

Keywords: Butyl levulinates, biomass, biofuel, thermodynamics determination, ion-exchange resins.

RESUM

Aquest projecte està relacionat amb la síntesi dels levulinats de butil, que són productes d'interès per fer-los servir com additius de combustible, tant per el dièsel com la gasolina, degut a les propietats que presenten.

Específicament aquest estudi es centra en la síntesi del *sec*-butil levulinat (SBL) que s'ha identificat com un efectiu antidetonant de la gasolina. El SBL es considera un biocombustible ja que es produeix a partir de l'àcid levulinic (LA), que és una font renovable de biomassa – ja que té origen lignocel·lulòsic- i l'1-butè (1B), que és una olefina de baix valor afegit. El camí de reacció proposat per dur a terme la síntesi del SBL és l'esterificació de l'LA amb 1B utilitzant una resina de bescanvi iònic com a catalitzador. A diferència dels processos més tradicionals, i per tant més estudiats, s'empra una olefina en lloc d'un alcohol per evitar la formació d'aigua com a producte secundari.

Degut a la possible implantació, a nivell industrial, d'aquesta síntesi s'han de determinar les condicions d'operació, el catalitzador òptim i la termodinàmica que envolta la reacció. Estudis anteriors han demostrat que les condicons d'operació més favorables per la reacció eren aquelles que es treballava a una temperatura entre 80 i 100 ºC, amb excés d'1B, i fent ús de l'Amberyst 15, una resina de bescanvi iònic, degut a l'elevat rendiment cap a la formación de SBL i la poca afectació de les reaccions secundàries.

Aquest projecte està dedicat a determinar la constant d'equilibri d'aquesta reacció a un rang de temperatures entre 90 i 120 ºC. Posteriorment es determina el valor de l'entalpia i l'entropia de reacció, el qual és comparat a un valor teòric que s'obté mitjançant diferents mètodes d'estimació.

Paraules clau: Levulinats de butil, biomassa, biocombustible, determinació termodinàmica, resines de bescanvi iònic.

1. INTRODUCTION

1.1. FOSSIL FUELS

Fossil fuels are hydrocarbon-containing materials of biological origin formed as a result of geologic processes acting on the remains of the organic matter. These non-renewable energy sources can be found in three different forms depending on the state of matter: in the form of gas, natural gas, in the form of liquid, petroleum and derivatives, and in solid form, coal. All fossil fuels can be burned in air or with oxygen derived from air to provide heat, which may be used directly, as in the case of home furnaces, or indirectly by producing steam to drive generators that can supply electricity [1].

The Industrial Revolution in the second half of the 18th century, meant a turning point in the consumption of fossil fuels, which have been consumed in an increasing rate ever since. The fact that new technologies implemented for the mass production, characteristic from the Industrial Revolution, required a higher energy consumption that could be no longer satisfied by the combustion of wood. By the late 18th century, coal began to be marketed on large scale and outpaced the use of wood [2].

As the time has gone by, the knowledge of the crude oil, as well as the improvement of the drilling technologies, has led to the commercialization of it in a world-wide scale [2]. It was discovered the possibility of obtaining intermediate materials and fuel products, with a potential use of interest in different areas, by distillation of the crude oil [3].

As a matter of fact, types of fuels that society relies on have shifted over the years, from solely coal towards a combination with oil and then gas, as can be seen in Figure 1. Coal consumption is falling in many parts of the world, but the consumption of oil and gas are still growing [4].

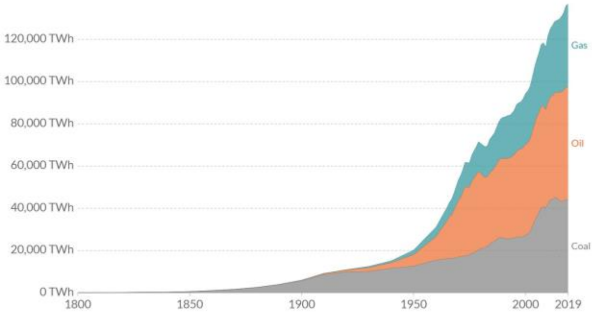


Figure 1. Energy transition from fossil fuels [4].

In recent years, the aim for alternative fuel has accelerated [3]. Although the new technologies such as fracking, rotatory drilling and directional drilling have made it possible to extract smaller deposits, the reserves of the principal fossil fuels are still limited [1]. Nowadays, fossil fuels supply more than 80 % of the energy consumed by the industrially developed countries of the world [1]. In addition, the search for alternative fuels is due to the environmental problems that fossil fuels have developed over the years, one of them is the emission of greenhouse gases directly related to the climate change.

Since the climate change has become a problem, the United Nations (UN) Framework Convention on Climate Change sets out an overall framework intended to stabilize atmospheric concentrations of greenhouse gases so to prevent anthropogenic interference with the climate system. In one of the latest conferences, an agreement was made between the countries that were part of the UN. The agreement made in 2015, known as the Paris Agreement, established a critical temperature limit which should be set at 1.5 ºC or 2 ºC above the preindustrial levels. Basically, the main goal is to achieve the zero net emissions in the early period of the 21st century, between 2030-2050 [5]. The Paris Agreement needs to be carried out by a coordinated political effort from both, the government and the private sector, meaning that a step towards the development and implantation of the alternatives fuels must be taken.

1.2. BIOMASS AND BIOFUELS

Biomass is a source of carbon from plant, animal of fungal organic matter which can be valued directly in the form of heat after a combustion or indirectly since it is, therefore, a suitable raw material to produce different products such as biofuels or biomaterials [6]. It is considered a renewable energy source because it can regrow in a relatively short time and as a matter of fact, whether trees are burned or whether they decompose naturally, the same amount of carbon dioxide would be released to the atmosphere. In other words, replacing fossil fuels with biomass would theoretically reduce the carbon emissions [7].

Biofuels are substances derived from biomass with the purpose to produce energy through combustion. These can be classified into different generations depending on the raw material used [8-9].

- First generation of biofuels: Fuels made from food crops grown on arable lands such as sugar or starch.
- Second generation of biofuels: Fuels made from lignocellulosic biomass or agricultural wastes.
- Third generation of biofuels: Based on algal biomass production.
- Fourth generation of biofuels: Solar biofuels using synthetic biotechnology.

At present, the most interesting alternative to produce biofuels is the second generation of biofuels. On one hand, first generation of biofuels must compete with food crops. On the other hand, the third and fourth generation are not able to compete with the other generations due to the lack of development. Even though the fourth generation has not been developed yet, it is the most hopeful and attractive option for the future because it is based on direct conversion of solar energy into fuel using raw materials that are inexhaustible, cheap and widely available [9].

Focusing on the biofuel production, three suitable groups of biomass-derived raw materials can be distinguished: starchy, triglycerides (oilseed) and lignocellulosic. A special importance will be added to the lignocellulosic biomass due to its abundance. This feedstock is made up of lignin, hemicellulose, and cellulose in variable proportions, where the hemicellulose is the minority of it. Hemicellulose is an easily hydrolysable polysaccharide, with an amorph small chain, which can lead to the production of acids, alcohols and sugars among other interesting products. Lignin is a hydrophobic aromatic polymer, with different ramifications, that provides structural rigidity to the plants. Cellulose, that is protected by the lignin, is made of glucose. The main structural difference between cellulose and the other components is the crystalline structure that it possesses [6].

In order to achieve the conversion of the lignocellulosic biomass into biofuel, the biomass must be pre-treated. Pre-treatment consists of breaking down the lignocellulose to its constituent parts, in other words, it consists in separating the cellulose from the other two polymers. To accomplish the degree of separation, physical, mechanic, physicochemical or chemical treatment must be employed.

From the transformation of the cellulose many products of great interest can be produced, such as the furfural and the 5-hydroxymethylfurfural (HMF) which both of them will lead to the production of the levulinic acid that can be transformed in many other valuable products. Therefore, the levulinic acid is a platform molecule being capable to produce a wide range of derivates such as levulinic esters that may substitute some petrol derivatives [6].

1.3. LEVULINIC ACID

Levulinic acid (LA), also known as 4-oxopentanoic acid, is a sugar-derived platform chemical that can be produced from biomass. Actually, it is an ideal platform chemical since it can be used to produce a great number of bio-chemicals such as polymers, biofuels or fuel additives among others [10].

It is a water-soluble compound with great reactivity due to their functional groups. Even though levulinic acid is an ideal intermediate, it is difficult to recover it [10].

The dehydration of the biomass with acid is one of the most widely used approach, however it is not that simple because of the side products [10]. In order to avoid these problems, the Biofine Corporation developed an acid hydrolysis process in a two-reactors system. In the first reactor the hydrolysis takes place at high temperature (210-230 ºC) in the presence of 1-5 wt.% mineral acid during 13-25 s, producing 5-HMF which is removed continuously and supplied to the second reactor. Then, in the second reactor, the hydroxymethylfurfural (HMF) is further hydrolyzed at 195-215 ºC for 15-30 min. The levulinic acid yield that can be reached is greater than 60 %, depending on the hexose content of the carbohydrate-containing starting material [11].

1.4. ALKYL LEVULINATES: *SEC*-BUTYL LEVULINATE

Alkyl levulinates are biobased chemicals compounds that can be used in a great variety of applications since they are potential substitutes of current chemicals coming from petro-chemical routes [12]. They possess outstanding properties, such as low toxicity, high lubricity, flash point stability and moderate flow properties under low temperatures conditions, making them suitable to be used as cold flow improvers in biodiesel or as oxygenate additives for gasoline and diesel fuels [13].

There are many ways to obtain alkyl levulinates. They can be directly obtained straight from the reaction between glucose or fructose with alcohols using heterogeneous catalysts or they can be obtained by esterification of levulinic acid with alcohols or olefins using a catalyst. Even though in the past homogeneous catalysts were used, such as the hydrochloric acid, it is preferable to implement heterogeneous catalysis since the solids are easier to separate, recycle, regenerate, reuse, limit the corrosion and even increase the levulinate yield [12]. Although it is not the common route, alkyl levulinates can be also produced by reacting angelica lactone and alcohols in the presence of acid or base catalysts or with alkenes and water using acid catalysts [12-13]. In Figure 2, the two available routes to obtain levulinate esters are shown.

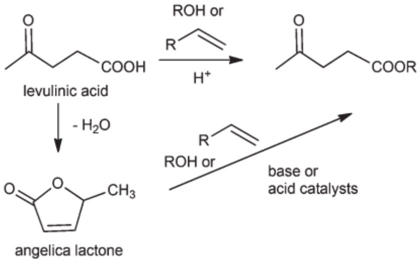


Figure 2. Different routes to obtain levulinate esters [13].

As it mentioned before, alkyl levulinates can be used as a biofuel. In order to guarantee the stablished quality indicated in the EN 590, which is included in the directive 2009/30 of the European Community. Even though a directive is not mandatory, it will guarantee the basic properties of an acceptable fuel [14].

Among all possible alkyl levulinates, ethyl and butyl levulinates are the main studied esters. Despite the better properties that butyl levulinate possess it is the synthesis of ethyl levulinate that has been studied the most [15]. There is a possible alternative to the alkyl levulinates mentioned above: *sec*-butyl levulinate (SBL). It is an interesting alternative because through this route side products formation, such as water or dialkylether, can be avoided [16]. SBL can be produced by esterification of an olefin instead of an alcohol in acidic conditions. Besides the interest of the SBL, the esterification could be able to revalorize olefins such as 1-butene (1B) because its unique use has been the production of poly-butene meaning that, with the object of preventing their accumulation, they are burned in case there is a low demand of poly-butene [17]. In Figure 3, possible routes of obtaining SBL by using different alkylating agents in the esterification of levulinic acid are shown.

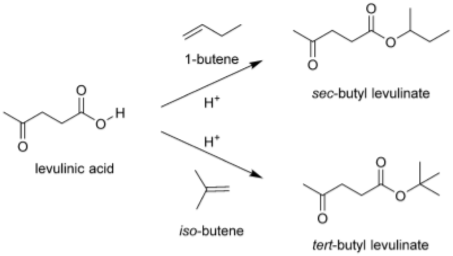
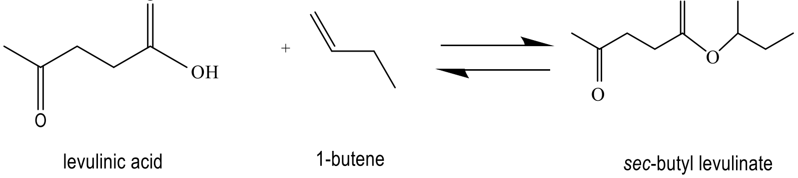
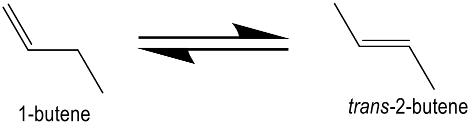


Figure 3. Routes of LA esterification using an olefin [16].

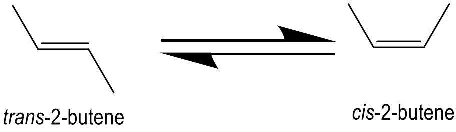
If LA is esterified in acidic conditions with 1B (see R1), to produce SBL, side reactions may occur. Those reactions come from the isomerization of the olefin to *trans*-2-butene (E-2B) (see R2) which later isomerizes to *cis*-2-butene (Z-2B) (see R3). The reactions that take place in the present work are shown below.



(R1)



(R2)



(R3)

1.5. ACIDIC ION EXCHANGE RESINS

A catalyst is a substance that increases the rate at which a chemical reaction approaches the equilibrium, without permanently intervening in the reaction. In other words, a small amount of catalyst can make a big change in the composition of the reacting system. A catalyzed process can be classified into three main groups:

1) Homogeneous, where the catalyst is in the same phase as the reactants.

2) Heterogeneous, where the reactants and the catalyst are in different phases.

3) Enzymatic, where the catalyst is an enzyme.

Most of the catalyzed processes used in the industry are heterogeneous, where 90 % of these use a solid catalyst [18].

Due to its importance, henceforward the focus of the present work is going to be the solid heterogeneous catalysis. This kind of catalysis requires at least one reactant to interact with the solid surface, specifically to the active center, to later be adsorbed onto it in order to form the activated complex. Then, the decomposition of the activated complex happens and finally the desorption of the product takes place. There are many things, such as structure, size, pores and even the selectivity, life cycle or activity, that need to be taken into an account to make the best election of a solid catalyst [18].

Focusing on the ion-exchange resins, which are organic compounds synthetically polymerized that contain charged sites that are able to attract an ion of opposite charge from the surrounding solution. This kind of resins are usually light and porous solids that are most of the times prepared in the form of granules, beads or sheets. There are some ion-exchange resins that can be used as an effective catalyst in esterification and hydrolysis reactions [19].

For the production of fuel ethers, among a wide variety of ion exchange resins, the matrix styrene-divinylbenzene is the most used. This kind of matrix is obtained as a result of a copolymerization of polystyrene cross-linked by divinylbenzene. The commercial ion-exchange resins can be classified in two main groups: gel-type resins, which present microporous and macroreticular resins that present permanent macroporous. The resins used in order to produce alkyl levulinates are required to be acidic resins. Its functionality is obtained by direct sulfonation with sulfuric acid, depending on the degree of sulfonation three main groups can be distinguished, from least to most, surface sulfonated, conventional sulfonated and over-sulfonated [20].

Other properties that should be taken into consideration to choose an ion exchange resins are the degree of cross-linking and swelling capacity among others. The degree of cross-linking is related to the divinylbenzene initial percentage before the polymerization, this degree provides the stiffness to the matrix reducing the number of large porous. The swelling capacity is dependent on the chemical properties of the resin matrix and the degree of cross-linking [21]. It could be defined as the volume variation of a resin owing to its interaction with a polar substance and difference osmotic pressure outside and inside of the particle [22].

In a nutshell, ion-exchange resins can be used as a solid heterogeneous catalyst, and thus, avoid many problems such the separation of the catalyst from the solution that contains the product. Based on the results obtained by Démolis et al, the most suitable ion-exchange resin is the Amberlyst-15 (A15) for the levulinic acid esterification using 1-butene, avoiding side products [16].

The esterification of the LA using 1B has been also carried out, in previous works, in a temperature range of 40-110 °C varying the initial molar ratio of levulinic acid to 1-butene between 0.4 and 3. Among the catalysts that have been used, A15 presented the highest activity being able to achieve a 66% SBL yield from the LA esterification with 1B, meaning that it is a suitable ion exchange resin for the reaction [22-24].

2. OBJECTIVES

The present work focuses on the synthesis of SBL by esterification of LA with 1B, using A15 as a catalyst. The aim of the study is to determine the thermodynamic properties of the esterification reaction, which have not been determined yet, to know the equilibrium conditions of the reaction. Due to the presence of side reactions as a result of the isomerization of 1B, thermodynamic properties of these reactions will be determined as well. Therefore, the following specific goals have been set:

1) To determine the experimental equilibrium constants of LA esterification reaction with 1B to obtain SBL (R1), isomerization of 1B (R2), and double-bond isomerization reaction of E-2B (R3), at different operating conditions in terms of reactants composition and temperature.
2) To estimate the theoretical equilibrium constants for the described reactions and to compare them to obtained experimental results.
3) To determine the liquid-phase entropy and enthalpy changes of the studied reactions.

3. THEORETICAL FRAMEWORK

3.1. ENTHALPY

By definition, enthalpy (H) is the sum of the internal energy and the product of pressure and volume [25]. So, it is a state function that fully depends on the temperature, pressure and internal energy. Usually, since absolute energetic states cannot be determined, the enthalpy is expressed as a change of enthalpy (ΔH) [26].

The enthalpy of formation of a given compound is defined as the enthalpy change to form such species in its standard state, 1 atm and 298.15 K and its most stable phase, by an isothermal reaction [27].

The enthalpy of the reaction is defined as the enthalpy variation produced by a reaction under constant conditions of pressure and temperature, which does not require to be in the standard form. Then, the enthalpy of the reaction is the sum of reactants and products enthalpy changes of formation (see eq.1). If the change is positive, the reaction is endothermic, meaning that heat is absorbed. In case the variation is negative, the reaction would be exothermic, meaning that heat would be released [26-27]. The enthalpy of the reaction can be calculated using the following expression:

$$\Delta H_r(T) = \sum_{j=1} \nu_j \cdot \Delta H_{f_j}(T) \qquad (1)$$

Where ν_i is the stoichiometric coefficient, which presents negative values when it is referred to reactants ($\nu_i<0$), and positive values for products ($\nu_i>0$).

3.2. ENTROPY

The state function of entropy (S), which is defined in the second law of thermodynamics, is related to the disorder of the substances. In a system that has reached the equilibrium if a change is made the entropy will increase. It gives an idea of the magnitude of non-usable energy contained in a system. When there is a reversible reaction, dS=0 whereas if there is an irreversible reaction, then dS>0 [28-29].

$$dS \geq \frac{\partial q}{T} \tag{2}$$

The entropy of the reaction can be obtained from the entropies of formation at a given state and temperature conditions [27].

$$\Delta S_r(T) = \sum_{j=1} \nu_j \cdot \Delta S_{f_j}(T) \tag{3}$$

3.3. EQUILIBRIUM

The chemical equilibrium of a reaction is a state where the rate of the global reaction equals zero. In other words, the direct rate of reaction equals the inverse reaction. In this kind of situation, the concentrations of products and reactants remain constant. Therefore, chemical equilibrium depends on pressure and temperature. If a change of temperature or pressure is produced, the reaction will reach a different equilibrium state [30]. The velocity in which a reaction approaches the equilibrium will be increased, when necessary, by the addition of a catalyst.

The equilibrium constant is a parameter that quantifies the chemical equilibrium. It is defined as the ratio of the direct and inverse reaction rate. As means of demonstration, an example of the equilibrium constant calculation is shown.

Considering the following reversible reaction:

$$\nu_A A + \nu_B B \rightleftharpoons \nu_R R + \nu_S S$$

The law of mass action states that reactions rate is proportional to the concentrations of the species raised to the stoichiometry coefficient. In this case, the global reaction can be separated into two reactions, forward and backward, where each reaction will have its rate.

$$\nu_A A + \nu_B B \rightarrow \nu_R R + \nu_S S \quad r_d = k_d x_a^{\nu_A} x_b^{\nu_B} \tag{4}$$

$$\nu_R R + \nu_S S \rightarrow \nu_A A + \nu_B B \quad r_i = k_i x_r^{\nu_R} x_s^{\nu_S} \tag{5}$$

As it was mentioned before, the equilibrium is reached once the direct and inverse reaction rate is equal.

$$r_d = r_i \tag{6}$$

$$k_d x_a^{\nu_A} x_b^{\nu_B} = k_i x_r^{\nu_R} x_s^{\nu_S} \tag{7}$$

Applying the given definition of the equilibrium constant.

$$K = \frac{k_d}{k_i} = \frac{c_r^{\nu_R} c_s^{\nu_S}}{c_a^{\nu_A} c_b^{\nu_B}} \tag{8}$$

Nevertheless, the law of mass action also states that the liquid-phase equilibrium is directly proportional to activities, rather than concentrations. Activity is defined as the product of the molar fraction (x_j) and the activity coefficient (γ_j). In ideal conditions, and an ideal mix, the activity coefficient would take the unit value not making any change on the equilibrium constant (see eq.9).

$$K = \frac{x_r^{\nu_R} x_s^{\nu_S}}{x_a^{\nu_A} x_b^{\nu_B}} \cdot \frac{\gamma_r^{\nu_R} \gamma_s^{\nu_S}}{\gamma_a^{\nu_A} \gamma_b^{\nu_B}} \tag{9}$$

4. EXPERIMENTAL SECTION

4.1. MATERIALS

In order to carry out the synthesis of the sec-butyl levulinate (SBL), levulinic acid (LA) (Acros Organics, 98% purity) and 1-butene (1B) (Air Liquide, 99.9% purity) are required. In Table 1, the main properties of the reactants, products, and major byproducts involved in the system are shown.

Table 1. Main properties of the reactants and products

Properties	1-butene [a]	2-butanol [b]	levulinic acid [c]	*sec*-butyl levulinate [a]	butyl levulinate [d]
CAS number	106-98-9	78-92-2	123-76-2	85734-01-6	2052-15-5
Chemical formula	C_4H_8	$C_4H_{10}O$	$C_5H_8O_3$	$C_9H_{16}O_3$	$C_9H_{16}O_3$
State at room temperature	Gas	Liquid	Solid	Liquid	Liquid
Density [kg/m³]	608	807	1134	-	974
Molecular weight [g/mol]	56.11	74.12	116.12	177.22	177.22
Melting point [ºC]	-185	-115	33	-	-
Boiling point [ºC]	-6.11	99.5	245	-	107
Flash Point [ºC] at 1 atm	-78.9	24	98	-	92
Purity [%]	>99	>99,5	>98	-	98
Supplier	Air liquide	PanReac AppliChem	Acros Organics	-	Sigma-Aldrich
Safety pictograms					

[a] Values obtained from PubChem [31].
[b] Values obtained from PanReac AppliChem [32].
[c] Values obtained from Acros Organics [33].
[d] Values obtained from Sigma-Aldrich [34].

Due to the no commercial availability of the *sec*-butyl levulinate, butyl levulinate was used as a chemical standard since these two molecules are almost identical in terms of chromatographic response.

The ion exchange resin used for the present work as the catalyst is A15, supplied by Du Pont, which has the properties, of the data sheet, listed in Table 2:

Table 2. Catalyst properties.

Catalyst	**Type**	**Sulfonation**	**Acid Capacity [mmolH$^+$/g]**	**DVB [%]**	**Water retention [%]**	**T_{max} [^{o}C]**	**ρ [g/cm^3]**
A15	macroporous	conventional	4.81	20	52-57	142	1.416

The gas used to pressurize the system, as well as to keep the 1-butene in liquid state, was nitrogen (99.9995% purity), and the chromatographic carrier gas was helium (99.9998% purity). Nitrogen was supplied by Linde Gas España S.A.U.

4.2. SETUP

The experimental setup consists of a 250 mL stainless-steel batch reactor (Autoclave Engineers, Inc) with 200 mL of useful volume. The reactor is heated by a jacket, connected to a thermostatic bath, with a mixture of propanediol and water. The system also includes a thermocouple, a stirrer, a relief valve, a pressure gauge and a baffle. A schematic diagram of the experimental setup is shown in Figure 4.

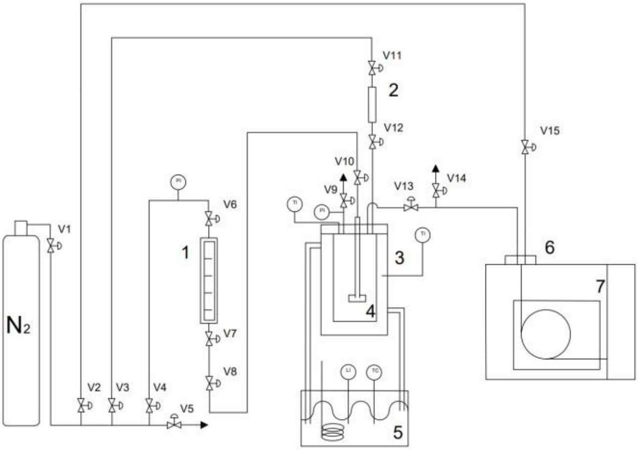


Figure 4. Schematic diagram of the batch reactor setup. 1: pressure burette, 2: catalyst injector, 3: batch reactor, 4: agitation system, 5: thermostatic bath, 6: sample injector, 7: gas chromatograph coupled to a mass selective detector

A manometer can be found between the reactor and the venting valve (V9) and is used to measure the pressure inside the reactor. The main point of the venting valve (V9) is to depressurize the system in cases where it is needed during the reaction or to open the system for cleaning tasks

The stirring system consists of a six-blade turbine mounted on a rotor connected to a frequency converter where the stirring speed can be regulated. A baffle is located beside the turbine, its main function is to break up the vortices due to the agitation. There is a thermocouple, with a precision of ±0.1 ºC, next to the stirring system where the reactor temperature can be measured.

A gas chromatograph (Agilent 7890B GC System), coupled to a mass-selective detector (Agilent 5977B GC/MSD), can be found connected to the reactor. Both, the GC and the MSD, are used to identify and quantify the different species inside the reactor. The sample goes through a heated conduction, to avoid its solidification, from the reactor to the inlet of the chromatograph. A 0.2 μL sample is injected, automatically by a mechanically operated valve using compressed air, in the GC which is equipped of a capillary column (HP-PONA 19091S-001, J&W Scientific, Santa Clara, US; 100 % dimethylpolysiloxane, 50m × 0.20 mm × 0.50 μm) and uses a helium flow of 0.5 mL/min. The total run time of the analysis was of 18.57 min where the GC oven temperature was set as follows:

1) 5 minutes hold at 313 K
2) A 35 K/min ramp up to 473 K.
3) A final 9 minutes hold at 473 K.

4.3. PROCEDURE

Catalyst pre-treatment

Due to ion exchange highly hygroscopic character, a pre-treatment must be applied to reduce their water content prior to every experiment since water inhibits the catalyst [35]. The followed procedure is listed below.

1) Weigh approximately the double of the desired amount of catalyst.
2) Pre-dry the resin in an atmospheric oven for 2 hours at 110 ºC.
3) Introduce the pre-dried ion exchange resin sample in a vacuum oven for at least 12h at 100 ºC at 10^{-3} MPa.

Reactor Loading

The procedure carried out, which was always the same, is listed below.

1) Since levulinic acid is solid at room, it must be heated in a water bath to surpass its melting point (33 ºC).
2) Once the levulinic acid is liquid, weigh the desired amount and pour it inside the reactor vessel.
3) Close the reactor. At this point, it's advisable to turn on the thermostatic bath (set the power at 60 % of full capacity while heating and once the mixture has reached the desired temperature, then the power should remain between 10-20% of full capacity).
4) Mount the stirring system, chain and cover, and turn it on by selecting a stirring speed
5) Weigh the desired amount of 1-butene by means of difference in a pressure burette. The pressure burette is used in order to have the 1B as a pressurized liquid since it is found as a gas at room temperature.
6) Place the burette into the system.
7) Screw the sample valve (V13) to close the sample system. The one-way valve (V10), that connects the burette with the reactor, must be screwed as well.
8) Once the temperature has reached its desired value the 1-butene needs to be introduced. This is step will be carried out by depression (without exceeding 15 bars).
9) Remove the catalyst from the vacuum oven, weigh the desired amount (5 g) and then place it into the catalyst injector.
10) Connect the catalyst injector to the nitrogen line and pressurize it up to 25 bars. After opening the valve (V12), the catalyst will be introduced into the reactor vessel by means of pressure difference.
11) Make sure that all the valves are closed and there are no leaks.
12) Run the experiment for 10 hours.
13) The sample analysis can be started once 7 hours of the experiment have been reached, following the procedure shown in “GC analysis”.

14) After reaching the expected 10 hours, turn off the agitation system as well as the thermostatic bath and the heating mantle. Then depressurize the reactor by opening the venting valve and make sure that all the other valves are closed.

GC analysis

In order to carry out the sample analysis, a gas chromatograph (GC) coupled to a mass selective detector (MSD), both of them connected to a computer, was used. The general procedure to analyze the samples with the GC-MSD system is described below:

1) Turn on the electric heating mantle for about 10 minutes before the GC analysis.
2) Select the method in the computer program.
3) Check that the circuit is at atmospheric pressure using V14 and open the sample valve (V13) which means, that the reactor mixture will flow through the sample circuit.
4) Press the green arrow on the program.
5) Save the analysis as the experimental conditions and press the "OK AND RUN METHOD". In Appendix 1, the computer program, the analysis results and the retention time of the present species can be found.
6) Close the sample valve (V13).
7) After waiting a couple of minutes and being sure that the mixture is inside the chromatograph, there are two options:
    - The first one is to open valve number 14 and clean the sample circuit with nitrogen. This is not the best option since the reaction's volume is not constant.
    - The second one is to depressurize the reactor to 20 bars and then add the 25 bars nitrogen in the sample circuit. By means of pressure difference, requiring the sample valve (V13) to be opened, the mix inside the sample circuit will go back to the reactor. This step should be done thrice at least.
    - Even though the second option is better since there are no changes in terms of design variables of the reactor, the first one has been used quite more often because there are less cleaning problems. The second one makes the circuit

pipes dirty which means that the analysis won't be reliable, however, it would be a better option in case the equilibrium wasn't reached.

8) Close the sample valve (V13).
9) Purge the nitrogen that may have stayed in the sample circuit.

Cleaning

Once the experiment was over, the following procedure was followed to clean the setup.

1) Depressurize the reactor opening the venting valve (V9).
2) Unscrew the sampling circuit from the sample valve (V13), the one-way valve (V10) and the nitrogen pipe connected to the catalyst injector.
3) Disassemble the agitation system.
4) Open the reactor.
5) Extract the mixtures from the inside of the reactor using a vacuum pump.
6) Filter the mixture in order to separate the catalyst. The mixture goes to the non-halogenated solvents and the catalyst to the solid resin waste container.
7) Extract the remaining catalyst from the reactor using acetone and filter it as the step 6.
8) Clean the reactor cover with acetone.
9) Dry the reactor cover and the reactor with pressurized air.
10) Make sure that there are no substances left either on the inside or the cover of the reactor.

4.4. REACTION CONDITIONS

The experiments carried out lasted between 8 and 10 hours, which was considered enough to ensure that the chemical equilibrium conditions had been met, at a constant stirring speed of 500 rpm and using commercial A15 as the catalyst. Pressure (25 bar) and temperature remained constant during every experiment. For the purpose of calculating the equilibrium constants for the studied reaction system, different temperatures were tested. Different initial molar ratios of LA to 1B ($R^{o}_{LA/1B}$) were also tested. Assayed experimental conditions are shown in Table 3:

Table 3. Experimental conditions for the thermodynamic determination.

Temperature [°C]	**Catalyst [g]**	**Molar ratio ($R_{LA/1B}$) [-]**
100	5	1.0
100	5	1.5
100	5	0.5
110	5	1.5
110	5	0.5
120	5	1.5
120	5	0.5
90	10	1.5
90	10	0.5

5. THEORETICAL ESTIMATION OF THE EQUILIBRIUM CONSTANT

The objective of the present work is to determine the equilibrium constant for the studied reactions in terms of involved compounds activities (K_a), as well as thermodynamic properties of reaction, such as the entropy and the enthalpy changes of reaction. Since the reaction took place in the liquid state, the equilibrium should depend only on temperature. Otherwise, pressure would also affect the equilibrium constant.

The equilibrium constant is related to the state functions enthalpy and entropy by the definition of the Gibbs energy change of reaction [27].

$$\Delta G^o(T) = \Delta H^o(T) - T \cdot \Delta S^o(T) \qquad (10)$$

$$\ln(K_a) = -\frac{\Delta G_r^o(T)}{R \cdot T} = -\frac{\Delta H_r^o(T)}{R \cdot T} + \frac{\Delta S_r^o(T)}{R} \qquad (11)$$

As can be seen in the equation above, the logarithm of the chemical equilibrium constant is a linear function that depends only on the enthalpy and entropy changes of reaction. As a matter of fact, the enthalpy and entropy of the reaction need to be on the temperature and state in which the reaction is carried out. In order to do so, it will be necessary to apply the Kirchhoff equations shown below [36-37].

$$\Delta H_r^o(T) = \Delta H_r^o(T_0) + \int_{T_0}^{T} \sum_{j=1} \nu_j \cdot c_{p_j}(T) dT \qquad (12)$$

$$\Delta S_r^o(T) = \Delta S_r^o(T_0) + \int_{T_0}^{T} \frac{\sum_{j=1} \nu_j \cdot c_{p_j}(T)}{T} dT \qquad (13)$$

Where c_{pj} is the specific heat of the j compound.

There is a need for determining the enthalpy and entropy changes of formation of each compound present in the reaction in order to calculate the enthalpy and entropy change of the reaction. At this point, an order of preference is stablished, consisting in the following criteria: i) if the thermodynamic parameter (either entropy or enthalpy) has been determined in earlier works, the values found in the literature should be used; ii) in case no records can be found regarding thermodynamic properties of some compounds, they will be calculated by means of an estimation method. In the present work, all compounds involved were found in earlier works except the main product, SBL.

5.1. ESTIMATION OF SBL THERMODYNAMIC PROPERTIES OF FORMATION

Firstly, in order to estimate the SBL enthalpy change of formation, two different estimation methods were assayed. On one hand there is the Benson's method, which estimate the thermodynamic properties of organic compounds. Although at first it was only used for compounds in gas phase, now it can also be used in the condensed phases [37]. On the other hand, there is the Joback method, which is used to calculate enthalpy of formation at gas state, combined to the Vetere method, which allows to find the enthalpy change of condensation. Combining those two methods, the enthalpy change of formation in the liquid state at the standard temperature can be calculated [27].

Henceforward, there is going to be a focus on the Benson's method due to its simplicity, while the combination of the other two methods is further described in the Appendix 2. The Bensons's method takes into account the energetic contribution of each constituent group present in the molecule (see Appendix 3), to calculate the enthalpy change of formation using the following expression [37]:

$$\Delta H_f^o(T^o, L) = \sum_k n_i \cdot \Delta H_f^o(T^o, L) \tag{14}$$

Where *k* is the type of group, n_i is the number of k-types groups, and ΔH^o_f is the energetic contribution of the k-type groups in kJ/mol.

In order to verify the results obtained through the Benson's method, a comparison between different methods was made. Results of SBL enthalpy and entropy changes of formation can be found in Table 4. As seen in the table, differences between values obtained with different methods were insignificant because the comparison between the estimation and the literature value only differed about 1% unless the case of E-2B. Since the estimation method applied is not able to distinguish the 2-butene isomers, the literature value was considered reliable.

Table 4. Comparison of the enthalpy change of formation of the different compounds.

Compound	Literature value	Benson's method [37]	Joback method [27]
SBL	—	-736.0	-731.86
LA	-683.8 [38]	-676.5 (1.0%)	-682.1 (0.2%)
1B	-20.8 [28]	-20.54 (1.3%)	-23.8 (14.4%)
E-2B	-29.8 [28]	-33.12 (11.1%)	-33.0 (10.7%)
Z-2B	-33.3 [28]	-33.12 (0.3%)	-33.0 (0.9%)

Furthermore, LA thermodynamic properties were also estimated to compare obtained values to those found in the literature, in order to assess the reliability of used methods for chemical species in the present reaction system (LA values are also included in Table 4. From values in the table, it can be seen that the -676.5 kJ/mol -value obtained by method Benson's method- was close to the previously reported value of -683.3 kJ/mol [38]. Therefore, Benson's method was considered a reliable method to estimate SBL enthalpy change of formation and was chosen over the combination of the Joback and Vetere method since it was able to predict better the olefin properties that is a well-studied compound. It also gives a greater confidence since every estimation method has an associated uncertainty, so the combination of two different methods should have a greater uncertainty than the use of the Benson method.

Secondly, the estimation of the entropy change was made. In this case, the Benson's method was used, since it can estimate entropy changes values successfully, and the method was considered reliable according to the assessment carried out for the enthalpy changes estimation. Benson's method to estimate entropy changes of formation is analogous to that for enthalpies, as can be seen in the following expression [37].

$$\Delta S_f^o(T^o, L) = \sum_k n_i \cdot \Delta S_f^o(T^o, L) \tag{15}$$

Where *k* is the type of group, n_i is the number of k-types groups, and $\Delta S^o{}_f$ is the energetic contribution of the k-type groups in J/mol·K.

Thirdly, in case appliance of the Kirchhoff equations is required, the specific heat of the compound need to be estimated. The Rùdzicka and Domalski method, that is a further development of the Benson method, is used to estimate the liquid-phase specific heat. The Rùdzicka and Domalski method takes into account the contribution of each constituent group present in the molecule (See Appendix 4) [27]. The specific heat of each compound is calculated by applying the following equation.

$$c_{p_L} = R \cdot \left(A + B \cdot \frac{T}{100} + D \cdot \left(\frac{T}{100} \right)^2 \right) \tag{16}$$

Where *R* is the gas constant expressed in J/mol·K and *T* is the temperature expressed in K. *A*, *B* and *C* are parameters that need to be calculated using the following expressions:

$$A = \sum_{i=1}^{k} n_i \cdot a_i \quad (17) \qquad B = \sum_{i=1}^{k} n_i \cdot b_i \quad (18) \qquad D = \sum_{i=1}^{k} n_i \cdot d_i \quad (19)$$

Where *a*, *b* and *c* are parameters related to the constituent groups and n_i is the number of times that the same group is present in the molecule.

Since the specific heat is a function of temperature, the estimation of this parameter is required for each compound of the present work because bibliographically specific heat values can only be found for definite temperatures. In order to verify the method employed it is necessary to compare the estimated results of the 1-butene, since LA specific heat has not been tabulated yet, to the tabulated values for a definite temperature. In standard conditions, 1-butene has a specific heat of 118 J/mol·K [28] while its estimated value is 121.9 J/mol·K, which makes the Rùdzika and Domalski method reliable. The specific heat, as a function of temperature, for the present substances is shown below:

$$c_{p_{SBL(L)}} = R \cdot \left(41.927 - 5.445 \cdot \frac{T}{100} + 1.592 \cdot \left(\frac{T}{100} \right)^2 \right) \tag{20}$$

$$c_{p_{LA(L)}} = R \cdot \left(24.298 - 1.252 \cdot \frac{T}{100} + 0.806 \cdot \left(\frac{T}{100} \right)^2 \right) \tag{21}$$

$$c_{p_{1B(L)}} = R \cdot \left(14.123 - 1.684 \cdot \frac{T}{100} + 0.625 \cdot \left(\frac{T}{100} \right)^2 \right) \tag{22}$$

$$c_{p_{2B(L)}} = R \cdot \left(15.840 - 2.827 \cdot \frac{T}{100} + 0.818 \cdot \left(\frac{T}{100} \right)^2 \right) \tag{23}$$

Where *R* is the gas constant in J/mol·K and *T* is the temperature in K.

5.2. ESTIMATION OF THE EQUILIBRIUM CONSTANT OF THE REACTIONS

The standard values of the parameters needed to estimate the equilibrium constant of the present reactions are listed in Table 5:

Table 5. Enthalpy and entropy changes of formation of compounds in the present reaction system.

Compound	CAS	ΔH^o_f[kJ/mol]	ΔS^o_f[J/mol·K]
1B [a]	106-98-9	-20.8	227.0
Cis-2B [a]	590-18-1	-29.8	219.9
Trans-2B [b]	624-64-6	-33.3	205.31
LA [c]	123-76-2	-683.8	268.6
SBL [d]	85734-01-6	-736.0	441.5

[a] Tabulated values from CRC Handbook of Chemistry and physics [28].
[b] Tabulated values from the NIST Webbok [39].
[c] Tabulated values from Emel'yanenko [38].
[d] Estimated values applying the Benson method [37].

Enthalpy and entropy changes of the studied reactions were calculated using equation 1, and results are listed in Table 6.

Table 6. Theoretical values of the thermodynamic reaction properties for the studied reaction system.

Reaction	ΔH^o_r[kJ/mol]	ΔS^o_r[J/mol·K]
SBL formation (R1)	-31.4	-54.1
1B isomerization to E2B (R2)	-12.5	-21.7
E2B-Z2B isomerization (R3)	3.5	14.6

The respective equilibrium constants can be represented as functions of temperature, and the equilibrium constants for every considered temperature can be calculated with equation 11. Results can be found in Table 7, where K_{a1} refers to SBL formation (R1), K_{a2} to 1B isomerization (R2) and K_{a3} to E-2B isomerization (R3).

Table 7. Estimated equilibrium constant at different temperatures

T [°C]	K_{a1}	K_{a2}	K_{a3}
90	49.00	4.62	1.81
100	37.08	4.14	1.87
110	28.48	3.73	1.93
120	22.16	3.37	1.98

6. EXPERIMENTAL RESULTS AND DISCUSSION

In this section the experimental thermodynamic parameters, at the operating conditions mentioned above, of the present reactions (R1, R2 and R3) are determined. Firstly, an explanation on how to determine the calibration equations is shown. Secondly, the experimental thermodynamic parameters are obtained and discussed by the effect of the non-ideality of the mix and the difference between the working pressure and the standard pressure, at which the theoretical values were obtained.

6.1. CALIBRATION

The calibration is done to find the proportionality relation between the relative mass and the relative GC-MSD area of every substance of the present work. It is started by designing some combinations of the species present in their expected rank. The calibration procedure is listed in Appendix 5.

Once the calibration procedure is done, the GC/MSD gives a % of area under each peak of the different species, which can be identified by their retention time that can be found in Appendix 1. Since the wt.% is known, and indeed is related to the response, the calibration equations can be done. In Table 8 all the calibration equations for the species of the present work. See Appendix 5 for their graphical representation.

Table 8. Calibration equations for the reaction species

Compound	Calibration equation	R^2
LA	$w_{LA}=(1.34\pm0.10)A_{LA}+(0.06\pm0.02)$	0.9703
1B	$w_{1B}=(3.23\pm0.29)A_{1B}$	0.9451
E-2B	$w_{E2B}=(3.23\pm0.29)A_{E2B}$	0.9451
Z-2B	$w_{Z2B}=(3.23\pm0.294)A_{Z2B}$	0.9451
SBL	$w_{SBL}= (0.48\pm0.04)A_{SBL}$	0.9947
BuOH	$w_{BuOH}=(0.99\pm0.03) A_{BuOH}$	0.9687

Where w_j is the mass fraction of the compound j and A_j is the area under each peak expressed in times one.

6.2. EXPERIMENTAL EQUILIBRIUM CONSTANT

The equilibrium constant is a combination of the molar fractions or concentrations and the activity coefficients as it was mentioned in the theoretical framework. So, for a liquid reaction of a non-ideal system the equilibrium constant is expressed as the following expression [40]:

$$K_a = \prod_{j=1}^{S} \left(a_j \right)^{\nu_j} = K_x \cdot K_\gamma \qquad (24)$$

Where K_x is referred to the molar fractions while K_γ is referred to the activity coefficients.

From the molar fractions obtained experimentally, K_x and K_γ can be calculated. Firstly, the K_x is calculated since it can be obtained directly from the experiments with no further treatment of the experimental data alike the K_γ. Due to the presence of three different reactions, three different K_x are calculated using the following expressions.

$$K_{x1} = \frac{x_{SBL}}{x_{LA} \cdot x_{1B}} \qquad (25)$$

$$K_{x2} = \frac{x_{E-2B}}{x_{1B}} \qquad (26)$$

$$K_{x3} = \frac{x_{Z-2B}}{x_{E-2B}} \qquad (27)$$

Where x_j is the molar fraction of the compound. K_{xi} is the equilibrium constant referred to one reaction.

In Table 9 the experimental results are presented along with their K_{xi} value (see next page).

Uncertainty is shown since different measures (between two and five) were used for each experiment.

Comparing the experimental equilibrium constant to the estimated value a difference is seen. All the reactions have higher values, in part, this is because it is considered as an ideal mixture.

UNIFAC

As mentioned above, the reaction mixture is non ideal and the deviation from the ideality is given by the activity coefficients. These coefficients are calculated by using the Modified UNIFAC (Dortmund) Model where the procedure is shown in Appendix 6. This model considers that the activity coefficients can be divided by a residual and a combinatorial part. In order to calculate the deviation, the molar fractions must be known, and the molecules need to be broken to their constituent groups to use the tabulated parameters [41]. The equilibrium constant referred to the activity coefficients is calculated using the following expressions.

$$K_{\gamma 1} = \frac{\gamma_{SBL}}{\gamma_{LA} \cdot \gamma_{1B}} \tag{28}$$

$$K_{\gamma 2} = \frac{\gamma_{E-2B}}{\gamma_{1B}} \tag{29}$$

$$K_{\gamma 3} = \frac{\gamma_{Z-2B}}{\gamma_{E-2B}} \tag{30}$$

Table 9. Experimental results along the equilibrium constant referred to the molar fractions.

Experimental run	T [^oC]	$R^o_{LA/1B}$	Molar fraction (10^2)						Kx_1	Kx_2	Kx_3
			1B	E-2B	Z-2B	2-BuOH	LA	SBL			
1	100	0.5	4.97 ± 0.04	49.70 ± 0.14	25.50 ± 0.09	1.025 ± 0.014	5.61 ± 0.18	13.20 ± 0.18	48 ± 2	10.01 ± 0.07	0.513 ± 0.002
2	100	0.5	4.89 ± 0.10	49.32 ± 0.10	25.30 ± 0.05	0.94 ± 0.02	6.02 ± 0.22	13.50 ± 0.13	46 ± 2	10.02 ± 0.05	0.5131 ± 0.0012
3	100	0.5	4.89 ± 0.02	49.47 ± 0.06	25.411 ± 0.008	1.08 ± 0.02	5.90 ± 0.04	13.20 ± 0.03	45.90 ± 0.35	10.12 ± 0.05	0.5137 ± 0.0005
4	110	0.5	5.34 ± 0.04	48.63 ± 0.12	25.68 ± 0.08	1.03 ± 0.03	6.75 ± 0.02	12.58 ± 0.18	34.94 ± 0.66	9.11 ± 0.056	0.5280 ± 0.0005
5	120	0.5	5.98 ± 0.02	47.99 ± 0.16	26.14 ± 0.08	1.21 ± 0.03	7.36 ± 0.08	11.32 ± 0.17	25.71 ± 0.35	8.02 ± 0.025	0.5447 ± 0.0004
6	90	0.5	4.47 ± 0.06	49.58 ± 0.06	24.60 ± 0.04	0.970 ± 0.011	5.68 ± 0.023	14.69 ± 0.26	58 ± 4	11.06 ± 0.16	0.4962 ± 0.0011
7 [a]	90	1	0.030	0.343	0.172	0.014	0.236	0.206	29.303	11.506	0.501
8 [a]	90	1	0.027	0.324	0.162	0.012	0.286	0.190	24.808	12.116	0.499
9 [a]	90	1	0.028	0.323	0.161	0.012	0.286	0.189	23.321	11.389	0.499
10 [a]	100	1	0.030	0.319	0.162	0.013	0.315	0.161	16.871	10.476	0.507
11 [a]	100	1	0.028	0.298	0.153	0.014	0.345	0.162	16.501	10.492	0.512
12 [a]	100	1	0.010	0.099	0.052	0.007	0.707	0.124	17.362	9.832	0.520
13 [a]	110	1	0.028	0.267	0.141	0.013	0.412	0.140	12.062	9.456	0.528
14 [a]	110	1	0.034	0.324	0.170	0.013	0.307	0.151	14.381	9.487	0.525
15 [a]	110	1	0.034	0.319	0.169	0.013	0.322	0.143	13.201	9.523	0.529
16 [a]	120	1	0.037	0.322	0.174	0.013	0.321	0.132	10.977	8.601	0.542
17 [a]	120	1	0.036	0.309	0.167	0.013	0.346	0.129	10.378	8.592	0.541
18 [a]	120	1	0.021	0.180	0.098	0.011	0.583	0.107	8.943	8.740	0.545
19	100	1.5	2.1513 ± 0.0010	23.52 ± 0.03	11.99 ± 0.02	1.215 ± 0.013	39.98 ± 0.15	21.15 ± 0.11	24.59 ± 0.23	20.93 ± 0.03	0.5095 ± 0.0007
20	100	1.5	2.16 ± 0.06	24.07 ± 0.27	12.20 ± 0.10	1.300 ± 0.002	39.31 ± 0.40	20.95 ± 0.02	24.65 ± 0.42	11.13 ± 0.17	0.507 ± 0.002
21	100	1.5	2.13 ± 0.08	22.07 ± 0.38	11.21 ± 0.29	1.07 ± 0.02	44 ± 1	19.74 ± 0.68	21.17 ± 0.61	10.36 ± 0.23	0.508 ± 0.005
22	110	1.5	2.19 ± 0.09	22.20 ± 0.72	11.75 ± 0.34	1.434 ± 0.004	44 ± 1	18.38 ± 0.16	19.11 ± 0.06	10.16 ± 0.09	0.529 ± 0.002
23	120	1.5	2.93 ± 0.04	25.50 ± 0.30	14.01 ± 0.17	1.63 ± 0.02	38.91 ± 0.54	17.03 ± 0.14	14.97 ± 0.17	8.71 ± 0.021	0.5494 ± 0.0002
24	90	1.5	1.61 ± 0.04	19.89 ± 0.10	9.82 ± 0.10	1.18 ± 0.02	44.44 ± 0.54	23.07 ± 0.27	32.291 ± 0.007	12.37 ± 0.23	0.494 ± 0.003

[a] Results obtained from [42].

In Table 10, the K_γ constants obtained at the different experimental conditions, as a result of applying the UNIFAC prediction method are shown.

Table 10. Equilibrium constant referred to the activity coefficients.

T [ºC]	$R^o_{LA/1B}$	$K_{\gamma1}$	$K_{\gamma2}$	$K_{\gamma3}$
90	0.5	0.2110 ± 0.002	1.0313 ± 0.0003	1 ± 0
100	0.5	0.1977 ± 0.0007	1.02872 ± 0.00014	1 ± 0
110	0.5	0.1912 ± 0.0010	1.0270 ± 0.0003	1 ± 0
120	0.5	0.1818 ± 0.0013	1.0243 ± 0.0003	1 ± 0
90	1	0.301 ± 0.002	1.0391 ± 0.0003	1 ± 0
100	1	0.314 ± 0.013	1.03346 ± 0.00009	1 ± 0
110	1	0.296 ± 0.006	1.0289 ± 0.0003	1 ± 0
120	1	0.296 ± 0.012	1.0241 ± 0.0009	1 ± 0
90	1.5	0.34064 ± 0.00001	1.04333 ± 0.00014	1 ± 0
100	1.5	0.3280 ± 0.0005	1.0376 ± 0.0002	1 ± 0
110	1.5	0.325 ± 0.002	1.0324 ± 0.0002	1 ± 0
120	1.5	0.3109 ± 0.0010	1.02867 ± 0.00015	1 ± 0

On one hand, the isomerizations are close to the ideality since the values are close to one. In fact, the $K_{\gamma3}$ value is the unit for all temperatures, meaning that there is no deviation from the ideality since it is not possible to distinguish both isomers, due to their exact molecular formula, while using the UNIFAC prediction method. On the other hand, the esterification is far from an ideal situation since its value is far from the unit.

Poynting correction factor

In addition, another deviation from ideality can occur due to the difference between the standard pressure and the working pressure. This deviation is characterized by means of the Poynting correction factor K_Γ [40] .

$$K_\Gamma = \exp\left(\frac{P-1}{R \cdot T} \cdot \sum_{j=1}^{s} \nu_j \cdot V_j \right) \tag{31}$$

Where *P* is expressed in atm, *T* in K and V_i, the molar volume of the compound i, in L/mol.

The Poynting factor for the different reactions at the different assayed conditions are shown in Table 11.

As can be seen, the difference between the working pressure and the standard pressure can be neglected, since the values of the Poynting factor are close to the unity.

Table 11. Poynting factor of the present reactions at different operating temperatures.

T [°C]	**$R^{o}_{LA/1B}$**	**$K_{\Gamma 1}$**	**$K_{\Gamma 2}$**	**$K_{\Gamma 3}$**
90	0.5	1.0130 ± 0.0006	1.03409 ± 0.00008	0.98161 ± 0.00006
100	0.5	1.0103 ± 0.0002	1.03275 ± 0.00006	0.98273 ± 0.00005
110	0.5	1.0080 ± 0.0003	1.03096 ± 0.00008	0.98396 ± 0.00003
120	0.5	1.0052 ± 0.0002	1.02925 ± 0.00010	0.98511 ± 0.00006
90	1	1.003 ± 0.002	1.0220 ± 0.0002	0.98814 ± 0.00010
100	1	0.983 ± 0.011	1.016 ± 0.005	0.992 ± 0.002
110	1	0.990 ± 0.003	1.0195 ± 0.0010	0.9899 ± 0.0005
120	1	0.982 ± 0.007	1.017 ± 0.003	0.9915 ± 0.0015
90	1.5	0.9950 ± 0.0008	1.01368 ± 0.00005	0.9925481 ± 0.0000009
100	1.5	0.9943 ± 0.0010	1.0154 ± 0.0002	0.99176 ± 0.00012
110	1.5	0.9889 ± 0.0012	1.0142 ± 0.0004	0.9927 ± 0.0003
120	1.5	0.9908 ± 0.0004	1.1056 ± 0.0002	0.99214 ± 0.00009

Taking into account the experimental results and their deviation, due to both the non-ideality of the mixture and the pressure-dependence assed by the Poynting factor, the equilibrium constant can be calculated. In the present work, the following equilibrium constants, which are shown in Table 12, have been obtained.

Table 12. Experimental equilibrium constant

T [ºC]	$R^o_{LA/1B}$	K_{a1}	K_{a2}	K_{a3}
90	0.5	12.48 ± 0.86	11.83 ± 0.17	0.4871 ± 0.0011
100	0.5	9.28 ± 0.21	10.66 ± 0.04	0.5043 ± 0.0007
110	0.5	6.74 ± 0.16	9.65 ± 0.06	0.5195 ± 0.0005
120	0.5	4.70 ± 0.09	8.46 ± 0.03	0.5366 ± 0.0004
90	1.0	7.80 ± 0.24	12.39 ± 0.24	0.4941 ± 0.0008
100	1.0	5.22 ± 0.22	10.78 ± 0.28	0.509 ± 0.005
110	1.0	3.86 ± 0.145	9.95 ± 0.03	0.5218 ± 0.0011
120	1.0	2.83 ± 0.09	9.00 ± 0.02	0.538 ± 0.002
90	1.5	10.945 ± 0.011	13.08 ± 0.24	0.490 ± 0.002
100	1.5	7.71 ± 0.22	11.41 ± 0.15	0.5040 ± 0.0012
110	1.5	6.15 ± 0.04	10.64 ± 0.09	0.526 ± 0.002
120	1.5	4.61 ± 0.06	9.10 ± 0.02	0.5451 ± 0.0002

Focusing on the values of the equilibrium constant at different initial molar ratio, the values obtained are pretty close between them. As a matter of fact, the values obtained at a molar ratio of 1.5 are lower than the ones obtained at 0.5, a suitable explanation would be that oligomers were formed which decreased the efficiency of the esterification. But, as can be seen, all the values are far from the estimated equilibrium constant, especially those related to the esterification. One way to find out where this deviation comes from is finding out the reactions change of enthalpy and entropy, which can be done by linear regression of the equilibrium constant logarithm against the inverse of the temperature (eq.11). The linear regressions of the esterification reaction at different initial molar ratio are shown below while its representation can be found in Figure 5:

$$\ln\left(K_{a1}\right)_{R^o_{LA/1B}=0.5} = \left(4035 \pm 222)\right) \cdot \frac{1}{T} - \left(10.22 \pm 0.59\right) \qquad (32)$$

$$\ln\left(K_{a1}\right)_{R^o_{LA/1B}=1} = \left(4775 \pm 277)\right) \cdot \frac{1}{T} - \left(11.09 \pm 0.73\right) \qquad (33)$$

$$\ln\left(K_{a1}\right)_{R^{o}_{LA/1B}=1.5}=\left(4029\pm201)\right)\cdot\frac{1}{T}-\left(8.72\pm0.53\right) \tag{34}$$

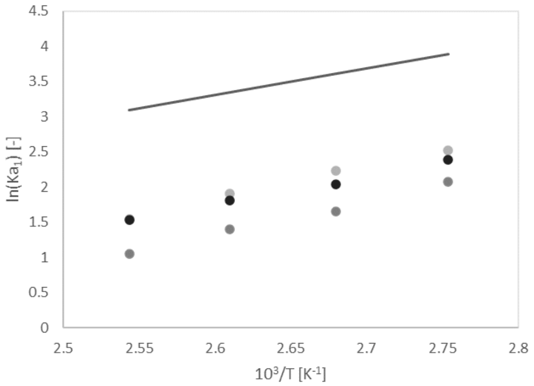


Figure 5. Comparison of the estimated and experimental equilibrium constant of the esterification reaction. Estimation (—), $R^{o}_{LA/1B}$=0.5 (•), $R^{o}_{LA/1B}$=1 (•), $R^{o}_{LA/1B}$=1.5 (•).

Taking a closer look at the representation of the constant, it is possible to see how the different initial ratios assayed in the present work, present a similar slope, while the main difference comes from the interception, which in turn is related to entropy change of reaction as deduced from Eq. 11. Although there is a big difference between the interceptions, the overall results are acceptable because they present a similar interception at different assayed conditions. As can be inferred from Figure 5, the main difference between estimated and experimental values is that the experimental values have a lower equilibrium constant. This is due to the non-possibility of considering simultaneous reactions while estimating the thermodynamic properties and the non-ideality of the mixture since the estimation of those properties was done by considering an ideal mixture.

The graphical representation of the isomerizations are shown in Figure 6 and 7.

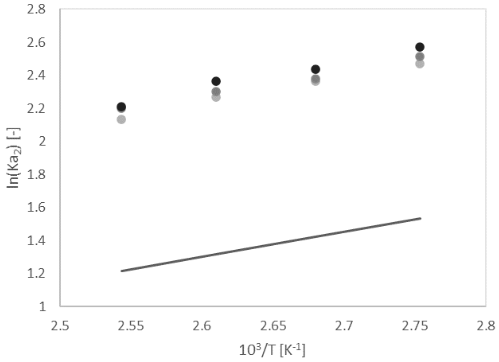


Figure 6. Comparison between the estimated and experimental equilibrium constant of the isomerization of 1B toE-2B. *Estimation (—), $R^o_{LA/1B}$=0.5 (•), $R^o_{LA/1B}$=1 (•), $R^o_{LA/1B}$=1.5 (•).*

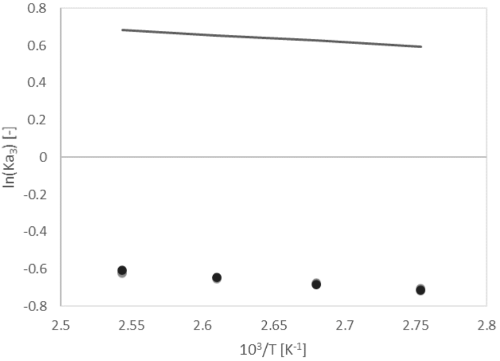


Figure 7. Comparison of the estimated and experimental equilibrium constant of the isomerization of E-2B to Z-2B. *Estimation (—), $R^o_{LA/1B}$=0.5 (•), $R^o_{LA/1B}$=1 (•), $R^o_{LA/1B}$=1.5 (•).*

As it can be seen, the isomerizations take close values for the different conditions assayed in the present work, while both of them are deviated from the theoretical values for each reaction. In Figure 6, a greater deviation can be seen when using an initial molar ratio of LA with 1B, this can be explained by the formation of oligomers, which affected the chromatographic analysis. In Figure 7, a strong difference between experimental and theoretical values can be seen, even though all the experiments exact same slope and interception. A suitable answer to the difference could be that estimation methods employed were unable to consider simultaneous reactions, which is the case of the present work.

From the equilibrium constant logarithms represented as a function of the temperature inverse, the enthalpy and entropy change of reaction can be calculated by using equation 11. These results are shown in Table 13 considering that the state functions were independent from temperature.

Table 13. Thermodynamic properties of the present reactions

Reaction	ΔHr [kJ/mol]	ΔSr [J/molK]
R1	-37 ± 2	-83 ± 6
R2	-13.0 ± 0.5	-15 ± 1
R3	3.80 ± 0.27	4.49 ± 0.72

As we can see, the values of the enthalpy change and entropy change are higher than the estimated values. It might be due to unavoidable experimental errors.

Comparing the enthalpy change of the isomerization, it can be seen that the enthalpy change is close to the theoretical value, proving that the experimental value obtained is reliable. Due to the difference of the interception values, more experiments at different conditions are required before being able to conclude anything to see if the error comes from the estimation method applied or not.

On one hand, it is possible to see the inverse proportionality between the Ka and temperature of the esterification and the isomerization of 1B to E-2B, meaning that the reaction is exothermic. On the other hand, the isomerization of E-2B to Z-2B is an endothermic reaction due to the direct proportionality between the temperature and the equilibrium constant.

Since the esterification has been carried out successfully using other esterification agents, a comparison of the enthalpy and entropy change of reaction is shown in Table 14. The esterifying agents are methanol (MeOH) to produce methyl levulinate (ML), ethanol (EtOH) for the production of ethyl levulinate (EL) and 1-butanol (1-BuOH) to produce butyl levulinate (BL).

Table 14. Comparison of the thermodynamic properties of the LA esterification using different esterifying agents

Reaction	ΔH^o_r (kJ/mol)	ΔS^o_r(J/mol·K)
$LA + MeOH \rightleftarrows ML + H_2O$ [38]	-13.6	-17.05
$LA + EtOH \rightleftarrows EL + H_2O$ [38]	-9.8	-125.95
$LA + 1 - BuOH \rightleftarrows BL + H_2O$ [38]	-10.8	-38.15
$LA + 1B \rightleftarrows SBL$	-37 ± 2	-83 ± 6

As it can be seen, in general terms, all the esterification reactions are exothermic. Comparing the reaction of the present work, esterification of LA with 1B, it can be seen that it is the most exothermic reaction due to the non-formation of water which increases the enthalpy change of reaction. Taking a closer look at the entropy changes of reaction it can be seen that all of them are negative, meaning that the results obtained at the present work might be reliable.

Comparing the value of the esterification reaction using 1B, there is evidence that the theoretical calculation made to estimate the entropy of the reaction did not take into account the simultaneous reactions that take place in the present work, resulting in a big difference of the estimated and experimental value.

7. CONCLUSIONS AND FUTURE WORK

The study of the liquid-phase esterification of LA with 1B in order to produce SBL has provided experimental data to determine the thermodynamic properties of the reaction, as well as of the side reactions that take place simultaneously with the main reaction.

Firstly, the equilibrium is shifted towards the formation of product, that is towards the SBL production, as it can be inferred from the high values presented by the experimental equilibrium constant in terms of molar fractions.

Secondly, a difference between the experimental and theoretical equilibrium constant was detected, which can be attributed to the simultaneous reactions that took place in the present work that could vary the theoretical estimation because as was mentioned above, all the experiments that were carried out presented similar results.

Finally, the thermodynamic parameters were determined from the obtained equilibrium constants considering that the enthalpy change of reaction is independent from temperature over the assayed temperature range. From obtained results, both the esterification reaction and the isomerization of 1B to E-2B are exothermic reactions, given that the values of the enthalpy change of reaction are negative (i.e., -37 ± 2 kJ/mol and -13.0 ± 0.5 kJ/mol, respectively). With regards to the isomerization of E-2B to Z-2B, results indicate that the reaction would be endothermic, since the obtained value of enthalpy change of reaction is positive (3.80 ± 0.27 kJ/mol). Taking into account the experimental uncertainty associated to calculated values of enthalpy changes of reaction, results are considered as reliable.

As for the future work, in order to continue with the study of the reaction system there are two tasks that should be done. The first one is to verify that the enthalpy and entropy change of reaction are independent of temperature. The second one, in order to go further in the study of the reaction system, it would be necessary to focus on the deactivation of the catalyst employed, A15, in ambition to reutilize it.

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ACRONYMS

a_i	Activity
A15	Amberlyst-15
T_b	Boiling temperature (K)
2-BuOH	2-butanol
1B	1-butene
BL	Butyl levulinates
Z-2B	*cis*-2-butene
P_c	Critical pressure (bar)
T_c	Critical temperature (K)
C_p	Heat capacity (J/mol·K)
HMF	Hydroxymethylfurfural
LA	Levulinic acid
V_i	Molar volume (L/mol)
SBL	*Sec*-butyl levulinate
ΔH_f^o	Enthalpy change of formation (kJ/mol)
ΔS_f^o	Entropy change of formation (J/mol·K)
ΔH_r^o	Enthalpy change of reaction (kJ/mol)
ΔS_r^o	Entropy change of reaction (J/mol·K)
P	Pressure (bar)
T	Temperature (K)
K_a	Thermodynamic equilibrium constant
K_x	Thermodynamic equilibrium constant referred to the molar fraction

K_γ	Thermodynamic equilibrium constant referred to the activity coefficients
E-2B	*trans*-2-butene
K_Γ	Poynting factor
γ_I	Activity coefficient

APPENDICES

APPENDIX 1: CHROMATOGRAPHIC ANALYSYS


Instrument Control

Run Status: Idle

Instrument Status: Ready

Sample Name:

Data File: E18_R15_T90_10G_10h20min.D

0,00 Run Time: 18,57

40 Oven Temperature

250 Inlet-F Temperature

0,5 Column-1 Flow Calc.

280 Aux-2 Temperature

230 MS Source (°C)

150 MS Quad (°C)

Superimposed Chromatograms (Normalize)

Scan(Centroid) EI[+] Time Segment: 1 18,57 min

Figure 8. Program for the chromatographic analysis.

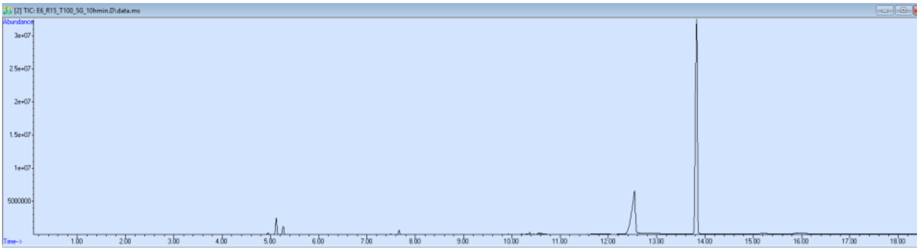
[2] TIC: E6_R15_T100_5G_10hmin.D\data.ms

Figure 9. Result of the analysis.

Table 15. Retention time of the different species.

Retention time [min]					
1B	**E-2B**	**Z-2B**	**2-BuOH**	**LA**	**SBL**
4.95	5.08	5.12	7.65	12.5	13.8

APPENDIX 2: JOBACK AND VETERE METHOD

In this appendix, the appliance of the Joback and Vetere method for the SBL enthalpy change of formation is shown. If other compounds need to be estimated, an analogous procedure must be followed.

Firstly, the "Joback Method" needs to be applied in order to calculate the enthalpy of formation change at standard conditions in gas state. This method takes into account the energy contribution of the functional groups presents in the molecule [27]. The expression to be used is the following:

$$\Delta H_f^o\left(298.15K\right) = 68.29 + \sum_k N_k \cdot \Delta hfk \tag{35}$$

Where N_k is the number of k-type groups presents in the molecule and Δhfk is the energy contribution characteristic of the k-group. The tabulated Δhfk values for the SBL, are shown in Table 16.

Table 16. Constituent groups to apply the Joback method.

	SBL	
Group	**N_k**	**hfk [kJ/mol]**
CH3(1)	3	-76.45
CH2(2)	3	-20.64
CH(3)	1	29.89
C=O(2)	1	-133.22
COO(2)	1	-337.92

Since the SBL is found, in the present work, as a liquid, the enthalpy change of condensation needs to be estimated as well. To do so the method of Joback uses the reevaluated Lyndersen's groups contributions. In order to apply the method, the boiling temperature (T_b) and the critical temperature (T_c) and pressure (P_c) need to be calculated as the following expressions [27].

$$T_b\left(K\right) = 198 + \sum_k N_k\left(tbk\right) \tag{36}$$

$$T_c\left(K\right)=T_b\cdot\left(0.584+0.965\cdot\left(\sum_k N_k\left(tck\right)\right)-\left(\sum_k N_k\left(tck\right)\right)^2\right)^{-1} \tag{37}$$

$$P_c\left(bar\right)=\left(0.113+0.0032\cdot N_{atoms}-\sum_k N_k\left(pck\right)\right)^{-2} \tag{38}$$

Where N_{atoms} is the number of atoms, N_k is the number of k-types groups present in the molecule and tbk, tck and pck are the contribution values of each group to calculate the boiling temperature, critical temperature and critical pressure. All the tabulated values can be found in Table 17.

Table 17. Tabulated parameters of the SBL molecule to apply the Vetere method.

		SBL		
Group	**N_k**	**tbk [K]**	**tck [K]**	**pck [bar]**
CH3(1)	3	23.58	0.0141	-0.0012
CH2(2)	3	22.88	0.0189	0
CH(3)	1	21.74	0.0164	0.002
C=O(2)	1	76.75	0.038	0.0031
COO(2)	1	81.1	0.0481	0.0005

The boiling temperature, the critical temperature and the critical pressure for the SBL, which has 28 atoms, are listed in Table 18.

Table 18. SBL T_b, T_c and P_c values.

T_b[K]	T_c[K]	P_c[bar]
517	701	24.9

Then, the condensation enthalpy change, which has the same value as the vaporization enthalpy change with the opposite sign, will be estimated. In the aim of estimating its change of enthalpy the Vetere method, which uses the values calculated above (T_b,T_c,P_c), will be employed [27]. The equation that needs to be applied can be found below:

$$\Delta H_{vb}=R\cdot T\cdot\left(\frac{\left(1-T_{br}\right)^{0.38}+0.5+\dfrac{0.5066}{P_c\cdot T_{br}{}^2}}{1-T_{br}+F\cdot\left(1-\left(1-T_{br}\right)^{0.38}\right)\cdot\ln\left(T_{br}\right)}\right) \tag{39}$$

Where T_{br} is the quotient between T_b and T_c, and F is 1 in this case.

Since the enthalpy of vaporization was obtained at the boiling temperature, it requires to be converted to the standard temperature by applying the Watson's ratio [27].

$$\Delta H_{vb}\left(T_o\right)=\Delta H_{vb}\left(T_b\right)\cdot\left(\frac{1-T_{or}}{1-T_b}\right)^{0.38} \qquad (40)$$

Where T_{or} is the division between T_o and T_c.

As a reminder, the enthalpy of condensation is the enthalpy of vaporization with its sign changed.

$$\Delta H_{vb}=-\Delta H_c \qquad (41)$$

The resulting enthalpy of formation in liquid state for the SBL is calculated as with the following expression.

$$\Delta H_f^0\left(T_0,L\right)=\Delta H_f^0\left(T_0,g\right)-\Delta H_c\left(T\right) \qquad (42)$$

In Table 19, the SBL enthalpy values obtained from the estimation procedure are listed.

Table 19. SBL enthalpy values.

$\Delta H^o_f(T_0, g)$ [kJ/mol]	**$\Delta H_v(Tb)$ [kJ/mol]**	**$\Delta Hc(T_0)$ [kJ/mol]**	**$\Delta H^o_f(T_0, L)$ [kJ/mol]**
-664.2	50.2	-67.6	-731.9

APPENDIX 3: BENSON METHOD

Table 20. LA constituent groups for the appliance of the Benson method.

		$LA_{(L)}$		
Groups	**N_k**	**Δ^oH_f [kJ/mol]**	**Δ^oS_f [J/mol·K]**	**c_p [J/mol·K]**
C-$(H)_3$(CO)	1	-47.61	83.3	36.48
CO-$(C)_2$	1	-152.76	33.81	52.97
C-$(H)_2$(CO)(C)	2	-24.14	39.87	29.29
CO-(C)(O)	1	-142.2	32.72	44.98
O-(H)(CO)	1	-285.64	38.28	37.82

Table 21. Constituent groups of SBL in order to apply the Benson method.

		$SBL_{(L)}$		
Groups	**N_k**	**Δ^oH_f [kJ/mol]**	**Δ^oS_f [J/mol·K]**	**c_p [J/mol·K]**
C-$(H)_3$(C)	2	-47.61	83.3	36.48
C-$(H)_3(C)_2$	1	-25.73	32.38	30.42
C-(H)(O)$(C)_2$	1	-21	-25.31	25.56
O-(C)(CO)	1	-196.02	38.28	19.58
C-$(H)_2$(CO)(C)	2	-24.14	39.87	29.29
CO-$(C)_2$	1	-152.76	33.81	52.97
C-$(H)_3$(CO)	1	-47.61	83.3	36.48
CO-(C)(O)	1	-149.37	32.72	44.98

Table 22. 1B constituent groups in order to apply the Benson's method

1B$_{(L)}$				
Groups	**N_k**	**Δ^oH_f [kJ/mol]**	**Δ^oS_f [J/mol·K]**	**c_p [J/mol·K]**
$C-(H)_3(C)$	1	-47.61	83.3	36.48
$C-(C)(H)_2(C_d)$	1	-25.73	31.67	29.29
$C_d-(H)(C)$	1	31.05	28.58	24.6
$C_d-(H)_2$	1	21.75	86.19	28.37

Table 23. 2B constituent groups in order to apply the Benson's method.

2B$_{(L)}$				
Groups	**N_k**	**Δ^oH_f [kJ/mol]**	**Δ^oS_f [J/mol·K]**	**c_p [J/mol·K]**
$C-(H)_3(C)$	2	-47.61	83.3	36.48
$C_d-(H)(C)$	2	31.05	28.58	24.6

APPENDIX 4: RÙDZICKA AND DOMALSKI

Table 24. Levulinic acid constituent groups with the a, b and c parameters.

		LA		
Group	**N_k**	**a_i**	**b_i**	**d_i**
$C\text{-}(H)_3(CO)$	1	3.8452	-0.33997	0.19489
$CO\text{-}(C)_2$	1	5.4375	0.72091	-0.18312
$C\text{-}(H)_2(CO)(C)$	2	6.6782	-2.4473	0.47121
$CO\text{-}(C)(O)$	1	29.246	3.4261	-2.8962
$O\text{-}(H)(CO)$	1	-27.587	-0.16485	2.7483

Table 25. Sec-butyl levulinate constituent groups with the a, b and c parameters

		SBL		
Group	**N_k**	**a_i**	**b_i**	**d_i**
$C\text{-}(H)_3(C)$	2	3.8452	-0.33997	0.19489
$C\text{-}(H)_3(C)_2$	1	2.7972	-0.054967	0.10679
$C\text{-}(H)(O)(C)_2$	1	0.9879	0.39403	-0.01612
$O\text{-}(C)(CO)$	1	-21.434	-4.0164	3.0531
$C\text{-}(H)_2(CO)(C)$	2	6.6782	-2.4473	0.47121
$CO\text{-}(C)_2$	1	5.4375	0.72091	-0.18312
$C\text{-}(H)_3(CO)$	1	3.8452	-0.33997	0.19489
$CO\text{-}(C)(O)$	1	29.246	3.4261	-2.8962

Table 26. 1-butene constituent group with the a, b and c parameters

		1B		
Group	**N_k**	**a_i**	**b_i**	**d_i**
$C\text{-}(H)_3(C)$	1	3.8452	-0.33997	0.19489
$C\text{-}(C)(H)_2(C_d)$	1	2.0268	0.20317	0.11624
$C_d\text{-}(H)(C)$	1	4.0749	-1.0735	0.21413
$C_d\text{-}(H)_2$	1	4.1763	-0.47392	0.099928

Table 27. 2-butene constituent groups with the a, b and c parameters

		2B		
Group	**N_k**	**a_i**	**b_i**	**d_i**
C-$(H)_3$(C)	2	3.8452	-0.33997	0.19489
C_d-(H)(C)	2	4.0749	-1.0735	0.21413

APPENDIX 5: CALIBRATION

The calibration procedure that has been followed is listed below.

1) Weigh the desired amount of levulinic acid.
2) Introduce the levulinic acid into the pressure burette using the liquid injector.
3) Tighten the liquid screw and make sure that no leaks exist.
4) Weigh the pressure burette.
5) Introduce the desired amount of 1-buten by using one of the valves of the burette.
6) Weigh the pressure burette. By means of difference it is possible to know the exact 1-butene mass introduced in the burette.
7) Join the top valve of the burette with the nitrogen line.
8) Join the bottom valve of the burette with the sample circuit.
9) Pressurize the burette, no more than 15 bars and introduce the sample.
10) Select the desired method in the computer (SBL_VALV.M).
11) Do the steps 4, 5, 7 (option 1), 8 and 9 from the GC analysis.

The next graphs show the calibration equations that have been used for the different species of the present work.

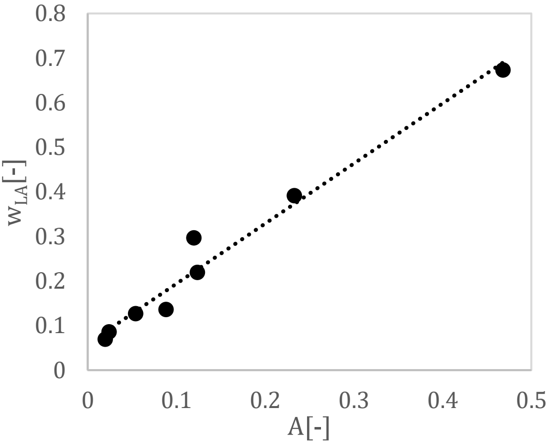

Figure 10. Calibration equation for levulinic acid.

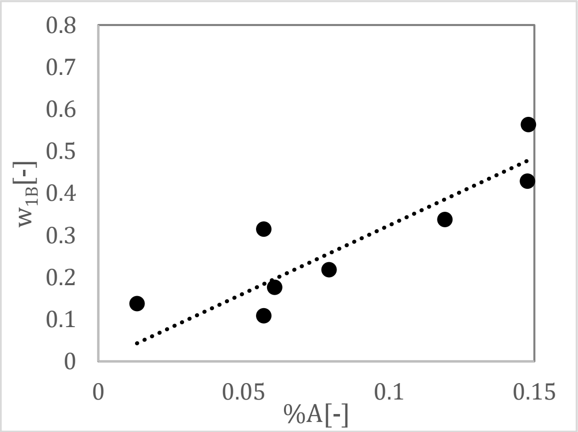

Figure 11. Calibration equation for 1-butene and 2-butene.

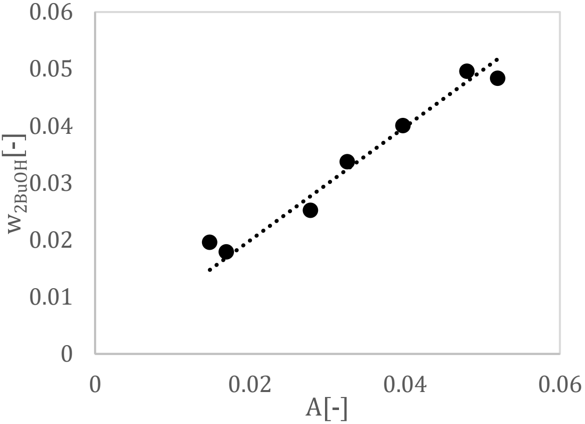

Figure 12. Calibration equation for 2-butanol.

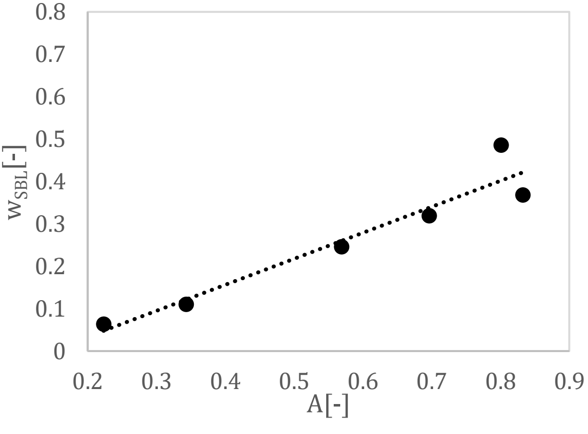

Figure 13. Calibration equation for sec-butyl levulinate*.*

APPENDIX 6: UNIFAC PREDICTION METHOD

The UNIFAC prediction method is used to estimate the non-ideality of the mixture by estimating the activity coeficients (γ_i), that are the sum of a combinatorial and residual part:

$$\ln(\gamma_i) = \ln(\gamma_i^C) + \ln(\gamma_i^R) \tag{43}$$

The combinatorial part is calculated using the following expression.

$$\ln(\gamma_i^C) = 1 - V_i' + \ln(V_i') - 5 \cdot q_i \cdot \left(1 - \frac{V_i}{F_i} + \ln\left(\frac{V_i}{F_i}\right)\right) \tag{44}$$

Where the equation parameters are the following expressions.

$$V_i' = \frac{r_i^{3/4}}{\sum_j x_j \cdot r_j^{3/4}} \tag{45}$$

$$V_i = \frac{r_i}{\sum_j x_j \cdot r_j} \tag{46}$$

$$r_i = \sum \nu_k^{(i)} \cdot R_k \tag{47}$$

$$F_i = \frac{q_i}{\sum_j x_j \cdot q_j} \tag{48}$$

$$q_i = \sum \nu_k^{(i)} \cdot Q_k \tag{49}$$

Where x_j is the molar fraction, v_k the times a k-grup repeat, Q_k and R_k are tabulated parameters [41]. So, in order to calculate the combinatorial part the molecule needs to be broken down to its constituent groups.

Table 28. Constituent groups of the molecules in the present work along the tabulated parameters for the combinatorial part calculation.

Compound	i	Group	Subgroup (k)	R_k	Q_k	v^i_k	r_i	q_i
1B	1	2	5	1.2832	1.6016	1	1.2832	1.6016
		1	1	0.6325	1.0608	1	0.6325	1.0608
			2	0.6325	0.7081	1	0.6325	0.7081
2B	2	1	1	0.6325	1.0608	2	1.265	2.1216
		2	6	1.2832	1.2489	1	1.2832	1.2489
2-BuOH	3	1	1	0.6325	1.0608	2	1.265	2.1216
			2	0.6325	0.7081	1	0.6325	0.7081
			3	0.6325	0.3554	1	0.6325	0.3554
		5	81	1.063	0.8663	1	1.063	0.8663
LA	4	1	2	0.6325	0.7081	2	1.265	1.4162
		9	18	1.7048	1.67	1	1.7048	1.67
		20	42	0.8	0.9215	1	0.8	0.9215
SBL	5	1	1	0.6325	1.0608	2	1.265	2.1216
			2	0.6325	0.7081	2	1.265	1.4162
			3	0.6325	0.3554	1	0.6325	0.3554
		11	22	1.27	1.4228	1	1.27	1.4228
		9	18	1.7048	1.67	1	1.7048	1.67

Then the residual part needs to be calculated. To do so the following expressions will be used.

$$\ln\left(\gamma_i^R\right) = \sum_k \nu_k^{(i)} \cdot \left(\ln\left(\Gamma_k\right) - \ln\left(\Gamma_k^i\right)\right) \tag{50}$$

$$\ln\left(\Gamma_k\right) = Q_k \cdot \left(1 - \ln\left(\sum_m \theta_m \cdot \psi_{mk}\right) - \sum_m \frac{\theta_m \cdot \psi_{mk}}{\sum_n \theta_n \cdot \psi_{nm}}\right) \tag{51}$$

$$\theta_m = \frac{Q_m \cdot X_m}{\sum Q_n \cdot X_n} \tag{52}$$

$$X_m = \frac{\sum_j \nu_k \cdot x_j}{\sum_n \sum_j \nu_n \cdot x_j} \tag{53}$$

$$\psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm} \cdot T + c_{nm} \cdot T^2}{T} \right) \tag{54}$$

Where T is the temperature in Kelvin, x_i the molar fraction, v_k the repetitions of the k-type groups and the parameters a_{nm}, b_{nm} and c_{nm} are tabulated parameters for each group that compose the molecule.

Table 29, 30 and 31. Tabulated parameters for the residual part calculation.

$a_{mn}\backslash a_{nm}$	1	2	5	9	11	20
1	0	189.66	2777	433.6	98.656	1182.2
2	-95.418	0	2649	179.8	980.74	-2026.1
5	1606.06	1566	0	-250	973.8	-1295
9	199	91.811	653.3	0	-16.486	-109.51
11	632.22	-582.82	310.4	33.415	0	62.031
20	2017.7	-347.5	1525.8	178.22	59.594	0

$b_{mn}\backslash b_{nm}$	1	2	5	9	11	20
1	0	-0.2723	-4.674	0.1473	1.9294	-3.2647
2	0.06171	0	-6.508	0.6991	-2.4224	8.1549
5	-4.746	-5.809	0	2.857	-5.663	4.3634
9	-0.8709	-0.7171	-1.412	0	-0.2792	0.9689
11	-3.3912	1.6732	1.538	0.2191	0	1.0567
20	-9.0933	1.216	-4.9155	-0.9168	-0.712	0

$c_{mn}\backslash c_{nm}$	1	2	5	9	11	20
1	0	0	0.001551	0	-0.003133	0.009198
2	0	0	0.004822	0	0	0
5	0.0009181	0.005197	0	-0.006022	0.00769	0
9	0	0	0.000954	0	0	0
11	0.003982	0	-0.00485	0	0	0
20	0.01024	0	0	0	0	0