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Màster en Enginyeria Química

Treball Final de Màster

Equilibrium thermodynamics of the liquid phase esterification of levulinic acid with octanol over an ion exchange resin

Estudi de la termodinàmica d'equilibri de la reacció d'esterificació en fase líquida d'àcid levulínic amb octanol emprant-se una resina de bescanvi iònic com a catalitzador

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Es diu que “es de bien nacido ser agradecido”. Jo diria, més aviat, que es tracta d’una qüestió d’educació. Quantes vegades hauré dit “gràcies” al llarg de la realització d’aquest treball? Massa? Massa poques? Jo diria que tantes com accions realitzades pels que m’han acompanyat aquests mesos amb l’objectiu de facilitar-me la feina, fer més agradables les estones de treball o en benefici de la consecució dels objectius plantejats. No són, doncs, aquestes línies, un reconeixement a res extraordinari ans el contrari: l’enèsim i darrer gràcies a aquelles persones que han convertit l’ordinari en extraordinari.

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SUMMARY

The objective of this work is to characterize the thermodynamics of the synthesis reaction of octyl levulinate from levulinic acid and 1-octanol in liquid phase. In the current context of depletion of the traditional resources of raw materials and fuels as well as the fight against climate change, numerous efforts are being carried out to develop material production processes from renewable resources.

This is the case of octyl levulinate, a compound that, due to its physical and chemical characteristics such as its density, volatility and viscosity, has a high potential as a substitute for lubricant bases traditionally obtained from crude oil. Octyl levulinate is considered a biomolecule as it is synthesized from levulinic acid, one of the 12 biomass-derived molecules with the greatest potential according to U.S. Department of Energy, and 1-octanol, which can also be obtained through bioprocesses.

As a previous step to the design of processes for its synthesis, the thermodynamic properties of this esterification need to be determined. Despite the existence of several kinetic studies of the esterification of levulinic acid with 1-octanol, the thermodynamic constant of this reaction is experimentally determined for the first time in this work. Its value at 80, 100 and 120 ºC is compared with those computed via estimation methods. Likewise, the enthalpy change and the entropy change of the reaction are experimentally determined and compared with theoretically estimated values.

On the other hand, an experimental purification method of the synthesized octyl levulinate based on the combination of washing the reaction medium with water followed by vacuum rectification is described. Finally, the value of the isobaric heat capacity of octyl levulinate is experimentally determined for the first time at different temperatures, and these values are compared with those obtained via a theoretical estimation method.

Key words: biomass, biolubricant, alkyl levulinates, ion exchange resin, thermodynamic characterization, enthalpy, entropy, chemical equilibrium.

1. INTRODUCTION

Throughout this chapter, various topics concerning the chemical reaction under study and its interest at a social, economic and environmental level are presented and discussed.

21st century society still relies heavily on non-renewable resources like natural gas, oil and coal to meet its needs on raw materials and fuels. However, there is a profound need to work to mitigate not only the environmental but also the economic and social negative effects of this fact. Chemical engineers must play a relevant role in this ecological transition.

The aspects discussed in this work are the basis justifying the interest in the study of a reactive system through which a product is obtained from renewable resources entailing a high potential to replace others obtained from petroleum derivatives.

1.1.Sustainable development

Raw materials are basic and elemental substances used in the manufacture of products or in the production of energy. Raw materials are the basis of any industrial process and their origin can be mineral, vegetable or animal.[1] Today's society is still largely dependent on non-renewable sources of energy and materials, and one of the main objectives of sustainable development is to reduce such dependency by promoting alternative and renewable sources.

1.1.1. The current landscape of energy resources

In its annual International Energy Outlook 2021 (IEO2021), the U.S. Energy Information Administration (EIA) predicted that global energy consumption will increase by about 50% over the next 30 years, if there is no major policy or technological change.

Crude oil and other fossil fuels will continue to play a particularly important role as they will still be the most widely used energy sources in 2050. However, renewable energy sources, which include biomass as well as hydro, solar and wind, are expected to grow at a similar rate.[2]

The same report forecasts strong growth in the use of renewable energy sources in both OECD and non-OECD countries as can be seen in Figure 1, driven by the optimization of technologies for exploiting these energy resources and government incentives. A significant decrease in the consumption of energy derived from coal and nuclear fission in OECD countries is also expected. In this regard, countries such as Spain and Germany are implementing plans to achieve progressive denuclearization, redoubling their commitment to fossil fuels with cleaner emissions such as gas and renewable energies. However, the positive environmental consequences of this trend would unfortunately be offset by an increase in absolute terms in the use of these energy sources in non-OECD countries.

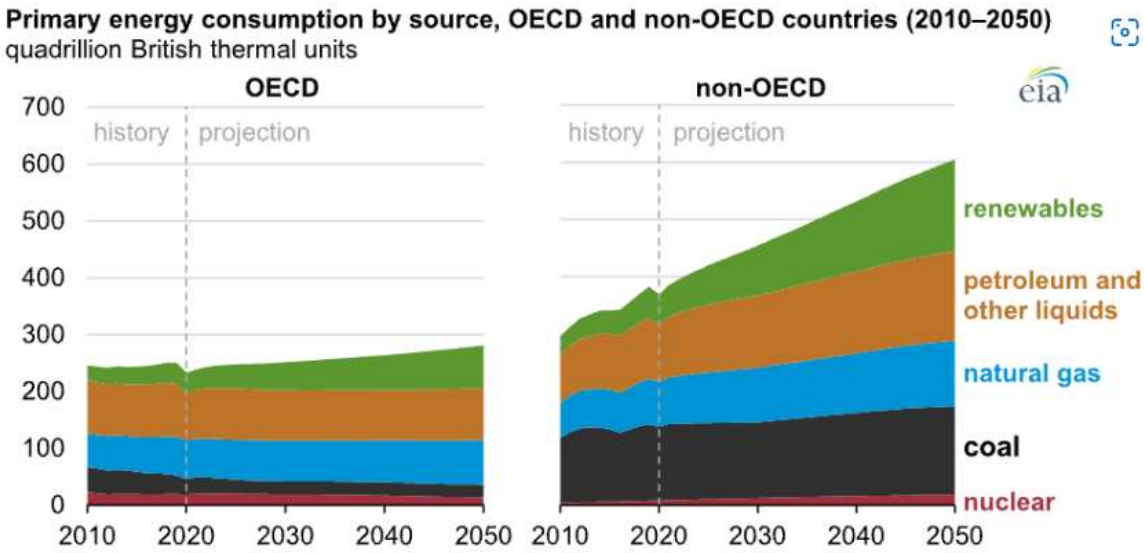


FIGURE 1. Primary energy consumption by source, OECD and non-OECD countries (2010-2050). Source: International Energy Outlook 2021, U.S. Energy Information Administration.

On the other hand, it is noted that although crude oil consumption will recover pre-pandemic levels in the member states of the organization, it is not expected that OECD countries will recover this threshold in the next 30 years, mainly due to improvements in the formulation of fuels and engines, leading to greater energy efficiency of petroleum-derived fuels.

Noteworthy, industry is the economic activity that will have the hardest time weaning itself from fossil fuels. The consumption of fuels derived from crude oil is predicted to increase threefold in industry compared to transport. Likewise, industry is also pointed out as the main responsible for the increase in natural gas consumption in non-OECD countries.

Finally, the emergence of the use of coal as a fuel in the steel and iron industries, especially in emerging and developing economies, is highlighted.

Coal is, even in 2022, the main source of electricity globally, and its combustion is the main activity generating greenhouse emissions.[3] Due to rising gas prices in the West as a side effect of the Ukraine-Russia war and industrial growth in the East, coal-fired power generation has picked up. Countries such as Germany, heavily dependent on Russian gas, have been forced to start up coal-fired power plants to meet their social and industrial energy needs. However, leaving aside the present situation, the road to decarbonization, although it will be arduous (coal consumption must be reduced at a rate of 11% per year to achieve zero carbon emission targets by 2050), is already being travelled: the number of final investment decisions (FIDs) in projects to increase coal-fired power is 80% lower than five years ago. Since the Paris climate summit, 21 countries have pledged to have all coal-fired plants closed by 2030. However, even if this commitment was to be fulfilled, the global environmental impact would be rather small, as these 21 countries are responsible for only 1% of total CO_2 emissions. The countries of East Asia, with their growing population and industry, are identified as holding the key to achieving the sustainable development goals by 2050, but these countries have not made concrete commitments to reduce coal consumption.

The conflict between Russia and Ukraine has led to great price volatility in the natural gas market, which in turn provoked an increase in the price of raw materials and consumer goods, triggering record inflation levels in this century and rate hikes and recession in the U.S. and European economies. Although gas generates cleaner emissions than oil or coal (between 2 and 2.5 times less NO_X and sulphur derivatives), its combustion is still one of the main contributors to greenhouse gas emissions. To achieve the goal of zero net carbon emissions by 2050, it will be essential to stop using this energy source. However, it is recognized that natural gas will play an important role in the next couple of decades and that its consumption will grow. To mitigate the resulting negative environmental effects, alternatives such as combined gas and hydrogen combustion plants or CCUS (Carbon Capture, Use and Storage technologies) projects should be pursued.[4] Obtention of biofuels and raw materials derived from biomass would be an example of those cleaner technologies.

1.1.2. The current landscape of raw material sourcing

Raw materials are those obtained directly from nature or from the transformation of other materials and that are used for the manufacture of other products of interest.

The basic raw material sources are water (from the sea, rivers and subway aquifers), air (mainly molecular nitrogen and oxygen are obtained), minerals, biomass, natural gas, crude oil and coal. Among them, the most important in terms of consumption and from which the greatest number of chemical compounds are obtained is crude oil.

Oil is a liquid complex mixture of hydrocarbons with traces of other elements, such as sulphur, nitrogen and various metals. Structurally, it consists of varying amounts of paraffinic, naphthenic and aromatic hydrocarbons. Since it is formed in a reducing, anaerobic atmosphere, it has no olefins in its composition. The most widely accepted theory holds that oil is formed from animal and plant residues subjected underground to high pressures and temperatures which, together with anaerobic bacterial action, trigger the formation of hydrocarbons. These hydrocarbons flow between various sedimentary layers until they concentrate in geological formations called reservoirs, which are non-permeable and porous. The reservoirs are stratified, with natural gas, composed mainly of methane, at the top, followed by a generally liquid layer of crude oil and finally, brackish water. The reservoirs can be found on the mainland or offshore, i.e. under the sea.[5]

Depending on the region in which the crude oil is extracted, the conditions during its formation and its age, its composition and quality may vary. The oil quality is defined by different parameters, e.g., density, sulphur content, the proportion between the different structural types of hydrocarbons and its TBP (true boiling point) curve, which reflects the molecular weight distribution of the hydrocarbons that make up the mixture. Oil is mainly used to produce fuels, lubricants, asphalts and raw materials for the petrochemical industry. In 2018, 14% of refined crude oil was destined to chemicals production.[6]

The crude oil, once extracted from the reservoir, is decanted at the wellhead to reduce its water content and stabilized to reduce its gas content and facilitate its transportation. It is then processed in a refinery, a plant in which the crude is subjected to various processes aimed at obtaining different hydrocarbon mixtures of a certain range of molecular weights, each with different applications. Lubricants are one of the products formulated using substances obtained from oil refining. These are substances that are interposed between two moving surfaces to reduce the friction between them, thereby

reducing wear and minimizing the energy that must be applied to make them move. On the other hand, lubricants can have other functions such as cooling, sealing, antioxidant or diluent.

Lubricants are formed by mixing a lubricant base together with various additives that allow the product to achieve the required quality, improving its lubrication capacity, service life, resistance to oxidation, wear, corrosion and deposit formation. The additives are added in variable proportions, from a few ppms, in the case of colorants and defoamers, to values of 20% in those lubricants used in metalworking.[7]

Industrial lubricating oils are classified according to ASTM D 2422 (Standard classification of industrial lubricants by Viscosity System) according to their viscosity. Similarly, the SAE J 300 standard classifies automotive lubricants according to their viscosity at different temperatures, with a twofold objective: to ensure that at low temperatures and when the engine is started the oil can flow sufficiently to access the engine parts requiring lubrication; and that, at high temperatures and with the engine running, the lubricant has a minimum viscosity that allows the formation and maintenance of an oil film on the surfaces of the engine's moving parts. On the other hand, there are other categories that classify lubricants according to their quality, for gasoline or diesel engines, for cars and trucks, motorcycles or tractors, for 2 or 4-stroke engines, for gas engines and for transmission oils. These categories are defined by API (American Petroleum Institute) in the United States and by ACEA (European Automobile Manufacturers Association) and are based on the sulphur content of the lubricant bases, their useful life or consumption needs.[7]

There are two main types of lubricating oils, depending on the method of obtaining the lubricant base: mineral oils, in which lubricant bases are mainly obtained as vacuum distillates from the residue of atmospheric distillation. These bases are called Neutral. There are also Bright stocks bases, which are obtained as extracts from the deasphalting of the residues obtained in vacuum distillation. The purpose of these refining operations is to obtain a hydrocarbon mixture with a high paraffin and naphthene content and low aromatic hydrocarbon content; and synthetic lubricants, generally polyalphaolefins obtained from synthesis reactions from petroleum derivatives such as ethylene. There are other synthetic lubricants based on polyglycols, esters and silicones. Synthetic lubricants were developed primarily for use at critically high temperatures, where minerals, with their heterogeneous molecular composition, offer inferior mechanical and thermal

performance. Synthetic oils generally have a higher viscosity index, which makes this property less dependent on temperature, have a longer service life, greater fluidity at low temperatures, lower freezing points and, due to their greater homogeneity, less friction between molecules, which translates into lower energy consumption by the engine during start-up. However, its price can be up to five times higher than that of a mineral oil. Finally, there is a last category of lubricants, semi-synthetic lubricants, formulated by mixing varying proportions of a mineral oil with a compatible synthetic oil.[8,9]

Whether mineral, synthetic or semi-synthetic, lubricants are manufactured from products obtained from crude oil, directly from its refining process, or from substances obtained in the refining process, which are then chemically transformed in processes specific to the petrochemical industry. Since oil is consumed at a higher rate than the rate of production, it is considered a non-renewable source of energy and resources. Although new oil extraction techniques such as fracking, rotatory and directional drilling have made it possible to discover and exploit new deposits and oil production levels have continued to grow since the plateau that began in 2005 and was broken in 2013, the reality is that oil, as a supplier of fuels and chemicals, is an exhaustible resource. The peak of the discovery curve of new oil reserves was reached in 1962 and in recent years a negative record has been reached in terms of finding new fields. In fact, around 70% of oil is extracted from wells discovered before 1970. In addition, the quality of the crude oil extracted today is increasingly lower (higher sulphur content and molecular weight), making the refining process more difficult in order to continue obtaining the levels of fractions of different qualities required to meet the needs of society. Moreover, the CAPEX and OPEX costs of operating oil wells and refining oil are increasing year after year. [10] Due to all these reasons, the development of new materials and energy resources has become an imperative need.

In addition, it is necessary to develop technologies that contribute to reducing carbon and greenhouse gas emissions and thus contribute to reducing the anthropogenic footprint on the environment in order to comply with the agreement adopted at COP26 in Glasgow to limit global warming to 1.5 ºC by the end of the current century.[11]

1.1.3. Green chemistry

Green chemistry goes far beyond its formal definition, which is the design of chemical products and processes to reduce the use or generation of substances hazardous to health

or the environment. Green chemistry is involved in the entire life cycle of chemical products, from their design through their manufacture, distribution, and multiple uses to their final disposal.[12]

Green chemistry has its origins in the 1990 US Pollution Prevention Act, which emphasizes the need to reduce the use of hazardous substances and the importance of treating waste in such a way that recycling is prioritized and that disposal in the natural environment is only the last option, and is always done in a way that is safe for public health and the health of nature.

The principles of green chemistry were originally proposed by Paul Anastas and John Warner in their book *Green Chemistry, theory and practice*, developing a vision that transcends the initial concerns about the hazardousness of certain raw materials, chemicals and wastes and establishes the guidelines for what should be the industry of the 21st century, operating in a framework of scarcity of traditional raw materials and a consensus on the need to reduce carbon emissions into the atmosphere: prevent waste generation, maximize atomic economy, design safer chemical syntheses, avoid the use of solvents, use renewable raw materials, avoid derivatization reactions, use catalysts, design chemical products that degrade easily after use, on-line control to prevent pollution and design products and processes to minimize risk are its twelve principles. [12]

The green chemistry concept lays the foundations for a chemical industry that is more responsible with the environment and the planet in general, aimed at the functional excellence of products and the operational excellence of processes, with a view to the dual sustainability - economic and environmental -.

Although they are not literal principles of the so-called green chemistry, the design and synthesis of processes to maximize the reuse of by-products, the internal or external valorisation of generated waste, the integration and optimization of separation units to recover unreacted reactants and by-products to give them a new use, the commitment to the circular economy and transforming the current industry into one that contributes to reducing the carbon footprint are some of the ideas that emerge from the principles of green chemistry wherein the efforts are being focused.

With-in such context, the development of processes based on biomass to obtain fuels and other chemicals that can be used as raw materials for manufacturing of valuable

products is one of the research fields with the greatest prospects that contribute to the reduction of carbon emissions and mitigate the depletion of natural resources.

1.1.4. Biomass as a raw material and energy source

Biomass is a source of organic carbon obtained from animal, plant or fungal resources. Biomass is considered one of the most important energy resources globally. In fact, until the Industrial Revolution, when it was displaced by fossil fuels, it was the most important fuel.

There are several ways to valorise biomass, e.g., its combustion in specially designed boilers to process this type of fuel, which generates gases at high pressure and temperature that can be used as heat input in industrial and domestic applications or expanded in a turbine coupled to an alternator to produce electricity. This is the process carried out in a biomass power plant, wherein biomass is burned with excess air (20-40 % more air than theoretically necessary stoichiometrically) reaching temperatures between 600 and 1300 ºC. Moreover, pyrolysis, which consists of subjecting biomass to temperatures of around 500 ºC and in the absence of air to decompose it into various gases, such as hydrogen or carbon oxides, and a solid residue of charcoal. Finally, gasification, a more complex combustion process with limiting oxygen (10-50% of the theoretically stoichiometrically necessary) in which the biomass first undergoes a process of pyrolysis and then oxidation of the carbonaceous residue generated in the previous stage generates syn gas, composed of CO, CO_2, CH_4, H_2O, H_2 and N_2 in variable proportions, which is used as a fuel with low calorific value compared to methane or hydrogen.[13,14,15]

There are also biological methods of biomass valorisation, already used in the Middle Ages, such as fermentation of grape juice to produce wine, fermentation of cereals to produce beer, or applications developed in contemporary times, such as fermentation of sugars obtained from corn, sugar cane or sugar beet to produce bioethanol, which can be used as transportation fuel. Furthermore, there is biodiesel, produced by esterification and transesterification reactions from oils obtained from vegetable or animal matter.

Finally, it is worth mentioning the conversion of biomass into a multitude of molecules that can be used for the manufacture of various chemical products. This is the activity carried out in biorefineries, industrial plants that break down and transform biomass into a multitude of derivatives with direct applications or into substances that can be used as raw materials in downstream processes in the chemical value chain.[16] In

addition to various chemical products, energy and fuels are produced in biorefineries. In the current context of depletion of fossil resources, increasing pressure on the environment, greater awareness of the need to tackle climate change and its consequences, and the depopulation and abandonment of rural areas, biomass becomes a source of materials and energy with great potential, and biorefineries the ideal substitute to traditional refineries for harvesting the future sustainable chemical industry.

There are two main types of biorefinery: Energy-driven, with processes oriented to obtain energy and fuels; and product-driven, oriented to the conversion of biomass into different chemical products. The by-products derived from the processes carried out in either type of facility are usually valorised for energy purposes. Regardless of whether they are energy-driven or product-driven, biorefineries fall into three categories depending on the origin of the biomass they process as feedstock. On the one hand, first-generation biorefineries use plant resources from agricultural crops that could be used as food. Examples of this type of biomass are sugar cane, sugar beet or corn; on the other hand, second-generation biorefineries use lignocellulosic biomass or waste from agricultural or livestock activities or urban waste. This category of biomass includes woody crops on forest land, waste generated in forestry activities or maintenance of forests and green spaces, waste generated in livestock farms such as manure or slurry, by-products of the food industry or the organic fraction of municipal waste; finally, third-generation biorefineries are those facilities that have bioreactors specially designed to house algae cultures that produce biofuels as by-products of their metabolic activity or as cellular energy reservoirs.

First generation biorefineries have the advantage of starting from a feedstock that requires simpler upstream processes prior to the actual refining process. However, they have the disadvantage of the need to use food crop areas to produce feedstock for fuels and other non-food products, which has a negative impact on the communities where these crops are grown. Third-generation facilities, on the other hand, have the theoretical advantage of greater sustainability. Algae, which only require brackish water, carbon in the form of CO_2 and exposure to sunlight, have shown remarkable yields in the production of certain fuel compounds, such as triacylglycerol. However, the complexity involved in the operation and maintenance of this type of plant, as well as the high investment required for the photobioreactors in which the algae are grown, make this type of facility a less competitive option. Second-generation biorefineries are currently the most

interesting option for the transformation of biomass into derivatives for direct and industrial application. Among their advantages are the non-competition of raw materials with food crops and the existence of a remarkable development of transforming processes.

Lignocellulose is the most abundant biopolymer on Earth. Lignocellulose is composed of three different types of polymers: cellulose, the most abundant of the three components, is a linear homopolymer consisting of ß-glucose residues linked by 1-4 bonds. Cellulose is characterized by its crystallinity and porosity and can be hydrolysed, not without some difficulty, in an acid medium. The cellulose fibres interact with each other by means of hydrogen bridges, forming microfibrils, which combine to form bundles of larger fibres. These bundles have amorphous and crystalline zones, the latter being the most resistant to hydrolysis; hemicelluloses, a group that shelters the rest of the polysaccharides present in the structure of the plant mass. These fibres are generally shorter than cellulose fibres and are composed of various monosaccharides: pentoses, hexoses, hexuronic acids and deoxyhexoses. Hemicellulose fibres are usually highly branched and can be homopolymers or heteropolymers. In addition, they are less resistant to hydrolysis than cellulose and their decomposition makes it possible to obtain various products with direct applications or industrial interest, such as sugars, alcohols or organic acids; lignin, the second most important polymer in the plant mass. Chemically, lignin is a polymer of aromatic character with an amorphous structure formed by phenylpropane units linked by carbon-carbon bonds. It is characterized by its low solubility and the formation of aggregates when exposed to certain solvents. Lignin is the component that is incorporated last during the cell wall formation process, and interacts with cellulose and other polysaccharides to stiffen the cell wall structure.[17] Lignin is the most complex component of plant mass to recover and has traditionally been used in pyrolysis or combustion processes to obtain direct energy. However, processes are gradually being developed that allow it to be used in other applications such as the formulation of polyurethane foams, filling in polylactic acid films, production of carbon fibres, as antioxidant and antimicrobial agents and in foodstuffs. Finally, the biomass contains variable proportions of ash and other low molecular weight organic compounds such as terpenes, aliphatic acids, waxes, alcohols, flavonoids, alkaloids or tannins, which can be easily extracted by washing with organic solvent.[18]

The use of lignocellulosic biomass in a biorefinery requires two upstream processes prior to the actual process of separating and refining the materials to obtain energy,

biofuels and high value-added chemical products: on the one hand, a set of mechanical operations for the adaptation of the harvested plant mass, to facilitate its transport and use as feed in the biorefinery; and on the other hand, a set of mechanical, physical and chemical operations aimed at separating the different polymers that make up the biomass and then hydrolysing these polymers to obtain their constituents. Polymer fractionation processes, such as organosolv, require the biomass to be subjected to high temperature and pressure conditions and the use of hazardous substances such as alcohols or sulfuric acid.[19]

It is clear that the development of biomass as a source of energy, fuels and derivatives, as described in the previous chapters, will not only provide an economic boost to rural and forest areas, but will also reduce dependence on fossil resources, which are in the process of depletion. Moreover, the production of energy from biomass contributes to the goal of zero net carbon emissions: theoretically, all the carbon present in the combusted plant mass is released in the form of CO_2 into the atmosphere; this CO_2 will be incorporated into the structures of living plants in the dark phase of photosynthesis, known as the Calvin cycle. The set of anabolic processes that constitute this cycle requires an energy input that the plant obtains from the oxidation of molecules that have been reduced in the light phase of photosynthesis thanks to the input of solar energy.[20]

Thus, biomass should be considered an abundant, inexhaustible and renewable resource, but only in theory. Numerous scientists have made efforts to raise awareness among legislators, eager to promote alternative sources of chemicals and energy in the context of the fight against climate change, that biomass is not a panacea: the assumption of zero net carbon emissions is only true if all the carbon released into the atmosphere is reabsorbed by living forest mass at an acceptable rate. This is only possible if the cultivation of fast-growing forest stands is encouraged and deforestation is curbed. Other arguments that add controversy to the use of biomass as a food and energy source, beyond deforestation, would be the fact that biomass combustion generates emissions richer in particulate matter, nitrogen oxides and sulphur than fossil fuels, its lower calorific value leading to a lower energy yield per unit mass burned, and the damage to ecosystems caused by the use of heavy machinery for biomass harvesting.[21]

1.1.5. Certifying the sustainability of supply chains

The European Directive 2009/28/WE, which promotes the use of biomass as a raw material for obtaining fuels and chemical products, made it necessary to develop tools to ensure that a certain fuel or chemical product has been manufactured from biomass or its derivatives.

In this way, various voluntary possession certifications were created that allow suppliers claiming to market a bioproduct to prove that this is indeed the case. The most popular are the German REDcert and the ISCC (International Sustainability and Carbon Certification). These certifications are available to farmers interested in using part of their land for energy crops, companies that store and distribute products made from biomass derivatives, biomass and biofuel producers, intermediaries that market products derived from biomass and industries that process biomass (oil mills, esterifiers, biorefineries, etc.). Major, those industries that are in the last links of the supply chains of a certain product, the origin of some of the raw materials from which it has been manufactured, which has been obtained from a biomass derivative, could also be interested in the application of these standards.

Therefore, these certifications are intended to demonstrate the sustainable and zero net carbon emissions-oriented nature of the entire supply chain arising from the marketing of a product. These certifications, in addition, often incorporate the requirement to comply with certain social responsibilities related to workers and communities, so that companies that have them benefit from social recognition as a company committed to sustainable development and, on the economic side, from a higher selling price for their products in a market that takes into account the renewable origin of the product.[22]

One of the main complexities of certifying the renewable origin of goods produced in the chemical and formulation industries lies in the fact that, in many cases, producers cannot aspire to rely solely on raw materials of renewable origin, but only partially. To illustrate this, the case of lubricants is presented. One of the raw materials for their manufacture could be octanol. This product can be obtained from crude oil, a non-renewable resource, or from biomass processing, a renewable source. The producer, for cost and delivery reliability reasons, cannot purchase only octanol derived from biomass, but it can receive part of the raw material from the renewable source and the rest from fossil origin. In this case, the standard applies the biomass balance approach, a verification method that makes it possible to analyse the traceability of the raw material

and to determine the percentage of fossil octanol that has been replaced by octanol obtained from biomass.[23]

1.2.The raw materials for the production of octyl levulinate

A possible way of producing octyl levulinate involves two reactive species: levulinic acid and 1-octanol. This chapter will describe the most relevant characteristics of both raw materials as well as their possible origins and methods of production.

1.2.1. Levulinic acid

Levulinic acid is one of the top derivatives that is obtained from six-carbon carbohydrates obtained from lignocellulosic biomass.[24] It was during the 19th century, when great advances were made in organic chemistry, that levulinic acid was first obtained by heating fructose with hydrochloric acid. Levulinic acid, traditionally produced from petroleum derivatives, can be easily and efficiently obtained from cellulose or its derivatives. According to the U.S. Department of Energy, this acid is one of the 12 biomolecules with the greatest potential, since it is a platform from which numerous products can be synthesized, such as polymers or lubricants, with properties and applications that can replace others obtained from crude oil or its derivatives.[25]

Levulinic acid is a compound soluble in water and in polar organic solvents with high reactivity due to its functional groups (a carbonyl group in the form of a ketone and a carboxyl group), electrophilic centres that can be subjected to nucleophilic attack. Although it is a chemical intermediate of enormous potential, its recovery from the reaction medium is difficult.

Levulinic acid is one of the few biomolecules that have passed the double test in which biomass-derived products usually fail: having reasonably low production costs and having characteristics and properties that make it a suitable platform for the production of derivatives of industrial interest.

Levulinic acid can be produced through several routes. The main step involves an acid-catalysed reaction starting from monosaccharides, pentoses or hexoses. Currently, only GF Biochemicals Ltd. produces levulinic acid at industrial level and the most technically and economically viable process to manufacture it is the Biofine process, consisting of three stages: pretreatment of the biomass to extract the polysaccharides;

hydrolysis of the polysaccharides to obtain monosaccharides; and transformation of the monosaccharides and their derivatives into levulinic acid.[26]

The pretreatment of biomass, as discussed above, depends on the nature of the feed. For example, cellulose is more complex to hydrolyse than starch and therefore the pretreatment required for lignocellulosic biomass is more severe than that required for biomass from a corn energy crop. In the case of the former, it is estimated that the pretreatment would be responsible for 18-20% of the total cost of the Biofine process. Weidener *et al.* proposed a pretreatment based on phosphoric acid as a recyclable catalyst that generates furfural, which can be converted into levulinic acid; Zhong *et al.* analysed an organosolv process with alkaline catalysis, which efficiently separates lignin and improves glucose accessibility; Schmidt *et al.* studied a thermo-enzymatic pretreatment from sugarcane bagasse biomass. [27]

The cellulose and hemicellulose obtained in pretreatment are composed of hexoses and pentoses. The hydrolysis process of these polysaccharides is catalysed by an acid. The protons supplied by the acid protonate the glycosidic oxygen of the sugar residues. This protonation is favoured at high temperatures. The protonated form of the glycoside slowly breaks down to a cyclic carbonium ion which, after rapid addition of water, triggers the generation of the 5- and 6-carbon monomers. The hexoses obtained will undergo a series of enolization and dehydration reactions that will generate 5-hydroxymethyl furfural. The pentoses will produce furfural. These reactions are carried out in plug-flow reactors.[27]

The hydroxymethyl furfural is transferred to a second stirred tank reactor, where a hydration reaction takes place. In this reaction, a water molecule is added to the C2-C3 bond of the furan ring generating an unstable intermediate that decomposes to form levulinic acid and formic acid. The levulinic acid formed at working conditions (about 200 °C and 10-15 bar) is liquid and is extracted from the bottom of the reactor. The furfural can be hydrogenated to produce furfuryl alcohol, which is boiled in ethyl methyl ketone in the presence of an acid to produce levulinic acid. Conversions of 70 to 80% of the theoretical maximum can be obtained if hydroxymethyl furfural is used as a starting point, or more than 90% if furfural is used as a starting point.[27]

The Biofine process requires a complex set of operations to purify the manufactured levulinic acid: initially, the mixture is neutralized with a base such as sodium hydroxide;

then, it is filtered to separate solid residues such as humins, produced in the reactions of hydrolysis of polysaccharides and conversion of monosaccharides; finally, the liquid is subjected to a series of between two and eight separation operations including distillations, extractions, evaporations and crystallizations to obtain purities of between 95 and 99%.[28]

1.2.2. 1-Octanol

1-Octanol is a primary alcohol whose carbon chain is linear and has eight carbon atoms. Octanol has low solubility in water and is a liquid at room temperature.

Octanol, which is considered a medium chain length alcohol, is of great value due to its use in the manufacture of surfactants for the cosmetics and detergent industries, its use in the production of pharmaceuticals and as a molecule required as a feed in the synthesis of other products of industrial interest. This compound is also used for the production of 1-octene, an important comonomer for polyethylene. Another of its applications is as an additive in polymeric materials and lubricants.

1-octanol has traditionally been produced by means of processes typical of the petrochemical industry, among which the following stand out: on the one hand, the oligomerization of ethylene in the presence of hydrogen and aluminium, to form the organometallic compound triethylaluminium, which is then oxidized with oxygen to obtain 1-octanol. In this process other alcohols are also obtained, which are then separated by a series of distillation operations; on the other hand, in a patent published in 2016 ABENGOA claimed recognition of an invention relating to the production of 1-octanol from ethanol and n-hexanol with a metal oxide catalyst derived from a hydratalcite in which said catalyst contains Ga and/or V combined with a noble metal, preferably Pd; finally, octanol can be obtained by oxosynthesis from n-heptane[29], a reaction in which organometallic catalysts are used.[30]

However, with the ambition to reduce dependence on fossil resources and with the aim of reducing the carbon footprint in the atmosphere, efforts are being made to develop technically and economically viable processes to produce green octanol. Although short-chain alcohols (four carbons or less) can be efficiently obtained through fermentation processes from sugars, and long-chain alcohols (more than twelve carbons) can be produced from the reduction of fatty acids from vegetable origin, the production of

medium-chain alcohols from biomass derivatives is more complex and its industrial development more incipient.

In the case of octanol Julis *et al.* propose a reaction system in which 1-octanol can be obtained from acetone and furfural. An aldol condensation permits the reaction between both raw materials to form furfuralacetone, which is then hydrogenated to form 4-(2-tetrahydrofuryl)-2-butanol. The latter is converted by selective deoxygenation and ring opening to 1-octanol. Ru nanoparticles together with a liquid acid make up the catalytic system that allows obtaining conversions greater than 90% of 1-octanol. Additionally, the authors mention the possibility of obtaining acetone, for example via the fermentation process of ketone-butanol-ethanol, from biomass derivatives to highlight the sustainable nature of the octanol produced.[31]

More recently, Qieng, X. *et al.* reported the possibility of producing n-octane from furfuralacetone in a cyclohexane medium with Pd-supported niobium phosphate catalyst. In this work, it was observed that to produce octene, 1-octanol was previously obtained. The authors developed the pertinent modifications in the catalyst as well as in the reaction medium in order to produce octanol from biomass derivatives obtaining yields higher than 60% under optimal conditions.[32]

Finally, on a more anecdotal level but to reflect the impetus of companies in valuing waste and betting on the circular economy, LanzaTech and BASF have developed a fermentation process with bacteria to produce 1-octanol from the treatment of gaseous emissions from the plant, mainly composed of carbon monoxide and hydrogen.[33]

1.3.The family of interest. Alkyl levulinates

Alkyl levulinates are bioderived materials with great potential for substituting other products traditionally obtained from crude oil by petrochemical synthesis routes, especially solvents and fuels, and as platforms for the synthesis of other substances. The applications of alkyl levulinates are due to their outstanding physicochemical characteristics: low toxicity, high lubricating power, good fluidity in wide temperature ranges and high flash point.[34]

The first studies on this family of compounds and their applications date back to the 19th century. However, in recent years intense work has been carried out on the possibility of obtaining these compounds from biomass derivatives. Alkyl levulinates can

be produced from simple chemical platforms derived from biomass, obtaining remarkable yields and selectivities. They can also be obtained directly from lignocellulosic biomass, but with significantly lower yields.[34]

One of the most studied possibilities is the production of alkyl levulinates by esterifying levulinic acid with alcohols in a reflux or non-reflux reactor depending on the boiling temperature of said alcohol.

The fact that it has been possible to obtain alkyl levulinates from simple derivatives of biomass such as levulinic acid has triggered research on the possibility of obtaining these compounds directly from lignocellulosic biomass. The recalcitrance and low solubility of this feedstock in the reaction medium entails the need to subject it to drastic conditions of temperature, pressure and acidity to carry out solvolysis and dehydration processes. This increase in the complexity of the process as well as in the complexity of the feedstock means that selectivity suffers. However, reactions such as the ones for the production of alkyl levulinates, which are carried out in alcohol, show higher selectivities and less tendency to trigger side reactions than those carried out in an aqueous medium, in which notable productions of humins are generated. On the other hand, the incorporation of the alkyl from the alcohol in the esterification process protects reactive groups that could trigger unwanted polymerization processes.[34]

Studies carried out by Garves on obtaining short-chain alkyl levulinates (methyl levulinate, isopropyl levulinate) using sulfuric acid[35], Tominaga *et al.*, who obtained yields of up to 75% in the transformation of cellulose to methyl levulinate in the presence of 2-naphtalene sulfonic acid[36] or the surprising yields of up to 90% obtained by Bianchi *et al.* in the transformation of coniferous wood into levulinates at 200 ºC by means of recycled sulfonated naphthalenes[37] are some of the outstanding works around the production of levulinates from complex biomass or its constituent polymers.

Other authors have tried to produce methyl levulinate from cellulose using solid catalysts, such as sulphated zirconia, sulfonated carbons and resins, as well as sulfonated TiO_2, obtaining more modest yields, between 10 and 40%. Wu *et al.* obtained methyl levulinate using Amberlyst-35 resin, achieving yields of around 10%.[34]

Likewise, obtaining alkyl levulinates from monosaccharides such as glucose, fructose or xylose has been studied. These processes require in the first instance the transformation of the monosaccharide into 5-hydroxymethyl furfural followed by an esterification

process for the formation of the ester or, alternatively, the formation of ethers from the monosaccharides, which then pass through a process of dehydration/rehydration to generate the ester. Zeolites, sulfonated metal oxides and ion exchange resins[38] have been tested as catalysts in conversion processes of these monosaccharides, obtaining yields of between 10 and 50% at temperatures between 140 and 200 ºC, the greatest handicap being the generation of alkyl ethers and dialkyl ethers that do not end up transforming into esters.[39]

Another way to obtain alkyl levulinates is from furfuryl alcohol. Furfuryl alcohol is obtained from the reduction of furfural, from hemicellulose. Furfuryl alcohol in aqueous medium and presence of acid is able to transform into levulinic acid which, in the presence of alcohol and the appropriate catalyst, can trigger the formation of alkyl levulinates. Van de Graaf *et al.* were the first to propose this route to obtain ethyl levulinate.[40,41] Various authors have studied the diverse chemical routes for obtaining levulinates from this alcohol, using zeolites, Amberlyst resins and ionic liquids. Finally, Cheng *et al.* carried out a one pot transformation of furfural into levulinic acid using a Pt catalyst in a reactor pressurized with H_2 in which furfural and ethanol are combined to obtain conversions of 92% and yields of up to 76%.[42]

As noted above, one of the applications of octyl levulinate, one of the highest value added alkyl levulinates, is as a base for the formulation of lubricants. Lubricant bases must have a series of properties to ensure excellent performance, and octyl levulinate more than fulfils them, even improving those of mineral-based lubricant bases. The properties of these esters are determined by the chain length of the alkyl group: on the one hand, the viscosity, which must be between 4 and 40 cSt to permanently maintain a layer of oil between the surfaces to be lubricated; on the other hand, the volatility index, which determines to what extent the viscosity varies with temperature.[43] In the case of octyl levulinate, the high viscosity index makes it a compound of high value as a lubricant, comparable to special oils; in addition, the freezing point, which must be low enough to ensure that even in the most severe cold conditions the oil will continue to flow; and, finally, volatility. In the case of octyl levulinate, the high boiling point is indicative of the non-generation of vapours that would occur during the operation of the engine.[5]

Thus, alkyl levulinates, and especially octyl levulinate, offer an optimistic horizon in which it will be possible to manufacture lubricants and fuel additives with excellent properties and that are also biodegradable and obtained from renewable resources.

1.4.State of the art of the obtention of biosourced alkyl levulinates

Several authors have studied the synthesis of alkyl levulinates, as highlighted in the previous chapter. However, the existing literature on the production of the ester of interest in the present work, octyl levulinate, is scarcer.

Khajone *et al.* carried out the esterification of levulinic acid with 1-octanol using a catalyst based on novel Bronsted acid functionalized on perylene diimide with ionic liquid that is activated by exposure to light. Optimal conditions were reached with an initial molar ratio of levulinic acid to octanol (LA:OH) of 1:1, obtaining a yield close to 96%, requiring 12 h to reach equilibrium. Similar yields were achieved in the production of other simpler alkyl levulinates. This work constitutes the first study of photocatalysis as an alternative for the production of octyl levulinate.[44]

Nandiwale and collaborators studied the synthesis of octyl levulinate from levulinic acid and 1-octanol using H-ZSM-5 and Meso-HZ-5 zeolite catalysts at temperatures between 100 and 120 ºC and molar ratios of OH:LA between 4:1 and 10:1, obtaining yields of up to 99% after around 4 h from the start of the reaction. No secondary reactions were observed in the study. The authors determined an endothermic nature of the reaction. They also demonstrated the high levels of efficiency and reusability of the zeolites tested, especially Meso-HZ-5.[45]

Zhoua *et al.* fabricated for the first time a catalyst based on lipase B from the species *C. antarctica* supported on an organosilicon material with a high-order three-dimensional macroporous structure. The catalytic activity of these materials was tested to obtain butyl, octyl and dodecyl levulinates by esterification of levulinic acid with the respective alcohol. In the case of octyl levulinate, yields of up to 85% were obtained after 4 h working at 40 ºC and starting from a 10:1 OH:LA molar ratio, with a decrease of around 4 percentage points after 9 cycles of use, which reflects better results than those obtained with commercial biocatalysts. Equilibrium was reached between 8 and 10 h of reaction.[46]

Pavlovic and his research group tested the performance of zeolite-clinoptilolite catalysts with sulphated and unsulphated SnO_2. Working at a temperature of 100 ºC and mass ratio LA:OH of 1:7, they obtained interesting activities, which decreased notably after five cycles due to the formation and deposition of coke in the catalyst structure. However, this study did not focus on analysing the thermodynamics of the process, not focusing on the yields obtained.[47]

Jia *et al.* conducted a further kinetic study around the production of long-chain alkyl levulinates via levulinic acid esterification. In this case, tungsten salts were used as catalysts and yields of up to 88% were achieved in just 15 minutes in a batch stirred tank reactor working at low temperature (70 ºC, although the authors claim that similar yields can be obtained working by below 50 ºC). Although the study was mainly carried out for the production of hexyl levulinate from 1-hexanol, the authors claim to have achieved similar results for octyl levulinate under the same working conditions.[48]

Finally, Hamryszak and Grzesik carried out a kinetic study for the conversion under non-isothermal conditions of levulinic acid and octanol to octyl levulinate using methanesulfonic acid as a catalyst. It was operated at temperatures between 100 and 155 ºC and molar ratios OH:LA from 3:1 to 10:1.[49]

None of the works cited refer to formation of two phases in the reactor due to the immiscibility of some of the components of the medium with the rest at the operating conditions.

If the works on the study of the production of long-chain alkyl levulinates are scarce, those in which an ion exchange resin is used as a catalyst are even more so. However, some authors have reported interesting results in the production of short-chain esters: Bringué *et al.* synthesized butyl levulinate using ion exchange resins at 110 °C[50], Badia *et al.* studied the synthesis of sec-butyl levulinate[51], Ramírez *et al.* obtained remarkable results in obtaining butyl levulinate by means of eight ion exchange resins based on sulfonic groups housed in a polystyrene-divinylbenzene matrix[52], Chaffey *et al.* produced different levulinates using Amberlyst-15[53] and Russo *et al.* obtained ethyl levulinate using Amberlite IR-120 as catalyst.[54]

Another point of great interest is the separation of the component of interest, in the case of this work octyl levulinate, from the rest of the substances (unreacted 1-octanol and levulinic acid and water) once the reaction has finished. This aspect is not only important for the study that is reflected in this work, but also as one of the issues to be resolved in order to achieve an industrial implementation of the production of long-chain esters through a technically viable process. The literature on this subject is equally scant.

On the one hand, Yaqi *et al.* describe a process for the separation of a system formed by water, an alcohol-type organic solvent with a certain solubility in water and a phtalate ester. This process is based on the addition of a salt to the system to trigger a salting out phenomenon, triggering the rapid appearance of two phases: an aqueous phase formed by water, and an organic phase, in which the alcohol and the ester would be found.[55] However, this process does not solve the need to obtain the pure ester, since its separation from the alcohol would still be necessary.

On the other hand, a patent filed by the company Kyowa Yuca Co., Ltd. describes a process for the purification of esters of methyl iso-butyrate or methyl methacrylate type obtained via esterification of an organic acid with methanol. Said process consists of a first distillation operation (at atmospheric pressure or vacuum) in which the alcohol is removed from the system in the form of a minimum boiling point azeotrope formed by the unreacted alcohol and a small part of the generated ester. In a second distillation (at vacuum) a first distillate is obtained formed by a water-ester azeotrope easily separable by decantation, and then the ester, leaving the organic acid as a residue of said rectification.[56]

2. OBJECTIVES

The present work focuses on the study of the thermodynamic properties of the synthesis reaction of octyl levulinate by esterification of levulinic acid with 1-octanol, which to the best of our knowledge are not available in the literature, and the determination of specific thermodynamic properties of the targeted product. The specific objectives of the work presented are listed below:

I. To determine the reaction equilibrium constant of the esterification of levulinic acid with 1-octanol from experimental runs at different temperature and initial composition of the reactants mixture.
II. To compare the equilibrium constants determined experimentally to those computed via estimation methods.
III. To determine the enthalpy and entropy changes of reaction and compare the values obtained experimentally to those calculated via estimation methods.

IV. To assess the eventual occurrence of side reactions and the phenomenon of phase separation.

V. To separate the product distribution in order to obtain octyl levulinate as pure as possible.

VI. To determine the specific heat at constant pressure of octyl levulinate experimentally and to compare it with theoretical estimations.

3. THEORETICAL FRAMEWORK

3.1.Chemical equilibrium and thermodynamic constant

A reversible chemical reaction is one in which the reactants, as soon as they react, give rise to products that also have the ability to transform into reactants.[57] Depending on the conditions of the reaction medium, mainly temperature and composition when it comes to reaction in liquid medium, the rate at which reactants are transformed into products (forward reaction) and the rate at which products are transformed into reactants (reverse reaction) differ.

A reversible reaction reaches equilibrium when the forward reaction and the reverse reaction proceed at the same rate. Thus, once the process reaches equilibrium, the concentration of the various species involved in the reaction remains constant.[57]

In the event of the following synthesis reaction:

$$\upsilon_A A + \upsilon_B B \leftrightarrow \upsilon_P P + \upsilon_Q Q$$

The law of mass action states that the rate of a chemical reaction is directly proportional to the concentration of the reactants, usually raised to their stoichiometric coefficient. Therefore, rates of forward and reverse reactions can be expressed according to Equations 1 and 2, respectively:

$$r_d = k \cdot C_A^{\upsilon_A} \cdot C_B^{\upsilon_B} \quad (1)$$

$$r_i = k' \cdot C_P^{\upsilon_P} \cdot C_Q^{\upsilon_Q} \quad (2)$$

At equilibrium, the global reaction rate is null. From this, it follows:

$$r_d = r_i \tag{3}$$

And, therefore:

$$k \cdot C_A^{\upsilon_A} \cdot C_B^{\upsilon_B} = k' \cdot C_P^{\upsilon_P} \cdot C_Q^{\upsilon_Q} \tag{4}$$

The thermodynamic constant of a reversible reaction is a parameter that quantifies to what extent one process -the forward or the reverse- prevails over the other in terms of rate. For this reason, it can be calculated as the quotient between the kinetic constant of the forward reaction and the kinetic constant of the reverse reaction. Thus, it holds that:

$$K = \frac{k}{k'} \tag{5}$$

On the other hand, the thermodynamic constant is a parameter that describes the composition of the reaction medium at equilibrium, insofar as it can be calculated, as is otherwise deduced from the combination of Equations 4 and 5, as the ratio between the product of reactants and products at equilibrium raised to their stoichiometric coefficients, as follows:

$$K = \frac{C_{Pe}^{\upsilon_P} \cdot C_{Qe}^{\upsilon_Q}}{C_{Ae}^{\upsilon_A} \cdot C_{Be}^{\upsilon_B}} \tag{6}$$

However, when the compounds involved in the chemical reaction do not behave ideally, microscopic interactions between the molecules are caused which, ultimately, result in deviations of certain thermodynamic properties. For liquid mixtures, such deviations are magnified when involved species present a notable polarity, as is the case due to the presence of water and levulinic acid. As a consequence, the thermodynamic reaction equilibrium constant, cannot be expressed in terms of concentrations of the different species, yet instead as a function of their activity. The activity of a component can be expressed as the product of its mole fraction and its activity coefficient. Said coefficient, which quantifies said deviations, depends on the temperature and the composition of the medium and can be estimated or predicted by means of various methods. Therefore, adapting Equation 6 to the case of non-ideal liquid mixtures:

$$K = \frac{a_{Pe}^{\upsilon_P} \cdot a_{Qe}^{\upsilon_Q}}{a_{Ae}^{\upsilon_A} \cdot a_{Be}^{\upsilon_B}} \tag{7}$$

And therefore:

$$K = \frac{x_{Pe}^{\upsilon_P} \cdot x_{Qe}^{\upsilon_Q}}{x_{Ae}^{\upsilon_A} \cdot x_{Be}^{\upsilon_B}} \cdot \frac{\gamma_{Pe}^{\upsilon_P} \cdot \gamma_{Qe}^{\upsilon_Q}}{\gamma_{Ae}^{\upsilon_A} \cdot \gamma_{Be}^{\upsilon_B}} = K_x \cdot K_\gamma \quad (8)$$

The equilibrium reached in a chemical reaction is characteristic of a specific temperature and is characterized by a certain relationship between the activity of reactants and products.

3.2.Enthalpy and entropy of reaction

Enthalpy is defined as the sum of the internal energy and the product of the pressure and volume of a thermodynamic system. It has dimensions of energy and it depends on the temperature and pressure and not on its history, being it how the system got to the actual state.[58]

As in the case of other state functions, it is not possible to refer to absolute enthalpy states, but rather to enthalpy variations that occur in a process through which the system changes its thermodynamic state.[58] Thus, in the case of chemical reactions, the enthalpy change of the reaction will be referred to as the difference in enthalpy between the initial state (reactants) and the final state (products).

When a chemical reaction takes place at constant pressure and temperature, the change in enthalpy coincides with the amount of heat released or absorbed by the reacting system. If the system releases heat, the enthalpy change will be negative and the reaction will be exothermic. Conversely, when said reaction occurs, the system absorbs heat energy, the enthalpy change will be positive and the reaction will be endothermic.[59]

The standard enthalpy of a reaction is the change in enthalpy that occurs when the reaction takes place at standard conditions, these being 1 atm pressure and the temperature of interest. On the other hand, the standard enthalpy of formation of a component is the enthalpy change that occurs when a given component is formed at 1 atm pressure and the desired temperature from its pure elements in its most stable form.[60] The standard enthalpy of a reaction can be calculated from the standard enthalpies of formation of products and reactants, as expressed in Equation 9, which constitutes the Hess law:

$$\Delta H^o(T) = \sum_{j=1} \upsilon_j \cdot \Delta H_{f_j}^o(T) \quad (9)$$

where the stoichiometric coefficients (*v*) of the products have a positive value and those of the reactants have a negative value.

Entropy is defined as the amount of thermal energy of a system per unit temperature that is not available for doing useful work. The amount of entropy of a system is also a measure of the degree of molecular disorder or randomness of said system.[61]

As in the case of enthalpy, reference will never be made to absolute states of entropy, but entropy variations of processes that produce a change in thermodynamic state will be calculated.

In the same way, the standard entropy of a reaction and the standard entropies of formation of products and reactants are defined, and they are related to each other as stated in Equation 10:

$$\Delta S^o(T) = \sum_{j=1} v_j \cdot \Delta S^o_{f_j}(T) \qquad (10)$$

where the stoichiometric coefficients (*v*) of the products have a positive value and those of the reactants have a negative value.

3.3.Gibbs free energy

Introduced by Josiah Willard Gibbs in 1870, it was initially defined as the available energy of the system. The sign that the Gibbs energy change of a reaction (ΔG) takes indicates whether it is spontaneous ($\Delta G<0$) or non-spontaneous ($\Delta G>0$).[62]

A reaction is spontaneous or exergonic under certain conditions of temperature, pressure, and system composition if, under these conditions, the formation of products is favoured. On the contrary, a reaction is non-spontaneous or endergonic when, under the referenced conditions, the formation of products is not favoured.[63]

The Gibbs free energy groups the enthalpy and entropy of the reaction in the same term. Thus, the standard Gibbs free energy of a reaction is related to the other two state functions according to Equation 11:

$$\Delta G^o(T) = \Delta H^o(T) - T \cdot \Delta S^o(T) \qquad (11)$$

On the other hand, the standard Gibbs free energy is related to the equilibrium constant as expressed in Equation 12:

$$\Delta G_{eq}^{0}(T) = -R \cdot T \cdot \ln(K) \tag{12}$$

And therefore, the equilibrium constant depends on the standard enthalpy and the standard entropy of the reaction according to Equation 13:

$$\ln(K) = -\frac{\Delta H^{o}(T)}{R \cdot T} + \frac{\Delta S^{o}(T)}{R} \tag{13}$$

If it is desired to determine the spontaneity of the reaction under conditions of medium composition other than equilibrium, Equation 14 must be used:

$$\Delta G^{o}(T) = \Delta G_{eq}^{0}(T) + R \cdot T \cdot \ln(Q) \tag{14}$$

where Q is the producer of the activities of the products raised to their stoichiometric coefficients divided by the producer of the activities of the reactants raised to their stoichiometric coefficients.

The Poynting factor allows quantifying the deviation from the thermodynamic constant due to the effect of pressure when it is significantly higher than atmospheric. It can be calculated according to Equation 15 and, conceptually, it calculates the deviation in the fugacity when pressure is increased from saturation to a certain value, isotermically.[64]

$$K_{\wp} = \frac{\phi}{\phi^{sat}} = \int_{P^{v}}^{P} \frac{V}{R \cdot T} \cdot dP = \exp\left(\left(\frac{P - P_{vm}}{R \cdot T}\right) \cdot \sum_{j=1} x_j \cdot V_j\right) \tag{15}$$

Where V_j is the molar volume of the compound j and P is the pressure expressed in atm and P_{vm} is the saturation pressure of the components mix. The molar volumes of the species are a function of the temperature and pressure. In Appendix 4 a method to estimate molar volumes at equilibrium is depicted as are all the methods required to estimate other thermodynamic properties from which molar volumes depend.

4. EXPERIMENTAL

4.1.Materials

4.1.1. Chemicals

Levulinic acid (Acros Organics, ≥98% purity) and 1-octanol (Acros Organics, 99% purity) were used as reactants. Apart from the product of interest, water is generated in the reaction. Table 1 below shows the most relevant physicochemical properties of the involved compounds:

TABLE 1. Main properties of chemicals employed in chemical reactions.

Properties	Units	Levulinic acid	1-Octanol	Water	Octyl levulinate
CAS Number	-	123-76-2	111-87-5	7732-18-5	41780-57-8
Molecular formula	-	$C_5H_8O_3$	$C_8H_{18}O$	H_2O	$C_{13}H_{24}O_3$
Molecular weight	g/mol	116.12	130.23	18.02	228.33
Density	kg/m^3	1133.5	828	1000	900
Melting point	ºC	30-33	-13.5	0	-
Boiling point	ºC	245-246	195	100	306.3
Viscosity	Pa·s	$7.7 \cdot 10^{-3}$	7.4	1.0	-
Solubility parameter	$Mpa^{1/2}$	26.9[a]	20.8[b]	48.0	15.0[a]
Purity	%	≥98	99	100	-
Flash point	ºC	98	86.5	-	129.0
State at room temp.	-	Solid	Liquid	Liquid	Solid
Data supplier	-	Merck	Merck		PubChem
Data supplier	-		Rotichrom		Chem Spider

[a]The value of this property has been calculated using the data available on their heat of vaporization and molar volume at 25 ºC. [b]The value of this property has been taken from available literature[65].

In order to perform the calibration of the chromatographic response, octyl levulinate obtained in the laboratory by distillation with a minimum purity of 95% was used as a standard.

4.1.2. Auxiliary gases

Nitrogen (N_2, Linde Gas España, ≥99.9995% purity) was used for the injection of the catalyst, as well as to pressurize the reactor during the experiments with the aim of maintaining a pressure widely above the vapour pressure of all the components at the highest temperature explored. Nitrogen was also used to facilitate the return of the excess

liquid from the sampling to the reactor through the piping system, as well as to facilitate the purging of the lines after each sampling. Helium (Linde Gas España, ≥99.998% purity) was used as carrier in the gas chromatography tests carried out.

4.1.3. Catalysts

The following ion exchange resins were tested in a screening prior to the experiments carried out to characterize the equilibrium. These resins were selected given their different morphological and compositional characteristics: Amberlyst^{TM} 35 (A-35, Dow DuPont), Purolite® CT-224 (CT-224, Purolite) and Purolite® CTA-196 (CTA-196, Purolite). Table 2 gathers a summary of the most relevant physical properties of the resins used:

TABLE 2. Main properties of ion exchange resins employed.

Catalyst	Type	Structure	Density [g/cm^3]	Capacity [eq H^+/L][a]	DVB [%]	Moisture [%]	Max. Operating [ºC]
A-35	Acid	macroreticular	0.51	1.9	20	55	150
CT-224	Acid	gel-type	1.42	4.3	4	55	150
CTA-196	Basic	macroreticular	1.04	1.8	NA	45-52	100

[a]*Dimensions are eq OH^-/L in the case of CTA-196.*

Before use, the resisns were subjected to a pretreatment aimed at reducing moisture. Pretreatment consisted in 24-48 h of drying at room temperature followed by atmospheric oven drying at 110 ºC. In the case of A-35 and CT-224, with higher maximum operating temperatures, they were placed for 24 h in a vacuum oven (0.01 bar) at 100 ºC as a final step of pretreatment. CTA-196 was previously washed with methanol and subjected to 80 ºC in the same vacuum oven overnight.

4.2.Experimental setup

Experiments were carried out in the experimental setup depicted in Figures 2-5. A batch reactor (Autoclave Engineers, Inc.) (E1) with a total volume of 250 mL was used. For each experiment, the volume occupied by the reactants at the beginning of the reaction (excluding the catalyst) was 180 mL. The reactor is operated in batch mode and at a pressure of 25 bar. A manometer allows to monitor the pressure inside the vessel. The reactor consists of a stainless-steel cylinder equipped with a 6-blade stirrer mounted on a rotor connected to a frequency variator from which the agitation speed can be manually controlled. In all experiments, this was set at 750 rpm. Around the agitator, there is a

baffle plate whose function is to break the vortices that are generated in the reactor as a result of agitation. The reactor is heated with a jacket (E2) connected to a thermostatic bath (3) with a mixture of dimethyl sulfoxide and water or thermal oil alternatively. Thermocouples are set in the jacket and inside the reactor that measure the temperature with an accuracy of ± 0.1 ºC. The reactor has a tab in the head where the catalyst injector (E4) is connected. This injector is connected to a pipe that transports nitrogen at the desired pressure to facilitate injection and pressurize the vessel at the start of the reaction.

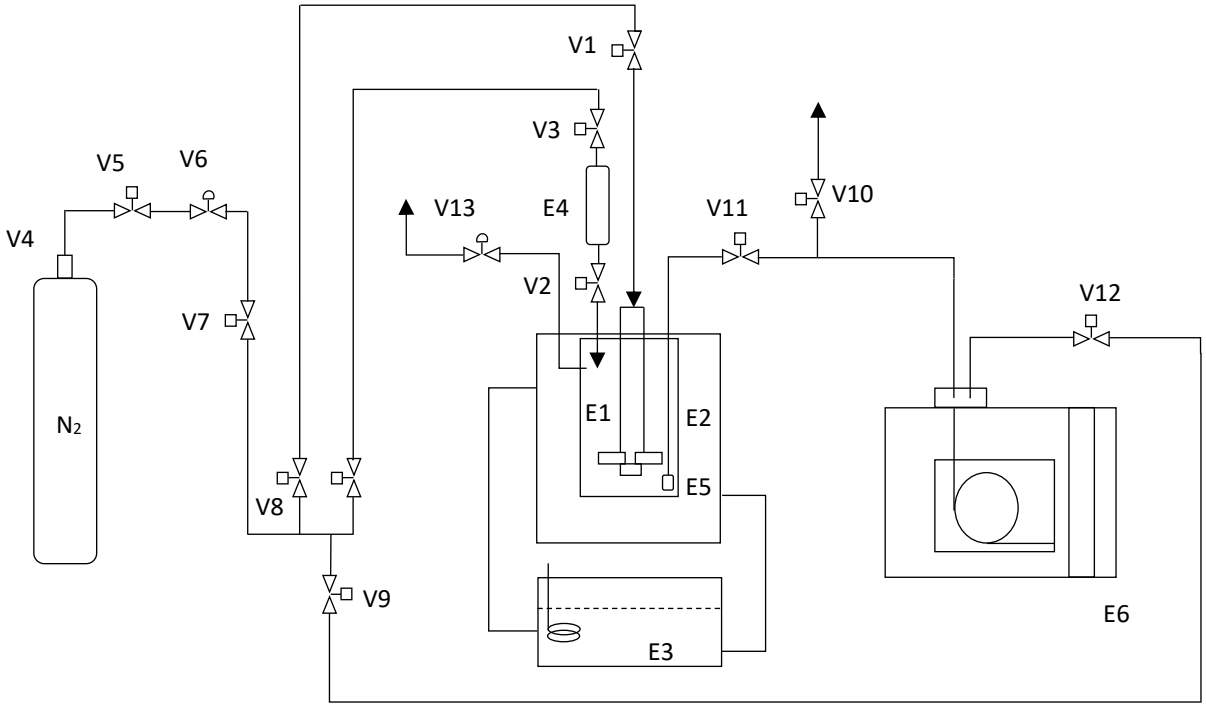


Figure 2. Experimental setup composed of a stirred tank batch reactor and a gas chromatograph coupled to a mass-selective detector.

Sampling is done through an iron filter (E5) with a 0.5 µm mesh that prevents catalyst suction. The sampled liquid is conducted towards the inlet of the gas chromatograph (E6) by depression through a heat-insulated pipe with an electric blanket to prevent the solidification of the components inside. An automatic injection valve using compressed air introduces an aliquot of 0.2 µL to the system made up of the gas chromatograph (Agilent 7890B GC System) and the mass-selective detector (Agilent 5977B GC/MSD), the equipment used to analyse the nature and quantity of each of the chemical species inside the reactor vessel. The gas chromatograph consists of a capillary column (HP-PONA 19091S-001, J&W Scientific, Santa Clara, US; 100% dimethylpolysiloxane, 50 m 0.20 mm x 0.50 µm nominal).

4.3.Procedure

The following steps were carried out in each of the experimental runs:

4.3.1. Catalyst pretreatment

Except for the CTA-196 resin, which was already pretreated, the ion exchange resins had to undergo a drying process to remove the adsorbed water given its hygroscopic character, especially CT-224, which is gel-type.

1) Weigh on an analytical balance a catalyst weight greater than that desired to load in the reactor (between 2-3 times the desired weight for A-35 and between 3-4 times the desired weight for CT-224). The resin has previously been pretreated submitting it to room temperature drying and 110 ºC oven drying.
2) Place the catalyst in a vacuum oven at 100 ºC and 0.01 bar for 24 hours.
3) After 24 hours of drying, break the vacuum of the oven by opening the relief valve a quarter of its stroke to avoid a sudden pressurization that can damage the seals.

4.3.2. Reactor load

1) Since levulinic acid is in the solid phase at room temperature, place the reactant bottle in a thermostatic bath at a temperature slightly above 33 ºC.
2) Once it is in the liquid phase, weigh the desired mass of levulinic acid by pouring the content of the bottle into a beaker. Proceed in the same way with 1-octanol.
3) Pour the contents of both beakers into the reactor vessel.
4) Place the head of the reactor together with the agitation system, the baffle plate and the sampling filter and screw it applying the necessary force to ensure the tightness of the seal.
5) Screw the sampling duct to the inlet of the reactor intended for such purpose, place the transmission chain from the rotor to the agitation system and install the protection casing around it.
6) Screw the duct enabled for the injection of reactants in the gas phase into the inlet located at the top of the reactor head. This duct will not be used. Make sure that the valve (V1) located in said duct is closed.
7) Check that the lower valve (V2) of the injector is closed to prevent the emanation of vapours through said duct.

8) Start the thermostatic bath to heat the content of the reactor. Set the temperature setpoint in the bath at 0-5 ºC above the desired temperature inside the reactor. Start the stirrer, setting its speed at 750 rpm using the manual selector.
9) Monitor the temperature inside the reactor through the reading of the thermocouple.
10) When the temperature in the reactor is 5 ºC below the temperature at which it is desired to carry out the experiment, remove the catalyst from the vacuum oven and weigh the desired mass (between 5 g and 8 g).
11) With the lower injector valve closed, open the upper injector valve (V3) and pour the catalyst into it using a funnel.
12) Screw the injector pressurization pipe to its inlet. Proceed to pressurize the injector: open the valve of the nitrogen lung bottle (V4); open the valve and open the stopcock (V5) that allows the conduction of nitrogen to the laboratory; adjust the desired pressure using the pressure reducer (V6); open the nitrogen access valve (V7) to the valve panel; open the injector pressurization valve (V9) and check that the upper injector valve is open; check that the nitrogen access valve (V10) to the sample recirculation circuit is closed.
13) When the temperature inside the reactor reaches the desired value, introduce the catalyst into the reactor vessel by quickly opening the lower valve of the injector. Along with the catalyst, nitrogen will enter the reactor, which will allow the pressure inside to rise up to the desired value. To make it difficult for resin particles to stick to the walls of the injector, apply sharp blows with a metal tool to the casing of the injector.
14) After catalyst injection is complete, close the upper and lower injector valves. This instant is considered the beginning of the reaction.

4.3.3. Sampling and analysis

A computer, with software Agilent GCMS, controls the sample analysis system, made up of the gas chromatograph and the mass-selective detector.

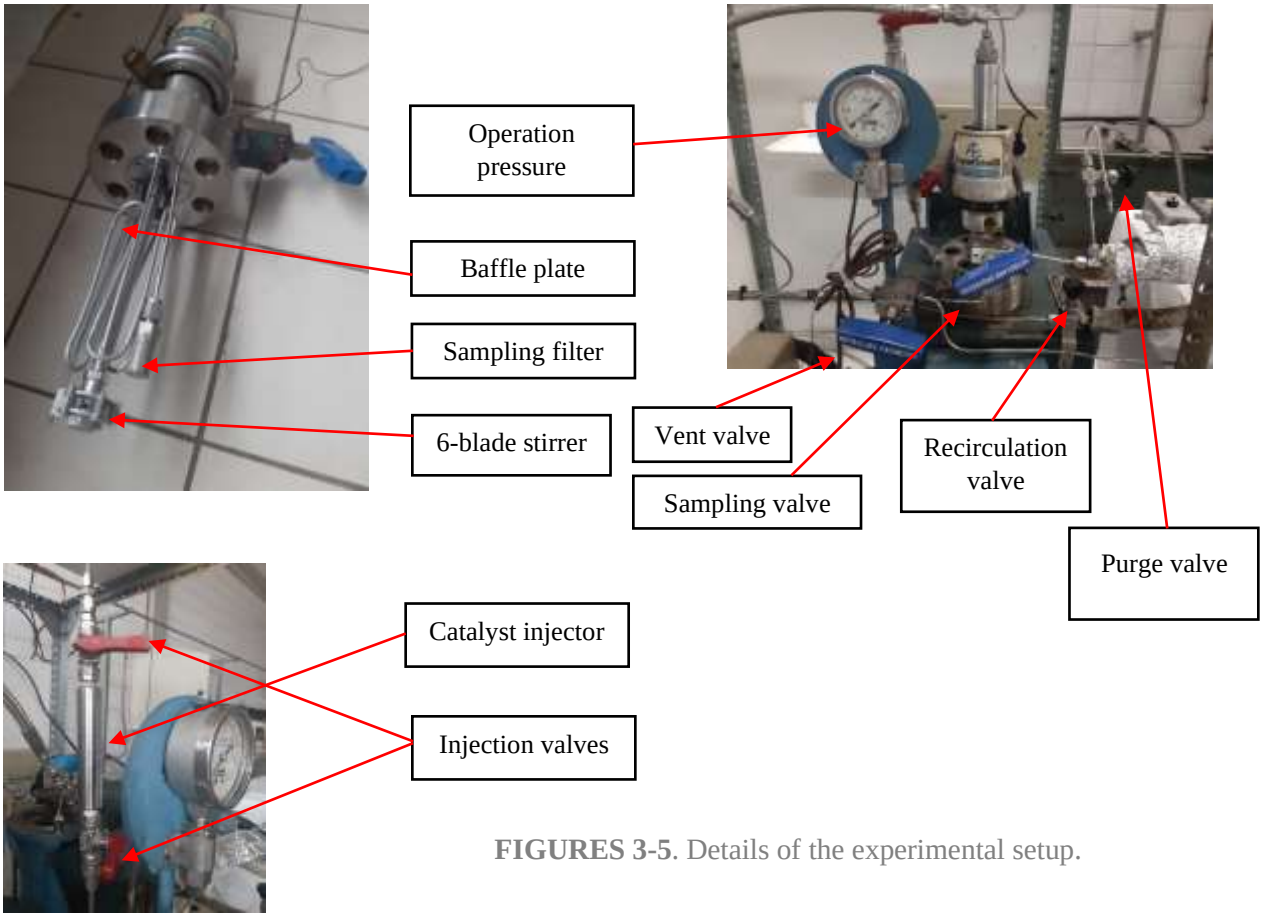
1) Experiments will be run until equilibrium is reached. Sampling and analysis will be carried out with a frequency of 15-20 minutes during the first 2 hours and with a frequency of 30-60 minutes until the reaction is completed.

2) For each sampling assay, load the chromatographic method into the online software and create the virtual sample by clicking on the green arrow on top of the screen.
3) Turn on the electrical insulation of the sampling line setting a medium power and open the purge valve (V10) of the sampling circuit to ensure that it is not pressurized.
4) Fully open the sampling valve (V11). Allow 1-2 minutes for the sampled liquid to circulate through depression to the chromatograph inlet, filling the entire volume of the sampling circuit.
5) Press the "OK and Run Method" button on the screen. This action will trigger the preparation of all the elements of the analyser to adjust to the characteristics of the designed method and the injection of the sample aliquot in the chromatograph will take place.
6) Close the sampling valve and check that the valve that allows nitrogen access to the recirculation circuit is open.
7) Open the recirculation valve (V12), allowing pressurized nitrogen access to the sampling line. Slightly open the reactor vent valve (V13) to generate a slight depression between the reactor vessel and the sampling circuit.
8) Open the sampling valve to allow reintroduction of the unanalysed sample content back to the reactor. Close said valve when it is observed on the manometer that the pressure in the reactor has reached the set value again.
9) Purge the residual content of the sampling circuit by opening the sampling valve and placing a collection cup in the outlet of the purging line. Close the recirculation valve and close the purge valve.

4.3.4. Termination of the experiment and cleaning

1) After taking the last sample, turn off the thermostatic bath and the stirrer.
2) Open the vent valve to depressurize the reactor and let the system cool overnight.
3) Unscrew the sampling pipe from the reactor inlet, as well as the gaseous reactants injection pipe.
4) Remove the transmission chain from the rotator to the agitation system as well as the protective casing.
5) Disconnect the thermocouple that measures the temperature inside the reactor.

6) Unscrew the head of the reactor and separate it from its body to clean it: apply plenty of water, especially to the baffle plate and the stirrer blades to loosen the adhered catalyst particles; circulate pressurized air countercurrently through the sampling valve and suction filter to clean it and dry the internal parts of the stirrer and the baffle plate.
7) Extract the content of the reactor using a vacuum system and collect it in an Erlenmeyer flask.
8) Filter the contents removed from the reactor by gravity, using a funnel and filter paper. In this filtration operation, the catalyst is retained. The liquid phase will be stored in a 2 L bottle for subsequent purification of the product of interest.
9) Open the upper and lower valves of the injector and circulate pressurized air through said cylinder to drop the remains of the catalyst into the reactor vessel.
10) Clean the reactor vessel with water, taking special care to remove the catalytic particles that could have stuck to the seal.
11) Extract the contents of the reactor with the vacuum system and filter it by gravity, retaining the catalytic particles.
12) Dry the reactor vessel with pressurized air.



FIGURES 3-5. Details of the experimental setup.

4.4.Security and environment

Apart from water, the three main substances used throughout the experimental tasks are levulinic acid, 1-octanol and octyl levulinate. The three substances are identified as moderately irritating to the skin and eyes. For this reason, gloves and laboratory glasses will be used as protective elements when carrying out the tasks of handling and weighing reactants, sampling and analysing samples, cleaning contaminated laboratory utensils, cleaning the reactor and waste disposal.

On the other hand, 1-octanol is identified as a combustible substance, capable of generating flammable vapours at temperatures close to 80 ºC. Levulinic acid and octyl levulinate, with flash points of 98 and 129 ºC respectively, also have a risk of flammability at working temperatures. For this reason, the chemical reaction will be carried out in an inert atmosphere (25 bar N_2).

Finally, the waste generated in the experimental tasks (reactor cleaning water and reaction product cleaning water) will be deposited in the non-halogenated organic solvents container, for subsequent management. The catalyst used in the reaction is separated from the liquid medium by filtration and placed in the waste container dedicated to resins.

4.5.Experimental design

With the aim of determining the equilibrium constant of the synthesis reaction of octyl levulinate via esterification of levulinic acid with 1-octanol and studying its dependence on temperature, several experiments were carried out at different working temperatures and initial molar ratios between both reactants. All the experiments were performed isothermally keeping constant the agitation speed. Assayed experimental conditions are shown in Table 3.

Prior to the chemical equilibrium study, a previous screening including the ion exchange resins mentioned in Section 4.1.3, which allow covering different properties (for instance, A-35 is an acid macroreticular resin, CT-224 is an acid gel-type resin and CTA-196 is a basic macroreticular resin) was carried out. These experiments were performed at 100 ºC and using an initial molar ratio LA:OH of 1:1 (see Section 6.3).

TABLE 3. Experimental design executed.

Temperature [ºC]	$R^{o}_{LA:OH}$	Speed [rpm]	Pressure [bar]
80	1:1	750	25
80	1:2	750	25
80	1:4	750	25
80	1:8	750	25
100	1:1	750	25
100	1:2	750	25
100	1:4	750	25
100	1:8	750	25
120	1:1	750	25
120	1:2	750	25
120	1:4	750	25
120	1:8	750	25

5. THEORETICAL ESTIMATION OF EQUILIBRIUM CONSTANT AND THERMODYNAMIC PROPERTIES

The objective of this chapter is to estimate theoretically the thermodynamic reaction equilibrium constant at various temperatures.

The equilibrium constants for each temperature will be estimated using Equation 13. For this, it is necessary to previously estimate the enthalpy and entropy variations of the reaction for each temperature of interest. The strategy that is applied is the following: the variations of enthalpy and entropy of formation at 298.15 K of the components involved in the reaction are estimated; from these data, the enthalpy change and the entropy change of the reaction at 298.15 K are calculated using Equations 9 and 10; next, the enthalpy and entropy variations of the reaction are calculated at the various temperatures of interest using the Kirchoff law, as stated in Equations 16 and 17:

$$\Delta H^{o}(T) = \Delta H^{o}(T_0) + \int_{T_0}^{T} \sum_{j=1} \upsilon_j \cdot C_{p_j}(T) \cdot dT \tag{16}$$

$$\Delta S^{o}(T) = \Delta S^{o}(T_0) + \int_{T_0}^{T} \frac{\sum_{j=1} \upsilon_j \cdot C_{p_j}(T)}{T} \cdot dT \tag{17}$$

According to this principle, the enthalpy change of a reaction at a certain temperature is equal to the change in enthalpy that occurs at a reference temperature plus the enthalpy required to change the temperature of the reaction medium from the reference temperature

to the temperature at which the reaction takes place. The same reasoning applies to the entropy change.

5.1.Estimation of enthalpy and entropy of formation

The following order of priority is set when establishing a value for a certain thermodynamic property: if the value has been previously determined experimentally and is available in the literature, it will be taken; if not, it will be estimated using contrasted estimation methods.

The enthalpy change of formation at 298.15 K is available in the literature for all components except for octyl levulinate. The entropy change of formation at 298.15 K is available for water and levulinic acid. Two methods will be used to estimate formation properties not available in the literature, which later will be validated.

On the one hand, the Benson method estimates both the enthalpies and entropies of formation of organic compounds in the gas phase. It has been subsequently developed to calculate the enthalpies and entropies of formation in the liquid phase. On the other hand, the Joback method allows calculating only enthalpies of formation in the gas phase. In order to be able to calculate enthalpies of formation in the liquid phase, this method must be used in combination with the Vetere method, allowing to compute enthalpies of condensation.

Benson method is based on the structural decomposition of the molecule and the integration of the energy contribution of each constituent group.[66] Joback method also requires the decomposition of the molecule into groups, and calculates the enthalpy of formation at the boiling temperature, which is added to the enthalpy of condensation, whose estimation requires the prior determination of the critical properties of the substance.[67] The application of both methods is developed in Appendixes 1 and 2, respectively. The results obtained with each estimation method are shown in Table 4.

From Table 4 it can be seen that the enthalpy of formation estimates obtained through the Benson method are practically identical to published literature values (0.0% deviation in the case of levulinic acid, and 0.63% in the case of 1-octanol). However, the results obtained using the Joback and Vetere methods are a little further from those reported in the literature (differences of 3.30% and 0.79%). The greater degree of precision of the Benson method may be due to the fact that, since the application of any estimation method

has an associated uncertainty, the error will be greater when combining two estimation methods, as occurs when applying the Joback and Vetere methods. Thus, henceforward the enthalpy of formation value obtained by Benson method is employed for octyl levulinate.

TABLE 4. Enthalpy and entropy change of formation at 298.15 K.

	ΔH^o_f (298.15 K) Literature [kJ/mol]	ΔS^o_f (298.15 K) Literature [J/K·mol]	ΔH^o_f (298.15 K) Benson [kJ/mol]	ΔS^o_f (298.15 K) Benson [J/K·mol]	ΔH^o_f (298.15 K) Joback [kJ/mol]
Levulinic acid	-683.8[a]	286.6[a]	-683.66	267.85	-706.37
1-Octanol	-426.6[b]	NA	-429.29	354.06	-423.25
Water	-285.83[c]	69.9[c]			
Octyl levulinate	NA	NA	-831.83	578.02	-861.43

[a/b/c]Data obtained from open literature and data banks[68,69,70].

In the case of the entropy of formation, the difference between the bibliographic value for levulinic acid differs by 0.28% with respect to the one estimated using the Benson method. The error, far less than 9 J/K·mol, is of the order of those reported by other publications that have estimated entropies of formation of various oxygenated organic compounds.[71] Therefore, it is considered that the Benson method offers reliable results for species of the nature of those that make up the system under study, and thus, the values of entropy of formation estimated for 1-octanol and octyl levulinate will be used.

Starting from the application of the Benson method, two possibilities arise: estimate the molecules enthalpy and entropy of formation by applying the method to all the groups that make up the molecule (results shown in Table 4); or starting from experimental results for said properties available in the literature for molecules of a similar nature and applying the method only to the groups of atoms that differentiate one from the other molecules. Emel'yanenko studied the thermodynamics of the esterification of levulinic acid with shorter chain alcohols (methanol, ethanol and butanol). As a part of this research enthalpies and entropies of formation of species involved were determined experimentally.[68] If applying the Benson method to estimate the enthalpy of formation of the 4 CH_2 groups from which 1-octanol and octyl levulinate differ from butanol and butyl levulinate and adding the results to the enthalpies of formation determined by Emel'yanenko -430.22 kJ/mol and -839.52 kJ/mol are obtained as enthalpies of formation of 1-octanol and octyl levulinate, which differ in 0.2% and 0.9% respectively from those

estimated using the Benson method for the whole molecules. Similar differences are obtained when applying this method to the estimation of the entropy of formation of 1-octanol from previous results obtained for butanol, as well as for the estimation of formation properties of butanol starting from results obtained for methanol or ethanol by Emel'yanenko. However, the entropy of formation of octyl levulinate estimated applying the Benson method for the whole molecule (578.02 J/K·mol) differs markedly (10.7%) from the value obtained applying Benson starting from butyl levulinate (515.92 J/K·mol). Taking into account the fact that the application of the Benson method based on bibliographic data for similar molecules gives practically the same results as applying the method for the entire molecule in all the cases tested except for the entropy of octyl levulinate formation; and, in addition, knowing that the application of an estimation method entails a greater error the greater the number of groups of atoms to which it is applied and complying with the principle of taking advantage of contrasted bibliographic and experimental information when available, it is considered that the results obtained by applying the Benson method only to the groups of atoms that differentiate the molecules of interest with respect to other similar ones and for which there is contrasted experimental data is the most reliable procedure to estimate the enthalpy and entropy of formation for the organic molecules involved in the system under study.

5.2.Estimation of enthalpy and entropy of the reaction

The enthalpy and entropy change of the synthesis reaction of octyl levulinate from levulinic acid and 1-octanol is calculated from the values of enthalpy and entropy of formation available in the literature or estimated, using Equations 9 and 10. The results are shown in Table 5.

TABLE 5. Estimated values for enthalpy and entropy change of the reaction at 298.15 K.

ΔH^o (298.15 K) [kJ/mol][a]	ΔH^o (298.15 K) [kJ/mol][b]	ΔS^o (298.15 K) [J/K·mol][a]	ΔS^o (298.15 K) [J/K·mol][b]
-14.95	-4.71	-38.00	26.01

[a]Values calculated using enthalpies and entropies of formation obtained from literature when available and applying the Benson method to groups of atoms differentiating molecules; [b]Values obtained applying the Benson method to all organic molecules and to their whole structure.

It is observed that the esterification reaction studied is slightly exothermic at the reference temperature regardless of the method selected for estimating the enthalpies of formation. However, in the case of entropy, great differences are obtained between methods (a sign inversion is even observed). This is due to the difference observed in the

value of the entropy of formation of octyl levulinate depending on the procedure applied for its estimation: the Benson method applied to the whole molecular structure or, alternatively, Benson applied to the CH_2 groups differentiating octyl levulinate from butyl levulinate, for which experimental data is available. As discussed above values of enthalpy and entropy of the reaction in columns 1 and 3 of Table 5 are considered the most reliable. However, differences derived from the method employed demonstrate that estimation methods are useful only for approximating values of thermodynamic properties. In this sense, using experimental values published by other authors or, when not available, determined them experimentally would be the most suitable way to obtain reliable and accurate enthalpy and entropy change values of chemical reactions.

5.3.Estimation of dependence of isobaric specific heat (C_p) from temperature

The enthalpy and entropy of reaction must be estimated at the various temperatures of interest. To do this, the Kirchoff principle will be used, expressed mathematically in Equations 16 and 17. To estimate these properties, it will be necessary to know the expressions that allow relating the specific heat of the various components to temperature. These expressions have a polynomial form (see Equation 18, where *A*, *B* and *D* are the coefficients to be estimated and *R* is the gas constant expressed in J/K·mol) and their coefficients are estimated satisfactorily, even more accurately than other methods like Lee-Kesler, for organic compounds from melting point to normal boiling point using the Rùdzicka and Domalski method.[72]

$$C_{p_j}(T) = R \cdot \left(A + B \cdot \frac{T}{100} + C \cdot \left(\frac{T}{100} \right)^2 \right) \tag{18}$$

Said method is a development that has its roots in the Benson method and that computes the contributions of the groups that constitute the molecules for the estimation of the equation of interest.[73] The development of the Rùdzicka and Domalski method for the system under study is deployed in Appendix 3. Equations 19, 20 and 21 state the results obtained for C_p estimation for levulinic acid, 1-octanol and octyl levulinate:

$$C_{p_{LA}}(T) = R \cdot \left(24.298 - 1.252 \cdot \frac{T}{100} + 0.806 \cdot \left(\frac{T}{100} \right)^2 \right) \tag{19}$$

$$C_{p_{OH}}(T) = R \cdot \left(35.040 - 9.349 \cdot \frac{T}{100} + 3.190 \cdot \left(\frac{T}{100} \right)^2 \right) \tag{20}$$

$$C_{p_{OL}}(T) = R \cdot \left(52.539 - 4.308 \cdot \frac{T}{100} + 1.675 \cdot \left(\frac{T}{100}\right)^2\right) \quad (21)$$

In order to validate the Rùdzicka and Domalski method for the studied system, the value of C_p at the reference temperature of 298.15 K estimated by the equation determined by this method is compared with the value for the same property that can be found in the literature for 1-octanol.[74] Values obtained (295.2 J/K·mol estimated and 304.0 J/K·mol bibliographic) differ only by 2.9%.

The equation that reflects the relationship between the C_p of water and temperature has been previously determined:

$$C_{p_w}(T) = 0.5263 \cdot 10^5 + 0.2412 \cdot 10^3 \cdot T - 0.8508 \cdot T^2 + 0.1 \cdot 10^{-2} \cdot T^3 \quad (22)$$

5.4.Estimation of enthalpy and entropy of the reaction at various temperatures

Equations 16 and 17, which constitute the Kirchoff principle, are used to estimate the enthalpy change and entropy change of the reaction at various temperatures. The results are presented in Table 6:

TABLE 6. Estimated values for enthalpy and entropy change of the reaction at various temperatures.

T [K]	ΔH^o [kJ/mol]	ΔS^o [J/K·mol]
298.15	-14.95	-38.00
353	-15.81	-40.55
363	-16.22	-41.68
373	-16.71	-43.02
383	-17.29	-44.56
393	-17.97	-46.30

The results show a slight increase in absolute terms in the exothermicity of the reaction as the temperature raises. A linear dependence with R^2 greater than 0.99 between 353 and 393 K is observed. On the other hand, a scarce increase in absolute terms in the entropy change is observed. The considerable variation of C_p in the range of working temperatures for the various components contributes to the state functions, enthalpy and entropy, showing non-negligible variation with temperature.

5.5.Estimation of equilibrium constant of the reaction

Table 7 shows the values of the thermodynamic equilibrium constant for the esterification of levulinic acid with 1-octanol estimated for various temperatures. These equilibrium constants have been obtained by applying the Van't Hoff equation (Equation 13) from the enthalpies and entropies of reaction estimated and presented in Table 6.

TABLE 7. Estimated values of equilibrium constant of the reaction at different temperatures.

T [K]	K	ΔG^o [kJ/mol]
298.15	4.32	-3.62
353	1.67	-1.50
363	1.44	-1.09
373	1.24	-0.66
383	1.07	-0.22
393	0.93	0.23

From results presented in Table 7, two aspects are worth noting: on the one hand, the equilibrium constants are greater than 1 except at 393 K. This means that, in equilibrium, for any of the working temperatures excluding 393 K, the moles of products would be, theoretically, superior to the moles of reactants. In other words, the forward reaction is favoured over the reverse reaction, except if working at 393 K, when the reverse reaction would be favoured. Table 7 also shows the estimated Gibbs free energy of reaction by applying Equation 11 and using estimated values for enthalpy and entropy change of the reaction from Table 6. The sign inversion as the temperature increases is characteristic of exothermic reactions in which the entropy of products is smaller than that of reactants: given that all systems tend to minimize energy, the forward reaction becomes unfavoured when the increase in temperature produces that the energy loss associated to enthalpy realising is less important that the increment of energy associated to the decrease in entropy of the system.

On the other hand, the equilibrium constant decreases as the temperature increases. This is a direct consequence of the application of Le Châtelier's principle in an exothermic reaction: since the heat of reaction is a product of the direct reaction, this will be less favoured at high temperatures as the internal energy of the system is greater the higher the temperature. In addition to observing a logical trend for the equilibrium constant, it moderately varies by 44.0% between extreme temperatures (353-393 K). This fact is due to the moderate exothermicity of the reaction: if the reaction releases moderate thermal energy, the increase in temperature and therefore in the internal energy of the system

makes the progress of the reaction a relatively important factor in moving the system away from the equilibrium.

6. EXPERIMENTAL RESULTS AND DISCUSSION

In this section, the values for the equilibrium constant of the reaction under study as well as the enthalpy and entropy determined from the experimental results are presented. Likewise, these values are compared with those obtained by applying estimation methods (Chapter 5). Finally, a discussion is offered around the results obtained in the purification operations of octyl levulinate as well as around the experimental determination of its C_p.

6.1.Optimization of chromatographic method

Before carrying out the experiments to study the thermodynamics of the system, a set of tests was carried out to design an analysis method with the following objectives: that the species are effectively separated in the chromatographic column and that high resolution chromatographic peaks are obtained.

The selected chromatographic method is characterized by the implementation of two temperature ramps of 50 ºC/min and 40 ºC/min, respectively, preceded each by temperature plateaus at 100 ºC and 150 ºC for 1.5 min, culminating the evolution of the oven temperature with a plateau at 240 ºC that is hold for 4 minutes; an inlet pressure of 1.2 bar, a maximum total flow of 328.66 mL/min and a split ratio of 200:1. The analysis time is fixed at 10 minutes. The retention times of the species present in the system are depicted in Table 8.

TABLE 8. Retention time of species present in the reaction system.

Retention time [min]			
1-Octanol	Octyl levulinate	NI	Levulinic acid
3.7	6.6	6.9	7.2

An unidentified substance appears for a retention time of around 6.9 minutes. However, since its presence in the reaction medium is practically negligible throughout the experiments, especially when the reaction is close to equilibrium, its presence does not affect the thermodynamic characterization of equilibrium.

6.2.Calibration

The use of the gas chromatograph together with the mass-selective detector allows to analyse the samples that are extracted from the reaction medium, obtaining for each substance a chromatographic peak area. The analysis of these peaks allows quantifying the area percentage corresponding to each substance.

The calibration is carried out to obtain the equations that relate the chromatographic area percentages with the molar fraction of each substance present in the reaction medium, which are presented in Table 9. The calibration curves are built from the chromatographic response obtained for a certain number of samples with a known molar composition of the various species that make up the system. Following the procedure detailed in Appendix 6, calibration equations for 1-octanol, levulinic acid and octyl levulinate have been obtained from between 11 and 14 samples of variable composition. The samples have been prepared in such a way that they cover the composition of the reaction medium for all the experiments carried out and from the beginning of the reaction until the equilibrium is reached.

TABLE 9. Calibration equations. Uncertainties have been calculated assuming a normal distribution with 95% confidence.

Specie	Calibration equation	R^2
Levulinic acid	$(-0.0028 \pm 0.0004)\cdot A_{LA}^2 + (0.053 \pm 0.003)\cdot A_{LA}$	0.98
1-Octanol	$(0.0078 \pm 0.0009)\cdot A_{OH} + 0.04 \pm 0.03$	0.97
Octyl levulinate	$(0.0047 \pm 0.0005)\cdot A_{OL} + 0.05 \pm 0.03$	0.98

Since water does not generate a chromatographic response when using the analysis method, its mole fraction must be estimated assuming that the sum of fractions of 1-octanol, levulinic acid, octyl levulinate, and water must add up to 1. The error made by underestimating the presence of the unrecognized substance when completing this balance is negligible if it is assumed that the percentage in chromatographic area is of the order of its mole fraction, since the percentage in area of this substance is barely higher than 5% at the beginning of the experiments and its presence falls below 0.5% at equilibrium.

Since the reaction between levulinic acid and 1-octanol generates one mole of water per every mole of octyl levulinate, one would expect the mole fractions of both products to always be the same, experimental error aside. However, it is observed that, if instead of assuming that the sum of mole fractions of the four species involved is one, the mole fraction of water is estimated assuming that it must be equal to that of octyl levulinate,

the balance of mole fractions is not always fulfilled: errors of between 15 and 20% are observed in experiments starting from a molar ratio LA:OH of 1:1, between 9 and 13% for initial molar ratio of 1:2 and between 6 and 1% for molar ratios 4:1 and 8:1.

In the experiments started with molar ratios closer to unity, that is, those experiments in which there will be a greater amount of water at equilibrium because a greater number of moles of both reactants will have been transformed, it is in those that the greatest differences are obtained. Furthermore, in all these experiments, the estimated mole fraction of water assuming sum of all mole fractions equals one is less than the mole fraction of octyl levulinate. These facts could be indicative that water shows a greater tendency to adsorb in the solid phase (surface of the ion exchange resin used as a catalyst) than other substances, perhaps because it has a smaller molecular size and is easier to diffuse through the pores of the resin. This would mean that the mole fraction of water would be higher in the solid phase than in the bulk liquid, triggering these differences in the mole fraction between both products. This hypothesis is considered probable given the high amount of catalyst (between 2.5 and 5% of the total mass of the reaction medium) injected into the reactor, which makes the solid phase a factor to take into account for the destabilization of the composition in the liquid phase. Since the object of study is the composition of the liquid phase at equilibrium, the effect on the determination of the thermodynamic properties of the reaction of this fact is null if the exposed hypothesis was true.

6.3.Previous catalyst screening

As exposed in Section 4.5, a catalyst screening was carried out in order to determine qualitatively if there was one ion exchange resin that triggered a faster equilibrium reaching. Three different ion exchange resins were tested (acid macroreticular, acid gel-type and basic). Experiments were carried out at 100 ºC and loading an initial molar ratio of reactants 1:1. 5 g of catalyst were injected. No phase separation was observed in any experiment and similar times were needed to reach equilibrium so no appreciable differences in terms of reaction rate were outlined. Figure 6 shows the evolution of octyl levulinate molar fraction with time for the three experiments.

As it can be seen in Figure 6, using CT-224 as catalyst allows to reach equilibrium approximately 60 minutes faster than using A-35 or CTA-196. However, CT-224 was discarded as the resin to use for main experiments due to the differential operational

difficulties associated to its use compared to A-35 and CTA-196. CT-224 resin is gel-type, which means that it has a higher capacity to adsorb water and swell. It was observed during the screening runs that this resin adsorbed environmental humidity during the transfer operations prior to its injection into the reactor, which led to the formation in the injector of a cohesive mass of particles that made it difficult to inject it to the reactor. Among the two macroporous resins, A-35 has been considered the most appropriate since its pretreatment is simpler, as discussed in Chapter 4. However, it is worth remarking that CTA-196 was also effective from the point of view of the reaction rate, which means that the acid/basic character of the resin employed does not have a notable effect.

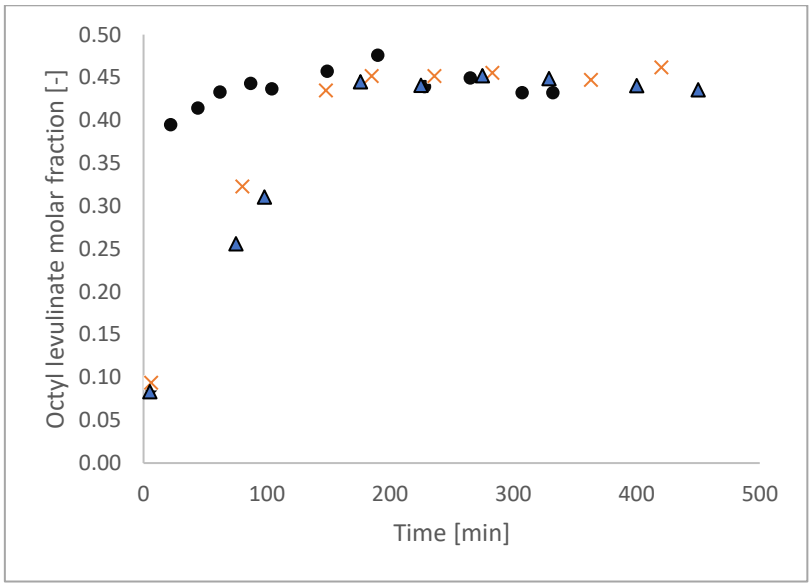


FIGURE 6. Evolution of molar fraction of octyl levulinate with time. Previous catalyst screening experiments carried at 100 ºC and initial molar ratio LA:OH of 1:1. 5g of catalyst injected of A-35 (×), CT-224 (•) and CTA-196 (▲).

6.4.Experimental determination of equilibrium constant

As explained in Section 4.5, twelve experiments have been carried out, working at three different temperatures, that is 80, 100 and 120 ºC, and starting from four different molar ratios between reactants ($R^{o}_{LA:OH}$), that is 1:1, 1:2, 1:4 and 1:8. Four of these experiments have been repeated to ensure the reproducibility of the obtained results.

As developed in Section 4.3, for each experiment samples were taken with variable frequency as the reaction progressed and they were analysed to determine the composition of the reaction medium. It was considered that chemical equilibrium was reached when the composition of the medium did not vary significantly. Then, between 2 and 5

additional samples were taken. From the analysis of the samples obtained at equilibrium, the molar fractions of the different components in the system are obtained.

As discussed in Chapter 3, the equilibrium constant of the reaction can be calculated as the product of the ratio of mole fractions and the ratio of activity coefficients, all multiplied by the Poynting factor to quantify the deviation of the system from ideality at high pressures, as follows:

$$K = \prod_{j=1} a_j = \prod_{j=1} x_j \cdot \prod_{j=1} \gamma_j \cdot K_{\wp} = K_x \cdot K_\gamma \cdot K_{\wp} \tag{23}$$

Unlike the ratio of activity coefficients (K_γ) and the Poynting factor ($K_{\wp}$), the mole fractions ratio (K_x) can be calculated directly from the experimental results.

Table 10 shows the equilibrium mole fractions of the four components involved in the reaction as well as the ratio between said mole fractions. The reported mole fractions correspond to the average value of the 2-5 samples taken at equilibrium for each experiment. The exposed ratios between mole fractions correspond to the average value of K_x calculated for each of the samples taken at equilibrium.

From the mole fractions shown in Table 10, the conversion (X) achieved in the reaction can be calculated according to Equation 24, taking into account that the limiting reactant is levulinic acid:

$$X = \frac{x_{LA,0} - x_{LA}}{x_{LA}} \tag{24}$$

where $x_{LA,0}$ is the initial molar fraction of levulinic acid and x_{LA} is the molar fraction at equilibrium of said component for each experiment. Values of conversion of approximately 70% were obtained for experiments carried out with an initial molar ratio LA:OH of 1:1. Starting from the assumption that thermodynamical equilibrium is not affected by the initial composition of the reaction medium, a decrease in the initial molar ratio, which triggers that an increasing number of moles of 1-octanol could not react, causes a higher percentage of moles of levulinic acid to react, leading to higher conversions. Thereby, conversions of around 88% were obtained starting from initial molar ratios of 1:2, and of 90-94% for initial molar ratios of 1:4 and 1:8.

The selectivity of the reaction between levulinic acid and 1-octanol, under tested conditions, is practically 100% towards the production of octyl levulinate, since no side

reactions were detected. As discussed in Section 6.1, only one specie is formed as a by-product. This substance has not been identified, but given the characteristics of its mass spectrum, it could be a levulinate with a lower molecular weight than octyl levulinate, probably a butyl levulinate. Indicatively, this substance would be formed from the esterification of the levulinic acid present in the system with butanol, a molecule that would be formed from the dimerization of 1-octanol. However, the presence of butanol in the system has not been detected, which is why this hypothesis cannot be validated.

This by-product appears in greater quantity (up to 5% in chromatographic area) in the first moments of the reaction (first 60 minutes), when the concentration of 1-octanol and levulinic acid are higher. However, its presence decreases until it practically disappears when equilibrium is reached. It seems, therefore, that the reaction or set of reactions that trigger the appearance of this by-product are reversible and, under the tested conditions, are disadvantaged with respect to the targeted esterification reaction. Other authors[75,51] have reported the occurrence of side reactions in systems with levulinic acid and short-chain alkenes (butene). These reactions are related to the hydration of the alkene generating the corresponding alcohol or its oligomerization. However, in the scarce literature around thermodynamic studies of the production of levulinates from alcohols, no secondary reactions are mentioned that produce a decrease in selectivity towards the desired levulinate.

TABLE 10. Molar fractions of levulinic acid, 1-octanol, octyl levulinate and water at equilibrium and molar fractions ratio (K_x). Uncertainties have been calculated assuming a normal distribution with 95% confidence.

Temperature [ºC]	$R^o_{LA:OH}$	$x_{LA}\cdot10^2$	$x_{OH}\cdot10^2$	$x_{OL}\cdot10^2$	$x_W\cdot10^2$	K_x
80	1:1	14.8 ± 0.3	12.74 ± 0.08	44.56 ± 0.09	27.9 ± 0.3	6.5 ± 0.2
80	1:1	15.0 ± 0.4	12.9 ± 0.3	44 ± 2	28.1 ± 0.9	6.39 ± 0.05
80	1:1	14.8 ± 0.4	12.80 ± 0.06	44.3 ± 0.2	28.10 ± 0.08	6.5 ± 0.2
100	1:1	16.2 ± 0.8	14.1 ± 0.4	44 ± 2	26.1 ± 0.8	5.3 ± 0.6
100	1:1	15.2 ± 0.7	13.8 ± 0.2	44.50 ± 0.04	26.5 ± 0.4	5.5 ± 0.3
100	1:1	15.43 ± 0.07	14.5 ± 0.4	43.7 ± 0.2	26.37 ± 0.09	5.2 ± 0.2
120	1:1	16.2 ± 0.9	14.8 ± 0.3	43.43 ± 0.04	25.6 ± 0.8	4.8 ± 0.4
120	1:1	15.3 ± 0.7	15.3 ± 0.7	43.43 ± 0.04	26 ± 1	4.5 ± 0.6
120	1:1	15.8 ± 0.9	15.53 ± 0.08	40.9 ± 0.3	28 ± 1	4.5 ± 0.3
80	1:2	3.9 ± 0.6	34 ± 2	38 ± 2	24 ± 2	6.7 ± 0.2
100	1:2	3.7 ± 0.5	37.1 ± 0.4	34.3 ± 0.9	24.890 ± 0.009	5.8 ± 0.9
120	1:2	4.1 ± 0.8	37.4 ± 0.8	34.0 ± 0.7	25 ± 2	5 ± 2
80	1:4	1.25 ± 0.09	61.3 ± 0.4	19.2 ± 0.3	18.3 ± 0.2	4.5 ± 0.3
100	1:4	1.48 ± 0.06	62.3 ± 0.7	18.7 ± 0.4	17.5 ± 0.6	3.7 ± 0.2
120	1:4	1.75 ± 0.07	62.1 ± 0.7	19 ± 2	17.6 ± 0.6	3.00 ± 0.05
80	1:8	0.9 ± 0.2	73 ± 2	11 ± 2	15.9 ± 0.3	2.76 ± 0.06
80	1:8	0.65 ± 0.08	75.1 ± 0.8	8.6 ± 0.7	15.58 ± 0.11	2.75 ± 0.09
80	1:8	0.69 ± 0.09	74.6 ± 0.9	9.9 ± 0.7	15 ± 2	2.8 ± 0.4
100	1:8	0.96 ± 0.09	72.4 ± 0.9	11 ± 2	15.8 ± 0.3	2.2 ± 0.5
120	1:8	1.03 ± 0.09	73.85 ± 1.01	9.7 ± 0.8	15.4 ± 0.1	1.95 ± 0.04

TABLE 11. Activity coefficients of levulinic acid, 1-octanol, octyl levulinate and water at equilibrium and molar activity coeffients ratio (K_γ). Uncertainties have been calculated assuming a normal distribution with 95% confidence.

Temperature [ºC]	$R^o_{LA:OH}$	γ_{LA}	γ_{OH}	γ_{OL}	γ_W	K_γ
80	1:1	1.5475 ± 0.0005	1.21943 ± 0.00013	1.1804 ± 0.0002	4.3840 ± 0.0008	2.7424 ± 0.0006
80	1:1	1.54 ± 0.02	1.226 ± 0.008	1.182 ± 0.015	4.38 ± 0.06	2.76 ± 0.03
80	1:1	1.528 ± 0.007	1.229 ± 0.003	1.183 ± 0.003	4.382 ± 0.012	2.759 ± 0.006
100	1:1	1.566 ± 0.014	1.135 ± 0.002	1.147 ± 0.003	3.966 ± 0.012	2.557 ± 0.017
100	1:1	1.568 ± 0.009	1.136 ± 0.003	1.146 ± 0.002	3.973 ± 0.018	2.557 ± 0.017
100	1:1	1.557 ± 0.002	1.1377 ± 0.0012	1.1489 ± 0.0006	3.968 ± 0.002	2.57412 ± 0.00105
120	1:1	1.5806 ± 0.0006	1.0699 ± 0.0002	1.1269 ± 0.0009	3.533 ± 0.006	2.354 ± 0.003
120	1:1	1.5805 ± 0.0009	1.0691 ± 0.0006	1.124 ± 0.002	3.551 ± 0.015	2.362 ± 0.008
120	1:1	1.544 ± 0.005	1.0755 ± 0.0009	1.1464 ± 0.0014	3.477 ± 0.012	2.4005 ± 0.0108
80	1:2	1.83 ± 0.05	1.121 ± 0.006	1.150 ± 0.016	4.652 ± 0.109	2.60 ± 0.03
100	1:2	1.793 ± 0.013	1.06795 ± 0.00009	1.128 ± 0.006	4.12 ± 0.02	2.428 ± 0.017
120	1:2	1.746 ± 0.012	1.0336 ± 0.0017	1.09735 ± 0.00108	3.662 ± 0.009	2.23 ± 0.03
80	1:4	2.105 ± 0.003	1.0448 ± 0.0003	1.2680 ± 0.0004	4.721 ± 0.003	2.722 ± 0.007
100	1:4	1.897 ± 0.004	1.0276 ± 0.0013	1.1892 ± 0.0012	4.201 ± 0.013	2.563 ± 0.009
120	1:4	1.724 ± 0.012	1.0140 ± 0.0008	1.133 ± 0.007	3.701 ± 0.016	2.40 ± 0.02
80	1:8	2.26 ± 0.03	1.021 ± 0.003	1.39 ± 0.03	4.755 ± 0.006	2.86 ± 0.03
80	1:8	2.291 ± 0.012	1.0187 ± 0.0009	1.413 ± 0.013	4.766 ± 0.004	2.886 ± 0.013
80	1:8	2.30 ± 0.02	1.0186 ± 0.0014	1.388 ± 0.013	4.82 ± 0.07	2.861 ± 0.009
100	1:8	1.933 ± 0.004	1.0144 ± 0.0013	1.260 ± 0.013	4.205 ± 0.003	2.70 ± 0.02
120	1:8	1.686 ± 0.006	1.0086 ± 0.0005	1.168 ± 0.005	3.691 ± 0.013	2.536 ±0.014

Having calculated the equilibrium constant referring to the mole fractions, the next step is to calculate the equilibrium constant referring to the activity coefficients (K_γ). These coefficients can be estimated from the UNIFAC Dortmund model, a predictive method that requires the structure of the molecules as the only input information. The application of this model to the reference system is developed in Appendix 5.

The values for the activity coefficients for the various components for the various experiments, as well as the values of the ratio between them (K_γ) are shown in Table 11. Activity coefficients for 1-octanol and octyl levulinate are in any case close to one (maximum values of 1.23 and 1.41, respectively), which means that the behaviour of these molecules in the reaction medium is close to ideality. On the opposite, water and levulinic acid, which are the most polar species in the system, show high values for their activity coefficients (maximum values of 4.77 and 2.30, respectively). In addition, these coefficients increase as the operation temperature decreases. At lower temperatures, less mobility of the molecules and greater proximity is at play, which implies greater interactions, and hence a greater deviation from the ideal behaviour.

These high values of the activity coefficients, which trigger the equilibrium constants referred to activity coefficients to deviate from 1, demonstrate the importance of considering the non-ideality of the liquid phase to calculate the thermodynamic equilibrium constants.

The last step before calculating the equilibrium constants is the calculation of the Poynting factors. These are a function of the working pressure and the molar volume of the substances, which in turn is a function of the working temperature. Equation 15 was used to calculate this factor. The procedure for estimating the molar volumes of the various molecules is depicted in Appendix 4. Table 12 shows the values obtained for this parameter.

Poynting correction factors are, in any case, between 12 and 14% higher than unity, which means that the working pressure does have an effect on the activity coefficients of the compounds in the system. Therefore, not taking it into account for the calculation of the equilibrium constants would mean underestimating its value by 12-14%.

TABLE 12. Poynting factors. Uncertainties have been calculated assuming a normal distribution with 95% confidence.

Temperature [ºC]	$R^{o}_{LA:OH}$	K_{φ}
80	1:1	1.12891 ± 0.00003
80	1:1	1.130 ± 0.002
80	1:1	1.1301 ± 0.0002
100	1:1	1.125 ± 0.002
100	1:1	1.126 ± 0.002
100	1:1	1.12641 ± 0.00011
120	1:1	1.1210 ± 0.0006
120	1:1	1.123 ± 0.002
120	1:1	1.118 ± 0.002
80	2:1	1.136 ± 0.005
100	2:1	1.1292 ± 0.0009
120	2:1	1.125 ± 0.002
80	4:1	1.1363 ± 0.0003
100	4:1	1.1315 ± 0.0007
120	4:1	1.127 ± 0.002
80	8:1	1.1343 ± 0.0006
80	8:1	1.13387 ± 0.00018
80	8:1	1.137 ± 0.004
100	8:1	1.1298 ± 0.0005
120	8:1	1.1255 ± 0.0002

TABLE 13. Equilibrium constants. Uncertainties have been calculated assuming a normal distribution with 95% confidence.

Temperature [ºC]	$R^{o}_{LA:OH}$	K
80	1:1	20.2 ± 0.7
80	1:1	19.9 ± 0.5
80	1:1	20.2 ± 0.5
100	1:1	15 ± 2
100	1:1	15.8 ± 0.9
100	1:1	15.2 ± 0.5
120	1:1	13 ± 2
120	1:1	12 ± 2
120	1:1	12.0 ± 0.9
80	2:1	19.8 ± 0.4
100	2:1	16 ± 3
120	2:1	11 ± 5
80	4:1	14 ± 2
100	4:1	10.6 ± 0.6
120	4:1	8.1 ± 0.2
80	8:1	9.0 ± 0.3
80	8:1	9.0 ± 0.3
80	8:1	9 ± 2
100	8:1	7 ± 2
120	8:1	5.6 ± 0.2

Table 13 shows the values for the experimental equilibrium constants of the esterification reaction of levulinic acid with 1-octanol. These values are a direct result of the application of Equation 23, based on the experimental values of K_x, K_γ and K_φ for each experiment. Three aspects are worth discussing from the results obtained: on the one hand, the equilibrium constant decreases when the temperature increases, regardless of the initial composition of the system. This aspect confirms what had already been concluded from the estimated equilibrium constants, that the reaction under study is exothermic. That is, since heat is a reaction product, the higher the operating temperature, the less the reaction moves towards the products to approach equilibrium.

On the other hand, the equilibrium constants are clearly higher (an order of magnitude) than those obtained by estimation methods. Experimental error aside, two elements can explain the differences between the theoretical and experimental values: on the one hand, it has been observed experimentally that the available analytical system has improvable sensitivity for the detection of levulinic acid, generating chromatographic peaks that, especially in the experiments that started with a smaller amount of levulinic acid, were overlapped with noise up to a point. This could have been the cause if, in the experiments starting from a 1:1 molar ratio, in which the presence of levulinic acid in the equilibrium was more important, generating well-defined peaks, the experimental equilibrium constants had been of the same value order of those estimated. However, an even larger difference is obtained between the theoretical and experimental equilibrium constants for such experiments.

Therefore, the difference between theoretical and experimental values must be due to the other cause: the error associated with the theoretical methods for estimating the enthalpy and entropy of the reaction. As seen in Chapter 5, differences of almost 100% in the estimation of the reaction enthalpies are observed depending on the method used to estimate the enthalpies of formation of the compounds. In the case of entropy, a sign change of the parameter is even observed depending on the estimation method used. This uncertainty when estimating these parameters generates an even greater uncertainty in the estimation of the equilibrium constants, since for this the estimated enthalpy and entropy values must be located in an exponential term.

Finally, a decreasing trend seems to be observed in the value of the equilibrium constant as the presence of levulinic acid in the system decreases, that is, as the initial molar ratio LA:OH decreases. It would be rash to claim that the equilibrium constant

depends on the composition of the system. And more so when said constants practically do not vary between the experiments carried out starting from a 1:1 molar ratio with respect to those started with a 1:2 ratio. The explanation for this observation could be the following: given the low sensitivity of the analytical system when it comes to detecting levulinic acid in low concentrations, its chromatographic peaks generated in the experiments at initial molar ratios 1:4 and 1: 8 are less defined, which implies some error in the chromatographic area determinations. Such error has a negligible effect when the levulinic acid peak is larger (LA:OH molar ratios of 1:1 and 1:2).

Therefore, if this hypothesis is assumed to be true, it is the experiments carried out starting from 1:1 and 1:2 molar ratios between reactants that yield the most reliable values for the thermodynamic equilibrium constants.

6.5.Experimental determination of enthalpy and entropy change of the reaction

Experimental values for the standard enthalpy and entropy change of the reaction can be calculated from the slope and intercept of the plot of the natural logarithm of the equilibrium constant versus the inverse of the temperature according to Equation 13. Figure 7 shows this representation for experimental results obtained for experiments carried out at initial molar ratios LA:OH of 1:1 and 1:2, which, as discussed in previous section, are considered the most reliable.

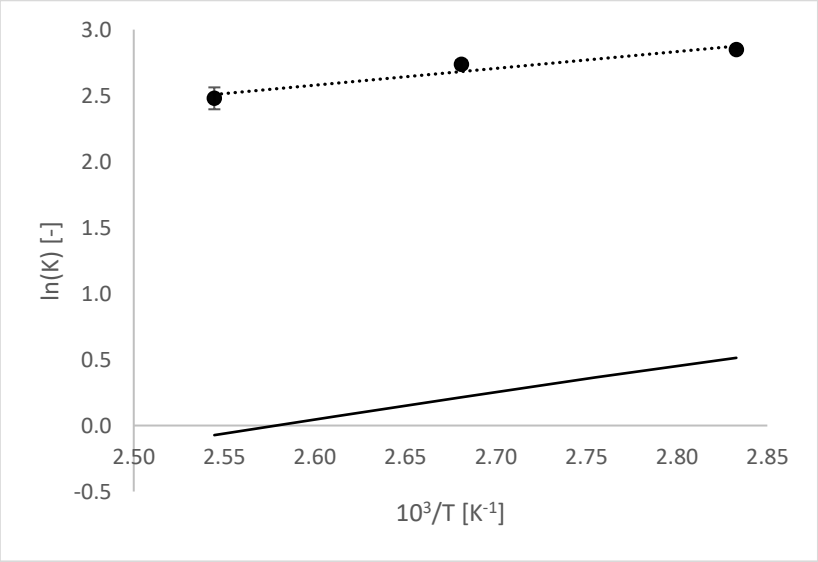


FIGURE 7. Estimated (-) and experimental values of the equilibrium constant assuming ΔH^O *and* ΔS^O *are independent from T.*

Equation 25 corresponds to the regression of the experimental points represented.

$$\ln(K) = (1799 \pm 248) \cdot \frac{1}{T} - (2.1 \pm 0.7) \quad (25)$$

Table 14 shows the experimental values of enthalpy and entropy change of the reaction assuming these parameters to be constant with temperature. Assuming this non-dependence on temperature would not be entirely justified considering the relatively low value of R^2 of the linear regressions (0.94), meaning that the slope (related with enthalpy) and intercept (related with entropy) change significantly from one experimental point to another. The large width of the confidence intervals for the slopes and the intercepts would be explained by the fact that the lines are constructed from only three experimental points (three assayed working temperatures). Although the experimental values for initial molar ratios LA:OH of 1:4 and 1:8 have not been graphically represented, the enthalpy value that would be obtained from their regression is not significantly different from that obtained from the experimental values for molar ratios 1:1 and 1:2. However, the entropy values would show significant differences due to the deviation between the values of the equilibrium thermodynamic constant of the reaction.

TABLE 14. Estimated and experimental values of enthalpy change and entropy change of the reaction.

ΔH^o Estimated [kJ/mol]	$\Delta H^o \neq f(T)$ [kJ/mol]	ΔH^o (298.15 K) = f(T) [kJ/mol]	ΔS^o Estimated [J/K·mol]	$\Delta S^o \neq f(T)$ [J/K·mol]	ΔS^o (298.15 K) = f(T) [J/K·mol]
-14.95	-15 ± 2	-13 ± 2	-38.00	-17 ± 6	-12 ± 5

Enthalpy and entropy change of the reaction under study are also calculated from experimental results assuming a dependence between these two functions with temperature. That means that enthalpy and entropy are determined at a reference temperature (298.15 K). Values obtained are shown in Table 14, together with those calculated assuming inexistent relation between enthalpy and entropy and temperature.

The Kirchoff law must be applied to carry out these calculations. In this sense, Equation 13 is transformed into Equation 26 when substituting enthalpy and entropy changes for their functions of temperature:

$$\ln(K) = -\frac{\Delta H^o(T_0)}{R \cdot T} - \frac{\int_{T_0}^{T} \sum_{j=1} \upsilon_j \cdot C_{p_j}(T) \cdot dT}{R \cdot T} + \frac{\Delta S^o(T_0)}{R} + \frac{\int_{T_0}^{T} \frac{\sum_{j=1} \upsilon_j \cdot C_{p_j}(T)}{T} \cdot dT}{R} \quad (26)$$

where T_0 is the reference temperature of 298.15 K. The functions $C_{pj}(T)$ are polynomials and therefore, so are the integrals of these functions. Thus, Equation 26 can be simplified into Equation 27, where *f(T)* represents these polynomial functions of temperature.

$$\ln(K) + f(T) = -\frac{\Delta H^o(T_0)}{R \cdot T} + \frac{\Delta S^o(T_0)}{R} \tag{27}$$

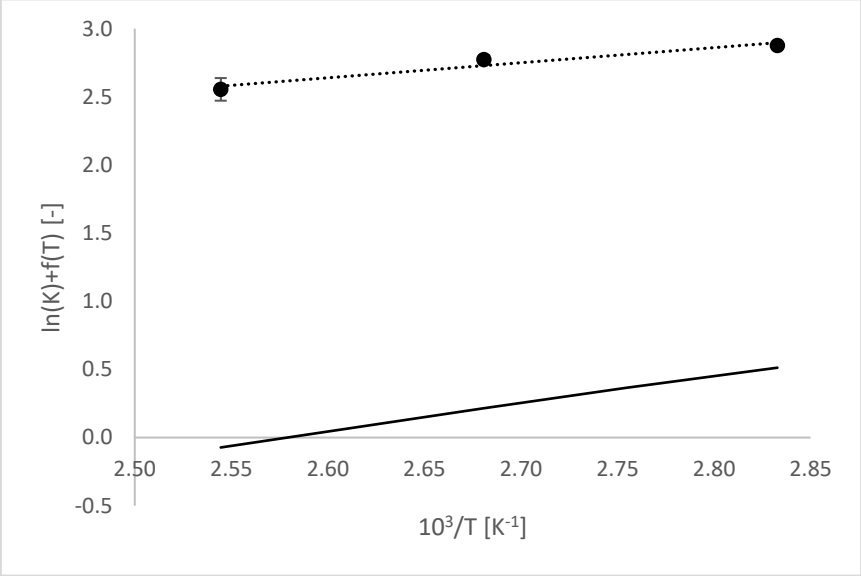


FIGURE 8. Estimated (-) and experimental values of the equilibrium constant assuming ΔH^O *and* ΔS^O *are a function of T.*

Figure 8 shows the representation of the natural logarithm of the experimental values of equilibrium constant plus the function of temperature resulting of the application of the Kirchoff law versus de inverse of temperature. Equation 28 corresponds to the regression of the experimental points represented.

$$\ln(K) + f(T) = (1588 \pm 247) \cdot \frac{1}{T} - (1.5 \pm 0.7) \tag{28}$$

There are noticeable differences between Figures 7 and 8 and between Equations 25 and 28, indicating that the enthalpy and entropy change of the reaction are not completely independent from temperature, meaning that assuming said functions constant with temperature introduces a significant element of error in the determination of the equilibrium constants of the reaction. Differences of up to 13% for enthalpy at 298.15 K and 29% for entropy at 298.15 K are observed in magnitude values depending on if these state functions are considered a function of temperature or not.

The values reported in Table 14 confirm the exotermicity of the esterification under study. Besides, a negative entropy change is observed, which means that the entropy of

the products is less than that of the reactants. This combination (negative enthalpy and negative entropy) will make the reaction thermodynamically spontaneous for one temperature range and non-spontaneous for another temperature range. That is to say, there will be a range of temperatures for which the equilibrium will be defined by a greater molar presence of products than of reactants and there will be another range of temperatures in which the inverse will occur.

On the other hand, the experimental values are in good agreement with those estimated theoretically, especially in the case of enthalpy (maximum difference of 13%). In the case of entropy, the differences (maximum 68%) are considerably larger. This may be due, as commented in Section 5.2, to the greater difficulty of estimating the entropies of formation with respect to the enthalpies. In fact, the great variability in the reaction entropy change values was already observed depending on the method used for estimating the entropy of formation of octyl levulinate.

Finally, the experimental results for the enthalpy and entropy changes of reaction are of the order of those obtained by Emel'yanenko *et al.* for esterifications of levulinic acid with shorter chain alcohols, reporting enthalpy values of -14.1, -10.3 and -11.3 kJ/mol for esterifications with methanol, ethanol and butanol, respectively[68]. Likewise, experimental values for the entropy of -17, -126 and -38 J/K·mol, respectively, are obtained.[75] The coincidence in the order should be indicative of a certain degree of validity of the experimental results obtained: since for the focused reaction the bonds that are broken and those that are formed are exactly the same as in the reactions studied by Emel'yanenko *et al.*, the energy that is emitted in said transformation must be similar a priori. The case of the entropy change is quite different. Although the chemical bonds of the species involved in the chemical reaction is the only input information that most entropy estimation methods demand, the entropy of a compound is a function of the number of microstates of said compound at a given temperature, being it a function of the whole structure of the chemical compound, being the cause of greater differences between entropies mentioned.

6.6.Purification of octyl levulinate

The objective of this experimental section was to obtain octyl levulinate of the highest possible purity from the product distribution final mixture collected from the experiments carried out. Once each experiment was finished, the reactor was emptied using vacuum

equipment and the mixture collected was filtered at atmospheric pressure to separate the catalyst particles. The liquid phases obtained as filtrate were stored and accumulated in the same container at room temperature until enough amount for proceeding to its separation was available. The composition of the mixture present in said container that was the feed for the separation operations tested for the purification of octyl levulinate is shown in Table 15.

TABLE 15. Molar fractions obtained in the successive stages of the octyl levulinate purification operations.

	Feed	Residue Vigreux	Organic phase from liquid-liquid extraction	Distillate vacuum distillation	Residue vacuum distillation
Levulinic acid	0.13	0.01	0.03	0.01	0.01
1-Octanol	0.34	0.05	0.32	0.08	0.04
Octyl levulinate	0.33	0.94	0.35	0.91	0.95

The first separation operation method tested was the simple distillation in a Vigreux column. Approximately 200 mL of feed was placed in the reboiler of the column, a balloon wrapped in an electric blanket that provided the necessary heat to boil the content of the reboiler. The heat supplied was controlled with a potentiometer. The Vigreux column consisted of a glass cylinder 200 mm high and 20 mm internal diameter filled inside with a set of conical-shaped glass slits, evenly distributed, which provide a better distribution of the liquid in the column, as well as a greater turbulence of the gas and the liquid, improving thereby the contact between phases and therefore the separation with respect to a conventional simple distillation column without packing. A total condenser with tap water and a distillate collection balloon completed the set up. The reboiler temperature was increased from 100 ºC to approximately 300 ºC, obtaining distillate fractions with increasing concentration of levulinic acid. The mixture that remained in the reboiler reached a molar purity of 94% in octyl levulinate, the least volatile component.

Despite having obtained a high purity of the desired product and having achieved a recovery yield of practically 100% (the presence of octyl levulinate in the distillate was practically negligible), two elements prevent the simple distillation carried out from becoming a successful operation of purification: on the one hand, the high boiling points of the species, especially levulinic acid, make it necessary to provide high amounts of heat to the reboiler; on the other hand, subjecting the mixture of components to such high

temperatures triggered humin formation reactions. Such undesired reactions would be triggered by the presence of levulinic acid[76,77] in the system and lead to the appearance of recalcitrant and insoluble substances that gave a black coloured aspect to the residue obtained in the reboiler.

Two possibilities were tested with the aim of avoiding the formation of humic compounds, both aimed at reducing the presence of levulinic acid in the system before distillation. On the one hand, the feed mixture was subjected to a low temperature (5ºC) in a refrigerator to favour the crystallization of levulinic acid or the product of interest. However, after 24 h there was no crystallization and the system continued to be homogeneous. On the other hand, the liquid-liquid extraction with water of the mixture of components and decantation was tested. The procedure applied was as follows: add 300 mL of feed and 150 mL of water to a 500 mL separatory funnel and shake gently. Vigorous agitation was found to inevitably lead to emulsification of the feed in the water. Then decant for 1 hour. Separate the aqueous phase and add additional 150 mL of water to the funnel. Shake vigorously and allow to decant for 24 h. Separate the aqueous phase. The high solubility of levulinic acid in water allowed reducing the presence of this compound in the feed from 13% mole to 3%.

The organic phase resulting from extraction (with a mole fraction of 3% in levulinic acid) was fed to the reboiler of a laboratory rectifying column 2 m high, 2 L reboiler capacity, packed with a random ring-type packing and equipped with a condenser with tap water, automatic reflux valve and vacuum pump. This set up allows reproducing the distillation carried out previously in the Vigreux column but with larger volumes of liquid and gas in the column, refluxing a part of the condensate to the column and working at pressure below atmospheric, which allows the content to boil at lower temperatures.

Throughout the operation, fractions of distillate with an increasing composition in octyl levulinate were extracted. The maximum purity of octyl levulinate achieved in the distillate was 91% mole. 240 g of mixture with a purity of octyl levulinate of 95% remained in the reboiler at the end of the operation. The residue at the end of the rectification had a dark orange coloration and, although the formation of humins and insoluble compounds was notably avoided, small insoluble particles did appear in very low amounts that were separated from the mixture by gravity filtration. The liquid medium resulting from said filtration was used to prepare the mixtures of known composition for calibrating the chromatographic response.

Being the recovery yield of octyl levulinate from washing and decantation greater than 99% and 32% from rectification, the total yield of the purification operations carried out is 32%, calculated as the quotient between the recovered mass of octyl levulinate and the available mass before the purification operations.

6.7.Determination of specific heat (C_p) of octyl levulinate

The specific heat at constant pressure of octyl levulinate was determined experimentally for the first time. The double objective of this chapter is to provide relevant thermodynamic data for the design of processes and operations involving octyl levulinate and, on the other hand, to compare the experimentally obtained C_p values with those estimated by a contrasted estimation method.

The estimation method that has been used to calculate C_p of the different components involved in the system for the estimation of reaction enthalpies and entropies is that of Rùdzicka and Domalski. The mathematical expression relating the C_p of octyl levulinate to temperature is given in Section 5.3, Equation 21.

The method used for the experimental determination of this parameter is based on subjecting a sample of the compound to a temperature sweep and quantifying the heat required to increase its temperature. Two different mixtures were analysed: the filtered highest purity distillate and the highest purity residue obtained in the vacuum rectification operation carried out in the laboratory. To do this, a small sample of each mixture is placed in a small metal pan under a nitrogen atmosphere, and then the temperature sweep is carried out.

Figure 9 shows the experimental results obtained for the distillate and for the residue, as well as the graphical representation of the equation estimated by the Rùdzicka and Domalski method. The estimated results are in good agreement with the experimental ones, especially with the C_p values obtained from the analysis of the residue samples. In addition, experimental values (residue) show a similar trend with respect to those estimated.

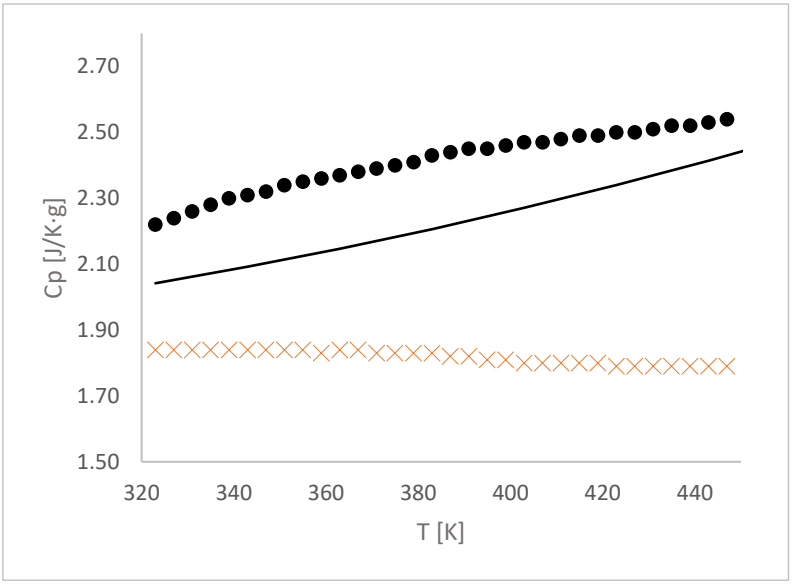


FIGURE 9. Estimated (-) and experimental values of the C_p of octyl levulinate as a function of temperature. Residue (•), distillate (×).

Table 16 shows the experimental and estimated values obtained at extreme temperatures assayed.

TABLE 16. Estimated and experimental values of the C_p of octyl levulinate at extreme temperatures assayed.

Temperature [K]	Distillate [J/K·g]	Residue [J/K·g]	Estimated [J/K·g]
323	1.80	2.22	2.04
447	1.84	2.54	2.44

Differences of 13% and 32% are observed between estimated and experimental values of distillate samples for extreme temperatures (323 K and 451 K, respectively). The differences are reduced to 8% and 4% respectively when the experimental values obtained from the residue samples are taken. A closer approximation to the experimental values of the residue was expected, since the purity of the octyl levulinate in the residue is notably higher than that achieved in the distillate. In these, other components influence to a greater extent in modifying the C_p with respect to that of pure octyl levulinate.

The small differences between the experimental and theoretical values validate the appropriateness of the Rùdzicka and Domalski method for estimating values of C_p for octyl levulinate.

7. CONCLUSIONS AND FUTURE WORK

The equilibrium reaction of the esterification of levulinic acid with 1-octanol to obtain octyl levulinate has been studied at different experimental conditions and relevant thermodynamic data has been obtained.

The reaction equilibrium constants at different temperature have been determined experimentally. Regardless of the initial composition of the reaction medium, the equilibrium constant decreases as the operating temperature increases. Thus, the reaction is exothermic. Relevant differences have been obtained between the experimental equilibrium constants and those computed by estimation methods. These differences are attributed to unavoidable inaccuracies derived from the application of estimation methods, especially in the case of estimating the entropy of formation of octyl levulinate.

Despite having observed notable differences between the experimental equilibrium constants determined in experiments starting from molar ratios LA:OH of 1:1 and 1:2 with respect to those obtained with ratios of 1:4 and 1:8, it is not considered that it can be affirmed that the equilibrium constant is a function of the initial composition of the medium, under the tested conditions. These differences are attributed to systematic errors and the limitations of the analytical equipment for an accurate quantification of levulinic acid at low concentrations.

Molar conversions of levulinic acid at equilibrium of up to 70% have been obtained in experiments starting from molar ratio LA:OH of 1:1. Conversion increased up to 94% in experiments working with initial molar ratio of 1:8.

No phase separation has been observed for any of the tested conditions. On the other hand, although there is formation of an unidentified by-product in the initial moments of the reaction (high concentrations of levulinic acid and 1-octanol), its presence is negligible at equilibrium, thus not affecting the reliability of the thermodynamic data obtained at equilibrium.

Experimental values of enthalpy of the reaction of -15 ± 2 kJ/mol considering enthalpy independent of temperature and of -13 ± 2 kJ/mol considering enthalpy as a function of temperature have been obtained. These values are very similar to those estimated using the Benson method (-15 kJ/mol). The experimental values of entropy (-

17 ± 6 and -12 ± 5 J/K·mol) show greater discrepancy with that obtained via the Benson method (-38 J/K·mol).

Vacuum rectification of the reaction products enabled to obtain octyl levulinate of high purity (95%) in the residue. Liquid-liquid extraction using water was effective to reduce notably the presence of levulinic acid but it was not enough for preventing the formation of humins in the column reboiler.

The C_p of octyl levulinate at various temperatures has been determined for the first time, obtaining remarkably similar results to those obtained by the Rùdzicka and Domalski estimation method. Experimental values between 2.22 and 2.54 J/K·g have been obtained for a temperature range of 323-447 K.

In conclusion, relevant thermodynamic data have been obtained which would enable to design an industrial process for the production of biolubricant octyl levulinate from biosourced levulinic acid and 1-octanol. However, in order to deepen the study of this synthesis, it would be pertinent to carry out a kinetic study of said reaction as well as a catalytic study to evaluate the activity of various catalysts based on ion exchange resins, not yet used in this synthesis. In addition, evaluating the same thermodynamic data at one or two more operating temperatures would strengthen the conclusions obtained.

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ACRONYMS

ω	Acentric factor
a	Activity
γ	Activity coefficient
T_b	Boiling temperature at atmospheric pressure
X	Conversion
P_c	Critical pressure
T_c	Critical temperature
V_c	Critical volume
ΔH_c	Enthalpy change of condensation
ΔH^o_f	Enthalpy change of formation
ΔH^o	Enthalpy change of the reaction
ΔH_v	Enthalpy change of vaporization
ΔS^o_f	Entropy change of formation
ΔS^o	Entropy change of the reaction
R	Gas constant
ΔG^o	Gibbs free energy change of the reaction
C_p	Isobaric specific heat
x	Molar fraction
$R^o_{LA:OH}$	Molar ratio levulinic acid:1-octanol
V	Molar volume
M	Molar weight
$K_{\wp}$	Poynting factor
P	Pressure
T_{br}	Reduced boiling temperature
P_r	Reduced pressure
T_r	Reduced temperature
T_0	Reference temperature

T	Temperature
K	Thermodynamic equilibrium constant
K_γ	Thermodynamic equilibrium constant referred to activity coefficients
K_x	Thermodynamic equilibrium constant referred to molar fractions
P_v	Vapour pressure

APPENDICES

APPENDIX 1: BENSON METHOD FOR ENTHALPY AND ENTROPY OF FORMATION ESTIMATION

To apply the Benson method it is required to decompose the molecules that constitute the system into groups of atoms, as shown in Tables 1A, 2A and 3A:

TABLE 1A. Constituent groups of levulinic acid for application of the Benson method.

Group	Count	ΔH^o_f (298.15 K) [kJ/mol]	ΔS^o_f (298.15 K) [J/K·mol]
C-(H)3(CO)	1	-47.61	83.3
CO-(C)2	1	-152.76	33.81
C-(H)2(CO)(C)	2	-24.14	39.87
CO-(C)(O)	1	-149.37	32.72
O-(H)-(CO)	1	-285.64	38.28

TABLE 2A. Constituent groups of 1-octanol for application of the Benson method.

Group	Count	ΔH^o_f (298.15 K) [kJ/mol]	ΔS^o_f (298.15 K) [J/K·mol]
C-(H)3(C)	1	-47.61	83.3
C-(H)2(C)2	6	-25.73	32.38
C-(H)2(O)(C)	1	-35.8	32.59
O-(H)(C)	1	-191.5	43.89

TABLE 3A. Constituent groups of octyl levulinate for application of the Benson method.

Group	Count	ΔH^o_f (298.15 K) [kJ/mol]	ΔS^o_f (298.15 K) [J/K·mol]
C-(H)3(C)	1	-47.61	83.30
C-(H)2(C)2	6	-25.73	32.38
C-(H)2(O)(C)	1	-35.80	32.59
CO-(C)(O)	1	-149.37	32.72
C-(H)2(CO)(C)	2	-24.14	39.87
CO-(C)2	1	-152.76	33.81
C-(H)3(CO)	1	-47.61	83.30
O-(C)(CO)	1	-196.02	38.28

In order to calculate the enthalpy change and the entropy change of formation of each component at 298.15 K, Equations 1A and 2A must be applied, respectively.

$$\Delta H_f^o(T_0) = \sum_j n_j \cdot \Delta H_{f_j}^o(T_0) \quad (1A)$$

$$\Delta S_f^o(T_0) = \sum_j n_j \cdot \Delta S_{f_j}^o(T_0) \quad (2A)$$

Where *j* refers to each constituent group and *n* is the number of groups of type *j* present in the molecule.

APPENDIX 2: JOBACK AND VETERE METHODS FOR ENTHALPY OF FORMATION ESTIMATION

The development of the calculation of the enthalpy of formation of octyl levulinate is developed in this appendix. The same procedure is applied to estimate the enthalpies of formation of the rest of the system's components.

First, the enthalpy of formation of the component in the gas phase and at 298.15 K must be calculated using Equation 3A:

$$\Delta H^{o}_{f(g)}(T_0) = 68.29 + \sum_{k} n_k \cdot \Delta hfk \qquad (3A)$$

In order to apply Equation 3A, the molecule must be broken down into groups, as shown in Table 4A:

TABLE 4A. Constituent groups of octyl levulinate for determination of enthalpy variation of formation in the gas phase applying the Joback and Vetere methods.

Group	Count	*Δhfk* [kJ/mol]
"-CH3"	2	-76.45
"-CH2-"	9	-20.64
"-COO-"	1	-337.92
">C=O"	1	-133.22

Enthalpy of formation of octyl levulinate at reference temperature and in the gas phase has a value of -741.51 kJ/mol. Values of this parameter for other species are shown in Table 5A:

TABLE 5A. Enthalpy of formation at 298.15 K and gas phase.

Specie	$\Delta H^{o}_{f(g)}$ (298.15 K) [kJ/mol]
Levulinic acid	-609.38
1-Octanol	-360.68
Octyl levulinate	-741.51

Next, the boiling temperature at atmospheric pressure and the critical pressure and critical temperature of the component must be estimated (in case no experimental values are available), using Equations 4A, 5A and 6A:

$$T_b = 198 + \sum_k n_k \cdot \ tbk \tag{4A}$$

$$T_c = T_b \cdot \left(0.584 + 0.965 \cdot \sum_k n_k \cdot \ tck - \left(\sum_j n_k \cdot tck \right)^2 \right)^{-1} \tag{5A}$$

$$P_c = \left(0.113 + 0.0032 \cdot N_{atoms} - \sum_k n_k \cdot \ pck \right)^{-2} \tag{6A}$$

where N_{atoms} is the number of atoms building the molecule, temperatures are in K and pressure in bar and *tbk*, *tck* and *pck* are respectively the contributions of each constituent group of the molecule for the calculation of each of the referenced properties. Its values are depicted in Table 6A:

TABLE 6A. Constituent groups of octyl levulinate and contributions for estimating boiling point, critical pressure and critical temperature.

Group	Count	*tbk*	*tck*	*pck*
"-CH3"	2	23.58	0.0141	-0.0012
"-CH2-"	9	22.88	0.0189	0
"-COO-"	1	81.10	0.0481	0.0005
">C=O"	1	76.75	0.0380	0.0031

Values for critical temperature and pressure and boiling point estimated according Equations 4A-6A for all species are shown in Table 7A:

TABLE 7A. Boiling point and estimated values for critical properties.

Specie	T_b [K]	T_c [K]	P_c [bar]
Levulinic acid	519	722.3	41.8
1-Octanol	468	625.5	25.1
Octyl levulinate	579.3	745.0	17.4

Next, Equation 7A, where T_{br} is the reduced boiling temperature calculated as the quotient between the boiling temperature and the critic temperature, and *F* takes a value of 1 according to the nature of the substances that make up the system, is applied to estimate enthalpy change of vaporization at boiling point from critical data calculated in the previous step:

$$\Delta H_v(T_b) = R \cdot T_b \cdot \frac{(1 - T_{br})^{0.38} \cdot \left(lnP_c - 0.513 + \frac{0.5066}{P_c \cdot T_{br}^2}\right)}{1 - T_{br} + F \cdot (1 - (1 - T_{br})^{0.38}) \cdot \ln(T_{br})} \quad (7A)$$

Given that the enthalpy of vaporization has been calculated at the boiling temperature, Equation 8A, where T_{0r} is the reduced temperature at 298.15 K, must be applied to obtain the value of said parameter at the reference temperature:

$$\Delta H_v(T_0) = \Delta H_v(T_b) \cdot \left(\frac{1 - T_{0r}}{1 - T_{br}}\right)^{0.38} \quad (8A)$$

Considering that the enthalpy of condensation is equal to the enthalpy of vaporization sign reversed:

$$\Delta H_c(T_0) = -\Delta H_v(T_0) \quad (9A)$$

The enthalpy of formation at 298.15 K in the liquid phase is calculated as the enthalpy of formation in the gas phase plus the heat released when condensing the product of said formation, according to Equation 10A:

$$\Delta H^o_{f(l)}(T_0) = \Delta H^o_{f(g)}(T_0) + \Delta H_c(T_0) \quad (10A)$$

Table 8A shows the enthalpy of vaporization at boiling point, the enthalpy of condensation at reference temperature and, finally, the enthalpy of formation at reference temperature for the various species:

TABLE 8A. Estimation of enthalpy of formation by Joback and Vetere method.

Specie	$\Delta H_v(T_b)$ [kJ/mol]	ΔH_c (298.15 K) [kJ/mol]	ΔH^o_f (298.15 K) [kJ/mol]
Levulinic acid	73.3	-97.0	-706.4
1-Octanol	47.4	-62.6	-423.3
Octyl levulinate	82.3	-119.9	-861.4

APPENDIX 3: RÙDZICKA AND DOMALSKI METHOD FOR ISOBARIC SPECIFIC HEAT ESTIMATION

To apply this method, it is required to break down the molecules into their constituent groups and calculate the parameters *A*, *B* and *D* as the sum of the value of the contributions of the different constituent groups to said parameters, as shown in Equations 11A, 12A and 13A:

$$A = \sum_k n_k \cdot a_k \qquad (11A)$$

$$B = \sum_k n_k \cdot b_k \qquad (12A)$$

$$D = \sum_k n_k \cdot d_k \qquad (13A)$$

Tables 9A, 10A and 11 A show how molecules are decomposed according to this method and the values for each group contribution to the three parameters:

TABLE 9A. Constituent groups of levulinic acid for application of the Rùdzicka and Domalski method.

Group	Count	*a*	*b*	*d*
C-(H)3(CO)	1	3.8452	-0.33997	0.19489
CO-(C)2	1	5.4375	0.72091	-0.18312
C-(H)2(CO)(C)	2	6.6782	-2.4473	0.47121
CO-(C)(O)	1	29.246	3.4261	-2.8962
O-(H)-(CO)	1	-27.587	-0.16485	2.7483

TABLE 10A. Constituent groups of 1-octanol for application of the Rùdzicka and Domalski method.

Group	Count	*a*	*b*	*d*
C-(H)3(C)	1	3.8452	-0.33997	0.19489
C-(H)2(C)2	6	2.7972	-0.054967	0.10679
C-(H)2(O)(C)	1	1.4596	1.4657	-0.2714
O-(H)(C)	1	12.952	-10.145	2.6261

TABLE 11A. Constituent groups of octyl levulinate for application of the Rùdzicka and Domalski method.

Group	Count	*a*	*b*	*d*
C-(H)3(C)	1	3.8452	-0.33997	0.19489
C-(H)2(C)2	6	2.7972	-0.054967	0.10679
C-(H)2(O)(C)	1	1.4596	1.4657	-0.2714
CO-(C)(O)	1	29.246	3.4261	-2.8962
C-(H)2(CO)(C)	2	6.6782	-2.4473	0.47121
CO-(C)2	1	5.4375	0.72091	-0.18312
C-(H)3(CO)	1	3.8452	-0.33997	0.19489
O-(C)(CO)	1	-21.434	-4.0164	3.0531

APPENDIX 4: ESTIMATION OF MOLAR VOLUMES

Hankinson and Thomson developed (1979) an equation to estimate the molar volume of substances in saturated liquid phase (HBT method).[78] Later, Thomson *et al.* extended the HBT method to apply to liquids compressed beyond the state of saturation, generalizing the constants of the Tait equation.[79] Equation 14A is used to estimate the molar volume of the species present in the reaction medium:

$$V = V_s \cdot \left(1 - c \cdot \ln\left(\frac{\beta + P}{\beta + P_v}\right)\right) \qquad (14A)$$

where *ß* is a parameter calculated using Equation 15A:

$$\frac{\beta}{P_c} = -1 + a \cdot (1 - T_r)^{\frac{1}{3}} + b \cdot (1 - T_r)^{\frac{2}{3}} + d \cdot (1 - T_r) + e \cdot (1 - T_r)^{\frac{4}{3}} \qquad (15A)$$

where parameters *a-e* take the following values:

$$a = -9.070217; b = 62.45326; d = -135.1102; f = 4.79594$$

$$g = 0.250047; h = 1.14188; j = 0.0861488; k = 0.0344483$$

$$e = \exp(f + g \cdot \omega_{SRK} + h \cdot \omega_{SRK}^2)\,;\; c = j + k \cdot \omega_{SRK}$$

With respect to Equation 14A P_v is the vapour pressure in bar and V_s is the saturated liquid volume in cm^3/mol at vapour pressure, and it is calculated according Equation 16A:

$$\frac{V_s}{V^*} = V_R^{(0)} \cdot \left(1 - \omega_{SRK} \cdot V_R^{(\delta)}\right) \qquad (16A)$$

Values of $V_R^{(0)}$ and $V_R^{(\delta)}$ can be obtained applying Equations 17A and 18A, respectively. Equation 16A can be applied in the range of $0.25<T_r<0.95$ and Equation 17A in the range $0.25<T_r<1.00$. Values of V^* are tabulated parameters which are close to the critical volume. Thus, when V^* are not available values of V_c can be used instead.

$$V_R^{(0)} = 1 + a \cdot (1 - T_r)^{\frac{1}{3}} + b \cdot (1 - T_r)^{\frac{2}{3}} + c \cdot (1 - T_r) + d \cdot (1 - T_r)^{\frac{4}{3}} \qquad (17A)$$

$$V_R^{(\delta)} = \frac{e + f \cdot T_r + g \cdot T_r^2 + h \cdot T_r^3}{T_r - 1.00001} \qquad (18A)$$

Where parameters a-h take the following values:

$$a = -1.52816; b = 1.43907; c = -0.81446; d = 0.190454$$

$$e = -0.296123; f = 0.386914; g = -0.0427258; h = -0.0480645$$

Regarding to Equation 16A the value of ω_{SRK} is the acentric factor that causes the Soave-Redlich-Kwong equation of state to give the best fit to pure component vapour pressures. It can be found as tabulated values for several components.[73] If not available, values of ω can be estimated instead.

Whith regard to Equation 14A, vapour pressure is estimated for all components following the Gomez-Thodos method, which is depicted below. This method tested for high complexity hydrocarbons can estimate vapour pressures from triple to critical point with higher accuracy than other extended-used methods like Riedel, Thek-Stiel and Zia-Thodos. Authors predict an excellent adaptation of reference method to estimate vapour pressures of complex organic compounds other than alkanes.[80]

Equation 19A is used to estimate vapour pressure at reduced temperature. Knowing the critical pressure of the compound, the vapour pressure at any temperature can be estimated:

$$\ln(P_{vr}) = \beta \cdot \left(\frac{1}{T_r^m} - 1\right) + \gamma \cdot (T_r^7 - 1) \qquad (19A)$$

Equations 20A-23A are required to obtain values for constituent parameters of Equation 19A:

$$\gamma = a \cdot h + b \cdot \beta \qquad (20A)$$

$$a = \frac{1 - \frac{1}{T_{br}}}{T_{br}^7 - 1} \qquad (21A)$$

$$b = \frac{1 - \frac{1}{T_{br}^m}}{T_{br}^7 - 1} \qquad (22A)$$

$$h = T_{br} \cdot \frac{\ln(P_c)}{1 - T_{br}} \qquad (23A)$$

where T_{br} is the reduced boiling point and P_c is the critical pressure of the compound. Parameters *ß* and *m* are calculated using different equations depending on the nature of the reference compound. For nonpolar compounds (it is the case of octyl levulinate), the following equations are used:

$$\beta = -4.26700 - \frac{221.79}{h^{2.5} \cdot \exp(0.0384 \cdot h^{2.5})} + \frac{3.8126}{\exp\left(\frac{2272.44}{h^3}\right)} + \Delta^* \quad (24A)$$

$$m = 0.78425 \cdot \exp(0.089315 \cdot h) - \frac{8.5217}{\exp(0.74826 \cdot h)} \quad (25A)$$

where Δ^* equals 0 except for hydrogen and helium. For water and alcohols, equations below are used:

$$m = 0.0052 \cdot M^{0.29} \cdot T_c^{0.72} \quad (26A)$$

$$\gamma = \frac{2.464}{M} \cdot \exp(9.8E - 06 \cdot M \cdot T_c) \quad (27A)$$

where M refers to the molecular weight and T_c to critical temperature. Finally, for polar compounds other than water and alcohols (it is the case of levulinic acid), following equations must be applied:

$$m = 0.466 \cdot T_c^{0.166} \quad (28A)$$

$$\gamma = 0.08594 \cdot \exp(7.462E - 04 \cdot T_c) \quad (29A)$$

For the latter two categories, ß is calculated using Equation 20A.

Next, the application of the methods outlined above is developed to estimate the molar volume of levulinic acid at 80 ºC. Initially, Equations 17A and 18A are used for the calculation of $V_R^{(0)}$ and $V_R^{(\delta)}$. Here, the reduced temperature will be the quotient between the operating temperature (353 K) and the critical temperature of levulinic acid (estimated value using the Joback method, see Appendix 2). Values of reference parameters are shown in Table 14A. Next, the value of V^* must be determined. Since value for levulinic acid is not tabulated in the literature, the critical volume will be used, which will be estimated using the Joback group contribution method, according to Equation 30A:

$$V_c = 17.5 + \sum_k n_k \cdot vck \quad (30A)$$

where *vck* is the contributions of each constituent group *k* of the molecule for the calculation of critical volume in cm^3/mol.

The breakdown of the levulinic acid molecule into constituent groups as well as the contribution of each group are shown in Table 12A:

TABLE 12A. Constituent groups of levulinic acid and contributions for estimating critical volume.

Group	Count	*vck*
"-CH3"	1	65
"-CH2-"	2	56
"-COOH-"	1	89
">C=O"	1	62

Value obtained for critical volume is shown in Table 14A. For the application of Equation 16A to estimate the saturate liquid molar volume, ω_{SRK} should be known. As the value of this parameter for levulinic acid is not available in literature, ω is estimated using the method developed by Ding Yu which can estimate acentric factors of high complexity organic molecules (overcoming the limitation of Lee-Kesler method or Watanisri *et al.*) with errors smaller than 4% and it can be applied to compounds other than alkanes, overcoming the main limitation of extended-used methods developed by authors such as Hoshino *et al.* [81] Equation 31A is used and the molecule breakdown in constituent groups is shown in Table 13A:

TABLE 13A. Constituent groups of levulinic acid and contributions for estimating acentric factor.

Group	Count	ω_k
"-CH3"	1	3.4381
"-CH2-"	2	3.4381
"-COOH-"	1	31.662
">C=O"	1	11.152

$$\omega = 0.004423 \cdot \left(\ln \left(3.3063 + \sum_k n_k \cdot \omega_k \right) \right)^{3.651} \qquad (31A)$$

The result of the application of this method to estimate acentric factor is shown in Table 14A. Next, Equation 15A must be used to calculate parameter *ß* for Equation 14A. Critical pressure of levulinic acid is estimated using the Joback method as depicted in Appendix 2. Finally, in order to apply Equation 14A to estimate molar volume at operating temperature, vapour pressure must be known. It is estimated according to procedure proposed by Gomez-Thodos, developed in the present appendix. Equations 19A, 20A, 21A, 22A, 23A, 28A and 29A are used and values for critical temperature and

reduced boiling point are required. Knowing all the constituent parameters of Equation 14A, molar volume can be estimated. Partial and final results are shown in Table 14A:

TABLE 14A. Molar volume of levulinic acid at 80 ºC and estimated values for acentric factor and other parameters required for molar volume estimation.

$V_R^{(0)}$	$V_R^{(\delta)}$	V_c [cm^3/mol]	V_s [cm^3/mol]	ω	P_v [bar]	V [cm^3/mol]
0.3596	0.2403	345.5	102.8	0.719	0.002515	103.1

APPENDIX 5: UNIFAC DORTMUND MODEL FOR ACTIVITY COEFFICIENTS ESTIMATION

The modified UNIFAC Dortmund method is a group contribution model which estimates liquid-phase activity coefficients in non electrolyte systems as a function of temperature and composition. These activity coefficients describe the deviation of the behaviour of the mixture from that of an ideal one.[82] The activity coefficients are calculated as the summation of a combinatorial part (γ_i^C), which represents the contribution of the excess entropy due to the different shapes and sizes of the considered molecules, and a residual part (γ_i^R) which represents the contribution of the excess enthalpy caused by energetic contributions between the molecules, as shown in Equation 32A:

$$\ln(\gamma_i) = \ln(\gamma_i^C) + \ln(\gamma_i^R) \qquad (32A)$$

The combinatorial part, which does not depend on temperature, can be calculated applying the following equations:

$$\ln(\gamma_i^C) = 1 - V_i' + \ln(V_i') - 5 \cdot q_i \cdot \left(1 - \frac{V_i}{F_i} + \ln\left(\frac{V_i}{F_i}\right)\right) \qquad (33A)$$

The parameters of Equation 33A can be calculated using the following correlations:

$$V_i' = \frac{r_i^{\frac{3}{4}}}{\sum_j x_j \cdot r_j^{\frac{3}{4}}} \qquad V_i = \frac{r_i}{\sum_j x_j \cdot r_j} \qquad F_i = \frac{q_i}{\sum_j x_j \cdot q_j} \qquad (34A)$$

$$r_i = \sum_k n_k^{(i)} \cdot R_k \qquad q_i = \sum_k n_k^{(i)} \cdot Q_k \qquad (35A)$$

where x_j is the molar fraction of the component j, n_k the times a group of k-type repeats and Q_k and R_k are tabulated parameters. Thus, in order to calculate the combinatorial part the molecules need to be broken down to its constituent groups. Table 15A shows the decomposition of the species present in the reaction mixture and their values for the required parameters.

On the other hand, the residual part can be calculated according to Equation 36A:

$$\ln\left(\gamma_i^R\right) = \sum_k n_k^{(i)} \cdot \left(\ln(\Gamma_k) - \ln\left(\Gamma_k^i\right)\right) \quad (36A)$$

The following correlations must be applied in order to calculate the constituent parameters of Equation 36A:

$$\ln(\Gamma_k) = Q_k \cdot \left(1 - \ln\left(\sum_m \theta_m \cdot \Psi_{mk}\right) - \sum_{m=1} \frac{\theta_m \cdot \Psi_{mk}}{\sum_n \theta_n \cdot \Psi_{nm}}\right) \quad (37A)$$

$$\theta_m = \frac{Q_m \cdot X_m}{\sum_n Q_n \cdot X_n} \qquad X_m = \frac{\sum_j n_m^{(j)} \cdot x_j}{\sum_j \sum_n n_n^{(j)} \cdot x_j} \quad (38A)$$

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm} \cdot T + c_{nm} \cdot T^2}{T}\right) \quad (39A)$$

where Γ_k and Γ_k^i are respectively the activity coefficients of the group k in the mixture and in the pure component i; Θ_m and X_m are respectively the area fraction and the mole fraction of the group m; Ψ_{nm} is the group interaction parameter, which is temperature dependent; and parameters a_{nm}, b_{nm} and c_{nm} are tabulated coefficients and are presented in Table 16A.

TABLE 15A. R_k and Q_k values and group assignment for the modified UNIFAC Dortmund model.

Specie	Group	Subgroup (k)	n_k	R_k	Q_k	Subgroup type
Levulinic acid	1	2	2	0.6325	0.7081	CH_2
	9	18	1	1.7048	1.6700	CH_3CO
	20	42	1	0.8000	0.9215	COOH
1-Octanol	1	1	1	0.6325	1.0608	CH_3
	1	2	7	0.6325	0.7081	CH_2
	5	14	1	1.2302	0.8927	OH (p)
Octyl levulinate	1	1	1	0.6325	1.0608	CH_3
	1	2	8	0.6325	0.7081	CH_2
	9	18	1	1.7048	1.6700	CH_3CO
	11	22	1	1.2700	1.4228	CH_2COO
Water	7	16	1	1.7334	2.4561	H_2O

TABLE 16A. *Values for binary interaction parameters.*

Group		a_{nm}	b_{nm}	c_{nm}	a_{mn}	b_{mn}	c_{mn}
n	*m*	[K]		[K^{-1}]	[K]		[K^{-1}]
1	5	2777.0	-4.6740	0.001551	1606.0	-4.7460	0.0009181
1	7	1391.3	-3.6156	0.001144	-17.253	0.8389	0.0009021
1	9	433.60	0.1473	0.0	199.00	-0.8709	0.0
1	11	98.656	1.9294	-0.003133	632.22	-3.3912	0.003928
1	20	1182.2	-3.2647	0.009198	2017.7	-9.0933	0.010240
5	7	-801.90	3.8240	-0.007514	1460.0	-8.6730	0.01641
5	9	-250.00	2.8570	-0.006022	653.30	-1.4120	0.0009540
5	11	973.80	-5.6330	0.007690	310.40	1.5380	-0.004885
5	20	-1295.0	4.3634	0.0	1525.8	-4.9155	0.0
7	9	190.50	-3.6690	0.008838	770.60	-0.5873	-0.003252
7	11	-675.50	3.6090	0.0	322.30	-1.3050	0.0
7	20	-1795.2	12.708	-0.01546	624.97	-4.6878	0.005237
9	11	-16.486	-0.2792	0.0	33.415	0.2191	0.0
9	20	-109.51	0.9689	0.0	178.22	-0.9168	0.0
11	20	62.031	1.0567	0.0	59.594	-0.7120	0.0

APPENDIX 6: CALIBRATION

The following steps have been followed in order to carry out calibration procedure:

1) Weigh the desired amount of levulinic acid, 1-octanol, octyl levulinate and water and introduce each substance in a small vial using a pipette for each compound.
2) Shake the vial to ensure that the substances are mixed to form a single phase.
3) Use a micrometric syringe to preload 0.2 µL of the mixture into the injection inlet of the gas chromatograph.
4) Select the chromatographic method for analysis of manually injected samples on the computer.
5) Press the plunger of the syringe to inject the sample into the chromatograph and, at the same time, press the selector which starts the analysis.
6) 30 seconds after the injection, remove the syringe from the inlet and wash it by applying three wipes with acetone.
7) Obtain the chromatographic area percentages by integrating the peaks offered by the mass-selective detector on the screen.

Figures 1A-3A show the calibration curves for substances involved in the chemical reaction under study:

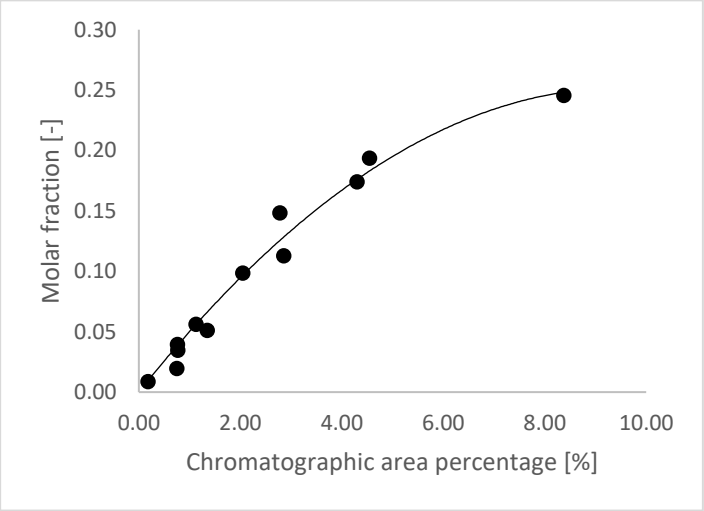

FIGURE 1A. Calibration curve for levulinic acid.

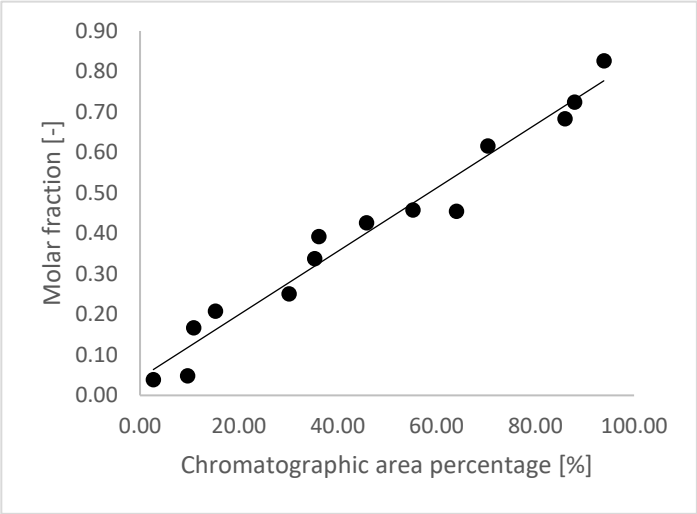

FIGURE 2A. Calibration curve for 1-octanol.

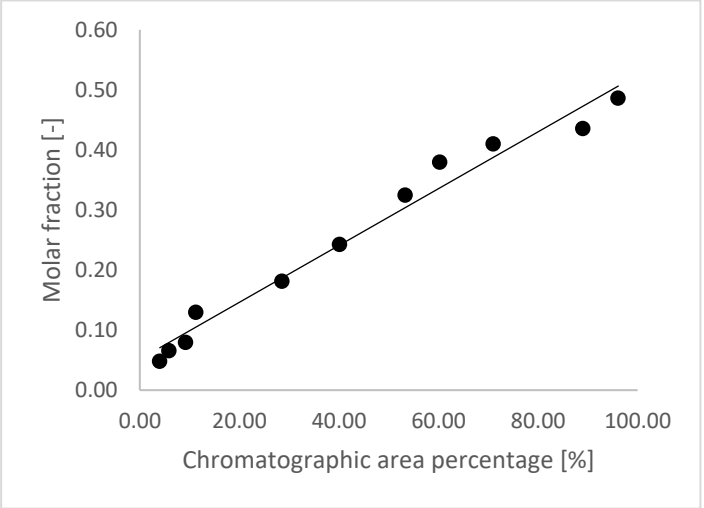

FIGURE 3A. Calibration curve for octyl levulinate.