Hydrothermal treatment of orange peel waste for production of fine chemicals

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“Walk on, walk on,
with hope in your heart
and you’ll never walk alone”

Richard Rodgers, Oscar Hammerstein
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Alla mia famiglia.
Chapter 1

Introduction

1.1 Objective and aims
The purpose of the present thesis is to explore acid-catalyzed hydrolysis as a valorization route to obtain LA from orange waste. Giving more value to food waste trying to recover more value added products is the real aims of the biorefinery concept. This is a process in which some food waste or simply biomass may be used to provide new intermediates compounds for the productions of widespread products. Moreover, LA is great potential intermediate for the production of other useful products.

In particularly, the aim of this work is to find the right parameters for the production of levulinic acid from orange peel. This may be done through a process optimization of LA production in a lab scale, by varying some parameters such as temperatures, acid-catalyst concentration, feed intake of raw material. Furthermore, it is also essential, in order to choose the perfect parameters values, gain insight of the behavior of the reaction conditions as function of the time, temperature, and acid concentration.
1.2 Structure of the thesis

The dissertation consists of five chapters.

In the present chapter, the aim and the goal of the project are discussed. The topic of the research is introduced and the outline of the experiments briefly illustrated.

Chapter 2 presents the state of the art in this field. Starting from needs of world energy demands, it is subsequently described the situation of the orange waste in the World, Europe and Italy. The researches in this field using orange peel are then illustrated. It is also illustrated the biorefinery concept, and an introduction of the Levulinic Acid, its uses and its potentially applications.

In the chapter 3 (Materials and methods) is described the experimental approach. The equipment and techniques used in this project are detailed illustrated.

Chapter 4 talks about the results of the experiments and subsequently these are described. In the first part the composition of the raw material is illustrated. Then are shown the results about the exploratory experiments performed by means of microwave reactors. In the last part, after the explanation of the effects of each parameters on the reaction conditions, the modelling of the optimization and its techniques are illustrated.

In the last chapter (chapter 5) conclusions of this project and future works are described.
Chapter 2

Literature review

2.1 Introduction

This chapter contains a review of the current literature on the fundamentals of the biorefinery concept and the production of levulinic acid by biomass. In the first part is shown the current situation of the world energy demand. In the second part the biorefinery concept, together with the situation of orange waste and its contemporary researches on the orange peel are expressed followed by the levulinic production system. Moreover are described all the levulinic acid production mechanism occurring in the reaction.

2.2 Biomass applications for energy generation and chemicals production

The world energy demand is one of the most important problem that the world population has to deal. Indeed, the world is highly dependent on the utilization of fossil resources (e.g. coal, natural gas and petroleum). The world energy consumption is shown in figure 2.1.
Moreover, a wide range of commonly used product, such as polymers, resins, fertilizers, lubricants, etc. are obtained from fossil resources. However, these are not healthy for the environment and they are also not renewable. Furthermore, burning fossil resources has produced an increase of the CO$_2$ concentration in the atmosphere. These and other issues brought to focus in seeking in more eco-friendly and alternative pathways to substitute fossils. One of the most suggested candidates is the biomass, because is the only renewable resource of fixed carbon, thus it can be used for the production of conventional hydrocarbon liquid transportation fuel and petrochemicals products.

To lead governments to an eco-friendly policy, the EU (European Union) has set an obligatory target of 20% renewable energy in gross final energy consumption as well as a 10% target for the share of renewable energy in transport for 2020.
2.3 Biomass: definition and valorisation using for biorefinery concept

The term biomass indicates any organic matter that is available on a renewable basis, including agricultural food and feed crop residues, wood and wood residues, dedicated energy crops and trees, animal wastes and other kind of waste materials.

As Girisuta et al. said, the utilisation of biomass for the production of non-food products has fostered research and development activities in various countries. To steer the research and development activities and to enhance market introduction, a novel concept was introduced: biorefining [3-6]. Among the several definition of biorefinery, the most exhaustive was performed by the IEA Bioenergy Task 42 “Biorefineries” [1]: “Biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy”. The biorefinery concept embraces a wide range of technologies able to separate biomass resources (wood, grasses, corn...) into their building blocks (carbohydrates, proteins, triglycerides...) which can be converted to value added products, biofuels and chemicals. A biorefinery is a facility (or network of facilities) that integrates biomass conversion processes and equipment to produce transportation biofuels, power, and chemicals from biomass. This concept is analogous to today’s petroleum refinery, which produces multiple fuels and products from petroleum [2].

Large-scale biorefinery systems are already operational; however, these existing systems deliver predominantly food products such as soy oil and soy protein, wheat starch and gluten, potato starch and protein. Generally, three stages of may be defined in biorefinery:
1. The first step is about the separation of the biomass into its components such as cellulose, hemicellulose, lignin, proteins, amino acids, fine chemicals and pharmaceutical compounds, in a primary depolymerization unit. Typically, this is carried out by means of traditional separation processes such as filtration, solvent extraction and distillation. There are also novel concepts such as supercritical CO$_2$ extraction and catalytic de-polymerization that have been exploring.

2. In the secondary step the conversion of the first step’s products to valuable end products and chemical intermediates occurs. Typical chemical intermediates generating from this step are alcohols, acids and platform chemicals such as levulinic acid, lactic acid or phenolic compounds. This process is generally characterized by thermo-chemical (e.g. gasification, liquefaction, hydrothermal conversion) and biochemical processes (fermentation).

3. Catalytic processes in order to converting chemical intermediates to high value added products characterize the third step.

A schematic representation of a biorefinery process is given in figure 2.2

![Figure 2.2: A simplified scheme of a biorefinery concept. (taken from 27)](image-url)
2.4 Orange waste

Orange is a citrus fruit consumed in high quantities all over the world in the natural and peeled forms and as a juice. It is associated with a low cost and contains many nutrients including vitamin C, A and B, minerals (calcium, phosphorus, potassium), dietary fiber and many phytochemicals, including flavonoids, amino acids, triterpenes, phenolic acids and carotenoids [7]. It is assumed that the orange originally came from Asia, particularly from southern China, north eastern India and perhaps Indonesia. Italian traders brought this fruit in Europe in 1450, and about ten years later orange were also brought by the Portuguese. In that period, oranges were mainly used for medicinal purposes, but soon it was used as luxurious food for wealthy people. Orange trees, like most citrus plants, need to grow up under subtropical conditions in a temperature range between 13°C and 38°C [10]. They are very sensitive to frost, especially during the first years. Generally, the favorable annual precipitations is about 125 – 500 mm but orange trees can survive and grow in areas where annual precipitation is about 1000 – 1500 mm [11].

In the figure 2.3 a section and the structure of an orange is shown. It is possible to see how the peel consists in two parts: the flavedo (exocarp) and the albedo (mesocarp). The flavedo is the outside skin of the peel and consists mostly of cellulosic material, but also contains essential oils, paraffin waxes, steroids and triterpenoids, fatty acids, pigments (carotenoids, chlorophylls, flavonoids), bitter principles (limonene) and enzymes [12]. The albedo is the inner part of the peel and is rich in pectin. [13]. Mainly varieties of orange can be included into common oranges, navel oranges, blood oranges and acidless oranges. The first ones represent the 66% of the whole orange production. “Valencia” and “Hamlin” belong to the category of common orange, and the first ones are also
the most important cultivation in California, Texas and South Africa. Hamlin is a small, smooth, seedless and juicy orange [14] [15].

![Figure 2.3: Structure and section of an orange taken from [13]](image)

Global Orange production for the years 2015/2016 is forecast to be about 47.9 million tons [8]. Even though orange production is declining from the previous year, this amount results to be substantially important in order to exploit orange waste. The Italian annual production of oranges is about 2.3 million tons per year. Most of them come from Sicily (52.6 %) and Calabria (31.7 %). In the figure 2.4 is shown European scenario in which Italy and Spain are the main producer.

![Figure 2.4: European scenario of production of oranges from 2005 up to 2012](image)
The largest producer is Brazil with 16.7 million tons expected for 2015/2016, followed in order by China (7 million tons), European Union (6.1 million tons), United States (4.8 million tons), Mexico (3.5 million tons), Egypt (2.7 million tons), Turkey (1.7 million tons), South Africa (1.7 million tons), Argentina (1 million tons) and Morocco (920,000 tons). Therefore, considering that during orange juice production, only around the half of orange weight is transformed into juice [9], it is necessary facing the problem of the great amount of residual such as peel, pulp, seeds, orange leaves and the whole orange fruit that do not reach the quality requirements. This hotchpotch of wastes is generally spread on soil near the production location, or alternatively burned through combustion contributing the global warming, even though plants abiding by the natural cycle assimilate the most of produced carbon dioxide. However, these methods of waste handling produce highly polluted wastewater in terms of chemical and biological oxygen values, which can negatively affect the soil and the ground and superficial waters.

It is extremely important and worthwhile finding a residuals management way in order to add values to orange waste. Thus, it would be useful to implement new processes for waste recovery, for instance, producing organic fertilizers, pectin, bio-oil, essential oils, and antioxidant compounds or based this processes for the production of several compounds with high added value, such as microbial proteins, organic acids, ethanol, enzymes and biologically active secondary metabolites and adsorbent materials. These are excellent alternatives to avoid environmental pollution and to add value to these substances.
Chapter 2: Literature review

2.5 Applications of orange waste

Extensive processes and technologies in order to enhance orange waste are illustrated in literature. It is possible to distinguish roughly two kind of categories for the valorization of the orange waste. The first one considers the application of the whole orange peel without differentiating individual constituents. The other one uses the biorefinery concept, which aims to obtain new useful compounds converting raw material. Examples of processes being part of the first category are the uses of orange peel, for instance, as animal feed or organic fertilizer.

2.5.1 Animal feed and organic fertilizer

Solid waste generated during orange juice production can be used to produce ingredients for animal feed (fresh or dried orange pulp). This system includes the most common procedures applied by orange juice production plants regarding the destination of the residues. Most plants make use of almost all the residue generated in the industrial process for the production of animal feed (Moreira et al., 2004). By means of some pressuring processes, the orange peel lose the water content also with the help of addition of calcium hydroxide or calcium oxide [7]. Since the water content in the fresh pulp is quite high (valuated around 70% - 75%), it is not easy to dry in the common industrial drying devices, and due to the high content of organic matter, it cannot be disposed easly (Crupi et al., 2001) [16]. However, as Tripoldi et al., 2004 say, there are some chemicals and enzymatic methods that facilitate the pressing and the loss of the water content allowing the drying process in the common industrial devices. In figure 2.5 a flowchart of industrial process of animal feed production by orange peel is shown.
Another direct use of orange peel waste is to use it converting it to a fertilizer by composting [17]. This is possible to gain it by modifying its C/N ratio, pH, and moisture content to 24:1, 6.3, and 60% respectively, and composted piling under shelter. The whole process can be completed in about 3 months.

As described in the chapter above, the biorefinery concept may be employed on the orange waste in order to gain potentially high value added products. Typically, extraction of essential oils and pectin, and conversion of lignocellulose to high value products are performed trying to use in a better way the orange waste.

2.5.2 Extraction of essential oils

Citrus fruit contains essential oils, which are widely employed in the food industry as flavors. They are located in oil sacs or glands that range in diameter
ranging from 0.4 to 0.6 mm and are located at irregular depths in the flavedo located at the outer rind of the fruit [18]. Orange peel typically contains more than 5 kg of oil per 1000 kg of oranges and approximately 90% of this is D-limonene (Braddock, Temelli, and Cadwallader, 1986; Hull, Lindsay, and Baier, 1953), a hydrocarbon, classified as a cyclic terpene. It is colorless liquid at room temperature, with an extremely strong orange odor. As the main odorous constituent of citrus (plant family Rutaceae), D-limonene is employed in the manufacture of food and medicines as a flavoring agent. It also has many applications in the chemical industry, cosmetics and domestic household products (Smyth and Lambert, 1998). The process of extracting D-limonene from orange peel is relatively simply and well established. It can be removed from the peel by cold pressing, steam distillation or solvent extraction, usually with hexane or carbon dioxide (Hull, Lindsay, and Baier, 1953).

Expression, also frequently referred to as pressing, is the process of applying physical pressure to a substance in order to extract. For orange waste, this can be used to extract essential oils from the peel. A conventional method is cold pressing, where the process takes place under low temperature. The main issue with this method is the low amount of preserved oils, as a large amount is soaked into the solid fraction of the waste [23].

Distillation is another commercially used method. The orange peel is exposed to boiling water or steam through which the essential oils are released by evaporation. The amount of essential oil recovered through distillation depends on four factors: distillation time, temperature, operating pressure and quality of the feedstock [13]. However, there are some disadvantages such as chemical modification of the oil components due to high temperatures and extended extraction time causing low quality oils.
There are other processes for extraction of essential oils such as *subcritical water extraction* which under pressure uses hot water (100°C – 374°C) as extractant [24], *microwave assisted extraction* which combines microwave heating with saturated steam which enhance the release of essential oils [25], *Microwave accelerated distillation* which combine with an extraction technique [26], *Microwave hydrodiffusion and gravity* which combines microwaves for hydrodiffusion from the inside, where it is collected and separated through gravity. A thermochemical method for oil extraction called *Instantaneous controlled pressure drop* (DIC), extracts volatile molecules by instant vaporization after which a condensation step is performed [27].

The solid residues remaining after the essential oil extraction could be reutilized. The maximum extraction yield for citrus oils is 0.4 g 100 g⁻¹, i.e., for every ton of fruit processed 4 kg of oil are produced [22]. Thus, from the total amount of solid residues generated in the production of juice (8000 t) and considering an extraction process with 40% efficiency, approximately 12.8 t of essential oils can be obtained.

### 2.5.3 Pectin extraction

The main part of the orange to be extracted after juice production are its essential oils. Additionally, pectin can be extracted, and extraction can be used for the production of animal feed from orange waste.

Pectin is an important component of plant cell walls, besides cellulose and hemicelluloses and it is probably the most complex macromolecule in nature, because it can be composed of as many as 17 different monosaccharides [13]. It is used as natural food additive widely in the food industry employed in fillings, sweets, as a stabilizer in fruit juices, milk drinks and in the pharmaceutical industry as detoxifying agent. Guo et. al (2012) compared three extraction
methods for pectin from orange peel: ultra-high pressure, microwave and traditional heating. Sub results included the yield of pectin being higher than the yield of traditional heating and microwave. The conclusion was that under optimal conditions, ultra-high pressure should be the more efficient, time saving, eco-friendly approach to extract pectin, especially if pectin with higher viscosity and stability is to be obtained [28]. Alternatively, microwave assisted extraction, as explained above for the extraction of essential oils, has gained increased interest among researchers. According to Maran et al. (2013) this method should be explored as it an interesting alternative because of its shorter time, less solvent use, higher extraction rate, better products and lower costs.

2.5.4 Pyrolysis

Pyrolysis is a thermochemical decomposition of organic material without the presence of oxygen or other reagents [29]. This process is used for the production of bio-oil, a black oil with a characteristic odor and high performance and can be obtained not only from pyrolysis but also from thermal degradation. Bio-oil may be used as an additive to conventional fuels, as transport fuel and to feedstock chemicals. The orange waste, being rich in cellulose, hemicellulose and lignin, is considered a good biomass to use for the production of bio-oil. The orange peel pyrolysis bio-oil contains valuable compounds as phenols, benzene, toluene, p-xylene, styrene, and carboxylic acids and the main component present is δ-limonene [30] [31].

2.5.5 General process

The first step of pyrolysis is the pre-treatment of the biomass, in this case orange peel. The orange peel is grinded; the particles of the orange peel should be reduced sufficiently before entering the pyrolysis reactor. The efficiency of pyrolysis depends on the particle size and the moisture content of the feedstock.
The second step is pyrolysis reaction: the pre-treated biomass is introduced in the reactor. At the same time, hot air is introduced in a combustor, but not in the reactor itself, since the pyrolysis reactor is a reaction with the absence of air. The combustor pre-heats the pyrolysis reactor, where the raw gasses are separated from the ash. The next step is char collection; the hot raw gasses are introduced in a separator to remove char. The purified gasses are then quenched with water. In this step, when the gasses are cooled down by quenched water, de bio oil is condensed at the bottom of the reactor and is collected. In the figure 2.6, a scheme of the general pyrolysis process is shown.

Figure 2.6: A scheme of a general pyrolysis process, taken from a work of S.E. Smith and M.E. Levenbach

As S.E. Smith and M.E. Levenbach said in their work, conventional pyrolysis has been applied for thousands of years and has been mainly used for the production of charcoal. In slow pyrolysis biomass is heated to 500 °C. The vapour residence time varies from 5 min to 20 min. As vapours do not escape as fast as they do in fast pyrolysis, some components being in vapour phase continue to react, and this is not desirable. Therefore, the heating rate of conventional pyrolysis is typically much slower than in fast pyrolysis.
On the other hand, fast pyrolysis is a high temperature process in which biomass is rapidly heated in the absence of oxygen. Biomass decomposes to generate vapours, aerosols and some charcoal-like char. After cooling and condensation of the vapours and aerosols, a dark brown liquid is formed. After the fast pyrolysis, 60-70 wt% of bio liquid is formed, together with 15-25 wt% of solid char and 10-20wt% of non-condensable gases (depending on the feedstock used). An advantage of fast pyrolysis is the zero waste, this is because the bio-oil and solid char can each be used as a fuel. As can be seen in the process in figure 5 above, the gas is recycled into the process.

2.6 Levulinic Acid

2.6.1 Conversion of biomass to Levulinic Acid

Researchers from NREL and PNNL (Pacific Northwest National Laboratory) have conducted an extensive study to identify valuable sugar-based building blocks for lignocellulosic biomass [32]. A long list of 30 interesting chemicals was obtained. By evaluating the potential markets of the building blocks and their derivatives, the list was reduced to 12. One of these promising building blocks is levulinic acid, which is accessible from lignocellulosic biomass using an acid catalyst. In figure 2.7, the conversion of a typical lignocellulosic biomass to LA)
Figure 2.7: Simplified reaction pathway for the conversion of lignocellulosic biomass to LA. (Taken from [33])

Levulinic Acid (LA), also know as 4-oxopentanoic acid or γ-ketovaleric acid, is a C5-chemical with a ketone and carboxylic group (figure 2.8.). LA is readily soluble in water, ethanol, diethyl ether, acetone and many other organic solvents. The dissociation constant (pKₐ) of LA is 4.59 [34], which is comparable with low molecular weight aliphatic carboxylic acids. In the table 2.1, some selected physical properties of LA are shown.

Figure 2.8: Molecule of Levulinic Acid
Table 2.1: Selected physical properties of LA

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pK_a$</td>
<td>4.59</td>
</tr>
<tr>
<td>Melting point</td>
<td>37°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>246°C</td>
</tr>
<tr>
<td>Density</td>
<td>1.14</td>
</tr>
<tr>
<td>Refractive index (20°C)</td>
<td>1.1447</td>
</tr>
<tr>
<td>Surface Tension (25°C)</td>
<td>39.7 dyne cm$^{-1}$</td>
</tr>
<tr>
<td>Heat of vaporization (150°C)</td>
<td>0.58 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>79.8 kJ mol$^{-1}$</td>
</tr>
</tbody>
</table>

2.6.2 Production of levulinic acid

LA was mentioned for the first time by the Dutch professor G. J. Mulder [35] in the 1840s, who, by heating sucrose at high temperature, prepared LA. An example of the reaction is shown in the figure 2.9.

As Girisuta et al. said, the controlled degradation of hexose (C6-sugars) by acids is still the most widely used approach to prepare LA from lignocellulosic biomass. The theoretical yield of LA from C6-sugars is 100 mol %, or 64.5 wt % due to the co-production of formic acid [41]. Commonly, LA yields of about two thirds (or even less) than the theoretical value are attained. These lower yields are due to the formation of undesired black insoluble-materials called humins. Another possible by-product of biomass hydrolysis is furfural, formed by the decomposition reactions of C5-sugars.
2.6.2.1 Continuous production of levulinic acid

Generally, the all levulinic acid production process by biomass are conducted in a laboratory scale, thus these are batch processes. A continuous process for the production of LA from corncob furfural residue at atmospheric pressure was proposed by Dunlop and Wells (1957) [36]. In this process, the carbohydrate feedstock (corncob furfural residue) is mixed with sulphuric acid and water to reach a concentration of corncob furfural residue of 21 wt % and an acid concentration of 3 wt %. Subsequently, the mixture is continuously passed through a reactor maintained at an elevated temperature (169 °C). Typical residence times are 2 h. The insoluble humins are separated from the product mixture in a filter unit. The aqueous mixture containing the acid catalyst and LA is then contacted with a water-immiscible solvent (methyl isobutyl ketone) to obtain an extract containing LA and an aqueous solution containing the acid catalyst. The latter is recycled to the mixer prior to the reactor. In an evaporator, the extraction solvent is separated from the LA and is recycled to the extraction column. Further concentration and purification of LA is carried out in a fractionation unit (vacuum distillation). With this process, a LA yield of 19.9 wt % based on the weight of the dry feedstock charged to the process was obtained.

A scheme of the continuous process for the production of levulinic acid proposed by Dunlop is shown in the figure 2.10.
Chapter 2: Literature review

Figure 2.10: Scheme of a continuous process for producing LA from corn cob furfural residue (taken from [33])

The first commercial-scale plant for the conversion of lignocellulosic biomass to LA has been built in Caserta, Italy [37,38]. In this plant, the process for producing the LA continuously is the Biofine technology [39]. In the figure 2.11 is given the Biofine technology scheme.

Figure 2.11: Scheme of Biofine technology for continuous production of LA
2.6.3 Mechanism of LA formation

The acid catalyzed degradation of hexoses into LA has been extensively studied; however, only a limited amount of information is available on the underlying reaction mechanism. The available information implies that hexose sugars initially dehydrate to form the intermediate product 5-hydroxymethylfurfural (HMF, 2), which is subsequently hydrated to give the final product LA. Scheme 1.1 shows the proposed mechanism for the conversion of hexose sugars, such as D-glucose (3), D-mannose (4) or D-fructose (5) to HMF. The conversion of HMF into LA is the result of water addition to the C2 – C3 bond of the furan ring to give the final products LA and formic acid (6). In the figure 2.12 is shown the scheme of the reaction formation taken from [33].

Figure 2.12: Scheme of dehydration reactions of hexose sugars to HMF
Chapter 2: Literature review

In the figure 2.13 is given a proposed scheme reaction of conversion of HMF to LA.

![Figure 2.13: A proposed scheme of conversion of HMF to LA](image)

2.6.4 Potential applications of LA and its derivatives

Currently, Levulinic acid has frequently been proposed as such a building block. Despite its status as an expensive and relatively small market specialty chemical (about 1 million lb:year at $4.00–$6.00:lb), LA and its derivatives have found use in highly diverse areas. Some applications of levulinic acid might be using LA as chiral reagents [40], biologically active materials [41], polyhydroxyalkanoates [42], polymers [43], polymerization initiators [44], antifouling compounds [45], personal cares products [46], lubricants [47], adsorbents [48], printing/inks [49], coatings [50], electronics [51], photography [52], batteries [53], drug delivery [54], corrosion inhibitors [55].

Moreover, levulinic acid is a very interesting intermediate, which lends to a widespread derivatives compounds. Indeed LA has been identified as a platform chemical for the synthesis of various organic chemicals with applications in the
polymer, fuel additive and organic solvent industries. In the figure 2.14 is shown a summary of the potential derivatives of LA.

**Figure 2.14**: Potentially derivatives compounds of LA
Chapter 3

Materials and Methods

3.1 Introduction

In this thesis, different data about hydrolysis of orange peel and the production of LA are collected and analyzed, and various experimental techniques have been used. In this chapter, the main equipment and procedure adopted during the experimentations are listed and explained. In particular are described the procedure in classic thermal hydrolysis, and the procedure by means of microwave technique, which it allowed to have a rapidly screening of the reactions. Furthermore, the primary treatment of raw material and the analytical equipment and procedures are described.

3.2 Preparation of Raw Material

The orange peel were obtained from a supermarket of Albert Heijn in Enschede (The Netherlands) and they were dried overnight in an oven at 80°C. Then, they were crushed in a blender and sieved to separate orange peel with particle size <100 µm and particle size between 100 µm and 300 µm, from the remainder.
3.3 Experimental procedures

3.3.1 Orange Peel characterization

Thermal gravimetric analysis (TGA) and Fourier transform infrared (FTIR) were used to determine the chemical composition (cellulose, hemicellulose, lignin and the organic ash content) of the orange peel in this study. The TGA was carried out in Mettler Toledo TGA/STDA851 (figure 3.1) by using Nitrogen atmosphere and air atmosphere with a flow rate of 100 mL min⁻¹. The samples were heated from 30°C up to 900°C at a constant heating rate of 10°C min⁻¹.

Figure 3.1: Mettler Toledo TGA/STDA851 equipment

The TGA is essential for characterization of the biomass, in so far it allows to identify approximately the composition. The TGA instrument continuously weighs a sample as it is heated to temperatures of up to 2000 °C, in our case up to 900°C. As the temperature increases, various components of the sample are decomposed and the weight percentage of each resulting mass change can be measured. Results are plotted with temperature on the X-axis and mass loss on
the Y-axis. Then, with the help of the first derivative curve it is possible to see in which range of temperature occurs the degradation, and based on that assume which compound may be in the biomass.

The spectrum was generated by Shimadzu IRTracer-100 (figure 3.2) by means of FTIR technique. FTIR stands for Fourier Transform Infrared.

**Figure 3.2: Shimadzu IRTracer-100 equipment**

When IR radiation is passed through a sample, some radiation is absorbed by the sample and some passes through (is transmitted). The resulting signal at the detector is a spectrum representing a molecular ‘fingerprint’ of the sample. The usefulness of infrared spectroscopy arises because different chemical structures (molecules) produce different spectral fingerprints [56]. The FTIR uses interferometry to record information about a material placed in the IR beam. The Fourier Transform results in spectra that analysts can use to identify or quantify the material. An FTIR spectrum arises from interferograms being ‘decoded’ into recognizable spectra. Patterns in spectra help identify the sample, since molecules exhibit specific IR fingerprints. In figure 3.3 the FTIR operation is shown.
Elemental analyses were performed at the Analytical Department of the University of Groningen using an automated Euro EA3000 CHNS analyzer. In figure 3.4 the Euro EA3000 CHNS is shown.
3.3.2 Microwave experiments

The screening hydrolysis reactions of orange peel carried out in single-mode microwave reactor were conducted with the equipment MW CEM Discover S-class System (figure 3.5). The reaction solution were prepared in a vial, which was housed in the internal cavity, which ensures the right positioning of the same vial. The cavity is larger enough to accommodate vials of different sizes (35ml and 10ml). In the instrument there is a continuous power generator, which is able to supply power from 0W to 300W. Power can be modulated by the instrument according to set-point values of temperature and pressure previously set by the operator. Temperature adjustment is carried out through a feedback control by using a compressed air-control cooling system. The furnace allows to work with two different operating modalities: the first keeps the temperature value to the set-point by varying the power, the latter allows to keep constant power. At the end of the process the instrument releases a report in which trends of T (°C), P (psi) and p (W) recorded during the reaction as a function of time are shown.

Figure 3.5: MW CEM Discover S-class System
3.3.3 Kinetic experiments

The reactions were carried out in 9ml glass tube reactors. The reactors were filled with a predetermined amount of dried orange peel. Subsequently, 5ml of aqueous solution of the sulfuric acid catalyst at the desired concentration was added. After putting in a stirrer, the reactors were sealed and placed in a constant temperature oil bath (± 3°C). At various reaction times, the reactors were taken from the oil and quenched in a water bath at ambient temperature to stop the reaction. The reactors were opened and the liquid separated from solid phase by means of 0.2 µm filter. A certain amount of clear liquid phase was taken and diluted with water (2 cm³). The composition of the solution was determined using HPLC equipment Agilent Technologies 1260 Infinity (figure 3.6) consisting of a Hewlett Packard 1050 pump, a Waters 410 refractive index detector and a BioRad organic acids column Aminex HPX-87H 300mm x 7.8 mm, which was operated at 60°C. The concentration of each compound in the liquid phase was determined using calibration curves obtained by analysing standard solutions with known concentrations.

Figure 3.6: HPLC Agilent Technologies 1260 Infinity
3.4 Definition of the yield and Severity Factor

The yield of levulinic acid is defined on weight base, as the ratio of the total amount of levulinic acid ($M_{LA}$) and the amount of the dried raw material in the reactor ($M_{OP}$).

$$Y_{LA} \ (wt \ \%) = \frac{M_{LA}}{M_{OP}} \times 100$$

The Severity Factor (SF) is calculated as:

$$SF = \log\{t \times \exp[(T_H - T_R)/14.75]\} - pH$$

where $t$ is the reaction time in minutes, $T_H$ the reaction temperature in °C, $T_R$ the reference temperature, most often 100 °C, and pH is the acidity of the aqueous solution in terms of acid concentration [57-59].

3.5 Modelling techniques and software

The optimization experiments were modelled using Design-Expert software (Stat-Ease). The yield of LA was modelled using a standard expression as given in the following equation

$$Y_{LA} = b_0 + \sum_{i=1}^{3} b_i x_i + \sum_{i=1}^{3} \sum_{j=1}^{3} b_{ij} x_i x_j$$

The operating variables (water hyacinth intake, temperature and acid catalyst concentration) are represented by the indices 1–3. The regression coefficients were obtained by statistical analyses of the data. Significance of factors was
determined by their p-value in the ANOVA analyses. A factor was considered significant if the p-value was lower than 0.05, meaning that the probability of noise causing the correlation between a factor and the response is lower than 0.05. Insignificant factors were eliminated using backward elimination, and the significant factors were used to model the data.
Chapter 4

Results and discussion

4.1 Introduction

As previous described, this chapter is divided essentially in four parts. In the first one, the results about the characterization of the orange peel are shown (4.2). In the second part are shown and discussed the results obtained from the experiments carried out in microwave system. The third part of the chapter talks about the optimization experiments carried out by classic hydrothermal approach. The results of the optimization experiments are shown together with the fundamental discussion of the effects of optimization parameters such as temperature, time, feed intake, acid concentration and particle size of the orange peel. In the last part are shown the results about modelling of the optimization reactions.

4.2 Determination of Orange Peel composition

Knowing the Orange Peel composition is crucial for the purposes of gaining insights into the highest theoretically possible LA yield. For this reason, a FTIR spectrum was performed in order to find the main functional group. The figure 4.1 shows the FTIR spectrum of the dried Orange Peel waste.
Figure 4.1: FTIR spectrum of the dried orange peel sample

The spectrum presents the characteristic bands corresponding to cellulose besides of lignin [60]. The most intense band in the high energy region is due to a large amount of OH groups, characteristic of carbohydrates. The intense band around 1010 cm\(^{-1}\) corresponds to the link C–O–H or C–O–R (alcohols or esters), while the peak at 2921 cm\(^{-1}\) represents the presence of C–H stretching vibration, and together with bending vibrations of aliphatic chains (–CH\(_2\)– and –CH\(_3\)–) at 1420 cm\(^{-1}\) forming the basic structure of lignocellulosic material. Indeed, the bands in the range between 1735 cm\(^{-1}\) and 1232 cm\(^{-1}\) are characteristics of lignin bond (Yang et. al. 2007). Lignin is rich of C=C and C=O bonds, which are related with peaks at 1605 cm\(^{-1}\) and 1735 cm\(^{-1}\). In the table 4.1, the main functional groups of the FTIR spectrum are shown.
Table 4.1: The main functional groups in the orange peel

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Functional Groups</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600–3000</td>
<td>OH stretching</td>
<td>Acid, methanol</td>
</tr>
<tr>
<td>2860–2970</td>
<td>C–H(_n) stretching</td>
<td>Alkyl, aliphatic, aromatic</td>
</tr>
<tr>
<td>1700–1735, 1510–1560</td>
<td>C=O stretching</td>
<td>Ketone and carbonyl</td>
</tr>
<tr>
<td>1605</td>
<td>C=C stretching</td>
<td>Benzene stretching ring</td>
</tr>
<tr>
<td>1440–1400</td>
<td>OH bending</td>
<td>Acid</td>
</tr>
<tr>
<td>1233</td>
<td>C–O–C stretching</td>
<td>Aryl-alkyl ether linkage</td>
</tr>
<tr>
<td>1092</td>
<td>C–O–C stretching vibration</td>
<td>Pyranose ring skeletal</td>
</tr>
<tr>
<td>1010</td>
<td>C–O stretching and deformation</td>
<td>C–O–C OH (ethanol)</td>
</tr>
<tr>
<td>700–900</td>
<td>C–H</td>
<td>Aromatic hydrogen</td>
</tr>
<tr>
<td>700–400</td>
<td>C–C stretching</td>
<td></td>
</tr>
</tbody>
</table>

The thermogravimetric analysis (TGA) is necessary to gain insight of the main constituent being part of the OP. The results of a thermogravimetric analysis of Orange Peel are given in the following figures. In the figure 4.2 the thermogravimetric (TG) and differential thermogravimetric (DTG) profiles in nitrogen atmosphere are shown.
The figure presents four distinct stages of weight losses. The first stage between 30°C and 100°C is associated with the release of weakly bonded water molecule. In the next stage, until 285°C the degradation of the Hemicellulose is shown. Afterwards, until 385°C occurs the decomposition of the Cellulose. The last stage represents the degradation of the Lignin, which takes place in the range between 400°C and 740°C. The residue in this case is the 20% in weight and represents just the solid residue. By performing the TGA in air atmosphere, it is possible to know the ash content of the raw material, inasmuch occurs the combustion reaction in the presence of the oxygen. The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of OP in air atmosphere are shown in the figure 4.3.
Figure 4.3: Thermo Gravimetric (TG) and Differential Thermo Gravimetric (DTG) curves of the oven-dried Orange Peel in air atmosphere

The results of these analyses are shown in Table 4.2

Table 4.2: Chemical composition of oven dried Orange Peel

<table>
<thead>
<tr>
<th>Thermal gravimetric analysis</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemicellulose(^a)</td>
<td>35</td>
</tr>
<tr>
<td>Cellulose</td>
<td>25</td>
</tr>
<tr>
<td>Lignin</td>
<td>11</td>
</tr>
<tr>
<td>Water</td>
<td>2.5</td>
</tr>
<tr>
<td>Ash</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Note \(^a\): The hemicellulose content is overrate due to the decomposition of the pectin
Based on TGA data it was obtained 35% corresponding to Hemicellulose. This value is overrate because in the same range of temperatures occurs the degradation of the pectin [61]. By analyzing the DTG profile of the figure 4.2, it is clearly notable the double peaks, in which one is referred to the degradation of the hemicellulose and the second to the degradation of the pectin. The proximity of both peaks may be avoid carrying out the TGA with an increase of temperature not as rapidly as the one used in this study.

The 25% correspond to Cellulose, 11% correspond to lignin, 2.5% corresponding to residual water and finally 2.8% correspond to ash content.

In the Table 4.3 it is possible to find the results of the elemental analysis. These data are the average of two analyzes.

Table 4.3: Elemental analysis of dried orange peel

<table>
<thead>
<tr>
<th>Elemental analysis (dried based)</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>42.89</td>
</tr>
<tr>
<td>H</td>
<td>6.15</td>
</tr>
<tr>
<td>O</td>
<td>49.79</td>
</tr>
<tr>
<td>N</td>
<td>1.17</td>
</tr>
<tr>
<td>S</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>
4.3 Hydrolysis reactions

4.3.1 Exploratory experiments

Exploratory experiments on the acid-catalyzed hydrolysis of orange peel to gain insights into the approximately yield of Levulinic Acid and the behavior of the reactions were carried out.

During the last two decades, the use of dielectric heating in the field of chemistry has become a powerful method to enhance chemical processes. Since the first experiments by Gedye et al. [62], scientists observed that microwave heating promoted increased reaction speed and reduced formation of side products compared with experiments under conventional heating providing and in many cases improved yields to give cleaner reaction profiles in significantly shorter reaction times [63].

The use of MW irradiation system has allowed having a quick analysis of the reaction conditions. Indeed, as Antonietti et al. [64] said, Microwave (MW) irradiation represents a very appropriate tool to make the hydrothermal process more efficient. This form of energy can interact very efficiently with polar molecules, thus allowing a rapid heating of the reaction environment and better yields and selectivity towards the desired products. MW radiation can penetrate lignocellulosic materials and the heat can be produced throughout the volume of the materials (in core volumetric heating) rather than an external source. Furthermore, in the case of lignocellulosic biomass, the effect of MW irradiation at a molecular level leads to a physical disruption of the internal composition of cells, increasing the rate of mass transfer. The application of microwave heating is a fast growing research area, where high reaction rates and selectivity can be achieved together with a significant reduction of the reaction time (often by orders of magnitude) and of energy consumption. [65-68].
In order to perform a preliminary screening of suitable reaction conditions for the synthesis of levulinic, some hydrolysis reactions in a MW reactor were carried out. The following parameters were used for each test:

- Feed intake: 1% wt.;
- Acid-catalyst concentration (H$_2$SO$_4$): 1M;
- Microwave system power: 100W;
- Volume of the vial: 35ml;
- Total sample weight (solid + solution): 7.5g;

By knowing that the main parameters influencing the hydrolysis reaction are temperature and time, it has been chosen to carry out the reactions at two different reaction times, 15min and 30min, and seven different temperatures: 110°C, 120°C, 130°C, 140°C, 150°C, 160°C, 170°C. In figure 4.4 and figure 4.5 yield (wt %) of glucose, xylose, arabinose, levulinic acid, formic acid and acetic acid as function of temperature, respectively for 15min and 30 min are shown.

**Figure 4.4**: Yield (wt %) in glucose (Glu), xylose (Xyl), arabinose (Ara), furfural (FA) and levulinic acid (LA) as function of the hydrolysis temperature for an orange peel sample. Operating condition: 0.075g biomass, 6.7g water, H$_2$SO$_4$ concentration 0.72 wt %. Hydrolysis time: 15 min.
Chapter 4: Results and discussion

Figure 4.5: Yield (wt %) in glucose (Glu), xylose (Xyl), arabinose (Ara), furfural (FA) and levulinic acid (LA) as function of the hydrolysis temperature for an orange peel sample. Operating condition: 0.075g biomass, 6.7g water, H_{2}SO_{4} concentration 0.72g. Hydrolysis time: 30 min.

Note: Tests at 150°C and 160°C were carried out with double operating conditions (0.15g biomass, 13.4g water, H_{2}SO_{4} concentration 1.44g.

By analyzing the two figures above, it is easy to note how the levulinic acid conversion reaction is already complete after 30 minutes at 160 °C, in fact, they are no longer registered sugars (in particular those C-6, then glucose) present in solution. With particular reference to figure 4.4, the yield value of levulinic acid and formic acid is almost equal both in the reaction at 160 °C that in the reaction at 170 °C. Comparing the reactions at the same temperature but different times, is, as predicted with increasing reaction time, an increase of levulinic acid amount to the detriment of the sugars present in the solution, a symptom of a progression of the conversion reaction. The same happens analyzing the reactions with changes in temperature by fixing the reaction times: the levulinic acid yield increases with temperature, while the yield of sugars decreases.
The presence of the sugars is due to the degradation of the polymers (cellulose and hemicellulose) to the sugar monomers. Glucose derived both from cellulose and hemicellulose (c-6 sugars), whereas xylose and arabinose come from the degradation of the C-5 part of the hemicellulose.

These reaction screenings are also useful for to gain insight of the reaction pathways and having a proof of the real reaction mechanism.

Looking to the reaction of formation of Levulinic acid (figure 4.6) is it possible to see the stoichiometry of the reaction. Indeed, together with the formation of LA occurs the co-production of FA.

![Reaction pathway](image)

**Figure 4.6:** Formation reaction of Levulinic Acid together with Formic Acid

By analyzing the figures 4.4 and 4.5 results clearly notable the co-formation of LA and FA. Moreover, at high temperatures, especially after 30 minutes, there is not an increase in yield both LA yield and FA yield.

The formation of the acetic acid is due to the acetylic groups present in the biomass. The yield of the acetic acid present in the solution after the reaction is almost the same for each kind of reaction. Both varying temperatures and times. It is settled between 1% wt. and 2.5% wt.
Regarding reactions at high temperatures, it is possible to note, especially in the figure 4.4 that, even halving reaction time, the LA yield and FA yield are quite high compared to maximum yield reachable. This occurs even though the glucose unreacted is still in the solution. This is symptom of the ease to hydrolyze the biomass.

In the table 4.4, the conversion of the reaction based on the glucose content is shown. The conversion is expressed on weight base.

**Table 4.4**: Reaction conditions, LA yield and glucose conversion for each reaction

<table>
<thead>
<tr>
<th>Test</th>
<th>T°C</th>
<th>min</th>
<th>LA yield (wt. %)</th>
<th>Conv. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>110</td>
<td>15</td>
<td>9,64</td>
<td>75,46</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>15</td>
<td>10,39</td>
<td>47,46</td>
</tr>
<tr>
<td>3</td>
<td>130</td>
<td>15</td>
<td>12,20</td>
<td>47,98</td>
</tr>
<tr>
<td>4</td>
<td>140</td>
<td>15</td>
<td>13,40</td>
<td>50,86</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>15</td>
<td>15,46</td>
<td>57,60</td>
</tr>
<tr>
<td>6</td>
<td>160</td>
<td>15</td>
<td>20,62</td>
<td>69,20</td>
</tr>
<tr>
<td>7</td>
<td>170</td>
<td>15</td>
<td>23,58</td>
<td>100,00</td>
</tr>
<tr>
<td>8</td>
<td>110</td>
<td>30</td>
<td>9,60</td>
<td>48,52</td>
</tr>
<tr>
<td>9</td>
<td>120</td>
<td>30</td>
<td>11,57</td>
<td>44,47</td>
</tr>
<tr>
<td>10</td>
<td>130</td>
<td>30</td>
<td>13,89</td>
<td>50,88</td>
</tr>
<tr>
<td>11</td>
<td>140</td>
<td>30</td>
<td>15,61</td>
<td>59,52</td>
</tr>
<tr>
<td>12</td>
<td>150</td>
<td>30</td>
<td>21,40</td>
<td>75,20</td>
</tr>
<tr>
<td>13</td>
<td>160</td>
<td>30</td>
<td>23,43</td>
<td>100,00</td>
</tr>
<tr>
<td>14</td>
<td>170</td>
<td>30</td>
<td>23,45</td>
<td>100,00</td>
</tr>
</tbody>
</table>
In figure 4.7, figure 4.8, figure 4.9, figure 4.10, figure 4.11 and figure 4.12 are shown respectively the yield (wt %) of levulinic acid, formic acid, acetic acid, glucose, xylose and arabinose for different temperatures as a function of the time (15min and 30min).

**Figure 4.7**: LA Yield (wt. %) for different temperatures as a function of time (15min, 30min)

**Figure 4.8**: FA Yield (wt. %) for different temperatures as a function of time (15min, 30min)
Figure 4.9: AA Yield (wt. %) for different temperatures as a function of time (15min, 30min)

Figure 4.10: Glucose Yield (wt. %) for different temperatures as a function of time (15min, 30min)
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Figure 4.11: Xylose Yield (wt. %) for different temperatures as a function of time (15min, 30min)

Figure 4.12: Arabinose Yield (wt. %) for different temperatures as a function of time (15min, 30min)
By analyzing the figures above, it is clearly notable how the main difference come out in temperatures in the middle of the range. This assumption fits for the acids, such as levulinic acid, acetic acid and formic acid, or rather for the final products of the reaction pathways. Looking the sugars, such as glucose, xylose and arabinose, which are the intermediate reaction products, the main differences are shown at low temperatures or high temperatures. Indeed, the first step for the path of the reaction is the solubilization of the sugars in the solution. Thus, at lower temperatures the time parameter plays an important role in yield terms. At high temperature, instead, it is possible observing the completely disappearance of the sugars in the solution, symptom of the totally conversion of the reaction.
4.3.2 Optimization experiments

4.3.2.1 Introduction

In this paragraph are shown and described the results about the optimization experiments. The first step was to carry out some experiments in order to choose the right particle size for having the best possible yield of levulinic acid. Once chosen the best particle size, that was used for the all next experiments.

In the next paragraphs there are also described the effects of the main parameters on the optimization of the levulinic acid production, in order to have an idea of the parameters playing the biggest role in the reaction.

4.3.2.2 Effect of particle size of raw material

Two experiments at 160°C with 1% wt of feed intake in a 1M sulfuric acid solution were carried out in order to find the right particle size for the optimization experiments. In the first experiment raw material with particle size between 300 µm e 100 µm was used. In the second experiment raw material with particle size <100 µm was used. In both cases times of investigation were 15min, 30min, 60min, 90min, 105min, and 120min. The two investigation temperatures were 160°C and 175°C in order to see if there are differences with medium and medium-high temperatures. In the figure 4.13, time trends of LA yield at 160°C as a function of feed intake particle size are shown.
Figure 4.13: Trend of the yields for particle size <100 µm and particle size between 100 µm and 300 µm at 160°C.

Two experiments at 175°C with 1% wt of intake in a 1M sulfuric acid solution were carried out. Since the main production of levulinic acid occurred in the first 30 minutes, for this experiment the investigation times were 5min, 10min, 15min, 30min, 60min, and 120min. In the figure 4.14, time trends of LA yield at 175°C as a function of feed intake particle size are shown.
Figure 4.14: Trend of the yields for particle size <100 µm and particle size between 100 µm and 300 µm at 175°C.

Apparently, analyzing these results, orange peel with smaller particle size gives better results than orange peel with higher particle size. For this reason, only orange peels with particle size <100 µm were used for the next studies.

In order to find the optimal parameters, some experiments were performed, differing in temperature, sulfuric acid concentration and initial intake of orange peel. For the whole experiments, orange peel with particle size <100 µm were used. The effects of the process conditions on the LA yield are discussed in the following section.
4.3.2.3 Temperature and time effects

Temperature is one of the most important parameters for the optimization of production of Levulinic Acid. This is due to the strong dependency of the reaction rate on the temperature. In this case, for the optimization experiments, four different temperatures were analyzed: 150°C, 160°C, 175°C and 180°C. In figure 4.15 the differences of Levulinic Acid yield, after 30min of reaction, among 4 kinds of reactions performed with 1% wt of feed intake in a 1M acid-catalytic solution, varying the temperature are shown.

![Figure 4.15: Levulinic Acid yield after reaction time of 30min at different temperature (1M acid-catalyst concentration, 1% wt feed intake)](image)

Another crucial parameter in order to evaluate the highest Levulinic Acid yield is surely the time. The production reaction of Levulinic Acid needs more or less time, mainly depending on temperature and concentration of the catalyst.
Taking in example reactions at 150°C and 180°C, it is possible to notice how the levulinic acid yield change after 120min. In figure 4.16 differences of levulinic acid yield between 30min and 120min for reaction at 150°C and reaction at 180°C are shown.

![Bar graph showing LA yield (%) wt for 150°C and 180°C at 30min and 120min](image)

**Figure 4.16:** Differences of Levulinic Acid Yield between reaction time of 30min and reaction time of 120min for two different reactions (1% wt feed intake, 1M acid-catalyst solution) differing in temperature: 150°C and 180°C

In both cases, there is an increase in Levulinic Acid yield. This might be due to the fact that completely conversion takes long time to be achieved especially operating at lower temperatures. In figure 4.17, time trends of Levulinic Acid yield for both reactions (150°C and 180°C) are shown.
Figure 4.17: Time trends of Levulinic Acid yield with 1% wt of feed intake and 1M Acid catalyst concentration as a function of the Temperature (150°C and 180°C)

Through this graphs, it is possible to analyze the correlation between time and temperature. It is possible to obtain the maximum possible yield after 15-30min by working at 180°C, whereas reaction at 150°C needs about 90-120min to reach the highest yield possible, as well as would be expected. Therefore, watching these results in terms of convenience, it is surely better to work at the highest possible temperature, since the maximum yield is obtainable with less reaction time.

4.3.2.4 Acid catalyst concentration effects

In this paragraph, the effects of the acid catalyst concentration are shown. Focusing on the reaction at 180°C, it is possible to evaluate how the Levulinic Acid yield varies, by changing the concentration of the catalyst. Concentrations 0.1M, 1M and 1.5M of Sulphuric Acid have been investigated. In the figure 4.18, differences of LA yield reached at 180°C, feed intake of 1%, among different concentrations are shown.
By analyzing the previous figure, it is possible to notice how the Levulinic Acid yield is not linearly dependent on the acid concentration. After reaction time of 30 min, the best yield, 19.3% wt, is achieved using a solution 1M (mol/L) of Sulphuric Acid, whereas using a solution 1.5M of Sulphuric Acid, the achieved yield is 18.5% wt. However, the same assumption is not valid if we consider how the Levulinic Acid yield changes as a function of concentration after 120 min, working with a temperature of 150°C (figure 4.19).
Figure 4.19: LA yield (% wt) after reaction time of 120min at 150°C using 1% wt feed intake at different acid catalyst concentrations

By observing the previous figure, it appears that working at 150°C, the yield increases by increasing the acid concentration. This is in contrast with the discussion above. The reason of this behavior might be that the reaction rate of secondary reactions (degradation of some thermos sensible compounds) varies by increasing temperature. Indeed, the changing acid concentrations has an effect on reaction time as well. An example is shown in the figure 4.20, which represents time trends of reactions working at 150°C with 5% wt of feed intake as a function of the acid concentration.
Figure 4.20: Time trends of Levulinic Acid yield with 5% wt of feed intake working at 150°C as a function of the acid-catalyst concentration

By analyzing the picture above, the function of the catalyst is to facilitate the Levulinic Acid production. Reactions operating at 1M and 1.5M acid catalyst concentration are faster than the reaction working at 0.1M. Furthermore they reach a higher yield value than the reaction working with lower acid concentration.

Under high temperature condition (180°C), a blank test in absence of H₂SO₄ was also carried out, and in this case there were no traces of levulinic acid, thus confirming the effectiveness of catalytic approach.
4.2.3.5 Feed intake effects

The last parameter used to the optimization analysis of production of Levulinic Acid is the amount of feed intake. In this study, two values of feed intake have been investigated: 1% wt and 5% wt based on the solution amount. In the figure 4.21 differences between LA yield reached after 30 min using 1% wt and 5% wt of feed intake at 180°C in a 1M acid solution are shown.

![Bar chart showing LA yield (% wt) for different feed intake (% wt)](image)

**Figure 4.21**: Levulinic Acid yield (% wt) after reaction time of 30 min for different reaction conditions as a function of feed intake

By analyzing the picture above, it easy to notice how the Levulinic Acid yield reached using 5% wt of feed intake is lower than the yield reached using 1% wt of feed intake. This assumption is also valid analyzing the whole duration of the reaction, as it is possible to see in the figure 4.22
Taking into consideration the same reaction times, it is clearly notable that the LA Yield using 5% of feed intake is always about 3% lower than LA yield obtained using 1% of feed intake.

### 4.2.3.6 Severity Factor

The combined severity parameter facilitates comparison of a broad range of yield data by coupling the reaction conditions of time, temperature, and acid concentration into a single variable. This parameter results very useful in order to having a clear background of the totally reactions plotted in a single graph. In the figure 4.23 the yield of levulinic acid for the completely reaction performed for the optimization is shown as a function of the severity factor differing for the feed intake parameter.

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**Figure 4.22**: Time trends of Levulinic Acid yield (wt%) working at 180°C in 1M Acid solution as a function of the feed intake
By analyzing the figure above, it is possible observing how the best yield of the production of levulinic acid is around the value 4.5 of severity factor. This means that all the reactions having parameters such ash acid catalyst concentration, temperature and time and giving 4.5 as severity factor provide the best yield. The graph shows also the differences between 1% wt. and 5% wt. of feed intake. As described before, indeed, using feed intake of 1% wt. on the total amount (soid + solution) instead of 5%, gives higher yields.
4.2.3.7 Optimization modelling

To quantify the effect of process conditions on the LA yield, the data were analyzed using the Design-Expert software.

A total of 14 experiments were performed, differing in temperature, acid catalyst concentration and initial intake of orange peel. In the Table 4.5 are shown the values of the parameters for each experiments and their response in term of LA Yield (wt. %) after 30min of reaction.

Table 4.5: Optimization experiments parameters and LA yield response

<table>
<thead>
<tr>
<th>Test</th>
<th>T (°C)</th>
<th>CH$_3$SO$_4$</th>
<th>Feed intake (wt. %)</th>
<th>LA Yield (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>0.1</td>
<td>1</td>
<td>2.7</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>0.1</td>
<td>5</td>
<td>2.4</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>1</td>
<td>1</td>
<td>13.9</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>1</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>1.5</td>
<td>1</td>
<td>15.1</td>
</tr>
<tr>
<td>6</td>
<td>150</td>
<td>1.5</td>
<td>5</td>
<td>12.6</td>
</tr>
<tr>
<td>7</td>
<td>165</td>
<td>0.8</td>
<td>1</td>
<td>18.8</td>
</tr>
<tr>
<td>8</td>
<td>165</td>
<td>0.8</td>
<td>5</td>
<td>15.6</td>
</tr>
<tr>
<td>9</td>
<td>180</td>
<td>0.1</td>
<td>1</td>
<td>7.9</td>
</tr>
<tr>
<td>10</td>
<td>180</td>
<td>0.1</td>
<td>5</td>
<td>7.3</td>
</tr>
<tr>
<td>11</td>
<td>180</td>
<td>1</td>
<td>1</td>
<td>19.3</td>
</tr>
<tr>
<td>12</td>
<td>180</td>
<td>1</td>
<td>5</td>
<td>16.1</td>
</tr>
<tr>
<td>13</td>
<td>180</td>
<td>1.5</td>
<td>1</td>
<td>18.5</td>
</tr>
<tr>
<td>14</td>
<td>180</td>
<td>1.5</td>
<td>5</td>
<td>16.3</td>
</tr>
</tbody>
</table>
The highest experimental yield was obtained at 180°C, acid catalyst concentration 1M, using 1% wt. of feed intake, and it is 19.3 wt. %. This is not the best yield reached during the optimization experiment, because the values present in the table 4.5 referred to 30min of reaction. Actually, it is possible reaching best values of LA yield increasing reaction time, but in term of convenience, taking values on 30min of reaction time results better than take them after more time, insofar the gain obtained in term of yield is not comparable with time which reaction needs to reach these values.

By analyzing the data with the software, the best model found is the following:

$$LA\ yield = -18.6508 + 0.15944 \, T + 7.76204 \, C_{H_2SO_4} - 0.56786 \times Feed\ intake$$

Even though this is the best model found, it fits not very well with the empirical data, in fact, the R-squared value is $$R^2 = 0.7851$$. In the table 4.6, analysis of variance of the model is shown.

**Table 4.6**: Analysis of variance of the preferred model

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F-Value</th>
<th>p-value Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>329.76</td>
<td>3</td>
<td>109.92</td>
<td>12.18</td>
<td>0.0011</td>
</tr>
<tr>
<td>T°C (A)</td>
<td>68.64</td>
<td>1</td>
<td>68.64</td>
<td>7.61</td>
<td>0.0202</td>
</tr>
<tr>
<td>CH$_2$SO$_4$ (B)</td>
<td>243.06</td>
<td>1</td>
<td>243.06</td>
<td>26.93</td>
<td>0.0004</td>
</tr>
<tr>
<td>Feed intake (C)</td>
<td>18.06</td>
<td>1</td>
<td>18.06</td>
<td>2</td>
<td>0.1876</td>
</tr>
<tr>
<td>Residual</td>
<td>90.25</td>
<td>10</td>
<td>9.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In the figure 4.24 is provide the parity plot for predicted and experimental values.

![Figure 4.24: Predicted vs. experimental data of LA yield (wt. %)](image)

The model predicts that both acid concentration and temperature have a profound effect on the levulinic acid yield. This is confirmed by the figure 4.25 and figure 4.26.

![Figure 4.25: Surface response of predicted model as function of acid concentration and temperature for 1% feed intake](image)
Figure 4.26: Surface response of predicted model as function of acid concentration and temperature for 5% feed intake
Chapter 5

Conclusions

In order to gain a deeper insight into the hydrolysis mechanism of the orange peel, several experiments were carried out. First of all, to know the main reaction conditions, the biomass was hydrolyzed using a MW reactor. The microwave system allows having considerable benefits in term of time and heating savings.

During these experiments, the main aim has been to find the perfect parameters for the production of levulinic acid by orange peel. Thanks to the MW experiments, it has been possible knowing the best possible LA yield reachable. Moreover, by analyzing the sugar contents during reactions, it was possible studying reaction trends, and to choose the ranges of parameters to investigate during optimization experiments. In order to find the perfect values of temperature, acid catalyst concentration and feed intake, a total of 14 experiments were carried out.

Data show great results in term of LA yield. The maximum yield reachable is around 20 wt. %. Considering other studies on different biomass, the production of levulinic acid by orange peel seems to have a great impact and a considerable convenience. For example, the maximum yield reached using water hyacinth plant as biomass is 9 wt.% (Girisuta et al. 2008). It is possible to obtain the same
value by orange peel, using giant reed (Arundo donax L.). In fact the study of Antonietti et al., around 22 wt.% of LA yield using HCl as acid catalyst was reached.

Furthermore, considering that orange peel is a food waste, recover add value products adopting the biorefinery concept results a great path for the challenges of green chemistry.

5.1 Future works

The experiments performed in this study, were carried out in a small lab scale, thus with only 5ml of solution in a 9ml reactor. Future works expect to reply the experiments carried out in this work, in a bigger scale, therefore in a bigger reactor. Moreover for a complete recovery of the whole biomass, it will be necessary carry out studies on the residual char obtained during hydrolysis reactions.
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(Available on 29 June 2016)


Appendix A

Other Graphs
Figure A.1: LA Yield (% wt) reached after reaction time of 30min using 1% feed intake at different acid catalyst concentrations as a function of the Temperature

Figure A.2: LA Yield (% wt) reached after reaction time of 30min using 5% feed intake at different acid catalyst concentrations as a function of the Temperature
Figure A.3: LA Yield (%wt) reached after reaction time of 120min using 1% feed intake at different acid catalyst concentrations as a function of the Temperature

Figure A.4: LA Yield (%wt) reached after reaction time of 120min using 5% feed intake at different acid catalyst concentrations as a function of the Temperature
Figure A.5: LA Yield (%wt) reached after reaction time of 30min at 150°C and different acid catalyst concentrations as a function of the Feed intake

Figure A.6: LA Yield (%wt) reached after reaction time of 30min at 180°C and different acid catalyst concentrations as a function of the Feed intake
Figure A.7: LA Yield (wt%) reached after reaction time of 120 min at 150°C and different acid catalyst concentrations as a function of the Feed intake.

Figure A.8: LA Yield (wt%) reached after reaction time of 120 min at 180°C and different acid catalyst concentrations as a function of the Feed intake.
Figure A.9: Time trend of LA Yield (%wt) with 1% wt of feed intake and 0.1M Acid catalyst concentration as a function of the Temperature

Figure A.10: Time trend of LA Yield (%wt) with 1% wt of feed intake and 1.5M Acid catalyst concentration as a function of the Temperature
Figure A.11: Time trend of LA Yield (%wt) with 5% wt of feed intake and 0.1M Acid catalyst concentration as a function of the Temperature

Figure A.12: Time trend of LA Yield (%wt) with 5% wt of feed intake and 1M Acid catalyst concentration as a function of the Temperature
Figure A.13: Time trend of LA Yield (%wt) with 5% wt of feed intake and 1.5M Acid catalyst concentration as a function of the Temperature

Figure A.14: Time trend of LA Yield (%wt) at 150°C and 0.1M Acid catalyst concentration as a function of the Feed intake
Figure A.15: Time trend of LA Yield (\%wt) at 150°C and 1M Acid catalyst concentration as a function of the Feed intake

Figure A.16: Time trend of LA Yield (\%wt) at 150°C and 1.5M Acid catalyst concentration as a function of the Feed intake
Figure A.17: Time trend of LA Yield (%wt) at 180°C and 0.1M Acid catalyst concentration as a function of the Feed intake

Figure A.18: Time trend of LA Yield (%wt) at 180°C and 1.5M Acid catalyst concentration as a function of the Feed intake
Figure A.19: Time trend of LA Yield (%wt) at 150°C with Feed intake of 1%wt as a function of the Acid catalyst concentration.

Figure A.20: Time trend of LA Yield (%wt) at 180°C with Feed intake of 1%wt as a function of the Acid catalyst concentration.
Figure A.21: Time trend of LA Yield (%wt) at 180°C with Feed intake of 5%wt as a function of the Acid catalyst concentration
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