Novel catalytic systems for sustainable chemical processes

Županić, Ana-Maria

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Ana-Maria Županić

NOVI KATALITIČKI SUSTAVI ZA ODRŽIVE KEMIJSKE PROCESE

DIPLOMSKI RAD

Voditelj rada: Izv. prof. dr. sc. Irena Škorić

Članovi ispitnog povjerenstva:

Izv. prof. dr. sc. Irena Škorić

Izv. prof. dr. sc. Marija Vuković Domanovac

Doc. dr. sc. Domagoj Vrsaljko

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Sažetak

Korištenje obnovljivih izvora biomase za održivu proizvodnju prepoznato je kao moguća zamjena za neobnovljiva fosilna goriva. Bio-utemeljeno gospodarstvo će značajno smanjiti ovisnost o naftnim sirovinama, ublažiti globalno zatopljenje, smanjenjem CO_2 emisija, smanjiti odlaganja otpada i konačno povećati ekonomsku korist. Trenutni pokušaji provode se s ciljem razvoja novih smjerova u sintezi alkil-levulinoata iz levulinske kiseline, kao polaznog materijala. Tijekom poslijednjih pet godina alkil-levulinoati privukli su pozornost istraživača, zbog svojih specifičnih fizikalno-kemijskih svojstava i mogućnosti primjene.

Osim korištenja obnovljivih izvora sirovine, heterogena kataliza privukla je puno pozornosti na području zelene kemije. Ovaj diplomski rad dio je širokog istraživačkog projekta, koji je bio proveden u Laboratoriju za zelenu sintetsku kemiju (Green S.O.C., Sveučilište Perugia, Italija) s ciljem razvoja potpuno zelene sintetske metodologije za pripremu bio-kemikalija dodatnih vrijednosti. Priprava alkil-levulinoata počevši od levulinske kiseline podrazumijeva korištenje alkohola kao reagensa i prisustvo kiselog katalizatora (tzv. reakcija esterifikacije). Pristup koji je korišten temelji se na pripremi novih heterogenih katalizatora, odnosno umreženih kiselih katalizatora temeljenih na polistirenu, a koji sadrže različita svojstva u pogledu gustoće aktivnih mjesta i fizičke morfologije. Da bi se potvrdila njihova katalitička aktivnost, provedene su reakcije esterifikacije s levulinskom kiselinom i različitim alkoholima.

Ključne riječi: biomasa, alkil-levulinoati, zelena kemija, heterogena kataliza, kiseli katalizatori

Summary

Utilisation of renewable biomass for sustainable production has been recognised as a possible substitute for non-renewable fossil fuels. A bio based economy will substantially reduce the dependence on petroleum feedstock, mitigate the global warming by reducing CO_2 emissions, reduce waste disposal and finally increase the economic benefits. Current efforts have been performed to develop new routes in the synthesis of alkyl levulinates from levulinic acid, as a starting material. Over the past five years, the alkyl levulinates have attracted the attention of researches due to their specific physical-chemical properties and possible applications.

Beside the use of renewable feedstock, heterogeneous catalysis has gain also a lot of attention in the area of green chemistry. This thesis work is part of broad research project carried out at the Laboratory of Green Synthetic Chemistry (Green S.O.C., University of Perugia, Italy) aiming at the development of fully green synthetic methodologies for the preparation of value-added bio-chemicals. The preparation of alkyl levulinates starting from levulinic acid implies the use of an alcohol as a reagent, in the present of an acid catalyst (so-called esterification reactions). The approach used is based on the preparation of novel heterogeneous catalysts, specifically cross-linked polystyrene-based acid catalysts, featuring different properties in term of density in active sites and physical morphologies. To verify their catalytic efficiency, esterification reactions of levulinic acid with different alcohols were conducted.

Key words: biomass, alkyl levulinates, green chemistry, heterogeneous catalysis, acid catalysts

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1. Introduction

Environmental protection is a prominent trend in the whole world, not only on individual continents or on sectors of interest. This is a wide and comprehensive concept, which is not only promoted by the scientists but it is the duty of the state policy, as well as European and world policy. Although it is called a trend, it must be considered also as a responsibility of all of us.

Most of the political parties have implemented the environmental obstacles into their policy, and their standpoints about sustainability are being emphasized so they could increase the awareness about the environment protection.

The rapid development of industries and technology has brought many negative effects, which are revealed in different aspects of pollution, especially in air, water and soil pollution. Other undesirable effects are: impact on climate change, the gradual decommissioning of the stratospheric ozone layer, degradation, deforestation, soil impoverishment and reduction of biodiversity. Need for change mitigation lead scientists and engineers to think to create greener and more sustainable technologies.

Global competitive tension forces chemical engineers to continually and constantly monitor the introduction of new technologies in the market, inform about their capabilities and apply the ones that will give the most efficient and effective results.

In this thesis, the development of new heterogeneous acid catalysts and their use in the production of alkyl levulinates is described.

2. Green Chemistry

The field that creates a framework for better and healthier conditions is the field of Green Chemistry, which should be in conjunction with the sustainable development. Green Chemistry is defined as the "design of chemical products and processes to reduce or eliminate the use and the generation of hazardous substances".[1]

Art of Green Chemistry is to devise a design, which considers efficient exploitation of raw materials (preferably renewable) without using toxic and/or hazardous reagents and solvents. Apart from that the developed systems should eliminate the generation of waste.[2,3]

On the other hand, sustainability considers beside the ecological component also the societal and economic component (Figure 1). To employ the optimal use of resources it is necessary to integrate technical, economic and social development, which are compliant with the necessity of environmental protection and advanced life ambience.[3]



Figure 1. Graphical display of sustainability.

In recent years, plenty of Countries jointly participated in the implementation of green and sustainable activities in academia and industries. Because of their extreme activities, there are a lot of examples of successful utilisation of green chemistry technologies.[4]

2.1. Principles of Green Chemistry

In 1998 Paul Anastas and John Warner presented the 12 principles of Green chemistry, although before them Trevor Kletz already entitled the next phrase: "*What you don't have, can't leak"*, and made the frames in which industrial and scientific work should have been defined.[1,5]

The following list helps to understand the meaning of the definition in practice and guides chemists towards fulfilling their role in achieving sustainable development.

The 12 principles are shown in table 1.

Table 1. 12 Principles of Green chemistry:[1]

1. *Prevention*	*It is better to prevent waste than to treat or clean up waste after it has been created.*
2. *Atom Economy*	Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. *Less Hazardous Chemical Synthesis*	Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. *Designing Safer Chemicals*	Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. *Safer Solvents and Auxiliaries*	The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. *Design for Energy Efficiency*	Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods

	should be conducted at ambient temperature and pressure.
7. *Use of Renewable Feedstock*	A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. *Reuse Derivatives*	Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. *Catalysis*	Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. *Design for Degradation*	Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. *Real-time analysis for Pollution Prevention*	Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. *Inherently Safer Chemistry for Accident Prevention*	Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

2.2. Metrics

In recent years, new systematic methods and tools are proposed in order to assess the sustainability of a process and therefore lot of progress is needed for the identification, design and development of appropriate products and processes that will produce sustainable and environmental acceptable processes.[6]

Reaction yield (RY) represents the quantity of a product (usually expressed as a fraction or a percentage) obtained in a chemical reaction from a given reactant.

Selectivity (S) indicates the ratio of one of the products (usually the desired one) emanating from the conversion of a certain reactant with respect to the other ones, or to the conversion of the starting material.[7]

The most commonly used metrics are: "Atom Economy", "Atom Efficiency", "Carbon Efficiency", "Environmental Factor (E-factor)", "Effective Mass Yield" and "Reaction Mass Efficiency".

Atom Economy (AE) has been introduced by Barry Trost in 1990s[8] and it refers to the concept of maximising the incorporation of atoms from reactants into the final products. It is defined as the ratio of molecular weight of the desired product over the molecular weights of all reactants, see eq. 1.1.[1,7]

$$AE = \frac{MW(products)}{\sum MW(reactants)} \tag{1.1}$$

The ideal reaction would be the one where all the atoms could be found in the desired product. If there is a multi-step process where intermediates are formed the calculation extends in the form shown in Figure 2.

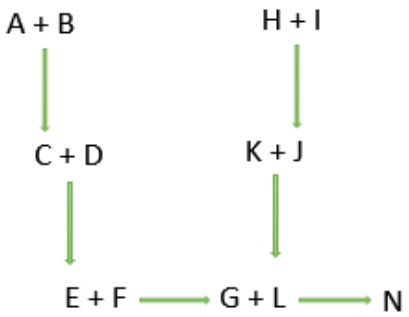


Figure 2. Multistep reaction.

$$\%\ AE\ of\ G = \frac{MW(G)}{MW(A+B+D+F)} * 100\% \quad (1.2.)$$

$$\%\ AE\ of\ N = \frac{MW(N)}{MW(A+B+D+F+H+I+K)} * 100\% \quad (1.3.)$$

Researchers from GlaxoSmithKline in 2001 presented a census of green metrics used by their company to promote sustainable chemistry. Among these, reaction mass efficiency (RME) was also represented. It is defined as ratio of product mass over the sum of the masses of reactants.

For a generic reaction: $A + B \rightarrow C$

$$RME(\%) = \frac{mass\ of\ C}{mass\ of\ A + mass\ of\ B} * 100\% \quad (1.4.)$$

It was also revealed that reaction mass efficiency relates Atom Economy, chemical yield and stoichiometry (actual molar quantities of reactants). Extended expression, that shows this connection is shown in Figure 3. [9,10]

	A	$+\ B$	$\rightarrow$	C
Mass:	m_1	m_2		m_3
Moles:	x	y		z
MW:	MW_1	MW_2		MW_3

$$RME = \frac{m3}{m1 + m2} = \frac{z(MW3)}{y(MW1) + z(MW2)}$$

$$= \frac{z(MW3)}{x(MW1) + (y - x + x)(MW2)} = \frac{z(MW3)}{x(MW1) + x(MW2) + (y - x)(MW2)}$$

$$= \frac{z}{x} * \frac{MW3}{MW1 + MW2 + x^{-1}(y - x)MW2} * \frac{(MW1 + MW2)^{-1}}{(MW1 + MW2)^{-1}}$$

$$= \frac{z}{x} * \frac{MW3}{MW1 + MW2} * \frac{1}{1 + \frac{(y - x)MW2}{x(MW1 + MW2)}}$$

$$= Yield * Atom\ Economy * \frac{1}{Stoichiometric\ \ Factor}$$

Figure 3. REM relates chemical yield, AE and stoichiometry.

Another often used parameter is process mass intensity (PMI, the reciprocal of reaction mass efficiency). General reaction assumes also the use of auxiliary materials such as reaction solvents (S), catalyst (C), work up materials (WPM) and purification materials (PM). Hence, the PMI is defined as a percentage of mass of all the inputs relative to the mass of desired product.[11]

$$PMI = \frac{mass\ of\ inputs}{mass\ of\ product} = \frac{m_A+m_B+m_S+m_C+m_{WPM}+m_{PM}}{m_P} \quad (1.5.)$$

The main limitation of PMI parameter is that it considers the mass of chemicals involved as a "lump sum" and does not consider their quality or ecological risks related to them. Hence, Hudlicky defined the term Effective mass yield (EMY), defined as a percentage of mass of the desired product relative to the mass of all non-benign materials used in its synthesis.[7]

$$EMY\ (\%) = \frac{mass\ of\ products}{mass\ of\ non\ benign\ materials} * 100\% \quad (1.6.)$$

Under the term "benign components", by-products, solvents or reagents that have no known environmental risk associated with them are defined. For example, water, dilute ethanol, low concentration saline solutions, autoclaved cell mass, etc.[7]

Due to the impossibility to determine if certain substances are non-benign, this parameter is not much useful.

Carbon efficiency (CE) is described as the percentage of carbon in the product respect to the total carbon in reactants.

$$CE(\%) = \frac{amount\ of\ carbon\ in\ products}{total\ carbon\ present\ in\ reactants} * 100\% \quad (1.7.)$$

This parameter does not take in account neither the solvent nor the additives, which are used in the reactions thus means it has a significant limitation and should be conjoined with other metrics.[7,10]

One of the simplest and most useful parameter that measures environmentally accessibility of chemical processes, or in other words respond to the question: "Is the

process sustainable?" is called Environmental Factor (E-factor). It is described as the ratio of the mass of waste to the final product.

$$E\ factor = \frac{mass\ of\ wastes\ (kg)}{mass\ of\ products\ (kg)} \quad (1.8)$$

Table 2. shows typical values of E-factor in different industrial sectors. The E-factor considers the reaction yield and includes reactants, solvents, all the additives/ coadjuvants and in principle the energy involved, although this latter is difficult to quantify. Higher E-factor values means more waste, and therefore bigger negative environmental impact.

Table 2. E-factor in various segments of chemical industry

Industry sector	Annual production(t)	E-factor	Waste production (t)
Oil refining	10^6-10^8	<0.1	10^4-10^6
Bulk chemicals	10^4-10^6	<1-5	10^4-5x10^6
Fine chemicals	10^2-10^4	5-50	5x10^2-5x10^5
Pharmaceuticals	10-10^3	25-100	2,5x10^2-10^5

From the table it can be concluded that processes, leading to the synthesis of fine chemicals or pharmaceuticals produce larger amount of waste, since they involve multiple syntheses and numerous purification steps.[7,12]

For measuring the environmental acceptability of processes, mass intensity (MI) is also used. Developed by Constable and co-workers of GlaxoSmithKline is defined as the total mass used in the process divided with the mass of the product.[12]

$$MI = E\ factor + 1 \quad (1.9.)$$

Considering the value of ideal conditions MI should be one in comparison to E-factor, where the expected value should be zero. As the value zero reminds to the terminal goal of zero waste, E-factor is considered the best metric, which gives a mental picture of how wasteful a process is.[12]

2.3.Solvents

Solvents are used in chemical laboratories and in chemical industries worldwide with global demand in the region of 20 million metric tonnes per annum.[13] As it mainly refers to hazardous, toxic or otherwise damaging solvents it means that they represent a large contribution to the environmental impact and also impact on cost, safety and health issues.[14,15,16]

It has been estimated that ca. 85% of mass wasted in synthesis and processes is constituted by the solvent, and the recovery efficiencies are typically 50-80%.[17,18] In the manufacture of active pharmaceutical ingredients (API) typical composition of the material used, is showed on Figure 4. The American Chemical Society Green Chemistry Institute Pharmaceutical Roundtable (ACS GCIPR) published this benchmark in 2008.

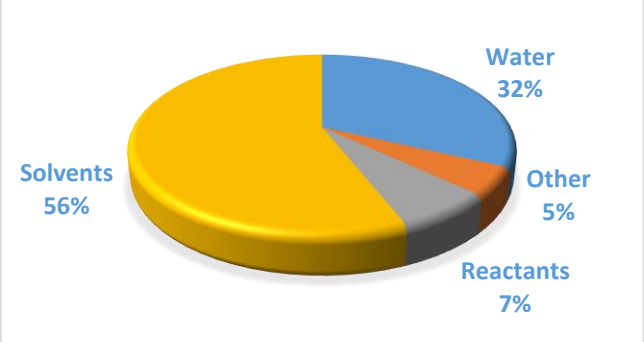


Figure 4. Composition by mass of the types of material used to manufacture an API.[14]

Customarily, solvents are used in the reaction as an unreactive auxiliary fluid with the primary purpose of dissolving reactants. Intermolecular interactions stabilise the solutes, promote the desired equilibrium position and can influence product selectivity. Their volatility and boiling temperature characteristics can facilitate their separation from the products by distillation but on the other hand, they may create undesired vapor emissions.[13,19]

Polar aprotic solvent, are also very common in organic synthesis, especially in nucleophilic substitutions. However, they have significant environmental and safety issues due to their toxity. Also, their miscibility with water enables their separation by washing with water but results with inevitably contaminated aqueous effluent.[18]

In addition to the problems connected with:

- health and safety factors such as toxicity, flammability,
- release of solvents in the environment, thus causing further environmental contaminations,
- subsequent reaction work up and separation

development of sustainable ones has become one of the most active area of Green Chemistry.[17,18]

Research on green solvents is an evolving field of interest and the promotion of this idea represents one of the principles of Green Chemistry.[13]

The ideal conditions would be avoiding the use of any kind of solvents, or in other words, "The best solvent is no solvent". Solvent-free processes are inescapable due to their crucial role in dissolving solids, heat and mass transfer, influencing viscosity and in separation and purification steps.[17,18]

The need of alternative solvents come up as the most acceptable solution to minimise the environmental impact and avoid problems with health and safety issues. There are four submitted ways to achieve that goal:[15]

1. Substitution of hazardous solvents with one that shows better EHS (Environmental, Health and Safe) properties
2. Use of "bio-solvents", i.e. solvents produced from renewable recourses
3. Substitution of organic solvents with supercritical fluids
4. Or with ionic liquids that show low vapour pressure, and thus less emissions in air.

Green solvents should have some of the following properties:

Low toxicity, non-flammable, safe to handle, easily biodegradable under environmental conditions, derived from renewable sources, high boiling point (not very volatile, low vapour emission) and easy to recycle.[20]

Liquid fatty acids, bioethanol, esters (biodiesel), limonene, glycerol, ethanol and acetic acid may all be produced from renewable resources and could be considered as possible replacement solvents. However, the use of alternative solvents is not sufficient to consider a process for a green one. As above mentioned every other aspects of the process should be examined and reach better outcome, for instance, the atom efficiency,

demands on non-renewable resources, energy use, transport costs, all must be taken into account.[20]

The evaluation of the greenness of a solvent can be determined by two environmental assessment methods with different scopes. The first method is Environmental, Health and Safety (EHS), which goal is to identify potential hazards of chemicals.[15,19]

The EHS method relies heavily on the availability of the process information and as in the early stage there is a lack of substance date, it could represent a problem. Applying these methods to process design therefore require expert judgment and large amount of time to create fate and effect date not only for the wellstudied substances but also for the new intermediates and products.[15,21]

Simplified EHS aspects are assessed in three categories with nine subgroup:

1. Environmental hazards – persistency, air hazard and water hazard
2. Health hazards – acute toxicity, irritation and chronic toxicity
3. Safety hazard – release potential, fire/explosion and reaction/decomposition.

For each category effect, an index between zero and one is calculated, one is used for dangerous substances whereas zero is for the harmless ones (Figure 5.).[15,9,21]

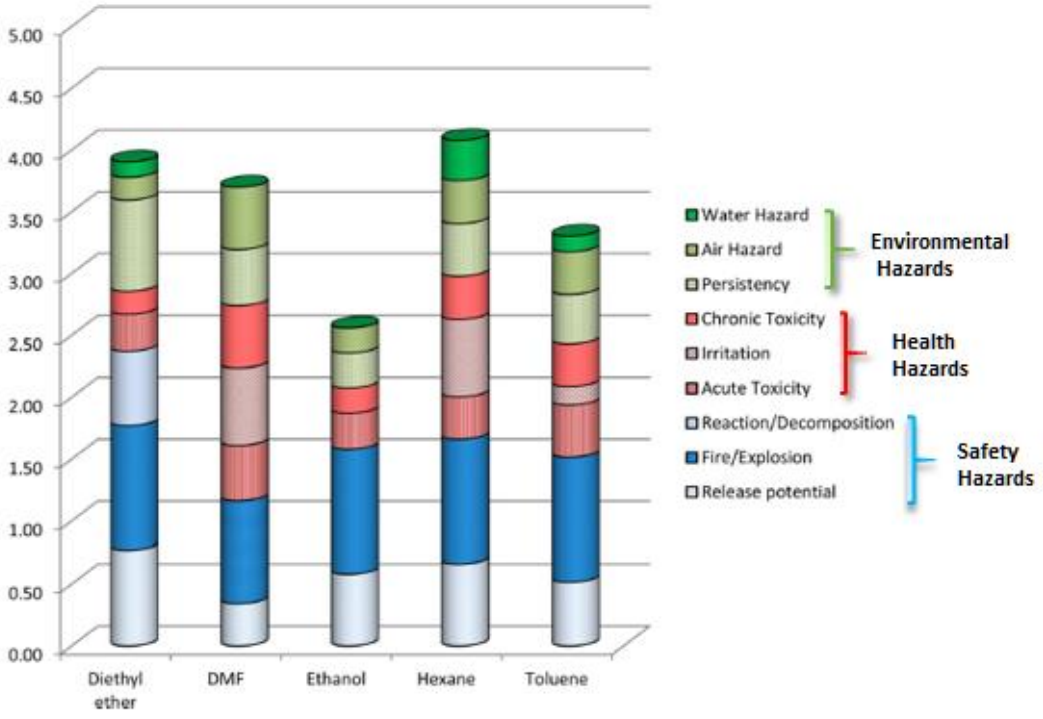


Figure 5. EHS rankings for five representative solvents.[19]

The second method is Life Cycle Assessment Method (LCA), a conceptual approach that comprises the consideration of all stages along the life cycle of a chemical (Figure 6). It is a flexible, interdisciplinary tool which principles can be applied to products and processes in any kind of industry or sector.[15,22,23]

Some of the metrics used in LCA are: (1) amount of inputs, (2) emissions to air, water and land (3) relative toxicities of materials (4) process or product costs (5) use of recycled materials.[23]

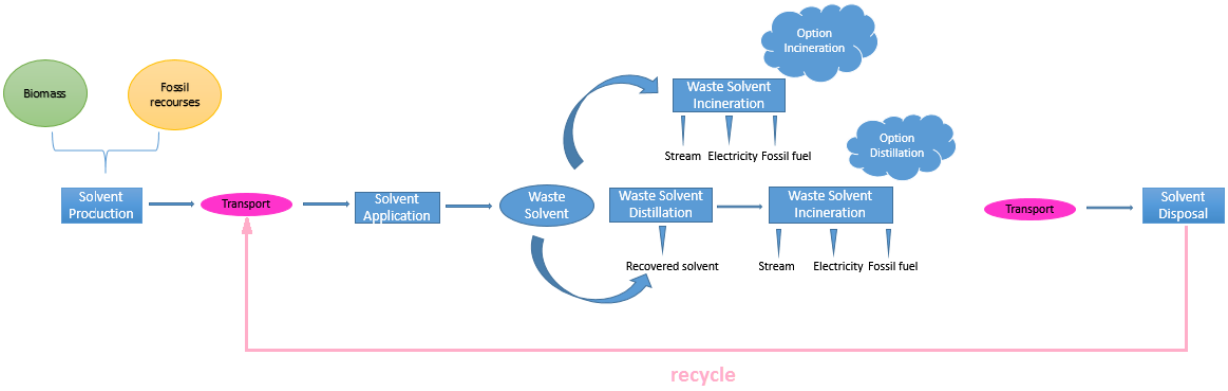


Figure 6. System model of the solvent assessment using the life-cycle assessment method.[13,15]

One of the quickest option to calculate LCA is the net cumulative energy demand (CED). On Figure 7. blue bars show the energy required for the production of 1 kg of solvent, red bars indicate the energy required for distillation rather than production, and the green bars show the energy recovered from incineration. Underneath, the light red and green bars illustrate the saved energy.[19]

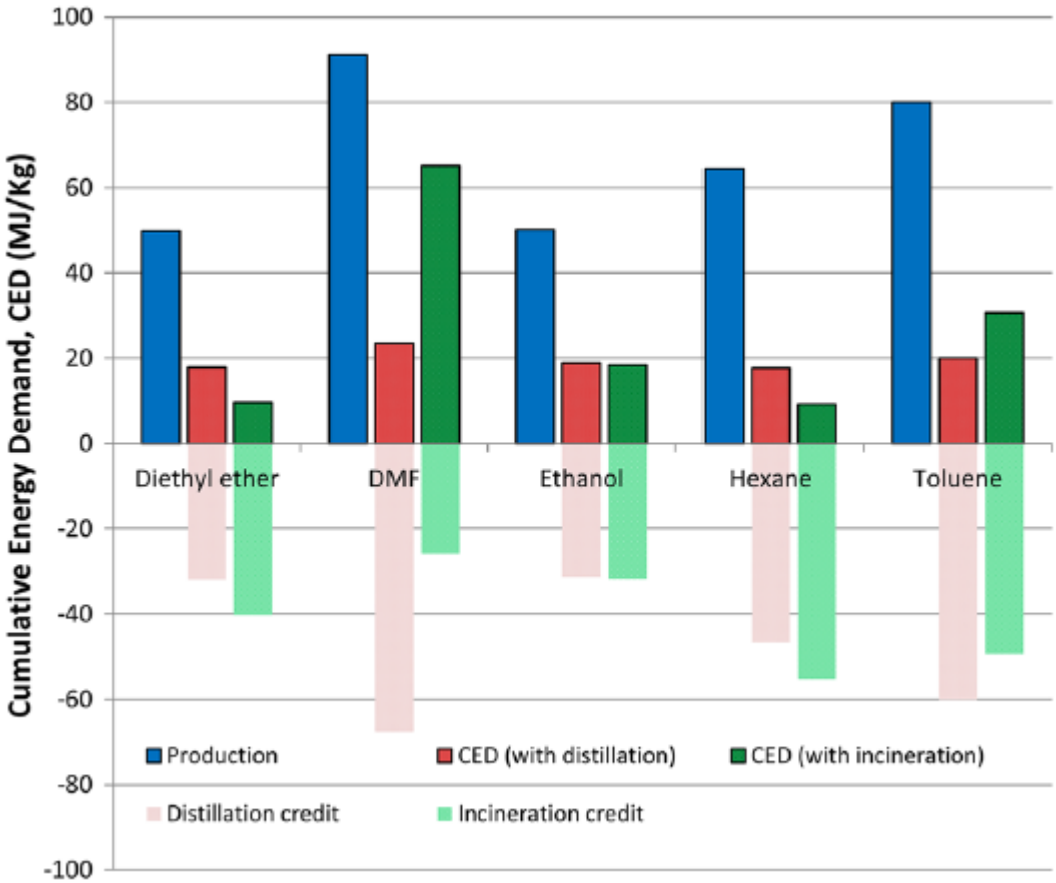


Figure 7. Energy demands associated with the production of five representative solvents.[19]

A multi-criteria evaluation or in other words combining the two mentioned methods would give the best solution for alternative solvent selection, providing results of practical relevance.[15]

Example of assembling the scores of two methods in order to get a bigger picture of solvent impact could be seen in Figure 8. Ethanol and ethyl acetate provide the optimum results from EHS perspective, and on the other hand, n-hexane and diethyl ether, because of their lower energy demand are considered more environmentally favourable solvents.[19]

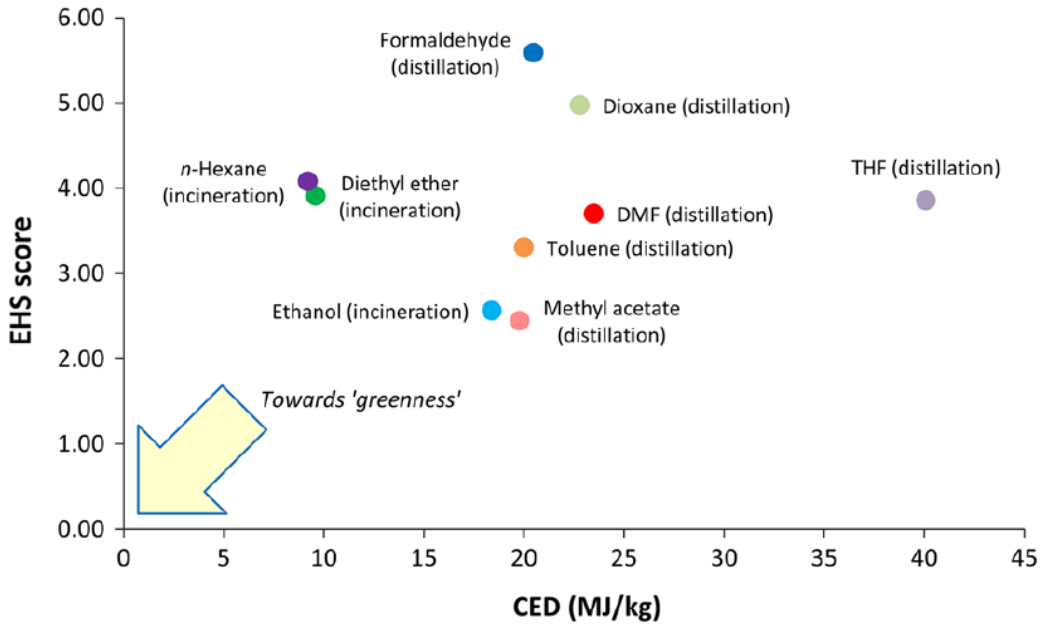


Figure 8. Map of EHS and CED values for representative solvents.

2.4. Heterogeneous catalysts

Organic catalysis is one of the most broadening fields of research in the modern organic chemistry.[24] Heterogeneous catalysis refers to the form of catalysis where heterogeneous catalyst exist in different phase to that of the reactants. The great majority of the catalyst are in solid phase; meanwhile the reactants occur in liquid or gas phase.[25]

Organic catalyst has recently been defined as "organic compound of relatively low molecular weight and simple structure capable of promoting a given transformation in substoichiometric quantity".[26,27] This definition, with its certain limitations, gives yet a clear picture what organic catalyst is not. Is not an enzyme nor a metal-based catalyst. In this term, "organic" refers to metal-free conditions. Some of advantages of such conditions might include: inter alia, the possibility to work under wet solvents and under aerobic atmosphere, dealing with a stable and firm catalyst, avoiding the problem of metal leaching into the organic product.[24,27]

Switching from stoichiometric methodologies to catalytic processes, the efficiency of the reaction improves by lowering the energy input required. The amount

of catalyst needed for reaction comes in smaller percentage in comparison to stoichiometric amount, thus the formation of waste is avoided and the E-factor value and higher economic losses are decreased. Beyond efficiency, some otherwise unfavourable reactions could be also realized by using the correct catalyst.[1]

Furthermore, immobilisation of catalyst over an inert solid support is highly investigated. The scope of immobilisation is to simplify the isolation of products and catalyst recycling and to facilitate the reuse and recovery of the catalyst.[24,28] Hence, this leads to increased productivity of the catalyst, economic and environmental advantages.[28,29] Many different materials have been studied and developed as supports for a large variety of species being able to successfully participate as catalysts for organic or organic cross-coupling reactions. Although, with all this advantages supported catalyst often suffers from lower activities and selectivities when compared with their nonsupported analogues. Thus further synthetic efforts have to be performed.[29,30]

The supported catalyst could be divided in two groups: organic and inorganic supports. Within the category of organic supports different types of polymers are incorporated, which range from insoluble resins to highly soluble oligomers.[30,31]

The work of this thesis is focused on the synthesis of heterogeneous acid catalysts, which are now preferred giving moderate to high yields in the synthesis of alkyl levulinates. Moreover in the case of solid acid catalyst, the corrosion and disposal issues that appear when liquid mineral acid are used, may be avoided.[32] The following chapters will give a review of the two types of heterogeneous catalysts.

2.4.1. Polystyrenes

The concept of solid-phase peptide synthesis using heterogenoeus chloromethylated polystyrene crosslinked by divynylbenzene (DVB) was reported by Merrifield in 1963.[33] Since then a very high number of research groups focused the attention on development of heterogeneous polystyrene, such as Merrifield resin[34], as well as of new crosslinkers for polystyrene.[35]

Polymer resin beads based on polystyrene have greatly attracted the interest of chemists, becoming one of the most studied and used polymeric materials. They were obtained by free-radical crosslinking copolymerization of styrene and crosslinker monomers using suspension polymerization.[36] Crosslinker constitutes a link between the chains, forming a stable network. Besides the monomer and crosslinker, initiator and immiscible water phase is included. Water phase indicates an aqueous solution, which contains a suspension stabilizer, often a water soluble polymer that helps avoid association of the organic-phase droplets. Polymerization and crosslinking reactions begin with the decomposition of initiator that produces free radicals. These conditions ensure the production of robust and spherical particles of an appropriate size and size distribution, that are essential in most of the applications.[37] Finally, the product needs to be washed in a Soxhlet extractor for 24 h and then vacuum dried in order to remove traces of unreacted monomers and initiator.

2.4.2. Gel-type resins

In order to obtain hard glassy transparent beads, in the case of gel-type polymer, the comonomer mixture of styrene and chosen crooslinker is required (Figure 9). Usually the range of crosslinker is between 0,5 – 20%, but when it is used for application as support the range is reduced at 0,5 – 2 %. In the dry state the resin shows a very low surface area (less than 10 m^2g^{-1}), thus the diffusion of even small molecules is very slow. In spite of that if solvent with the solubility parameter similar to that of the polymer is used, “solvent porosity” is created, allowing the diffusion of small molecules to the polymer network.

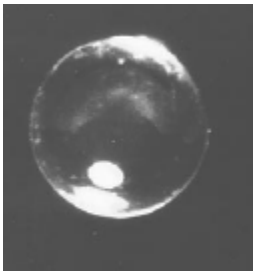


Figure 9. Opthical photograph of gel-type bead.

As it can be seen on the Figure 10.a) when the swelling process begins, it occurs from the outside to the interior, forming an expanded exterior pellicular layer and

leaving the central unswollen glassy core. With time, the central core shrinks and finally disappears. The second part of the Figure 10 (Figure 10.b)) shows a diverse process of swelling. Pressure of the interior swollen core is caused by the lost of solvent in the external layer. Hence, the external dry layer can lead to fracture or burst of the resin particles. The described phenomenon is known as the phenomenon of the "osmotick shock". The matrix that can undergo many cycles of swelling and deswelling without any mechanical damage is considered to be usefull.

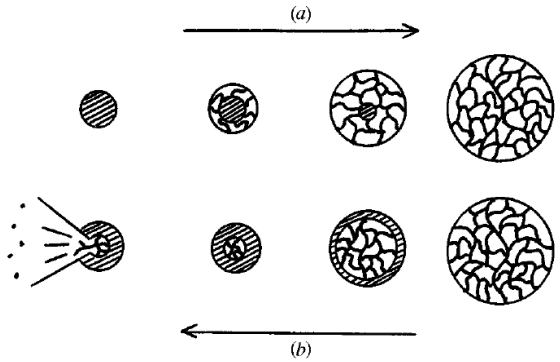


Figure 10. Solvent response of gel-type resin.

2.4.3. Macroporous resins

The term macroporous resin refers to permanent well-developed porous structure that is almost independent from the solvent nature and presists in the dry state.[28] Unlike gel-type resins, these beads have higher surface areas, typically around 50 to 1000 m^2g^{-1}. Macroporous resin is obtained when in the comonomer mixture an appropriate organic solvent (diluent or porogen) is added. The product consists of hard but opaque spherical beads with a rough surface (Figure 11). Such permanent network of pores allows access to the interior of the pore structure by essentially all solvents whether categorised as "good" or "bad".

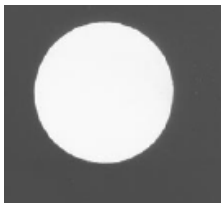


Figure 11. Opthical photograph of macroporous bead.

The key role of the porogen is to create a phase sepration of the polymer matrix that is mainly responsible for the formation of porous structures in the dried state (Figure 12).[36] Mixture of monomer, crosslinker and porogen is an isotropic solution (a). Polymer network must occur during the process of polymerization (b) (c). Macroporous beads, finally, consist of a crosslinked polymer phase and a discrete porogen phase, that latter begins to act as a template (d) (e). The product is washed in a Soxhlet extractor in order to remove all the unreacted reagents, including porogen (f).

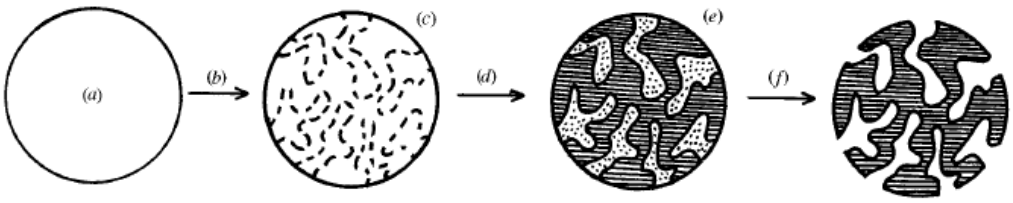


Figure 12. Action of porogen in forming porous morphology in a macroporous resin.

Porogen types have significant influence on the pore structure. Various types of porogen lead to different pore size, pore volume, surface area and so.[38] One of the most used porogens are: 2-ethyl-hexanoic acid, 1-chlorodecane, toluene and cyclohexanol. For the synthesis of catalysts m-SP-SO_3H described in this thesis, 1-chlorodecane has been employed as a novel pore-forming agent to produce macroporous beads, bearing in mind its effectiveness in generating the required structure.[38,39,40]

According to literature, catalytic activity of macroporous resin should give better results, due to the nature of the resin. As it is depicted in Figure 13 macroporous resin own large surface area and high speed ion exchange ability. Moreover, plenty of apertures and large pore diameter of resin allow faster access to molecules of reactants to inner of resins. On the other hand, the surface area and the pore diameter of gel resins are smaller, allowing interaction of reactants with the active group only on the surface of gel resin. Consequently, lower yields are expected.[41]

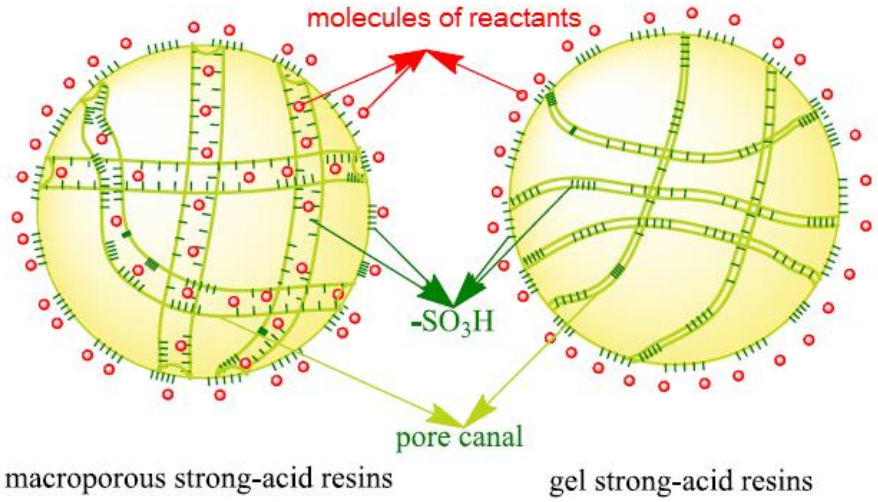


Figure 13. The schematic diagram of the interaction between the different resins and reactant molecules.[41]

For further verifying, different type of synthesized and commercially available catalyst were compared in the work of this thesis.

3. Biomass

3.1. Advantages of renewable resources

With today's lifestyle and advanced technology, requirements for energy consumption are in perpetual increase. Current industrial economies are still largely depend on non-renewable recourses, such as crude oil, coal and natural gas, what can lead to early depletion of their reserves.[42] Apart from that, the use of petro-based fuels and chemicals creates a negative impact on the environment, accounting for more than two thirds of the GHG emissions addressed by the Kyoto Protocol.[43,44] The development countries were responsible for over 50 % of global growth of carbon dioxide (CO_2).[44] Hence, an urgent need to develop more sustainable energy systems has come up as a solution to overcome the aforementioned problems.[45]

Another great challenge in the 21st century is to diminish the enlargement of waste disposal. Environmental legislation have given stringent requirements not only to reduce the waste but also to make use of that waste through reuse and recycling.[42]

The deployment of alternative sources of energy considers substitution of unsustainable raw materials with the renewable feedstocks.[46] Renewable resources, like solar radiation, geothermal energy, winds, tides and biomass can be replenished by the environment over relatively short periods of time and can be a good replacement for fossil fuels.(Figure 14).[42]

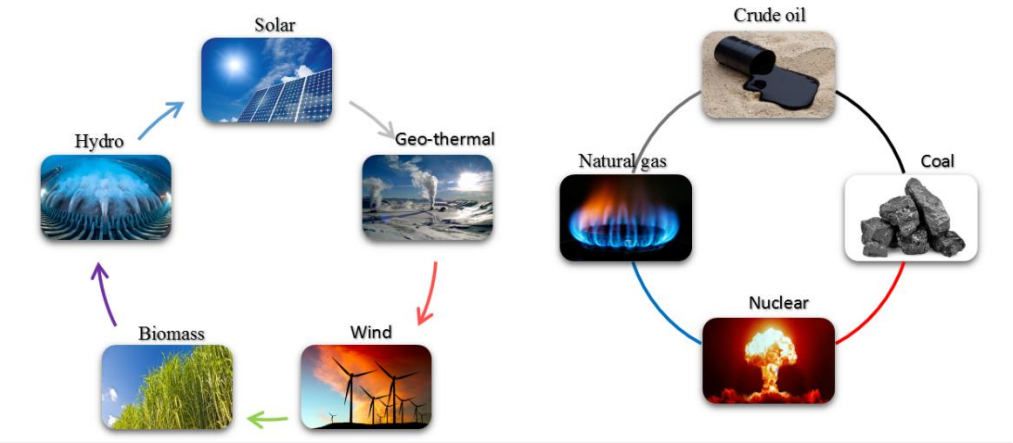


Figure 14. Different types of renewable and non-renewable resources.

The applicability of biomass as a renewable resource has been recognised as most promising solution to substantially reduce emissions, make contributions in all sectors and gain more profit.[47,48] Biomass is most copious resource in the world and it correspondents to any organic matter that is renewed rapidly as of the carbon cycle.[42,48] It encompasses feed crops, agricultural food, dedicated energy crops and trees, forestry and agricultural residues, aquatic plants and animal and municipal waste (Figure 15.).[49]



Figure 15. Different types of biomass.

Incorporation of biomass into manufacturing processes and establishing a bio-based economy affords various economic, environmental and social benefits.[49]

Biomass is the only renewable source that can be used to produce not only energy but also a whole portfolio of valuable products.[5,42] From the economic point of view coproduction of platform chemicals and materials can afford an additional benefit to industries with integrated biorefineries.[50]

The switch to renewable feedstock gives advantageous reduction in the carbon footprint of liquid fuels and chemicals. Biomass compounds take up carbon dioxide from the air trough photosynthesis, while they are growing. At the end of life cycle, when such organic matter decomposes or burns (while clean energy is created - Figure 3x) carbon dioxide from the matter returns back to atmosphere, thereby creating a "closed loop".[42] Studies suggest that bio-fuels reduce greenhouse gases up to 65 %.[51]

And finally social benefit is achieved through more stable and profitable agricultural economy.[49]

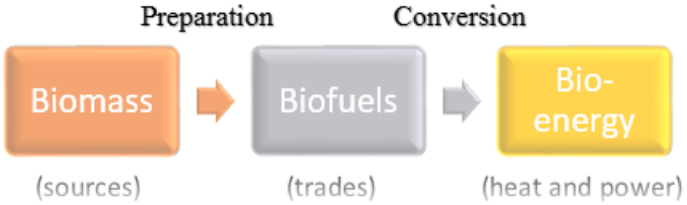


Figure 16. Bio-energy production flow.

Although the accent is still focused on conversion of biomass into bio-energy, that may be derived in the form of heat or transformed into electricity for distribution, growing emphasis is also on manufacture of commodity chemicals and liquid fuels. Figure 16 also explains one role of the biofuels, which is that they can be used as feedstock intended for the production of bio-energy, produced directly or indirectly from biomass.[44]

3.2. Composition of biomass

Presently, the global production of plant biomass is estimated around $1.0*10^{11}$ tonnes per year.[52] First generation biomass feedstock considers food commodities, such as edible oil seeds, sucrose, starch and maize. As it competes directly or indirectly with food production, it appears as an unsustainable solution.[49,50,53] In contrast, the second generation of bio-based fuels and platform chemicals refers largely to lignocellulosic biomass and inedible oil seed crops as feedstock in integrated biorefineries. It avoids competition with food sector, is cheap and abundant and does not require as much land and fertilisers to grow, thus is considered as a potential alternative for bioenergy resources.[42,53]

Moreover, the utilisation of organic waste, which is generated in the processing, harvesting and use of agricultural products, contributes not only the minimisation of the waste but also maximising the value of biomass, creating the spirit “waste equals feedstock”.[42,50]

A major concern for biomass is the variability of biomass; therefore, the development of economically viable methods is still in progress. Chemical transformations required to establish renewable chemicals industry still remain to be discovered. However, the great potential in the use of plant biomass to produce liquid biofuels is widely recognised by governments and scientists.[53,54]

As noted above, lignocellulose, the fibrous material that constitutes the cell walls of plants, is the most important resource of biomass.[32,49] It is mainly composed of three major polymeric components: lignin (ca. 20%), cellulose (ca. 40 %) and hemicellulose (ca. 20%) (Figure 17).[32,45,46,50] These polymers create a hetero-matrix, which composition depends on the species type and even resource of biomass.

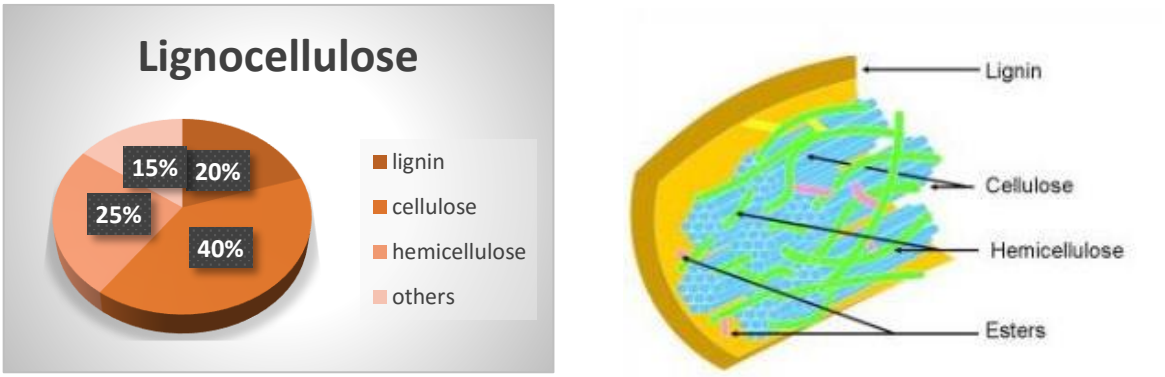


Figure 17. Composition of lignocellulose.

Lignin is a three-dimensional biopolymer, that is generally accepted as the "glue" that binds the different components of lignocellulosic biomass together, thus making it insoluble in water. Its non-uniform structure that imparts rigidity and resistance to plant cell walls. Lignin is formed of methoxylated phenyl propane structures, therefore it is the only one composed entirely of aromatic subunits.[32,45,50] It can be used to generate electricity.[49]

Cellulose and hemicellulose are polymers composed of glucose or different carbohydrate units. Cellulose is the main constituent of plant cell wall conferring structural support and it refers to unbranched homopolymer. Unlike cellulose, hemicelluloses are branched, heterogeneous polymers of pentoses, hexoses and acetylated sugars. Depolymerisation of cellulose and hemicellulose can give fermentable sugars and derivate, which are of crucial importance due to their potential

for use and transformation to important commodity platform chemicals (Figure 18).[32,45,46]

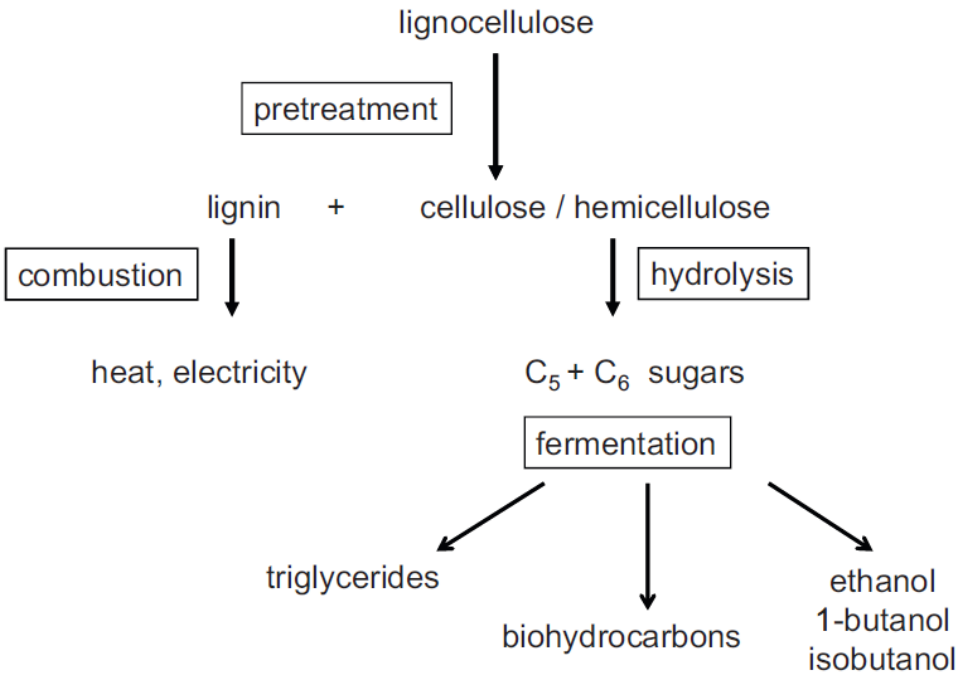


Figure 18. Different approaches to 2nd generation of biofuels from lignocellulose.[49]

3.3. Conversion of biomass to commodity chemicals

Nowadays, the biorefinery products compete with the existing petroleum-derived products. The key to success in the bio-based production is to choose the right biomass as the raw material and to develop a cost-effective infrastructure for production, storage and pre-treatment of biomass.[5,42]

Hexoses and pentoses, the building blocks of cellulose and hemicellulose can subsequently be used as raw materials for conversion to many different industrial products by either fermentation or chemocatalytic processes. One approach is to design a process that will give different types of hydrocarbons, meanwhile the other approach focuses to obtain oxygenates or amino acids, as biobased platform chemicals. Glycerol, as the co-product in the transesterification of triglycerides also represents a significant feedstock for various C_3 commodity chemicals, that are currently petroleum-based chemicals, obtained from propylene.[5,49]

Hydroxymethylfurfural (HMF) and furfural are produced from C_5 and C_6 sugars through acid catalysed dehydration process.[55] Due the specific functional groups of HMF, a wide range of chemicals, polymers and biofuels can be produced, but its production has not yet been reduced to commercial practice.[5,55] HMF can be further converted to γ-valerolactone (GVL), furan-2,5-dicarboxylic acid (FDCA) or to levulinic acid (LA), on which is the main focus of this work.[5,49]

Investigation on LA has been decided to run, because LA is considered to be one of the most imperative biochemical, originated from cellulose and has been highlighted as a promising building block for chemistry.[55] LA is classified as green solvent, that can be used in number of industrial processes.[32,56] Moreover, LA, as an representative organic compound from biomass may be acknowledged more favourable industrial replacement in comparison to other alternative solvents (e.g. ionic liquids, supercritical fluids or fluorous solvents) considering that technologies required for their use are similar to the current ones, which means lower economical costs.[56,57] LA has been used in the synthesis of alkyl levulinates.

3.4. Synthesis of alkyl levulinates and their application

Alkyl levulinates, as a potential industrial substitutes can be obtain in high yield from simple biomass derived products such as levulinic acid or furfuryl alcohol or directly from lignocellulosic resources in lower yields (Figure 19).[32]

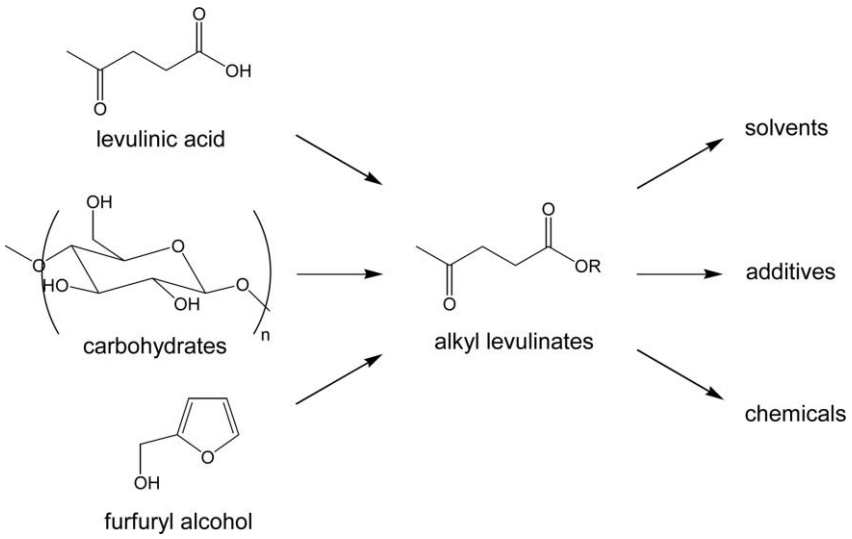


Figure 19. Routes for production of alkyl levulinates.[32]

In this thesis the route from LA as a starting material for synthesis of alkyl levulinates have been chosen (Figure 20).

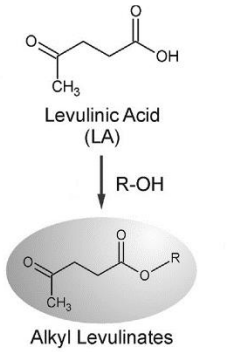


Figure 20. Production of alkyl-levulinates from levulinic acid.[47]

Alkyl levulinates have been prepared by the esterification of levulinic acid in the presence of following alcohols: methanol, ethanol, propanol and buthanol. To avoid very slow reaction conditions and to achieve equilibrium conversion in a reasonable period of time, the reaction has been conducted on elevated temperatures in the presence of different types of catalysts.[47]

Alkyl levulinates have extensive field of possibility to be used. Due their specific physicochemical properties they have been recognised as an alternative green solvents. Moreover, they can find applications, as additives to conventional diesel or gasoline fuels, (Fisher-Tropsch) gas oil-based fuels, and even biodiesels. Their use leads to cleaner combustion processes with lower NO_x emissions. Furthermore, it has been pointed out that they can be used as building blocks in the area of chemical synthesis (Figure 6x).[32] Transformation of alkyl levulinates into γ-Valerolactone (GVL) is getting the major of attention. GVL has unique physical and chemical properties, which represents an ideal chemical for use as a solvent or intermediate in chemical industry or energy storage. Beside that it is a colourless liquid, with specific odour, which makes it suitable for the production of perfumes and food additives.[57,58]

To conclude, the recent researches confirm that application and development of alkyl levulinates will contribute to future greener and sustainable processes.

4. Aim of the work

In recent years, awareness of the need for greener and more sustainable technologies has been recognised. Through the fundamental principles of green chemistry economic, environmental and social goals can be accomplished. Therefore, flowing the newest trends, this thesis has been focused on the topics such as renewable feedstock and catalysis.

Utilisation of the biomass can assure large numbers of platform chemicals. Levulinic acid has been chosen as the starting material because it is one of the most imperative biochemical that can be used in esterification reactions to obtain alkyl levulinates that can be used in various applications, such as solvents, additives or speciality chemicals.[32]

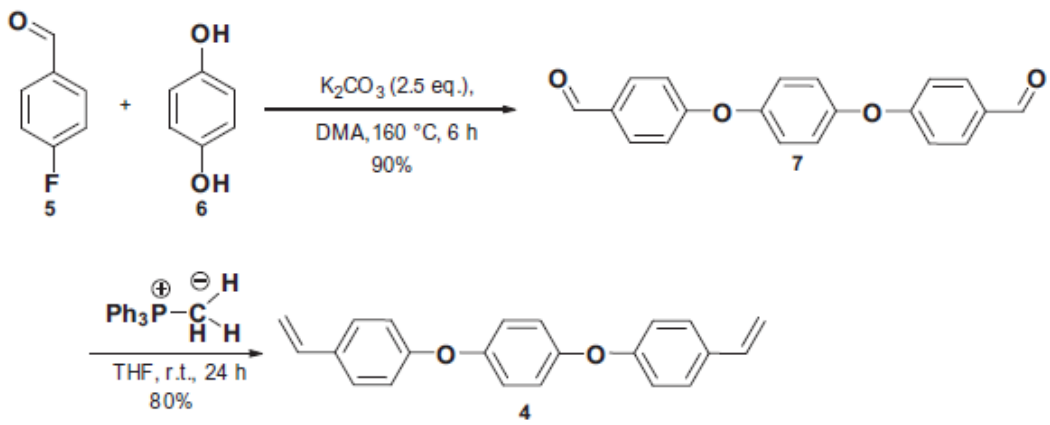
On the other hand, catalysis, or more specifically, development of heterogeneous systems has also attracted the interest of the chemists because it simplifies the isolation of products and catalyst recycling, leading to economic and environmental advantages.[28]

The experimental part has been carried out at the Laboratory of Synthetic Green Organic Chemistry (Green S.O.C.) on the Department of Chemistry, Biology and Biotechnology at the University of Perugia. The aim of this current thesis was the preparation of two polystyrene based acid catalyst and test their efficiency in esterification reactions with LA.

5. Results and Discussion

5.1. Synthesis of 1,4-bis(4-vinylphenoxy)benzene 4

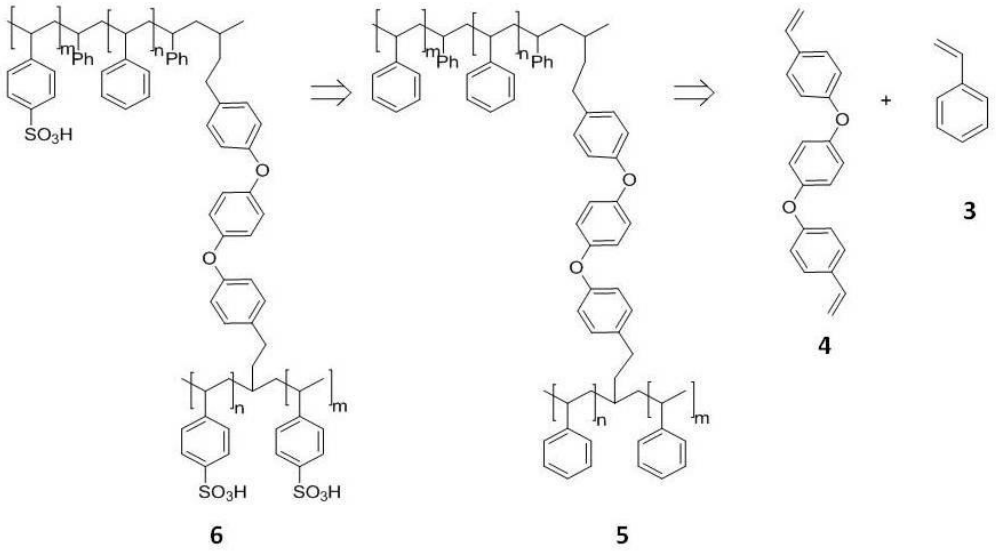
1,4-Bis(4-vinylphenoxy)benzene cross-linker **4** was synthesized as outlined in Scheme 1. Two step synthesis begins with the reaction of 4-fluorobenzaldehyde and hydroquinone in the presence of K_2CO_3.[59] Within this conditions ether-linked dialdehyde 4,40-[1,4-phenylenebis(oxy)]dibenzaldehyde **7** occurs, which is subjected to subsequent reaction with methyltriphenyl phosphonium bromide under Wittig conditions to afford the target product in good overall yield (72%). Noticeably, a major advantage of the proposed cross-linker is that it can be readily synthesized from easily accessible precursors, does not require rare materials, reducing risks regarding materials supply or costs; and, finally, the compound can easily be isolated by re-crystallization.



Scheme 1. Synthetic route for 1,4-Bis(4-vinylphenoxy)benzene **4**

5.2. Polymerization

New gel-type and macroporous polystyrene-supported heterogeneous acid catalysts (namely SP-SO_3H and m-SP-SO_3H) were developed in order to investigate their application in the production of alkyl levulinates from lignocellulosic biomass. General approach for the synthesis of polystyrene based catalysts is shown on scheme 2.

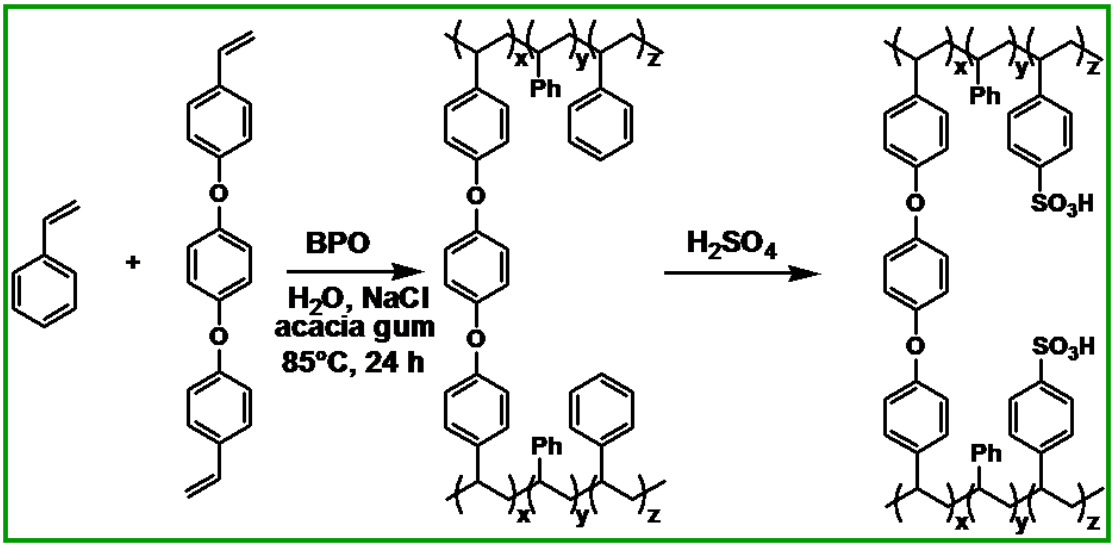


Scheme 2. Synthetic route for catalysts SP-SO_3H and m-SP-SO_3H

In this thesis work will be discussed first the preparation of the two types of polymer-supported catalysts synthesized and afterwards will be shown the results of the esterification reactions promoted by gel-type SP-SO_3H and by macroporous resin m-SP-SO_3H catalysts, where their efficiency was tested. Application of the mentioned catalysts in esterification reactions in water solution were also conducted in order to get a more extensive picture about their efficiency.

5.2.1. Synthesis of gel-type polystyrene resins SP

Novel sulfonic acid functionalized polystyrene-based resin SP-SO_3H has been prepared by following synthetic strategy depicted in scheme 3.



Scheme 3. Synthesis of SP and SP-SO_3H

The synthesis of unfunctionalized polystyrene resin SP proceed through conventional free radical suspension polymerization method. (Figure 27) A liquid mixture of the co-monomers (styrene and 1,4- bis(4-vinylphenoxy)benzene **4** as cross-linker (2 mol%)) dissolved in chlorobenzene was dispersed in an excess of immiscible water phase under stirring. In the optimization process, it was found that the best stabilizer is Acacia Gum, hence the aquatic solution consisted of Acacia Gum (4%) and NaCl (3%) in distilled water and it stirred for 30 minutes under room temperature. Benzoyl peroxide was used as polymerization initiator and after 24 h under stirring at 85 ^{o}C the resulting product have consisted hard transparent resin beads. They were washed in a Soxhlet extractor (Figure 21) for 24 hours with water, THF and hexane in order to remove residual monomers and then vacuum dried overnight.

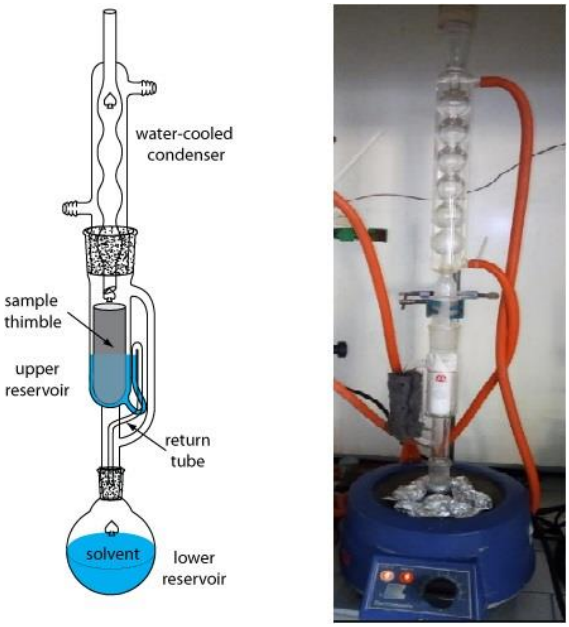
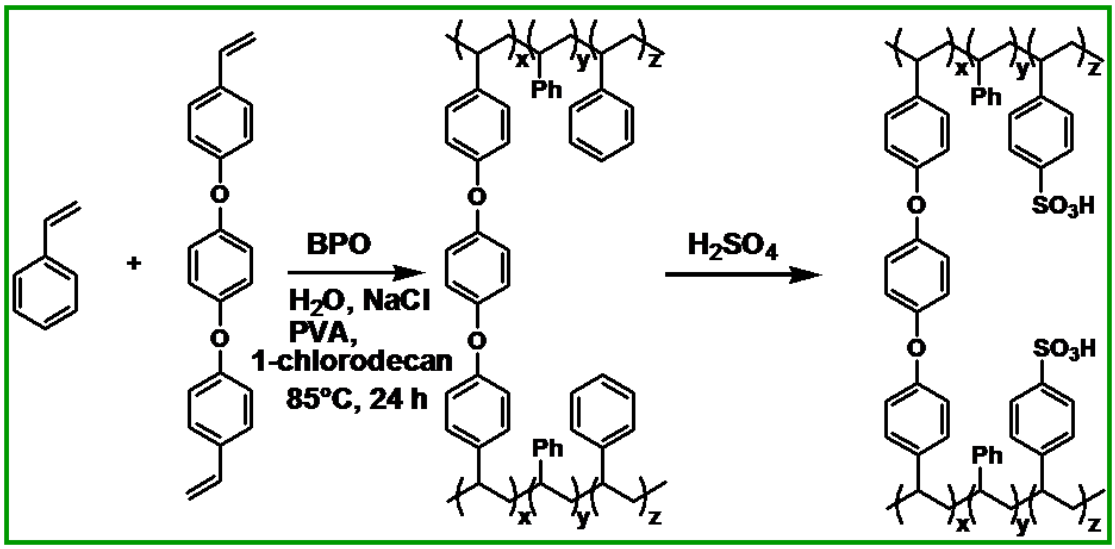


Figure 21. Scheme of Soxhlet extractor (on the left) and Soxhlet extractor used in laboratory (on the right).

5.2.2. Synthesis of macroporous polystyrene resins m-SP

Macroporous polystyrene-based resin (m-SP) has been synthesized in a similar way as the previous, with suspension polymerization method, conducted in a three-necked glass reactor (Figure 27). Synthetic strategy of the mentioned polymer is depicted on the scheme 4, along with the preparation of m-SP-SO_3H catalysts (see below).



Scheme 4. Synthesis of m-SP and m-SP-SO_3H

The aqueous solution of NaCl and high molecular weight PVA stabilizer (MW85,000-124,000) was put under vigorous mechanical stirring, after 24 h to this solution was added the organic phase composed by styrene, cross linker (1,4- bis(4-vinylphenoxy)benzene **4**) and chlorobenzene as a solvent. The solvent must be soluble in the monomer mixture but insoluble in the continuous phase of the polymerization suspension. Chlorodecan, as a porogen, was selected bearing in mind its effectiveness in generating macroporous structure.[38-40,60] The polymerization starts with the addition of radical initiator.[28] In this case two different initiators were used in order to investigate which one of them could give better yields, i.e. benzoyl peroxide or AIBN. The reaction was carried out at 85 ºC for 24h. Glassy and opaque beads were extracted in Soxhlet with water, THF and hexane in order to remove the unreacted monomers and porogens. Finally the product was vacuum dried overnight. All the conditions used in such process of optimisation are given in the table 3.

Table 3. Conditions for polymerization optimization

Entry	*Styrene,%*	*Cross Linker,%*	*PVA,mg*	*Initiator,mg*	*Porogen(mL) Chlorodecan*	*Yield,%*
1	98	2	16	131,12 (benzoylperoxide)	0,4	71,47
2	98	2	24	131,12 (benzoylperoxide)	0,4	n.a.
3	98	2	32	40 (AIBN)	2	n.a.
4	98	2	64	40 (AIBN)	2	11

* n.a. → not applicable, the product was obtained but the yield couldn't be determine

In entry 3 and 4, where AIBN was used the gain reaction yields were very small, and in the case of entry 3 the yield wasn't calculated because during the washing of the polymer beads, they were dissolved. In the second case (entry 4) amount of AIBN was increased in order to increase polymerization rate and, ultimately, obtain mechanically more resistant beads. With new created beads, solubility tests were performed, which showed, indeed, that the synthesized polymer wasn't soluble in neither of the solvents used in Soxhlet extractor.

The condition in entry 1 was pointed out as the best one. Spherical beads were obtained. Increasing the amount of PVA (entry 2) sticky solution was gained, without formation of the required beads.

The functionalization of the macroporous, described in the subsequent chapter was enforced on the polymer synthesized in the conditions reported in entry 1.

5.3. Functionalization of novel synthesized polymers: preparation of catalysts SP-SO_3H and m-SP-SO_3H

The introduction of sulfonic acid group (-SO_3H) into above mentioned polymer beads, creating acid catalysts SP-SO_3H **(**scheme 3 and 4**)** featuring three different loadings (A,B,C) is realized with the use of concentrated sulphuric acid. Sulphonation reactions are carried out in a round–bottomed flask, containing a magnetic stirrer with the mixture of polymer and sulphuric acid and used as a standard batch reactor. Different conditions are performed, depending on the desired loading.[61,62] The loading was determined by Elemental microanalysis and acid-base titration. Table 4. shows the conditions and results of the mentioned process for achieving different loadings of gel-type polymer. To achieve high and medium loading SP-SO_3H the reaction was conducted at 60 ^oC for 15 and 6h, while achieving low loading catalyst the reaction was carried out at room temperature for 6h.

Table 4. Reaction conditions used to obtain sulphonated acid gel-type polymers with different loadings.

Sulfonating Agent	*Temp.(°C)*	*Time(h)*	*Loading* (mmol/g)*	*Loading** (mmol/g)*	*Polymer SP-SO_3H*
H_2SO_4 (96%)	60	15	4.10	4.68	A
H_2SO_4 (96%)	60	6	3.11	2.92	B
H_2SO_4 (96%)	r.t.	6	0.46	0.89	C

* Determined by Elemental microanalyses

** Determined by acid-base titration

Table 5. Loadings and percentage of cross-linker in the newly synthesized catalysts SP-SO_3H and the commercially available ones.

Catalyst	*Cross-linker(mol%)*	*Loading (mmol/g)*
SP-SO_3H A	**4** (2)	4.68
SP-SO_3H B	**4** (2)	2.98
SP-SO_3H C	**4** (2)	0.89
m-SP-SO_3H A	**4** (2)	4.7
Amberlyst 15	DVB (20)	4.7
PS-p-TSA	DVB (2-5)	2.9

Catalyst were tested in activity and recoverability in the synthesis of alkyl levulinates and were compared with the commercially available ones (Amberlyst 15 and polystyrene (PS) supported p-toluensulphonic acid – p-TSA). Table 5 illustrates the loadings (determined with acid-base titration) of all catalyst and the type of crosslinker used in crosslinking polymerization reaction carried out for the purpose of this thesis.

Amberlyst 15 (Figure 22) is a macroreticular polystyrene based ion exchange resin with strongly acidic sulfonic group, which is used as heterogeneous catalysis.[63]

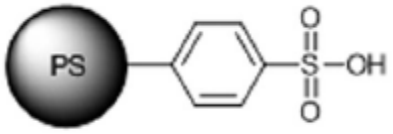


Figure 22. Structure schematization of commercially available acid catalysts, Amberlyst 15 and PS-p-TSA.[63]

The other commercially used catalyst is PS-p-Toluenesulfonic acid (PS-p-TAS). It may be schematically represented similarly to Amberlyst 15 (Figure 22), but unlike Amberlyst 15, PS-p-TSA has smaller amount of cross-linker (table 5), which result is less degree of crosslinking, and it is PS-p-TSA macroporous.

Another main difference between the commercially available catalyst and catalyst synthetized in laboratory is the kind of cross-linker used. Instead of divinylbenzene (DVB), that is used to form polymer network in the commercially available catalysts, all the novel ones are made with the cross-linker described in the previous chapter (table 5).

General procedure, mechanism and results of test reactions used are reported in the following chapter.

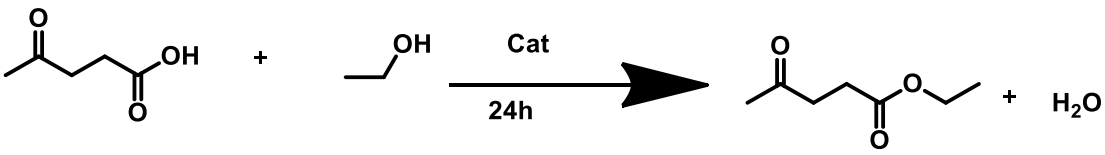
5.4. Catalytic activity tests

The efficiency of the synthetized polymeric supported catalysts have been tested in esterification reactions between levulinic acid and different alcohols in order to obtain alkyl levulinates, as the new challenge in modern green chemistry.

5.4.1. Esterification reactions of levulinic acid promoted by gel-type SP-SO_3H catalyst

As mentioned before alkyl levulinates are recognised as bio based chemicals with strong potential to substitute chemicals manufactured from non-renewable resources. They are considered for attainable green solvents and effective chemicals, which can convert renewable biomass into fuel.

The esterification reaction of LA with ethanol is showed in scheme 5.



Scheme 5. Esterification reaction of LA with ethanol

The results of reaction described in scheme 5 are summarized in the table 6.

Table 6. Synthesis of Ethyl-levulinate in the presence of catalyst SP-SO_3H

Entry	*LA/EtOH*	*Cat.(mol%)**	*T (°C)*	*t (h)*	*C (%)***
1	1:5	/	70	24	1
2	1:5	A(4.3)	70	24	47
3	1:5	A (8)	70	5	71
4	1:5	A(8)	70	24	54
5	1:10	A(8)	70	24	80
6	1:5	A(10)	70	24	76
7	1:10	A(10)	70	24	70
8	1:10	B(8)	70	24	47
9	1:5	B (10)	70	24	72
10	1:10	B (10)	70	24	65
11	1:10	C (8)	70	24	36

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversion are determined by 1H-NMR Spectroscopy.

Results obtained with esterification reaction seem to suggest the main factor affecting the catalytic efficiency is represented by the loading values. The best result in table 6 is highlighted in green (table 6, entry 5) and refers to use of catalyst with high loading. This may be (at least partially) attributed to the greater reaction mixing efficiency. In Table 6, entry 11 could only achieved 36 % of conversion, indicating that catalyst with low loading gives unsatisfactory results. Entry 6 and entry 9 have given similar results (entry 6 – 76% of conversion, entry 9 – 72% of conversion) in comparison to the best obtained ones (entry 5 – 80 %), they use less amount of alcohol, but in both case the amount of catalyst is bigger. As it is easier and more economic to put less amount of catalyst, indeed the entry 5 represents the best conditions.

Table 7. Synthesis of Ethyl-levulinate in the presence of commercially available Amberlyst 15

Entry	*LA/EtOH*	*Cat.(mol%)**	*T (°C)*	*t (h)*	*C (%)***
1	1:5	Amberlyst 15 (4.3)	70	24	33
2	1:5	Amberlyst 15 (8)	70	24	47
3	1:10	Amberlyst 15 (8)	70	24	60
4	1:5	Amberlyst 15 (10)	70	24	66
5	1:10	Amberlyst 15 (10)	70	24	65

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversions are determined by 1H-NMR Spectroscopy.

Table 8. Synthesis of Ethyl-levulinate in the presence of commercially available PS-p-TSA

Entry	*LA/EtOH*	*Cat.(mol%)**	*T (°C)*	*t (h)*	*C (%)***
1	1:5	PS-p-TSA (4.3)	70	24	16
2	1:5	PS-p-TSA (8)	70	24	57
3	1:10	PS-p-TSA (8)	70	24	62
4	1:5	PS-p-TSA (10)	70	24	66

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversions are determined by 1H-NMR Spectroscopy.

In table 7 and table 8 the results of esterification reactions with the commercially available catalyst are shown. The best conditions are highlighted in green. In both cases the best outcome use 10% of catalyst, which is more than the best obtained result with the synthetized polymer SP-SO_3H A that uses 8% of catalyst. The overall reaction conversion in both cases is 66%, which is again less than with the newly synthesized catalyst (80%) obtained in more favourable condition (condition with less amount of catalyst).

If the same reaction conditions are scrutinized with different catalyst (table 6, entry 6 and entry 9, table 7 entry 4 and table 8 entry 4) the conclusion that could be drawn is that in all conditions better results are achieved with newly synthesized catalysts.

Comparison of best achieved results with new synthetized gel-type SP-SO_3H and commercially available Amberlyst 15 and PS-p-TSA are also demonstrated in a graphical form, showed in Figure 23.

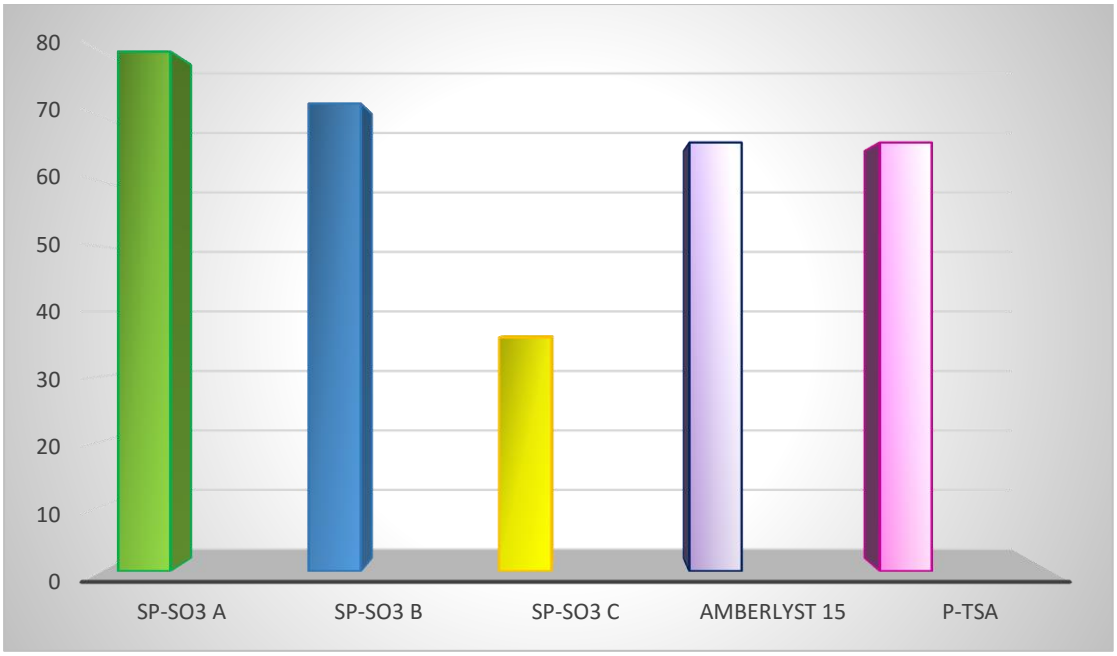
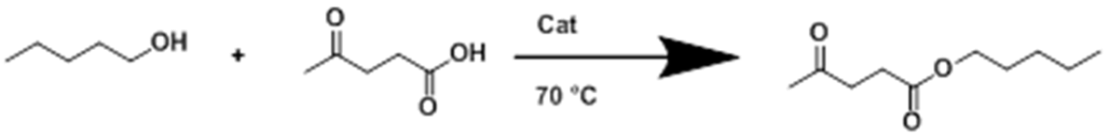


Figure 23. Comparison of best achieved results with newly synthesized gel-type SP-SO_3H and commercially available Amberlyst 15 and PS-p-TSA.

The esterification reaction of LA with pentanol was investigated to broaden the SP-SO_3H scope. The esterification reaction with pentanol is showed in scheme 6. The most significative results are summarized in table 9 and table 10.



Scheme 6. Esterification reaction of LA with pentanol

Table 9. Synthesis of Pentyl-levulinate in the presence of catalyst SP-SO_3H

Entry	*LA/PeOH*	*Cat.(mol%)**	*T (°C)*	*t (h)*	*C (%)***	***B/P******
1	1:5	A(8)	70	24	52	
2	1:10	A(8)	70	24	72	
3	1:5	A(10)	70	5	70	0:100
4	1:5	A(10)	50	3	47	0:100

5	1:5	A(10)	50	5	55	0.34:99.6
6	1:5	A(10)	70	24	70	
7	1:10	A(10)	70	5	80	
8	1:10	A(10)	70	24	82	
9	1:10	A(10)	70	48	92	
10	5:1	A(10)	70	24	88	
11	1:10	B(8)	70	24	70	
12	1:5	B(10)	70	24	78	
13	1:10	C(8)	70	24	54	

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversions are determined by 1H-NMR Spectroscopy.

*** B/P refers to ratio of by-product and product.

Table 10. Synthesis of Pentyl-levulinate in the presence of commercially available Amberlyst 15

Entry	***LA/PeOH***	***Cat.(mol%)****	***T (°C)***	***t (h)***	***C (%)*****	***B/P******
1	1:10	Amberlyst 15 (8)	70	24	70	
2	1:5	Amberlyst 15 (10)	70	24	62	2:98
3	1:10	Amberlyst 15 (8)	70	5	60	
4	1:5	Amberlyst 15 (10)	50	3	9	12:88
5	1:5	Amberlyst 15 (10)	50	5	30	5:95
6	1:5	Amberlyst 15 (10)	70	24	66	
7	1:10	Amberlyst 15 (10)	70	5	65	

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversions are determined by 1H-NMR Spectroscopy.

*** B/P refers to ratio of by-product and product.

The best result given in the production of pentyl-levulinates are obtained with the novel synthetized gel-type polymer with highest loading. The results with Amberlyst 15 are worse (Figure 24) in comparison of reactions preformed in same conditions using gel-type SP-SO_3H catalyst. For example table 9 entry 6 and 12 and table 10 entry 6 have been performed in the same conditions; molar ratio of levulinic acid and pentanol was 1:5 and they were conducted at 70 °C for 24 h. The only difference is the catalyst. In entry 7 (table 9) SP-SO_3H A is used, in entry 12 (table 9)

SP-SO_3H B, and in entry 6 (table 10) Amberlyst 15. The highest conversion have been obtained with the catalyst with medium loading, the lowest with Amberlyst 15. It should be noted that in the mentioned conditions better results were obtained with medium loading catalyst in comparison with the high loading ones. The alkyl chain of pentanol is longer than in ethanol, used in previous reactions, therefore when high loading catalyst is used, there may be occurred some sort of steric hindrance, which might explain better activity of the SP-SO_3H catalyst with medium loading.

Notably, it was also found that polystyrene based novel polymer reached better selectivity (entry 3,4,5 of table 9 in comparison with entry 2,4,5 of table 10). The side product, which is formed in the presence of Amberlyst15 may derive from the undesired attack of pentanol to carbonyl function of LA, and subsequent cyclization.[64]

Some of the reaction conditions were conducted at lower temperatures, at 50 ^oC for 3 and 5h. Reactions with Amberlyst 15 show negligible conversions (Table 10: entry 4 – 9% and 5 – 30%), but the one performed with SP-SO_3H A (entry 4 and 5 of table 9) have reached higher conversion yields. Entry 4 reached 47 % , and entry 5 reached 55% of yield, which is almost high as the one performed in the conditions of higher temperatures. Studies of the reactions conducted at lower temperatures could be further investigated.

Figure 24 shows the best results in graphic display that are highlighted in green in the tables above.

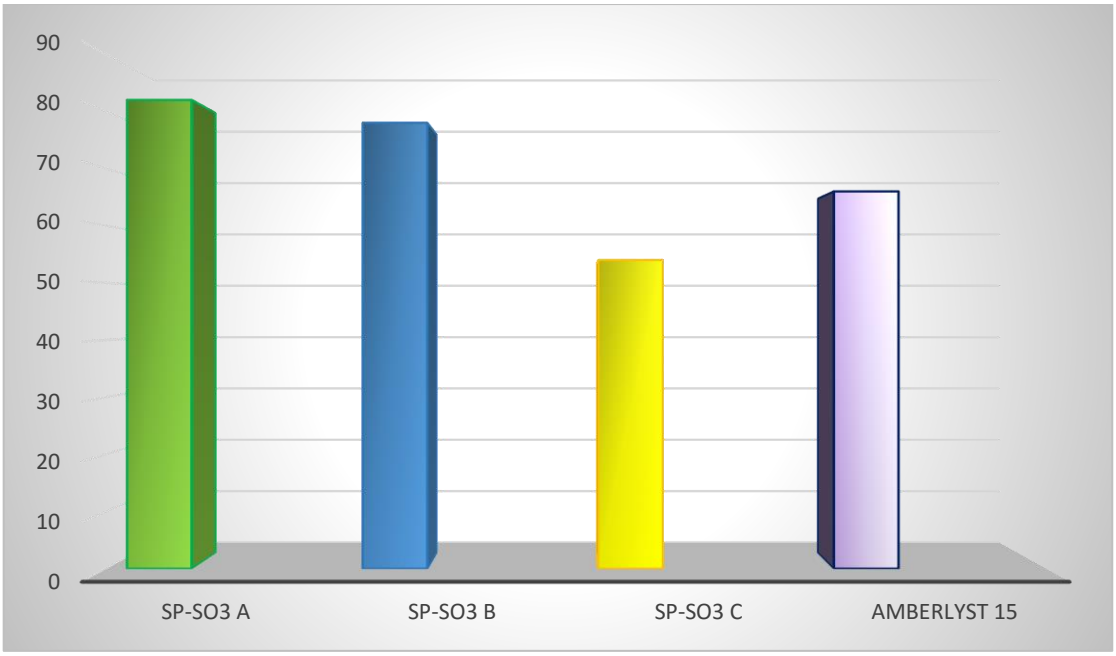


Figure 24. Comparison of best achieved results with new synthesized gel-type SP-SO_3H catalysts and commercially available Amberlyst 15.

Studies on the recoverability and recyclability of the polymer are currently in the progress.

5.4.2. Esterification reactions of levulinic acid with the use of macroporous m-SP-SO_3H catalyst

Macroporous resin have been synthetized to compare its efficiency with other above mentioned polymers. The esterification reaction were conducted at 70 ^oC for 24h. Esterification reaction with ethanol and pentanol are showed in scheme 5 and 6. In this case, to broaden the scope of catalysts, esterification reaction with butanol and methanol were also performed in order to try to synthesize methyl-levulinates and butyl-levulinates. Remarked reactions are showed in scheme 7 and 8. The collected results are summerized in table 11 to 14.

Table 11. Synthesis of Ethyl-levulinate in the presence of synthesized macroporous m-SP-SO_3H

Entry	*LA/EtOH*	*Cat(mol%)**	*T(°C)*	*t(h)*	*C(%)***
1	1:5	m-SP-SO_3H (10)	70	24	75
2	1:5	m-SP-SO_3H (7)	70	24	51
3	1:10	m-SP-SO_3H (5)	70	24	65

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversions are determined by 1H-NMR Spectroscopy.

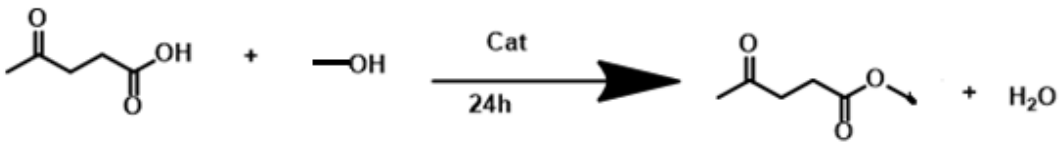
Table 12. Synthesis of Pentyl-levulinate in the presence of synthesized macroporous m-SP-SO_3H

Entry	*LA/PeOH*	*Cat(mol%)**	*T(°C)*	*t(h)*	*C(%)***
1	1:5	m-SP-SO_3H (10)	70	24	85
2	1:5	m-SP-SO_3H (7)	70	24	57
3	1:10	m-SP-SO_3H (5)	70	24	45

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversions are determined by 1H-NMR Spectroscopy.

Entry 1 in the table 11 and 12 shows the best result. The conditions that gave those results were performed in molar ratio of LA/ alcohol=1:5 with 10 % of catalysts. Furthermore, results obtained in synthesis of pentyl-levulinates and ethyl-levulinates, in the case where gel-type catalyst with medium loading SP-SO_3H B and macroporous catalyst m-SP-SO_3H were used, in the aforementioned conditions could be compared. Table 6 entry 9 – 72% and table 9 entry 12 – 78% give the conversion yields promoted by gel-type catalysts, while table 11 entry 1 – 75% and table 12 entry 1 – 85% give the results obtained with the use of macroporous resin. In both cases higher yields were obtained synthesizing pentyl-levulinates. Additionally, it can be noticed that entry 1 of table 12 with the conversion yield of 85 % is considered as the best overall result if we compare all the reactions carried out with employment of new synthetized polymer.



Scheme 7. Esterification reaction of LA with methanol

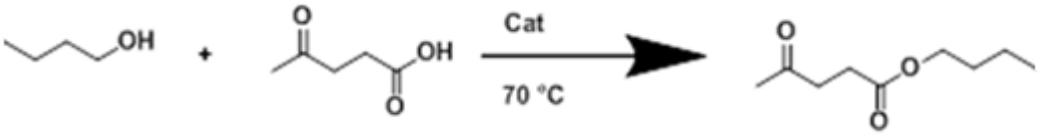
Table 13. Synthesis of Methyl-levulinate in the presence of synthesized macroporous m-SP-SO_3H, commercially available PS-p-TSA and Amberlyst 15.

Entry	*LA/MeOH*	*Cat(mol%)**	*T(°C)*	*t(h)*	*C(%)***
1	1:5	m-SP-SO_3H (10)	70	24	40
2	1:10	m-SP-SO_3H (8)	70	24	50
3	1:5	p-TSA (10)	70	24	45
4	1:10	p-TSA (8)	70	24	63
5	1:5	Amberlyst 15 (10)	70	24	74
6	1:10	Amberlyst 15 (8)	70	24	52

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversions are determined by 1H-NMR Spectroscopy.

In contrast with the majority of cases in which Amberlyst 15 showed lowest conversion yields, in the synthesis of methyl-levulinates gave the best result (entry 5), in conditions where molar ration of LA/methanol was 1/5 with the addition of 10% of Amberlyst 15. Remarkable results have not been obtain with the use of macroporous m-SP-SO_3H yet, so further investigations have to be conducted.



Scheme 8. Esterification reaction of LA with butanol

Table 14. Synthesis of Butyl-levulinate in the presence of synthesized macroporous m-SP-SO_3H, commercially available PS-p-TSA and Amberlyst 15

Entry	*LA/BuOH*	*Cat(mol%)**	*T(^oC)*	*t(h)*	*C(%**)*
1	1:5	m-SP-SO_3H (10)	70	24	49
2	1:10	m-SP-SO_3H (8)	70	24	67
3	1:5	PS-p-TSA (10)	70	24	87
4	1:10	PS-p-TSA (8)	70	24	89
5	1:5	Amberlyst 15 (10)	70	24	44
6	1:10	Amberlyst 15 (8)	70	24	60

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversions are determined by 1H-NMR Spectroscopy.

In the synthesis of butyl-levulinates highest efficiency is obtain with PS-p-TSA (entry 4), with conversion yields of 89%. Macroporous resin (67 %) gave slightly lower conversion (entry 2) and the lowest reaction yields have been obtained with Amberlyst 15.

Figure 25 shows graphical display of conversion obtained with m-SP-SO_3H in various conditions. From that can be noticed that ethyl – and pentyl – levulinates provide better results with the conditions of higher amount of catalyst m-SP-SO_3H and less volume of alcohol. On the other hand, butyl – and methyl – levulinates give better results in conditions with lower amount of catalyst m-SP-SO_3H and in molar ratio of LA/alcohol 1:10.

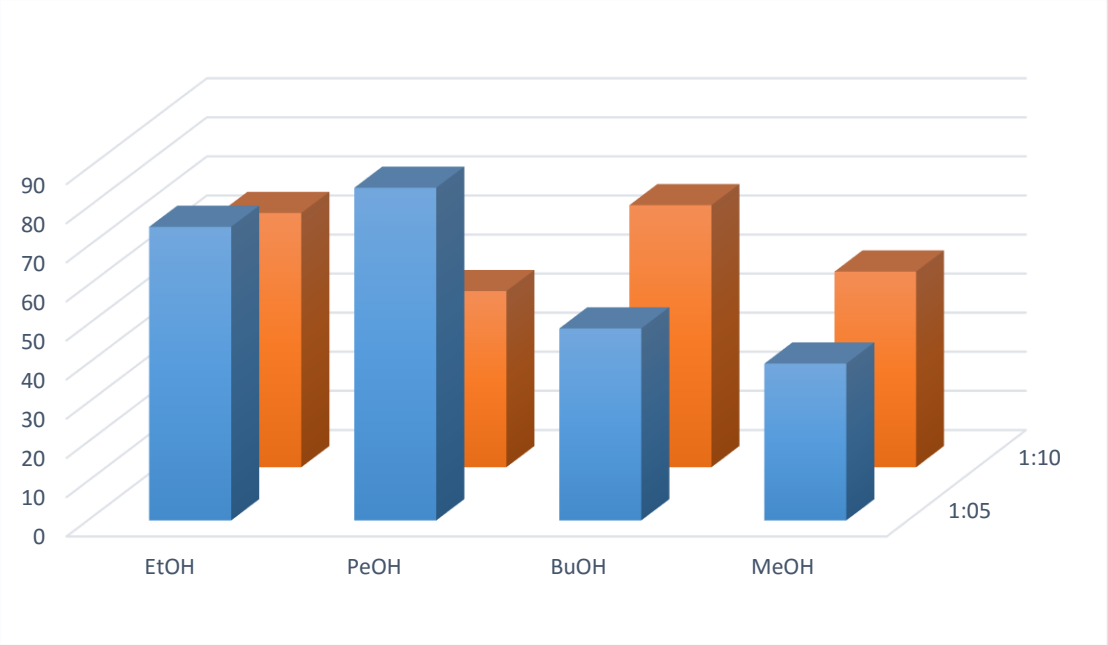


Figure 25. Graphical display of conversion obtained in various conditions.

5.4.3. Activity of SP-SO_3H and m-SP-SO_3H in esterification reactions of levulinic acid in water solution conditions

Generally biomass has approximately between 70-50 % of water content. If the solid acid catalyst could carry out the esterification reactions, it would mean saving the time and money for unnecessary procedure of concentration processes. Esterification reaction with the employment of novel catalyst were examined in order to check is it possible to run the reaction in water solution conditions. The given results are collected in the following tables (table 15,16,17 and 18).

Table 15. Esterification reaction of LA (70 % in water) with ethanol

Entry	*LA/EtOH*	*Cat (mol%)**	*T(°C)*	*t (h)*	*C (%)***
1	1:10	A(8)	70	24	50
2	1:5	A(10)	70	24	77
3	1:10	A(10)	70	24	67
4	1:5	B(10)	70	24	37
5	1:5	Amberlyst15(10)	70	24	43

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversions are determined by 1H-NMR Spectroscopy.

Table 16. Esterification reaction of LA (50% in water) with ethanol

Entry	*LA/EtOH*	*Cat (mol%)**	*T (°C)*	*t (h)*	*C (%)***
1	1:5	A(8)	70	24	25
2	1:5	A(10)	70	24	31
4	1:5	B(10)	70	24	30
5	1:5	Amberlyst15(10)	70	24	16

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversions are determined by 1H-NMR Spectroscopy.

Table 17. Esterification reaction of LA (50% in water) with ethanol

Entry	*LA/EtOH*	*Cat(mol%)**	*T(°C)*	*t(h)*	*C(%)***
1	1:5 (70%)	mSP-SO_3H (10)	70	24	24
2	1:5 (50%)	mSP-SO_3H (10)	70	24	12

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversions are determined by 1H-NMR Spectroscopy.

Table 18. Esterification reaction of LA (50% in water) with pentanol

Entry	*LA/PeOH*	*Cat(mol%)**	*T(°C)*	*t(h)*	*C(%)***
1	1:5 (70%)	mSP-SO_3H (10)	70	24	45
2	1:5 (50%)	mSP-SO_3H (10)	70	24	22

* Catalyst mol% refers to the amount of immobilized acid moieties used.

** Conversions are determined by 1H-NMR Spectroscopy.

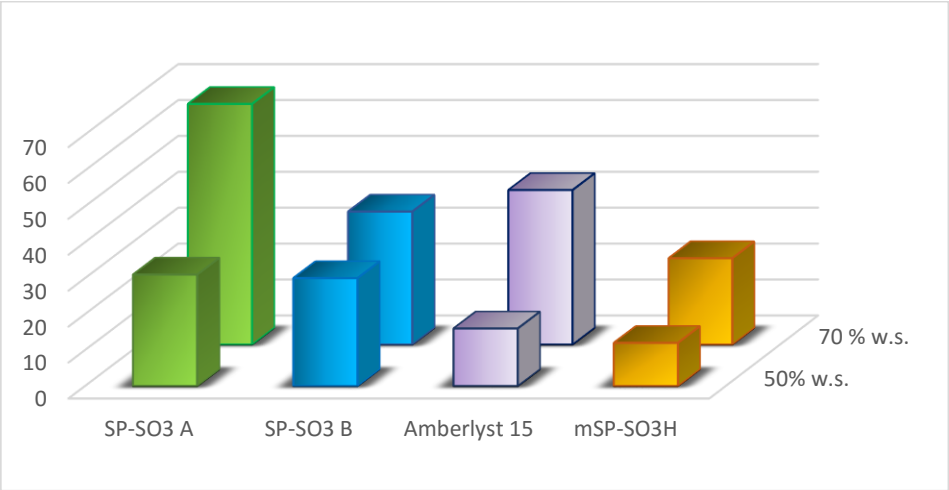


Figure 26. Graphical display of reaction conversions obtained in water solution conditions, with use of different catalyst.

Table 15, 16 and 17 show the results obtained for the synthesis of ethyl-levulinate. The gel-type polymer with highest loading seems to be the best choice for achieving highest conversions.

As expected, higher conversion yields are obtained in conditions with 70% of water solution. Increasing the water content the yield of ethyl-levulinate noticeably decreased, and part of ethanol was probably been reacting with the water to form levulinic acid. Thus, higher water content in the reaction medium become subjected to the competing processes of alcoholysis and hydrolysis.

Alcohols with longer hydrocarbon chain, like pentanol are less soluble in water, so the synthesis of pentyl-levulinate have given higher yields in comparison with the synthesis of ethyl-levulinate, where the yields are unsatisfactory.

6. Experimental part

6.1. General remarks

All chemicals were purchased and used without any further purification unless otherwise noted. Suspension polymerizations were run using a three-neck cylinder-shaped glass vessel, equipped with a mechanical stirrer, condenser and nitrogen inlet. A silicon oil bath was used as heating source.

Elemental microanalyses were performed using a Fison's EA1106CHN analyzer using atropine, 2,5-bis-2-(5-tert-butylbenzoxazol-yl)-thiophene (BBOT) and phenanthrene as reference standard, with an accuracy of ca. 2 lmol/g.

GLC analyses were performed by using Hewlett–Packard HP 5890A equipped with a capillary column DB-35MS (30 m, 0.53 mm), a FID detector and hydrogen as gas carrier. GLC-EIMS analyses were carried out by using a Hewlett–Packard HP 6890 N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV.

All ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100.6 MHz, respectively, using $CDCl_3$ as deuterated solvent and bromoanisole as internal standard.

6.2. Synthesis of 1,4-bis(4-vinylphenoxy)benzene 4

In a round bottomed flask equipped with a condenser and a magnetic stirrer, 4-fluorobenzaldehyde 5 (3.18 g, 25.6 mmol), hydroquinone 6 (1.54 g, 14.0 mmol) were dissolved in *N*,*N*-dimethylformamemide (20.0 mL), and potassium carbonate (4.84 g, 12.60 mmol) was added. The reaction mixture was left under stirring at 160 ^{o}C for 6 h, then poured into cold water (20 mL) and filtered to afford 4,4'-[1,4-phenylen-bis-(oxy)]dibenzaldehyde **7** as brown solid, with a yield of 82% , which was pure according to NMR analysis and was used without further purification. ^{1}H NMR ($CDCl_3$) δ 7.04–7.16 (m, 8H), 7.84–7.93 (m, 4H), 9.99 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 117.9, 118.5, 129.8, 131.3, 150.1, 162.7, 190.6.

In a three-neck round bottom flask, equipped with a magnetic stirrer and a nitrogen inlet/outlet, methyltriphenylphosphoniumbromide (5.167 g, 14.49 mmol) was dissolved in dry THF (55 mL) at 0 ^{o}C. A solution of nBuLi (9.04mL, 1.6 M in n-hexane, 14.49 mmol) was then added dropwise, and the reaction mixture was left under stirring at 0 ^{o}C for 3 h, then allowed to warm at room temperature. Next, a solution of 4,4'-[1,4-phenylenebis(oxy)]dibenzaldehyde 7 (2.0 g, 6.29 mmol) in dry THF (15.0 mL) was added, and this mixture was stirred at room temperature for an additional 24 h. After this time, THF was removed under vacuum, and the residue was recrystallized from methanol, affording 1,4-bis(4-vinylphenoxy) benzene 4 (1.77g, 89.5% yield) as a white solid (m.p. 146–146.5 ^{o}C). ^{1}H NMR ($CDCl_3$) δ 5.18–5.21 (d, 1H, J = 11.08 Hz), 5.64–5.68 (d, 1H, J = 17.52 Hz), 6.65–6.72 (dd, 1H, J = 11.08, 6.6 Hz), 6.95–6.97 (d, 2H, J = 8.66 Hz), 7.00 (s, 2H), 7.36–7.39 (d, 2H, J = 8.66); ^{13}C NMR ($CDCl_3$) δ 112.79, 118.25, 120.43, 127.54, 132.65, 135.95, 152.62, 157.40. An. Calcd. For $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%. Found: C, 84.11; H, 5.76%.

6.3. Polymerization

6.3.1. General procedure for the preparation of gel-type polymer SP

A three neck round bottom cylinder shaped glass vessel (Figure 27) was filled with a solution of acacia gum (4.80 g, 4% w) and NaCl (3.60 g, 3% w) in distilled water (120 mL) and stirred for 30 minutes under room temperature. A mixture of styrene (6.55 g, 63.04mmol), cross-linker 4 (0.395 g, 1.26 mmol), chlorobenzene (8 mL) and benzoyl proxide (131.12 mg, 0.54 mmol) represents the organic phase, which was added to the aqueous solution under stirring. Then, the reaction was warmed up to 85 ^{o}C under mechanical stirring. After 24 h, the reaction was allowed to reach room temperature and the polymer beads were filtred. The product was washed in a Soxhlet extractor for 24 h with water, THF and hexanes and vacuum dried overnight (yield 71 %).



Figure 27. Suspension polymerization reactor used in laboratory

6.3.2. General procedure for the preparation of macroporous resin m-SP

A reaction vessel immersed in an oil bath, equipped with condenser, mechanical stirrer and nitrogen inlet/outlet was charged with water (80ml), poly(vinyl alcohol) (MW 85.000-124.000, 99% hydrolysed) (2%) and NaCl (g) and stirred for 24 h at room temperature. A mixture of styrene (6.55g, 63.04 mmol), croos-linker (0.395 g, 0.54 mmol), chlorobenzene (0,4 ml) and benzoyl proxide (131.12 mg,0.54 mmol) represents the organic phase, which was added to the aqueous solution under stirring. The system was kept under stirring and purged with nitrogen for 30 min. Then, the reaction was warmed up to 85 ^{o}C under mechanical stirring. After 24 h, the reaction was allowed to reach room temperature and the polymer beads (Figure 28) were filtred. The product was washed in a Soxhlet extractor for 24 h with water, THF and hexanes and vacuum dried overnight (yield 71 %).

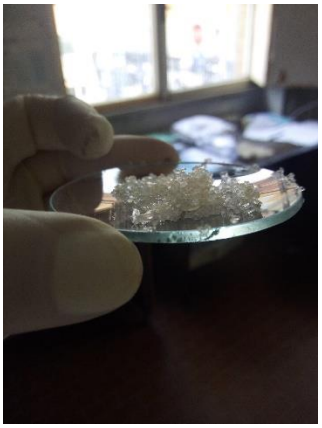


Figure 28. Synthesized polymer beads.

6.4. Synthesis of catalysts SP-SO_3H and m-SP-SO_3H

A series of partially sulfonated resins were prepared. In order to achieve low-to-high sulfonation degrees, 300 mg of the selected polymer beads were placed in 2 mL of concentrated sulfuric acid and afterwards, the mixture was stirred and heated for 6 h at a temperature selected to achieve the desired degree of sulfonation (T = 0–60 ^{o}C). The sulfonation reaction time and temperature (to control the conversion) were selected with the aim of limiting differences in the sulfonation degree at the periphery and center of the polymer beads. The product was washed with deionised water until neutral pH of the eluent. If gel-type polymer were sulphonated, the polymer was pre-swollen in 2 mL of dichloromethane.

Table 19. General elemental analysis date for the two type of catalysts:

Catalyst	*N (%)*	*C (%)*	*H (%)*	*S (%)*	*Loading(mmol/g)*
SP-SO_3H	0	38.73	4.50	13.70	4.68
m-SP-SO_3H	0	47	5	14.5	4.7

6.5. Representative esterification reaction of Levulinic acid with ethanol in optimal condition

In a screw capped vial equipped with a magnetic stirrer Levulinic acid (0.174 g, 1.50 mmol), ethanol (330 μL) and synthesized polymer, as acid catalyst were consecutively added and the resulting mixture was left under stirring at 70 ^{o}C. After 24 h, dichloromethane was added, the catalyst recovered by filtration and the organic solvent evaporated under vacuum to give ethyil levulinate. Conversion value was determined by NMR Spectroscopy. All the other reaction were carried out in the same way.

^{1}H NMR ($CDCl_3$) δ (ppm) 1.23-1.26 (m, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.55-2.64 (m, 2H, CH_2), 2.74-2.77 (m, 2H,CH_2), 4.10-4.16 (m, 2H, CH_2).

6.6. Representative esterification reaction of Levulinic acid in water solution conditions with pentanol

In a screw capped vial equipped with a magnetic stirrer Levulinic acid (0.174 g, 1.50 mmol), pentanol (811 μL), distilled water (248 μL) and synthesized polymer, as acid catalyst were consecutively added and the resulting mixture was left under stirring at 70 ^{o}C. After 24 h, dichloromethane was added, the catalyst recovered by filtration and the organic solvent evaporated under vacuum to give ethyil levulinate. Conversion value was determined by NMR Spectroscopy. All the other reaction were carried out in the same way.

^{1}H NMR ($CDCl_3$) δ (ppm) 0,80-0,83 (m, 3H, CH_3), 1,24 (m, 4H, CH_2), 1.52-1.55 (m, 2H, CH_2), 2.02 (s, 3H, CH3), 2.46-2.49 (m, 2H,CH_2), 2.65-2.68 (m, 2H, CH_2), 3.96-4.03 (m, 2H, CH_2).

7. Conclusion

During the work of this thesis a series of novel polystyrene based gel-type acid catalysts namely SP-SO_3H, containing the 1,4-bis(4-vinylphenoxy)benzene cross-linker, and featuring three different loadings has been prepared. Additionally, a high loading macroporous polystyrene-based resin (m- SP-SO_3H) has been developed, by employing the same cross-linking agent. Full structural/morphological characterization is in due course. The activity of this catalytic systems has been preliminary evaluated in esterification reaction of levulinic acid with different alcohols to give the corresponding alkyl levulinates. The best conversion yield was, indeed, obtain with the use of newly synthesized macroporous SP-SO_3H, in the esterification reaction of levulinic acid with pentanol, but remarkable results were obtained with the both of the synthesized catalysts. Conversion yields obtained with the use of synthesized ones were generally higher than the ones with the use of commercially available catalysts hence, good efficiency of gel-type catalyst and macroporous resin was proved. Esterification reaction of levulinic acid in water solution conditions were also conducted in order to broaden the catalyst scope. As expected, better results were obtained in condition with less amount of water content. Futher investigations are due in course.

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Curriculum vitae

Ana-Maria Županić was born in 1991 in Zagreb. Part of her childhood, she spent in Hungary, where her primary education has begun. Returning back in Croatia, she finishes primary school Julije Klovića in Zagreb and high school IV. Gymnasium. In 2010 she has enrolled in the Faculty of Chemical Engineering and Technology in Zagreb and she has completed her undergraduate studies in Environmental Engineering. She has than continued the graduate studies in Chemical Engineering, on the same Faculty. On the summer semester of the academic year 2015/2016 she has applied for the Erasmus Student Exchange Program. Within this Program, she has carried out the experimental part of her master thesis at the Department of Chemistry, Biology and Biotechnologies, of the University of Perugia, in Italy. After finishing the graduate studies, she would like to broad her knowledge in the aforementioned fields. In her free time, she likes to travel, learn about other cultures and other foreign languages, and spend some quality time with her family and friends. She hopes that in the near future she could improve her riding skills.