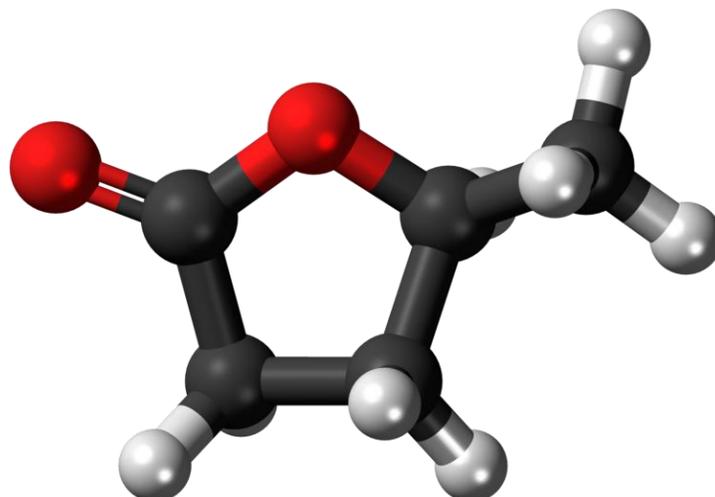




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Hydrogenation of Levulinic Acid to γ -Valerolactone in a Continuous Packed Bed Reactor



Master Thesis

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Abstract

Levulinic acid (LA), derived from lignocellulosic biomass, is recently selected as one of the 15 most promising carbohydrate-derived platform chemicals by the US Department of Energy. The presence of a ketone and carboxyl group makes it a versatile component, which can be converted to a number of derivatives. Among the derivatives of LA, γ -valerolactone (GVL) is identified as a sustainable platform chemical for the production of carbon-based chemicals and fuels. A significant amount of literature is available about the production of GVL in batch set-ups with the use of different solvents and catalysts. Nevertheless, limited literature is available about studies using continuous set-ups. For eventual scaling up to industrial level, continuous processes are preferred above batch processes for a bulk chemical like GVL.

This study is focused on the catalytic hydrogenation of LA in water to produce GVL through the intermediate 4-hydroxypentanoic acid (4-HPA) in a continuous packed bed reactor. A catalyst screening study with heterogeneous catalysts was performed using ruthenium on different supports (typical conditions: 90°C, 1 mL/min feed flow, 30 mL/min H₂ flow, 2 gram catalyst, column pressure 45 bar). Ru/Al₂O₃ was found to be unstable under the applied hydrothermal conditions and acid environment and dissolved slowly. Ru/TiO₂ showed high stability, but a low conversion of LA was achieved. The best performance of all tested catalysts was demonstrated by Ru/C. The catalyst showed high activity (almost full conversion of LA) and stability over 6 hours on stream. Because of its excellent performance, Ru/C was chosen as base catalyst for further process studies. The effect of LA feed concentration on the conversion of LA and reaction rate was investigated by using feed streams of different LA concentrations under the same reaction conditions. It was found that the initial LA concentration has a significant influence on the LA conversion. The conversion of LA in concentrated LA solution was increased by alteration of the process conditions and using higher catalyst intakes. This showed that Ru/C is able to convert concentrated streams of LA to GVL.

Finally, a long duration test was performed with diluted LA (1 mol/L), using Ru/C (0.5 wt.% of Ru) as catalyst. A slow decrease in conversion of LA was observed over 52 hours on stream. The initial conversion of LA was 95%, and after 52 hours on stream 82% of LA conversion was observed. A significant decrease in specific surface area of the catalyst (BET) was observed, from 1108 m²/g to 391 m²/g after 52 hours on stream. This was most likely the cause of decrease in activity, since no measurable leaching of ruthenium was detected during the experiment.

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1 Introduction

Nowadays our society heavily depends on petroleum as the carbon source to produce chemicals and fuels [1,2]. However, this goes on the expense of extensive consumption of natural sources such as petroleum, natural gas and coal. It took millions of years to form these fossil resources, and currently they are consumed at a much higher rate than their natural regeneration cycle. Another important issue is the emission of CO₂, a strong greenhouse gas, which is released to the atmosphere by combustion of fossil fuels. In a few decades a large amount of carbon, which was stored in the earth for million years, was released causing environmental issues and climate change. The demand on fossil resources is still growing and ultimately these resources will be depleted. Therefore, a renewable source for chemicals and fuels has to be found. Solar, wind, hydroelectric and geothermal energy have been suggested as excellent alternatives to coal and natural gas for heat and electricity production. However, for the production of fuels and chemicals a carbon source is necessary. Biomass is the only sustainable source of organic carbon which is currently available on earth and is considered as an ideal alternative for petroleum in the production of fuels, chemicals and carbon-based products [3].

Levulinic acid (LA) is an important derivative of second generation lignocellulosic biomass. It is a versatile platform chemical, which can be used for a number of applications. Examples are the production of polymers, lubricants, fuels, coatings or pharmaceuticals [4]. LA has recently been selected as one of the 15 most promising carbohydrate-derived platform chemicals by the US department of Energy [3,5].

Among the derivatives of LA, γ -valerolactone (GVL) is identified as promising platform chemical for the synthesis of both biofuels and biochemicals. GVL can be obtained by catalytic hydrogenation of LA and can be used as a fuel additive, food ingredient, intermediate for the production of chemicals and fuels, solvent, polymer precursor and nylon intermediate [6].

Extensive research has been performed on the hydrogenation of LA in batch systems using both homogeneous and heterogeneous catalysts by several groups [6]. However, despite the high interest, limited studies have been reported about the production of GVL in a continuous manner. Keeping scaling up to industrial scale in mind, a continuous process is favorable above a batch process [7]. Therefore, this study is focused on the hydrogenation of LA to produce GVL in a continuous set-up. It is an extension on the work of Chalid et al. who studied LA hydrogenation reactions in a batch set-up [8], and the unpublished work of Piskun et al. about a kinetic study on the hydrogenation of LA with Ru/C in water using a batch set-up [9].

1.1 Literature review

A detailed overview of available literature is given in this section. Biomass will first be discussed from a general point of view. This will be followed by a review of available literature about LA hydrogenation to produce GVL in batch and continuous systems.

1.1.1 Sorts of biomass

Biomass for first generation biofuels

Biodiesel and bioethanol derived from edible biomass sources, such as sugar cane or corn for bioethanol and vegetable oils for biodiesel, can be identified as first generation biofuels. They can be produced in a relatively simple way using conventional technologies. The production process of bioethanol consists of biomass pre-treatment to produce sugar monomers, which can subsequently be fermented with the use of microorganisms to form bioethanol. After a distillation step, the bioethanol can directly be used as fuel or fuel additive. Biodiesel can be produced by the esterification of fatty acids or transesterification of oils (triglycerides) in an alcohol using a basic or acidic catalyst. After separation from glycerol by decantation and purification, the produced fatty acids can be used as fuel or fuel additive. Despite the fact that first generation biofuels can be produced in a simple and commercially available way, they have some important drawbacks. Bioethanol is slightly corrosive and therefore it has to be mixed with gasoline to prevent engine damage. Moreover, it has a tendency to attract water which can lead to an increased risk of phase separation when blended with gasoline and, subsequently, engine damages. Biodiesel is also corrosive and therefore it has to be combined with regular diesel. The high cloud point of biodiesel, compared with regular diesel, increases the risk of blockages in fuel hoses or filters at low temperatures. In addition to these problems, it is preferable to use non-edible biomass to be sure that the production of chemicals and fuels is not in competition with food supply [1,10].

Biomass for second generation biofuels

In contrast with first generation biofuels, which are produced from only a part of biomass, second generation biofuels use the entire biomass (lignocellulosic biomass). In addition, the biomass used for second generation biofuels is non-edible, so it does not compete with food supply [1]. Lignocellulosic biomass has the potential to replace fossil resources for the production of fuels and chemicals [11]. A general overview of the conversion of biomass into first and second generation biofuels is shown in Figure 1.1.

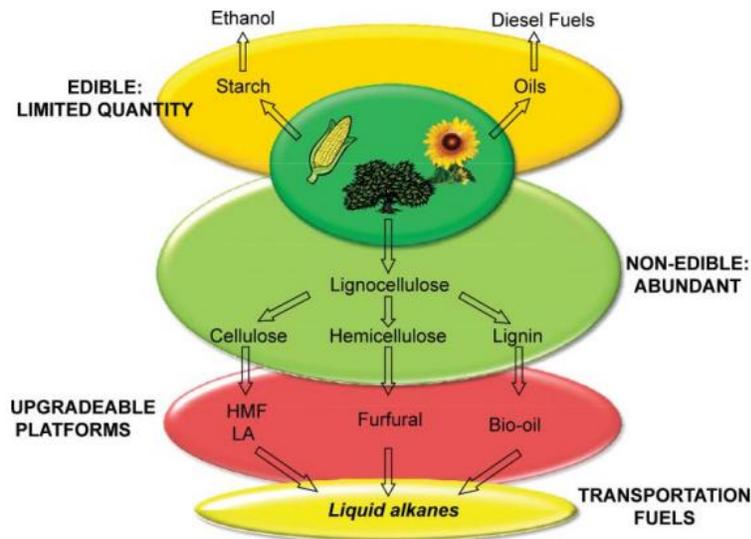


Figure 1.1: Conversion of biomass to biofuels, adapted from [1]

From the scheme in Figure 1.1 it can be observed that lignocellulosic biomass consists of three components, which can be converted into a variety of chemicals and fuels:

Lignin (15-20 %)

Lignin is an amorphous polymer, which is composed of methoxylated phenylpropane structures, and surrounds hemicelluloses and cellulose. Therefore biomass has to be pre-treated to depolymerize the lignin seal to make carbohydrates accessible, using chemical methods. The lignin fraction can be upgraded to phenolic resins, bio-oils and aromatics.

Hemicellulose (25-35%)

Hemicellulose is an amorphous polymer, consisting of five different sugar monomers: D-xylose (most prevalent), L-arabinose, D-galactose, D-glucose and D-mannose. Hemicellulose binds to lignin and strands of cellulose are interlaced with hemicellulose. To recover glucose from cellulose by hydrolysis, it is preferred to remove hemicellulose from biomass during pre-treatment. The extraction of hemicellulose can be achieved with physical methods or both physical and chemical methods. The xylose monomers, derived from hemicellulose, can be fermented to ethanol or dehydrated to furfural.

Cellulose (40-50%)

Cellulose is a polymer of glucose units, which are linked via β -glycosidic bonds. It is isolated within the lignin/hemicellulose matrix and therefore biomass has to be pre-treated before cellulose can be hydrolysed. This pre-treatment can be performed with the use of milling and physical/chemical techniques. Cellulose can be converted into glucose using enzymatic hydrolysis [1]. The formed glucose can subsequently be converted to: hydroxymethylfurfural (HMF), LA, formic acid (FA) and insoluble humins [1,4].

1.1.2 Upgrading of lignocellulosic biomass

Lignocellulosic biomass can be converted to fuels and chemicals via thermochemical treatment or hydrolysis. The main pathways are represented in Figure 1.2.

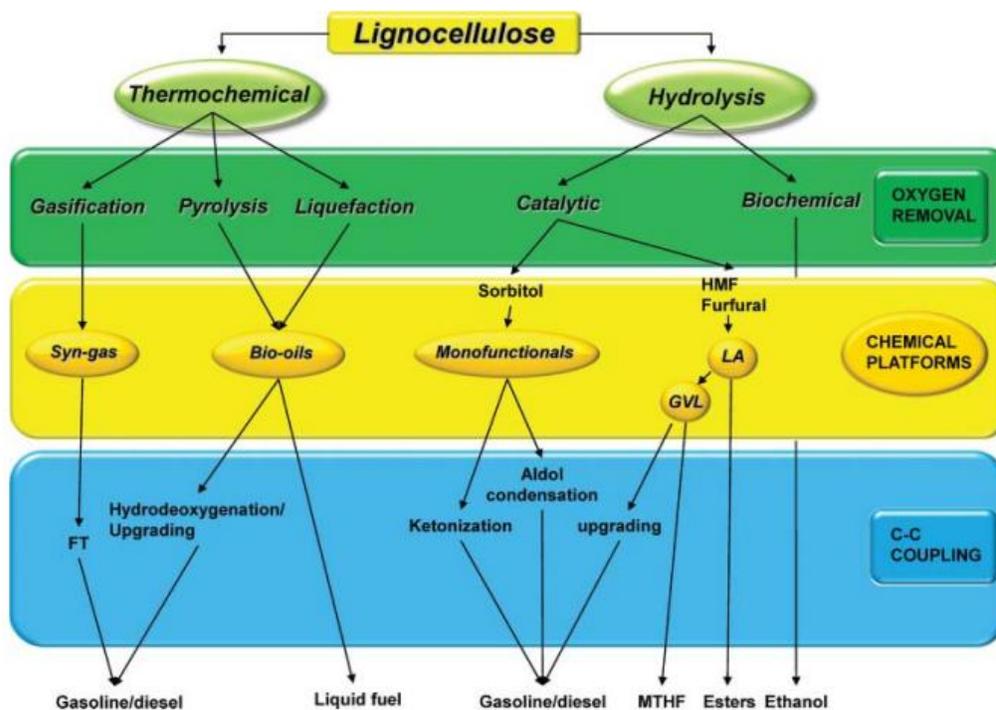


Figure 1.2: Pathways for upgrading of lignocellulosic biomass, adapted from [1]

Thermochemical

Gasification

Gasification of lignocellulosic biomass to syngas (a mixture of H_2 and CO) is carried out at temperatures over $700^\circ C$. The high temperature is necessary for the endothermic formation of the syngas mixture [11]. The formed syngas can subsequently be converted to gasoline or diesel using Fischer-Tropsch synthesis. All sorts of biomass can be subjected to the gasification process, thus it is not constrained to a particular feedstock. However, the Fischer-Tropsch process needs a clean gas feed. Thus, water content and impurities in the produced syngas can cause problems in this downstream process.

Pyrolysis

Pyrolysis is a thermal anaerobic decomposition of biomass at temperatures ranging from 380 to $530^\circ C$ and at short residence times (seconds). The result is a liquid mixture of more than 350 compounds such as acids, aldehydes, alcohols, sugars, esters, ketones and aromatics, which are known as bio-oil. The produced bio-oil cannot directly be used for combustion engines because of a high oxygen content and high acidity. Therefore, the product has to be treated in order to overcome the low energy density and corrosive properties [1].

Liquefaction

Liquefaction is carried out at lower temperatures than pyrolysis (250-450°C), higher pressures (5-20 bar) and longer residence times. This leads to a bio-oil with less oxygen content compared to bio-oil produced by pyrolysis. However, the resulting bio-oil shows instability for long term storage. Therefore, it needs to be upgraded, for example by hydrodeoxygenation, to solve these stability problems and transform the oils into fuels [1].

Hydrolysis

In comparison to thermochemical pathways, where all fractions of lignocellulose are used, in hydrolysis processes only the hemicellulose and cellulose part can be used. Besides this, for the conversion to fuels and chemicals, relatively mild reaction conditions are required.

Chemo-catalytic

After the separation of lignin from the cellulose and hemicellulose, the sugars can be isolated by hydrolysis [1]. The sugars and the products of their conversion have high degree of functionality (-OH, -COOH and -C=O groups). Therefore, oxygen removal reactions (dehydration, hydrogenation or hydrogenolysis) have to be carried out for the production of fuels and chemicals. The produced chemical platform molecules can contain a maximum of 6 carbon atoms. Hence, C-C coupling reactions are necessary to upgrade these platform chemicals to fuels, since hydrocarbon fuels can consist of chains with a maximum of 20 carbon atoms [3].

Biochemical

The sugars, which are isolated from cellulose and hemicellulose, can also be fermented to produce second generation bio-ethanol. This eliminates the need for an edible feedstock [3].

Unless the more extensive reaction pathways, hydrolysis offers selective processing options and platform chemicals which cannot be achieved with thermochemical pathways. However, combination of both pathways can offer interesting opportunities for an integrated bio-refinery [1].

1.1.3 LA as platform chemical

Levulinic acid (4-oxopentanoic acid) has recently been identified by the US department of Energy as one of the 15 most promising platform chemicals derived of the carbohydrate part of lignocellulosic biomass [5]. Some physical properties of LA are shown in Table 1.1:

Table 1.1: Physical properties of LA, adapted from [8]

| Property | Value |
|------------------------------|--------|
| MW (g/mol) | 116.11 |
| Melting point (°C) | 38 |
| Boiling point (°C) | 247 |
| Density (g/cm ³) | 1.14 |
| pKa | 4.59 |

LA is an interesting building block because of the presence of two functional groups: a ketone group (-C=O) and a carboxyl group (-COOH). This makes LA a versatile component, which can be converted into a number of derivatives. Products, obtained from LA, can be used as intermediates in the production of chemicals, directly as fuel additives or converted into biofuels [4,12]. The structural formula of LA and some of the derivatives are represented in Figure 1.3.

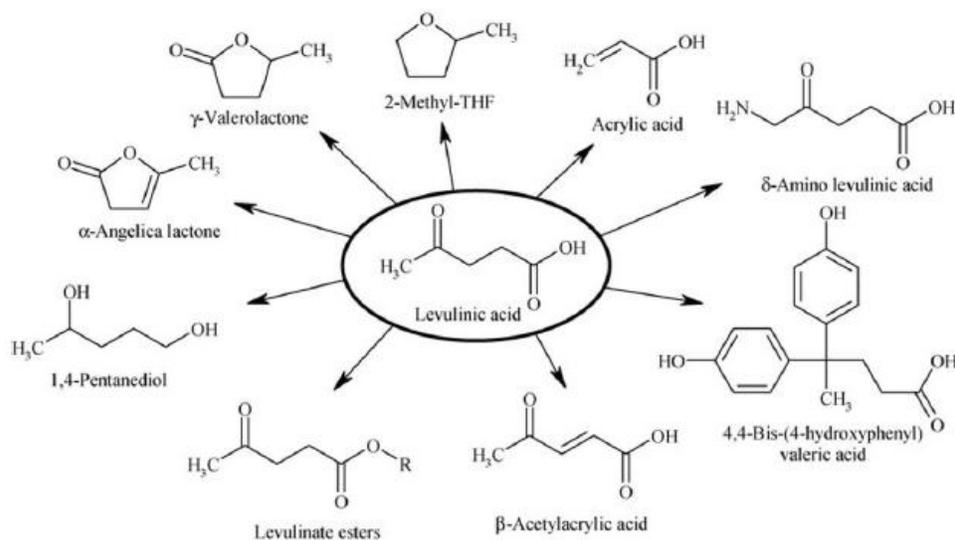


Figure 1.3: Levulinic acid and its derivatives, adapted from [12]

A promising technology to produce LA on an industrial scale was developed by the Biofine Corporation and is known as the Biofine process [13,14]. The process converts lignocellulosic biomass to valuable platform chemicals, which are especially LA and furfural. The feedstock for the Biofine process consists of cellulose containing materials, such as paper mill sludge, urban waste paper, agricultural residues and cellulose fines from paper making [4]. The Biofine process is schematically represented in Figure 1.4.

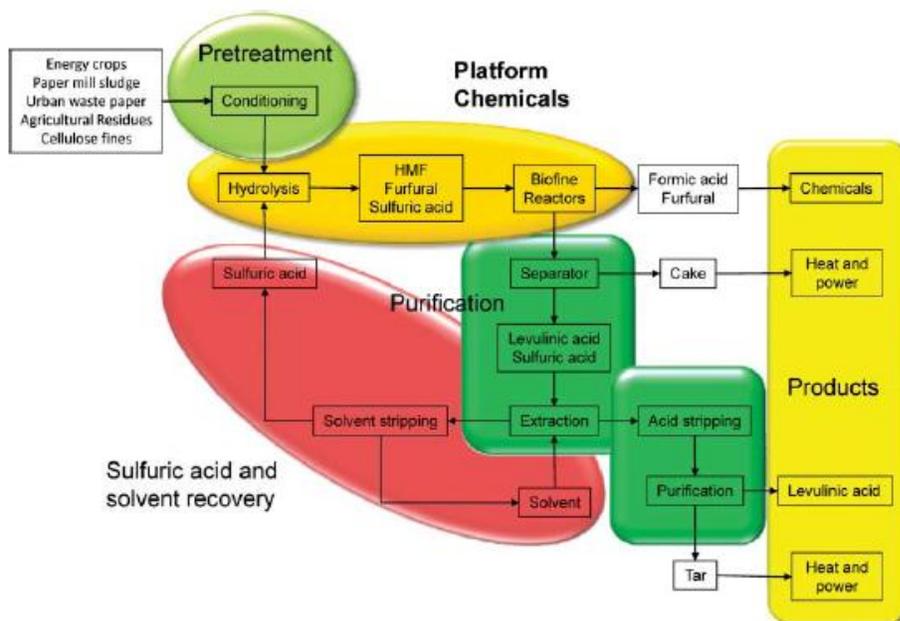


Figure 1.4: Biofine process, adapted from [1]

The biomass feedstock is mixed with sulphuric acid (1.5-3 wt.%) and introduced into a plug-flow reactor to hydrolyse the carbohydrates at 210-220°C and a pressure of 25 bar with a short residence time (12 s.). During this hydrolysis step, C₅ and C₆ sugars are converted into respectively furfural and hydroxymethylfurfural (HMF). In a second plug-flow reactor the HMF reacts further to form LA and FA at 190-200°C and a pressure of 14 bar with a residence time of 20 minutes. The conditions in the second reactor result in separation of the formed furfural and FA from the LA. The formed LA is separated from the sulphuric acid and subsequently purified [13,14].

1.1.4 GVL synthesis and potential as sustainable liquid

Among the derivatives of LA, GVL is identified as a sustainable platform chemical for the production of chemicals and fuels. It can be used as fuel additive, food ingredient, intermediate for the production of chemicals and fuels, solvent and polymer precursor [6]. GVL can be obtained by the hydrogenation of LA using either heterogeneous or homogeneous catalysts in the liquid or gas phase. The reaction pathways from LA to GVL are shown in Figure 1.5.

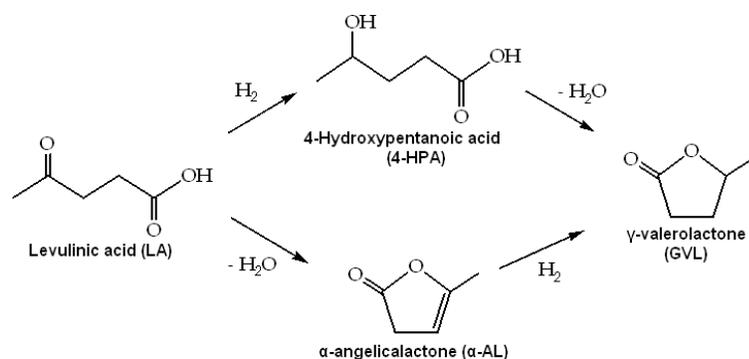


Figure 1.5: Hydrogenation pathways of LA to GVL, adapted from [8]

The conversion of LA to GVL may proceed through two possible pathways: via the intermediate α -angelica lactone (α -AL) or 4-hydroxypentanoic acid (4-HPA). In the presence of a non-acidic metal catalyst (e.g. Ru/C) and by operating at lower temperatures ($< 200^{\circ}\text{C}$), the reaction likely proceeds via the intermediate 4-HPA. The formed 4-HPA is unstable and will undergo ring closure due to interaction of the hydroxyl group with the carboxyl group and lose a water molecule to form GVL. In the presence of strong mineral or solid acids, LA dehydrates at moderate temperatures ($300\text{-}350^{\circ}\text{C}$) yielding α -AL followed by hydrogenation to form GVL. α -AL polymerizes over acidic surfaces and it typically leads to deactivation of the catalyst, therefore this reaction pathway is not preferred [4,11,15,16].

Horváth et al. reported a study about the sustainability of GVL [17]. They demonstrated that GVL could be considered as a sustainable liquid, since it has several very attractive physical and chemical properties (Table 1.2).

Table 1.2: Physical properties of various oxygenates, adapted from [17]

| Property | Methanol | Ethanol | MTBE | ETBE | GVL |
|---|----------|---------|-------|--------|---------|
| MW (g/mol) | 32.04 | 46.07 | 88.15 | 102.17 | 100.12 |
| Carbon (wt.%) | 37.5 | 52.2 | 66.1 | 70.53 | 60 |
| Hydrogen (wt.%) | 12.6 | 13.1 | 13.7 | 13.81 | 8 |
| Oxygen (wt.%) | 49.9 | 34.7 | 18.2 | 15.66 | 32 |
| Boiling point ($^{\circ}\text{C}$) | 65 | 78 | 55 | 72-73 | 207-208 |
| Melting point ($^{\circ}\text{C}$) | -98 | -114 | -109 | -94 | -31 |
| Density (g/cm^3) | 0.791 | 0.8 | 0.74 | 0.742 | 1.05 |
| Open cup flash point ($^{\circ}\text{C}$) | 16.1 | 14 | -33 | -19 | 96 |

GVL has a high boiling point (207°C), which makes it easy to separate from water since it does not form an azeotrope. Besides this, GVL has a high open cup flash point (96°C), compared to the other oxygenates. Additional temperature dependent vapor experiments showed a minimal increase of vapor pressure from 0.65 kPa (25°C) to 3.5 kPa (80°C) for GVL. The other oxygenates demonstrated much higher numbers. Taking this into account, the authors concluded that GVL is a safe liquid to store. GVL has all the characteristics of a sustainable liquid: the possibility to convert to fuels and chemicals, renewable, easy and safe to store, low melting point, high boiling and flash point, a distinctive and

acceptable smell to recognize leaks and spills, low or no toxicity and solubility in water to assist biodegradation.

GVL can be used as a fuel blend, though its low hydrogen content results in blending limits. Therefore it can be interesting to upgrade GVL to other derivatives, such as MTHF. Recently researches on the conversion of GVL into other components have been performed by several groups [15,18-25]. An overview of GVL derivatives is shown in Figure 1.6.

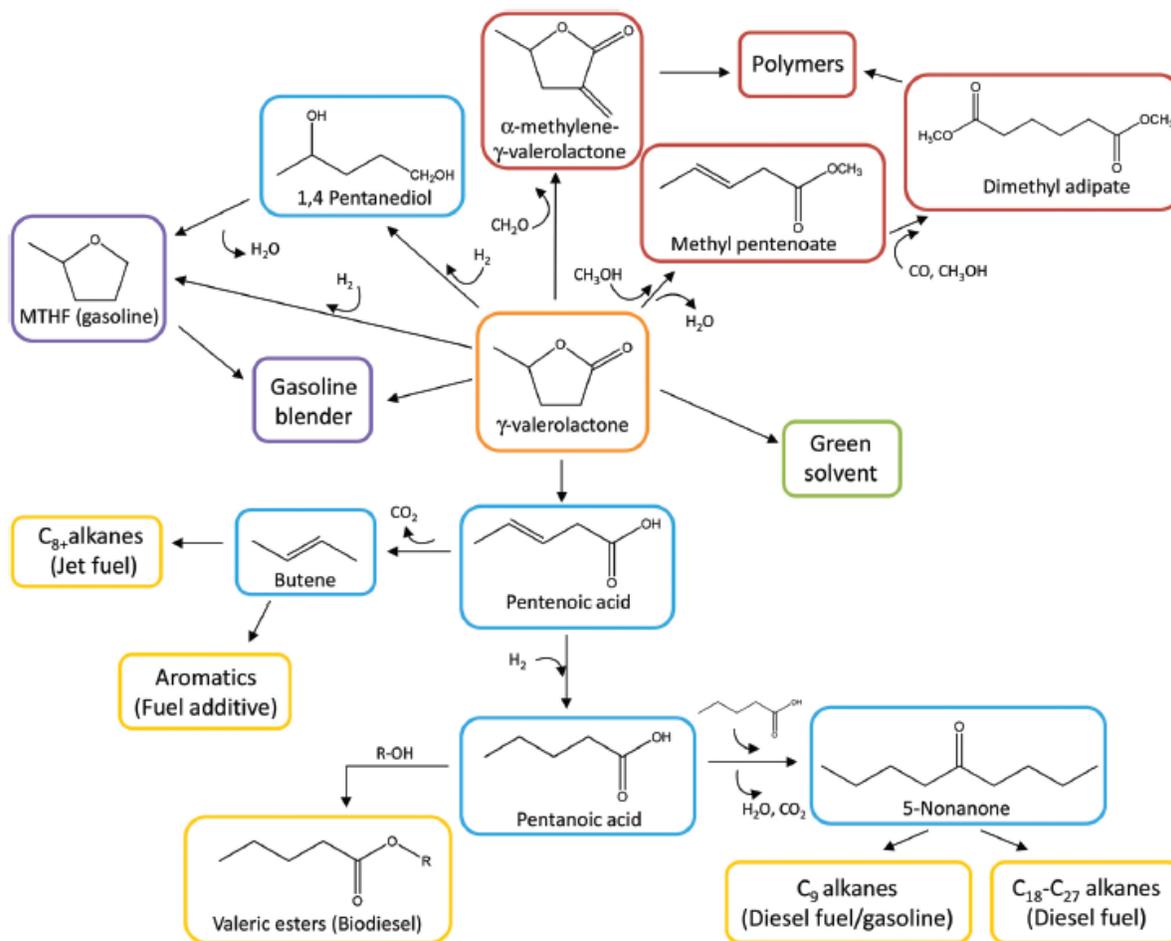


Figure 1.6: Reaction pathways to convert GVL into fuels, fuel additives and chemicals, adapted from [16]

1.1.5 LA hydrogenation in batch set-ups

The versatility of GVL has initiated numerous studies, to screen the suitability of hydrogenation catalysts for the synthesis of GVL from LA. Homogeneous catalysts for the hydrogenation of LA to produce GVL have been developed over recent years, leading to well-functioning systems [26-30]. However, these systems are not suitable for eventual large-scale production, because of the high boiling point of GVL (207-208°C) [17]. This makes homogeneous processes uneconomical, because GVL has to be separated from the homogeneous catalyst by means of distillation.

Therefore, the use of heterogeneous catalysts is more interesting for the targeted production of GVL on larger scales. A significant amount of research has been done in recent years to develop heterogeneous systems and it is still in development. Recently, Wright et al. published a detailed review with broad variations of heterogeneous catalysts and solvents for the hydrogenation of LA to produce GVL [6]. A substantial number of catalysts have been used with the most common being supported transition metals. An overview of heterogeneous catalysts and process conditions using solvents other than water is given in Table 1.3 (the optimized conditions as reported are depicted).

Table 1.3: Hydrogenation of LA in different solvents with heterogeneous ruthenium catalysts

| Catalyst | Solvent | Hydrogen Pressure (bar) | Temperature (°C) | Reaction Time (min.) | LA Conversion (%) | GVL Selectivity (%) | Reference |
|---------------------------------|-------------|-------------------------|------------------|----------------------|-------------------|---------------------|-----------|
| Ru/C (5 wt.% Ru) | Methanol | 12 | 130 | 160 | 92.0 | 99.0 | [31] |
| Ru/C (5 wt.% Ru) | 1,4-Dioxane | 34 | 150 | 240 | 100 | >97 | [18] |
| Ru/C (5 wt.% Ru) | 1,4-Dioxane | 12 | 130 | 160 | 98.8 | 97.7 | [32] |
| Ru/C (5 wt.% Ru) | Methanol | 12 | 130 | 160 | 99.0 | 85.3 | [32] |
| Ru/TiO ₂ (1 wt.% Ru) | 1,4-Dioxane | 40 | 200 | 240 | 100 | 95.8 | [33] |

The largest screening study was performed by Manzer, who compared the activity and selectivity of the transition metals (Ir, Rh, Pd, Ru, Pt, Re and Ni), supported on active carbon [18]. Ru/C showed excellent activity for the conversion of LA and selectivity to GVL. The excellent performance of ruthenium stimulated the interest for ruthenium supported catalysts for LA hydrogenation. The reactions are normally carried out at temperatures of 100-150°C, hydrogen pressures between 10 and 35 bar and reaction times between 60 and 240 minutes. Ruthenium supported on active carbon is most prevalent in solvents as methanol and 1,4-dioxane with LA conversions higher than 92%. A possible explanation for the good performance of Ru/C is a combination of the small particle size and high surface metal dispersion degree of ruthenium [31]. At higher temperatures, ruthenium supported on TiO₂ showed excellent performance as was reported by Luo et al. [33]. They obtained full LA conversion with 95.8% GVL selectivity. Though, minor amounts of the deep hydrogenation products MTHF and 1,4-pentanediol were found in the reaction mixture.

Reactions in water

Despite promising results in different organic solvents, water can be a more interesting solvent for the LA hydrogenation reactions. Some reasons why water is preferred:

- cheap in comparison to other solvents;
- environmental friendly;
- the LA product stream, coming from the hydrolysis of lignocellulosic biomass, is an aqueous solution. This can be an advantage for scaling up to targeted integrated bio refineries.

An overview of heterogeneous catalysts and process conditions with the use of water as solvent is given in Table 1.4 (the optimized conditions as reported are depicted).

Table 1.4: Hydrogenation of LA in water with heterogeneous ruthenium catalysts

| Catalyst | Hydrogen Pressure (bar) | Temperature (°C) | Reaction Time (min.) | LA Conversion (%) | GVL Selectivity (%) | Reference |
|--|-------------------------|------------------|----------------------|-------------------|---------------------|-----------|
| Ru/Al ₂ O ₃ (5 wt.% Ru) | 30 | 70 | 180 | 24.0 | 96.0 ^a | [34] |
| Ru/C (5 wt.% Ru) | 30 | 70 | 180 | 48.0 | 97.5 ^a | [34] |
| Ru/TiO ₂ (0.55 wt.% Ru) | 45 | 170 | 120 | 95.0 | 92.0 | [35] |
| Ru/C (5 wt.% Ru) | 12 | 130 | 160 | 99.5 | 86.6 | [32] |
| Ru/ZrO ₂ (0.1 mol% Ru) | 40 | 150 | 60 | 99.9 | Unknown | [36] |
| Ru/C (5 wt.% Ru) | 45 | 90 | 60 | 99.0 | 78 ^a | [8] |

^a Only other product 4-HPA

The hydrogenation reactions in water are generally carried out at temperatures between 50 and 170°C, hydrogen pressures between 10 and 45 bar with reaction times ranging from 60 to 180 minutes. The results reported in literature about hydrogenation reactions in water using Ru/C are different. Galletti et al. reported 48% LA conversion with 97.5% GVL selectivity, Al-Shaal et al. - 99.5% LA conversion with 86.6% GVL selectivity and Chalid et al. - 99% LA conversion with 78% GVL selectivity. These differences can be explained by different reaction conditions in all cases. It was already investigated by Liu et al. that the hydrogen pressure has an effect on the LA conversion and GVL selectivity [31]. Besides this, Chalid et al. showed the influence of temperature and reaction time on the conversion of LA and selectivity to GVL [8]. Galletti et al. improved their process by addition of Amberlyst A-70, a heterogeneous acid co-catalyst. This co-catalyst activates the carbonyl group to form the intermediate 4-HPA. This resulted in an increase of LA conversion to 100% and 99.9% GVL selectivity after 180 minutes of reaction under the same reaction conditions as the experiment without addition of Amberlyst A-70.

Ru/Al₂O₃ showed poor results for LA hydrogenation reactions in water. A possible explanation for the low activity is the low surface area of Ru/Al₂O₃, which is about 10 times lower than that of Ru/C [34]. Furthermore it has already been reported by Osada et al. that Ru/Al₂O₃ has a low hydrothermal stability, which resulted in structural damages and loss of ruthenium to the solution during gasification of lignin in supercritical water in a batch reactor (400°C, 3.7 bar, 180 min.) [37].

It was observed by Du et al. that Ru/ZrO₂ also showed high level of conversion of LA (99.9%), though no information was given about the selectivity to GVL [36].

The positive effect of water on the hydrogenation reaction was investigated by Al-Shaal et al. [32]. They performed experiments with ruthenium on different supports in ethanol at 130°C and 12 bar H₂ for 160 minutes. The experiments were repeated at the same reaction conditions in an ethanol/water mixture, which resulted in an increase of conversion for all supports.

Recently Deng et al. invented a two-step conversion system of LA and FA [35]. In the first step the FA from the FA/LA mixture was converted into H₂ and CO₂ using a Ru-P/SiO₂ catalyst, which resulted in almost full FA conversion. The remaining mixture was hydrogenated with an external hydrogen source (45 bar) using a Ru/TiO₂ catalyst at a relatively high reaction temperature (170°C) for 120 minutes; this resulted in a high level of LA conversion (95%) and GVL selectivity (92%). However, the support seems to have an influence on the hydrogenation reaction as was investigated by Al-Shaal et al. [32]. They performed LA hydrogenation experiments in ethanol and ethanol-water mixtures with ruthenium on two different TiO₂ supports. Ru/TiO₂ with support from Tronox (rutile phase) was unable to catalyze LA hydrogenation, while with support from Degussa (P25 form, mixture of anatase and rutile phase) 81% conversion was obtained under the same conditions (130°C, 12 bar H₂, 160 min.). The support from Degussa had a higher specific surface area, which enhanced the catalysis either by facilitating substrate absorption or enabling higher ruthenium dispersion. This can be confirmed by the work of Primo et al. who studied the hydrogenation of functionalized carboxylic acids using Ru/TiO₂ [38]. They concluded that the activity of Ru/TiO₂ catalysts depends on the particle size of ruthenium and the nature of the TiO₂ support, since the carbonyl group is activated on the support.

Reactions with neat LA

The process efficiency can be increased by hydrogenation of neat levulinic acid instead of using solvents. Nevertheless, limited literature is available about this subject. The results of two groups who performed hydrogenation experiments with neat levulinic acid are given in Table 1.5.

Table 1.5: Hydrogenation of neat LA with heterogeneous ruthenium catalysts

| Catalyst | Hydrogen Pressure (bar) | Temperature (°C) | Reaction Time (min.) | LA Conversion (%) | GVL Selectivity (%) | Reference |
|---------------------------------|-------------------------|------------------|----------------------|-------------------|---------------------|-----------|
| Ru/C (5 wt.% Ru) | 12 | 190 | 40 | 100 | Unknown | [32] |
| Ru/C (5 wt.% Ru) | 12 | 25 | 3000 | 100 | 97.5 | [32] |
| Ru/TiO ₂ (1 wt.% Ru) | 40 | 200 | 240 | 98.8 | 98.9 | [33] |
| Ru/TiO ₂ (1 wt.% Ru) | 40 | 200 | 600 | 100 | 97.5 | [33] |

Ru/C was able to achieve 100% conversion of LA at a temperature of 190°C within 40 minutes, though no information was given about the GVL selectivity. The possibility to achieve 100% conversion at a lower temperature (25°C) was also shown but required much longer reaction time (50 hours) [32]. Ru/TiO₂ showed excellent activity, though a higher hydrogen pressure was applied and longer reaction times were necessary to obtain 100% LA conversion. The product mixture contained minor amounts of the deep hydrogenation products MTHF, pentanoic acid (PA) and 1,4-propanediol [33].

LA hydrogenation in aqueous solution with FA as hydrogen source

Most of the processes for GVL synthesis use petroleum-derived hydrogen, which makes the processes less sustainable. During the synthesis of LA, FA is co-produced [13,14]. Since FA can be decomposed into H₂ and CO₂, it is an interesting source of hydrogen. Therefore, also research has been performed to hydrogenate LA with *in-situ* formed hydrogen from FA, and is still going on [21,27,35,36]. This can be an interesting route for integrated bio-refineries. Though, there are some important issues which arise during these processes. The product stream from LA synthesis contains sulphuric acid (H₂SO₄), which is used for the hydrolysis of carbohydrates. Sulphur adsorbs on the surface of the ruthenium catalyst and leads to deactivation. Therefore, a neutralization step is required or alternatives for H₂SO₄ should be used for the hydrolysis step [39]. Besides this, FA is initially converted into H₂ and CO₂ by the ruthenium catalyst (e.g. Ru/C), but the selectivity is decreasing with time. This leads to formation of CO and H₂O, which reduces the hydrogen production. In addition, the ruthenium catalyst leads to methanation of CO to form CH₄. This reaction consumes hydrogen, which is required for the hydrogenation of LA [19,40]. This was confirmed by Du et al. by performing LA hydrogenation experiments over different platinum group metals [36]. When they added 1000 ppm CO to the reaction system, the LA conversion was strongly reduced. Possible solutions for this problem will be discussed in the following section about hydrogenation of LA in continuous set-ups.

1.1.6 LA hydrogenation in continuous set-ups

LA hydrogenation in batch has already shown to be very effective with excellent LA conversions and GVL selectivities at different reaction conditions. However, continuous processes are preferred above batch processes for targeted production on an industrial scale. Several advantages were reported by Serrano-Ruiz et al. [7]:

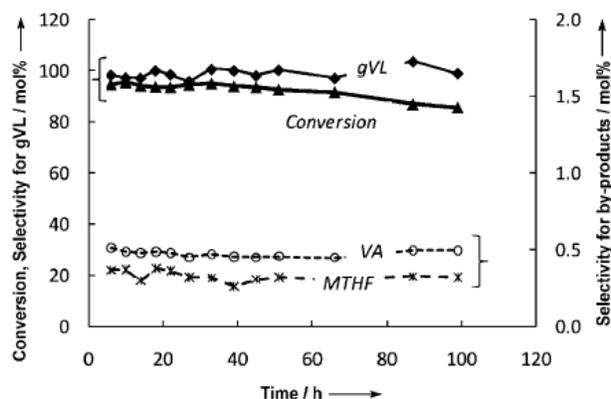
- better control of reaction conditions;
- facilitates scaling up;
- intensification of the chemical processes to convert feedstocks into desired products;
- catalyst separation from the products is not necessary in case of fixed bed reactors;
- catalyst regeneration can be performed over the same bed without removal of the catalyst;
- gasses, which are generated during reaction (normally CO and CO₂), can be removed constantly;
- higher product yields per unit time.

An overview of reported literature about continuous set-ups for hydrogenation reactions of LA, including process conditions, is given in Table 1.6.

Table 1.6: Hydrogenation of LA in continuous set-ups using heterogeneous catalysts

| Reactor Type | Catalyst | Solvent | Hydrogen Source | Pressure (bar) | Temperature (°C) | WHSV ($\text{g}_{\text{feed}}/\text{g}_{\text{cat}}\cdot\text{hr}$) | LA Conversion (%) | GVL Selectivity (%) | Reference |
|-------------------------|--|----------------------|--|----------------|------------------|---|----------------------------|-------------------------------|-----------|
| Packed Bed Up-flow | Pt/SiO ₂ (0.8 wt.% Pt) Extrudates | Water/ GVL | Extern | 40 | 200 | 2 | 15 hr.: 85 460 hr.: 22 | 15 hr.: 92 460 hr.: 83 | [41] |
| Packed Bed Up-flow | Ru/C (5 wt.% Ru) Powder | Water | Extern | 35 | 150 | 32 | Start: 90 106 hr.: 68 | Start: 96 106 hr.: unknown | [15] |
| Packed Bed | Pt/TiO ₂ (1 wt.% Pt) Extrudates | GVL | Extern | 40 | 200 | 9 | Start: 98 100 hr.: 85 | >95 | [20] |
| Packed Bed Down-flow | Ru/C (5 wt.% Ru) Powder | 1-Butanol/ water | Extern | 35 | 180 | 0.9 | 91 | 97.8 | [19] |
| Packed Bed Down-flow | Pd/C (10 wt.% Pd) + (Ru/C 5 wt.% Ru) Powder | None | FA/ Butylformate + co-feed H ₂ | 35 | 180 | 0.9 | 96 | 99 | [19] |
| Packed Bed Down-flow | Ru/C (5 wt.% Ru) Powder | Water | FA + co-feed H ₂ | 35 | 150 | Unknown | 35 | >98 | [42] |
| Packed Bed Down-flow | RuRe(3:4)/C (15 wt.% RuRe) Powder | Water | FA + co-feed H ₂ | 35 | 150 | Unknown | 15-40 | >95 | [42] |
| Packed Bed Up-flow | RuSn (3,6:1)/C (5 wt.% RuSn) Powder | 2-Sec butylphenol | Extern | 35 | 220 | 2.2 | 98 | 95.8 | [40] |
| Packed Bed Up-flow | RuSn (3,6:1)/C (5 wt.% RuSn) Powder | 2-Sec butylphenol | FA + co-feed H ₂ | 35 | 220 | 1.5 | 46 | 93.4 | [40] |
| Packed Bed Down-flow | Ru/C (5 wt.% Ru) Powder | 1,4-Dioxane | Extern | 1-25 | 265 | 0.5 | Start: 100 240 hr.: 100 | Start: 98.6 240 hr.: 96.6 | [43] |

The reactions are normally carried out in packed bed reactors at temperatures ranging from 150 to 220°C and pressures of 35 to 40 bar. Shell patented a system for the conversion of LA to PA, with GVL as intermediate [41]. The system consists of 2 reactors. In the first packed bed reactor LA is converted to GVL at 200°C and 40 bar H₂, while in the second packed bed reactor GVL is converted to PA. They performed an experiment of 500 hours with the use of Pt/SiO₂ extrudates to convert LA to GVL. The feed consisted of LA (91 wt.%), GVL (7.8 wt.%) and water (1.2 wt.%) with a small recycle of the reactor effluent. The catalyst showed significant deactivation with time on stream. The conversion decreased from 85% (15 hours) to 22% (460 hours) and the selectivity to GVL decreased from 92% (15 hours) to 83% (460 hours). However, it was shown that the catalyst restored its initial activity after regeneration. Minor amounts of PA, MTHF and unknown organic components were found in the product mixture. A system for the conversion of LA to GVL followed by GVL conversion into PA and subsequently formation of 5-nonanone out of PA was reported by Serrano-Ruiz et al. [15]. The hydrogenation reaction of LA in aqueous solution was carried out in a packed bed reactor filled with Ru/C powder at 150°C and 35 bar H₂. The space velocity was relatively high (WHSV= 32 g_{feed}/g_{cat}.hr) to keep the conversion below 100%, in order to check for catalyst stability. The initial conversion of LA was 90% and decreased slowly with time on stream to 68% after 106 hours. The initial selectivity towards GVL was high (96%), though no information was given about the selectivity for GVL after 106 hours. The other products were 4-HPA and 1,4-pentanediol. No information was provided about catalyst characterization. Lange et al. performed a catalyst screening with 50 different catalysts using a packed bed reactor [20]. The feed consisted of LA (89 wt.%) and GVL (11 wt.%). Pt/TiO₂ showed the best performance and was subsequently tested for 100 hours at 200 °C and 40 bar H₂. In contrast, Pt/C showed low activity which can be confirmed with the work of Manzer [18]. The results of the long duration experiment are shown in Graph 1.1.

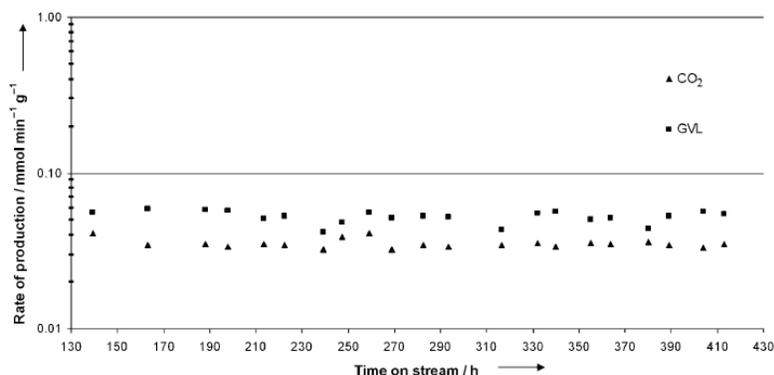


Graph 1.1: Hydrogenation of LA over Pt/TiO₂ (VA=PA) at 200°C and 40 bar H₂, adapted from [20]

The catalyst showed slow deactivation with time on stream. The conversion decreased from 98% to 80% over 100 hours, while the average selectivity to GVL remained the same (>95%). Also traces of the deep hydrogenation products MTHF and PA were found in the product stream. Analysis of the catalyst showed no significant loss or sintering of the active metal.

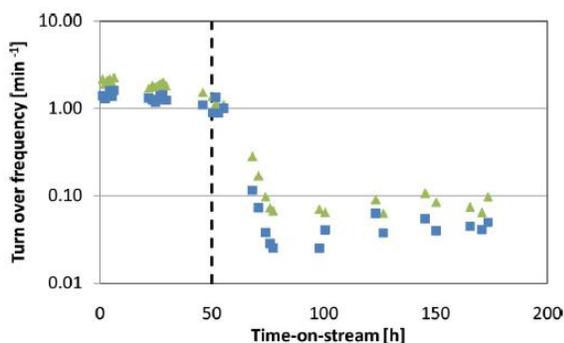
An alternative pathway was developed by Gürbüz et al. [19]. They prepared an aqueous solution of LA and FA by hydrolysis of cellulose with H₂SO₄. When LA and FA were treated with butene, which can be

produced from GVL, sec-butyllevulinate (BL) and sec-butylformate (BF) were generated. These esters are hydrophobic and separated spontaneously from the aqueous solution, which enabled the recycling of H_2SO_4 . In addition, it prevented deactivation of the catalyst by H_2SO_4 . The formed BL and BF could subsequently be processed over a dual bed reactor containing Pd/C and Ru/C. In this catalytic system Pd/C facilitated BF decomposition into CO_2 and H_2 , and Ru/C the hydrogenation of BL to form GVL and 2-butanol. This could be followed by the conversion of the product stream to butene over a $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst. To test the ability of Ru/C for the hydrogenation of BL, an experiment was performed in a fixed bed down-flow reactor with a water/1-butanol solution of BL over a Ru/C (5 wt.% of Ru) catalyst using external hydrogen (12 mL/min) at 180°C and 35 bar H_2 . This resulted in a high level of BL conversion (91%) and selectivity towards GVL (97.8%). Another experiment with the same feed and reaction conditions with addition of BF was performed over a Ru/C (5 wt.% of Ru) catalyst, which resulted in a low conversion of BL (24%) and selectivity towards GVL of 91.7%. This can be explained by the fact that Ru/C was incapable for the conversion of BF and FA to CO_2 and H_2 since the selectivity was changed, resulting in CO formation as discussed in part 1.1.5. In addition, Pd/C is not a very active catalyst for LA hydrogenation [18], but showed to be an excellent catalyst for the conversion of FA to CO_2 and H_2 [44]. To test the capability of the dual catalyst bed, a long duration experiment was performed at 180°C and 35 bar H_2 with a BL/BF feed coming from the beginning of the process (as described), which also contained traces of H_2SO_4 . In the catalyst bed, the feed was first contacted with Pd/C to form H_2 and CO_2 followed by Ru/C where the BL was hydrogenated with the *in-situ* formed H_2 . A co-feed of hydrogen was added (12 mL/min) during the experiment to be sure that the catalysts remained in a reduced state. The results of the long duration experiment are shown in Graph 1.2.



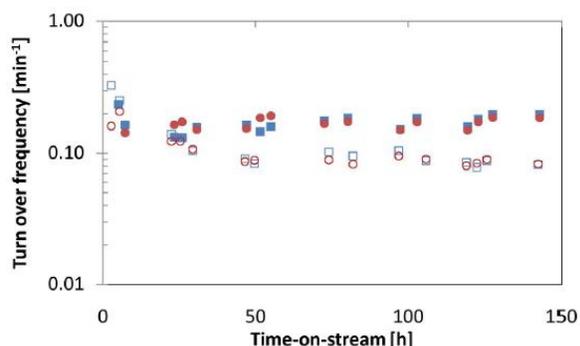
Graph 1.2: BL and BF conversion over a Pd/C-Ru/C dual catalyst bed at 180°C and 35 bar H_2 , adapted from [19]

The dual-bed catalytic system showed excellent stability with time on stream over 400 hours. A high level of BL conversion was achieved (96%) with high selectivity towards GVL (99%). The effect of H_2SO_4 on Ru/C and the bimetallic catalyst RuRe(3:4)/C was explored by Braden et al. [42]. An experiment was carried out to test the stability of Ru/C with a feed stream consisting of an aqueous solution of 0.3 mol/L of both LA and FA in a packed bed reactor at 150°C and 35 bar H_2 . Sulphuric acid was added after 50 hours on stream. A co-feed of hydrogen was added (5 mL/min) during the experiment to be sure that the catalyst remained in a reduced state. The results are shown in Graph 1.3.



Graph 1.3: Ru/C stability test with a LA(□)/FA(Δ) feed stream at 150°C and 35 bar H₂, adapted from [42]

The Ru/C catalyst showed slow deactivation over the first 50 hours. The conversion of LA at the beginning of the experiment was relatively low (35 %). In contrast to the effect of FA on Ru/C described in other literature, only traces of methane were found in the gas phase and FA was almost completely converted to CO₂ (>98%) with a high selectivity (>99%). After addition of H₂SO₄, the conversion of LA decreased rapidly (< 5%). In addition, the GVL selectivity decreased from > 98% to 60-70%. The addition of the more oxophilic metal rhenium to Ru/C increased the activity of the catalyst and made the catalyst resistant for H₂SO₄. Graph 1.4 shows the stability of the catalyst over 150 hours on stream at 150°C and 35 bar H₂.



Graph 1.4: LA(□) conversion to GVL(○) using 15 wt.% RuRe/C at 150°C and 35 bar H₂, adapted from [42]

The open symbols represent a reaction without addition of H₂SO₄, while the solid symbols represent a reaction with addition of H₂SO₄. The feedstock of the reactor consisted of 2.2 mol/L of both LA and FA in an aqueous solution (higher than the experiment with Ru/C). A stable catalytic activity was achieved, even with addition of H₂SO₄. The LA conversions, of all points which were measured, were between 15 and 40% with GVL selectivity higher than 95%. FA was completely converted to CO₂ with a selectivity higher than 99%. Additional experiments were performed with 2.2 mol/L of both LA and FA at high LA conversion (> 80%) with Ru/C (5 wt.% of Ru) and RuRe(3:4)/C (15 wt.% of RuRe).

The steady state production rate of GVL for Ru/C (0.0028 mmol min⁻¹ g-cat⁻¹) was more than 10 times lower than for RuRe/C (0.034 mmol min⁻¹ g-cat⁻¹). The steady state production rate of GVL for Ru/C at the lower concentration of 0.3 mol/L (of both LA and FA) was shown to be 0.02 mmol min⁻¹ g-cat⁻¹, which showed that the conversion of LA is also a function of the concentration of LA. In summary it was

concluded that rhenium is an effective promoter for ruthenium for the conversion of LA and FA in the presence of H_2SO_4 .

The performance of another bimetallic catalyst, RuSn/C, was explored by Alonso et al. [40].

Hydrogenation experiments with a LA/FA feedstock in sec-butylphenol as solvent through a packed bed reactor with Ru/C (5 wt.% of Ru) at 220°C and 35 bar H_2 , showed a drastic deactivation of the catalyst with time on stream. This was caused by the loss of selectivity towards CO_2 and H_2 during the decomposition of FA, as described in section 1.1.5. Furthermore, the Ru/C catalyst hydrogenated the C=C bond in the solvent. Addition of tin improved the selectivity towards CO_2 and H_2 for the conversion of FA (> 99%). Besides this, the selectivity of the catalyst was modified to hydrogenate the C=O bond of LA instead of the C=C bond of the solvent. An experiment in a packed bed reactor filled with RuSn(3.6:1)/C (5 wt.% of RuSn) with 2 mol/L LA in 2-sec-butylphenol was performed using external hydrogen at 220°C and 35 bar H_2 , which resulted in excellent conversion of LA (98%) and selectivity towards GVL (95.8%). The same experiment was carried out again, but in this case also 2 mol/L FA was added (additional hydrogen source). This resulted in a lower LA conversion (46%), but still a high level of GVL selectivity (93.4%). In both cases, the catalyst showed slow deactivation over the first 100 hours on stream and then achieved a stable performance over more than 230 hours. During both experiments, small amounts of MTHF and unknown organic components were found in the product mixtures. The positive effect of tin can be explained by its ability to activate C=O groups, which will facilitate hydrogen transfer from adjacent ruthenium sites [45].

An exception to the processes described above is the work of Upare et al. [43]. The reported process was carried out in the vapor phase instead of the liquid phase. A solution of LA in 1,4-dioxane was hydrogenated in a packed bed reactor with Ru/C (5 wt.% of Ru) powder. The reaction was performed at atmospheric pressure at 265°C, after 168 hours the hydrogen pressure was increased to 25 bar. The conversion of LA was 100% at the beginning of the experiment and remained the same over 240 hours on stream. The initial selectivity towards GVL was 98.6% and decreased to 96.6% after 240 hours on stream, which was most likely caused by the increased hydrogen pressure. Also small amounts of α -AL and MTHF were found in the product stream. The vapor phase process shows excellent performance and has the ability to operate at atmospheric pressure. However, the process will be energy intensive due to the high boiling point of LA (247°C).

In conclusion, the use of FA as hydrogen source can be very interesting since it is co-produced during LA synthesis and excludes the need of an external hydrogen source. This can be promising for integrated biorefineries. However, this strategy can cause problems for the hydrogenation reaction of LA to produce GVL and therefore more research is needed on systems which can treat mixtures of LA, FA and H_2SO_4 . Reactions in the vapor phase showed excellent results, but the processes will be energy intensive. The most promising results were reported about hydrogenation of LA in the liquid phase using external hydrogen. Therefore, this study is focused on the hydrogenation of LA in the liquid phase in a packed bed reactor using external hydrogen.

1.2 Objectives

The hydrogenation of LA with water as solvent in batch systems, reported in literature, showed interesting results [8,9,32,34-36]. However, limited studies have been reported about hydrogenation of LA with water as solvent in continuous set-ups. There is only one group who studied the process with the use of exclusively LA in water as reactor feed and an external hydrogen source [15]. In other studies different additives, other solvents or feedstocks consisting of LA and FA were used as depicted in Table 1.6 in section 1.1.6.

The work described in this study, is an extension of the work of Chalid et al. [8] and the recent unpublished work of Piskun et al. [9]. In both studies, LA hydrogenation experiments were performed in a batch set-up (in aqueous solution) with the use of an external hydrogen source and a heterogeneous Ru/C catalyst. Catalyst recycling experiments were carried out to test the stability of the catalyst. The first experiment showed excellent LA conversion (99%) with a GVL selectivity of 54%. For a second experiment the catalyst was reused, which resulted in a LA conversion of 80 % with the same selectivity towards GVL. For both cycles, only 4-HPA was identified as an intermediate. The BET surface area of the catalyst decreased from 900 m²/g to 170 m²/g. The decrease in activity was probably caused by coke formation on the catalyst surface, another suggestion was the polymerisation of α -AL on the catalyst surface.

To get more insight in the catalyst stability, further studies in a continuous set-up are required. Besides this, continuous processes are preferred above batch processes for eventual scaling up to industrial scale [7]. Therefore, this study is focused on the hydrogenation of an aqueous LA solution in a continuous set-up, using a heterogeneous catalyst with the main objective being:

Study the catalytic hydrogenation of LA in a continuous set-up with an emphasis on catalyst activity and stability.

To achieve this goal, a couple of sub aims were set:

- design and building of an appropriate continuous set-up for LA hydrogenation;
- perform catalyst screening tests with heterogeneous ruthenium catalysts on different supports and find the best performing catalyst for further studies;
- get insight in the effect of LA concentration on LA conversion and the reaction rate;
- test the ability of the system to work with concentrated LA;
- test the stability of the catalytic system by performing a long duration test.

1.3 Approach

Design and building of the continuous set-up

The continuous set-up, which was delivered by the technical department, was tested for the ability to convert LA to GVL. Therefore, initial experiments were carried out at low LA concentrations. The reactor was modified where necessary to obtain a more stable system for LA hydrogenation.

Catalyst screening

The catalyst screening study was performed using Ru/Al₂O₃, Ru/TiO₂ and Ru/C as catalyst with different ruthenium loading. To make the test comparable, the study was carried out at the same reaction conditions, catalyst intake and LA concentration. The catalysts were evaluated on stability and LA conversion.

Effect of LA feed concentration

To get insight in the effect of LA feed concentration, a number of experiments was carried out at different initial concentrations of LA (from 0.1 mol/L to 97 wt.% LA). The reaction conditions and catalyst intake were kept the same to make the results comparable.

Conversion of concentrated LA solution

Reactions without the use of solvent can be advantageously for eventually scaling up to industrial scale, since distillation steps to separate GVL from the solvent will be eliminated. To obtain higher conversions with concentrated LA, the process conditions were altered and higher catalysts intakes were applied.

Catalyst stability test

To test the stability of the catalytic system, a long duration test was performed for 52 hours. The same reaction conditions were applied as for the catalyst screening tests. The stability of the system was evaluated by LA conversion and catalyst deactivation/degradation.

2 Materials and methods

2.1 Materials

Levulinic acid (purity >98%) and 1,4-dioxane (purity >99%) were purchased from Acros Organics, deuterium oxide (purity 99.9%) was purchased from Sigma-Aldrich. Hydrogen and nitrogen gas were from Linde Gas (purity 99.5%). All chemicals were used without purification.

The catalysts were obtained from:

- Johnson Matthey (JM): Ru/C (0.5 and 2 wt.% of Ru), Ru/Al₂O₃ (0.5 wt.% of Ru)
- Evonik: Ru/C (5 wt.% of Ru)
- BASF: Ru/Al₂O₃ (0.3 wt.% of Ru), TiO₂ support (anatase phase)

Ru/TiO₂ was prepared in house by wet impregnation using RuCl₃ as precursor and the TiO₂ support obtained from BASF. The catalyst was dried at 50°C for 24 hours in an orbital shaker. Subsequently, the catalyst was reduced for 4 hours at 450°C with 10% H₂/N₂.

2.2 Methods

In this section an overview will be given about the experimental and analytical procedures.

2.2.1 Reactor description

The reactor consists of two parts: a preheating section and a reaction section placed on top (see Figure 2.1 for details). The preheating section is filled with a static mixing element, which is kept in place with fine mesh gauzes. The section is equipped with tracing, which is controlled by an Eurotherm 2208e controller. The temperature inside the preheating section is controlled by the temperature of the wall of the preheating section. Therefore the temperature sensor present in the tracing spiral is used. The reactor tube has an internal diameter of 0.6 cm and a length of 13.5 cm. It is filled with catalyst of choice, which is kept in place with the same sort of fine mesh gauzes as used in the preheating section. When 2 gram Ru/C was used, the reaction section was totally filled with catalyst. The rest of the reaction section was filled with woven glass sheets for the runs where 2 gram of Ru/Al₂O₃ or Ru/TiO₂ was used, because of the higher particle density of Al₂O₃ and TiO₂. The temperature of the reactor is controlled at the same way as the preheating section, with the difference that the controller is an Eurotherm 2132. The liquid feed is pumped into the preheating section by a Williams P250 V225 piston pump. The feed pipe is equipped with two backflow preventers to make sure that no liquid or hydrogen flows back to the pump and no pressure fluctuations will arise. Additionally, the feed pipe and vessel are equipped with a tracing (40°C) which was used at high LA concentration to prevent LA crystallization due to the high melting point of LA (38°C). Hydrogen is entering the reactor at the same point as the liquid feed and is controlled by a Brooks 5866 pressure controller and a Bronkhorst F-211-C-FA-11-V flow controller. The hydrogen feed pipe is fitted with a needle valve to close the hydrogen flow, and a backflow preventer to prevent liquid entering the controllers and pressure fluctuations.

Pressure manometers are placed before the preheating section and after the reaction section to determine the column pressure. Before and after the reaction section, a thermocouple is placed to determine the temperature of the reaction mixture. The liquid/gas mixture coming from the reaction section is filtered through a 5 micron filter to prevent contamination of the back pressure valve. The back pressure valve is a Tescom 26-1726-24, which is placed behind the filter and reduces the pressure to atmospheric pressure. The liquid/gas mixture then enters a gas/liquid separator, after which the liquid will flow to a product vessel placed on a balance. The gas, mainly hydrogen, is mixed with nitrogen and is vented to the extraction system. All pipes, valves and fittings are of stainless steel 316L purchased from Swagelok. A P&ID of the reactor is shown in Figure 2.1.

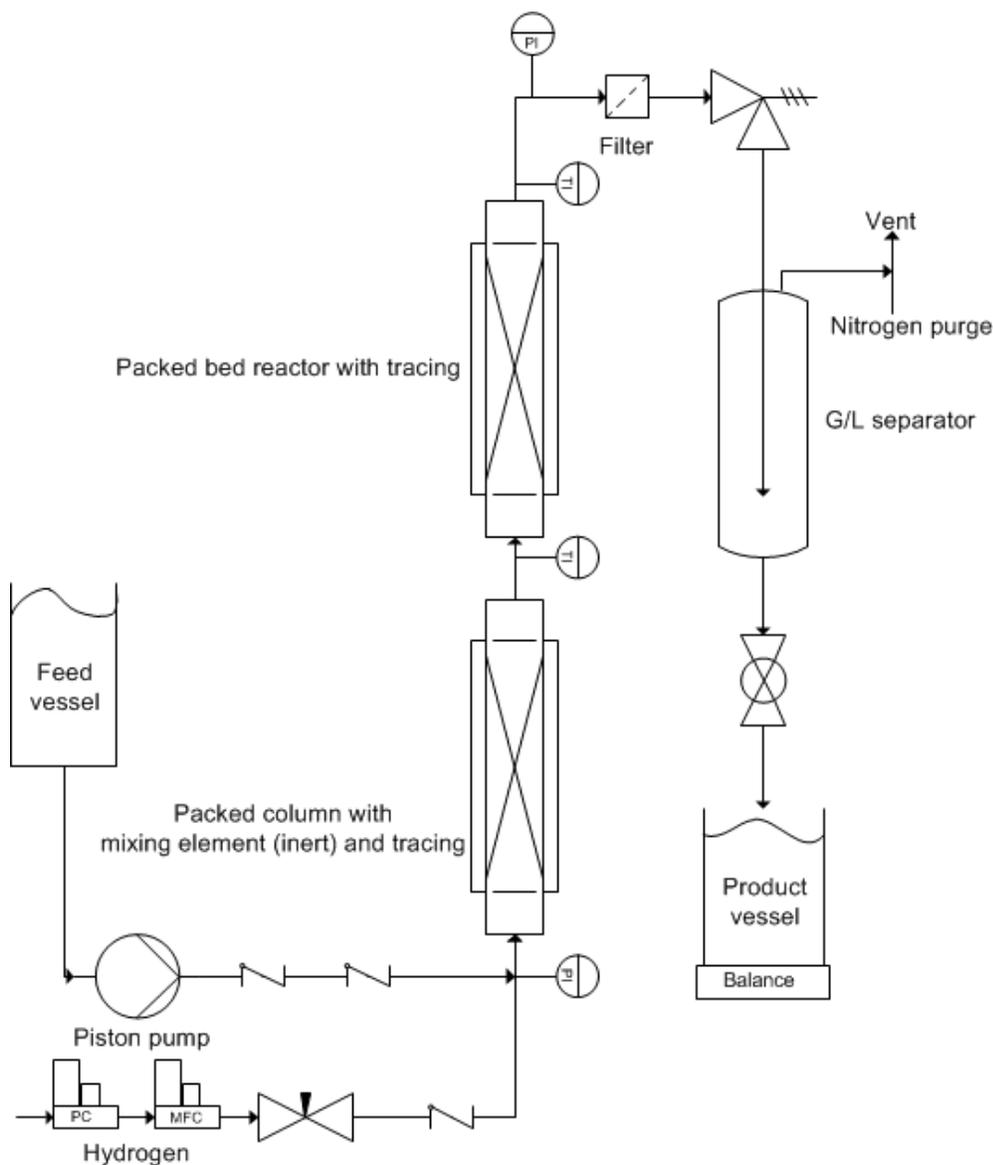


Figure 2.1: P&ID reactor set-up

A photo of the reactor with and without insulation is shown in Figure 2.2.

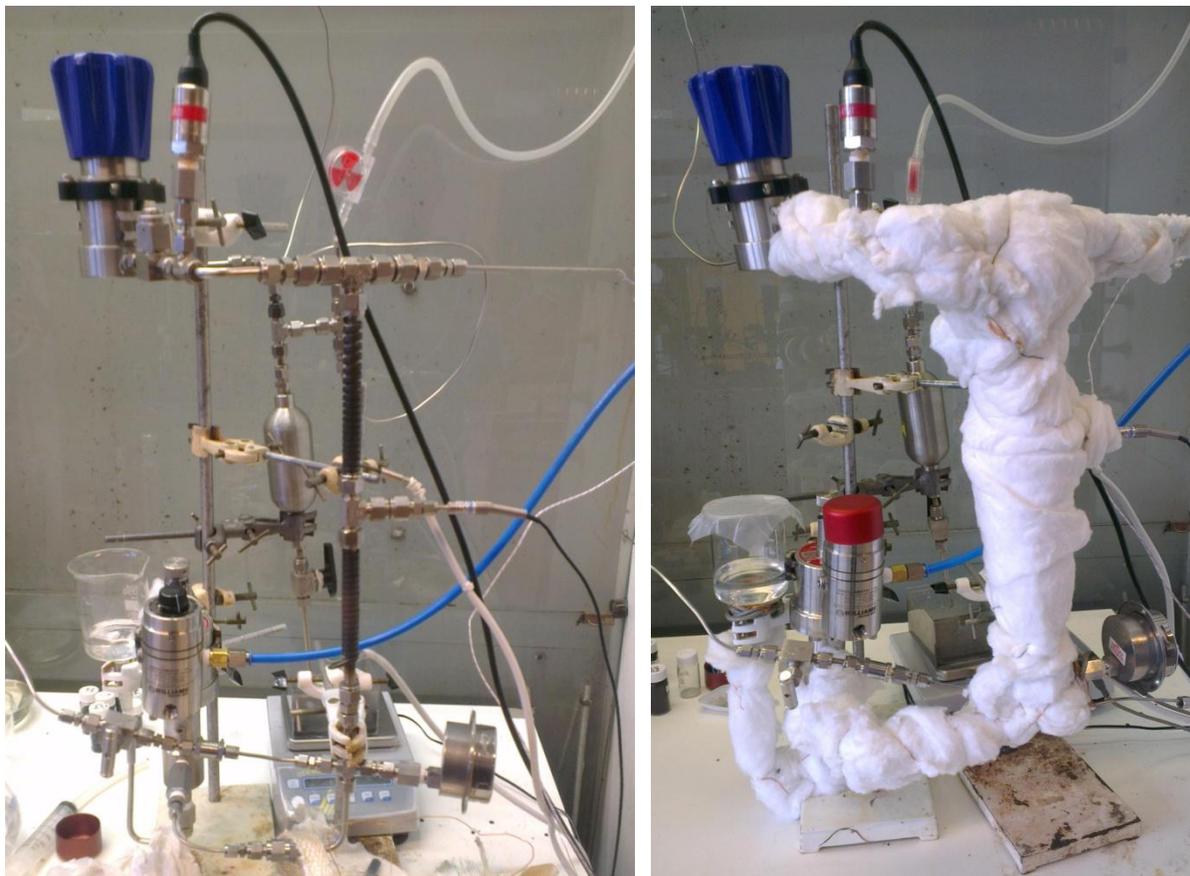


Figure 2.2: Reactor set-up without insulation (left) and with insulation (right)

2.2.2 Experimental procedures

All experiments were carried out in the packed bed reactor as described in section 2.2.1. The only exceptions are the experiments with concentrated LA (section 3.4), for which a larger reaction section was used (height 33 cm). When the catalyst was charged to the reaction section, the reactor was brought to 45 bar pressure by pumping the aqueous LA solution into the reactor. The catalysts were not activated before the experiments. During all experiments, a volumetric feed flow of approximately 1 mL/min was applied. When no leakage was detected, the reactor was insulated to prevent heat loss to the environment. The heaters were subsequently turned on and after approximately 10-15 minutes the hydrogen flow was started. When the temperature of the outgoing stream from the reaction section was 85°C (normally after 10-20 minutes), the outlet valve of the gas/liquid separator was closed and the timer was started ($t=0$). From this moment each 15 minutes samples were taken by emptying the content of the gas/liquid separator into a vial. It was assumed, and later verified, that the reactor reached a steady state after 2 hours on stream. Therefore, the samples obtained after 2 hours on stream were the first analysed samples.

The aqueous solutions of LA were prepared by diluting LA with deionized water (Milli-Q water) to the desired concentrations in a round bottom flask of 1 liter under open air.

All catalysts/supports were provided in mm range and were crushed and/or sieved beforehand when required. The catalysts which were used for this study are shown in Figure 2.3.

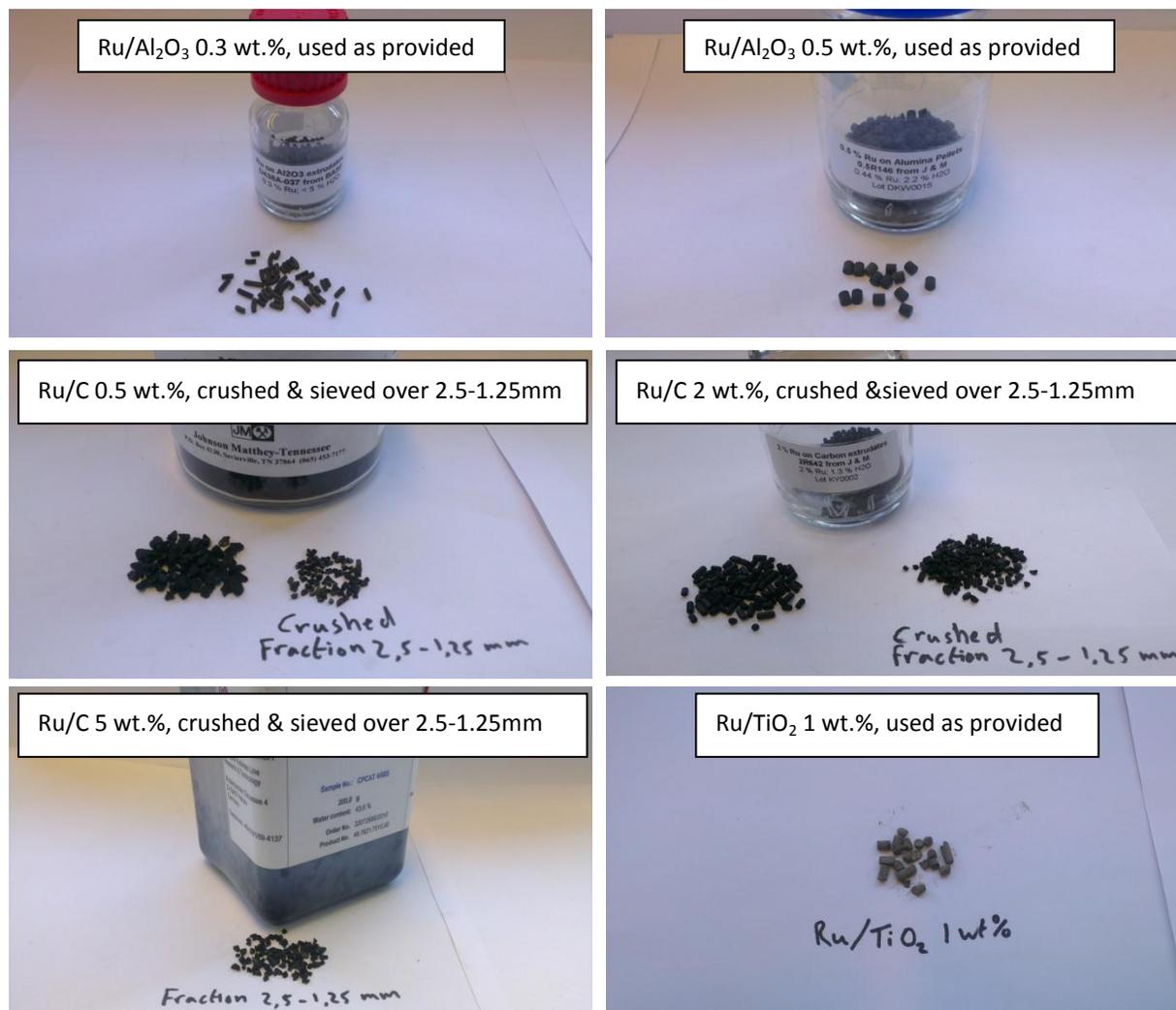


Figure 2.3: Catalysts used for experiments

2.2.3 Analytical procedures

The first analysed sample is the sample after 2 hours on stream. Subsequently, the samples after each hour were analysed. The most commonly used technique to analyse the liquid phase was ¹H-NMR. All spectra were recorded on a Varian 200 MHz spectrometer using D₂O as solvent and 1,4-dioxane as internal standard. The main advantage of this technique is that it can provide a quick insight in the product distribution. The preparation of the samples and the measurement itself does not take much time. Besides, 4-HPA (which is instable) is not converted into GVL during this analysis technique and thereby a good picture of the product distribution is obtained. On the other hand, ¹H-NMR is sensitive for measurement errors and inaccurate at lower concentrations. However, this is not a problem for this study since most of the experiments were carried out at a concentration of 1 mol/L or higher.

Another technique which was used to analyse the liquid phase was HPLC, since it is a proven technique with good accuracy. The used HPLC machine was an Agilent 1260 infinity. The mobile phase consisted of an aqueous solution of sulphuric acid (5 mmol/L) operated at a flow rate of 0.55 mL/min. The column (Biorad Aminex HPX-97H) was operated at 60°C. Though, a drawback of this technique is that the analysis costs considerable time (40 min. per sample) and thereby it is not possible to get a quick insight in the product distribution. In addition, 4-HPA is converted to GVL in the column by the mobile phase (H_2SO_4), which catalyses the ring closure of 4-HPA. Thereby, no 4-HPA was detected and the only components seen on the spectra were LA and GVL.

To test the catalysts for leaching of ruthenium to the liquid phase, inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements were performed using a Perkin Elmer Optima 7000 DV. The liquids of the runs using catalysts with Al_2O_3 and TiO_2 support were additionally analysed for aluminium or titanium content with ICP-OES to evaluate the support stability.

Calculation of concentrations by HPLC analysis

All product samples were filtered over a 20 micron filter (Minisart) to prevent any solids entering the HPLC column. The samples were made by dissolving 20 μL of product in 1.75 mL of deionized water (Milli-Q water) with the use of Gilson pipettes. All amounts were weighted on a 4 decimal balance (Mettler AE240). The dilution factor was calculated using Equation 6.1 in Appendix 6.1.1. The concentrations of LA and GVL were calculated by a computer program using calibration curves obtained from standard solutions. The obtained concentrations were multiplied by the calculated dilution factors to calculate the real concentrations. The conversion of LA was calculated using Equation 6.2 in Appendix 6.1.1. The HPLC technique was used to check the $^1\text{H-NMR}$ measurements of the long duration test. A typical HPLC spectrum is shown in Figure 2.4.

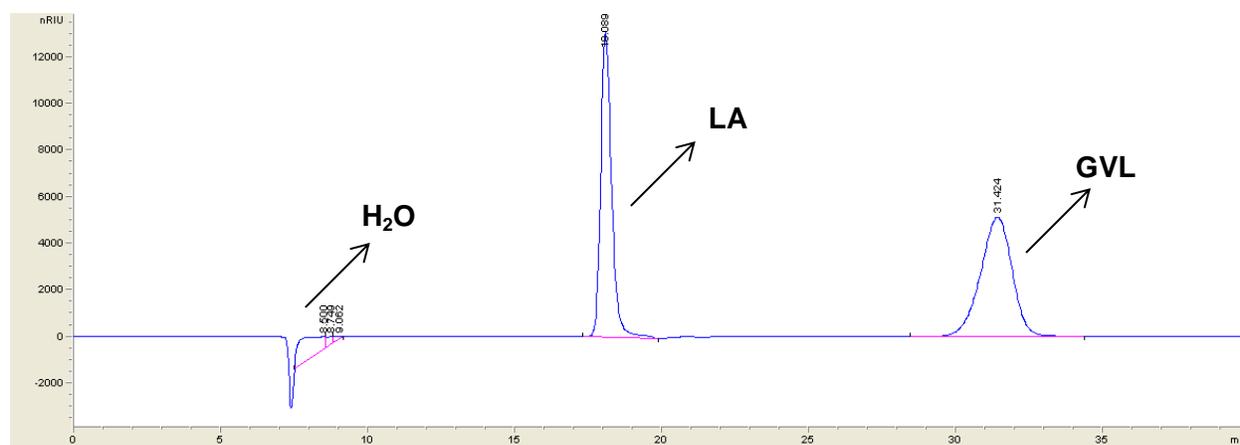


Figure 2.4: Typical HPLC spectrum

The retention times are approximately 18 and 31 minutes respectively for LA and GVL. The negative water peak has a retention time of approximately 7 minutes.

Calculation of concentrations by $^1\text{H-NMR}$ analysis

All product samples were filtered over a 20 micron filter (Minisart) in the same way as for HPLC analysis. The samples were made by adding 600 μL of product sample, 10 μL of 1,4-dioxane (internal standard) and 800 μL of D_2O (solvent) into a NMR tube with the use of Gilson pipettes. For the runs with respectively 5 mol/L and 97% LA, 400 and 200 μL of sample were added. The amounts were weighted on the same 4 decimal balance as used for HPLC analysis. A typical $^1\text{H-NMR}$ spectrum including the hydrogen labeling scheme, adapted from a LA hydrogenation experiment in batch set-up [9], is shown in Figure 2.5.

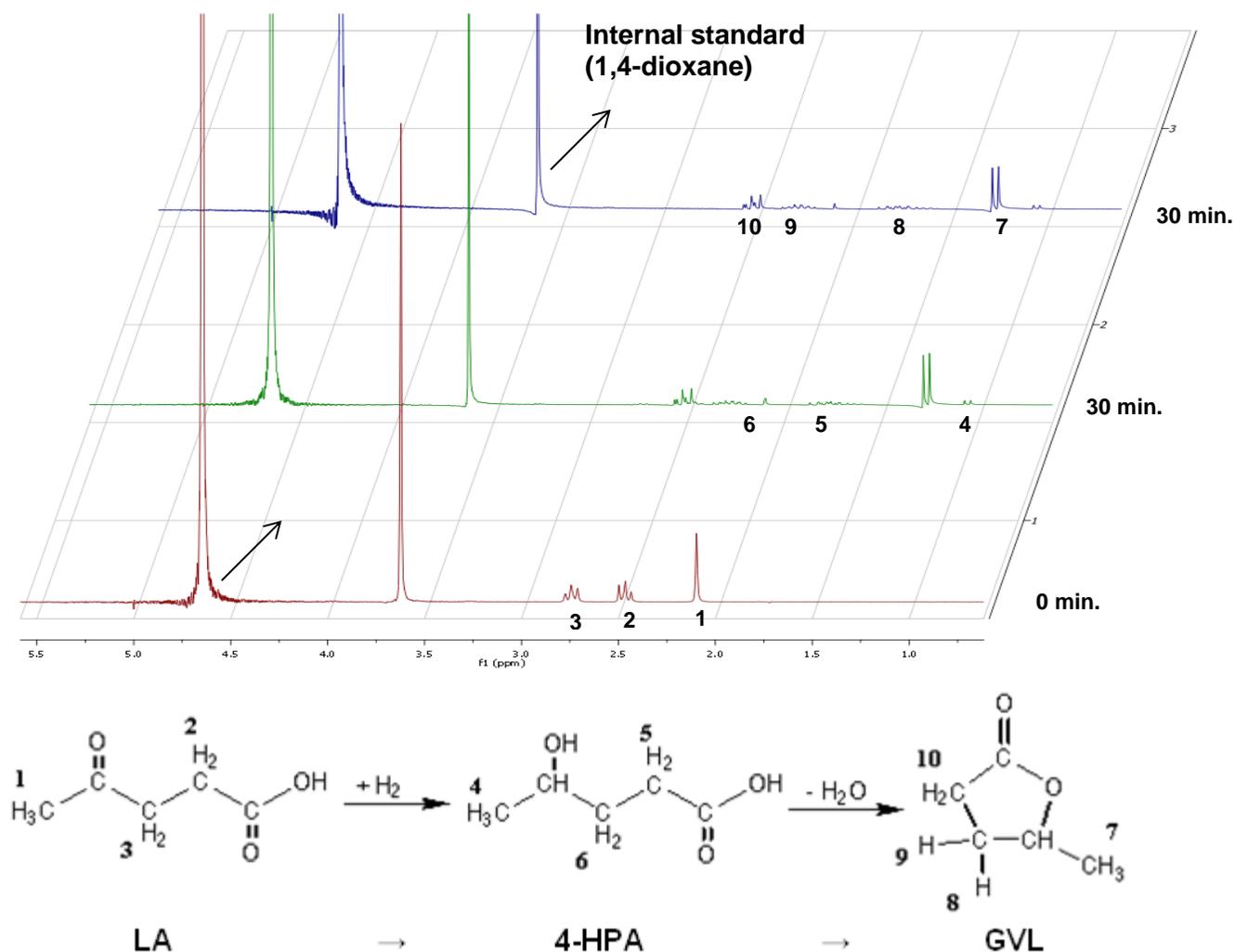


Figure 2.5: Typical $^1\text{H-NMR}$ spectrum with hydrogen labeling scheme, adapted from [9]

The concentrations of LA, 4-HPA and GVL were calculated using Equation 6.3 to 6.7 in section 6.1.2. The conversion of LA was calculated using Equation 6.2 in section 6.1.1. The yields and selectivities of the products were calculated with Equation 6.8 to 6.11 in section 6.1.2.

Catalyst analysis

All catalysts were washed with deionized water (Milli-Q water) after reaction and subsequently dried in a Binder vacuum oven (25 mbar) at 60°C for 23 hours. The BET specific surface area of fresh and spent catalysts was measured on a Micromeritics ASAP 2024 using nitrogen gas. All catalyst samples were degassed before BET analysis. In addition, ICP-OES analysis was performed with fresh and spent catalysts to check the ruthenium loading and for leaching of ruthenium to the liquid phase. The same machine was used as for the elemental analysis of the liquid phase (Perkin Elmer Optima 7000 DV). The Ru/Al₂O₃ catalysts were also analysed with X-Ray Diffraction (XRD) to check if there were structural changes during the experiment. The used machine was a Bruker D8 Advance. The fresh and spent catalysts of the long duration test are currently also tested with variable techniques by University Utrecht to gain more insight in catalyst deactivation. The techniques that will be used are:

- Transmission electron microscopy (TEM)
- X-Ray Fluorescence (XRF)
- H₂-chemisorption
- Thermal Gravimetric Analysis (TGA)

3 Results

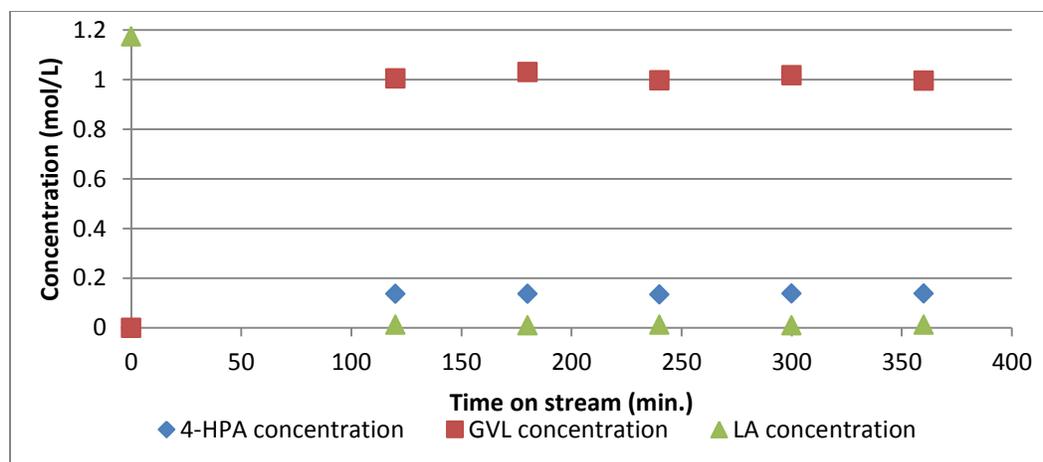
3.1 Initial experiments

3.1.1 Reactor design

Initially, a Swagelok R3A-K1B back pressure valve was used. However, this valve was not able to give a stable pressure profile. Therefore, it was replaced by a Tescom back pressure valve as described in section 2.2.1. Another problem that arose was the temperature control. The heaters of the preheating- and reaction section were controlled on the temperature supplied by a thermocouple placed inside the reactor before the reaction section. It was not possible to obtain a matching ingoing and outgoing temperature of the reaction section. Besides this, the temperatures kept fluctuating since the controllers could not reach a stable control. A possible explanation for this problem is that hydrogen was passing along the thermocouple, causing measurement errors. To overcome this problem, a second controller was placed to control the temperature of the reaction section separate from the preheating section. In addition, temperature sensors present inside the heating spirals were used for the temperature measurement instead of the thermocouple inside the reactor. This made it possible to control the temperature inside the reactor by the temperature of the reactor wall. The temperature inside the reactor was now measured manually by reading of values supplied by thermocouples placed before and after the reaction section. After the optimization of the reactor, an experiment of 6 hours runtime was performed to determine the performance and operational stability. The applied reaction conditions were as follows:

- Initial LA concentration: 1.17 mol/L
- Volumetric flow rate feed: +/- 1 mL/min
- Volumetric flow rate H₂: 30 mL/min
- Column pressure: 45 bar
- Temperature: 130°C
- Catalyst (Ru/C, 0.5 wt.% of Ru): 2.00 gram
- WHSV: 30 ($\frac{g_{\text{feed}}}{g_{\text{cat}} \cdot \text{hr}}$)

The results are shown in the concentration profile in Graph 3.1.



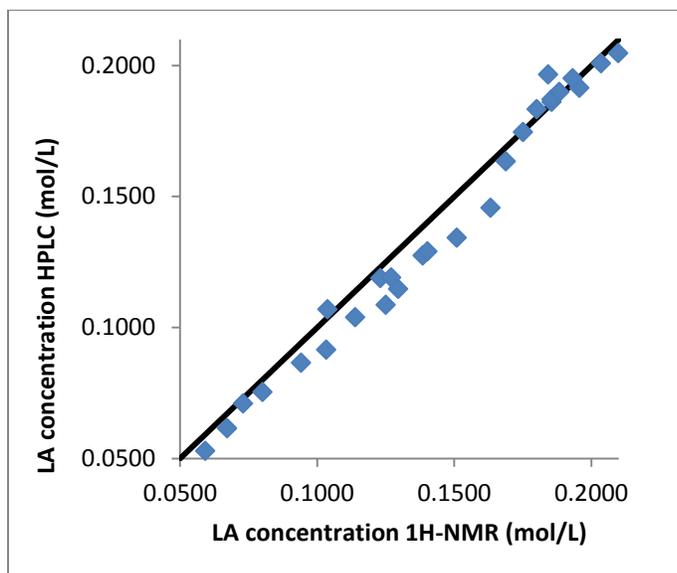
Graph 3.1: LA hydrogenation concentration profile at 130 °C using Ru/C as catalyst (0.5 wt.% of Ru)

The experiment resulted in almost full LA conversion (99%), only traces of LA were found during 6 hours on stream. The selectivity towards GVL was 88% with the only by-product being 4-HPA (see $^1\text{H-NMR}$ spectrum 6.1 in Appendix 6.2.1 and HPLC spectrum 6.10 in Appendix 6.3.1), the selectivity towards 4-HPA + GVL was 100%. The mole balance closed for 98.6%. The other 1.4% can presumably be attributed to carbon which was left on the catalyst surface in the form of coke or measurement errors. No temperature or pressure fluctuations were observed during the experiment. For evaluation of catalyst stability, the conversion of LA should be lower. The effect of reaction temperature on LA conversion and selectivity to GVL was already investigated by several groups [8,9,31]. For this reason, the rest of the experiments were carried out at a lower temperature (90°C). The initial experiments have led to the following benchmark conditions:

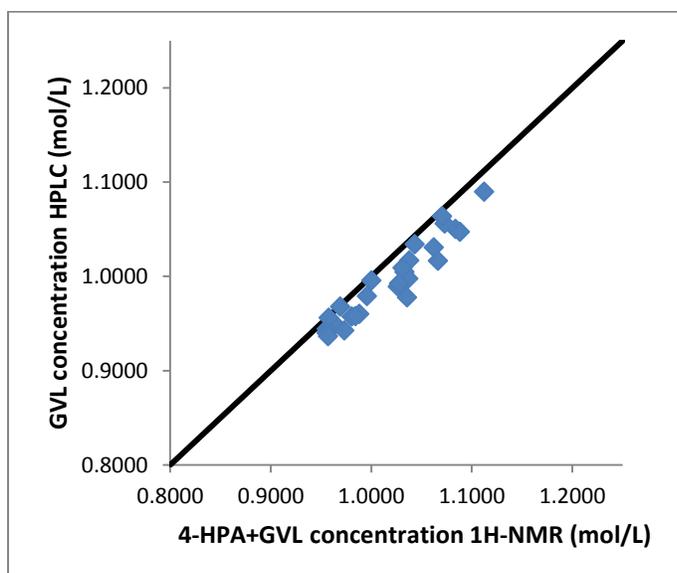
- Initial LA concentration: +/- 1 mol/L
- Volumetric flow rate feed: +/- 1 mL/min
- Volumetric flow rate H_2 : 30 mL/min
- Column pressure: 45 bar
- Temperature: 90°C
- Amount of catalyst: 2.00 gram
- WHSV: 30 ($\text{g}_{\text{feed}}/\text{g}_{\text{cat}}\cdot\text{hr}$)

3.1.2 HPLC/ $^1\text{H-NMR}$ comparison

Two techniques are available for the analysis of the liquid phase, as described in section 2.2.3. $^1\text{H-NMR}$ is a quick method to get insight in the product distribution. The liquid phase of the long duration test (section 3.5.1) was also analysed with HPLC to check the accuracy of $^1\text{H-NMR}$. To get insight in the difference between the concentrations obtained by $^1\text{H-NMR}$ and HPLC, parity plots were made for LA and GVL. 4-HPA was converted into GVL during analysis with HPLC resulting in peaks for only LA and GVL. Therefore, the 4-HPA concentration was counted up to the GVL concentration, both obtained by $^1\text{H-NMR}$, to make the results comparable. The data for the parity plots was obtained from the long duration test (section 3.5.1), the plots are shown in Graph 3.2 and 3.3.



Graph 3.2: Parity plot LA



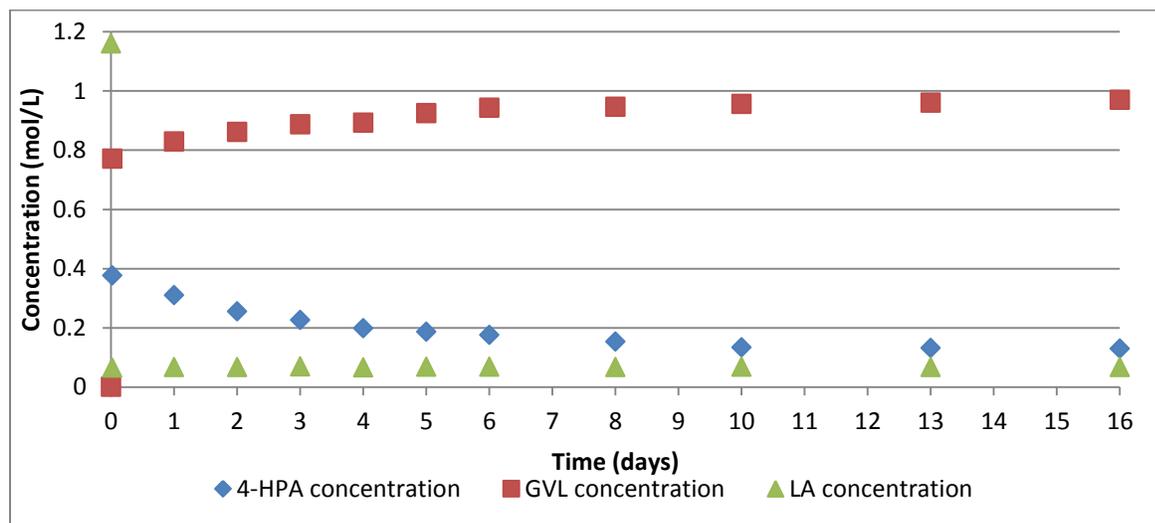
Graph 3.3: Parity plot GVL

The plots show that $^1\text{H-NMR}$ measures slightly higher concentrations for both LA and 4-HPA + GVL compared to HPLC. The average difference between the LA concentrations of $^1\text{H-NMR}$ and HPLC was 4.8%. However, the concentrations were low which presumably caused measurement errors for one or both technique(s). In addition, only a slight difference in concentration will result in a high percentage of difference because of the low concentrations. The average difference between the 4-HPA + GVL concentration of $^1\text{H-NMR}$ and GVL concentration of HPLC was 2.3%. This was probably also caused by measurement errors by one or both technique(s). The preparation procedure of the samples and calibration method of both techniques could also have an influence on the measured concentrations. Despite of the small difference between both techniques, $^1\text{H-NMR}$ was chosen as technique for analysis

of the liquid phase of further experiments. The main reason is the fact that it gives a quick insight in the product distribution. Measurement of the samples only takes minimal time (3 min. per sample) compared to HPLC (40 min. per sample). Another advantage of $^1\text{H-NMR}$ is that 4-HPA is also measured, while it is converted to GVL during HPLC analysis.

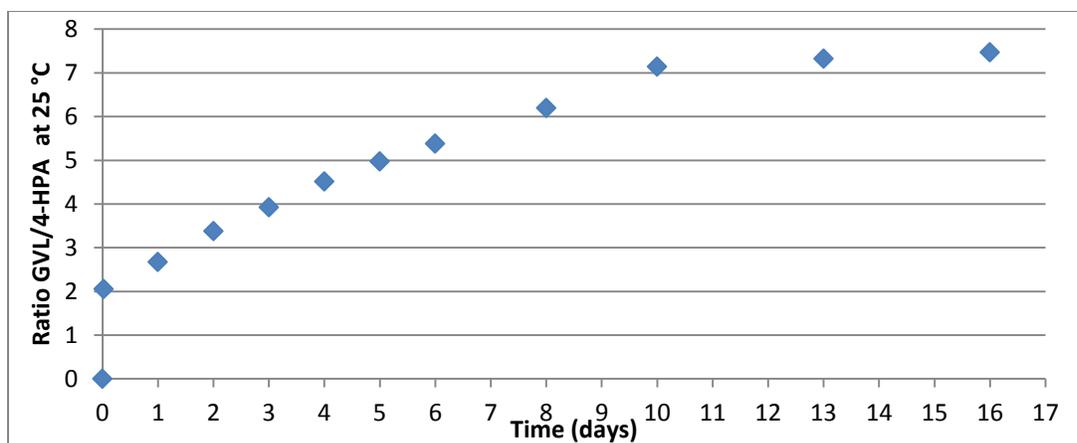
3.1.3 4-HPA \leftrightarrow GVL equilibrium

Even at room temperature, 4-HPA slowly converts to GVL until the ring closure reaction reaches equilibrium. Therefore, to investigate this equilibrium, a test was performed with 1 sample from the long duration test (section 3.5.1). Sample number 14 (3.5 hours on stream) was analysed within 30 minutes after it was taken from the reactor using $^1\text{H-NMR}$. The sample was left at room temperature and subsequently analysed every 24 hours. After 6 days, this interval was expanded to every 48 hours and after 10 days to 64 hours. The last measurement was 16 days after the sample was taken from the reactor. The results are shown in Graph 3.4.



Graph 3.4: 4-HPA \leftrightarrow GVL equilibrium over 16 days at room temperature (sample taken from long duration test)

A significant decrease of 4-HPA concentration and increase of GVL concentration was observed within 10 days after the experiment. After these 10 days, the ring closure reaction of 4-HPA to form GVL came slowly to an equilibrium. To get a better insight in the equilibrium, the GVL/4-HPA ratio for all points measured was calculated by dividing the GVL concentration by the 4-HPA concentration. The ratio at room temperature (25°C) in time is shown in Graph 3.5.

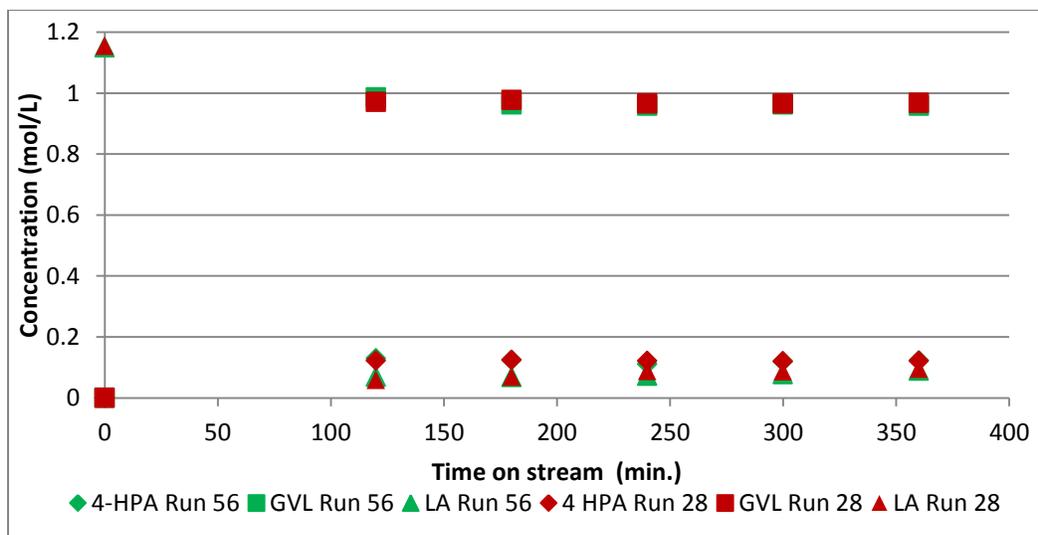


Graph 3.5: GVL/4-HPA ratio at room temperature (sample taken from the long duration test)

The main change of the concentrations indeed occurs within the first 10 days, as can be seen from the change in GVL/4-HPA ratio. After these 10 days, the rate of change decreases and is almost at equilibrium after 16 days with an equilibrium constant of approximately 7.5.

3.1.4 Reproducibility

To check the reproducibility of the experiments, two experiments were performed with Ru/C with 0.5 wt.% of ruthenium at the same conditions (90°C, 1 mL/min feed flow, 30 mL/min H₂ flow, 2 gram catalyst, column pressure 45 bar). The results are shown in Graph 3.6.



Graph 3.6: Original (Run 28) and duplo experiment (Run 56) of LA hydrogenation at 90°C using Ru/C (0.5wt.% of Ru)

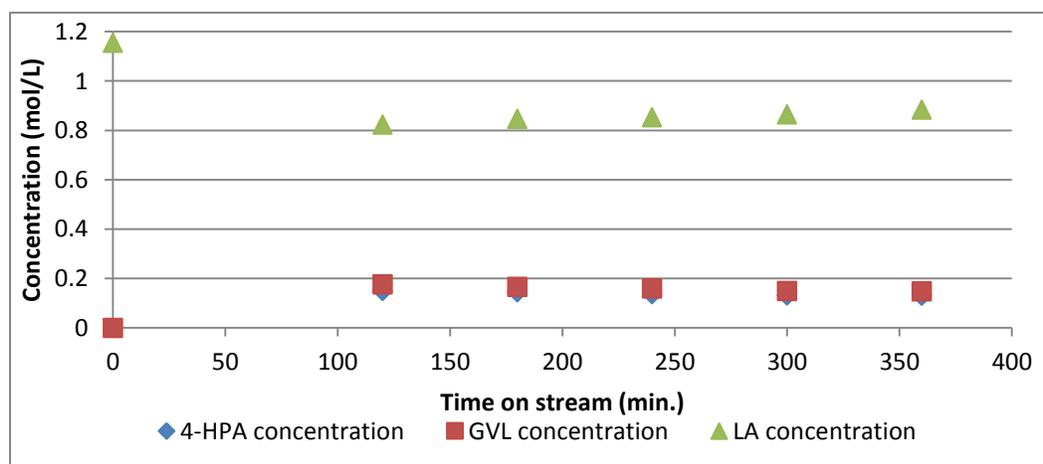
The samples were measured after some time of storage at room temperature to be sure that the 4-HPA \leftrightarrow GVL reaction was at equilibrium. Both experiments showed similar concentration profiles, which indicates that the experiments are reproducible.

3.2 Catalyst screening

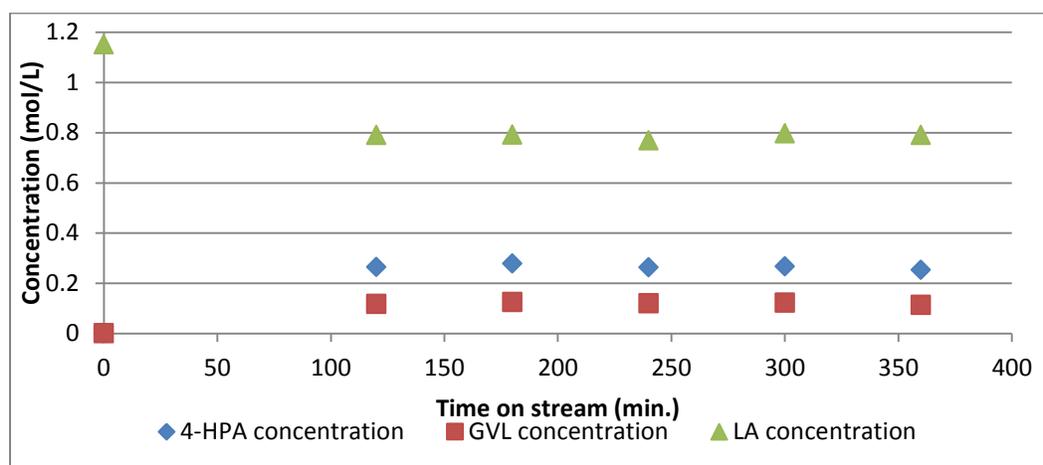
A catalyst screening study was performed with ruthenium on different supports. The catalysts which were used are described in section 2.1. All screening experiments were carried out at benchmark conditions, as described in section 3.1.1, for a runtime of 6 hours. The catalysts were evaluated on their activity and stability as will be discussed in the following sections.

3.2.1 Liquid phase product analysis

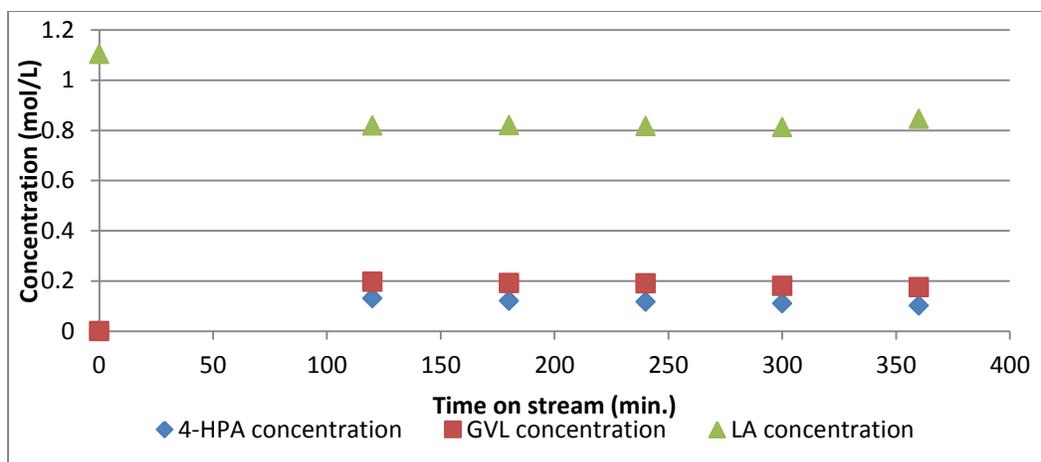
The samples taken from the reactor were analysed using $^1\text{H-NMR}$ with an interval of 60 minutes starting from 2 hours on stream. The only by-product found in all product mixtures was 4-HPA (see NMR spectra 6.2 to 6.7 in appendix 6.2.2 and HPLC spectra 6.12 to 6.17 in Appendix 6.3.2). The concentration profiles obtained during screening of the different catalysts are shown in graph 3.7 to 3.12.



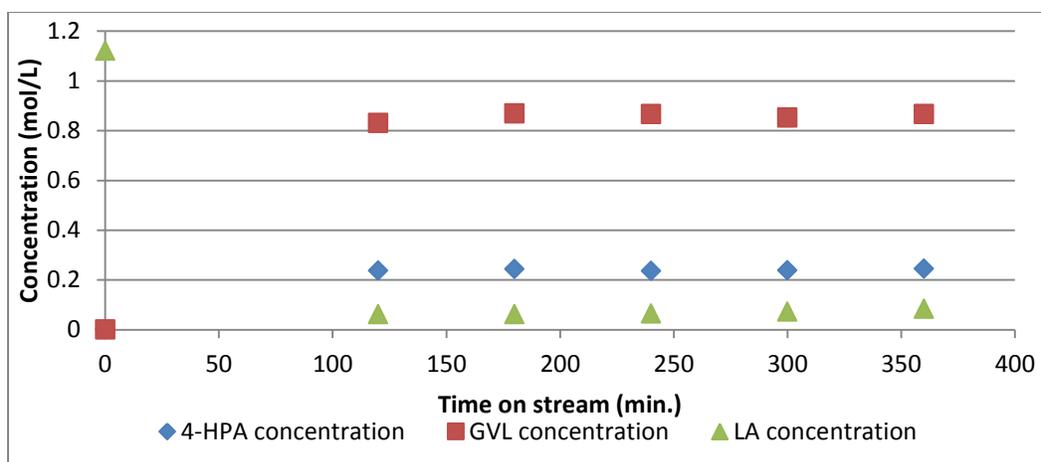
Graph 3.7: LA hydrogenation concentration profile at 90°C using Ru/TiO_2 as catalyst (1 wt.% of Ru)



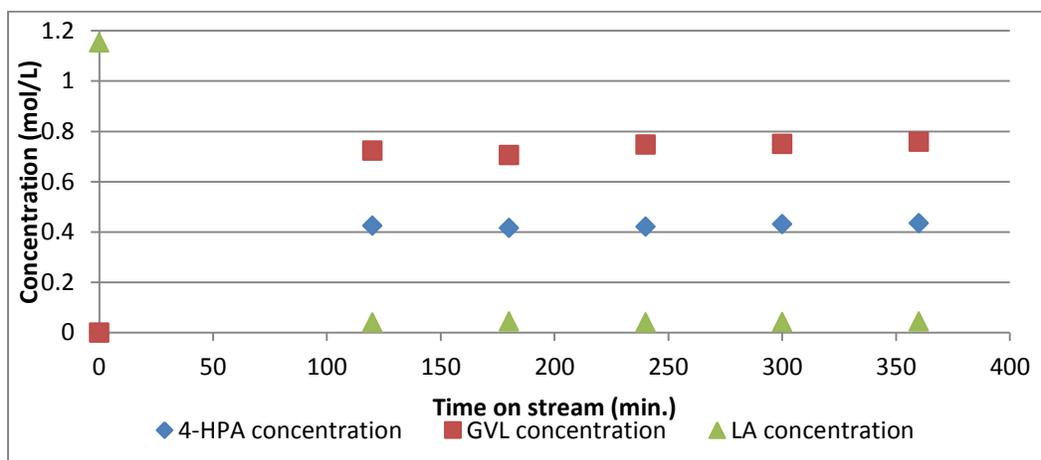
Graph 3.8: LA hydrogenation concentration profile at 90°C using $\text{Ru}/\text{Al}_2\text{O}_3$ as catalyst (0.3 wt.% of Ru)



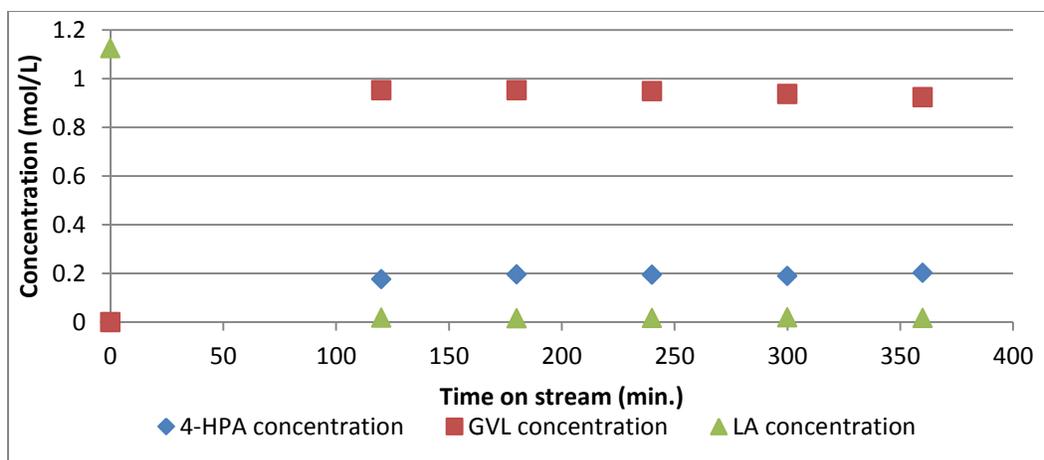
Graph 3.9: LA hydrogenation concentration profile at 90°C using Ru/Al₂O₃ as catalyst (0.5 wt.% of Ru)



Graph 3.10: LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (0.5 wt.% of Ru)

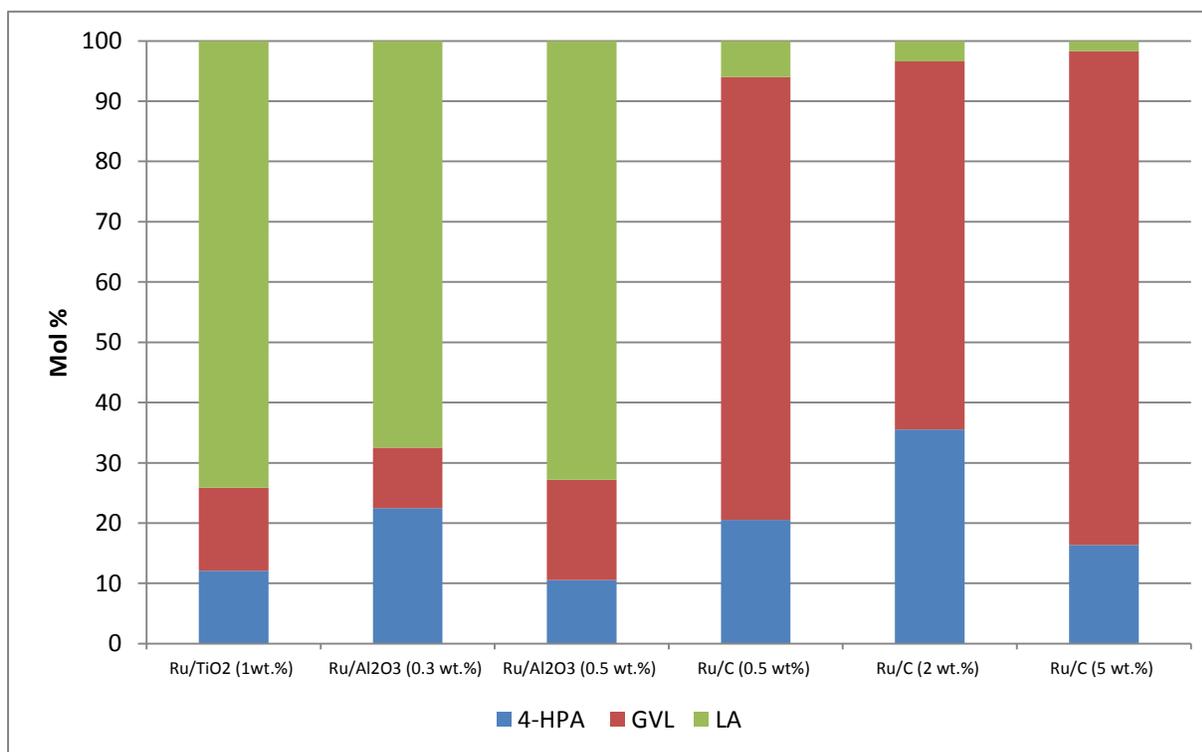


Graph 3.11: LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (2 wt.% of Ru)



Graph 3.12: LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (5 wt.% Ru)

Marginal decrease in LA conversion during a run was observed for all catalysts over 6 hours on stream. However, large differences were found in the LA conversion and product distribution for the different catalysts. To make the performance of the catalysts more comparable, the average molar distribution over 6 hours on stream of the reactor effluent is shown in Graph 3.13.



Graph 3.13: Product distribution of the hydrogenation of LA over different catalysts at 90 °C (average over 6 hours)

An overview of the LA conversions and selectivities to 4-HPA and GVL obtained during the catalyst screening experiments is given in Table 3.1.

Table 3.1: Performance of different catalysts in the hydrogenation reaction of LA at 90°C (average over 6 hours)

| Catalyst | Conversion LA (%) | Selectivity GVL (%) | Selectivity 4-HPA (%) | GVL/4-HPA ratio | Selectivity 4-HPA+GVL (%) |
|---|-------------------|---------------------|-----------------------|-----------------|---------------------------|
| Ru/TiO ₂ (1 wt.% Ru) | 25 | 54 | 47 | 1.15 | 101 |
| Ru/Al ₂ O ₃ (0.3 wt.% Ru) | 31 | 31 | 69 | 0.44 | 100 |
| Ru/Al ₂ O ₃ (0.5 wt.% Ru) | 26 | 62 | 38 | 1.63 | 100 |
| Ru/C (0.5 wt.% Ru) | 94 | 78 | 22 | 3.54 | 100 |
| Ru/C (2 wt.% Ru) | 96 | 63 | 36 | 1.75 | 99 |
| Ru/C (5 wt.% Ru) | 98 | 83 | 15 | 5.53 | 98 |

The selectivity towards 4-HPA + GVL was approximately 100% with small differences for Ru/TiO₂ and Ru/C with 2 and 5 wt.% of ruthenium. These differences are presumably caused by measurement errors. The difference between the GVL/4-HPA ratios can be explained by the fact that not all samples were measured at the same time after the reaction. As discussed in section 3.1.3, it was observed that 4-HPA slowly converts to GVL at room temperature. An overview of the days between the experiment and analysis is given in Table 3.2.

Table 3.2: Time between experiment and analysis

| Catalyst | Time between experiment and analysis (days) |
|---|---|
| Ru/TiO ₂ (1 wt.% Ru) | 1 |
| Ru/Al ₂ O ₃ (0.3 wt.% Ru) | 1 |
| Ru/Al ₂ O ₃ (0.5 wt.% Ru) | 3 |
| Ru/C (0.5 wt.% Ru) | 3 |
| Ru/C (2 wt.% Ru) | 1 |
| Ru/C (5 wt.% Ru) | 3 |

The GVL/4-HPA ratio of the samples analysed after 3 days was higher than for the samples analysed after 1 day. The reason is that the experiments performed on Friday were analysed on Monday. For a better comparison of the GVL/4-HPA ratios, it would have been better to analyse the samples of all experiments at the same amount of time after the experiment.

Ru/TiO₂ showed poor activity in contrary to the expectations. Batch experiments showed that 1 wt.% ruthenium supported on TiO₂ was able to achieve 95% conversion of LA in 240 minutes of reaction time. The same reaction conditions were applied during continuous experiments with the only difference being the initial LA concentration, 1.1 mol/L in contrast to 0.6 mol/L for the experiment in the batch set-up. During batch experiments in water, Ru/TiO₂ (1 wt.% of Ru) showed comparable results with Ru/C (1 wt.% of Ru). This was not observed during the catalyst screening study in the packed bed reactor. Ru/C with only 0.5 wt.% of ruthenium showed much better performance than Ru/TiO₂ with 1 wt.% of ruthenium. Experiments in batch systems performed by other groups also showed excellent activity of Ru/TiO₂. As discussed in section 1.1.5, Deng et al. achieved 95% conversion of aqueous LA over Ru/TiO₂ (0.55 wt.% of Ru) within 120 minutes in a batch set-up [35]. Though, these results are not comparable, since a higher reaction temperature was applied (170°C). Luo et al. achieved 98.8% LA conversion within 240 minutes over Ru/TiO₂ (1 wt.% of Ru) using 1,4-dioxane as solvent in a batch set-up [33]. These

results are also not comparable to the results obtained with the catalyst screening study, because of the other solvent and a higher reaction temperature which was applied (200°C). Unless the incomparable results, it was shown that Ru/TiO₂ was able to catalyse LA hydrogenation to GVL. It was reported by Primo et al., that ruthenium crystallites (small particle size) activate hydrogen, while the TiO₂ support adsorbs and activates the acid [38]. Therefore, a possible explanation for the low activity of the Ru/TiO₂ catalyst used in the present continuous set-up is the fact that the nature of the support and the preparation method of the catalyst may have an influence on the catalyst activity. The effect of TiO₂ support on catalyst activity was also observed by Al-Shaal et al. [32]. They performed LA hydrogenation experiments in ethanol-water mixtures over two different types of TiO₂ support in a batch set-up. TiO₂ obtained from Tronox (rutile phase) showed no activity, while TiO₂ obtained from Degussa (mixture of rutile and anatase phase) was able to achieve 81% LA conversion under the same conditions (130°C, 12 bar H₂, 160 min.). The support from Degussa had a higher specific surface area, which enhanced the catalysis either by facilitating substrate absorption or enabling higher ruthenium dispersion.

Ru/Al₂O₃ also showed poor results for the hydrogenation of LA in the packed bed reactor. The same low activity of Ru/Al₂O₃ was observed by Galetti et al., who performed hydrogenation experiments in a batch reactor with an aqueous LA solution using Ru/Al₂O₃ (5 wt.% of Ru) at 180°C and 35 bar H₂ [34]. The low activity of the catalysts could also be caused by the low surface area of Ru/TiO₂ and Ru/Al₂O₃ (approximately 10 times lower than for Ru/C).

During the catalyst screening study, Ru/C showed the best results, which is in line with results reported in literature. Ru/C (0.5 wt.% of Ru) already achieved 94% of LA conversion, though a relatively small difference of activity was observed between the catalysts with different ruthenium loading. A potential reason for this observation will be explained in the next section. The major difference between the catalysts used in the continuous set-up (for this study) and batch set-up, is the particle size. In this study all catalysts were used in the form of pellets, while in batch experiments powders were used. Ru/C was crushed and sieved over 2.5-1.25 mm, Ru/Al₂O₃ and Ru/TiO₂ were used as provided in the range of 2-5 mm. The main disadvantage of using pellets is the presence of diffusional and mass transfer limitations. On the other hand, catalysts in powder form in continuous systems result in higher pressure drops, which is undesirable [46].

The turnover frequency (TOF) and turnover number (TON) were calculated using respectively Equation 6.13 and 6.14 in Appendix 6.1.3 to further evaluate the performance of the different catalysts in the continuous system. Average concentrations were used over 6 hours on stream, assuming there was no deactivation. The actual ruthenium loadings (Table 3.7 in section 3.2.3) were used for the calculation based on gram of ruthenium. The results are shown in Table 3.3.

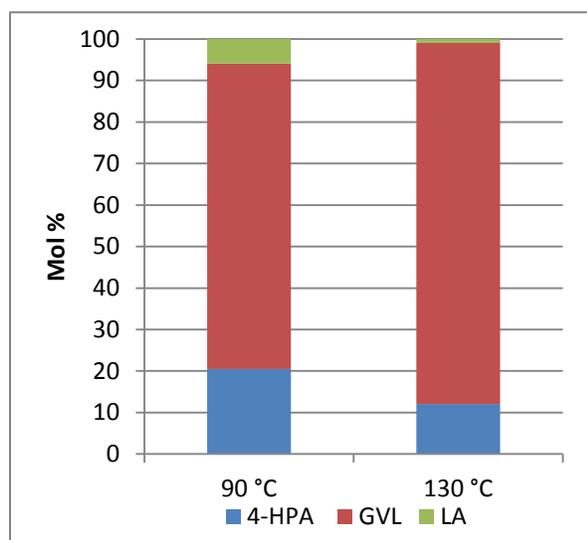
Table 3.3: Average TOF and TON over 6 hours on stream for different catalysts at 90°C

| Catalyst | ΔC_{LA} (mol/L) | TOF (g LA/g cat.hr) | TON (g LA/g cat) | TOF (g LA/g Ru.hr) | TON (g LA/g Ru) |
|---|----------------------------|------------------------|---------------------|-----------------------|--------------------|
| Ru/TiO ₂ (1 wt.% Ru) | 0.30 | 1.04 | 6.27 | 124.32 | 745.91 |
| Ru/Al ₂ O ₃ (0.3 wt.% Ru) | 0.36 | 1.27 | 7.60 | 633.21 | 3799.26 |
| Ru/Al ₂ O ₃ (0.5 wt.% Ru) | 0.28 | 0.98 | 5.89 | 222.98 | 1337.86 |
| Ru/C (0.5 wt.% Ru) | 1.05 | 3.66 | 21.98 | 1220.90 | 7325.39 |
| Ru/C (2 wt.% Ru) | 1.11 | 3.87 | 23.23 | 265.21 | 1591.27 |
| Ru/C (5 wt.% Ru) | 1.11 | 3.85 | 23.13 | 199.73 | 1198.36 |

All catalysts showed a TOF within the desired boundaries for hydrogenation (0.1-10 g LA/g cat.hr) [47]. However, Ru/C showed a higher activity than the other catalysts, as already discussed before. This also resulted in a higher productivity over 6 hours on stream, as can be seen from the turnover numbers. Ru/C with 0.5 wt.% of ruthenium showed the highest activity and productivity per gram ruthenium of the three Ru/C catalysts which were tested.

Temperature effect

The positive effect of reaction temperature on the conversion of LA and product distribution can be seen by comparing the experiment using Ru/C (0.5 wt.% of Ru) described in section 3.1.1 and the experiment with Ru/C (0.5 wt.% of Ru) of the catalyst screening study. The same reaction conditions were applied for both experiments (1 mL/min feed flow, 30 mL/min H₂ flow, 2 gram catalyst, column pressure 45 bar), the only difference being the reaction temperature (130°C versus 90°C). A comparison is shown in Graph 3.14.



Graph 3.14: Temperature effect on hydrogenation of LA over Ru/C (0.5 wt.% of Ru), average over 6 hours on stream

The average LA conversion over 6 hours on stream, obtained during the catalyst screening test at 90°C, was 94% compared to 99% conversion at 130°C. The selectivity towards 4-HPA + GVL was 100% for both

experiments, while the selectivity towards GVL was 78% at 90°C compared to 88% at 130°C. The effect of temperature on the conversion of LA and product distribution was also observed in literature [8,9,31]. The higher selectivity towards GVL can be explained by the fact that the ring closure reaction of 4-HPA is endothermic, therefore applying more heat to the reaction will lead to higher GVL selectivity and lower 4-HPA selectivity [11]. There was no analysis time effect, since both experiments were analysed at the same time after the experiment.

3.2.2 Mole balance closure

The mole balance closure was evaluated by counting up the concentrations of the products and remaining LA and subsequently subtracting this value from the initial LA concentration. Average values were used over 6 hours on stream. The results are shown in table 3.4.

Table 3.4: Average mole balance closure over 6 hours on stream for different catalysts at 90°C

| Catalyst | Average total mole balance over 6 hours (%) | Average concentration difference over 6 hours (mol/L) | Mole balance difference based on initial LA concentration (%) |
|---|---|---|---|
| Ru/TiO ₂ (1 wt.% Ru) | 99.9 | +0.002 | +0.1 |
| Ru/Al ₂ O ₃ (0.3 wt.% Ru) | 101.8 | -0.021 | -1.8 |
| Ru/Al ₂ O ₃ (0.5 wt. Ru) | 101.5 | -0.016 | -1.5 |
| Ru/C (0.5 wt.% Ru) | 102.2 | -0.025 | -2.2 |
| Ru/C (2 wt.% Ru) | 101.9 | -0.022 | -1.9 |
| Ru/C (5 wt.% Ru) | 102.2 | -0.025 | -2.2 |

The small difference in mole balance for all experiments is presumably caused by measurement errors of ¹H-NMR, integration errors of the peaks or errors during the preparation of the samples. In addition, it was possible that carbon was left on the catalyst surface in the form of coke.

3.2.3 Catalyst stability

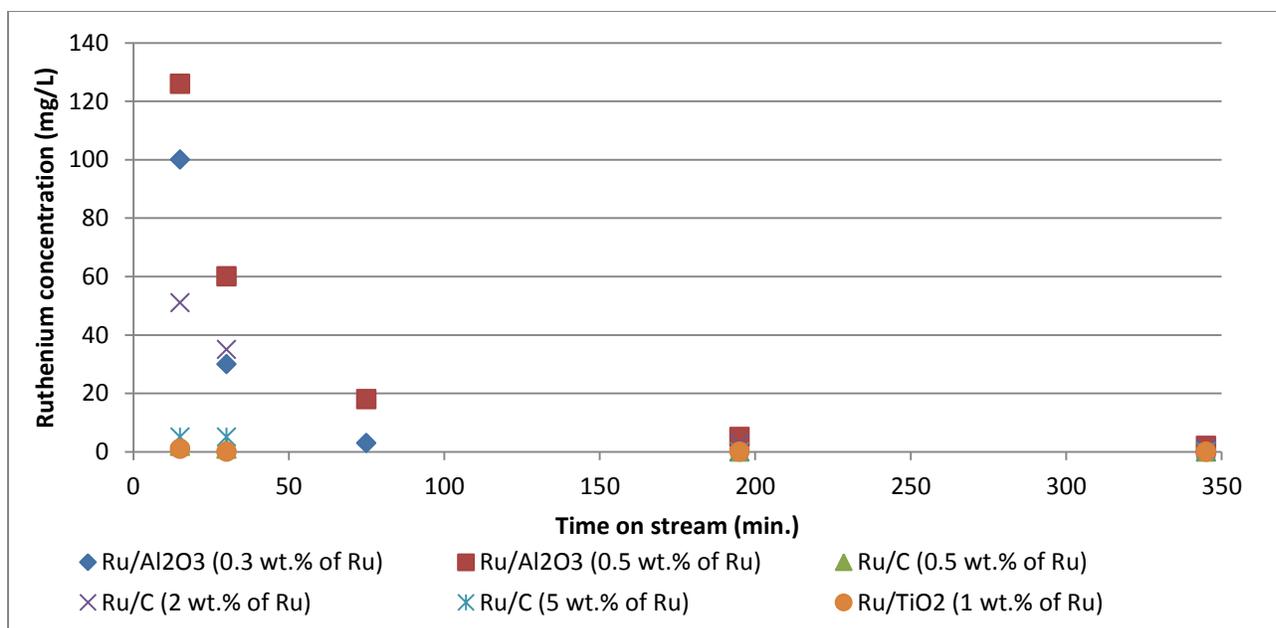
Liquid analysis

Liquid samples from the beginning, middle and end of the experiments were analysed for ruthenium content using ICP-OES. The results are represented in Table 3.5.

Table 3.5: Liquid analysis for ruthenium content

| Catalyst | Time on stream (min.) | Concentration Ru (mg/L) | Leached Ru from initial amount on catalyst (%) | Total leached Ru (%) |
|--|-----------------------|-------------------------|--|----------------------|
| Ru/Al ₂ O ₃ (0.3 wt.% Ru) | 15 | 100 | 48.75 | 62.43 |
| | 30 | 30 | 12.17 | |
| | 75 | 3 | 1.10 | |
| | 195 | 1 | 0.41 | |
| | 345 | <1 | 0 | |
| Ru/Al ₂ O ₃ (0.5 wt.% Ru) | 15 | 126 | 31.96 | 48.24 |
| | 30 | 60 | 11.57 | |
| | 75 | 18 | 3.48 | |
| | 195 | 5 | 0.86 | |
| | 345 | 2 | 0.37 | |
| Ru/C (0.5 wt.% Ru) | 15 | 2 | 0.55 | 0.82 |
| | 30 | 1 | 0.27 | |
| | 195 | <1 | 0 | |
| | 345 | <1 | 0 | |
| Ru/C (2 wt.% Ru) | 15 | 51 | 3.60 | 5.93 |
| | 30 | 35 | 2.10 | |
| | 195 | 3 | 0.17 | |
| | 345 | 1 | 0.06 | |
| Ru/C (5 wt.% Ru) | 15 | 5 | 0.30 | 0.60 |
| | 30 | 5 | 0.30 | |
| | 195 | <1 | 0 | |
| | 345 | <1 | 0 | |
| Ru/TiO ₂ (1 wt.% Ru) | 15 | 1 | 0.09 | 0.09 |
| | 30 | <1 | 0 | |
| | 195 | <1 | 0 | |
| | 345 | <1 | 0 | |

The total amount of leached ruthenium is in fact higher, because not all samples were measured. To get a better insight in the quantity of ruthenium leaching, the results are also represented in Graph 3.15.



Graph 3.15: Liquid analysis for ruthenium content

Ru/TiO₂ showed no measurable leaching of ruthenium to the liquid phase, except for a trace amount in the beginning of the experiment. In addition, no titanium was found in the liquid phase.

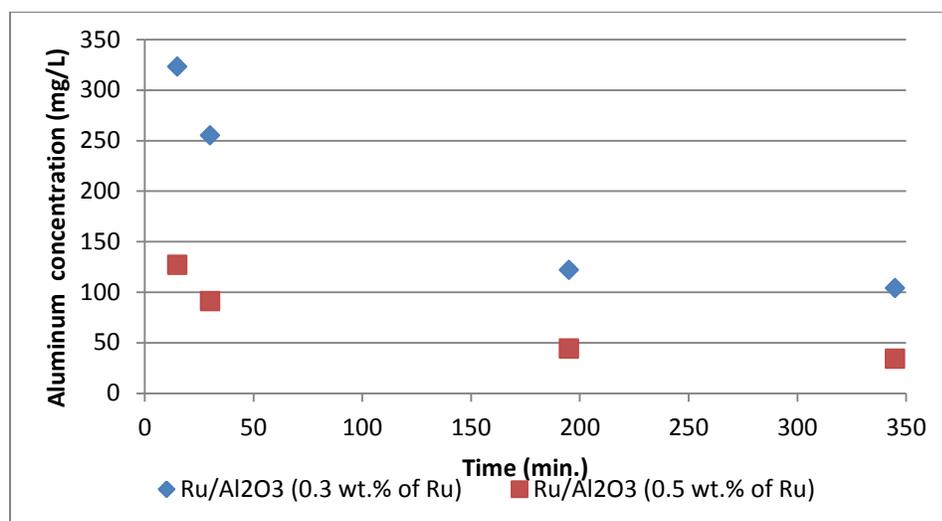
Ru/C (0.5 and 5 wt.% of Ru) only showed leaching of ruthenium in small amounts in the beginning of the experiment and kept stable for the rest of 6 hours on stream. Ru/C with 2 wt.% of ruthenium showed higher amounts of ruthenium leaching to the liquid phase in the beginning of the experiment and kept leaching in small amounts during 6 hours on stream.

High amounts of ruthenium were found in the liquids of the runs with Ru/Al₂O₃ catalysts. Both catalysts kept leaching ruthenium to the liquid phase during 6 hours on stream. Because of the high amounts of ruthenium in the liquids, the samples were also analysed for aluminium content to check for support stability. The results are shown in Table 3.6.

Table 3.6: Liquid analysis for aluminium content

| Catalyst | Time on stream (min.) | Concentration Al (mg/L) | Leached Al from initial amount (%) | Total leached Al (%) |
|---|-----------------------|-------------------------|------------------------------------|----------------------|
| Ru/Al ₂ O ₃ (0.3 wt.% Ru) | 15 | 323 | 0.66 | 1.46 |
| | 30 | 255 | 0.43 | |
| | 195 | 122 | 0.21 | |
| | 345 | 104 | 0.16 | |
| Ru/Al ₂ O ₃ (0.5 wt.% Ru) | 15 | 127 | 0.27 | 0.53 |
| | 30 | 91 | 0.15 | |
| | 195 | 44 | 0.06 | |
| | 345 | 34 | 0.05 | |

The total amount of aluminium leaching is in fact higher, because not all samples were measured. To get a better insight in the quantity of Al leaching, the results are also represented in Graph 3.16.



Graph 3.16: Liquid analysis for aluminium content

The amount of aluminium in the liquid phase decreased with time on stream, but at the end of the experiment still a significant amount was detected. Ru/Al₂O₃ seems to be unstable under the applied hydrothermal conditions and acid environment during the hydrogenation of LA in this study.

Comparable hydrothermal instability of Ru/Al₂O₃ was observed by Osada et al. for the gasification of lignin at 400°C and 3.7 bar in supercritical water [37].

Leaching analysis of catalysts

The ruthenium content of the fresh and spent catalysts was also checked using ICP-OES analysis; the results are represented in Table 3.7.

Table 3.7: Ruthenium leaching analysis of catalysts

| Catalyst | Manufacturer | wt.% Ru |
|--|--------------|---------|
| Ru/Al ₂ O ₃ (0.3 wt.% Ru), fresh | BASF | 0.22 |
| Ru/Al ₂ O ₃ (0.3 wt.% Ru), spent | | 0.028 |
| Ru/Al ₂ O ₃ (0.5 wt.% Ru), fresh | JM | 0.44 |
| Ru/Al ₂ O ₃ (0.5 wt.% Ru), spent | | 0.13 |
| Ru/C (0.5 wt.% Ru), fresh | JM | 0.30 |
| Ru/C (0.5 wt.% Ru), spent | | 0.28 |
| Ru/C (2 wt.% Ru), fresh | JM | 1.46 |
| Ru/C (2 wt.% Ru), spent | | 1.08 |
| Ru/C (5 wt.% Ru), fresh | Evonik | 1.93 |
| Ru/C (5 wt.% Ru), spent | | 1.73 |
| Ru/TiO ₂ (1 wt.% Ru), fresh | Home made | 0.83 |
| Ru/TiO ₂ (1 wt.% Ru), spent | BASF support | 0.84 |

All fresh catalysts demonstrated a lower ruthenium content than was mentioned by the supplier. Ru/TiO₂ showed no measurable leaching of ruthenium over 6 hours on stream. Both Ru/Al₂O₃ catalysts showed significant decrease in ruthenium content after 6 hours on stream. This reduction in ruthenium content was confirmed by the ruthenium detected in the liquid phase. Ru/C with 0.5 wt.% of ruthenium only showed a marginal decrease in ruthenium content after 6 hours on stream, while Ru/C with 5 wt.% of ruthenium showed a higher level of ruthenium leaching. However, analysis of the liquids proved that the main leaching occurs during the first 30 minutes of the experiments. For Ru/C with 5 wt.% of ruthenium it was proved that the actual ruthenium content was significant lower than specified by the supplier. The stability of Ru/C with 2 wt.% of ruthenium is an exception compared to the two other tested Ru/C catalysts, because a significant amount of leaching of ruthenium was observed. The minimal differences between the LA conversions for the experiments with Ru/C catalysts could be caused by a minimal difference in actual ruthenium content.

Surface area analysis of catalysts

To check the difference in the specific surface area of the fresh and spent catalysts, BET analysis was carried out for all catalysts. The results are shown in Table 3.8.

Table 3.8: Specific surface area of fresh and spent catalysts

| Catalyst | BET surface area (m ² /g) | Difference (m ² /g) |
|--|--------------------------------------|--------------------------------|
| Ru/Al ₂ O ₃ (0.3 wt.% Ru), fresh | 178 | |
| Ru/Al ₂ O ₃ (0.3 wt.% Ru), spent | 214 | +36 |
| Ru/Al ₂ O ₃ (0.5 wt.% Ru), fresh | 102 | |
| Ru/Al ₂ O ₃ (0.5 wt.% Ru), spent | 104 | +2 |
| Ru/C (0.5 wt.% Ru), fresh | 1108 | |
| Ru/C (0.5 wt.% Ru), spent | 849 | -259 |
| Ru/C (2 wt.% Ru), fresh | 949 | |
| Ru/C (2 wt.% Ru), spent | 592 | -357 |
| Ru/C (5 wt.% Ru), fresh | 1031 | |
| Ru/C (5 wt.% Ru), spent | 941 | -90 |
| Ru/TiO ₂ (1 wt.% Ru), fresh | 96 | |
| Ru/TiO ₂ (1 wt.% Ru), spent | 105 | +9 |

The increase in specific surface area of Ru/Al₂O₃ could be caused by dissolving of both ruthenium and alumina in the liquid phase. The increase in specific surface area of Ru/Al₂O₃ with 0.3 wt.% of ruthenium was higher, which was confirmed by more aluminium found in the liquid phase than for Ru/Al₂O₃ with 0.5 wt.% of ruthenium.

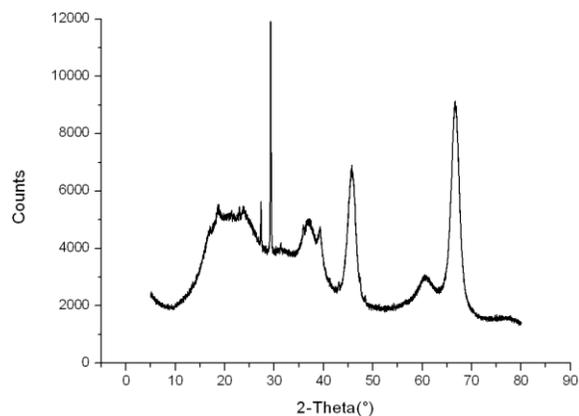
All Ru/C catalysts showed a drop in specific surface area after 6 hours on stream. Chalid et al. observed the same during batch experiments with Ru/C [8]. A possible explanation for this effect is the formation of coke on the catalyst surface. Another suggestion is the polymerisation of α -AL on the catalyst surface. Despite of the absence of this component in the liquid phase, it can be formed in low amounts on the catalyst surface and have affinity for the carbon support [16].

Ru/TiO₂ demonstrated a small increase in specific surface area. It was presumable caused by differences in the structure of the support particles. Particles used for the analysis of the fresh catalyst could have had a higher specific surface area than the particles used during the experiment. Additionally, precursor (remaining of the catalyst synthesis) could be present on the catalyst surface, which was washed off during the experiment. In addition, the dispersion of ruthenium is likely not homogeneous, because the catalyst was home made.

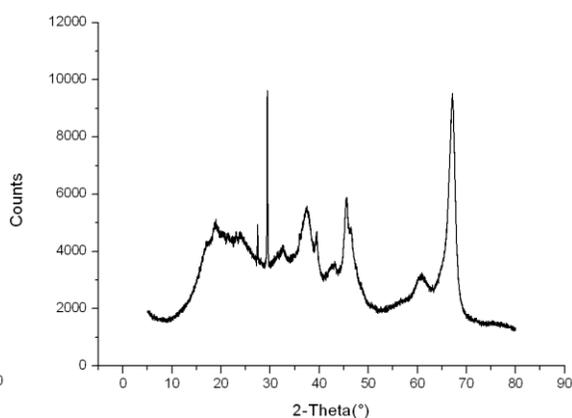
In conclusion, Ru/C catalysts with 0.5 and 5 wt.% of ruthenium and Ru/TiO₂ with 1 wt.% of ruthenium showed the highest stability of all catalysts which were used during the catalyst screening. However, both Ru/C catalysts showed significant higher activity than Ru/TiO₂. Therefore, these two Ru/C catalysts were used for further experiments during this study.

Catalyst structure analysis of Ru/Al₂O₃

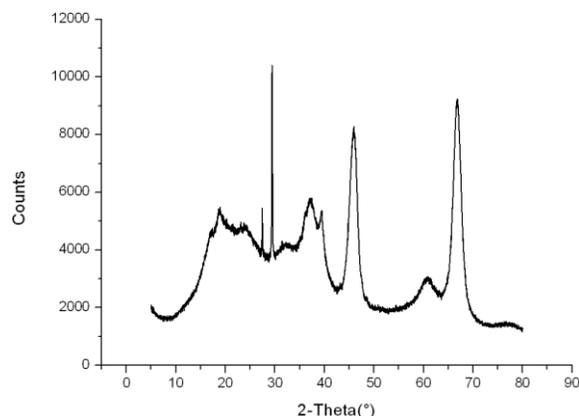
High amounts of ruthenium and aluminium were found in the liquid phase of experiments where Ru/Al₂O₃ was used . Therefore, XRD analysis was performed with fresh and spent Ru/Al₂O₃ catalysts to check if the structure changed during the experiment. The XRD patterns are represented in Graph 3.17 to 3.20.



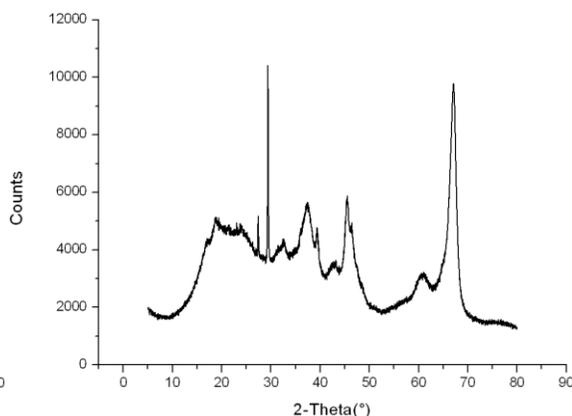
Graph 3.17: Pattern fresh Ru/Al₂O₃ (0.3 wt.% Ru)



Graph 3.18: Pattern fresh Ru/Al₂O₃ (0.5 wt.% Ru)



Graph 3.19: Pattern spent Ru/Al₂O₃ (0.3 wt.% Ru)



Graph 3.20: Pattern spent Ru/Al₂O₃ (0.5 wt.% Ru)

The XRD patterns show that the catalysts are ruthenium supported on γ -Al₂O₃. The structure was not changed during 6 hours on stream. Therefore, it can be concluded that layers of the Ru/Al₂O₃ catalysts are slowly dissolved in the liquid phase without significant changes in structure. This is most likely caused by the hydrothermal conditions and acid environment.

3.3 Effect of LA feed concentration

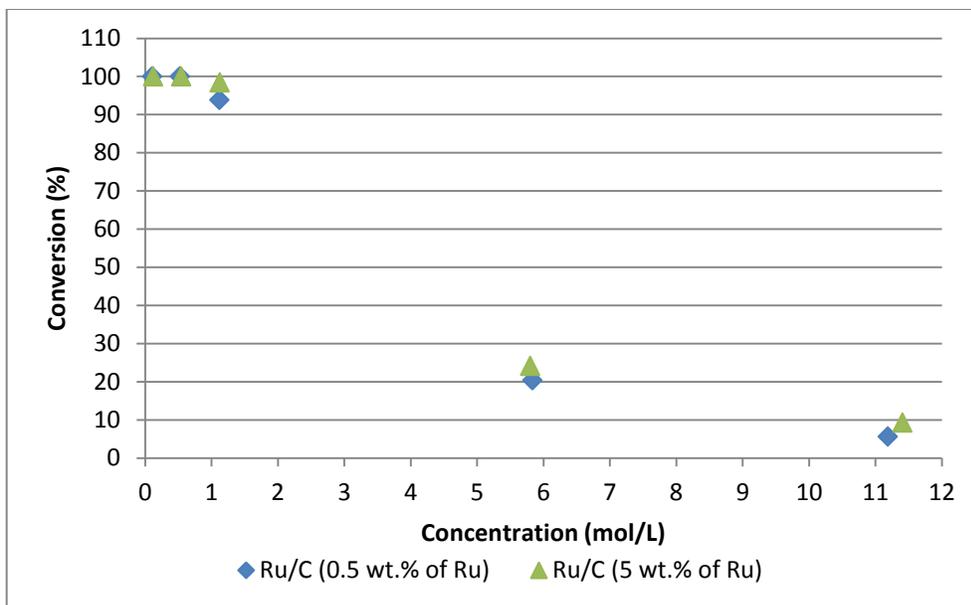
To get insight in the effect of initial LA concentration on conversion and reaction rate, a number of experiments were performed at benchmark conditions using Ru/C catalysts with 0.5 and 5 wt.% of ruthenium with different initial LA concentrations. The conditions, which were used for all experiments were as follows:

- Volumetric flow rate feed: +/- 1 mL/min
- Volumetric flow rate H₂: 30 mL/min
- Column pressure: 45 bar
- Temperature: 90°C
- Amount of catalyst: 2.00 gram
- WHSV: 30 (g_{feed}/g_{cat}·hr)

The used concentrations of LA were as follows:

- 0.1 mol/L
- 0.5 mol/L
- 1 mol/L
- 5 mol/L
- 97% LA (3% water)

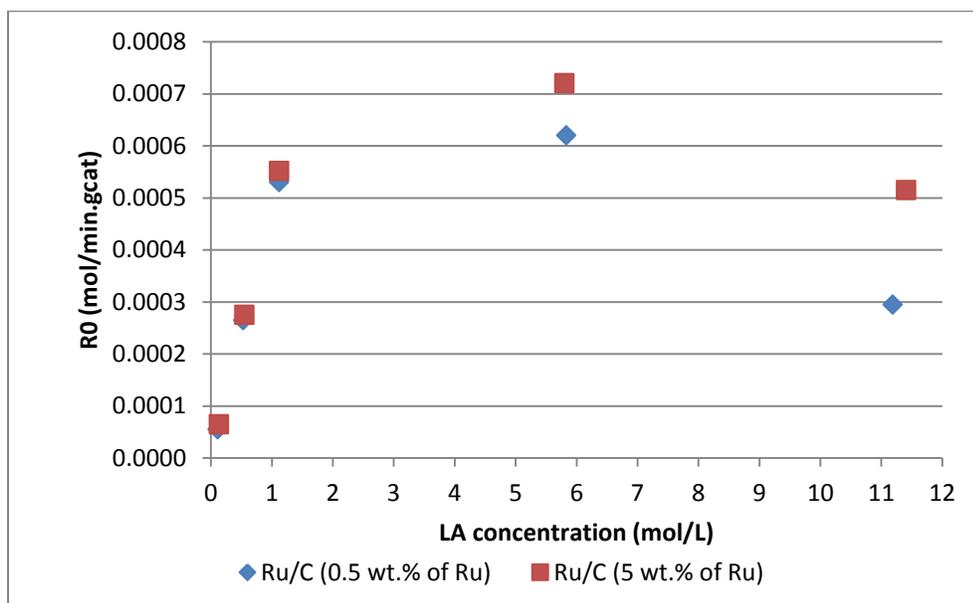
The concentration profiles of all separate experiments can be found in Appendix 6.4 (Graph 6.1 to 6.10). Analysis of the samples was carried out using ¹H-NMR with the same intervals as described in section 3.2.1. A summary of the average conversions over 6 hours on stream for all experiments is shown in Graph 3.21.



Graph3.21: Effect of initial LA concentration on average LA conversion over 6 hours on stream at 90°C

A strong effect of initial LA concentration on the conversion of LA was observed. Both catalysts were able to achieve 100% LA conversion at LA concentrations of 0.1 and 0.5 mol/L. The conversion of LA starts to decrease with increasing concentration.

To determine the order of reaction, the initial reaction rates were calculated using Equation 6.15 in section 6.1.3. The results are shown in Graph 3.22.



Graph 3.22: Effect of initial LA concentration on initial reaction rate at 90°C

The reaction is first order at low concentration, zero order at average concentration and negative order at high concentration, with respect to LA. This is in agreement with batch experiments coupled to this

study [9]. Though, the maximum concentration which was applied during these batch experiments was 2 mol/L, and therefore the negative reaction order was not observed. In addition, Braden et al. discovered the same by performing an experiment with a feed consisting of 0.3 mol/L of both LA and FA and an experiment with a feed consisting of 2.2 mol/L of both LA and FA at 150°C and 35 bar H₂ [42]. Because of the higher concentrations, fewer vacancies are available on the catalyst surface, resulting in lower conversions. The higher difference between the initial reaction rate for both catalysts at approximately 11 mol/L, compared to the difference at approximately 5 mol/L, can be explained by the fact that the initial LA concentration for the run with Ru/C with 5 wt.% of ruthenium was slightly higher. The second important observation from these experiments is that there is only a small difference in LA conversion for both catalysts with different ruthenium loading. This effect has also been observed during the catalyst screening experiments (section 3.2.1). The minor difference in catalyst activity can be explained by the lower ruthenium loading for Ru/C (5 wt.% of Ru) than indicated by the supplier (1.9 wt.% instead of 5 wt.%). Besides this, the type of carbon used as support and the catalyst preparation procedure may also have an influence on the activity of the catalyst. It was also seen during the catalyst screening study, that during the start-up of the reactor and beginning of the experiment, more ruthenium was leached from the Ru/C (5 wt.% of Ru) supplied by Evonik than the Ru/C (0.5 wt.% of Ru) supplied by Johnson Matthey. Therefore the catalyst supplied by Johnson Matthey seems to be of a better quality.

3.4 High LA concentration experiments

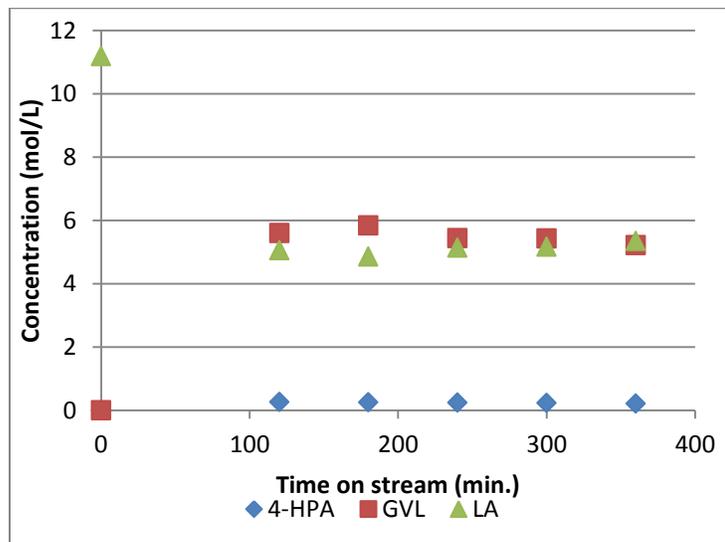
During the experiments discussed in section 3.3, it was shown that Ru/C with 0.5 and 5 wt.% of ruthenium demonstrated a lower activity at high initial concentrations of LA. For eventual scaling up to industrial scale, it is better to keep the amount of solvent as low as possible to eliminate additional distillation steps of the product stream. Therefore, additional experiments were performed at higher reaction temperature, hydrogen flow and catalyst intake to test the ability of the system to convert concentrated LA streams. To be able to use higher catalyst intakes, a longer reaction section was used during these experiments (33 cm instead of 13.5 cm). The rest of the reactor was used in the same form as for the rest of the experiments. The reaction conditions applied during the experiments with concentrated LA were as follows:

- Initial LA concentration: 97% LA (3% water)
- Volumetric flow rate feed: +/- 1 mL/min
- Volumetric flow rate H₂: 120 mL/min
- Column pressure: 45 bar
- Temperature: 150°C
- Amount of catalyst: 5.00 gram
- WHSV: 12 ($\frac{g_{\text{feed}}}{g_{\text{cat}} \cdot \text{hr}}$)

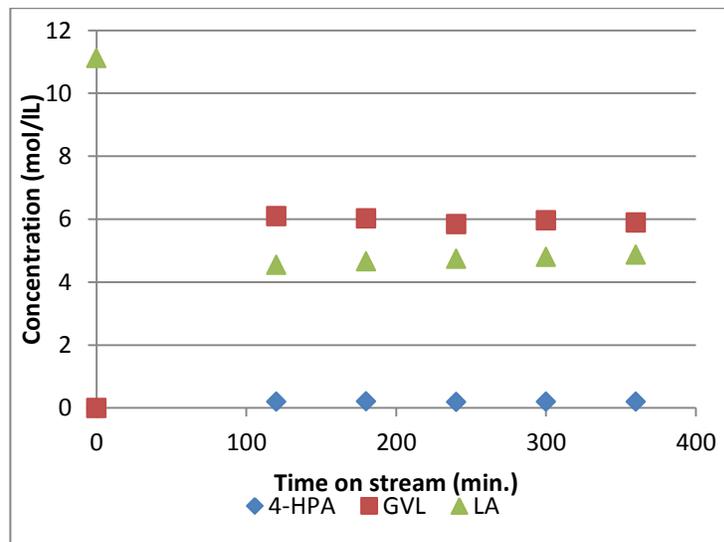
The activity and stability of Ru/C (0.5 wt.% of Ru) from JM and Ru/C (5 wt.% of Ru) from Evonik at described conditions are evaluated in the following sections.

3.4.1 Liquid phase product analysis

Analysis of the samples was carried out using $^1\text{H-NMR}$ with the same intervals as described in section 3.2.1. The results are shown in Graph 3.23 and 3.24.



Graph 3.23: Concentration profile 97% LA over Ru/C (0.5 wt.% Ru) at 150°C



Graph 3.24: Concentration profile 97% LA over Ru/C (5 wt.% Ru) at 150°C

A slight reduction in LA conversion with time on stream was observed for both catalysts. The average conversion and selectivity to the products over 6 hours on stream for both catalysts are represented in Table 3.9.

Table 3.9: Activity of Ru/C catalysts in hydrogenation of concentrated LA (average over 6 hours) at 150°C

| Catalyst | Conversion LA (%) | Selectivity GVL (%) | Selectivity 4-HPA (%) | GVL/4-HPA ratio | Selectivity 4-HPA+GVL |
|--------------------|-------------------|---------------------|-----------------------|-----------------|-----------------------|
| Ru/C (0.5 wt.% Ru) | 54 | 96 | 8 | 12 | 104 |
| Ru/C (5 wt.% Ru) | 57 | 97 | 6 | 16 | 103 |

The altered reaction conditions resulted in LA conversions higher than 50 % for both catalysts. The GVL/4-HPA ratio was higher than achieved at benchmark conditions for both catalysts, as discussed in section 3.2.1. This was an effect of the higher reaction temperature, since the ring closure reaction of 4-HPA to GVL is endothermic [11]. Therefore, this reaction will be accelerated when a higher reaction temperature is applied leading to higher amounts of GVL. The selectivity towards 4-HPA + GVL was detected to be slightly higher than 100%, probably caused by measurement errors. The higher hydrogen flow also had a positive effect on the conversion of LA, because the H_2/LA ratio for the reaction was higher than for the experiments with concentrated LA discussed in section 3.3. Not enough hydrogen was available for the reaction with LA during these experiments. The mole balance of the experiment at 150°C with Ru/C (0.5 wt.% of Ru) and Ru/C (5 wt.% of Ru) closed respectively with 97.2% and 97.9%. The difference is presumably caused by a combination of measurement errors and carbon left on the catalyst surface in the form of coke. The only other product observed in the liquid phase was 4-HPA (see

NMR spectra 6.8 and 6.9 in Appendix 6.2.3 and HPLC spectra 6.18 and 6.19 in Appendix 6.3.3). Al-Shaal et al. showed that Ru/C was able to achieve 100% LA conversion when using neat LA within 40 minutes in a batch set-up [32]. However, they applied different reaction conditions (190°C, 12 bar H₂ and Ru/C in powder form).

The TOF and TON were calculated respectively using Equation 6.13 and 6.14 in Appendix 6.1.3 to further evaluate the performance of the catalytic system at high LA concentration and the altered process conditions. Average concentrations over 6 hours on stream and the actual ruthenium loading were used for the calculations. The results are shown in table 3.10.

Table 3.10: Table 3.3: Average TOF and TON over 6 hours at high LA concentration at 150°C

| Catalyst | ΔC_{LA} (mol/L) | TOF (g LA/g cat.hr) | TON (g LA/g cat.hr) | TOF (g LA/g Ru) | TON (g LA/g Ru) |
|--------------------|----------------------------|------------------------|------------------------|--------------------|--------------------|
| Ru/C (0.5 wt.% Ru) | 6.07 | 8.46 | 50.73 | 16910.33 | 101461.96 |
| Ru/C (5 wt.% Ru) | 6.40 | 8.92 | 53.51 | 2772.47 | 16634.85 |

Both catalysts showed a TOF within the desired boundaries for hydrogenation (0.1-10 g LA/g cat.hr) with the changed process conditions [47]. It was again proved that Ru/C with 0.5 wt.% of ruthenium showed the highest activity and productivity based on the amount of ruthenium over 6 hours on stream.

3.4.2 Catalyst stability

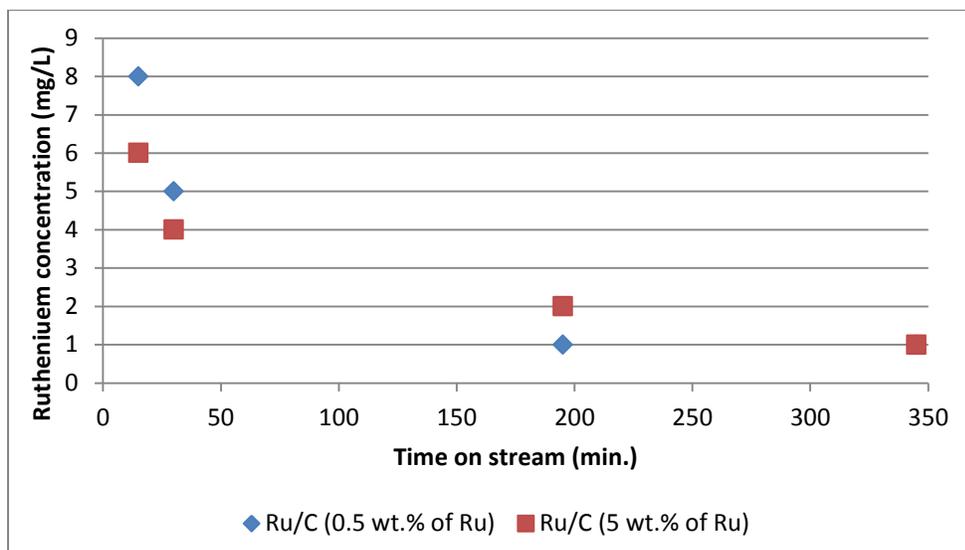
Liquid analysis

Liquid samples from the beginning, middle and end of each experiment were analysed for ruthenium content using ICP-OES to check the catalysts for leaching of ruthenium. The results are represented in Table 3.11.

Table 3.11: Liquid analysis for ruthenium content

| Catalyst | Time on stream (min.) | Concentration Ru (mg/L) | Leached Ru from initial amount on catalyst (%) | Total leached Ru (%) |
|-----------------------|--------------------------|----------------------------|---|-------------------------|
| Ru/C (0.5 wt.% Ru) | 15 | 8 | 0.95 | 1.78 |
| | 30 | 5 | 0.60 | |
| | 195 | 1 | 0.11 | |
| | 345 | 1 | 0.12 | |
| Ru/C 5 (5 wt.% Ru) | 15 | 6 | 0.11 | 0.22 |
| | 30 | 4 | 0.07 | |
| | 195 | 2 | 0.02 | |
| | 345 | 1 | 0.02 | |

The total amount of ruthenium leaching is in fact higher, because not all samples were measured. To get a better insight into the quantity of ruthenium leaching, the results are also represented in Graph 3.25.



Graph 3.25: Liquid analysis for ruthenium content

At the beginning of the experiment and start-up of the reactor, small amounts of ruthenium were leached to the liquid phase from both catalysts. The same catalyst behavior was observed during the catalyst screening experiments. However, the higher reaction temperature in combination with concentrated LA resulted in leaching of ruthenium during all 6 hours on stream, though in lower amounts than at the beginning of the experiment.

Leaching analysis of catalysts

The ruthenium content of the fresh and spent catalysts was also checked using ICP-OES analysis, the results are represented in Table 3.12.

Table 3.12: Ruthenium leaching analysis of catalysts

| Catalyst | Manufacturer | wt.% Ru |
|------------------------------|--------------|---------|
| Ru/C (0.5 wt.% of Ru), fresh | JM | 0.3 |
| Ru/C (0.5 wt.% of Ru), spent | | 0.17 |
| Ru/C (5 wt.% of Ru), fresh | Evonik | 1.93 |
| Ru/C (5 wt.% of Ru), spent | | 1.44 |

Both catalysts showed a decrease in ruthenium content after 6 hours on stream, which was confirmed by ruthenium found in the liquid phase. It can be concluded that both catalysts show a slight degradation under the harsher reaction conditions which were applied.

Surface area analysis of catalysts

The specific surface area of all Ru/C catalysts during catalyst screening experiments was decreased. Therefore, both Ru/C catalysts used for reaction with concentrated LA were also checked for specific surface area using BET analysis. The results are shown in Table 3.13.

Table 3.13: Specific surface area of fresh and spent Ru/C catalysts

| Catalyst | BET surface area (m ² /g) | Difference (m ² /g) |
|------------------------------|--------------------------------------|--------------------------------|
| Ru/C (0.5 wt.% of Ru), fresh | 1108 | |
| Ru/C (0.5 wt.% of Ru), spent | 792 | -316 |
| Ru/C (5 wt.% of Ru), fresh | 1031 | |
| Ru/C (5 wt.% of Ru), spent | 821 | -210 |

Both catalysts showed a decrease in specific surface area after 6 hours on stream. This is possibly caused by the formation of coke on the catalyst surface. Another suggestion is the formation of α -AL in small amounts, as described in section 3.2.2.

3.5 Long duration catalyst stability test

For eventual scaling up to industrial scale, the continuous reactor should be able to operate in a full continuous way (24/7). Therefore a long duration test was carried out, to get more insight in the stability of the catalytic system. The experiment was performed at benchmark conditions, which were as follows:

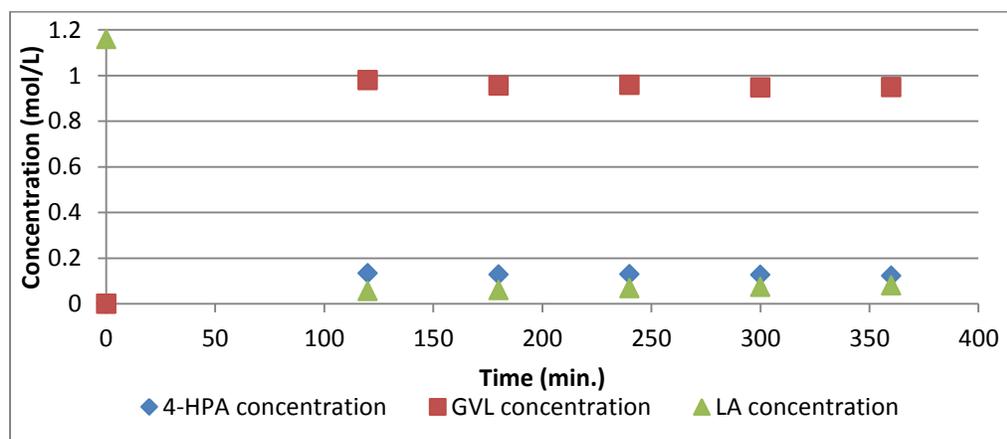
- Initial LA concentration: 1.15 mol/L
- Volumetric flow rate feed: +/- 1 mL/min
- Volumetric flow rate H₂: 30 mL/min
- Column pressure: 45 bar
- Temperature: 90°C
- Amount of catalyst: 2.00 gram
- WHSV: 30 (g_{feed}/g_{cat}·hr)

The catalyst of choice for this long duration experiment was Ru/C with 0.5 wt.% of ruthenium, obtained from JM. This catalyst showed the best stability of the carbon supported ruthenium catalysts during the catalyst screening tests. Besides this, for its ruthenium content, Ru/C (0.5 wt.% of Ru) from JM showed the highest activity and productivity. In addition, from economical point of view, it is preferred to use as less ruthenium as possible.

The results of the experiment are discussed in the following sections.

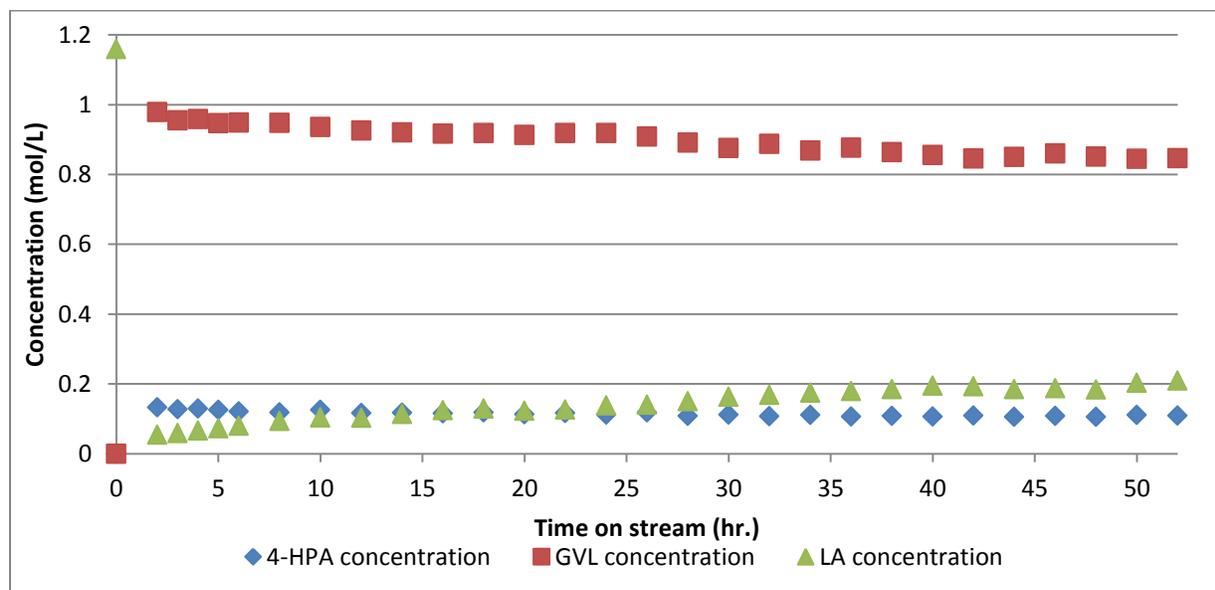
3.5.1 Liquid phase product analysis

The samples taken from the reactor of the first 6 hours on stream were analysed with an interval of 60 minutes starting from 2 hours on stream using ¹H-NMR. The concentration profile is shown in Graph 3.26.

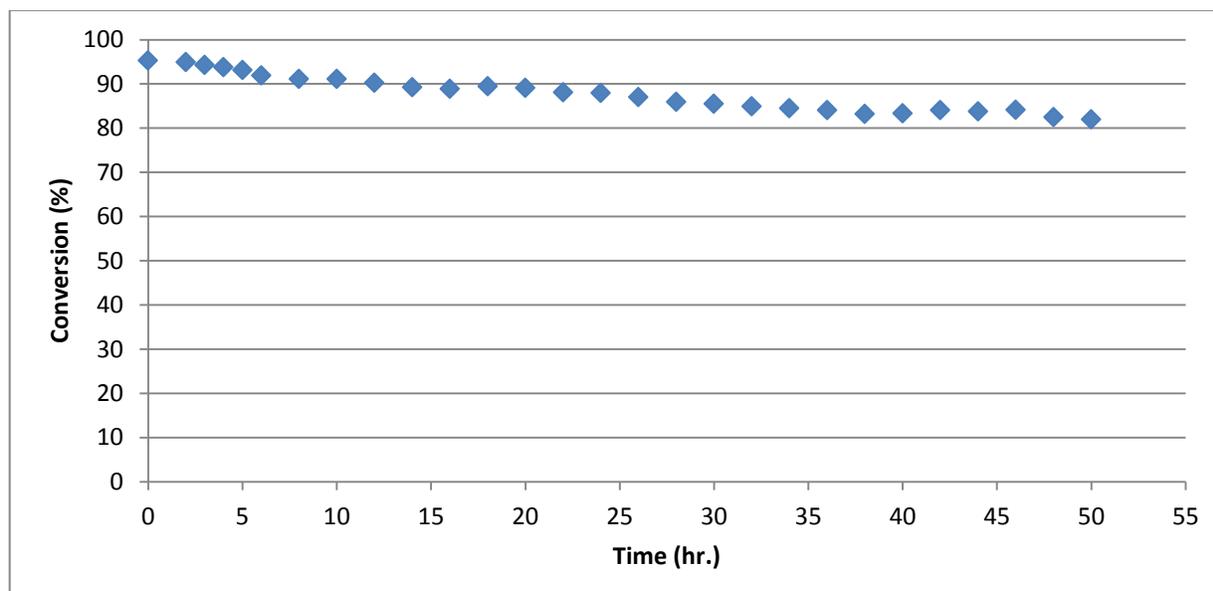


Graph 3.26: Concentration profile long duration experiment (first 6 hours on stream) at 90°C using Ru/C (0.5 wt.% of Ru)

The concentration profile of the first 6 hours on stream shows a similar trend as the concentration profile for Ru/C (0.5 wt.% of Ru) obtained during the catalyst screening study (Graph 3.10). The 4-HPA concentration is slightly lower, while the GVL concentration is slightly higher. This is caused by the fact that the samples were left at room temperature for 2 weeks after the experiment to be sure that the GVL/4-HPA ratio was at equilibrium. The rest of the samples were analysed with an interval of 120 minutes and the results were added to Graph 3.26. The concentration profile over 52 hours on stream is shown in Graph 3.27. In addition, the conversion profile of LA is shown in Graph 3.28.



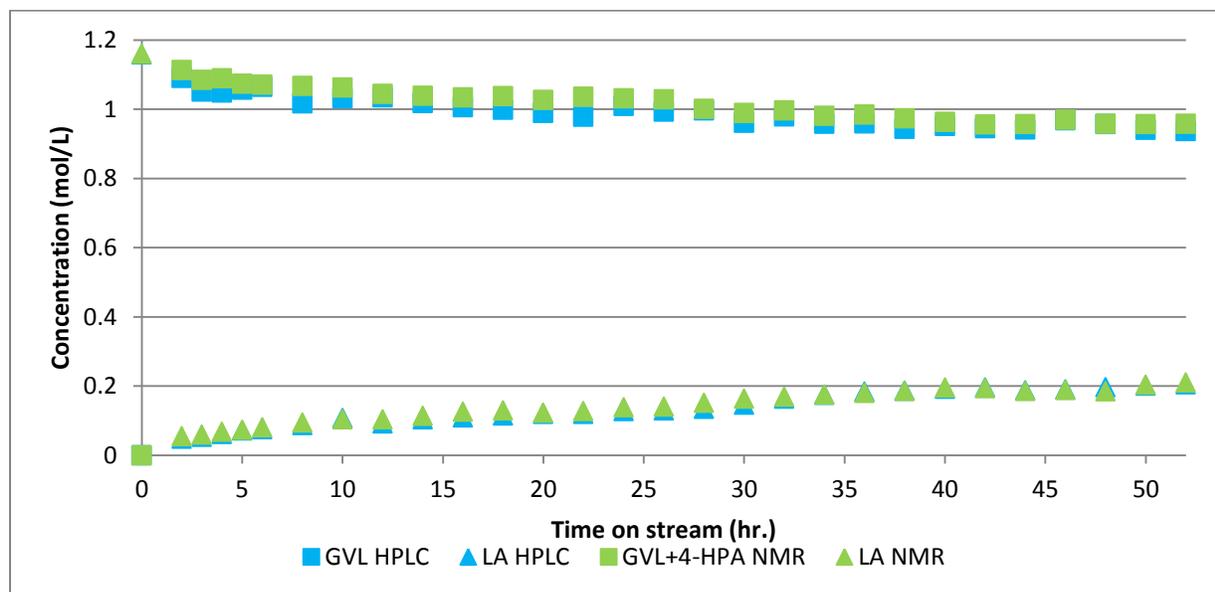
Graph 3.27: Concentration profile long duration experiment over 52 hours on stream at 90°C using Ru/C (0.5 wt.% of Ru)



Graph 3.28: Conversion of LA over 52 hours on stream at 90°C using Ru/C (0.5 wt.% of Ru)

A reduction in LA conversion was observed over 52 hours on stream. The initial LA conversion of 95% decreased to 82% after 52 hours on stream. The conversion of LA decreased with a value of approximately 0.25% per hour, which is an indication for catalyst deactivation during the experiment. The selectivity towards 4-HPA + GVL remained the same during the experiment with a value of 100%. The GVL/4-HPA ratio was 7.64 with a GVL selectivity of 89%. However, it should be mentioned that these samples were analysed after 2 weeks of storage at room temperature. The same degree of catalyst deactivation was observed during experiments reported in literature. As discussed in section 1.1.6, Serrano-Ruiz et al. used a packed bed reactor filled with Ru/C (5 wt.% of Ru) powder [15]. A higher concentration (8.6 mol/L) and temperature (150°C) were applied than during this study, the space velocity was comparable ($WHSV=32 \text{ g}_{\text{feed}}/\text{g}_{\text{cat}}\cdot\text{hr}$). The conversion of LA decreased from 90% to 68% after 106 hours on stream. Unless the different conditions, the same degree of decrease in LA conversion was observed, which was approximately 0.20% per hour. No explanation was given for this reduction in catalyst activity. In addition, a higher selectivity towards GVL instead of 4-HPA was achieved because of the higher reaction temperature. Braden et al. also used Ru/C (5 wt.% of Ru) powder in a packed bed at 150°C and 35 bar H_2 with a feed consisting of 0.3 mol/L of both LA and FA [42]. They observed a slow decrease in LA conversion over 50 hours on stream. Though, the results are not fully comparable because the feedstock of the reactor consisted of LA and FA. No quantitative information was given about catalyst intake, space velocity and decrease in LA conversion. The reason for reduction in catalytic activity during this study is discussed in the following sections.

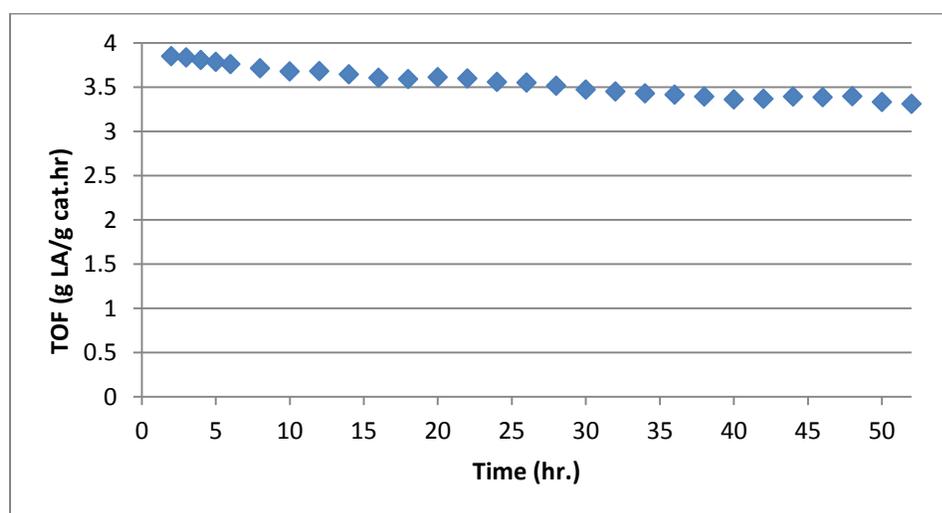
To check the accuracy of $^1\text{H-NMR}$, the same samples taken from the reactor were also analysed using HPLC. As mentioned in section 2.2.3, no 4-HPA was measured during this analysis technique, because the eluent (H_2SO_4) catalysed the ring closure reaction to form GVL. The concentrations of 4-HPA and GVL calculated from $^1\text{H NMR}$ were counted up to compare it with the GVL concentrations calculated using HPLC. The concentrations calculated using both techniques are shown in Graph 3.29.



Graph 3.29: Concentrations profile of the long duration experiment at 90°C, analysed by HPLC and $^1\text{H-NMR}$

The concentration profiles of $^1\text{H-NMR}$ and HPLC show comparable trends. The LA concentrations are approximately the same. A small difference can be observed between the trends of GVL for HPLC and GVL + 4-HPA for $^1\text{H-NMR}$. The average difference between the two trends is 2.3% and is most likely caused by measurement errors by one or both technique(s), integration errors of the peaks or errors during the preparation of the samples. It can be concluded that both techniques are suitable for liquid phase analysis of LA hydrogenation. Both techniques can be used to analyse the conversion of LA. Though, for an insight in the whole product distribution, $^1\text{H-NMR}$ is the only technique which is useful.

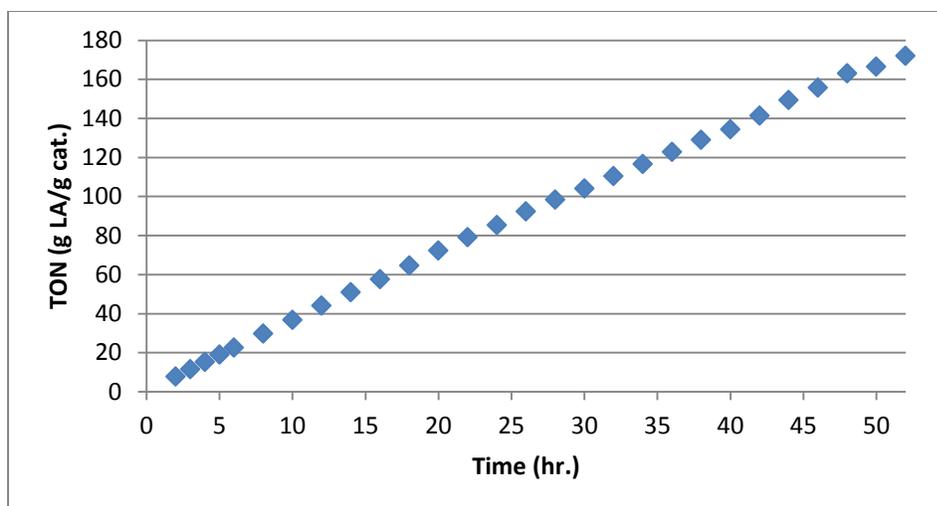
To evaluate the catalyst activity, the TOF was calculated using Equation 6.13 in Appendix 6.1.3. The results over 52 hours on stream are shown in Graph 3.30.



Graph 3.30: TOF over 52 hours on stream at 90°C using Ru/C (0.5 wt.% of Ru)

The initial activity was the same as for Ru/C (0.5 wt.% Ru) seen during the catalyst screening study. A slow reduction in TOF was observed over 52 hours on stream, confirming the reduction in conversion. The TOF remained within the desired boundaries of 0.1-10 g LA/g cat.hr [47].

The TON over 52 hours on stream was calculated using Equation 6.14 in Appendix 6.1.3. The TON calculation was corrected for the decreasing TOF. The results are shown in Graph 3.31.



Graph 3.31: TON over 52 hours on stream at 90°C using Ru/C (0.5 wt.% of Ru)

The total productivity after 52 hours on stream was 172 g LA/g cat, and the total productivity based on the amount of ruthenium was 1103 g LA/g Ru after 52 hours on stream.

3.5.2 Catalyst stability

Liquid analysis

ICP-OES analysis was carried out especially on liquid samples of the beginning of the experiment, followed by samples spread over the rest of the experiment, to check if there was leaching of ruthenium to the liquid phase from the Ru/C catalyst. The results are represented in Table 3.14.

Table 3.14: Liquid analysis for ruthenium content

| Time on stream (min.) | Concentration Ru (mg/L) | Leached Ru from initial amount on catalyst (%) | Total leached Ru (%) |
|-----------------------|-------------------------|--|----------------------|
| 15 | 7 | 2.40 | |
| 30 | 3 | 0.80 | |
| 45 | 1 | 0.27 | |
| 60 | <1 | 0 | |
| 105 | <1 | 0 | |
| 270 | <1 | 0 | |
| 420 | <1 | 0 | |
| 570 | <1 | 0 | |
| 1110 | <1 | 0 | |
| 1620 | <1 | 0 | |
| 2130 | <1 | 0 | |
| 2625 | <1 | 0 | |
| 3105 | <1 | 0 | 3.47 |

Only a minor amount of ruthenium leaching from the Ru/C catalyst was observed during the beginning of the experiment. No measurable amount of ruthenium was found in the samples after 45 minutes on stream. The same behavior was observed for this catalyst during the catalyst screening study, discussed in section 3.2.2. Because the catalyst stopped leaching ruthenium to the liquid phase after 45 minutes, it can be concluded that this is not the reason for the decrease in LA conversion.

Leaching analysis of catalyst

In addition to the analysis for ruthenium content in the liquid phase, the catalyst was also checked for ruthenium content using ICP-OES analysis. The results are represented in Table 3.15.

Table 3.15: Ruthenium leaching analysis of catalyst

| Catalyst | Manufacturer | wt.% Ru |
|------------------------------|--------------|---------|
| Ru/C (0.5 wt.% of Ru), fresh | JM | 0.30 |
| Ru/C (0.5 wt.% of Ru), spent | | 0.28 |

There was only a small decrease in ruthenium content over 52 hours on stream. This was confirmed by ruthenium found in the liquid phase at the beginning of the experiment. The leaching of ruthenium only took place during the start-up of the reactor.

Surface area analysis of the catalyst

During the catalyst screening experiments, a significant decrease in specific surface area was observed for all Ru/C catalysts. Therefore, the spent catalyst of the long duration test was also analysed using BET analysis. The results are shown in Table 3.16.

Table 3.16: Specific surface area of fresh and spent catalyst

| Catalyst | BET surface area (m ² /g) | Difference (m ² /g) |
|------------------------------|--------------------------------------|--------------------------------|
| Ru/C (0.5 wt.% of Ru), fresh | 1108 | |
| Ru/C (0.5 wt.% of Ru), spent | 391 | -717 |

There was a significant decrease in specific surface area after 52 hours on stream. The decrease in specific surface area was almost 3 times higher than measured for the Ru/C catalyst with 0.5 wt.% of ruthenium used during the catalyst screening over 6 hours on stream. This is most likely the reason why the conversion of LA kept decreasing over 52 hours on stream. As already discussed in section 3.2.2, the decrease in specific surface area is probably caused by the formation of coke on the catalyst surface. Another suggestion is the polymerisation of small amounts of α -AL on the catalyst surface. Sintering of the ruthenium particles is not expected to cause the decrease in activity, because of the relatively low reaction temperature which was applied. However, additional catalyst characterization techniques are required to exclude this. These analysis methods are currently carried out by University Utrecht.

4 Conclusions

Catalytic LA hydrogenation experiments were carried out in a packed-bed reactor for the synthesis of GVL. A number of initial experiments were carried out to test the reactor performance. Through modifications of the reactor, a stable pressure and isothermal temperature profile were obtained. A test with Ru/C (0.5 wt.% of Ru) as catalyst, showed the ability of the reactor to achieve almost full conversion of LA when operating at a temperature of 130°C.

A catalyst screening study was performed to test the activity and stability of ruthenium on several supports at a reaction temperature of 90°C. Ru/Al₂O₃ was able to catalyse the hydrogenation reaction, though low activities were observed. Besides this, ICP-OES analysis proved that significant amounts of ruthenium and aluminium were leached to the liquid phase. XRD analysis indicated that the structure of the support was not changed. Hence, it was concluded that layers of Ru/Al₂O₃ were slowly dissolved to the liquid phase. Therefore, it was found that Ru/Al₂O₃ is not an appropriate catalyst for the hydrogenation of LA under hydrothermal conditions. Home made Ru/TiO₂ was also able to catalyse the reaction, but showed a poor activity. Despite of the low activity, the stability was excellent since no ruthenium and titanium leaching was observed. Batch experiments coupled to this study and experiments reported in literature have shown that Ru/TiO₂ should be able to achieve high level of conversion of LA. However, it was also reported that the nature of support and preparation procedure have an important influence on the activity of the catalyst. It is most likely that this was the reason for the low activity.

The best results were obtained with Ru/C. Ru/C with 0.5 wt.% of ruthenium was already able to achieve 94% conversion of LA at 90°C. Ru/C with 0.5 and 5 wt.% of ruthenium showed small amounts of ruthenium leaching at the start-up of the experiments and kept stable over 6 hours on stream. Therefore, it was found that Ru/C is an active and stable heterogeneous catalyst for the hydrogenation of LA in water. Because of its excellent performance, the support of choice for further studies was active carbon.

To investigate the influence of LA feed concentration, experiments were carried out at 90°C with Ru/C with 0.5 and 5 wt.% of ruthenium at the same reaction conditions using different initial LA concentrations. Both catalysts were able to achieve 100% conversion at low concentrations (0.1 and 0.5 mol/L). Lower LA conversions were observed for both catalysts at higher concentrations. Ru/C with 0.5 and 5 wt.% of ruthenium achieved respectively 6 and 9% of conversion for a feed containing 97% LA and 3% water. It was concluded that the reaction is first order at low concentration, zero order at average concentration and negative order at high concentration, with respect to LA. Additional experiments with altered process conditions (150°C instead of 90°C, 120 mL/min flow of hydrogen instead of 30 mL/min and 5 gram catalyst intake instead of 2 gram) resulted in higher catalyst activity for Ru/C with 0.5 and 5 wt.% of ruthenium. The conversion increased respectively from 6 and 9% to 54 and 57%. It was concluded that the temperature, hydrogen flow and catalyst intake have a significant influence on the reaction. However, a slight decrease in conversion was observed for both catalysts and ruthenium was found in small amounts in the liquid phase over 6 hours on stream. Ru/C showed a slight deactivation under the applied harsher reaction conditions. The temperature also had an influence on the GVL/4-HPA ratio, since the ring closure reaction of 4-HPA is endothermic. A higher reaction temperature led to

higher GVL selectivities and lower 4-HPA selectivities. A study on the 4-HPA \leftrightarrow GVL equilibrium also showed that the composition of the product mixture was changing at room temperature. A significant change in 4-HPA and GVL concentration was observed within 10 days after the experiment. After these 10 days the reaction came slowly to equilibrium.

As an extension on the catalyst screening study, a long duration test was performed with Ru/C with 0.5 wt.% of ruthenium. This catalyst was chosen because of its excellent performance and stability over 6 hours on stream. At the start of the experiment, 95% LA conversion was observed followed by a slow reduction over 52 hours on stream. However, after 52 hours on stream still 83% conversion of LA was achieved. The BET specific surface area of the catalyst showed a significant decrease from 1108 m²/g to 391 m²/g. This is most likely the cause of the decrease in activity, since no leaching of ruthenium was observed after the start-up period of the reactor. During the start-up only small amounts of ruthenium were leached to the liquid phase, which resulted in a minimal decrease of ruthenium content, from 0.30 wt.% to 0.28 wt.%. The decrease in BET specific surface area is presumably caused by the formation of coke. Another suggestion is the polymerization of α -AL in low amounts (since it was not found in the liquid phase) on the catalyst surface.

In conclusion, ruthenium supported on active carbon showed to be an active and stable catalyst for hydrogenation of LA under hydrothermal conditions in a packed bed reactor. The main issue with Ru/C is the decrease in specific surface area with time on stream, caused by coke formation on the catalyst surface. The decrease in specific surface area leads to reduction of LA conversion and therefore regeneration of the catalyst will be necessary from time to time. This can become a problem for eventual scaling up to industrial scale, since carbon supports do not survive frequent regeneration by coke burn-off [20].

The reactor was able to operate in a full continuous way, though modifications will be necessary for 24/7 operation. Therefore, safety switches should be installed for tracing, pressure and hydrogen flow.

5 Recommendations

It will be interesting to get more insight in the effect of the weight hourly space velocity on the conversion of LA. This can be performed by changing the catalyst intake or the flow of LA entering the reactor. A lower flow or higher catalyst intake will result in a longer residence time of the reactants in the reaction section. It is expected that this will result in higher conversions. This will especially be interesting for the conversion of concentrated LA solutions. Also the effect of temperature on product distribution and catalyst stability should be investigated in further detail.

During this study, catalysts in the form of pellets were used. It is known from literature that pellets cause diffusion and mass transfer limitations causing lower reaction rates [46]. This should be checked with a kinetic model, which is currently under development. To overcome the diffusion and mass transfer limitations, powders should be used instead of pellets.

Ru/C showed excellent performance for hydrogenation of LA in water. Though, the decrease in specific surface area with time on stream, caused by coke formation, makes it necessary to regenerate the catalyst from time to time. Carbon supports do not survive frequent regeneration by coke burn-off [20]. This means that it will be required to replace the catalyst once in a while. This is a disadvantage for eventual scaling up to industrial level and it will have a negative influence on the process economics. Therefore, further studies in the packed bed reactor should focus on Ru/TiO₂, since TiO₂ is stable to decoking conditions [20]. During this study Ru/TiO₂ gave poor results, but showed to be stable. Though, results reported in literature and batch experiments coupled to this study have shown that Ru/TiO₂ should be able to achieve high levels of LA conversion. The preparation procedure and nature of the support seemed to have a significant influence on the activity of the catalyst. Hence, improved preparation procedures should be applied and different sorts of TiO₂ should be tested. Another catalyst which should be tested in the continuous reactor is Pt/TiO₂. Lange et al. performed an experiment in a packed bed reactor for 100 hours with this catalyst at 200°C [20]. The catalyst showed a high initial activity with 98% conversion of LA, which slowly decreased to 80% conversion of LA over 100 hours on stream. The catalyst showed no significant loss or sintering of the active metal. Therefore, the catalyst could be regenerated to restore its initial activity. Hence, Pt/TiO₂ is an interesting alternative for Ru/C.

To achieve a more stable liquid flow profile, it would probably be better to use another pump instead of the piston pump, which is currently used and gives a pulsating flow. Most studies reported in literature used a HPLC pump, which is able to generate a continuous flow into the column. During this study, the process parameters were logged manually. This can be improved by logging to a computer, since deviating process conditions can be recognized faster in that way.

Finally, another analysis technique is required to check the product distribution (including 4-HPA) provided by ¹H-NMR. Gas chromatography is an interesting technique, but it is required to treat the product mixture to prevent for conversion of 4-HPA to GVL during analysis.

6 Appendix

6.1 Used equations

The Equations which were used for this study are represented and explained in this section.

6.1.1 Calculation of concentrations by HPLC

The dilution factor of the samples was calculated with Equation 6.1.

$$Df = \frac{M_s + M_{H_2O}}{M_s} \quad (6.1)$$

Where:

- D_f = dilution factor
 M_s = mass product sample (g)
 M_{H_2O} = mass deionized water (g)

The conversion of LA was calculated with Equation 6.2.

$$X_{LA} = \frac{C_{LA,0} - C_{LA}}{C_{LA,0}} * 100 \quad (6.2)$$

Where:

- X_{LA} = conversion LA (%)
 $C_{LA,0}$ = initial concentration LA (mol/L)
 C_{LA} = concentration LA (mol/L)

6.1.2 Calculation of concentrations by ¹H-NMR

The concentrations of LA, 4-HPA and GVL were calculated using Equation 6.3 to 6.7.

$$Mol_a = mol_s \frac{I_a}{I_s} * \frac{N_s}{N_a} \quad (6.3)$$

Where:

- Mol_a = moles of analyte
 Mol_s = moles of internal standard (mass of 1,4-dioxane divided by molar mass (88,1))
 I_a = integral analyte
 I_s = integral internal standard
 N_a = number of nuclei giving rise to the relevant analyte signals (3)
 N_s = number of nuclei giving rise to the standard signals (8)

$$C_a = \frac{mol_a}{V_{total}} * Df \quad (6.4)$$

$$Df = \frac{M_s + M_{dioxane} + M_{D_2O}}{M_s} \quad (6.5)$$

$$V_{total} = \frac{M_s + M_{dioxane} + M_{D_2O}}{1000 * \rho_{average}} \quad (6.6)$$

$$\rho_{average} = \frac{M_s * \rho_s + M_{dioxane} * \rho_{dioxane} + M_{D_2O} * \rho_{D_2O}}{M_{total}} \quad (6.7)$$

Where:

- C_a = concentration analyte (mol/L)
- Mol_a = moles of analyte
- V_{total} = total volume of solution (L)
- Df = dilution factor
- M_s = mass of sample (g)
- $M_{dioxane}$ = mass of 1,4-dioxane (g)
- M_{D_2O} = mass of D_2O (g)
- $\rho_{average}$ = average density of the solution (g/cm^3)
- ρ_s = density sample (g/cm^3)
- $\rho_{dioxane}$ = density 1,4-dioxane (g/cm^3)
- ρ_{D_2O} = density D_2O (g/cm^3)
- M_{total} = total mass of solution (g)

It was assumed that the density of the sample was the same as water ($1 g/cm^3$)

The yields and selectivities of the products were calculated with Equation 6.8 to 6.11.

$$Y_{GVL} = \frac{C_{LA,0} - C_{LA} - C_{4-HPA}}{C_{LA,0}} * 100 \quad (6.8)$$

$$Y_{4-HPA} = \frac{C_{LA,0} - C_{LA} - C_{GVL}}{C_{LA,0}} * 100 \quad (6.9)$$

$$S_{GVL} = \frac{Y_{GVL}}{X_{LA}} * 100 \quad (6.10)$$

$$S_{4-HPA} = \frac{Y_{4-HPA}}{X_{LA}} * 100 \quad (6.11)$$

Where:

- X_{LA} = conversion LA (%)
- $C_{LA,0}$ = initial concentration LA (mol/L)
- C_{LA} = concentration LA (mol/L)

| | |
|-------------|---------------------------------|
| Y_{GVL} | = yield GVL (%) |
| C_{4-HPA} | = concentration 4-HPA (mol/L) |
| Y_{4-HPA} | = yield 4-HPA (%) |
| C_{GVL} | = concentration GVL (mol/L) |
| S_{GVL} | = selectivity towards GVL (%) |
| S_{4-HPA} | = selectivity towards 4-HPA (%) |

6.1.3 Process calculations

The weight hourly space velocity was calculated with Equation 6.12.

$$WHSV = \frac{\Phi_v}{m_{cat}} * 60 \quad (6.12)$$

Where:

| | |
|-----------|--|
| $WHSV$ | = weight hourly space velocity ($g_{feed}/g_{cat} \cdot hr$) |
| Φ_v | = volumetric flow rate feed (mL/min) |
| m_{cat} | = mass of catalyst (g) |

The turnover frequency was calculated with Equation 6.13.

$$TOF = \frac{(C_{LA,0} - C_{LA}) * \Phi_v * M_{LA}}{m_{cat}} \quad (6.13)$$

Where:

| | |
|------------|--------------------------------------|
| TOF | = turnover frequency (g LA/g cat.hr) |
| $C_{LA,0}$ | = initial LA concentration (mol/L) |
| C_{LA} | = LA concentration (mol/L) |
| Φ_v | = volumetric flow rate feed (L/hr) |
| M_{LA} | = molar mass LA (g/mol) |
| m_{cat} | = mass of catalyst (g) |

The turnover number was calculated with Equation 6.14.

$$TON = TOF * t \quad (6.14)$$

Where:

| | |
|-------|--------------------------------|
| TON | = turnover number (g LA/g cat) |
| t | = time on stream (hr) |

The initial reaction rates were calculated with Equation 6.15.

$$R_0 = \frac{\Phi_v \cdot (C_{LA,0} - C_{LA})}{m_{cat}} \quad (6.15)$$

Where:

- R_0 = initial reaction rate (mol/min*g)
- Φ_v = volumetric flow rate feed (mL/min)
- $C_{LA,0}$ = initial LA concentration (mol/L)
- C_{LA} = LA concentration (mol/L)
- m_{cat} = mass of catalyst (g)



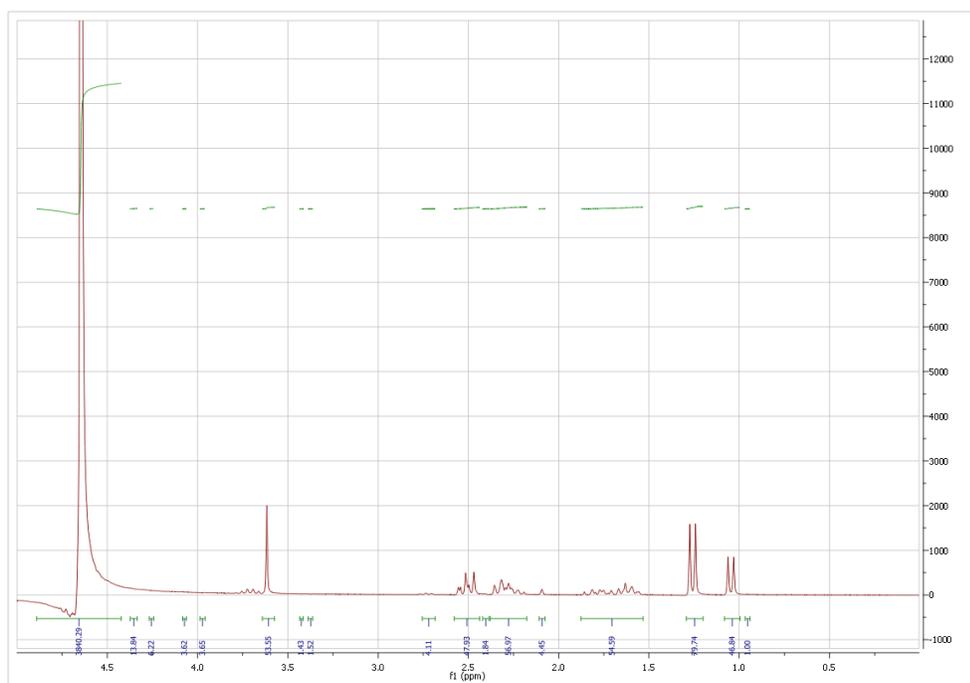
Spectrum 6.3: Hydrogenation reaction of LA using Ru/Al₂O₃ (0.3 wt.% Ru) at 2 hours on stream



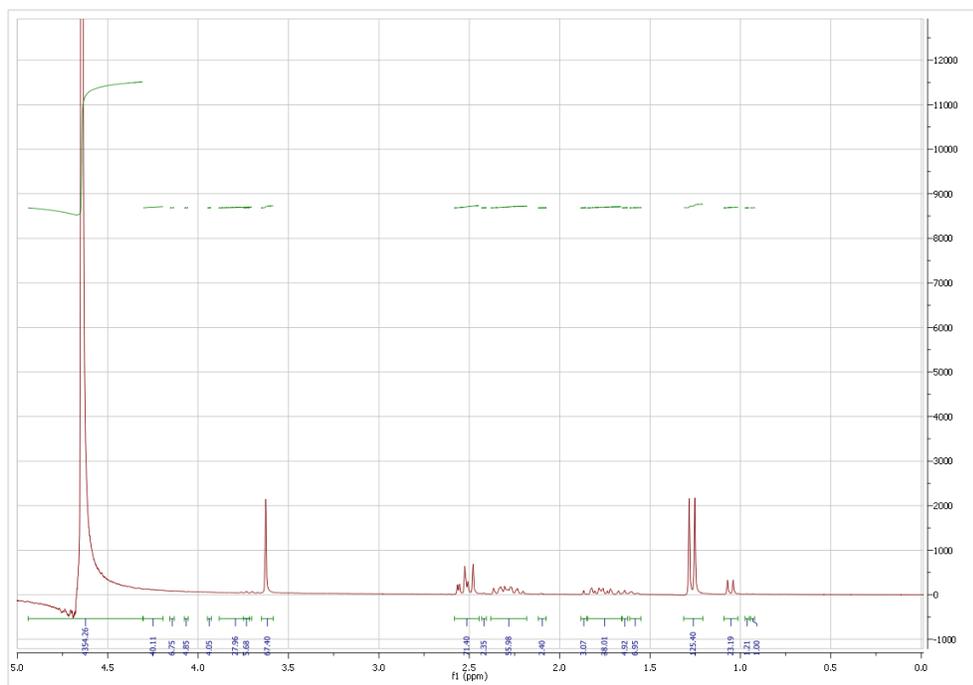
Spectrum 6.4: Hydrogenation reaction of LA using Ru/Al₂O₃ (0.5 wt.% Ru) at 2 hours on stream



Spectrum 6.5: Hydrogenation reaction of LA using Ru/C (0.5 wt.% Ru) at 2 hours on stream

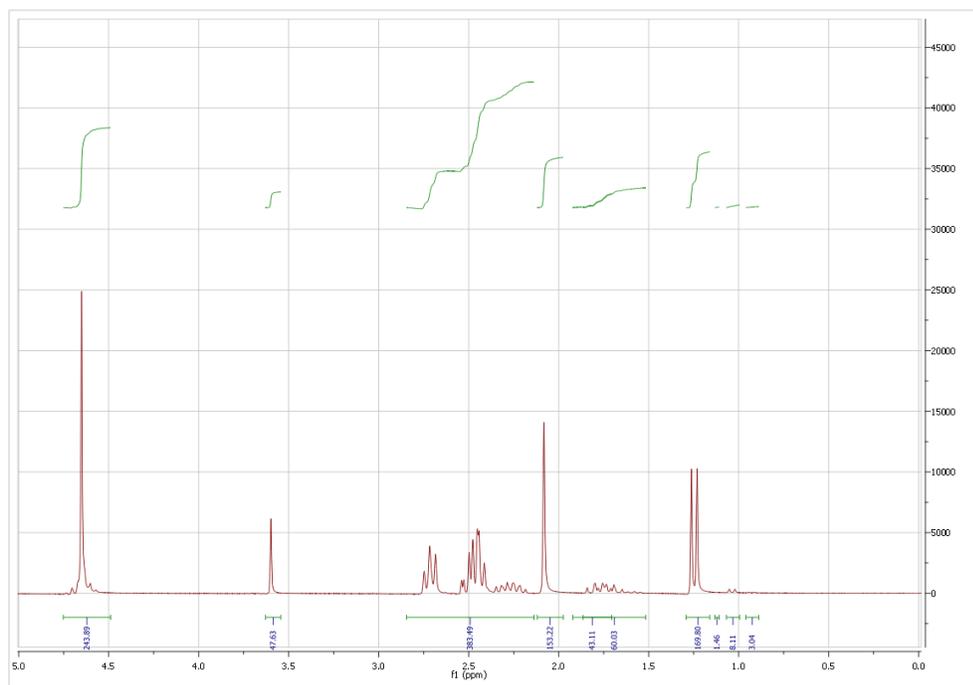


Spectrum 6.6: Hydrogenation reaction of LA using Ru/C (2 wt.% Ru) at 2 hours on stream

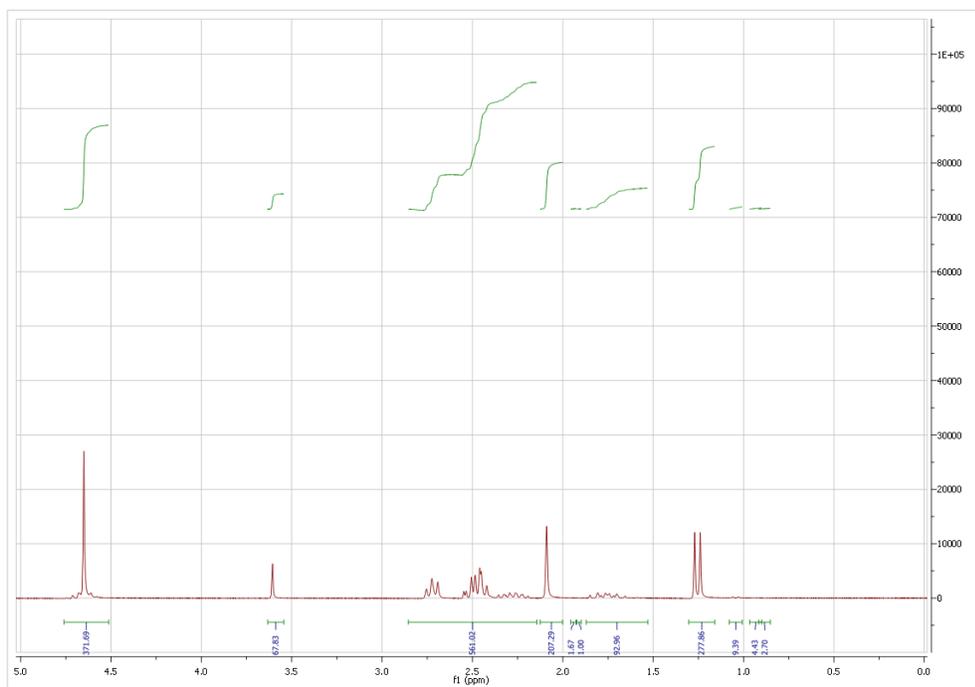


Spectrum 6.7: Hydrogenation reaction of LA using Ru/C (5 wt.% Ru) at 2 hours on stream

6.2.3 High LA concentration experiments



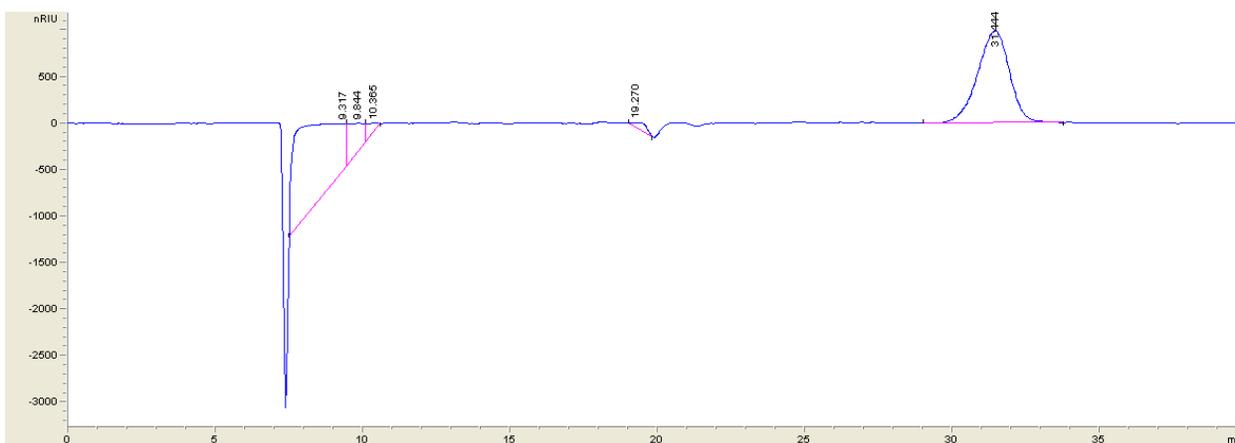
Spectrum 6.8: Hydrogenation reaction of 97 % LA using Ru/C (0.5 wt.% Ru) at 2 hours on stream



Spectrum 6.9: Hydrogenation reaction of 97 % LA using Ru/C (5 wt.% Ru) at 2 hours on stream

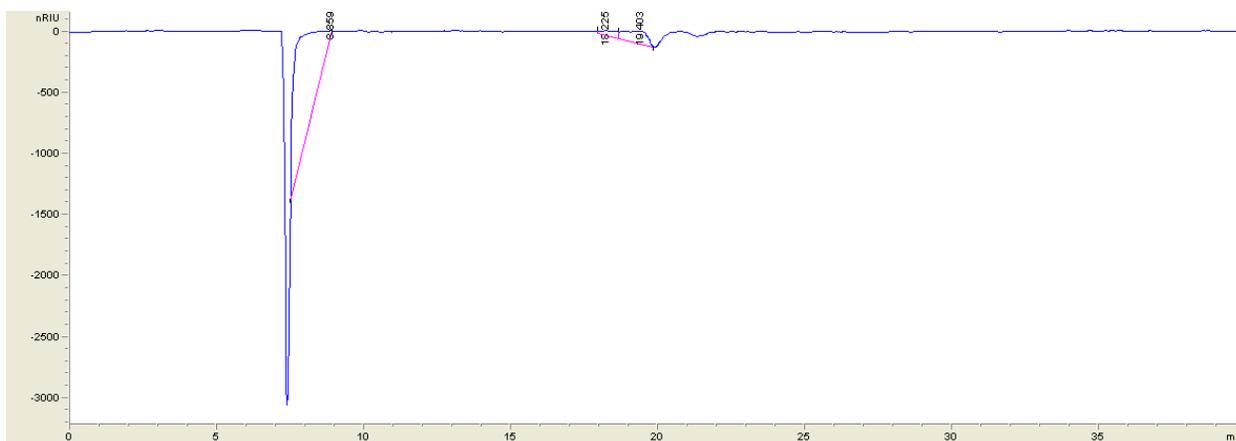
6.3 HPLC spectra

6.3.1 Initial experiments



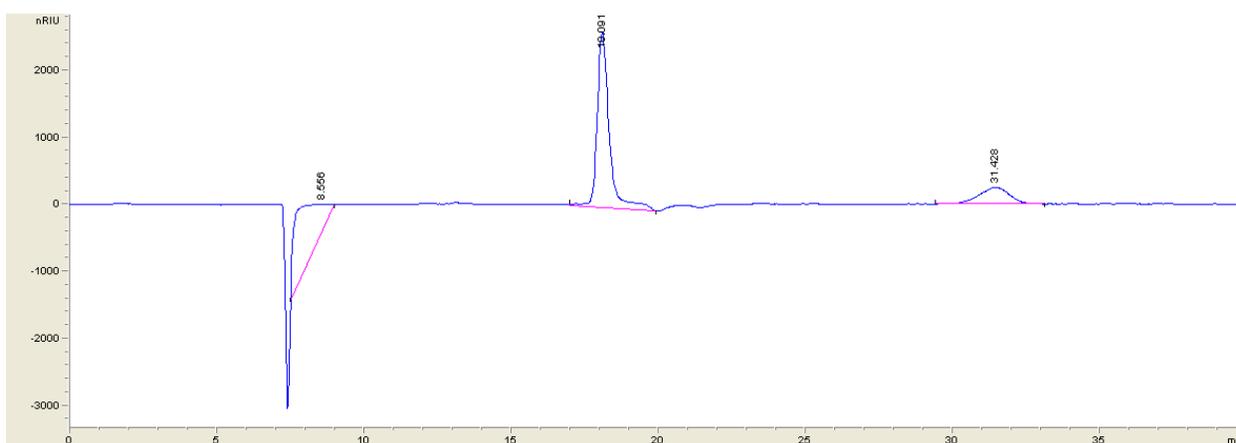
Spectrum 6.10: Hydrogenation reaction of LA at 130°C using Ru/C (0.5 wt.% Ru) at 2 hours on stream

The negative peak at approximately 20 minutes retention time was also observed in a measurement with only water, it is presumably caused by contamination of the HPLC column. The HPLC spectrum of the measurement with only water is shown in Spectrum 6.11.

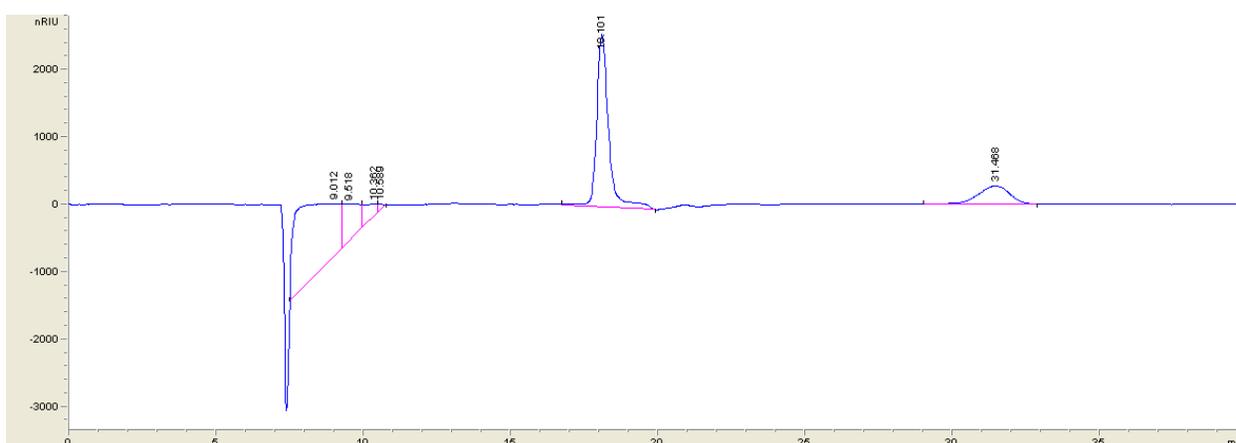


Spectrum 6.11: HPLC spectrum blank measurement with only water

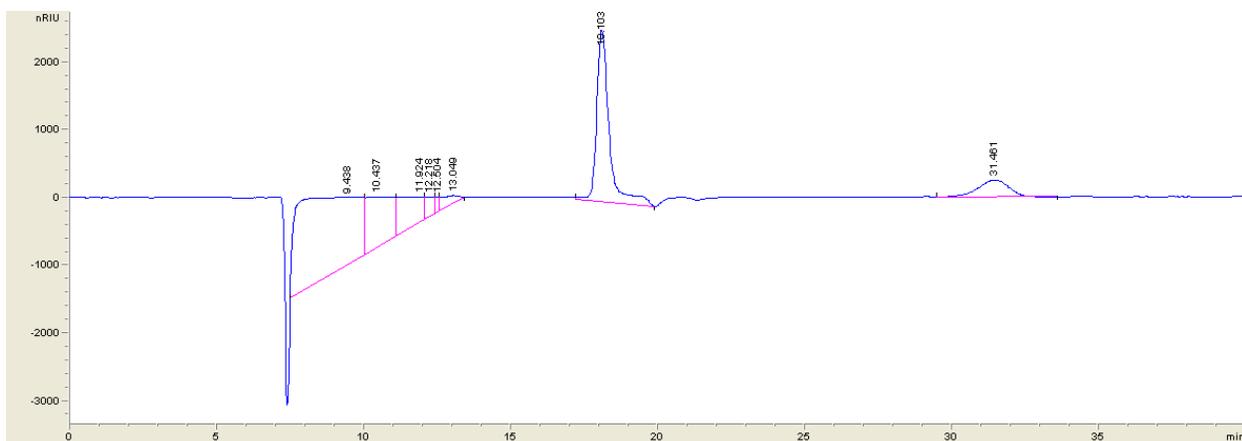
6.3.2 Catalyst screening



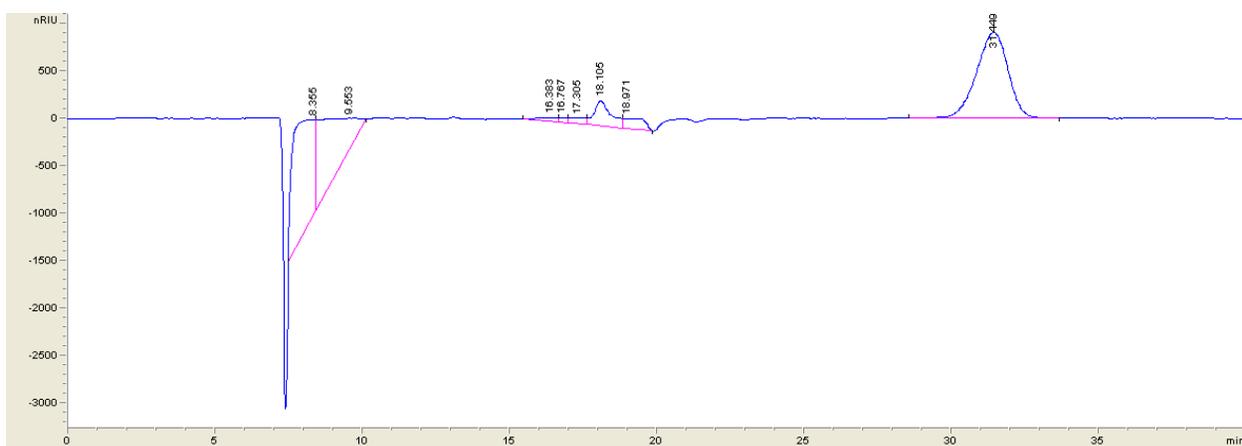
Spectrum 6.12: Hydrogenation reaction of LA at 90°C using Ru/TiO₂ (1 wt.% Ru) at 2 hours on stream



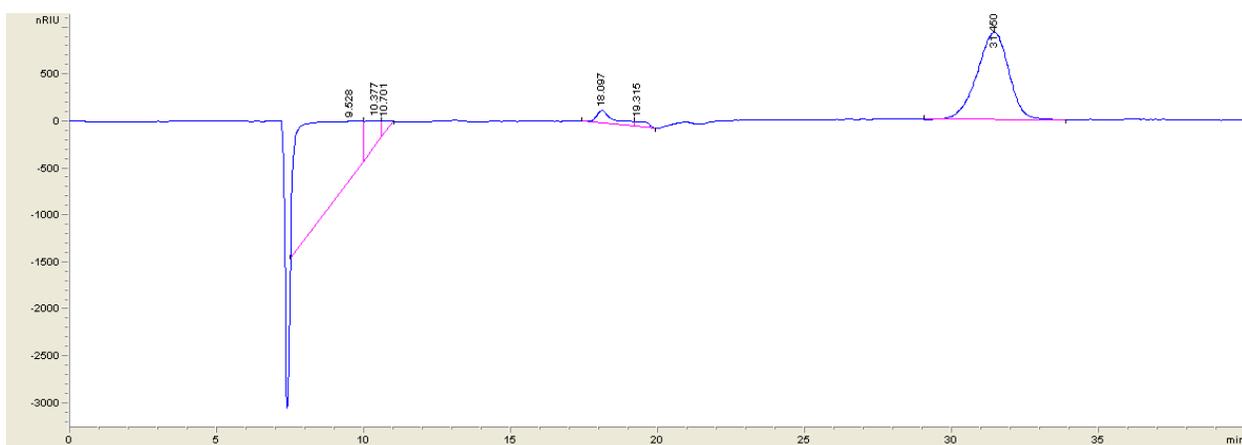
Spectrum 6.13: Hydrogenation reaction of LA at 90°C using Ru/Al₂O₃ (0.3 wt.% Ru) at 2 hours on stream



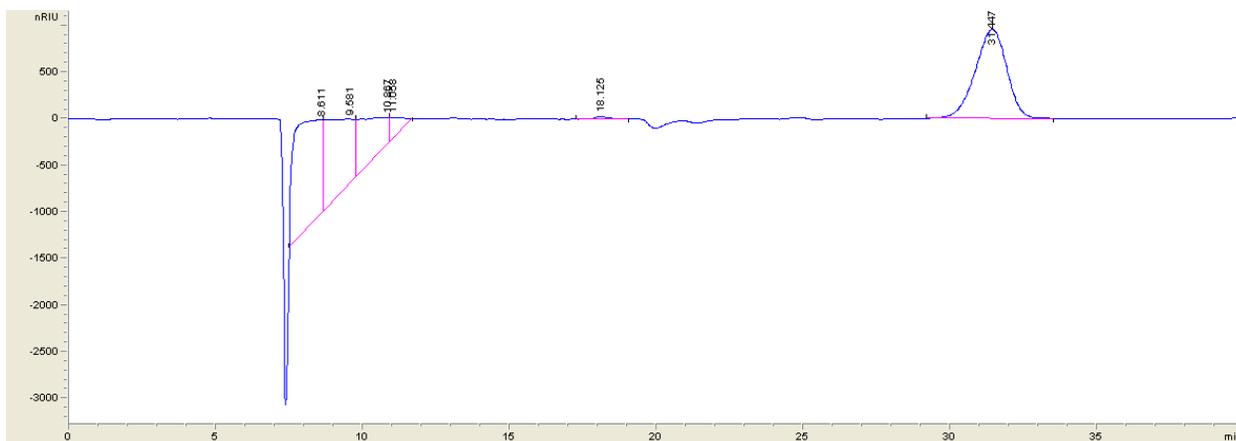
Spectrum 6.14: Hydrogenation reaction of LA using Ru/Al₂O₃ (0.5 wt.% Ru) at 2 hours on stream



Spectrum 6.15: Hydrogenation reaction of LA using Ru/C (0.5 wt.% Ru) at 2 hours on stream

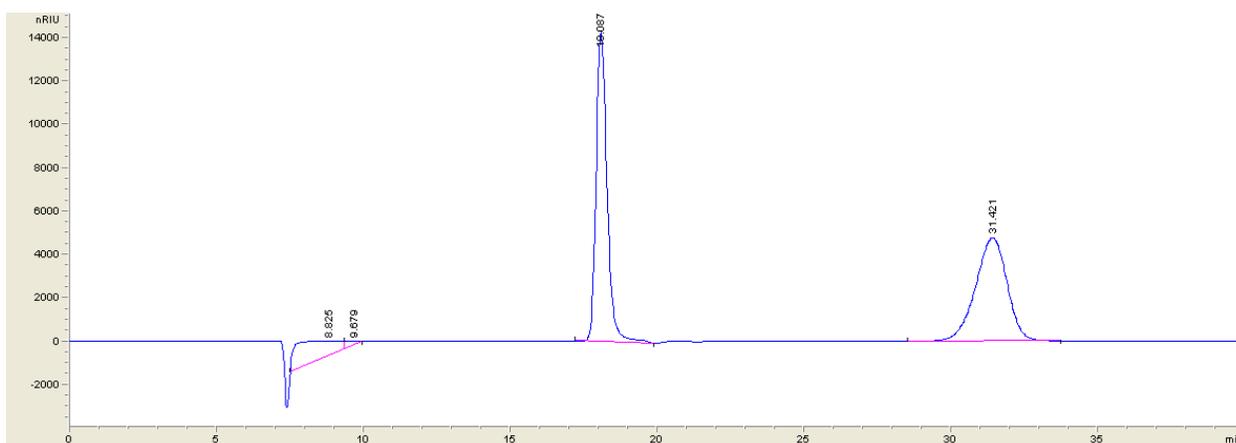


Spectrum 6.16: Hydrogenation reaction of LA using Ru/C (2 wt.% Ru) at 2 hours on stream

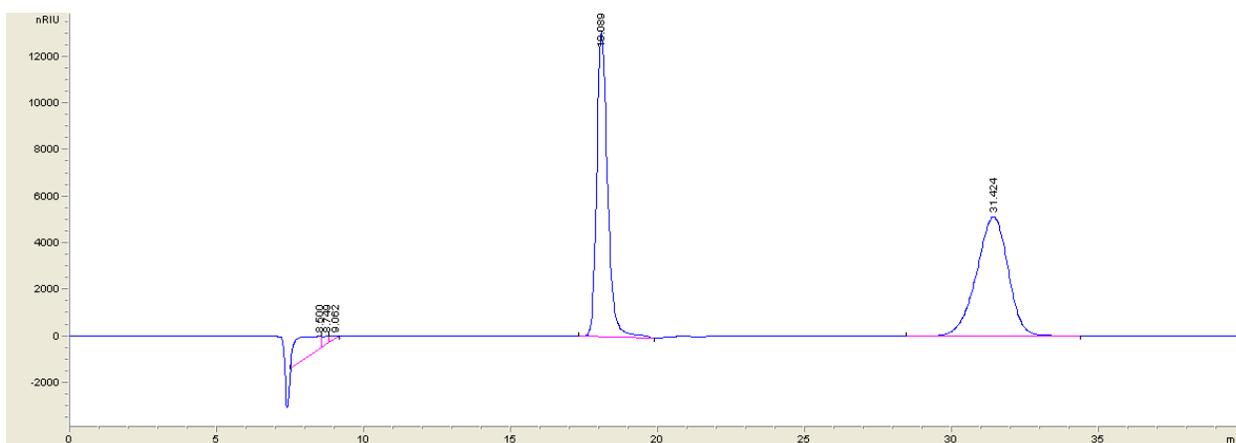


Spectrum 6.17: Hydrogenation reaction of LA using Ru/C (5 wt.% Ru) at 2 hours on stream

6.3.3 High LA concentration experiments



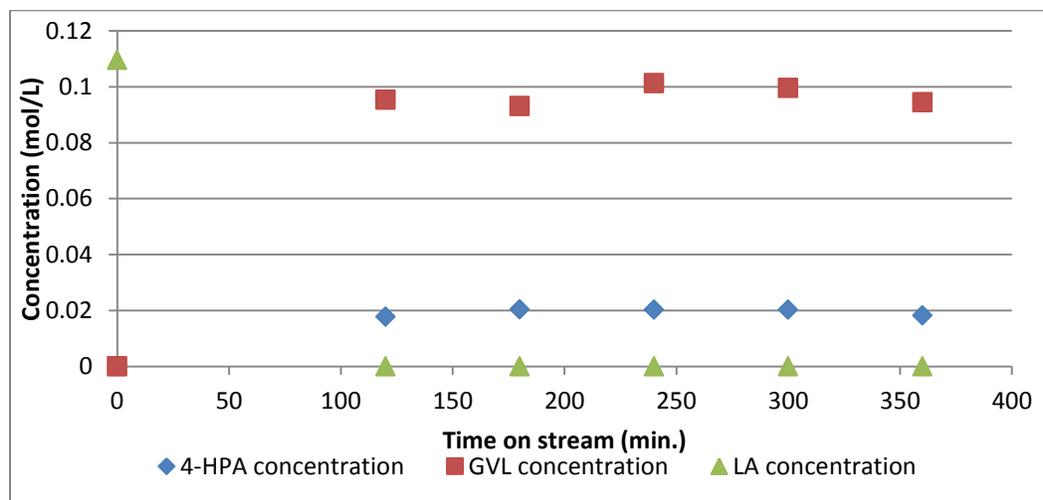
Spectrum 6.18: Hydrogenation reaction of 97% LA using Ru/C (0.5 wt.% Ru) at 2 hours on stream



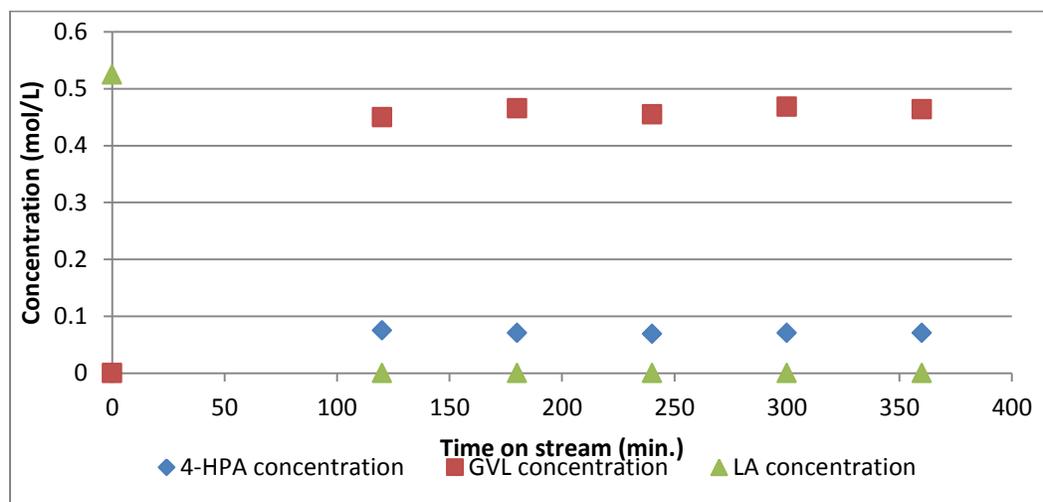
Spectrum 6.19: Hydrogenation reaction of 97% LA using Ru/C (5 wt.% Ru) at 2 hours on stream

6.4 Concentration profiles

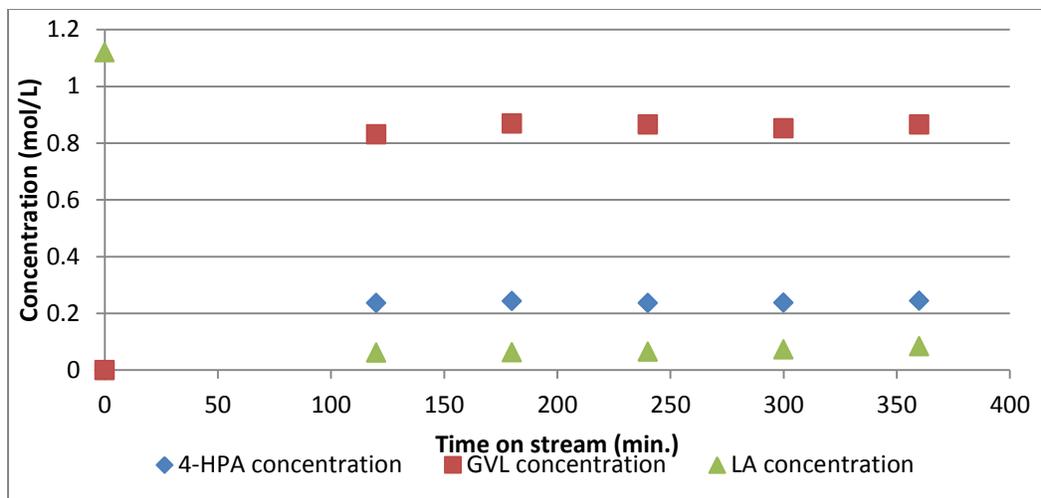
Graph 6.1 to 6.5 represent experiments performed with Ru/C with 0.5 wt.% of ruthenium.



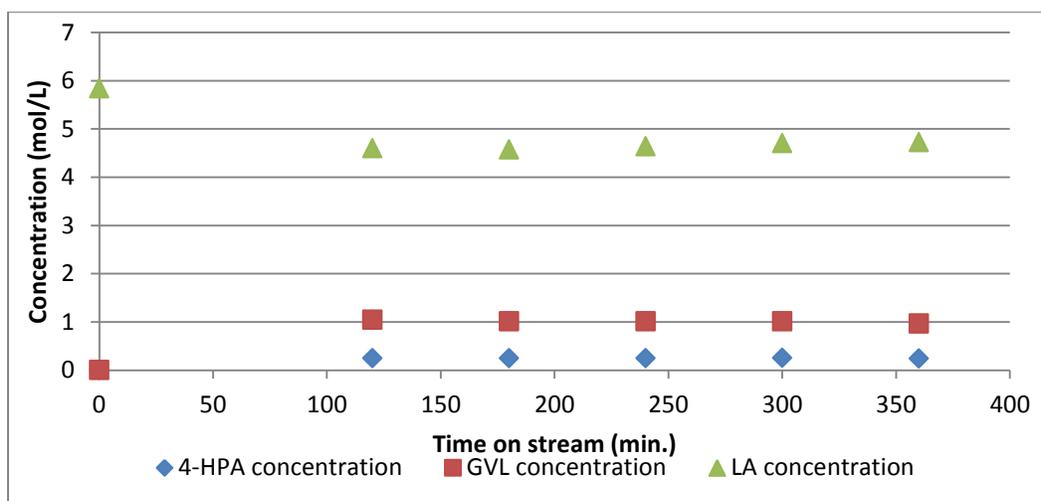
Graph 6.1: 0.1 mol/L LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (0.5 wt.% Ru)



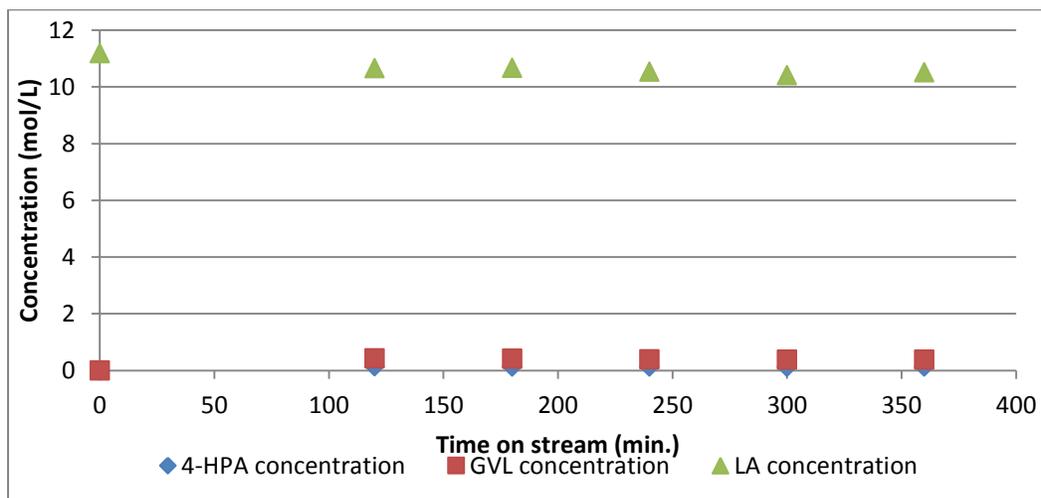
Graph 6.2: 0.5 mol/L LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (0.5 wt.% Ru)



Graph 6.3: 1 mol/L LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (0.5 wt.% Ru)

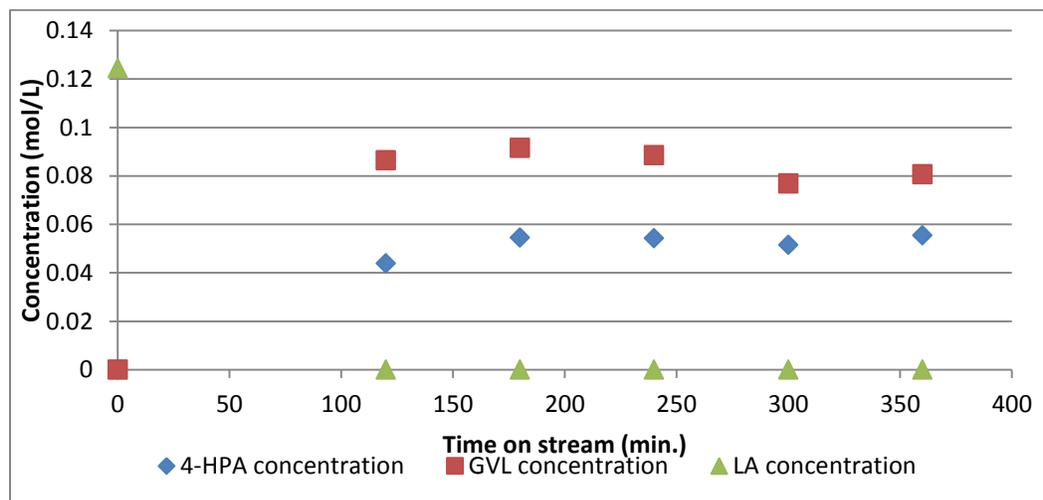


Graph 6.4: 5 mol/L LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (0.5 wt.% Ru)

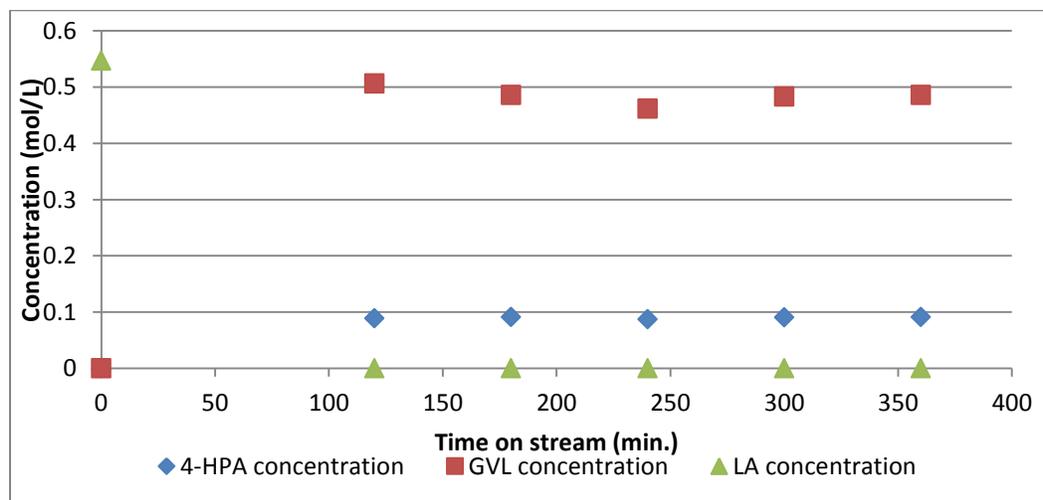


Graph 6.5: 97% LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (0.5 wt.% Ru)

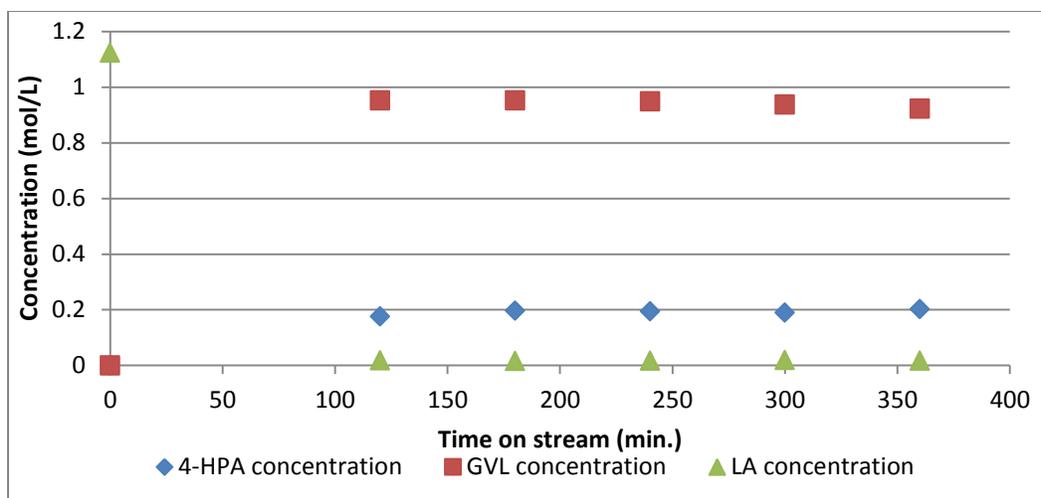
Graph 6.6 to 6.10 represent experiments performed Ru/C with 5 wt.% of ruthenium.



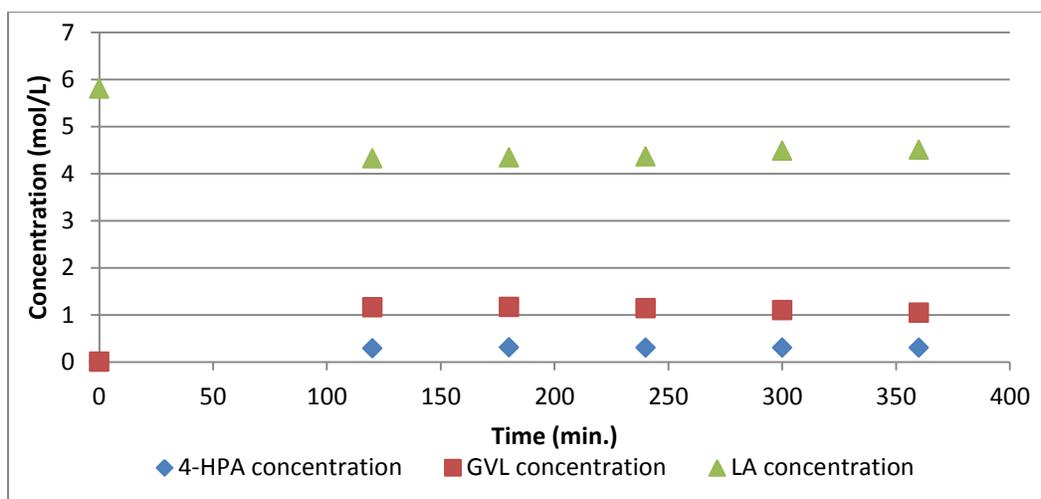
Graph 6.6: 0.1 mol/L LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (5 wt.% Ru)



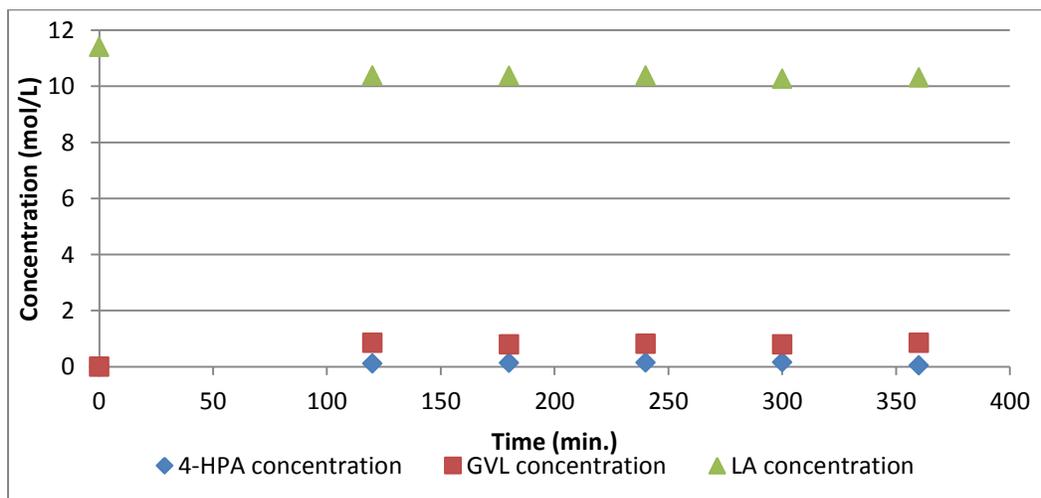
Graph 6.7: 0.5 mol/L LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (5 wt.% Ru)



Graph 6.8: 1 mol/L LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (5 wt.% Ru)



Graph 6.9: 5 mol/L LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (5 wt.% Ru)



Graph 6.10: 97% LA hydrogenation concentration profile at 90°C using Ru/C as catalyst (5 wt.% of Ru)

6.5 Overview experiments

Table 6.1: Overview experimental conditions and results

| Catalyst | Wt.% Ru | Mass catalyst (g) | Initial LA concentration (mol/L) | WHSV ($g_{\text{feed}}/g_{\text{cat}} \cdot \text{hr}$) | Temperature (°C) | Flow H ₂ (mL/min) | Duration (hr.) | LA conversion (%) | 4-HPA+ GVL Selectivity (%) | Mole balance closure (%) | Described in section |
|-----------------------------------|---------|-------------------|----------------------------------|---|------------------|------------------------------|----------------|-------------------|----------------------------|--------------------------|----------------------|
| Ru/C | 0.5 | 2.00 | 1.17 | 30 | 130 | 30 | 6 | 99 | 100 | 98.6 | 3.1.1 + 3.2.1 |
| Ru/C | 0.5 | 2.01 | 1.15 | 30 | 90 | 30 | 6 | 93 | 100 | 101.4 | 3.1.4 |
| Ru/TiO ₂ | 1 | 2.00 | 1.15 | 30 | 90 | 30 | 6 | 25 | 101 | 99.9 | 3.2 |
| Ru/Al ₂ O ₃ | 0.3 | 2.00 | 1.15 | 30 | 90 | 30 | 6 | 31 | 100 | 101.8 | 3.2 |
| Ru/Al ₂ O ₃ | 0.5 | 2.01 | 1.10 | 30 | 90 | 30 | 6 | 26 | 100 | 101.5 | 3.2 |
| Ru/C | 0.5 | 2.00 | 1.12 | 30 | 90 | 30 | 6 | 94 | 100 | 102.2 | 3.1.4 + 3.2 + 3.3 |
| Ru/C | 2 | 1.98 | 1.15 | 30 | 90 | 30 | 6 | 96 | 99 | 101.9 | 3.2 |
| Ru/C | 5 | 2.00 | 1.12 | 30 | 90 | 30 | 6 | 98 | 98 | 102.2 | 3.2 + 3.3 |
| Ru/C | 0.5 | 1.99 | 0.11 | 30 | 90 | 30 | 6 | 100 | 97 | 106.0 ^a | 3.3 |
| Ru/C | 0.5 | 2.03 | 0.52 | 30 | 90 | 30 | 6 | 100 | 100 | 101.3 | 3.3 |
| Ru/C | 0.5 | 1.95 | 5.83 | 30 | 90 | 30 | 6 | 20 | 101 | 101.1 | 3.3 |
| Ru/C | 0.5 | 2.00 | 11.19 | 30 | 90 | 30 | 6 | 6 | 101 | 99.2 | 3.3 |
| Ru/C | 5 | 1.94 | 0.12 | 30 | 90 | 30 | 6 | 100 | 97 | 109.9 ^a | 3.3 |
| Ru/C | 5 | 2.00 | 0.55 | 30 | 90 | 30 | 6 | 100 | 100 | 105.0 ^a | 3.3 |
| Ru/C | 5 | 2.00 | 5.80 | 30 | 90 | 30 | 6 | 24 | 101 | 100.3 | 3.3 |
| Ru/C | 5 | 2.00 | 11.41 | 30 | 90 | 30 | 6 | 9 | 106 | 101.0 | 3.3 |
| Ru/C | 0.5 | 5.00 | 11.19 | 12 | 150 | 120 | 6 | 54 | 104 | 102.8 | 3.4 |
| Ru/C | 5 | 5.00 | 11.12 | 12 | 150 | 120 | 6 | 57 | 103 | 102.1 | 3.4 |
| Ru/C | 0.5 | 2.00 | 1.16 | 30 | 90 | 30 | 52 | 95→82 | 100 | 99.7 | 3.5 |

^a High difference caused by measurement errors of ¹H-NMR (inaccurate at low concentrations). For all experiments: column pressure +/- 45 bar and volumetric flow rate feed +/- 1 mL/min.

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