



BUDAPESTI MŰSZAKI ÉS GAZDASÁGTUDOMÁNYI EGYETEM
VEGYÉSZMÉRNÖKI ÉS BIOMÉRNÖKI KAR

Separation studies on mixtures generated in biomass conversion

/Biomassza átalakítása során keletkező komponensek elválasztási lehetőségeinek vizsgálata/

Proposed theses based on PhD dissertation

Dávid Havasi

Department of Chemical and Environmental Process Engineering
Budapest University of Technology and Economics

Supervisor: Dr. László T. Mika

Department of Chemical and Environmental Process Engineering
Budapest University of Technology and Economics

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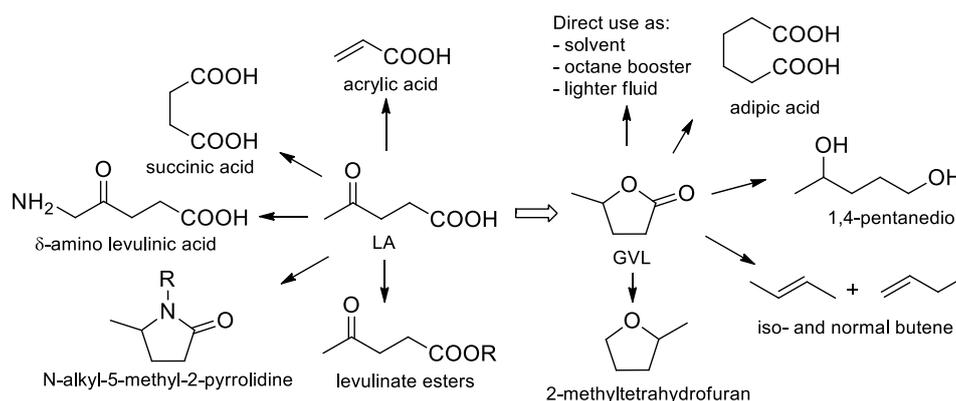
1. Introduction

The production of chemicals and therefore most of nowadays consumer goods require fossil materials. In the past decades various researches aimed on finding technologies that could provide similar materials from alternative, renewable sources.

The increasing life standards and population continuously elevates the demand for fossil resources which not only speeds up the use of limited materials, but also generates more and more wastes. Therefore, the development of biomass based chemical technologies and researches focusing on the application of biomass wastes is gathering more attention from the industrial sector. Recently, a variety of platform chemicals has been identified, that could partially or completely replace certain fossil-derived chemicals.

Such platform chemicals are levulinic acid (LA) ¹ and its esters (e.g. methyl-, ethyl- and 2-propyllevulinate) that could be directly generated from biomass wastes, and γ -valerolactone (GVL) gathered from their catalytic conversion. ²

The possible application of these molecules directly or as raw material for other chemicals were investigated by various researches, some selected uses are shown in the following figure (Fig. 1).



1. Figure Some possible uses of LA and GVL³

Similarly to other chemical technologies, the final costs are greatly affected by the efficiency of the required separation and recirculation steps. Although various researches focused on the production and application of these chemicals, the separation

¹ Bozell, J. J.; Moens, L.; Elliott, D. C.; Wang, Y.; Neuenschwander, G. G.; Fitzpatrick, S. W.; Bilski, R. J.; Jarnefeld, J. L. *Resour. Conserv. Recy.* **2000**, 28, 227-239.

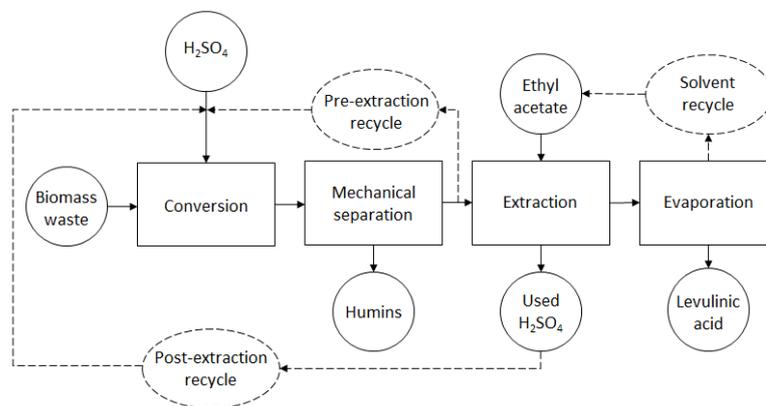
² Horváth, I. T.; Mehdi, H.; Fábos, V.; Mika, L. T. *Green Chem.* **2008**, 2, 238-242.

³ (a) Girisuta, B.; Janssen, L. P. B. M.; Heeres, H. J. *Chem. Eng. Res. Des.* **2006**, 84, 339-349.; (b) Mika, L. T.; Cséfalvay, E.; Németh, Á. *Chem. Rev.* **2017**, DOI: 10.1021/acs.chemrev.7b00395

and recirculation steps were so far studied only in limited cases.

LA can be produced from mono-, di- and polysaccharides, and also from food and agricultural wastes that contain such materials by acid catalysed hydrolysis. In practice, the acid catalyst could be sulfuric acid, while for heating conventional and microwave assistance are suitable.⁴ Literature data shows that various materials could be applied for the generation of LA with such acid solutions.⁵ After the conversion the products and by-products are present in the aqueous solution.

After the extraction of the final product, the aqueous catalyst solution would be the largest waste of the conversion. The reuse of this solution would greatly decrease the environmental effect and material demand of the process; however, no detailed information is available on the effects of the reuse. In the present work my aim was to investigate the possible reuse of sulfuric acid in the production of LA (Fig. 2).

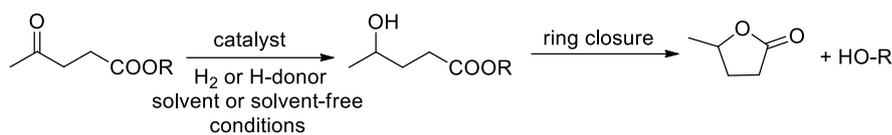


2. Figure The acid catalysed production of LA, showing the possible reuse routes of sulfuric acid (dashed)

The LA gathered from biomass wastes and the esters generated from it in the presence of acid catalyst and alcohol, could be converted to GVL via catalytic hydrogenation. For these reaction different homogeneous and heterogeneous catalysts and hydrogen sources could be applied, including molecular hydrogen, formic acid and 2-propanol. The reactions provide different mixture compositions, however in most cases 100% conversion could be achieved. The following figure shows some of the possible reaction routes along with the by-products (Fig. 3).

⁴ Szabolcs, Á.; Molnár, M.; Dibó, G.; Mika, L. T. *Green Chem.* **2013**, *15*, 439–445.

⁵ (a) Antonetti, C.; Licursi, D.; Fulignati, S.; Valentini, G.; Galetti, A. M. R. *Catalysts* **2016**, *6*, 196 – 224; (b) Tukacs, J. M.; Holló, A. T.; Rétfalvi, N.; Cséfalvay, E.; Dibó, G.; Havasi, D.; Mika, L. T. *ChemistrySelect* **2017**, *2*, 1375-1380.



R	starting material	by-product	solvent	H-donor
H	levulinic acid	water	water	HCOOH
-CH ₃	methyl levulinate	methanol	GVL	2-propanol
-C ₂ H ₅	ethyl levulinate	ethanol	2-propanol	
-C ₃ H ₇	2-propyl levulinate	2-propanol		

3. Figure Selected routes for producing GVL with different H-donors and raw materials (LA and esters)

The overall efficiency of producing GVL is mainly affected by the separation of the final product mixture, therefore the comparison of separations could help choosing the most suitable reaction route. Apart from the dissolved or heterogeneous catalysts, the final mixture is composed of liquids and considering their ratios, a distillation process could be considered for product purification. The proper design and software modelling of such columns require certain thermodynamic data.

The vapor-liquid equilibria (VLE) of mixtures containing GVL were not available so far and therefore the experimental investigation of binary mixtures is required. With the experiments, the possible liquid-liquid equilibria and azeotrope formation could also be observed, which could require alternative or special separation units. In the present work I investigated the VLE of five binary mixtures that contained GVL.

Nowadays for the investigation of VLE vapor condensate and liquid circulation stills are applied,⁶ that allow the simultaneous sampling of both vapor and liquid phases. The stills presented in most researches are usually applied to mixtures where the boiling point of the pure compounds show only a smaller difference (usually below 100 °C).

Since the boiling point of GVL is more than 100 °C higher than all of the other investigated compounds (water, methanol, ethanol, 2-propanol and formic acid), an equilibrium still redesigned in the present work was applied for the experiments. Experimental VLE data should usually be tested for thermodynamic consistency, for which the original⁷ and modified⁸ Herington tests and the L-W test⁹ proposed by Wisniak was applied.

⁶ Malanowski, S. *Fluid Phase Equilibria* **1982**, 8, 197-219.

⁷ Herington, E. F. G. *Inst. Petrol. J.* **1951**, 37, 457-470

⁸ Wisniak, J. *Ind. Eng. Chem. Res.* **1993**, 32, 1531-1533

⁹ Wisniak, J. *Ind. Eng. Chem. Res.* **1994**, 33, 177-180.

2. Experimental procedures

The possible reuse of sulfuric acid in the production of LA was investigated in Ace Glass pressure tubes with PTFE sealing by applying conventional heating and magnetic stirring. By each reaction 500 mg of biomass was mixed in 10 mL of $2 \text{ mol} \times \text{dm}^{-3}$ aqueous sulfuric acid solution and the mixture was heated to $170 \text{ }^\circ\text{C}$ for 8 hours. First, D-fructose was applied as a model substrate, then as “real” biomass waste cooked tea leaves and a mixture of different wastes (vegetable- and fruit peels, spent coffee grounds and cooked tea leaves). The biomass materials were grinded to $<2 \text{ mm}$ particle size and dried at $105 \text{ }^\circ\text{C}$.

The conversion of biomass to LA generates solid by-products, that were separated with a G3 glass filter, the final product was extracted with ethyl acetate. The product yields were determined with a Shimadzu GCMS-QP2010 SE gas chromatograph, equipped with mass spectrometer and a Bruker Avance-250 NMR spectrometer.

For the VLE experiments first a still designed by Manczinger and Tettamanti was applied,¹⁰ then after equipping certain modifications, the tests were started with the water-GVL system. Based on the first experiments the equilibrium still was redesigned in AutoCAD and the new equipment was applied for the VLE experiments.

The composition of the VLE samples was determined with a Zeiss Abbe type G thermostated refractometer. Since all the investigated compounds showed a greater difference in refractive indices to GVL and the indices changed monotonically with the concentration, the method was found suitable for my experiments. The composition of certain mixtures was checked with a HP 6890N gas chromatograph equipped with a FID detector and with the previously mentioned GCMS and NMR equipments.

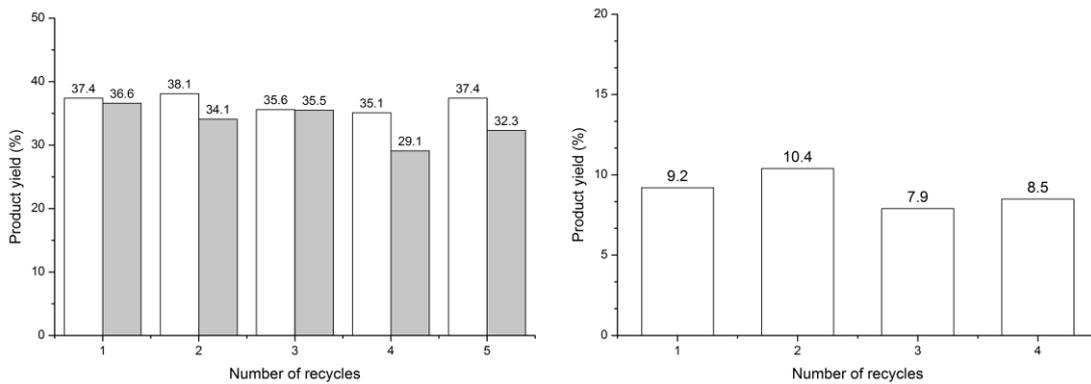
The experimentally determined VLE data were used in ChemCAD[®] (7.1.4.10142) to gather binary interaction parameters. Based on these parameters the optimization of different separations could be performed and compared.

¹⁰ Manczinger, J.; Tettamanti, K. *Period. Polytech. Chem. Eng.* **1966**, *10*, 183-195.

3. Results

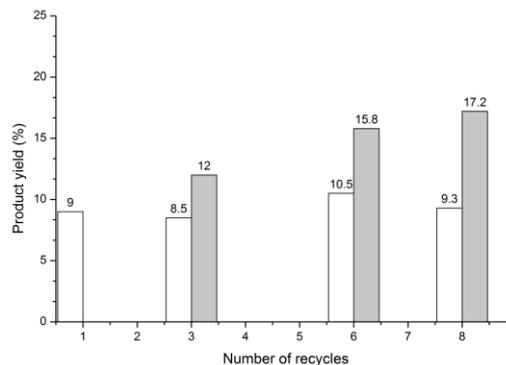
Two possible recycling routes were identified in the acid catalysed hydrolysis of biomass to LA: after the separation of solid by-products the aqueous phase could be fed back to the reactor without extracting the LA (pre-extraction recycle) or the product can be extracted, and the catalyst solution could be reused (post-extraction recycle). The results show that both routes could be chosen without significant change in the LA yield.

By applying D-fructose as raw material, the LA yield did not change after five reuses by both pre- and post-extraction recycling. The post-extraction route was further investigated with cooked tea leaves, where no significant change was found after four reuses (Fig. 4 shows the results with D-fructose and cooked tea leaves).



4. Figure The comparison of the two identified recycle routes with D-fructose and the results of post-extraction recycle with cooked tea leaves

When applying the prepared biomass waste mix (BWM), a maximum of eight pre-extraction reuses were performed without change in the LA yield. After the extraction, the acid solutions were once again reintroduced to the reactor and the new step showed elevated yields (Fig. 5).



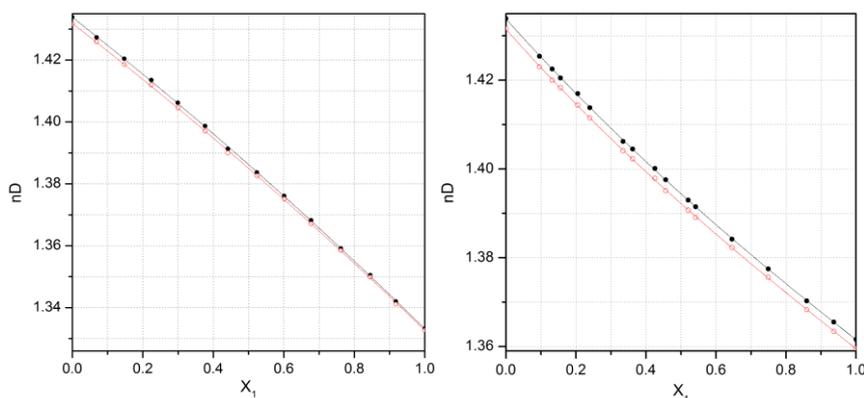
5. Figure LA yields with BWM by pre-extraction recycle (white bars) and an additional post extraction reuse (grey bars).

The boiling temperatures of GVL was investigated between 0.67 and 101.19

kPa with the modified equilibrium still. The data were used to define constants for the Antoine equation and to calculate the temperature independent heat of vaporization of GVL. The results showed a good fit to other literature data.

In a recently published study¹¹ (Ruzicka) the available vapor pressures of GVL were compared, including my experimental data. The results showed that the data published by Zaitseva et.al.¹² and from my work 10 of 14 data points (between 10.3 and 101.19 kPa) were consistent with the new experimental data and calculations. The four excluded data points were measured at smaller pressures (0.67 and 5.07 kPa) where the uncertainty has a greater effect. The experimental vapor pressure data showed a good fit to the results provided by Zaitseva et.al.

The composition of the binary equilibrium samples was determined with refractometry. Therefore, the refractive indices of the five investigated mixtures (water-GVL, methanol-GVL, ethanol-GVL, 2-propanol-GVL and formic acid-GVL) were investigated in the whole concentration spectra at 20 and 25 °C with a thermostated refractometer (Fig. 6).

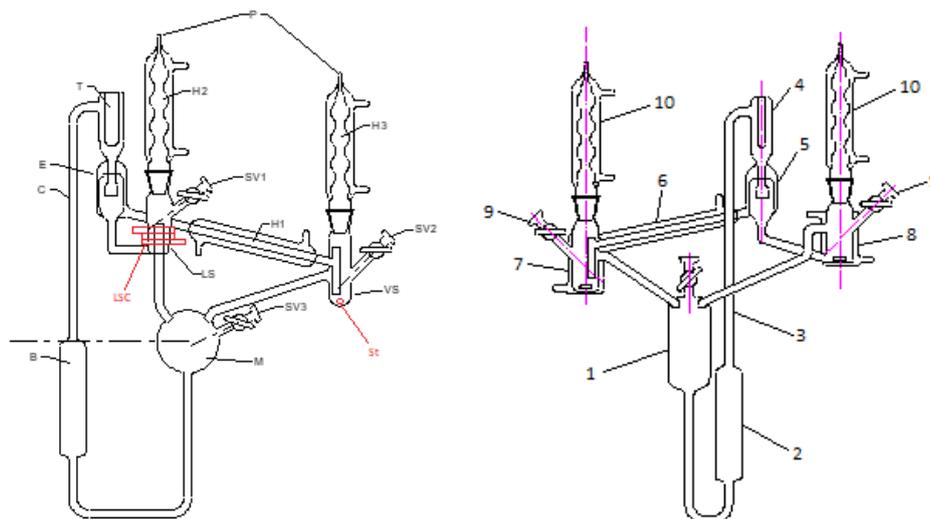


6. Figure The refractive indices of water-GVL and ethanol-GVL by different compositions (mass fraction; red – 25 °C, black – 20 °C)

Although the modified still was found good for investigating the equilibrium of water and GVL, based on the experiences the still was redesigned (Fig. 7 shows the modified and the redesigned equilibrium stills). The redesigned still was tested with the mixture of ethanol and ethylene glycol (as a mixture with greater difference between boiling points) and comparison with literature data showed good results.

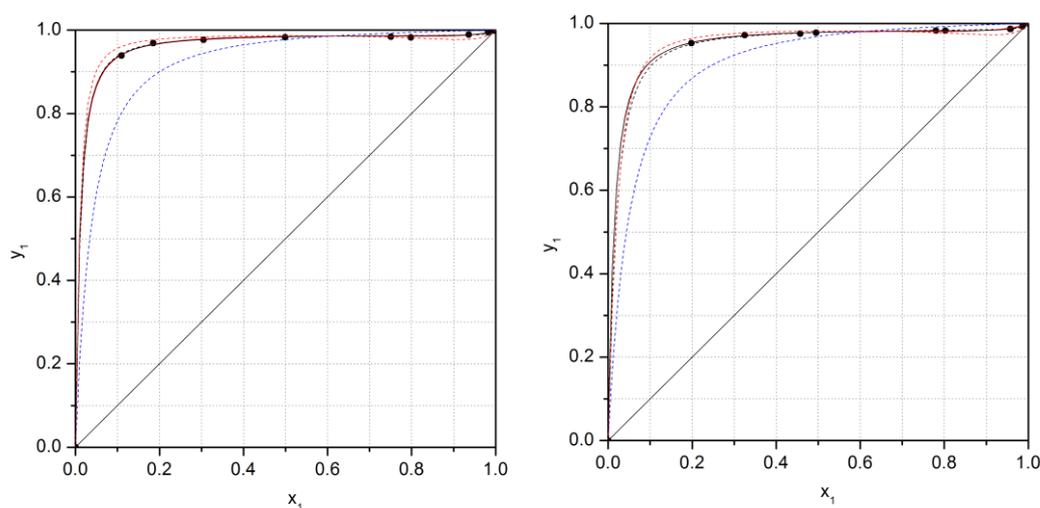
¹¹ Pokorny, V.; Stejfa, V.; Fulem, M.; Cervinka, C.; Ruzicka, K. *J. Chem. Eng. Data* **2017**, *62*, 4174-4186.

¹² Zaitseva, A.; Pokki, J.-P.; Le, H. Q.; Alopaeus, V.; Sixta, H. *J. Chem. Eng. Data* **2016**, *61*, 881-890.



7. Figure The modified (liquid sampler cooling (LSC), stirring of vapor sampler (St), sampling valves (SV1-2)) and the redesigned still with duplicated sampler walls (7-8), stirring by both samplers, cylinder shaped container (1)

The vapor-liquid equilibrium of GVL with water, ethanol, methanol, 2-propanol and water was investigated. By the mixtures containing water the experiments were performed at 10, 51 and 101 kPa (Fig. 8). The results showed that water does not form azeotrope with GVL, they could be completely separated from each other. Simultaneously to my experiments, Zaitseva et.al.¹³ published isothermal equilibrium data for the system water-GVL, where similar observations were made.



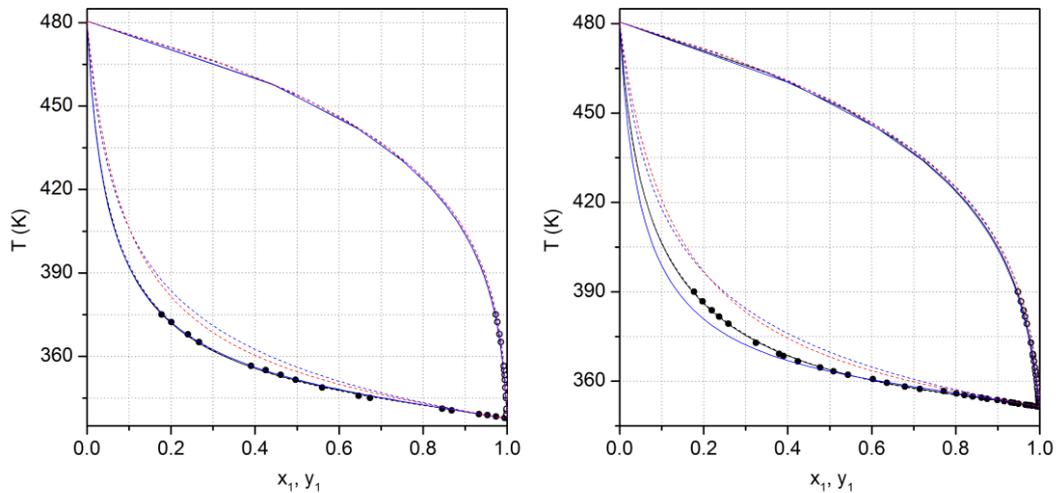
8. Figure The x-y plot of water and GVL at 10 and 51 kPa. (●) – experimental data; (---) – Ideal Vapor Pressure calculations; (---) – Modified UNIFAC model calculations; Equilibrium curves calculated with activity coefficient models (based on experimental data): (—) – NRTL; (---) – Wilson; (---) - UNIQUAC

The behaviour of the water deviated from the ideal behaviour, showing a posi-

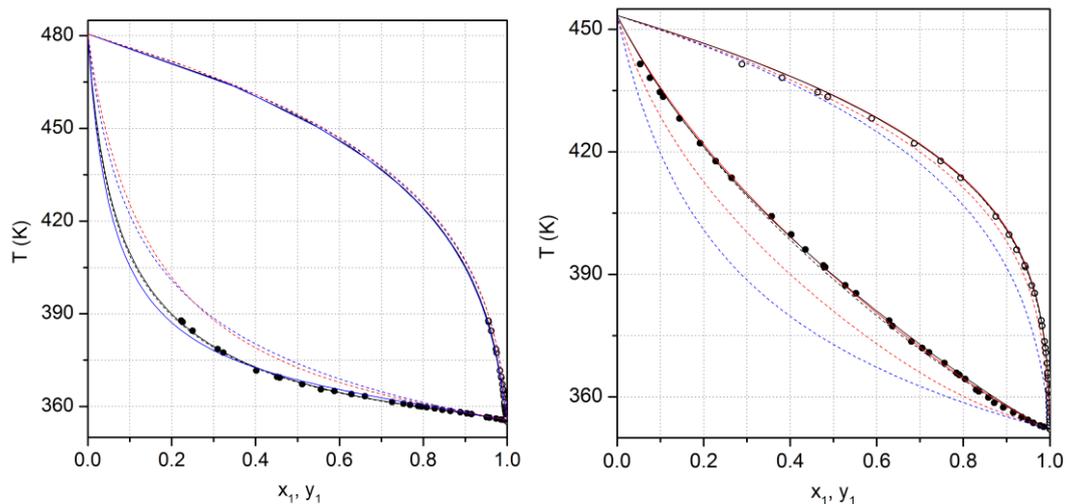
¹³ Zaitseva, A.; Pokki, J.-P.; Le, H. Q.; Alopaeus, V.; Sixta, H. *J. Chem. Eng. Data* **2016**, *61*, 881-890.

tive deviation in most of the concentration range, however by small GVL concentrations a pinch tangent is visible.

The equilibrium of GVL with methanol, ethanol (Fig. 9) and 2-propanol (Fig. 10) was investigated at 101 kPa. The results showed that none of these alcohols form azeotrope with GVL and all show a positive deviation from the ideal behaviour.



9. Figure The T-x-y plot of methanol and ethanol with GVL at 101 kPa. (●) – experimental data; (- -) – Ideal Vapor Pressure calculations; (- · -) – Modified UNIFAC model calculations; Equilibrium curves calculated with activity coefficient models (based on experimental data): (–) – NRTL; (- -) – Wilson; (—) – UNIQUAC



10. Figure The T-x-y plot of methanol with GVL at 101 kPa, and formic acid with GVL at 51 kPa. (●) – experimental data; (- -) – Ideal Vapor Pressure calculations; (- · -) – Modified UNIFAC model calculations; Equilibrium curves calculated with activity coefficient models (based on experimental data): (–) – NRTL; (- -) – Wilson; (—) – UNIQUAC

The equilibrium of formic acid and GVL was investigated at 51 kPa to avoid interaction with moisture in the air. The results show that this mixture does not form azeotrope (Fig. 10). The mixture shows negative deviation from the ideal behaviour, possibly due to secondary bonds.

All the experimental data were tested with the original Herington test,¹⁴ since it is still applied by NIST (National Institute of Standards and Technology) for preliminary testing data before publication. I also applied the modified version of the Herington test¹⁵ and the L-W integral and point-to-point tests.¹⁶ The results of the consistency could only show probable consistency and inconsistency; however, the L-W test was also performed for the UNIFAC model generated data and the results were compared with the ones gathered for the experimental data. Although not all the data could fulfil the consistency criteria, the similarity of experimental and UNIFAC results suggest a possible consistency.

Based on the gathered VLE data binary interaction parameters for Wilson, NRTL and UNIQUAC activity coefficient models, that could be used for software modelling of separations.

By using these parameters, the separation of 13 different mixtures containing GVL were compared. Based on primary considerations the following GVL production routes could be chosen: when conversion with the least reaction steps is considered, the direct conversion of LA with molecular hydrogen could be suitable; when an easier separation is required, the hydrogenation of methyl levulinate could be chosen. When high pressures should be avoided, the transfer hydrogenation of LA with 2-propanol or formic acid could be considered, the latter resulting less separable components. If the separation of by-products is also important, then the transfer hydrogenation of 2-propyl levulinate with 2-propanol could be selected, as it only generates a binary or ternary mixture.

¹⁴ Herington, E. F. G. *Inst. Petrol. J.* **1951**, 37, 457-470.

¹⁵ Wisniak, J. *Ind. Eng. Chem. Res.* **1994**, 33, 177-180.

¹⁶ Wisniak, J. *Ind. Eng. Chem. Res.* **1993**, 32, 1531-1533.

4. Proposed theses

1. I investigated the possible recycle of the aqueous sulfuric acid catalyst solution in the production of levulinic acid. I showed that the solution could be recycle multiple times by applying either model substrates or real biomass wastes. At least 9 consequent reuses could be performed.

Publication related to proposed thesis: **H4**

2. I determined the refractive indexes of 5 different GVL-containing binary mixture in the whole concentration range at two different temperatures. The results show that the refractive indexes change monotonically in the whole concentration range.

Publication related to proposed thesis: **H1, H2, H3**

3. I investigated the vapor-liquid equilibrium of water and GVL under isobaric conditions at three different pressures. It was shown that the mixture does not form azeotrope and shows a positive deviation from the ideal behaviour in most of the concentration range. Independent to the experiments, parallel to the publication process, a separate research group performed the isothermal investigation of the same mixture¹⁷ where the non-azeotropic behaviour was confirmed.

Publication related to proposed thesis: **H1**

4. I investigated the isobaric vapor-liquid equilibrium of GVL with methanol, ethanol and 2-propanol, where no azeotrope formation was observed, and all the mixtures showed positive deviation from the ideal behaviour.

Publication related to proposed thesis: **H2**

5. I investigated the vapor-liquid equilibrium of formic acid and GVL at reduced pressure. It was shown that the mixture does not form azeotrope and shows a negative deviation from the ideal behaviour, while the vapor-phase association of formic acid was observed.

Publication related to proposed thesis: **H3**

¹⁷ Zaitseva, A.; Pokki, J.-P.; Le, H. Q.; Alopaeus, V.; Sixta, H. *J. Chem. Eng. Data* **2016**, *61*, 881-890.

5. Possible applications

The experimental results show that the sulfuric acid applied for producing LA could be reused multiple times in the process without decreasing the yield of LA. Therefore, the material demand of the process and the amount of generated wastes could be reduced. With the two recycle routes different strategies could be made for achieving the most optimal LA yield.

The redesigned VLE still could be used for investigating binary mixtures, including other systems with GVL or with components that have greater difference between their boiling points.

The refractive indices of mixture containing GVL could be used for the analysis of binary mixture compositions in future equilibrium measurements.

The VLE data and the binary interaction parameters gathered by their use could be applied in the software modelling and design of separation units, concerning such mixtures. The results could help identifying the most suitable GVL production line by giving a primary comparison of the separation steps.

Since none of the investigated mixtures showed azeotrope formation, GVL could be completely separated from mixtures that contain water, methanol, ethanol, 2-propanol or formic acid.

The results of recirculation and VLE experiments could help in designing and improving an efficient, biomass-based GVL production line.

6. Publications and lectures

Publications related to theses

H4. Havasi, D., Pátzay, Gy., Stelén, G., Tukacs, J. M., Mika, L. T. Recycling of Sulfuric Acid in the Valorization of Biomass Residues. *Per. Pol. Chem. Eng.* **2017**, *61*, 283–287. (<https://doi.org/10.3311/PPch.11175>) /90%; IF (2018): 0.877/ (Q3), Independent citation: 1

H3. Havasi, D., Hajnal, Á., Pátzay, Gy., Mika, L. T. Vapor–Liquid Equilibrium of γ -Valerolactone and Formic Acid at $p = 51$ kPa. *J. Chem. Eng. Data* **2017**, *62*, 1058–1062. (<https://doi.org/10.1021/acs.jced.6b00867>) /70%; IF (2017): 2.196/ (Q1, D1)

H2. Havasi, D., Pátzay, Gy., Kolarovszki, Z., Mika, L. T. Isobaric Vapor–Liquid Equilibria for Binary Mixtures of γ -Valerolactone + Methanol, Ethanol, and 2-Propanol. *J. Chem. Eng. Data* **2016**, *61*, 3326–3333. (<https://doi.org/10.1021/acs.jced.6b00384>) /90%; IF (2017): 2.196/ (Q1, D1), Independent citation: 1

H1. Havasi, D., Mizsey, P., Mika, L. T. Vapor–Liquid Equilibrium Study of the Gamma-Valerolactone–Water Binary System. *J. Chem. Eng. Data*, **2016**, *61*, 1502–1508. (<https://doi.org/10.1021/acs.jced.5b00849>) /100%; IF (2017): 2.196/ (Q1, D1), Independent citations: 5

Conference lectures

2. Havasi, D., Pátzay, Gy., Rozgonyi, P., Kolarovszki, Z., Mika, L. T. Binary Isobaric Vapor–Liquid Equilibrium Study of gamma-valerolactone and Aliphatic Alcohols. *Proceedings of the 43rd International Conference of Slovak Society of Chemical Engineering* **2016**, 159. (ISBN:978-80-89597-35-2)

1. Havasi, D., Mika, L. T. Vapor-liquid equilibrium study on the γ -valerolactone-water binary system. *Proceedings of the 42nd International Conference of Slovak Society of Chemical Engineering*, **2015**, 199. (ISBN:978-80-89475-14-8)

Other publications

2. Tukacs, J. M., Holló, A. T., Rétfalvi, N., Cséfalvay, E., Dibó, G., Havasi D., Mika, L. T. Microwave-Assisted Valorization of Biowastes to Levulinic Acid. *ChemistrySelect*, **2017**, 2, 1375-1380. ([https://doi.org/ 10.1002/slct.201700037](https://doi.org/10.1002/slct.201700037))

1. Nagy, M., Rácz, D., Havasi, D., Zsuga, M., Kéki, S. Izoindol tartalmú polimerek. *Műanyag és gumi*, **2013**, 50, 368-373.