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Table of Contents

A Novel Process to Produce Adipic Acid by Catalytic Dehydroxylation of Biomass-derived Mucic Acid **1**
Florian M. Harth, Brigita Hočevar, Blaž Likozar, Miha Grilc

One-pot Algae Conversion Into Sustainable Biofuel by Catalytic Hydroprocessing **11**
Dana Marinič, Brigita Hočevar, Miha Grilc, Blaž Likozar

Development of FT–IR, UV and Fluorescence Based Analytical Methodology for Lignin Characterisation **19**
Rok Pogorevc, Tina Ročnik, Blaž Likozar, Edita Jasiukaitytė-Grojzdek, Miha Grilc

A NOVEL PROCESS TO PRODUCE ADIPIC ACID BY CATALYTIC DEHYDROXYLATION OF BIOMASS-DERIVED MUCIC ACID

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Abstract The heterogeneously catalyzed dehydroxylation of mucic acid to produce adipic acid, a highly relevant polymer precursor, was investigated. The use of methanol as solvent is particularly important since it not only acts as reducing agent but also protects the carboxylic acid functionality by esterification. Re/C was found a well-suited catalyst for this reaction and not only showed high activity but was also reusable with suitable reactivation procedure. Under optimized reaction conditions, 98 % of dehydroxylated products could be obtained from mucic acid. Moreover, combining Re/C with a suitable hydrogenation catalyst (e.g. Pd/C) and performing the reaction under H2 atmosphere steers the reaction towards adipic acid ester. Therefore, it could be shown that adipic acid derivatives are available from biomass-accessible mucic by this novel and renewable approach.

Keywords:
adipic acid,
biomass,
dehydroxylation,
heterogeneous catalysis,
rhenium

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1 Introduction

The production of industrially demanded and value added chemicals from renewable resources such as lignocellulosic biomass is an extensively researched challenge. Adipic acid is a dicarboxylic acid and one of the most important polymer precursors, in particular for the polyamide industry and sustainable processes are shought for its production. A newly developed strategy to produce adipic acid from lignocellulosic biomass is presented here. Lignocellulose-derived sugars, possessing six carbon atoms like adipic acid, are a promising starting point. They can be catalytically oxidized into aldaric acids (e.g. mucic acid). Subsequently, the key reaction step is the selective catalytic dehydroxylation of mucic acid into adipic acid (Fig. 1).

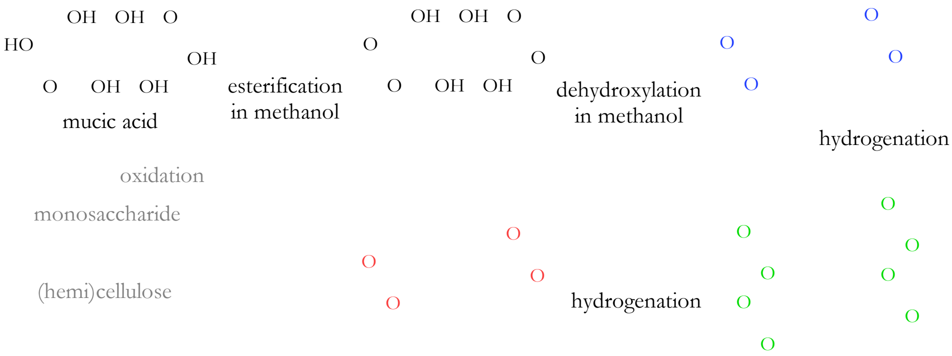

Figure 1: Scheme of the renewable production of adipic acid via selective catalytic dehydroxylation of mucic acid.

Sourec: own.

Previously, Re-based homogeneous catalysts (e.g. CH_3ReO_3, $HReO_4$ or $KReO_4$) and alcohol solvents have successfully been used for this reaction (Shiramizu & Toste, 2012, 2013; Li *et al.*, 2014; Larson *et al.*, 2017). Following the characteristic deoxydehydration route, pairs of vicinal hydroxyl groups are removed and a double bonds are formed. Further hydrogenation then yields adipic acid.

To enable catalyst recycling, the use of solid catalyst in advantageous. Examples of heterogeneously catalyzed processes have been reported for similar reactants (Denning *et al.*, 2013; Ota *et al.*, 2015, 2016; Sandbrink *et al.*, 2016; Tazawa *et al.*, 2016; Nakagawa *et al.*, 2018; Sharkey *et al.*, 2018; Xi *et al.*, 2018). Only very recently, this was shown to be possible also for the case of adipic acid (Hočevar *et al.*, 2021), which is presented here. The initial study, which also led to a patent application (Hočevar *et al.*, 2019), was soon confirmed by additional studies (Deng *et al.*, 2021; Jang *et al.*, 2021).

Here, we present insights into how the Re-catalyzed dehydroxylation of mucic acid is influenced by various process parameters, including the type of Re catalyst, the role of the solvent, the influence of the presence of H_2 gas and/or hydrogenation co-catalysts as well as the effect of reaction temperature.

2 Materials and Methods

Throughout the study, commercial catalysts were used: Re/C, Re/SiO_2 and Re/Al_2O_3 (each 5 wt.-% Re loading, powders; Riogen, USA) as well as Pd/C (5 wt.-% Pd loading, powder; Sigma Aldrich, USA). Prior to catalytic experiments, the catalyst(s) were reduced in a flow of H_2 (200 mL min^{-1}) at 400 °C for 3 h.

Catalytic experiments were conducted in stirred and heated autoclave reactors (Amar Equipment Pvt. Ltd., India). The reactor was loaded with mucic acid (97 % , Sigma Aldrich, USA), methanol and the catalyst(s), pressurized with nitrogen or hydrogen, heated up to the desired reaction temperature and kept for typically 72 hours. Different commercially available catalysts (Re/C, Re/SiO_2, Re/Al_2O_3) were tested. While there was always a solid Re catalyst present (typically Re/C), in some experiments Pd/C was added as a co-catalyst. Moreover, the reaction conditions were varied, namely the reaction temperature in the range of 120-175 °C and the composition of the gas phase (nitrogen or hydrogen) prior to the catalytic experiments.

The final reaction mixtures were filtered and analyzed by gas chromatography-mass spectrometry (GC-MS). A GCMS–QP 2010 Ultra (Shimadzu, Japan) was used equipped with a nonpolar column (ZebronTM ZB–5MSi, 60 m, diameter 0.25 mm, film thickness 0.25 µm). Compounds were identified by mass spectrometry and quantified based on external calibrations using the FID signal.

3 Results and Discussion

3.1 Dehydroxylation over Re/C

First, mucic acid dehydroxylation was investigated over a commercially available Re/C catalyst under inert N_2 atmosphere. These results are shown in Fig. 2 (left columns). Since there is no H_2 or other additional reducing agents are, methanol serves as the reducing agent. Moreover, methanol readily forms esters with mucic acid under reaction conditions. Consequently, all detected products are dimethyl esters of the respective dicarboxylic acids.

The dehydroxylation reaction already proceeds at 120 °C, where ca. 93 % of dehydroxylated products were found after 72 hours reaction over Re/C. The main product is the twice-unsaturated analogue of dimethyl adipate (62 %), which is the direct product of full deoxydehydration of mucic acid dimethyl ester, i.e. where all four vicinal hydroxyl groups are removed. Moreover, a considerable amount of this intermediate product was partially hydrogenated to a group of isomers with one double bond (28 % yield) and some even fully hydrogenated to dimethyl adipate.

Increasing temperature to 175 °C lead to a slight increase in product yield (98 % of dehydroxylated products in total). More importantly, a shift in selectivity is apparent and only traces of the primary, twice-unsaturated product were found in the product mixture. While mostly partially hydrogenated products were formed, there was also a substantial amount of dimethyl adipate (31 %). It was confirmed by gas chromatography that in both cases under initially inert atmosphere the hydrogenation activity is related to H_2 formation by methanol decomposition.

When the initial gas phase composition in the reactor was changed from inert N_2 to H_2, hydrogenation activity is similarly enhanced (Fig. 2, right column). While under N_2 atmosphere at 120 °C only around 30 % yield of hydrogenated products was formed over Re/C, under H_2 pressure of initially 10 bar all detected products were either partially (58 % yield) or fully hydrogenated (25 %). These experiments prove that under suitable reaction conditions the combined dehydroxylation and subsequent hydrogenation of mucic acid to adipic acid derivatives is feasible. Moreover, product selectivity can be steered to a certain degree by the choice of the reaction conditions.

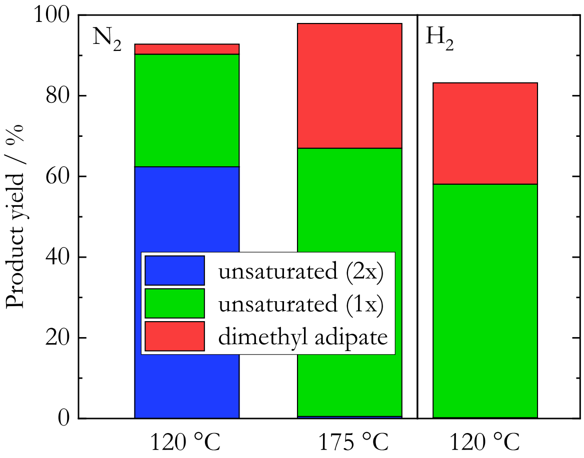

Figure 2: Product yields after 72 h from mucic acid dehydroxylation in methanol over Re/C under different reaction conditions.

Sourec: own.

3.2 Influence of catalyst support material

Besides Re/C, two other commercially available Re-based catalysts were studied regarding their activity in mucic acid dehydroxylation (Fig. 3). It should be noted that, unlike for the previously discussed results, the catalysts were used as-obtained without reduction before the catalytic experiments. This explains the considerably lower hydrogenation activity over Re/C at 120 °C. Comparing Re/C with Re/SiO_2 and Re/Al_2O_3 it is apparent that the latter two are by a factor of ca. 10 less active in catalyzing the dehydroxylation of mucic acid. Moreover, Re/Al_2O_3 was found to rather catalyze undesired decarboxylation and hydrodeoxygenation reactions resulting in the formation of short-chain as well as cyclization products. Overall, Re/C is exceptionally suited as a catalyst for the dehydroxylation reaction.

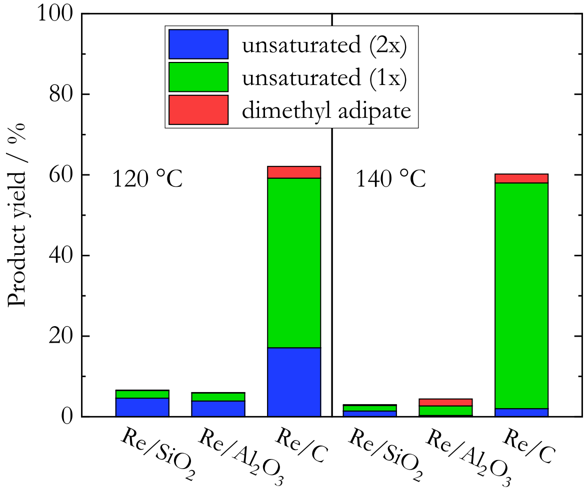

Figure 3: Product yields after 72 h from mucic acid dehydroxylation in methanol over different solid Re catalysts under H_2 atmosphere at different temperatures.

Sourec: own.

2.3 Influence of a hydrogenation co-catalyst

The formation of the twice-unsaturated dehydroxylation product proceeds considerably more facile over Re/C than the subsequent hydrogenation reactions, as was shown in section 2.1. Therefore, the addition of a hydrogenation co-catalyst is one option to increase selectivity for hydrogenated products, in particular dimethyl adipate, without resorting to harsher reaction conditions. The results in Fig. 4 clearly show that the presence of additional Pd/C (molar ratios $n_{Pd}\, n_{Re}^{-1} = 1{:}6$ or 1:4) shifts product selectivity almost completely towards fully hydrogenated dimethyl adipate. Yields of up to 60 % were obtained with only ca. 3 % of unsaturated products. Therefore, the use of Pd/C as a hydrogenation co-catalyst facilitates hydrogenation and enables the efficient one-pot dehydroxylation and hydrogenation of mucic acid into adipic acid.

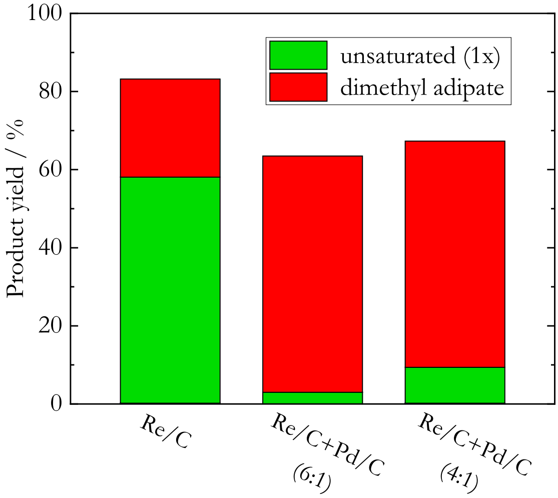

Figure 4: Product yields after 72 h from mucic acid dehydroxylation in methanol over Re/C with or without co-catalyst Pd/C under H_2 atmosphere at 120 °C.

Sourec: own.

4 Conclusions

The use of solid Re-based catalysts for the dehydroxylation of mucic acid in coimbination with subsequent hydrogenation to adipic acid was investigated. One important aspect is the use of methanol as a solvent that also protects the carboxylic groups by esterification and can serve as a reducing agent and a H_2 source. Re/C was shown to be a highly efficient catalyst for the heterogeneously catalyzed dehydroxylation reaction, in particular compared to other solid Re catalysts. Moreover, the reaction conditions and the presence or absence of an additional Pd/C hydrogenation catalyst are influential parameters that allow to steer product selectivity of the process. Under N_2 atmosphere, methanol serves as reducing agent and mostly the direct dehydroxylation product, which contains two double bonds, is obtained over Re/C at 120 °C in yields of up to 62 %. Overall, the yield of dehydroxylated product was up to 98 %. This includes also partially hydrogenated as well as fully hydrogenated products, the latter being the target product dimethyl adipate. These subsequent hydrogenation reactions are enhanced by higher reaction temperature, H_2 atmosphere as well as the use of a Pd/C co-catalyst. Adjusting the reaction conditions in this manner allows for selective production of dimethyl adipate from biomass-derived mucic acid. Due to the heterogeneous catalytic nature of the process, which enables catalyst recycling, as well as the non-toxic and renewable reactants the presented process is a considerable improvement compared to conventional processes for the production of adipic acid.

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One-pot Algae Conversion Into Sustainable Biofuel by Catalytic Hydroprocessing

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Abstract Microalgae have emerged as a promising feedstock for third generation biofuels. This study aims to investigate the reaction conditions for biodiesel production from microalgae. Microalgae were liquefied and transformed into a mixture of diesel like hydrocarbons using commercial bifunctional NiMo/γ-Al_2O_3 catalyst. GC-MS analysis revealed that the produced bio-oils are a complex mixtures of partially or completely deoxygenated compounds. The most promising experiment using 25 wt% of catalyst at 350 °C of reaction temperature and 50 bar of initial hydrogen pressure yielded 22.6 wt% of liquid alkanes with the high selectivity towards pentadecane, hexadecane, heptadecane and octadecane.

Keywords:
adipic acid,
biomass,
dehydroxylation,
heterogeneous catalysis,
rhenium

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1 Introduction

Environmental problems among with the increasing energy demand, instable fuel prices and limited fossil fuel have led to the growing interest in renewable fuels. Expensive raw materials and consequently higher biodiesel price compared to petroleum fuels represent the main obstacle for general use of biofuels.

Microalgae have recently emerged as an attractive and suitable feedstock for biofuel production, mostly because of its high biomass productivity and photosynthetic efficiency. Furthermore, microalgae exhibit high growth rate and high accumulation capacity of lipids and fatty acids. Moreover, it can grow on waste, it does not require arable land of fresh water, hence it's not a threat to traditional agricultural goods. Low carbon footprint and GHG emissions make biofuel technology even more interesting (Bwapwa et al., 2017; Delrue et al., 2013). The advantage of having high tolerance to CO_2 makes microalgae a promising organism for CO_2 mitigation. (Moreira & Pires, 2016).

The algal biofuel technology has been the subject of numerous studies throughout the previous decade. The three principal bio-fuel pathways used for the biofuel production are pyrolysis, the lipid extraction and conversion into bio-diesel through transesterification and the hydrothermal liquefaction (HTL). The latter was developed to be the most practical one due to the algal high water content (Yang et al., 2016). In comparison to HTL, which can convert biomass with high moisture content (above 50% mass fraction), pyrolysis can decompose only dry organic matter (Hognon et al., 2015). Additional drying cause high electricity and heat consumption (Delrue et al., 2012).

HTL is a thermochemical process, where the biomass is transformed directly into liquid biocrude while using high pressures (10-25 MPa) and temperatures (280-370 °C) for 5-120 minutes (Xu et al., 2018). Due to the high oxygen and nitrogen concentrations in bio-crude and consequently poor product quality, further catalytic hydrotreatment is required (Yang et al., 2016). Additional treatment leads to the energy, time and cost prohibitive processes, which limits the options for general use. Since high pressure and temperature are already some of the major HTL drawbacks (Delrue et al., 2013), the improvement is necessary. In this study the one-pot algae conversion into sustainable biofuel was carried out by catalytic hydroprocessing. The main goal was to combine liquefaction and hydrotreatment processes.

This study is a part of a bilateral research project in collaboration with the French Alternative Energies and Atomic Energy Commission (CEA). Microalgae cultivation, harvesting and lipid extraction was done by CEA. Our department at the National Institute of Chemistry carried out the hydrotreatment of microalgae oils.

2 Methods

The catalytic hydrotreatment of Chlorella microalgae was performed in a 300 mL cylindrical stainless steel slurry reactor equipped with a Rushton turbine impeller (Fig. 1). The reactor was filled with 120 mL of reaction mixture that contained 5 wt% of algae, the rest being dodecane. Commercially available $NiMo/Al_2O_3$ catalyst was used in this study. The catalyst mass was set to 25 wt% with respect to the initial mass of microalgae. The system was purged with nitrogen twice to ensure inert gaseous headspace and then pressurized with hydrogen to the desired pressure (Table 1). The reaction mixture was heated-up by increasing the temperature from room temperature with the heating ramp of 5 °C/min to the desired reaction temperature. The reaction conditions were maintained constant for 4 hours before rapid cooling down. Decompressed gas phase from the reactor was analyzed by micro-GC. Before opening, the reactor was purged with nitrogen. The reaction mixture was filtered. The solid samples collected from the filtration were washed three times with dodecane and once with hexane, then analyzed by Fourier transform infrared (FTIR) spectroscopy. The liquid samples collected from the filtration were analyzed by Gas Chromatography – Mass spectroscopy (GC-MS, Shimadzu Ultra 2010) and by FTIR.

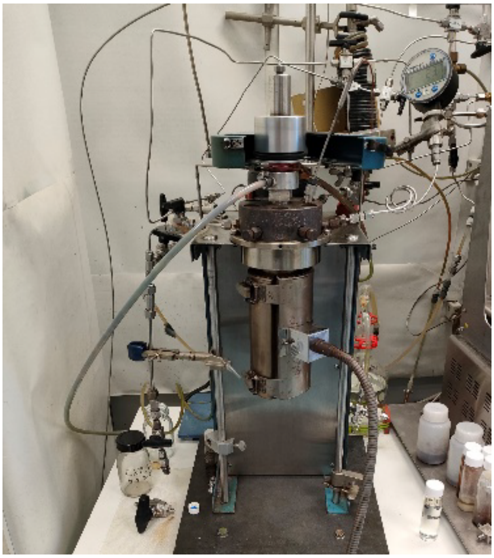

Figure 1: 300 mL high-temperature and high-pressure reactor.

Source: own.

Table 1: Reaction conditions for each run in batch slurry reactor.

Run	Catalyst form	T^a (°C)	P^b (bar)	W_{cat} (wt%)
1	Sulf NiMo/γ-Al_2O_3	200	50^c	25
2	Sulf NiMo/γ-Al_2O_3	300	50^c	25
3	Sulf NiMo/γ-Al_2O_3	312	50^c	25
4	Sulf NiMo/γ-Al_2O_3	325	50^c	25
5	Sulf NiMo/γ-Al_2O_3	350	50^c	25
6	Sulf NiMo/γ-Al_2O_3	325	30^c	25
7	Sulf NiMo/γ-Al_2O_3	325	20^c	25
8	Sulf NiMo/γ-Al_2O_3	325	50^d	25
9	Sulf NiMo/γ-Al_2O_3	350	30^c	25
10	Sulf NiMo/γ-Al_2O_3	350	20^c	25
11	Ox NiMo/γ-Al_2O_3	325	50^c	25
12	Red NiMo/γ-Al_2O_3	325	50^c	25
13	/	325	50^c	0^e
14	/	325	50^c	0^f

[a] Set temperature of plateau.

[b] Initial pressure in reactor.

[c] Hydrogen atmosphere.

[d] Nitrogen atmosphere.

[e] Blank – no catalyst

[f] Blank – no algae and catalyst

3 Results

3.1 Liquid phase analysis

GC-MS analysis revealed that the produced bio-oils are a complex mixtures of partially or completely deoxygenated compounds. The most promising experiment using 25 wt% of catalyst at 350 °C of reaction temperature and 50 bar of initial hydrogen pressure yielded 22.6 wt% of liquid alkanes with respect to the initial mass of microalgae. The results showed high reaction selectivity towards pentadecane, hexadecane, heptadecane and octadecane. The chromatogram shown in Fig. 2 confirmed low oxygen and nitrogen content, where the main oxygen compound was nonadecanol. The removal of unwanted heteroatom compounds was reached by hydrodeoxygenation (HDO). Hydrogenation and hydrogenolysis reactions transform oxygen composed molecules into o-free hydrocarbon chains, which are suitable for the use as biofuel (Valencia et al., 2018).

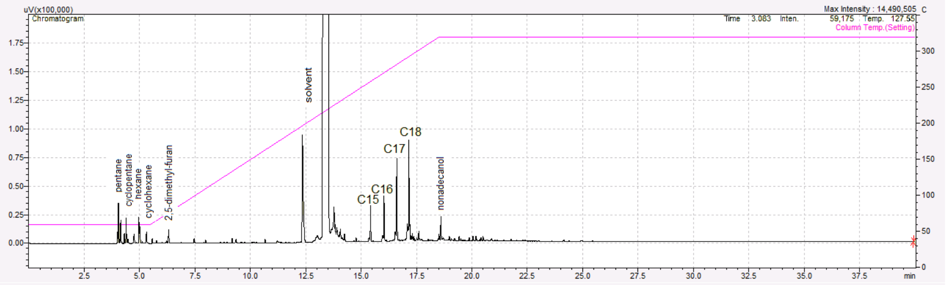

Figure 2: GC-MS chromatogram of produced biooil at optimal reaction conditions (350 °C and 50 bar of initial hydrogen pressure).

Source: own.

Higher temperature resulted in higher alkane concentration (up to 4,53 mg/ml) and higher yields (up to 22.6 wt%). The higher the hydrogen pressure, the more hydrogenation reactions of alkenes occurred. In addition, stricter reaction conditions (such as higher temperature and higher hydrogen pressure) resulted in lower mass residue, suggesting that the liquefaction was more intense.

NiMo/Al_2O_3 is being widely used as a commercial catalyst in petrochemical industry. Among the reduced, oxygenated and sulfided form, the latter was found to be the most promising, while the first two were much less active. GC-MS chromatogram of produced biooils using different catalyst form is presented in Fig. 3.

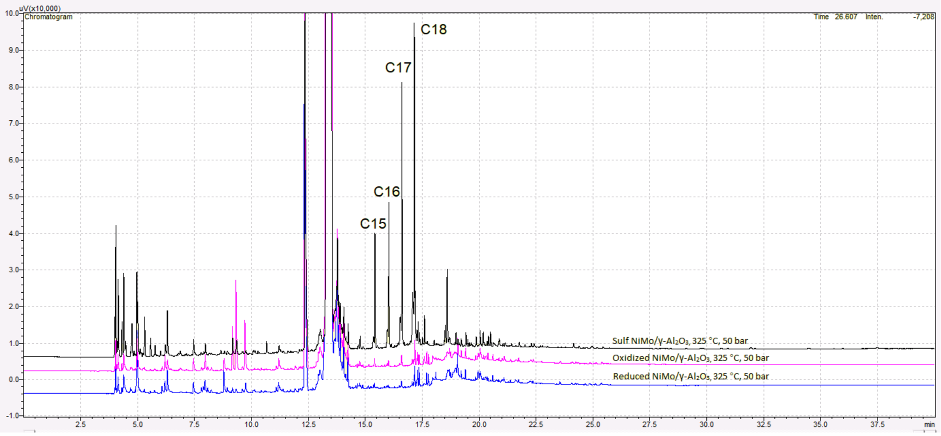

Figure 3: GC-MS chromatogram of produced biooils using reduced, oxygenated and sulfided catalyst form.

Source: own.

The FTIR spectra of liquid (Fig. 4) and solid samples were obtained in the range of 4500 – 400 cm^{-1} for determining the functional groups present in the feedstock and the product. FTIR spectrum of liquid product match quite well with the spectrum of the dodecane, since the solvent represents a high proportion of the product. The major difference were two weak bands around 3700 cm^{-1} and 1070 cm^{-1} which are related to O—H stretching vibration.

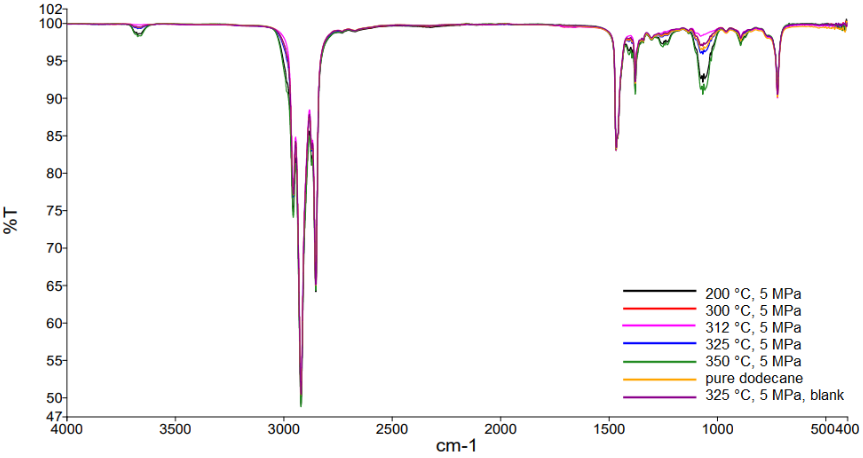

Figure 4: FTIR analysis results of produced biooils.

Source: own.

3.1 Gas phase analysis

Gas products were mostly composed of H_20, CO, CO_2 and light hydrocarbons such as CH_4 and C_2H_6. Fatty acids under hydrogen pressure can undergo three main deoxygenation routes; hydrodeoxygenation, decarbonylation or decarboxylation. From the gas composition we can conclude that hydrodeoxygenation (removal of O atoms as H_2O) is more dominant deoxygenation pathway than decarbonylation and decarboxylation (DCO, removal of O atoms as CO and CO_2) (Arora et al., 2021; Soni et al., 2017; Yang et al., 2016).

4 Conclusion

Microalgae slurry was successfully processed in a cylindrical reactor at temperature of 300 – 350 °C, hydrogen pressure of 20 – 50 bar and reaction times of 4 hours. The catalytic hydroprocessing led to the conversion of microalgae into a complex mixture of diesel like hydrocarbons (C14–C18). The oil yields were higher (up to 22.6 wt%) at higher temperature and H_2 pressure.

Acknowledgments

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DEVELOPMENT OF FT–IR, UV AND FLUORESCENCE BASED ANALYTICAL METHODOLOGY FOR LIGNIN CHARACTERISATION

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Abstract The development of the novel analytical methodologies for lignin chracterisation is presented. Lignin fractions were characterized by NMR, SEC/GPC as well new analytical methodologies were implemented such as FT–IR, UV and fluorescence. FT–IR and fluorescence results show a promising correlation to the NMR and SEC/GPC analysis. Main findings from the SEC/GPC and NMR results indicates that by adding more water to the organosolv spent liquor isolated lignin contains lower amount of β-O 4 linking motif and also has a lower molecular weight. The following is also confirmed by the straightforward analysis using FT–IR and fluorescence giving the opportunity to replace time-consuming and complex lignin characterisation methods with a simple and quick analytics and the possibility to be applied for the in-process control in continuous production processes.

Keywords:
lignin,
molecular weight,
FT–IR spectroscopy,
fractionation,
UV

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1 Introduction

Lignocellulosic biomass, one of the renewable resources representing an alternative to fossil oil and gas, is composed of cellulose (50 %-source of carbohydrates), hemicellulose (25 %-source of carbohydrates) and lignin (25 %) which could be used in production of biofuels, chemical, biopolymers and sugars (Liao et al., 2020; Liu et al., 2018). Lignin is a by-product of pulp and paper industry processes (kraft, sulfite and soda) and is usually burned to produce energy for the pulping but it could be used to produce value added chemicals and fuels by reducing its heterogeneity and overall molecular weight (Liao et al., 2020; Pang et al., 2021; Sadeghifar et al., 2020; Yáñez-S et al., 2014). More environmentally friendly organosolv process coupled with a certain lignin recovery/fractionation protocol is a promising way to isolate lignin with a particular properties (molecular weight and structural features). Several fractionation processes using different solvents have been developed (Liu et al., 2018).

Lignin is synthetized via radical polymerization using three monolignols, specifically sinapyl alcohol (syringyl (S)), coniferyl alcohol (guaiacyl (G)) and p-coumaryl alcohol (H), inside the plants such as softwood (mostly G units are present), hardwood (G and S units are present), and some grasses (all three of the units are present (H, G and S)) (Lahive et al., 2020; Liao et al., 2020; Liu et al., 2018; Pang et al., 2021). During the polymerization monolignols are coupled forming specific lignin motifs such as β-O-4, β-5 and β-β (Lahive et al., 2020).

Conventionally used analytics in lignin chemistry Nuclear Magnetic Resonance (NMR) and Size-Exclusion Chromatography (SEC)/ Gel-Permeation Chromatography (GPC) are complex and time-consuming. NMR provides information on lignin structural properties, but the sample preparation and analysis by itself are quite long. SEC/GPC provides the molecular weight of lignin, but again sample preparation takes even more time, because of the derivatization procedure. New analytical methodologies has to be developed for lignin characterization to get particular information faster and easier (Zevallos Torres et al., 2020).

The aim of this paper is to characterize lignin fractions with new analytical methodologies such as UV-vis, fluorescence and Fourier-transform infrared spectroscopy (FT–IR) and to establish a relationship with the conventionally used analytics in lignin chemistry such as NMR and SEC/GPC.

2 Methods

Delignification of beech wood was made in 300 mL reactor (Autoclave engineering, Figure 1) at around 150 °C using mixture of solvents (ethanol and water) and diluted sulfuric acid. Filtration of the cold reaction mixture was then applied followed by drying solid residue in the oven and fractionation of the filtered liquid by adding various volumes of water to recover lignin with specific molecular weight. Recovered lignin was then freeze-dried and characterized using NMR, SEC/GPC, FT–IR , UV and fluorescence.

FT–IR spectra were recorded on FT–IR-ATR spectrophotometer (PerkinElmer, Spectrum Two), in the region 4000-400 cm^{-1} with resolution of 4 cm^{-1} and accumulation 64. The average spectrum of the ten paralell measurements of each sample was considered as a representative spectrum. Molecular weights of derivatized lignin samples were determined using size-exclusion chromatographic system (Thermo Scientific Ultimate 3000, ThermoFisher) equipped with UV detector set at 280 nm using THF as an eluent and Plgel 5 μm MIXED D 7.5 × 300 mm column. Calibration was performed using PS standards. NMR spectra were recorded using a Bruker AVANCE NEO 600 MHz NMR spectrometer following the protocol reported by Tran et al. (Tran et al., 2015). Fluorescence spectra in spectral range of 300 nm to 530 nm with emission step 2 nm was recorded on a Synergy H1 microplate reader (Biotek).

Figure 1: Autoclave Engineering.
Source: own.

3 Results

SEC/GPC chromatogram profiles (Figure 2a) show higher molecular weights at the fraction 1 (lowest amount of water was added) compared to fraction 5 (the highest amount of water was added). Using water as an anti-solvent it is possible to separate lignins with the specific properties, for instance average molecular weight. Initial lignin was used as a reference and was isolated adding the excess volume of the anti-solvent.

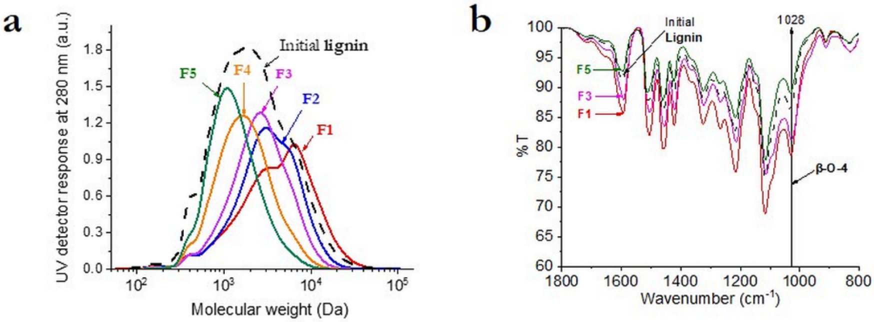

Figure 1: a) molecular weight distributions of the isolated lignins, b) enlarged FT–IR spectrum between 800 cm^{-1} and 1800 cm^{-1} of the initial lignin and three fractions.
Source: own.

FT–IR analysis identifies β-O-4 linkage with a corresponding signal around 1030 cm^{-1} from which the assumption of the number/quantity of it was made (Yáñez-S et al., 2014). The comparison of FT–IR spectra (Fig. 2b) shows a clear increase of the signal at 1026 cm^{-1} from last (F5) to first (F1) fraction which indicates higher content of this linking motif in F1 then in F5 (Yáñez-S et al., 2014). The comparison of the transmittance perversely mentioned signal with integrated surface of signal in NMR spectra which are 14.0, 12.9 and 8.5 per 100 C9 units, for F1, F3 and F5 fractions respectively, show similar pattern (lower integrated number higher transmittance) meaning those two analyses can be correlated.

Combination of fluorescence and SEC/GPC (Fig. 3) analysis indicates that the maximum intensity at 320 - 330 nm is align with the molecular weight which could be used to calculate the approximate molecular weight of initial or any other lignin isolated using EtOH/water organosolv pulping.

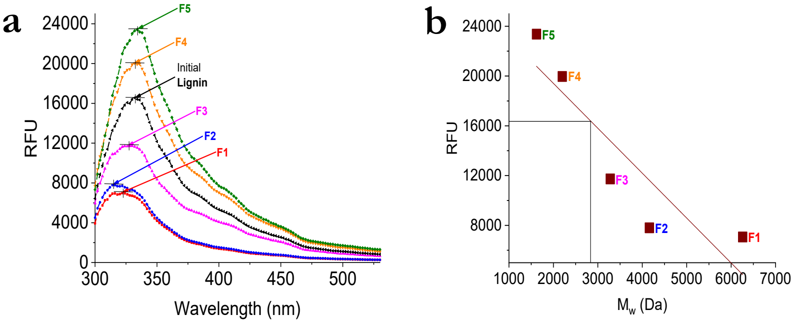

Figure 3: a) fluorescence measurements of initial lignin and all fractions. b) highlighted maximum values are used to correlate fluorescence and SEC analytical data

Source: own.

4 Conclusion

Straightforward FT–IR, fluorescence analysis show a promising correlation with NMR and SEC analytical data when used for lignin characterisation. The outstanding relationship between fluorescence and SEC analysis could be used for the in-process control in continuous production processes, for instance isolating specific lignin/fractions. Further, the SEC-fluorescence relationship will certainly be applied for the development of more complex analytical methodologies including UV, FT–IR and NMR analytical data.

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4TH INTERNATIONAL CONFERENCE ON TECHNOLOGIES & BUSINESS MODELS FOR CIRCULAR ECONOMY: CONFERENCE PROCEEDINGS

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Abstract The 4th International Conference on Technologies & Business Models for Circular Economy (TBMCE) was organized by the Faculty of Chemistry and Chemical Engineering, University of Maribor in collaboration with the Strategic Research and Innovation Partnership - Networks for the Transition into Circular Economy (SRIP- Circular Economy). The conference was held in Portorož, Slovenia, at the Grand Hotel Bernardin from September 13th to September 15th, 2021. TBMCE 2021 was devoted to presentations of circular economy concepts, technologies and methodologies that contribute to the shift of business entities and society as a whole to a more responsible, circular management of resources. The conference program included panel discussions, plenary and keynote sessions, oral and poster presentations on the following topics: Sustainable energy, Biomass and alternative raw materials, Circular business models, Secondary raw materials and functional materials, ICT in Circular Economy, Processes and technologies. The event was under the patronage of Ministry of Economic Development and Technology.

Keywords: sircular economy, sustainable development, processes and technologies, circular business models, research and development

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