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Arabinogalactan hydrolysis and hydrolytic hydrogenation using functionalized carbon materials

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ABSTRACT

Hydrolysis of the hemicellulose arabinogalactan was studied in this work over several functionalized carbon materials, which were specifically treated to increase their acidities. Hydrolytic hydrogenation of arabinogalactan was investigated using the same materials in a mechanical mixture with ruthenium supported on active carbon.

Application of these mixtures resulted in formation of polyols, suppressing simultaneously the generation of side products hydroxymethylfurfural (HMF) and furfural. Formation of high molecular weight compounds (aggregates of sugars and humins) was still quite substantial with a mechanical mixture of Ru/C and a carbon material prepared from sucrose by activation with zinc chloride to increase porosity. Post-treatment of this carbonaceous material with sulphuric acid significantly influenced kinetics of high molecular weight products formation resulting also in elevation of sugar alcohols yields.

1. Introduction

Catalytic conversion of lignocellulosic biomass gained a recent revival in the interest due to a general interest in catalytic valorization of biomass [1–3], especially because lignocellulose does not compete with food resources. The main chemical components of lignocellulosic biomass are cellulose (40–50%), hemicelluloses (25–35%) and lignin (23–33%), as well as minor amounts (<5%) of extractives and mineral matter [1–3].

Among various options for transformation of biomass, mild hydrolysis of cellulose and hemicellulose is one of the most promising since it leads to depolymerisation yielding a pool of molecules which could be used as platform chemicals. A review on hydrolysis of cellulose as an entry point to biorefinery schemes has been published recently [4]. During the acid hydrolysis of cellulose and hemicelluloses, the glycosidic bonds between the sugar units are cleaved to form partially hydrolyzed oligomers and, if the hydrolysis is complete, to produce the respective monosaccharides.

The main focus in the literature is on hydrolysis of cellulose [5], even if hemicelluloses are easier to hydrolyze than cellulose, due to their branched and non-crystalline structures [6–8]. Hydrolysis of lignocellulose using homogeneous acid catalysts was implemented industrially [1,4] using for example mineral acids such as H_2SO_4 as catalysts [9]. However, several disadvantages (corrosion, treatment of generated waste, etc.) call for the introduction of heterogeneous catalysts to conduct this reaction in an aqueous environment without the above mentioned drawbacks [4,10]. A range of solid acids has been used for hydrolysis of cellulose, including metal oxides, polymer based acids, heteropolyacids, proton forms of zeolites and sulfonated carbonaceous based acids as discussed recently in a comprehensive review [10]. Due to cellulose crystallinity, ball-milling is typically applied prior to hydrolysis. Among the materials tested sulfonated carbons or silica/carbon nanocomposites displayed high activity and good recyclability [10,11]. Hemicelluloses can be even easier to hydrolyze using heterogeneous catalysts, as demonstrated for arabinogalactan [12] and xylan [13] with sulfonic acid functionalized polymers and for xylan with proton form of zeolites [13]. For xylan it was concluded that leaching of sulfonic groups is rather strong, while proton form zeolites were much more stable and active.

One of the attractive options to increase the selectivity in hydrolysis of either cellulose or hemicellulose is to combine hydrolysis and hydrogenation to a single step using only water as a solvent and molecular hydrogen [14–29]. This bifunctional catalysis leading to sugar alcohols helps to avoid generation of furan compounds, which are formed on the acid sites favouring dehydration of the sugars. Such strategy was pioneered by Balandin et al. [14] and reintroduced by Fukuoka and Dhepe [15–17]. The first step in the one-pot

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process is hydrolysis of cellulose or hemicellulose into free sugars in the liquid phase (in the presence of a diluted mineral acid) and/or over an acidic support material. Hydrogenation of the free sugars affording polyols takes place on the active metal sites deposited on the support material. Typically transition metals (Pt or Ru) are used as the active phase for hydrogenation [5]. There are quite a number of studies on hydrolytic hydrogenation of cellulose and hemicellulose using a variety of solid acids, such as acid-functionalized mesoporous silica [18], zeolites and mesoporous materials [19–25]. Various carbon supported metal catalysts have been applied for hydrolytic hydrogenation of cellulose [26–32].

Changes of the acidic properties of the parent support after deposition of a metal are well documented resulting in loss of strong Bronsted and Lewis sites in case of metal modified zeolites [33,34]. An interesting option for hydrolytic hydrogenation could be thus to apply in hydrolytic hydrogenation a mechanical mixture of a solid acid catalyst and the most effective catalyst for hydrogenation of sugars, namely Ru/C. This has been done for hydrolytic hydrogenation of cellulose using Ru/C and sulfonic acid functionalized mesoporous silica MCM-41 [35] or heteropoly acids [36]. In the former case, leaching of sulfonic groups was very rapid, which also implies that contribution of homogeneous catalysis to the hydrolysis becomes significant.

Cellulose consists of polymerized glucose units, whereas hemicelluloses are hetero-polymers made up of different units of hexoses and pentoses. Arabinogalactan appears in large quantities in larch species such as *Larix sibirica*. The structural basis of arabinogalactan is a backbone of β-D-galactopyranose with D-galactopyranose and L-arabinofuranose side chains (Scheme 1). The average molar ratio of galactose to arabinose in arabinogalactan is about 6:1 and the molar mass is 20 000–100 000 g/mol [4]. Arabinogalactan can easily be extracted from wood chips with water under moderate conditions in industrial scale [37].

In the previous work of the authors [22], Ru–beta zeolites with different Si/Al ratio were used in hydrolytic hydrogenation of arabinogalactan because they contain Brønsted acid sites similar to mineral acids such as HCl and H_2SO_4, i.e. well-known homogeneous catalysts for hydrolysis of cellulose and hemicelluloses. Incorporation of ruthenium by impregnation resulted in the decrease of the overall strength of the acid sites. Hydrolysis of AG was ascribed [22] to the acid sites on the zeolite support material as well as homogeneous catalysis by H_3O^+. The latter is becoming more prominent with the temperature increase being related to a decrease of pK_w value of water (14 at 298 K compared to 11.4 at 458 K). Ru sites are needed for hydrogenation of the sugars and the introduction of Ru metal influences the selectivity by suppressing the formation of dehydration and degradation products.

As evident from the literature overview above, compared to cellulose, there is almost no effort reported in the literature devoted to hydrolytic hydrogenation of hemicelluloses using sulfonic acid functionalized carbons containing Ru or applying a combination of Ru/C and such functionalized carbons. The current work is aimed to fill this gap by performing hydrolytic hydrogenation of one of the hexose hemicellulose – arabinogalactan applying a one pot tandem approach, i.e. combining a commercial Ru/C catalyst with several functionalized nanoporous carbons. Hydrolysis of hemicellulose was also carried out with the functionalized carbons alone in the absence of a hydrogenation catalyst albeit in hydrogen atmosphere.

2. Experimental

2.1. Catalyst preparation

The CMK-3 material (CI), which is a carbon replica of mesoporous molecular sieve SBA-15, was obtained by matrix synthesis from sucrose [38]. The structure of the carbon is composed of a hexagonal arrangement of 1-D carbon rods. CI material being conventional mesoporous carbon is not acidic. Since it was proposed in the literature that mesoporous carbons such as CMK-3 can catalyze the hydrolysis of cellulose to glucose even in the absence of strong acidity [39], it was interesting to test performance of this material also for hydrolytic hydrogenation of hemicelluloses.

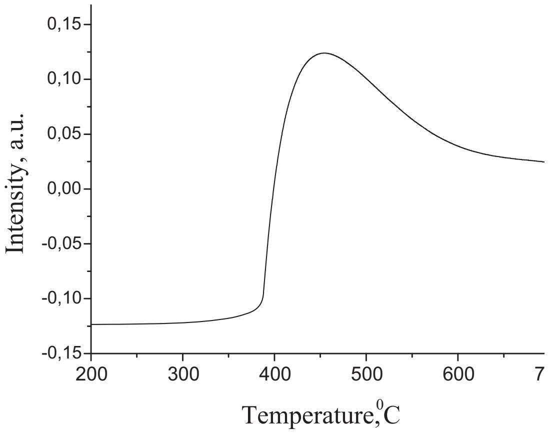

Fig. 1. NH_3-TPD profile of the sample CIII.

Mesoporous carbon (CII) was obtained via activation of sucrose with zinc chloride. A weighted amount of sucrose was stirred in 60% solution of $ZnCl_2$ (mass ratio $ZnCl_2$/sucrose was 7) for 30 min, then it was evaporated at 85 °C for 1 h. Thereafter the obtained mixture was heated at 110 °C for 1 day and subjected to pyrolysis in an inert atmosphere (argon) for 3 h at 700 °C (heating rate 3 °C/min). After cooling, the obtained samples were washed with distilled water, then with 1.2 M hydrochloric acid and with hot (85–90 °C) distilled water until the pH of the washing water was ∼6–7.

The treatment with zinc chloride as an activating agent is applied in bulk carbonization of some organic compounds in order to promote the development of porosity of carbon framework. Among the substances that are easily polymerized besides cellulose or lignin, also sucrose is often used, while such activating agents as phosphoric acid or zinc chloride were found to be efficient [40]. Such carbon materials with well developed surface and high mesoporous volume were described in details in our previous work [40]. During the material preparation HCl was used for dissolving of the products of hydrolysis and subsequent thermal transformation of zinc chloride. The obtained carbon CII is similarly to CI not acidic.

A mesoporous carbon catalyst (CIII) was prepared by sulfonation of mesoporous carbon (CII) similar to a conventionally used approach for treatment of for example CMK3 [39]. For sulfonation, 1 g of the carbon sample was added to 15 ml of concentrated sulphuric acid (98%). Then, the mixture was placed in a Teflon-sealed autoclave and maintained at 180 °C for 24 h. The obtained black product was filtered and washed with water up to neutral pH in the wash water, and then dried at 100 °C overnight. The structure and sorption properties of the sample CIII were almost the same as for the starting material (the reduction of the sorption parameters is not more than 10%). The concentration of acid sites in this sample is about 2.9 mmol/g, which was determined through back titration. In a typical procedure, a weighted amount of the sample (ca. about 0.5 g) was added into 20 ml of 0.1 M NaOH aqueous solution. The resulting suspension was stirred at room temperature for 24 h until an equilibrium was reached and titrated by drop wise addition of 0.1 M HCl. The acid strength of the sample was determined by thermo-programmed desorption of ammonia (NH_3-TPD). The results (Fig. 1) showed that CIII had strong acid sites, as ammonia was only desorbed at 400–600 °C.

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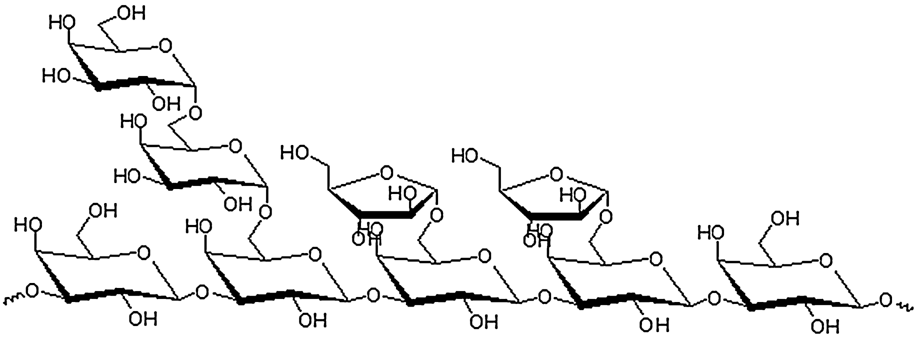

Scheme 1. Structure of arabinogalactan.

A commercial Ru/C catalyst (4.6 wt% Ru, surface area 700 m^2/g, metal cluster size according to TEM 2–3 nm) was applied in the mechanical mixtures with the carbon materials.

2.2. Catalyst characterization

Nitrogen and hydrogen adsorption isotherms with a purity of 99.99% were measured by volumetric method at 77 K up to atmospheric pressure ($p \sim 1 \times 10^{-3}$–760 Torr) on Sorptomatic 1990. The specific surface area (S_{BET}) was estimated by the BET equation. The mesopore size was determined by Barrett–Joyner–Halenda and Dollimore Heal methods. The mesopore size was determined by the adsorption branch in the cases where the ad(de)sorption hysteresis on the isotherms ended in the ultimate strength of the meniscus of the liquid adsorbate (nitrogen) to break (at $p/p_0 \sim 0.45$–0.50). The micropore size was calculated from Horvath–Kavazoe equation. The values of the micropore volume were refined with the comparative *t*-plot method for porous materials which contain micro- and mesopores in the one structure. The surface area, as well as the pore volumes of the carbon materials are shown in Table 1. The carbon materials are characterized by a high surface area and large mesopore volume. More detailed characterization of CII sample is provided in [40].

The metal loading of Ru/C catalyst was determined by ICP-OES using a Spectro-CircoSCCD ICP-spectrometer. Approximately 50 mg of the sample was inserted into a teflon bomb; 4 ml of HF, 1 ml of HCl and 0.5 ml of HNO_3 were added. The sample was dissolved in a microwave oven, and diluted with deionized water and analysed in the spectrometer. The Ru particle morphology was analysed by transmission electron microscopy (TEM) in a MET JEOL-2000 EX II microscope. Analyzing the morphology of 100 particles observed in these micrographs it was possible to determine the size metal distributions.

2.3. Experimental setup

Hydrolysis in the presence of hydrogen over functionalized carbons and hydrolytic hydrogenation experiments over the same materials and also 5%Ru/C were carried out in a 300 ml Parr autoclave reactor connected to a pre-reactor with a 200 ml volume. The autoclave was equipped with a 0.5 μm filtered sampling outlet, which prevented the small catalyst particles from passing through it. The temperature was measured with a thermocouple and controlled automatically (Brooks Instrument). At the beginning of each experiment, 250 mg of the reactant, arabinogalactan, was dissolved in 90 ml of deionized water, loaded to the pre-reactor and subsequently bubbled with hydrogen. Thereafter, 200 mg of carbon materials along with 200 mg of 5%Ru/C catalyst (when the later was used) with a particle size below 63 μm to suppress internal diffusion limitations were loaded into the reactor containing 10 ml of deionized water. The total pressure was 31 bar, which implied the hydrogen partial pressure of 20 bar at 185 °C. The stirring rate was 1000 rpm to minimize external diffusion affecting activity measurements. When the desired temperature was reached, stirring was applied and the reactant solution from the pre-reactor was fed into the reactor. This was considered as the initial reaction time. These conditions were chosen in order to make easier the direct comparison of these results to the previously reported by our group [20,22]. Liquid samples from the reaction mixture were periodically withdrawn for analysis. The amounts of withdrawn samples were considered in the calculations of the reactant and product concentrations.

2.4. Product analysis

The liquid phase samples taken from the reaction mixture with an Acrodisc LC 13 mm syringe through 0.45 μm PVDF membrane filter were quantitatively analysed by HPLC without any further pretreatment. Two different columns were used according to the different groups of compounds that can be analysed by each one. The Bio-Rad Aminex HPX-87C column connected to a refractive index (RI) detector was used to analyse arabinogalactan, sugars, sugar alcohols and furan compounds. A diluted calcium sulphate $CaSO_4$ solution was used as the mobile phase, with a concentration of 1.2 mM. The eluent flow rate was 0.4 ml/min and the temperature was set to 353 K. In order to analyse the acid compounds and other degradation products, an Aminex cation H+ column was used, with a 0.005 M sulphuric acid solution as mobile phase. The eluent flow rate was 0.5 ml/min and the column temperature was set to 338 K. The individual components were identified by GC–MS analysis of the silylated components with a HP 6890-5973 GC-quadrupole-MSD instrument (Hewlett-Packard, Palo Alto, CA, USA) equipped with a HP-1 GC column (25 m × 0.20 mm i.d., 0.11 μm). More details are given in [20,22]. The total organic carbon (TOC-V CSN, Shimadzu) analysis was conducted to determine the amount of total organic carbon dissolved in the liquid phase. The carbon mass balance was calculated considering the concentration of arabinogalactan, sugars, polyols, furfurals and low molecular weight compounds analysed by HPLC.

3. Results and discussion

3.1. Hydrolysis and hydrolytic hydrogenation of arabinogalactan

Hydrolysis of arabinogalactan in the presence of hydrogen was studied using different carbon containing materials. For the sake of comparison, results in the absence of any catalysts as well as with a beta zeolite (Si/Al ratio equal to 11) reported previously [22] are also briefly discussed.

The acid nature of the solid catalysts is a parameter which can play a role in the first step of hydrolysis of the hemicellulose. The mechanism, which has been proposed for the acid catalyzed

Table 1
Textural properties of carbon materials.

	S_{BET}, m^2/g	$V_{t.}$, cm^3/g	S_{meso}, m^2/g	V_{meso}, cm^3/g	D_{meso}, nm	V_{micro}, cm^3/g	D_{micro}, nm
SBA-15	600	1.00	540	0.95	6.8	0.05	1.16
CI	1120	1.22	865	1.10	3.6	0.12	0.48
CII	1557	1.59	1450	1.54	3.8 ± 0.35.4 ± 1.1	0.001	–

$V_{t.}$ – total pore volume.
S_{meso}, V_{meso}, D_{meso} – mesopore specific surface area, volume and diameter.
V_{micro} – micropore volume calculated by the method *t*-plot.
D_{micro} – micropore diameter.

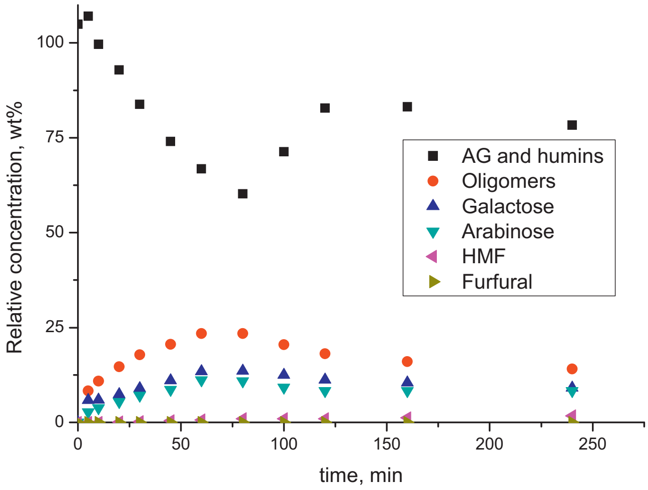

Fig. 2. Non catalytic hydrolysis of arabinogalactan at 185 °C.

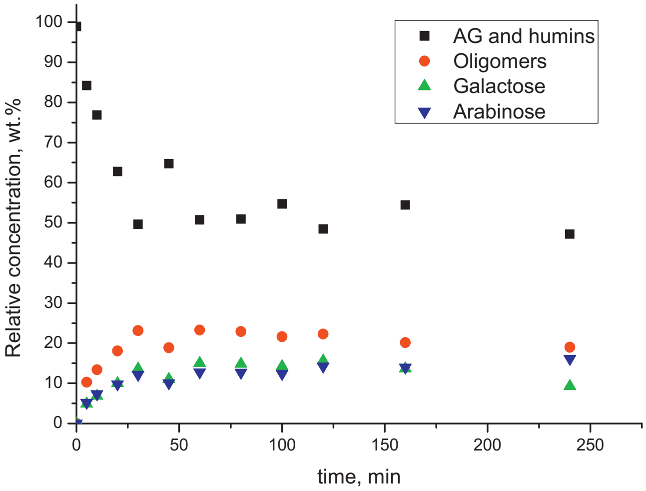

Fig. 3. Hydrolysis of AG at 185 °C in the presence of hydrogen with CI material.

hydrolysis of hemicelluloses in the aqueous phase, proceeds via the protonation of the glycosic bonds between the sugar units in the hemicellulose chain, resulting in the formation of t monosaccharides [20].

A noncatalytic experiment conducted at 458 K and total pressure 21 bar was described in ref. [22] demonstrating (Fig. 2) that even in the absence of any acid catalyst arabinose and galactose were formed along with oligomers.

The reason for such behaviour is the presence of in-situ generated protons which enhance the hydrolysis step even without any heterogeneous catalyst. In the hydrolysis of hemicelluloses H_3O^+ from water acts as a homogeneous acid catalyst. Besides the main sugars originating from the hemicellulose also dehydration products of sugars, such as furfural and 5-hydroxymethyl furfural were detected in inferior quantities. Their formation can be also attributed to H_3O^+ generated in-situ at high temperature.

A rather strange behaviour of the AG–hunins curve in Fig. 2 is the attributed to co-production of polymeric humins, which are formed during acid catalyzed conversion of hexoses with HMF [41] or through transformations of HMF first to 2,5-dioxo-6-hydrohexanal [10]. AG and humins cannot be separated in applied HPLC analysis procedure as these polymers elute at the same time. It was mentioned in ref. [22] that when arabinose is removed from the side chain of the hemicellulose it can lead to aggregation of galactose.

It was interesting to compare the hydrolysis in the case of blank experiments with the results for CI carbon, which is not acidic. The results presented in Fig. 3 clearly demonstrate that even if there is a difference between a noncatalytic experiment and the case when CI carbon is utilized, namely lower humins formation, the overall reaction also completely stops although at a somewhat higher conversion (ca. 50% for CI and 75% for a noncatalytic experiment).

Introduction of ruthenium on carbon catalyst (Fig. 4) does not substantially change the overall picture. Fig. 4 demonstrates that the formed sugars are hydrogenated to corresponding alcohols and that the formation of dehydration products is very minimal.

3.2. Influence of functionalized carbon on hydrolysis and hydrolytic hydrogenation

Modification of the carbon properties by thermal treatment of sucrose in the presence of zinc chloride and following with hydrochloric acid for removing the salt (CII carbon) significantly changed the hydrolysis of arabinogalactan (Fig. 5).

As can be seen from Fig. 5, the conversion of AG is substantially higher that for CI. Moreover, one could see clearly formation of degradation products. An unusual behaviour of AG and the concentration profiles of humins can be associated with the fact that the curve represents a sum of their concentrations. While AG is depolymerized humins are formed simultaneously.

In [22] a general reaction network for hydrolytic hydrogenation of arabinogalactan was proposed which included formation of humins from furfural and five HMF as well as a possible formation of aggregates (not separable from humins in HPLC) from sugars and sugar alcohols due to hydrogenation of the former. In the case of arabinogalactan hydrolysis in the absence of hydrogen and the metal catalyst this general scheme could be modified (Fig. 6).

A set of differential equations considering for simplicity first order reactions with concentrations directly taken from Fig. 5 can be easily written based on the reaction network in Fig. 6. Numerical data fitting of this set for the experimental data in Fig. 5 was done with the backward difference method by minimization of the sum of residual squares, *SRS*, with non-linear regression analysis using the Simplex and Levenberg–Marquardt optimization algorithms implemented in the a parameter estimation software ModEst [42].

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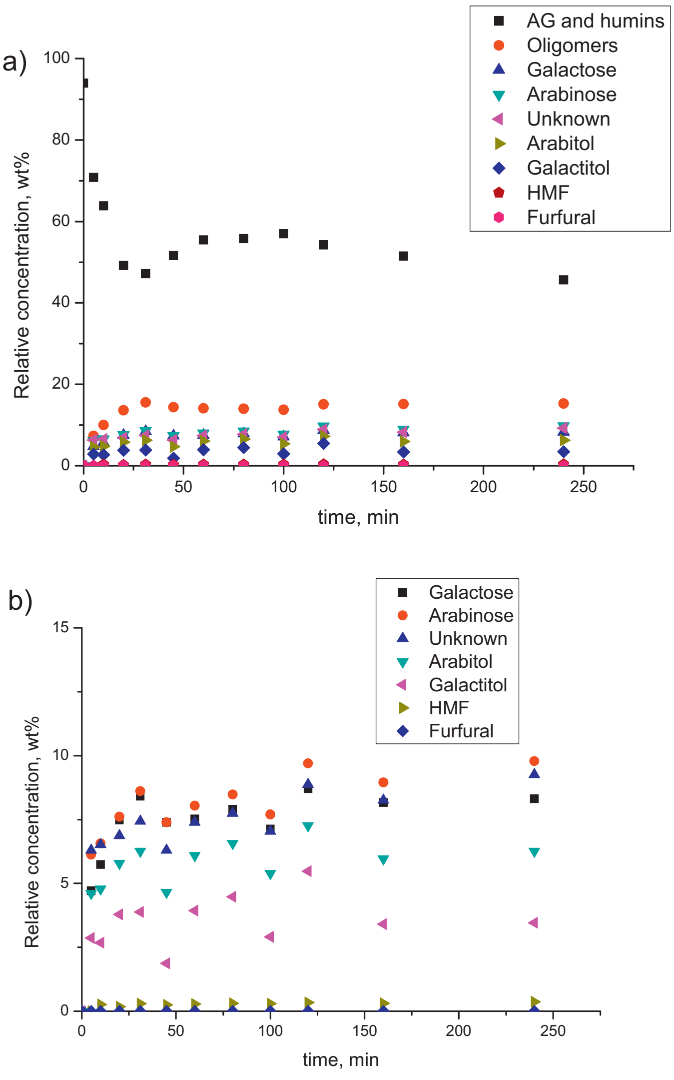

Fig. 4. Hydrogenation of AG at 185 °C with CI material and Ru/C: a) all concentrations, b) concentration of low molecular mass products.

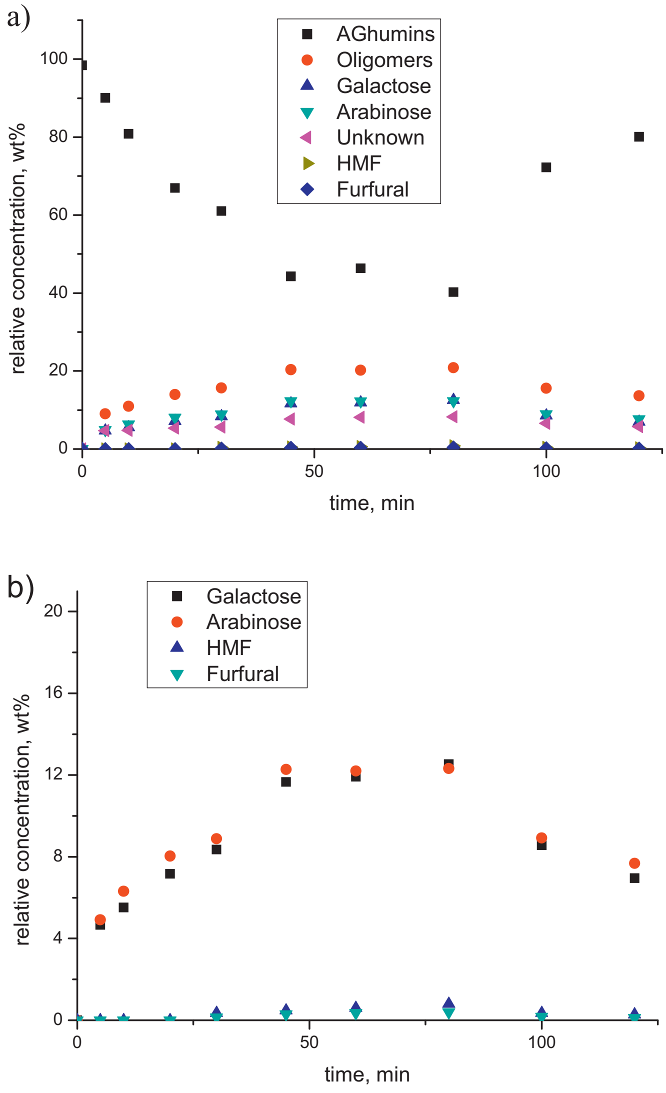

Fig. 5. Hydrolysis of AG at 185 °C in hydrogen atmosphere with CII material: a) all concentrations, b) concentration of low molecular mass products.

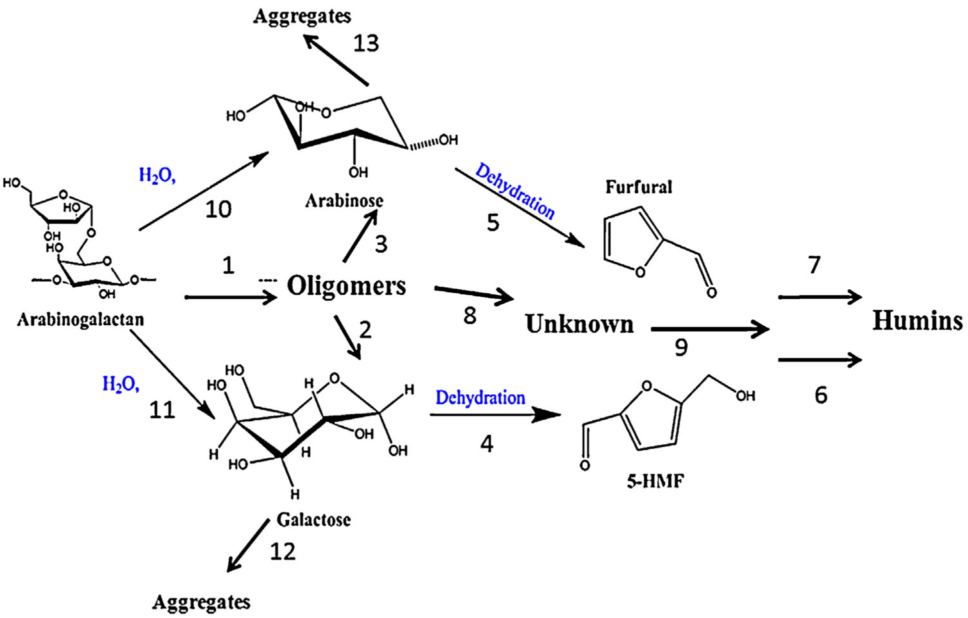

Fig. 6. Reaction network for hydrolysis of arabinogalactan.

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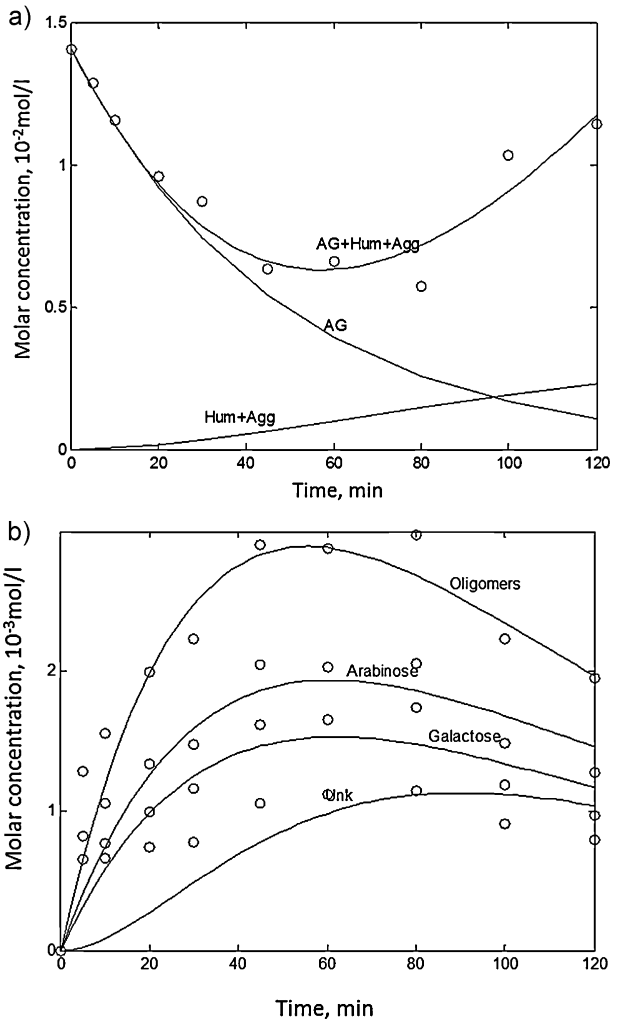

Fig. 7. Comparison between experimental data (Fig. 5) and calculations: a) higher molecular weight compounds, b) oligomers and lower molecular weight compounds.

The sum of squares was minimized starting with Simplex and thereafter switching to Levenberg–Marquardt method.

Estimated parameters (numbering corresponds to reactions in Fig. 6) and the standard errors are presented in Table 2, while the results are displayed in Fig. 7, showing a good correspondence between the experimental and calculated data with a degree of explanation above 99%. The majority of parameters are rather well identified, while few have large errors, which is understandable taking into account a relatively limited set of experimental data. In the parameter estimation the rate constants of steps 2 and 3 were negligible compared to other constants thus not being included in the Table 2.

Table 2
Values of parameters for Fig. 7.

Constant	Value	Error, %
k_1	1.77	11.0
k_4	0.99×10^{-7}	>100
k_5	1.48	>100
k_6	9.05	>100
k_7	7.06	>100
k_8	2.65	7.3
k_9	6.07	4.0
k_{10}	1.1	7.0
k_{11}	0.85	5.2
k_{12}	2.17	2.6
k_{13}	0.38	>100

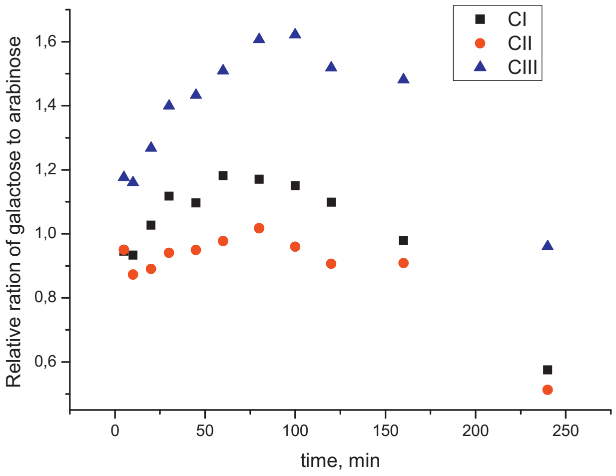

Fig. 8. Weight yields of arabinose and galactose for tested catalysts in hydrolysis of AG and 185 °C.

The galactose-to-arabinose ratio during hydrolysis is close to unity (Fig. 8) and is much smaller than one would expect from the stoichiometry (six in native AG). This implies that the release

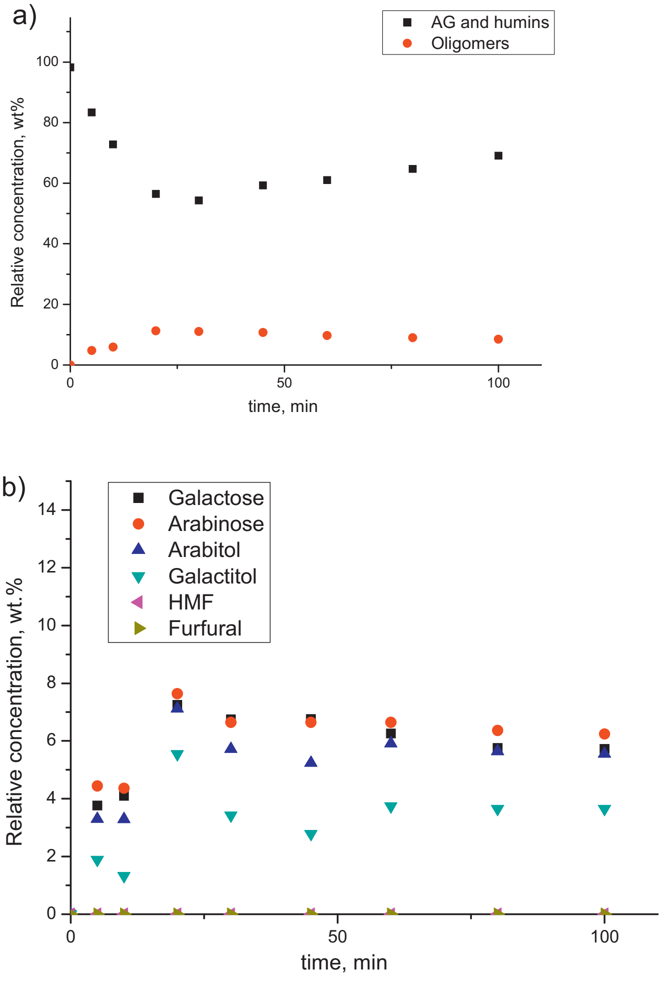

Fig. 9. Hydrogenation of AG at 185 °C with CII material and 5%Ru/C at 31 bar: a) concentration of AG, humins and oligomers, b) concentration of low molecular mass products.

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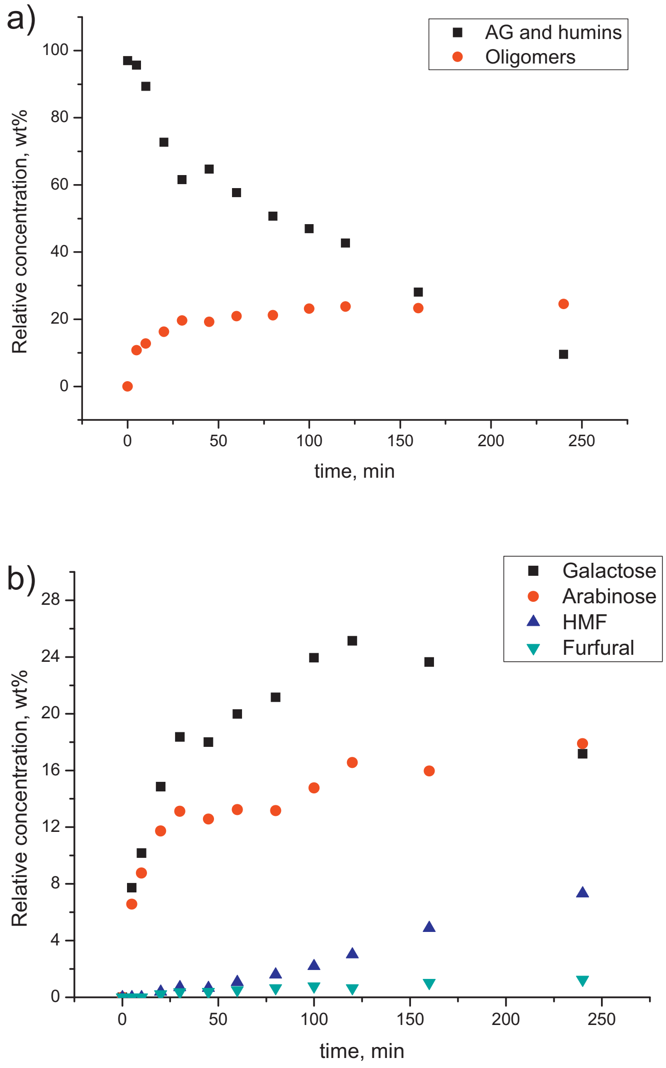

Fig. 10. Hydrolysis of AG at 185 °C with CIII material: a) concentration of AG, humins and oligomers, b) concentration of low molecular mass products.

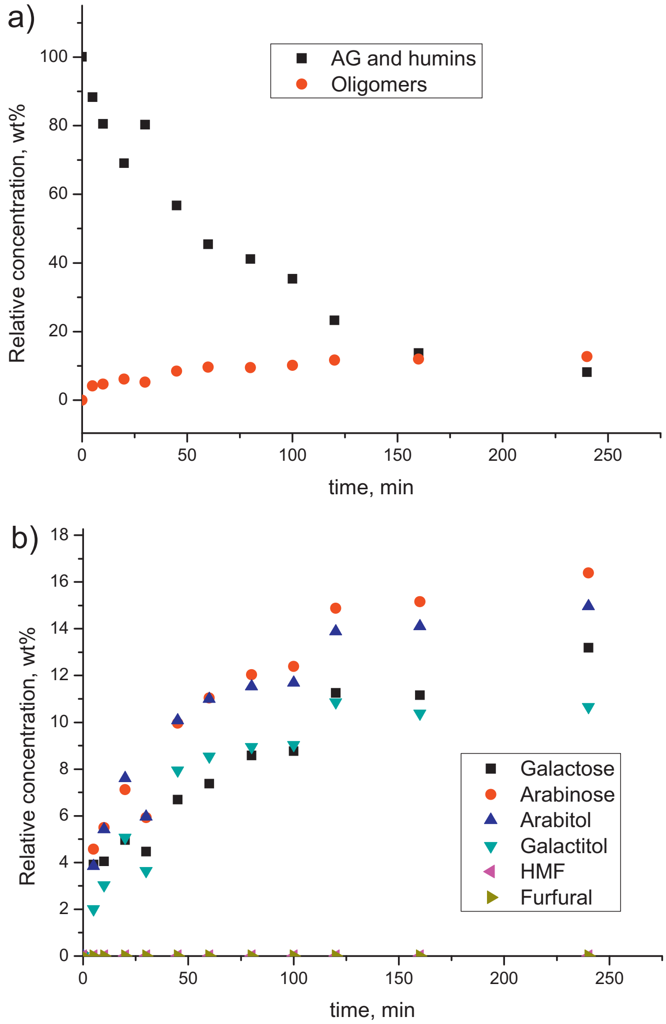

Fig. 11. Hydrogenation of AG at 185 °C with CIII material and 5%Ru/C at 31 bar: a) concentration of AG, humins and oligomers, b) concentration of low molecular mass products.

rate of arabinose is higher than for galactose reflecting preferential cleavage of the side chain containing the former sugar.

This behaviour was reported previously for AG hydrolysis using an ion-exchange resin with sulphonic groups at milder conditions (e.g. ca. 90 °C) [43]. Utilization of mineral acids such as HCl leads to the ratio of sugars consistent with stoichiometry [43].

It was previously shown [22] that when hydrolysis is carried out in water but in the presence of a Ru/C catalyst, the galactose- to-arabinose ratio is ca. 2.5 decreasing from this value to ca. 1.25 when an acidic Ru/beta zeolite is applied. Interestingly enough, the ratio of sugars is much smaller for the tested carbon materials being even below unity for CII, clearly illustrating the preferential cleavage of side arabinose groups.

The same material in the presence of a commercial 5%Ru/C catalyst accelerated the reaction leading to a higher conversion of AG (Fig. 9). Moreover, introduction of Ru in the reaction mixture completely suppressed the formation of furanic compounds and resulted in formation of sugar alcohols. A similar influence of the metal has been described for metal-modified Ru zeolites [22] also giving polyols with fewer amounts of degradation products. The hemicellulose, AG, is hydrolyzed first to the corresponding sugars, arabinose and galactose, which are subsequently hydrogenated to arabitol and galactitol. A clear difference between experiments with different carbon supports can be explained that not only H_3O^+ but also the acid sites of the support influence the hydrolysis.

From Fig. 9 it also follows that the ratio between arabitol and galactitol is even higher than the ratio between corresponding sugars, which in fact implies that arabinose is preferentially hydrogenated under actual experimental conditions.

It was interesting to further investigate the catalytic properties of carbon CII when sulfonic groups are introduced into this material (Fig. 10).

This carbon material is the most acidic one, thus it could be expected that hydrolysis would be most prominent in the presence of it. It should be noted that in a special leaching test (the heating of the catalyst in distilled water at 185 °C for 4 h) it was shown that the amount of sulfonic groups leaching from carbon in the experimental conditions is about 1–2%, which is within the error of the performed titrations. Thus the catalytic influence should be predominantly ascribed to the carbon material. It should be also noted that the ratio between galactose and arabinose is somewhat higher for CIII being still much lower than the stoichiometric one observed previously for mineral acids used in hydrolysis under milder conditions (ca. 100 °C). This result might imply that some minor hydrolysis happens also in the liquid phase due to presence of a homogeneous catalyst because of some inferior leaching of sulfonic groups. As can be seen from Fig. 10 the disappearance of AG is

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not accompanied with any increase in the concentration of humins. Not surprisingly formation of furans due to dehydration reactions was not negligible.

When CIII functionalized carbon was used together with 5%Ru/C catalyst, the rate of AG disappearance was almost the same (Fig. 11a), while the formation of sugar alcohols was visible as well as suppression of furan formation (compare Fig. 11b with Fig. 10b). The combined yield of sugar alcohols was also higher than for the mechanical mixture of CII and 5%Ru/C (Fig. 9).

The final carbon balance closure in the liquid phase with the products that could be reasonably well identified was checked to be around 90% with the least acidic catalyst CI and close to 70% for the most acidic ones. The latter results imply that besides sugars, sugar alcohols and furans also degradation products are present in the reaction milieu. Previously with H-β-11 some C2–C5 degradation products from the released monomers were detected, such as ethylene glycol, propylene glycol, glycerol, dihydroxy-propanoic and butanoic acids, butanediol (-triol), pentanediol (-triol) and their derivatives [22] being formed through various degradation reactions. These reactions of unstable monosaccharides take place at high temperatures and especially with increasing acidity of catalysts.

4. Conclusions

The majority of studies in the literature on hydrolytic hydrogenation of polysaccharides deals with cellulose as the feedstock, while the present work describes transformation of a hemicellulose arabinogalactan.

Besides using a different feedstock the focus of the current work was on detailed understanding of the reaction pathways including formation of humins, aggregates and oligomers, which is happening during hydrolytic hydrogenation, but typically either not reported or quantified.

In the current work the hydrolytic hydrogenation of arabinogalactan was studied over mechanical mixtures of functionalized carbon and Ru/C. Moreover hydrolysis of arabinogalactan using only the former carbon materials was conducted. Hydrolysis of the hemicellulose is due to acidity of the carbons materials as well as homogeneous catalysis by H_3O^+ originating from water. Carbon materials functionalized with sulfonic groups afforded hydrolytic hydrogenation of arabinogalactan with hydrogenation occurring on Ru/C. This catalytic system clearly diminished the formation of humins and dehydration products.

Finally the experimental data for arabinogalactan hydrolysis were modelled based on the proposed reaction network covering formation not only of the main reaction products, but also oligomers and heavy molecular weight products eluting at the same time as the initial substrate.

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