**A one-pot microwave-assisted NaCl-H2O/GVL solvent system for cellulose conversion to 5-hydroxymethylfurfural and saccharides with *in situ* separation of the products**

Zhicheng Jianga,b,c, Javier Remón\*b, Tianzong Li b, Vitaliy L. Budarin b, Jiajun Fan b, Changwei Hu\*a, James H. Clarkb

a Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan, 610064, P. R. China.

b Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, YO10 5DD, UK.

c National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu, Sichuan, 610064, P. R. China.

Corresponding author:

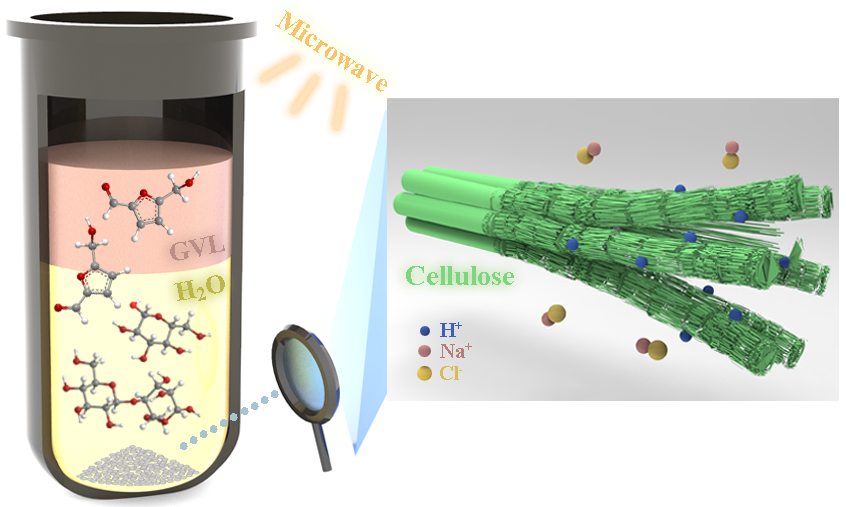
Javier Remón: [javier.remonnunez@york.ac.uk](mailto:javier.remonnunez@york.ac.uk); +44-0-1904322511

Changwei Hu: [changweihu@scu.edu.cn](mailto:changweihu@scu.edu.cn); +86-28-85411105

**Abstract**

This work addresses a microwave-assisted, NaCl-H2O/γ-valerolactone (GVL) solvent system for the co-production of 5-hydroxymethylfurfural (HMF) and saccharides from cellulose, examining the effects of the solvent system (H2O/GVL), NaCl concentration and reaction time. Oligosaccharides and glucose were completely recovered in the aqueous phase and their yields varied between 4-67 wt.% and 0-16 wt.%, respectively, while HMF was largely recovered in the organic phase, in a yield between 0-13 wt.%. Increasing the proportion of H2O in the system promoted cellulose depolymerisation and increased the production of oligosaccharides and glucose. This latter underwent a further decomposition to yield HMF and carboxylic acids when long times were used. An increase in NaCl not only kinetically promoted cellulose decomposition, but also modified the solubility of cellulose decomposition products in the aqueous phase, thus playing a very important role on the products distribution within both phases. With a solvent system consisting of 67/33 vol.% H2O/GVL, with 30 wt.% NaCl at 220 ºC for 18 min, it is possible to selectively convert 76% of the cellulose into a sugar-rich aqueous solution and a rich HMF organic phase. The former was made up of glucose (25 %) and oligosaccharides (64 %), while the later mainly comprised HMF (75 %). This might help the development of new biomass pre-processing technologies, allowing the co-production of precursors for the chemical and biological industries.

**Graphical abstract**



**Keywords:** Cellulose; Depolymerisation; Microwaves, NaCl, Water, γ-Valerolactone.

**Introduction**

The widespread use of fossil fuels is receiving some criticisms in terms of environmental and geopolitical implications as a result of new global poolicies to decrease the current over-dependency on crude oil and mitigate environmental pollution ([Jiang and Hu 2016](#_ENREF_22)). As part of this, the bio-refinery concept, i.e. using biomass and/or biomass residues and wastes as a feedstock to produce energy and chemicals, is gaining increasing attention. Lignocellulosic biomass largely consists of cellulose, hemicellulose and lignin, the relative amount of each structural component depending on the species. Herein, cellulose is the most abundant compound within the lignocellulosic biomass ([Sadula et al. 2017](#_ENREF_37)), as well as the most copious natural biopolymer on the Earth, thus converting this bio-based material into a very promising feedstock from which a bio-refinery concept could be built around.

Hydrothermal depolymerisation of cellulose is normally considered a promising approach for cellulose valorisation ([Abdullah et al. 2014](#_ENREF_1)). This process allows a liquid solution containing oligo- and mono-saccharides to be produced. Furthermore, a lot of different platform chemicals can be subsequently produced from these sugars via thermochemical and/or biological treatments ([Huang and Fu 2013](#_ENREF_15)). However, the intensive hydrogen bonds within the cellulose structure hinder the depolymerisation of cellulose ([Jiang et al. 2015](#_ENREF_19); [Mosier et al. 2005](#_ENREF_30)). In addition, 5-hydroxymethylfurfural (HMF) is another interesting platform molecule that can be produced from cellulose via glucose dehydration using hydrothermal treatments. This chemical is capable of connecting the biomass-based carbohydrate chemistry with the petroleum-based industry ([Zhao et al. 2007](#_ENREF_53)). Specifically, HMF can be converted into a large number of chemicals and platforms molecules and therefore, its production is gaining increasing attention ([De et al. 2011](#_ENREF_10); [Roman-Leshkov et al. 2007](#_ENREF_36); [Yang et al. 2016](#_ENREF_50)). HMF has traditionally been produced from glucose and fructose rather than from cellulose, and much higher HMF yields were obtained from these sugars than using cellulose. However, although new insights are being gained into the direct conversion of cellulose in HMF ([Bodachivskyi et al. 2018](#_ENREF_7)), new processes and more sustainable strategies need to be developed.

In this respect, various solvents have been attempted to explore an environmentally friendly reaction system for cellulose depolymerisation. Among them, water has been widely used as the reaction media. The use of water not only is economically feasible, but also it allows the production of high yields of oligosaccharides and glucose ([Li et al. 2017a](#_ENREF_24)). However, the yield and selectivity of HMF obtained from cellulose depolymerisation in aqueous systems are relatively low. To achieve an effective conversion of cellulose into HMF, elevated temperatures and long reaction times are to be used. This leads to the formation of by-products from side reactions, such as repolymerisation and decomposition of HMF, which leads to the formation of humins and carboxylic acids, among other compounds ([Tong et al. 2010](#_ENREF_42)).

This circumstance has led to the development of biphasic solvent systems in order to reduce the extent of side reactions. These systems are made up of an aqueous and an organic phase for a selective distribution of the reactants, intermediates and target products, thus helping the prevalence of some reactions over another. In particular, all the products from depolymerisation and decomposition of cellulose, including saccharides and HMF, are produced in the aqueous phase. Then, HMF can spontaneously be transferred to the organic phase if an appropriate organic solvent is used. This hinders the subsequent hydrolysis of HMF in water, thus increasing the yield of HMF ([Román-Leshkov and Dumesic 2009](#_ENREF_35)). Besides, the concentration of HMF in the aqueous phase is reduced as this compound moves from the aqueous phase to the organic phase, which shifts the equilibrium of saccharides conversion in the aqueous phase, resulting in an increase in the conversion rate and the yield of HMF.

Regarding the organic compounds used in H2O/co-solvent systems, miscible and partially miscible in water organic solvents have been used ([Jiang et al. 2018c](#_ENREF_20); [Li et al. 2016b](#_ENREF_28)). Partially miscible solvents include butanol, 2-methyltetrahydrofuran (MeTHF) and methyl isobutyl ketone (MIBK). Atanda et al. used a catalytic (TiO2) biphasic H2O/MeTHF solvent system for HMF production from rice husk and sugarcane bagasse. HMF yields of 65 wt.% and 72 wt.%, were respectively reported at 180 oC for 30 min ([Atanda et al. 2016](#_ENREF_4)). Cao et al. achieved 40 wt.% HMF yield from cellulose at 160 oC for 120 min using a H2O-DMSO/MIBK biphasic system catalysed by HCl ([Cao et al. 2015](#_ENREF_8)).

Miscible solvents used in biphasic systems mainly comprise aprotic polar solvents, such as tetrahydrofuran (THF) and γ-valerolactone (GVL). Among all the different solvent parameters affecting the solvent properties in these water/organic bi-phasic systems, *β and δ*h are normally regarded as the most influential parameters controlling the hydrolysis reactions. In particular, a low *β* value increases the acidity of the system and a good *δ*h value in the Hansen space improves the solubility of oligosaccharides ([Zhang and Yan 2017](#_ENREF_52)). For these solvents, inorganic salts, like NaCl, have been widely used to separate organic phase from aqueous phase and also modify the solubility of some organic compounds in the aqueous phase. This allows the solubility of cellulose decomposition products in the system to be tailored, thus helping to improve the performance of the reaction system. In addition, it must be borne in mind that these salts can also catalytically promote cellulose decomposition reactions. This catalytic effect was investigated during the cellulose decomposition by Jiang et al. using a NaCl-H2O system. These authors found that the presence of NaCl increased the formation of carboxylic acids, which exerted a positive catalytic effect on the process. As a result, 74% of the cellulose was converted into soluble oligosaccharides (53 wt.% yield) in a batch reactor (220 oC for 120 min) ([Jiang et al. 2015](#_ENREF_19)). In addition, Yang et al. studied the decomposition of cellulose using a Fe-resin solid catalyst in a water solution containing 5 wt.% NaCl at 200 oC for 300 min. They found that NaCl promoted cellulose depolymerisation and reported a glucose yield of up to 39 wt.% ([Yang et al. 2014](#_ENREF_49)). THF has also been used in aqueous/organic systems for the direct conversion of cellulose to HMF ([Shen et al. 2014](#_ENREF_38); [Xu et al. 2016](#_ENREF_47)). In this respect, cellulosic eucalyptus was converted into HMF (45 wt.% yield) using a NaCl-H2O-THF biphasic system catalysed by InCl3. The comparison between the aqueous and binary water/organic system (NaCl-H2O and NaCl-H2O-THF) revealed that a more efficient cellulose conversion was produced with the latter than the former ([Jiang et al. 2018d](#_ENREF_21)). The addition of NaCl prevented the possible HMF dehydration, thus enhancing the HMF yield and cellulose conversion. However, the possible catalytic effect of NaCl was not taken into account ([Wei and Wu 2016](#_ENREF_44)). Furthermore, γ-valerolactone (GVL) has been also used to produce HMF from cellulose ([Alonso et al. 2013a](#_ENREF_2); [Alonso et al. 2013b](#_ENREF_3); [Li et al. 2016a](#_ENREF_27); [Luterbacher et al. 2014](#_ENREF_29)). In some of these works, NaCl was also used to modify the solubility of GVL in water. Wettstein et al. addressed the catalytic conversion of cellulose using a H2O-GVL solvent containing different amounts of HCl (acid based catalyst) and NaCl (solubility modifier) at 155 ºC ([Wettstein et al. 2012](#_ENREF_45)). However the effect of NaCl on cellulose conversion was not observed as the process was conducted at relatively low temperature and cellulose can only be activated over 180 ºC in the absence of acids ([Fan et al. 2013](#_ENREF_11)).

These works reported to date provide good insights into cellulose depolymerisation to produce mono/oligo saccharides or HMF; however, to the best of the authors’ knowledge, this approach has always been used for the individual production of one or the other. In addition, the possible catalytic effect of NaCl during cellulose depolymerisation is not yet well understood. Given this scenario, this work addresses a novel microwave-assisted NaCl-H2O/GVL solvent system for the simultaneous production of (mono/oligo) saccharides and HMF with *in situ* separation of the products, analysing the effects of the NaCl concentration, solvent system (H2O/GVL) and holding time on the process. GVL was selected as the organic solvent having regard to its biomass-derived nature and relatively high boiling point, thus preventing pressure increases. Others system based on cheaper renewable solvents could include NaCl-H2O-THF ([Jiang et al. 2018d](#_ENREF_21)), and the information included in this work could be used for the optimisation of other NaCl-H2O/organic biphasic solvent systems. Microwave heating was used as it represents a potentially faster, more efficient and selective process for the thermal treatment of biomass ([Li et al. 2018](#_ENREF_25); [Li et al. 2017b](#_ENREF_26)). The comparison between microwave-assisted and conventional hydrolysis for the depolymerisation of cellulose, revealed that microwave heating was more effective and selective ([Fan et al. 2013](#_ENREF_11)). Polar solvents are highly effective in microwave energy absorption; therefore, the combination of these solvents together with microwave assisted heating offers an interesting and environmentally friendly technology for the valorisation of cellulosic materials. Besides, strong ionic solution has been reported to couple more efficiently with microwaves, and thus a concentrated NaCl solution can decrease the total energy consumed during microwave heating ([Jiang et al. 2018a](#_ENREF_17); [Xiouras et al. 2016](#_ENREF_46)). The fact that water/organic systems have never used to simultaneously produce saccharides and HMF demonstrate, together with the results provided by the in-depth study and the optimisation conducted addressing both NaCl solubility and catalytic effects, that this work represents a novel investigation in this field, which can help to develop novel, green and energy efficient methods for the production of energy carriers for the biological and chemical sectors.

**Materials and methods**

**Materials**

Microcrystalline cellulose, NaCl and GVL, all with a purity greater than 99 wt.%, were purchased from Sigma-Aldrich and used as received.

**Microwave experiments**

The experiments were carried out in an Anton Paar microwave system. For each reaction, 0.2 g of cellulose along with 4 mL of solvent (H2O+GVL), containing varying amounts of NaCl, were loaded into a 10 mL glass reactor. The solvent composition and the amount of NaCl in the reaction mixture were modified for each reaction according to the experimental design used for the experimentation. Before placing the reactor into the microwave unit, the reaction mixture was pre-stirred at room temperature for 5 min. A ramping time (time to reach the designed reaction temperature) of 5 min and a temperature of 220 ºC were used for all the experiments, while the reaction time was varied between 0 (to take into account the possible cellulose conversion during the heating up step) and 30 min (6 times higher than the ramping time to properly analyse this variable). According to our previous work, cellulose reacts very slowly when a reaction temperature below 220 oC is used ([Jiang et al. 2018b](#_ENREF_18)). After reaction, the reactor was quickly cooled down to room temperature by the default microwave system-cooling programme. Then, it was taken out from the microwave system and left 5 minutes at room temperature to achieve a complete separation of the solvent phases, i.e. the aqueous (NaCl-H2O) and the organic (GVL) phase. After this, three phases were clearly observed: an upper (organic) phase made up of GVL together with some cellulose decomposition products; a middle (aqueous) phase containing NaCl and cellulose water-soluble decomposition products, and a bottom phase containing unreacted solid cellulose. The upper phase (GVL phase) was recovered by means of a pipette. Then, the solid phase was separated from the aqueous phase by filtration. The solid residue was dried overnight at 105°C in an oven.

**Response variables and analytical methods**

Several response variables (Eq. 1 and 2) were used to analyse the effect of the operating conditions on the process. These include the overall cellulose conversion together with the yield of the different products recovered in each of the two phases, i.e. the yield of oligomers, the yield of glucose produced and recovered in the aqueous phase along with the yields of HMF, levulinic and formic acids produced and recovered in both, the aqueous phase and organic (GVL) phase. Oligomers identified and quantified included cellotriose (DP3), cellotetraose (DP4), cellopentaose and (DP5) and cellohexaose (DP6).

(Eq. 1)

(Eq. 2)

The aqueous and GVL phases were analysed by High Performance Liquid Chromatography (HPLC). The analyses were conducted using an Agilent 1260 apparatus fitted with an Infinity II RI Detector using two different columns. Sugars and carboxylic acids were determined with an Agilent Hi-Plex H (7.7 × 300 mm, 8 µm (p/n PL1170-6830), using a 0.005 M H2SO4 solution as the mobile phase. Besides, an ACE C18 (250 × 4.6 mm, 5 um particle size) column was used to analyse HMF and furfural, employing an acetonitrile/water (25/75, vol/vol) solution as the mobile phase. A liquid flow rate of 0.8 mL/min was used for both columns. The traditional chemical titration method was used for the calculation of cellulose and humins contents in the solid residue ([Hu et al. 2014](#_ENREF_13)).

**Experimental design and data analysis**

The influence of the concentration of NaCl in the aqueous phase (10-30 wt.%), the solvent composition H2O/GVL (1:4 to 4:1, vol:vol) and reaction time (0 to 30 min) during the microwave-assisted cellulose conversion at 220 ºC was experimentally investigated. The experiments were planned according to a 2 level 3-factor Box-Wilson Central Composite Face Centred (CCF, α: ±1) design. This corresponds to a 2k factorial design, where k indicates the number of factors studied (in this case 3 operating variables) and 2k represents the number of runs (in this case 8) for the simple factorial design. 8 axial experiments were also performed to study non-linear effects and interactions and 3 replicates at centre of the variation interval of each factor were carried out in order to evaluate the experimental error. This experimental design is suitable for studying the influence of each variable (linear and quadratic effects) together with all the possible interactions between them. All the results were studied with an analysis of variance (ANOVA) with 95% confidence. The ANOVA analysis assists to select the operating variables and interactions that significantly affect the response variables under consideration. For each response variable, the results predicted with the statistical model developed with the ANOVA analysis have been compared with the experimental value. For all the models, the lack of fit was not statistically significant in relation to the pure error with 95% confidence (p-value > 0.05) and their R2 is higher than 0.95, which validates the models developed. Figures show the interaction plots obtained with the models developed with the ANOVA analyses of the results of the 18 experiments performed. Experimental points have been added to these figures, when possible, to visually show that the lack of fit is not significant and to include more information in the figures. In addition, the cause-effect Pareto principle was employed to calculate the relative importance of the operating variables in the response variables. In these analyses, the lower and upper limits of all the operating variables were normalised from -1 to 1 (codec variables), which allows all operating variables (factors) to vary within the same interval and helps to investigate their effect in comparable terms.

**Results and discussion**

Table 1 lists the overall cellulose conversion and the yields of the major cellulose decomposition products recovered and quantified in both phases: H2O (aqueous) and GVL (organic). The relative influence of the operating variables on the results according to the ANOVA analysis and the cause-effect Pareto principle is shown in Table 2.

***Effects of the operating conditions on the total cellulose conversion***

The cellulose conversion varied between 17 and 99%, which indicates that our solvent system is very effective for cellulose depolymerisation under microwave heating at the operating conditions tested in this work. The cause-effect Pareto analysis reveals that the reaction time is the operating variable exerting the greatest influence on the overall conversion of cellulose with 33% of influence, followed by the concentration of NaCl with 22% of influence. Besides, the interactions between the reaction time and the NaCl concentration also exert a significant influence, although their relative influence is less important (13%). Figure 1 shows the interaction plots developed with the ANOVA analysis to explain the effect of the operating conditions on the conversion of cellulose. In particular, Figure 1 illustrates the effect of the solvent system (H2O/GVL) and the reaction time on the overall conversion of cellulose for different concentrations of NaCl: 10 wt.% (A) 20 wt.% (B) and 30 wt.% (C).

As regards the effect of the solvent system (H2O/GVL) on cellulose conversion, Figure 1 shows that regardless of the other operating conditions, increasing the proportion of water in the system leads to a significant increase in the overall cellulose conversion. A higher proportion of water in the solvent system experimentally results into an increase in the water/cellulose ratio. This produces a greater spread of cellulose hydrolysis reactions, thus augmenting the overall cellulose conversion ([Yang et al. 2012](#_ENREF_51)). This is accounted for by the stronger interactions occurring between cellulose and water than those taking place between cellulose and GVL. Cellulose has abundant hydroxyl groups on its surface, which are more likely to interact with H2O than with GVL ([Shi et al. 2013](#_ENREF_39)).

**Table 1** Experimental conditions: reaction time (min), solvent system (H2O/GVL, vol:vol) and NaCl/H2O (wt. %) and the original results obtained in the experiments

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9-12 | 13 | 14 | 15 | 16 | 17 | 18 |
| Time (min) | 0 | 30 | 0 | 30 | 0 | 30 | 0 | 30 | 15 | 0 | 30 | 15 | 15 | 15 | 15 |
| NaCl/H2O (wt. %) | 10 | 10 | 30 | 30 | 10 | 10 | 30 | 30 | 20 | 20 | 20 | 10 | 30 | 20 | 20 |
| H2O/GVL (vol : vol) | 1:4 | 1:4 | 1:4 | 1:4 | 4:1 | 4:1 | 4:1 | 4:1 | 1:1 | 1:1 | 1:1 | 1:1 | 1:1 | 1:4 | 4:1 |
| Overall conversion (%) | 18.4 | 48.8 | 20.1 | 45.7 | 28.3 | 97.9 | 28.0 | 99.8 | 64.5±1.0 | 17.3 | 61.1 | 50.7 | 64.9 | 30.3 | 73.9 |
| Humins yield (wt.%) | 1.5 | 5.7 | 3.5 | 5.7 | 2.5 | 3.4 | 3.9 | 1.0 | 5.3±0.4 | 2.6 | 12.7 | 3.9 | 6.0 | 4.3 | 4.8 |
| Oligomers yield (wt. %) | 14.0 | 26.6 | 10.5 | 24.7 | 20.8 | 63.3 | 15.1 | 68.4 | 25.0±2.1 | 3.6 | 18.8 | 20.5 | 19.7 | 13.8 | 27.4 |
| Glucose yield in H2O (wt. %) | 0.0 | 2.6 | 0.1 | 2.0 | 1.9 | 12.3 | 3.2 | 0.0 | 11.8±0.6 | 1.9 | 6.6 | 8.4 | 11.4 | 1.2 | 16.0 |
| HMF yield in H2O (wt. %) | 0.0 | 3.4 | 1.0 | 1.6 | 0.2 | 5.7 | 0.2 | 4.1 | 0.8±0.3 | 0.1 | 0.4 | 0.8 | 1.1 | 0.8 | 2.7 |
| HMF yield in GVL (wt. %) | 0.2 | 1.8 | 0.5 | 2.9 | 0.0 | 0.0 | 0.1 | 2.6 | 10.5±1.4 | 1.1 | 6.4 | 5.5 | 11.8 | 1.0 | 9.3 |
| LeA yield in H2O (wt. %) | 2.3 | 3.6 | 1.7 | 1.9 | 1.3 | 6.1 | 1.0 | 8.3 | 0.6±0.1 | 0.8 | 0.6 | 0.8 | 0.7 | 2.3 | 1.4 |
| LeA yield in GVL (wt. %) | 1.7 | 1.7 | 3.1 | 3.1 | 0.0 | 0.0 | 2.1 | 4.9 | 3.8±0.4 | 2.7 | 4.6 | 2.9 | 4.1 | 2.5 | 3.2 |
| FA yield in H2O (wt. %) | 0.2 | 0.2 | 0.0 | 0.2 | 0.1 | 3.1 | 0.1 | 3.9 | 0.1±0.0 | 0.1 | 0.2 | 0.1 | 0.2 | 0.1 | 0.8 |
| FA yield in GVL (wt. %) | 0.0 | 0.1 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.7 | 1.0±0.3 | 0.0 | 0.4 | 0.4 | 1.1 | 0.0 | 0.43 |

**Table 2** Relative influence of the operating conditions according to the ANOVA analysis.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Variable | R2 | I.Term | A (time) | B (H2O/GVL) | C (NaCl/H2O) | AB | AC | BC | ABC | A2 | B2 | C2 | A2B | A2C | AB2 | A2B2 |
| Overall results |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Overall conversion (%) | 0.99 | 59.30 | 21.88 | 7.12 | 21.82 | n.s. | 10.67 | n.s. | n.s. | -25.29 | -6.80 | -12.43 | -7.10 | -6.70 | 2.79 | 28.36 |
|  |  |  | (33) | (5) | (22) |  | (13) |  |  | (10) | (3) | (1) | (4) | (3) | (1) | (5) |
| Oligomers yield (wt. %) | 0.99 | 25.36 | 7.60 | n.s. | 11.82 | 1.86 | 8.92 | n.s. | n.s. | -14.11 | -5.06. | n.s. | n.s. | n.s. | 7.55 | 25.02 |
|  |  |  | (26) |  | (23) | (4) | (15) |  |  | (4) | (8) |  |  |  | (6) | (14) |
| Glucose yield in H2O (wt. %) | 0.99 | 11.76 | 1.65 | 1.50 | 7.38 | -1.80 | n.s. | -1.32 | -1.63 | -7.51 | -1.85 | -3.14 | -2.94 | -5.79 | n.s. | 3.53 |
|  |  |  | (8) | (4) | (13) | (7) |  | (5) | (7) | (18) | (15) | (4) | (5) | (11) |  | (3) |
| HMF yield in H2O (wt. %) | 0.98 | 0.84 | n.s. | n.s. | 0.70 | -0.44 | 0.57 | n.s. | n.s. | -0.60 | n.s. | 0.92 | -0.43 | n.s. | 1.79 | 0.73 |
|  |  |  |  |  | (15) | (8) | (11) |  |  | (7) |  | (15) | (8) |  | (32) | (4) |
| HMF yield in GVL (wt. %) | 0.95 | 9.65 | 1.17 | 3.18 | 4.15 | n.s. | n.s. | n.s. | n.s. | -5.10 | n.s. | -3.74 | -2.67 | -4.47 | n.s. | n.s. |
|  |  |  | (9) | (8) | (5) |  |  |  |  | (38) |  | (17) | (9) | (14) |  |  |
| LeA yield in H2O (wt. %) | 0.99 | 0.67 | n.s. | n.s. | -0.46 | 0.18 | 1.33 | 0.53 | 0.44 | n.s. | n.s. | 1.16 | n.s. | 1.35 | 1.31 | 1.44 |
|  |  |  |  |  | (9) | (1) | (17) | (7) | (6) |  |  | (22) |  | (8) | (22) | (8) |
| LeA yield in GVL (wt. %) | 0.97 | 3.81 | 0.95 | 0.59 | n.s. | 0.36 | 0.35 | 0.54 | 0.34 | n.s. | -0.51 | -1.17 | 0.63 | -0.31 | -0.61 | n.s. |
|  |  |  | (9) | (22) |  | (6) | (6) | (10) | (6) |  | (6) | (19) | (5) | (6) | (5) |  |
| FA yield in H2O (wt. %) | 0.99 | 0.14 | 0.07 | 0.08 | 0.32 | 0.10 | 0.82 | 0.12 | 0.08 | n.s. | n.s. | 0.29 | n.s. | 0.49 | 0.83 | 0.53 |
|  |  |  | (19) | (2) | (19) | (2) | (20) | (3) | (2) |  |  | (13) |  | (5) | (9) | (6) |
| FA yield in GVL (wt. %) | 0.58 | 0.81 | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | -0.37 | n.s. | -0.38. | n.s. | n.s. | n.s. | n.s. |
| n.s: Non significant with 95% confidence. Response = Indep. + Coefficient A·A + Coefficient B·B + Coefficient C·C + Coefficient AB·AB + Coefficient AC·AC + Coefficient BC·BC + Coefficient ABC·ABC + Coefficient A2·A2 + Coefficient B2·B2 + Coefficient C2·C2 + Coefficient A2B·A2B+ Coefficient A2C·A2C + Coefficient AB2·AB2 + Coefficient A2B2·A2B2  Numbers in brackets indicate the percentage Pareto influence of each factor on the response variable. Pareto values represent the percentage of the orthogonal estimated total value. | | | | | | | | | | | | | | | | |

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**Fig. 1** Interaction plots between the solvent system (H2O/GVL) and the holding time with different NaCl/H2O ratios for the overall conversion of cellulose. Bars are LSD intervals with 95% confidence.

The effects of the reaction time on the overall cellulose conversion depend on the solvent system and the concentration of NaCl in the mixture. In general, an increase in the reaction time increases the cellulose conversion due to longer exposure of the material to microwave energy. However, the concentration of NaCl modifies the effect of the reaction time due to the significant interaction between these two variables. For a low concentration of this salt (10 wt.%), Figure 1A shows that an increase in the reaction time results into a progressive increase in the overall cellulose conversion. However, this increase depends on the solvent system, i.e. a higher conversion takes place for rich aqueous mixtures than for those containing a high amount of GVL, due to the positive effect that water exerts on the hydrolysis of cellulose, as described earlier.

Increasing the NaCl concentration up to 20 wt.% leads to a rapid increase in the cellulose conversion, especially between 0 and 15 min. At this reaction time (15 min), a much higher cellulose conversion is obtained for a solution containing 20 wt.% of NaCl (74%) than for the same solution having 10 wt.% NaCl (60%). This suggests a positive catalytic effect of NaCl on the decomposition of cellulose. The presence of NaCl in the solution promotes the formation of acidic products from the decomposition of polysaccharides and sugars ([Tang et al. 2017](#_ENREF_40)), thus increasing the concentration of protons in water. These protons can be strongly adsorbed on the cellulose surface in the presence of high concentration of salts due to the increase in the ionic strength of the solution ([Jiang et al. 2018b](#_ENREF_18)). In addition, Cl- can generate hydrogen bonding with hydroxyl groups of cellulose, and breaks the original intermolecular hydrogen bonding among the cellulose chains, improving the disaggregation of cellulose strands and the solubilisation of cellulose ([Jiang et al. 2018b](#_ENREF_18); [Jiang et al. 2015](#_ENREF_19)). However, a further increase in the reaction time from 15 to 30 min does not increase the cellulose conversion regardless of the solvent system. When long reaction times are used, the formation of solid species (such as char and humins, Table 1) and their deposition on the cellulose surface inhibit the conversion of cellulose by blocking the interaction of cellulose and reagents and decrease the selectivity to liquid products. The presence of salts favours dehydration reactions ([Atia et al. 2011](#_ENREF_5); [Haber et al. 2002](#_ENREF_12)), promoting condensation and cross-polymerisation reactions and leading to the formation of humic acids and large organic compounds ([Chheda and Dumesic 2007](#_ENREF_9); [Huber and Dumesic 2006](#_ENREF_16); [Kirilin et al. 2012](#_ENREF_23); [Rackemann et al. 2014](#_ENREF_31); [Taylor et al. 2016](#_ENREF_41); [Tuteja et al. 2012](#_ENREF_43); [Yan et al. 2014](#_ENREF_48)). The formation of these macromolecules can occur from the furfural and HMF obtained from sugars ([Remón et al. 2016a](#_ENREF_32); [Remón et al. 2016b](#_ENREF_33); [Remón et al. 2016c](#_ENREF_34)).

Very interestingly, a further increase in the concentration of NaCl increases cellulose conversion. In particular, while an increase in the concentration of NaCl between 20 and 30 wt.% does not significantly change the cellulose conversion between 0 and 15 minutes, the conversion shows a progressive increase between 15 and 30 min for a 30 wt.% NaCl solution, rather than a plateau trace in this variable for a 20 wt.% NaCl solution. This is the consequence of two developments. A further increase in NaCl up to 30 wt.% promotes cellulose conversion to HMF, but it also decreases the solubility in water of this latter compound, thus helping its transference from the aqueous to the GVL phase. The removal of HMF from the aqueous phase might help prevent its dehydration, thus decreasing solid (humins and char) formation, and therefore, avoiding the deposition of humins on the cellulose surface, thus aiding cellulose conversion and selectivity to liquid products.

***Effects of the operating conditions on the yields of oligosaccharides and glucose***

The chemical analysis of the H2O and GVL phases reveals that under the operating conditions tested in this work, cellulose largely decomposes into a mixture of oligomers, glucose, HMF, levulinic acid and formic acid. Oligomers comprise a mixture of DP 3-6 oligosaccharides, including cellotriose (DP3), cellotetraose (DP4), cellopentaose and (DP5) and cellohexaose (DP6); DP4-6 species accounting for more than 90 wt.% of this fraction. Oligomers and glucose remain in the aqueous phase after the process, while HMF and both carboxylic acids distribute between the aqueous and organic phase in different proportionsdepending on the solvent system, NaCl concentration and reaction time. This product distribution is of paramount importance for the simultaneous production of sugar rich solutions and HMF in a single process. The effects of the operating conditions on the yields of these compounds in both phases are presented and discussed as follows.

The oligosaccharides yield and glucose yield in the aqueous phase vary by 4-69 wt.% and by 0-16 wt.%, respectively. According to the cause-effect Pareto analysis (Table 2), the reaction time and the concentration of NaCl are the operating variables exerting the greatest impact on the yield of oligomers with 26% and 23% of influence, respectively. Glucose formation is equally influenced by the three operating variables. In addition, several interactions between the operating variables also affect the yields of these two compounds. Figure 2 illustrates the effect of the solvent system (H2O/GVL) and the reaction time on the yields of oligomers and glucose produced in the process and recovered in the aqueous phase after the microwave treatment using different concentrations of NaCl: 10 wt.%, (A/D) 20 wt.% (B/E) and 30 wt.% (C/F).

In general, the effect of the solvent system (H2O/GVL) on the yields of these two compounds is fairly similar as that described for the cellulose conversion, i.e. a high H2O/cellulose ratio favours the depolymerisation of cellulose to yield oligomers via hydrolysis, as well as the further reactions of these oligomers to produce glucose. Besides, the reaction time has a negligible effect on the oligosaccharides and glucose yields when a solvent system contains a high proportion of GVL. This suggests that it is necessary to use a H2O/GVL solvent system with high proportion of H2O to see the effect of the reaction time on these two products at the relatively low temperature (220 ºC) used in this work for cellulose depolymerisation.

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**Fig. 2** Interaction plots between the solvent system (H2O/GVL) and the holding time with different NaCl/H2O ratios for the oligomers and glucose yields. Bars are LSD intervals with 95% confidence.

For a solvent system having a high proportion of water (H2O/GVL 4:1 vol/vol), the effect of the reaction time depends on the concentration of NaCl. In particular, when a low concentration (10 wt.%) of NaCl is used, the yield of oligomers rises slowly for the first 15 minutes, while a significant increase occurs during the next 15 minutes of reaction. A further increase in the concentration of NaCl up to 20 wt.% leads to a decrease in the oligomers yield within the entire reaction. This may be ascribed to the positive kinetic effect of NaCl on the process, which helps increase the oligomers decomposition rate. In this case, the oligomers yield increases during the first 15 minutes and remains steady afterwards. However, an increase in the concentration of NaCl up to 30 wt.% leads to an increase in the oligomers yield due to the greater promoting effect of NaCl on the depolymerisation of cellulose, together with the possible accumulation of oligomers with the advancement of the reaction.

Regarding glucose, the influence of the reaction time depends on the concentration of NaCl. In particular, an increase in the reaction time between 0 and 15 min leads to a substantial increase in the glucose yield regardless of the NaCl concentration (10-30 wt.%). The positive kinetic effect that the reaction time has on the process accounts for this increment. However, a further increase in the reaction time (from 15 to 30 min) produces a decrease in the glucose yield. When long reaction times are used, glucose undergoes a further NaCl catalytic decomposition towards the formation of HMF and carboxylic acids ([Bicker et al. 2003](#_ENREF_6); [Huang et al. 2010](#_ENREF_14)), thus decreasing the yield of this sugar. The concentration of NaCl also has a significant influence on glucose formation. Figure 2 shows how an increase in the concentration of NaCl reduces the reaction time at which the maximum for the glucose yield takes place. This shifts this maximum from around 20 min for 10 wt.% NaCl to around 10 min for 30 wt.% NaCl, due to the accelerated hydrolysis of cellulose and glucose assisted by this salt ([Bicker et al. 2003](#_ENREF_6); [Huang et al. 2010](#_ENREF_14)). However, if long reaction times (>15 min) are used, this increase in NaCl concentration reduces the glucose yield as this sugar might experience a further decomposition.

***Effects of the operating conditions on the generation of HMF and its further decomposition into other products***

HMF is produced in the aqueous phase but it can be transferred to the GVL phase if the appropriate solvent composition and NaCl concentration are used. Formic acid and levulinic acid are simultaneously produced from the decomposition of HMF in the aqueous phase. These two acids can also be transferred from the aqueous phase to the GVL phase and vice versa. The transference from the aqueous to the organic phase is more efficient for levulinic acid than for formic acid and/or that the reverse transference (from the organic to the aqueous phase) is more favoured for formic acid than for levulinic acid, due to the more polar character of formic acid than levulinic acid. The HMF yield in the aqueous phase shifts between 0 and 6 wt.%, while in the GVL phase it varies from 0 to 14 wt.%. The yields of levulinic acid in H2O and GVL vary by 0-8 wt.% and 0-5 wt.%, respectively, while formic acid yield in the aqueous and GVLphases range between 0 and 4 wt.% and 0 and 1 wt.%, respectively.

The cause-effect Pareto analysis (Table 2) reveals that the concentration of NaCl is the operating variable with the highest influence on the generation of HMF and its further decomposition in the aqueous phase. The concentration of NaCl and the solvent system (H2O/GVL) regulates the efficiency of HMF and levulinic acid extraction from the aqueous to the organic phase as it can control the solubility of these two compounds in water, while the reaction time might have a significant influence on the kinetics of HMF formation/consumption. In addition, several interactions between the operating variables have a strong impact on these products yield in both phases. Figure 3 and Figure 4 plot the effect of the solvent system (H2O/GVL) and the reaction time on the HMF and levulinic acid yield produced in the H2O and GVL phases, and formic acid yield produced in the H2O phase using different concentrations of NaCl. The proportion of this latter acid in the GVL phase is negligible and is not affected by the operating conditions.

An increase in the proportion of H2O enhances the conversion of cellulose and its subsequent conversion to HMF in the aqueous phase. Then, this increment in the HMF concentration in the aqueous phase increases the concentration gradient for this compound between the two phases (H2O and GVL), which allows a better and quicker diffusion between phases, thus increasing the HMF yield in the GVL phase. The HMF yield in the aqueous phase varies with the course of the reaction. However, the variations observed depend on the solvent system and the concentration of NaCl. For a low concentration of this salt (10 wt.%), the HMF yield in the H2O phase progressively increases with the reaction time regardless of the solvent system. Under these conditions, NaCl exerts a kinetic effect on cellulose and glucose decomposition, increasing the total yield of HMF in H2O and GVL phases. However, the concentration of this salt might not be high enough to fully control the solubility properties of the solvent system, i.e. to enhance the transference of HMF from the aqueous phase to the organic phase by decreasing the solubility of HMF in water.

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**Fig. 3** Interaction plots between the solvent system (H2O/GVL) and the holding time with different NaCl/H2O ratios for HMF yield in H2O phase (A-C) and GVL phase (D-F). Bars are LSD intervals with 95% confidence.

Conversely, a further increase in the concentration of this salt (20 wt.%) improves the solubility control of the solvent system and, as a result, the reaction time does not exert a significant influence on the yield of HMF in the aqueous phase. This suggests that a steady state in the aqueous phase between HMF production and phase transference of HMF could have been reached. However, an increase in the NaCl concentration up to 30 wt.% leads to further increase in the HMF yield in the aqueous phase and also shifts the maximum value of the HMF yield in the GVL phase. For this salt concentration, the positive kinetic effect of NaCl might be higher than the modified effect of solubility by NaCl, which accounts for the increase in the HMF yield observed in the aqueous phase. NaCl not only does potentiate the HMF formation, but also it helps the HMF transference from the aqueous to the organic phase, thus increasing the yield of this compound in the GVL phase.

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**Fig. 4** Interaction plots between the solvent system (H2O/GVL) and the holding time with different NaCl/H2O ratios for the levulinic acid and formic acid yields in H2O phase (A-C, G-I) and GVL phase (D-F). Bars are LSD intervals with 95% confidence.

A further increase in the reaction time (over 15 min) leads to a quick decrease in the total yield of HMF due to the decomposition of this species to formic and levulinic acids. In addition, a sharp increase in the yield of levulinic acid is observed when increasing the reaction time up to 30 min. HMF formation is enhanced during the first 15 min of reaction, where a maximum for HMF production takes place before the HMF yield drops with increasing reaction time. In addition, within this time interval (15-30 min), the concentration of NaCl significantly influences the yield of this carboxylic acid: an initial increase in the concentration of NaCl from 10 to 20 wt.% diminishes the yield of carboxylic acid, while a subsequent increase up to 30 wt.% leads to an increase in this yield. This result can be attributed to the counteracting effect of two developments: the positive kinetic effect of NaCl increasing the rate of the hydrolysis and dehydration reactions, and the negative effect of this salt on the solubility of the organic compounds in the aqueous phase. This latter decreases the solubility of formic acid in the aqueous phase, thus hindering its transference from the GVL to the aqueous phase.

***Optimisation of saccharides and HMF production from cellulose***

Optimum conditions were sought for the simultaneous production of saccharides and HMF from cellulose making use of the empirical models developed. The predicted R2 for all the models is greater than 0.95, which allows their use for prediction purposes within the interval of variation considered in this work. The optimisation aims to maximise the cellulose conversion and the amounts of (mono/oligo) saccharides as well as HMF recovered in the water and organic phase, respectively. In addition, it minimises the yield of HMF in the aqueous phase and the yields of levulinic and formic acids in both phases. To achieve this goal, optimum values for all the response variables were sought by assigning a relative importance (from 1 to 5) to each of the objectives in order to come up with a solution that satisfies all the criteria. Table 3 lists the relative importance assigned to each variable, and the optimisation results, which include both, the theoretical and experimental values.

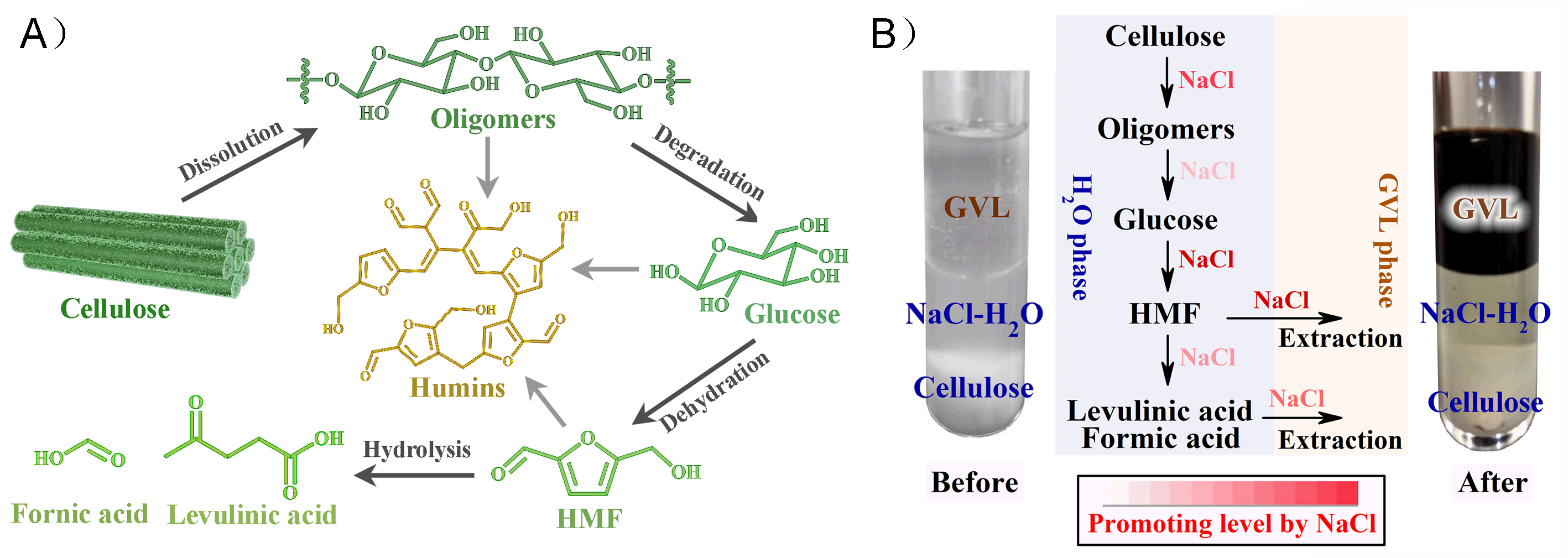
Taking these conditions into account, the optimisation predicts an optimum using a solvent system consisting of 67 vol.% H2O and 33 vol.% GVL (2:1, vol/vol) and a concentration of NaCl of 30 wt.% in H2O at 220 ºC for 18 min. This optimum was checked experimentally (Table 3) and non-significant differences were found between the theoretical and experimental values (p-value > 0.05). Under these conditions, it is possible to strike a compromise between cellulose conversion, saccharides and HMF production and products separation, i.e. maximising the yields of saccharides and HMF recovered in the aqueous and GVL phase, respectively, and minimising the decomposition of HMF towards levulinic and formic acids. Specifically, 73% of cellulose can be directly converted into HMF with an overall yield recovered in the GVL phase of 14 wt.%. The decomposition of HMF to levulinic and formic acids is also inhibited (1.7 wt.% and 4 wt.% total yield of carboxylic acids in the aqueous and the organic phases, respectively). These species account for the 91% of the total amount of products produced. The rest 9% includes carboxylic acids (0.2 wt.% lactic acid and 0.8 wt.% acetic acid), furfural (2.1 wt.%), and other sugars (2.1 % levoglucosan, 0.4 wt.% cellobiose, 0.3 wt.% fructose and 0.1 wt.% rhamnose) in the two phases, as well as 0.7 wt.% formic acid in the GVL phase.

**Table 3** Theoretical optimisation: operating conditions and response variables, including objectives, the interval of variations, relative importance, theoretical and experimental optimum values.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Variables | Objective | Interval of variation | Relative importance (1-5) | Optimum  Theoretical | Optimum  Experimental |
| Time (min) | none | 0-30 |  | 18 |  |
| H2O/GVL (vol:vol) | none | 1:4-4:1 |  | 2:1 |  |
| NaCl/H2O (wt.%) | none | 10-30 |  | 30 |  |
| Overall Conversion (%) | maximise | 0-100 | 3 | 73.1 | 75.8 |
| Oligomers yield (wt.%) | maximise | 0-100 | 5 | 32.1 | 32.2 |
| Glucose yield in H2O (wt.%) | maximise | 0-100 | 5 | 13.4 | 12.6 |
| HMF yield in H2O (wt.%) | minimise | 0-100 | 3 | 1.9 | 3.0 |
| HMF yield in GVL (wt.%) | maximise | 0-100 | 5 | 13.8 | 14.1 |
| LeA yield in H2O (wt.%) | minimise | 0-100 | 3 | 1.8 | 1.8 |
| LeA yield in GVL (wt.%) | minimise | 0-100 | 3 | 4.0 | 4.9 |
| FA yield in H2O (wt.%) | minimise | 0-100 | 3 | 0.9 | 0.7 |

The concentration of NaCl and the composition of the H2O-GVL solvent system exert an important role on cellulose conversion and products distribution/separation. Figure 5A shows an overall reaction pathway for cellulose decomposition, showing the formation of desired and undesired products, while Figure 5B shows a simplified reaction pathway showing the most representative products obtained during the hydrothermal depolymerisation of cellulose in the binary H2O-GVL solvent system used in this work. This includes the initial formation of water soluble oligomers and glucose, as well as both the subsequent transformation of this latter to HMF and its transportation to the GVL phase to hinder its further decomposition to levulinic and formic acids.

The good selectivity and controllability of this process might represent an opportunity in future production of energy and platform molecules from biomass, as it allows the simultaneous production and separation of saccharides and HMF in one single unit (one pot). In particular, 50% of cellulose is converted into a water-soluble fraction made up of glucose (25 %) and oligosaccharides (64 %) with small amounts of carboxylic acids (5 %). The rest (26% of the cellulose) is converted into platform molecules that are recovered in the GVL phase; this latter phase containing 75 % of HMF and 25 % of carboxylic acids. Future work should explore different alternatives addressing the recovering and re-usability of the solvent system after reaction. Concerning the sustainability and reusability of this biphasic co-solvent system, concentrated seawater could be used as a promising alternative reaction medium to replace the NaCl-H2O solvent, as seawater shows an extraordinary performance on the depolymerisation of oligosaccharides ([Jiang et al. 2018a](#_ENREF_17)). Besides, the GVL solvent after reaction can be separated by supercritical CO2 extraction for further use ([Luterbacher et al. 2014](#_ENREF_29)). Therefore, this bi-phasic co-solvent system can be regarded as a green and sustainable reaction system for the conversion of cellulose.



**Fig. 5** General reaction network for cellulose decomposition (A). Reaction pathway of cellulose decomposition in the H2O/GVL solvent system and effect of NaCl on the conversion of cellulose and the extraction of the products (B).

**Conclusions**

This work addresses the selective and simultaneous conversion of cellulose to saccharides and HMF using a novel microwave-assisted NaCl-H2O/GVL solvent system at 220 ºC. The effects of the solvent system composition (H2O/GVL, 1:4-4:1, vol/vol), NaCl concentration (10-30 wt.% NaCl/H2O) and reaction time (0-30 min) on the process have been analysed and thoroughly discussed. The most important conclusions are summarised as follows.

1. The statistical analysis of the results revealed that the solvent system (H2O/GVL), NaCl concentration and reaction time have a significant influence on the process under the operating conditions used in this work. The cellulose conversion varied between 15 and 99%; the cellulose being depolymerised into oligosaccharides, glucose, HMF and levulinic and formic acids.

2. Oligosaccharides, glucose and levulinic and formic acids were largely recovered in the aqueous phase and their yields (g/g cellulose) varied by 4-67 wt.%, 0-16 wt.%, 0-8 wt.% and 0-4 wt.%, respectively, while HMF was recovered in both phases with yields shifting between 0-6 wt. % and 0-13 wt.%, in the aqueous and organic phases, respectively.

3. Kinetics and thermodynamics effects are accounted for by the significant influence on the solvent system (H2O/GVL), NaCl concentration and reaction time on the process. An increase in the proportion of water in the solvent system produced a greater spread of depolymerisation and hydrolysis reactions of cellulose to yield oligosaccharides and glucose. This latter compound underwent a further decomposition to yield HMF and carboxylic acids when long reaction times were used. The proportion of NaCl in the solvent system had both thermodynamics and kinetics effects. This salt promotes cellulose decomposition and modifies the solubility of cellulose decomposition products in the aqueous phase. An increase in NaCl decreases the solubility of some organics. This helps increase their transference from the H2O phase to the GVL phase.

4. The optimisation of the process revealed that when using a solvent system consisting of 67 vol.% H2O and 33 vol.% GVL with a concentration of NaCl of 30 wt.% in H2O at 220 ºC for 18 min, is possible to maximise the cellulose conversion (76%) and the production of saccharides and HMF in the aqueous and organic phase, respectively. The aqueous phase was made up of glucose (25 %) and oligosaccharides (64 %), while the GVL phase contained up of 75 % of HMF along with a small proportion of carboxylic acids (25 %).

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