

Carbon materials as phase transfer promoters for obtaining 5-hydroxymethylfurfural from cellulose in a biphasic system

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Abstract: Different carbonaceous materials are tested as mass-transfer promoters for increasing the 5-HMF yields in biphasic cellulose hydrolysis. The benefits of working with a biphasic system (water/MIBK) under soft acid conditions are taken as starting point (no humins or levulinic acid production), being the slow extraction kinetics the weakest point of this approach. Carbon nanotubes (CNT) and activated carbon (AC) are proposed to improve 5-HMF L-L mass transfer. A kinetic analysis of extraction process allows proposing the competence between HMF and glucose adsorption as the main cause of the poor results obtained with the AC. On the contrary, very promising results were obtained with the CNT, mainly at 1.5 % loading, with a total transfer of HMF and a high global mass-transfer coefficient. The use of this CNT improves the amount of 5-HMF in the organic phase in more than 270 %.

Introduction

The increasing demand of chemicals and drop-in fuels produced from renewable resources has boosted the interest in biomass upgrading.^[1] Cellulose is the main polymeric constituent of lignocellulosic biomass, with a high crystalline polymer structure, consisting of thousands of D-glucose molecules.^[2] This polymer can be hydrolysed to glucose sugars, which can be transformed to a huge variety of valuable chemicals, generally known as bio-platform molecules.^[3] 5-HMF is considered as one of the most relevant one, with many interesting valorisation routes as building block for the production of polymers (biopolyester building blocks), fuel additives (2,5-dimethylfuran, 5-ethoxymethylfurfural, ethyl levulinate, etc.), and even drop-in fuels after a condensation and hydrodeoxygenations steps.^[4]

5-HMF production from cellulose requires two main steps, as it is summarized in Figure 1: (1) the hydrolysis of cellulose towards glucose; and (2) the glucose dehydration to produce 5-HMF. The hydrolysis can be enzymatically catalysed.^[5] However, the high sensitivity of these technologies, as well as their high cost, limit its industrial implementation. Therefore, chemical hydrolysis is nowadays in the spotlight as a promising alternative to the enzymatic route. Severe conditions, in terms of pressure and temperature, as well as mineral acids such as HCl and H₂SO₄ with Brønsted acid sites are the most referred ones.^[6,7] Despite the

well-known disadvantages of using homogeneous catalysts; cellulose is an insoluble polymer, which hinders the effective use of heterogeneous ones. In fact, most of the previous works proposing solid catalysts report the need of expensive pretreatments of the cellulose,^[8] and the importance of catalyst fouling caused by the humins.^[9] Because of these reasons, homogeneous catalysis is nowadays considered as technically more viable and current works are focused on the process optimization by minimizing mineral acid process inventories, and reducing the reaction temperature.

Once the glucose is obtained, under acid conditions, it has to undergo a further dehydration, removing three water molecules, and obtaining 5-HMF. This reaction must be carried out at softer conditions than the previous hydrolysis to prevent side reactions, such as the decomposition into levulinic and formic acid and different glucose and 5-HMF polymerization routes, yielding insoluble and invaluable humins.^[10] However, these soft conditions also limit the productivity of this compound, requiring longer reaction times. Several authors propose a previous isomerization of glucose into fructose, reducing the humins formation (since most of these undesired products are obtained by oligomerization and side reactions of unreacted glucose), and allowing working at higher temperatures, with the subsequent reaction rate increase.^[11,12] This isomerization requires the co-presence of a Brønsted acid catalyst (homogeneous, HCl) and a Lewis one (heterogeneous, such as acid zeolites or mesoporous silicates). The production of 5-HMF is strongly enhanced by this route,^[13] with decreases in the activation energy of dehydration step higher than 30 %, but adsorptions usually condition the carbon balances.^[11]

If the whole process, from cellulose to 5-HMF, is carried out in an one-pot configuration, the mechanism and mass-transfer limitations would be difficult to control. Thus, this process is mainly studied considering mineral acids (HCl, typically). In this case, side reaction products (acids and humins) cannot be prevented, since experiments are typically conditioned by the pressure and temperature required in the first step.^[10a,14,15] In order to overcome this drawback, different ionic liquids, and polar aprotic organic solvents are proposed.^[16] In all the cases, results are limited by the slow kinetics when hydrolysis is carried out in any non-aqueous solvent. With these premises, biphasic systems are proposed,^[17] based on the hydrophilic character of all the compounds involved, except 5-HMF. Under ideal conditions, the continuous extraction of 5-HMF to an organic phase prevents its further degradation to levulinic acid or humins polymers, also minimizing the need of subsequent purification steps. However, the solvent chosen is a key parameter, since the extraction kinetic must be fast enough to prevent that reaction continues in the

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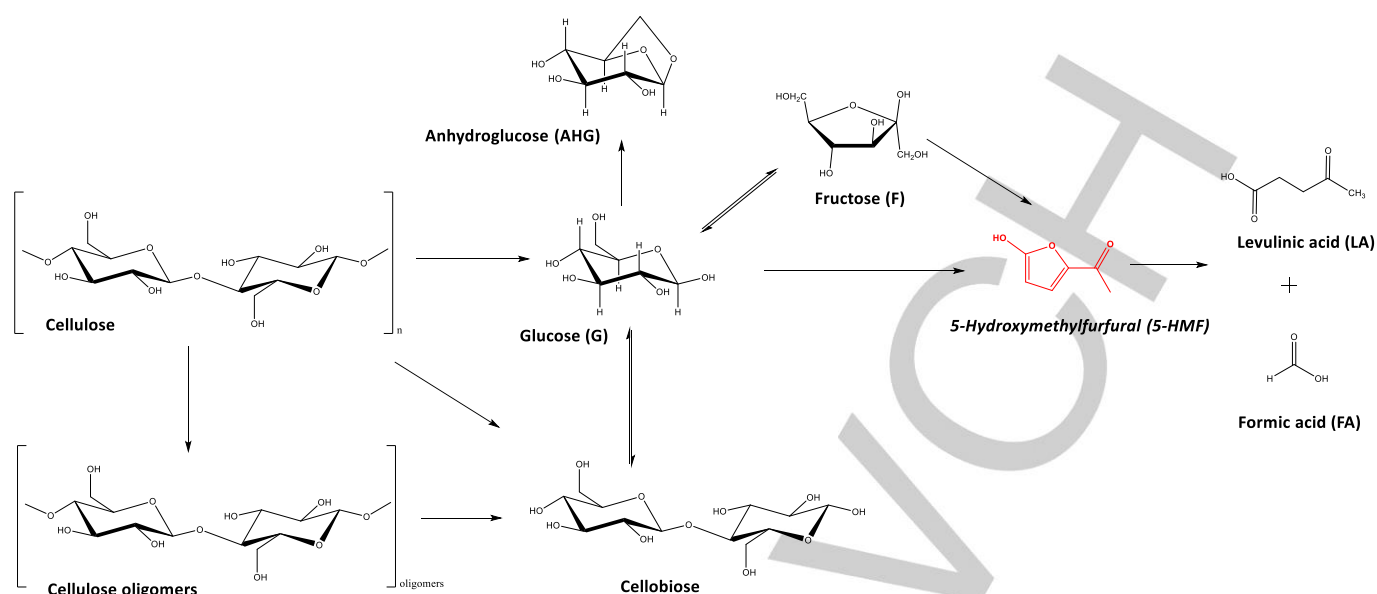


Figure 1. Reaction pathway of cellulose conversion into 5-HMF

aqueous phase with the HMF that has not been efficiently extracted.

Mass transfer limitations are the weakest point of these multiphase reactions. Several works have dealt with this topic, concluding that even under high stirring and a small disperse phase droplet size, the liquid-liquid mass transfer resistance usually controls the overall kinetics.^[18] A poor contact hinders HMF transfer, despite of being thermodynamically favoured. Thus, increasing the interfacial area between organic and aqueous phase is required to promote the intrinsic transport rate.^[16]

One of the possibilities to enhance this mass transfer is the use of amphiphilic materials, such as carbonaceous materials (nanofibers, nanotubes, graphite, active carbons, etc.). This kind of materials tend to adsorb non-hydrophilic molecules in the aqueous phase, desorbing them in the organic phases. The equilibrium between these processes will depend on the solubility of the solute in both solvents and on the surface properties of the adsorbent. Furthermore, the amphiphilic character of these materials also promotes liquid-liquid dispersion, decreasing the disperse phase droplet size, and promoting the mass transfer.^[20] Although these effects have been explored for organic reactions, they have not been studied for promoting the cellulose upgrading.

The aim of this work is to study the role of carbonaceous materials as mass transfer promoters in the context of the cellulose selective transformation into 5-HMF using a biphasic system. In addition to the use of these mass transfer promoters, the system MIBK/water applied to the cellulose transformation without any pretreatment and at these conditions is also a novelty in the literature, since the previous works propose the use of microwaves and ultrasonication to pre-treat the cellulose^[21] or complex catalytic/solvent systems.^[22,23] MIBK (methyl isobutyl ketone) is a good alternative from the point of view of the sustainability of the process, considering its green origin, its large availability, the high solubility of 5-HMF in this solvent and the low

toxicity and boiling point in comparison to other alternatives tested for biphasic systems, such as THF, acetonitrile or dimethylsulfoxide (DMSO).^[21a,22] Two different types of carbons were tested as mass transfer agents: active carbon (AC) and carbon nanotubes (CNT). The amount of material required was optimized with the best one (CNT) and results are explained in terms of extraction kinetic and equilibrium. The motivation for selecting these materials were the high adsorption capacity of the AC and the regular structure and weak surface functionalization of the CNT. Other carbonaceous materials (as activated graphites or carbon nanofibers) are supposed to have intermediate behaviours.

Results and Discussion

Performance in absence of phase transfer promoters

Trying to optimize the 5-HMF production without promoting the side products formation, this reaction was studied with low acid concentration and proposing a biphasic system (MIBK/water), with the aim of selectively extract the 5-HMF, the only compound with larger solubility in the organic phase than in the aqueous one. Despite MIBK has a relative solubility in water (19g/L at reaction conditions), the ratio MIBK/water (1:1 wt.) guarantees a perfect defined biphasic system. In addition to allow obtaining a selective extraction of the desired compound, this methodology introduces an extra advantage for HMF purification to isolate the HMF as solid. Despite the scarce studies about this topic, two different alternatives are proposed in the literature, distillation and crystallization.^[24] The first one would be discarded, according to the high boiling point of MIBK (117°C), whereas crystallization is entirely feasible, since the high different freezing points of MIBK (-84°C) and HMF (30°C). In order to analyse if the presence of the biphasic system has a negative role in the normal activity, results

plotted in Figures 2 and 3 are compared to the corresponding ones obtained in a monophasic (aqueous) medium. In this case, reaction is carried out using 0.175 L of water as solvent.

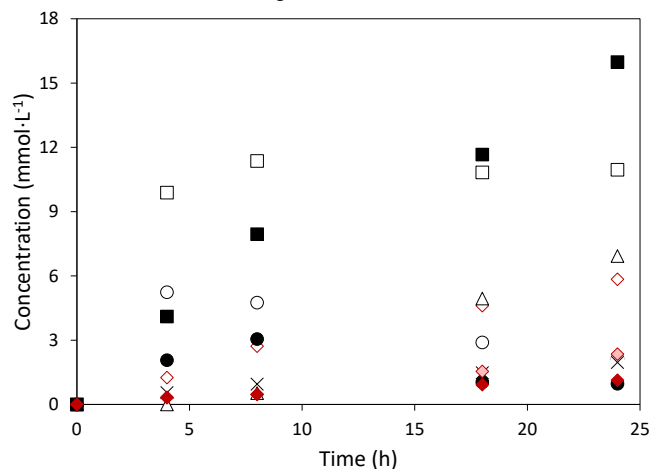


Figure 2. Temporal evolution of main products involved in the 5.83 g cellulose hydrolysis at 413 K with 200 ppm of HCl as catalyst. Empty symbols correspond to aqueous solvent, whereas the filled ones correspond to the biphasic MIBK/water system. Legend: (□) cellobiose; (○) glucose; (◇) 5-HMF; (×) AHG; and (△) levulinic acid.

Figure 2 shows the temporal evolution of main compounds involved in the reaction. All the results shown are the average value after carrying out each experiment twice. Experimental errors were estimated in terms of standard deviation, being always lower than 5%. It must be highlighted that, according to the mechanism and in good agreement with experimental data and previous results presented in the literature,^[14,15] levulinic and formic acids are equimolecular obtained, being the two compounds produced by the rehydration of 5-HMF. Levulinic acid is more relevant as bio-platform molecule than formic acid, and its production at these conditions can be also relevant since the reaction conditions are soft enough to prevent side reactions involving this molecule. These facts justify that only levulinic acid is plotted in the figure, since the concentration of both reaction products is similar and follows the same trend.

Main product in monophasic (empty symbols) and biphasic system (filled ones) is the glucose dimer, the cellobiose, with a continuous increasing trend in the biphasic system, and a more stable trend in the monophasic one. Two different reaction steps can produce this compound. On the one hand, this dimer can be a hydrolytic intermediate between the cellulose and the glucose. On the other one, this compound is also obtained in reactions feeding glucose, being produced by intermolecular dehydration reactions.^[25,26] This second route is proposed as the main one in this case, since it is largely promoted at temperatures close to the glucose melting point (419 K)^[27] and there is not any reason to consider a partial hydrolysis of cellulose producing cellobiose but not any other oligomer with three or four sugar units, compounds that would be detected in the liquid phase if they were produced in the reaction. This hypothesis is corroborated by the thermogravimetric decomposition analyses explained below. This etherification is a reversible reaction, being congruent with the profiles obtained, and explained the high amount of dimer

observed during all the reaction despite glucose is consumed in the subsequent steps.

Glucose is also relevant, observing in both cases the typical behaviour of an intermediate, with a maximum concentration of 943 ppm in the monophasic system and 550 ppm in the biphasic one (selectivities of 19.5 and 15.7%, respectively), after which a decreasing trend is clearly observed, a typical consequence of the advance to subsequent steps. Both components, glucose and cellobiose, are obtained only in the aqueous phase of the biphasic system. The combined analyses of both evolutions suggest that reaction in the biphasic system follows the same mechanism than in aqueous one, with a slower kinetic, more relevant in the first hydrolytic step (all these steps require water as solvent, but the first one is the most sensitive, since it requires more severe conditions). As consequence of the slower kinetic affecting also to the sugar dehydration, there is more glucose available to produce cellobiose, justifying the continuous increasing trend obtained in the biphasic system, whereas the concentration reaches a stable value when working with just water as solvent. 5-HMF has an increasing profile in both systems, reaching a maximum of 736 ppm (selectivity of 15.6%) when reaction is carried out in aqueous phase. However, if the process is carried out in a biphasic configuration, 5-HMF is observed in both phases, with a concentration distribution only relevant in the last points, with 296 ppm and 143 ppm, in aqueous and organic phase after 24 h, respectively. These results indicate that the distribution coefficient (expressed as the ratio of concentrations of 5-HMF in both phases) has a value of 0.48. At this point, it must be remarked that there is not any solubility limit in the concentration range studied, as it was experimentally tested in the laboratory. These data correspond to a HMF yield of 10.26% in the biphasic system, and 11.6% in the monophasic one.

As to secondary compounds, such as anhydroglucose (AHG) and levulinic and formic acid, the desired effect was reached, without detecting these compounds when reaction is carried out in a biphasic system, whereas the concentration of these products reach values of 318 and 804 ppm for AHG and levulinic acid, respectively, after 24 h if the reaction is carried out with only water. In fact, the selectivity to levulinic acid rises up to 14.8%, same value as the desired compound (15% of 5-HMF selectivity at 24 h). As both maxima correspond to the same time, the presence of this side-product is the most relevant drawback of this monophasic system, justifying the use of a biphasic one, since the extraction of 5-HMF in MIBK is 100% selective. The low distribution coefficient, however, reduces its productivity to only 55% of the obtained one in the monophasic system. All these results suggest a relevant mass transfer limitation, justifying the need of promoting mass-transfer between both phases.

An accurate analysis of cellulose conversion in these systems is not possible because of the different phases involved. Since cellulose is a solid (whereas all the compounds analysed are liquids), its conversion must be measured by the difference in weight before and after the reaction (only liquid samples are extracted for the temporal evolution). However, the mass measurement would be conditioned by any solid intermediate (heavy oligomers) or humins produced, obtaining by this technique a glucose conversion lower than the real one.

Considering this situation, the evolution of cellulose was analysed according to the "liquid-phase carbon yield", concept defined in the methodology section. As it is measured considering the liquid phases (water and MIBK), the evolution analysis is possible, whereas the conversion calculated by mass difference can also be analysed at the final point of each reaction.

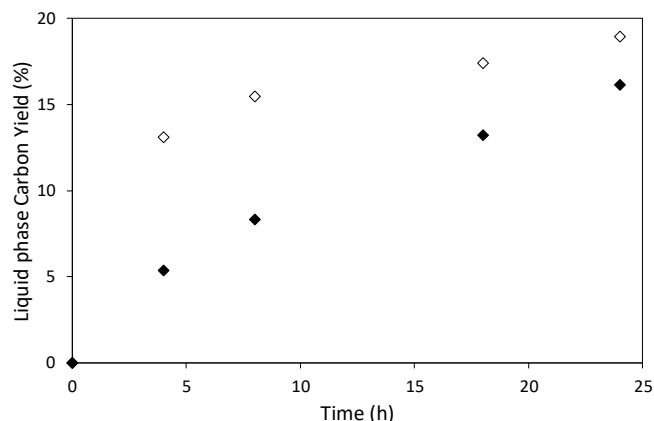


Figure 3. Temporal comparison of liquid phase carbon yield obtained with reaction carried out in aqueous phase (◇) and with the biphasic MIBK/water system (◆)

The temporal evolution of this parameter is compared in Figure 3. Results suggest a higher glucose conversion in the monophasic system (with symbols) than in the biphasic one (black symbols), being the differences more noticeable in the initial 8 h. However, theoretical conversions after 24 h are very close: 18.9 and 16.4 % for both cases. The low difference observed with the monophasic system between 18 and 24 h suggests that reaction conditions are not harsh enough to continue hydrolysing the most stable cellulose structure, once the terminal units have reacted. This result is congruent with the high crystallinity of this raw material (94.09 %, according to XRD analyses). In good agreement with this hypothesis, the biphasic system has the same trend, suggesting the same final point, but with a clear slower kinetic. These results, congruent with the products' profiles obtained, indicate that the biphasic system could be a good option to carry out the reaction, being the acidity and thermic conditions (and not the organic phase) the most probable limiting parameters to obtain a higher conversion.

In order to know if the liquid-phase carbon yield can be directly related to the cellulose conversion, thermogravimetric analyses were carried out, comparing the profiles obtained with the decomposition profile of the raw material and a sample of humins. This sample was obtained after a specific glucose hydrolysis test, at very severe conditions (24 h, 413 K and 400 ppm of HCl), once the solid phase was recovered by filtration and dried. Results are plotted in Figure 4. As it can be observed, both profiles after the reaction suggest the presence of cellulose (decomposition temperature at 590 – 610 K), whereas the weakest humins signal is at 660 K. The lower mass disappearance obtained with the humins sample in comparison to the other analyses also suggests the presence of more stable humins deposited on the surface, compounds that are not decomposed even at the maximum temperature of this analysis. However, final masses of samples

after reactions are the same as the one obtained with the fresh cellulose, discarding the presence of any of these side-compounds.

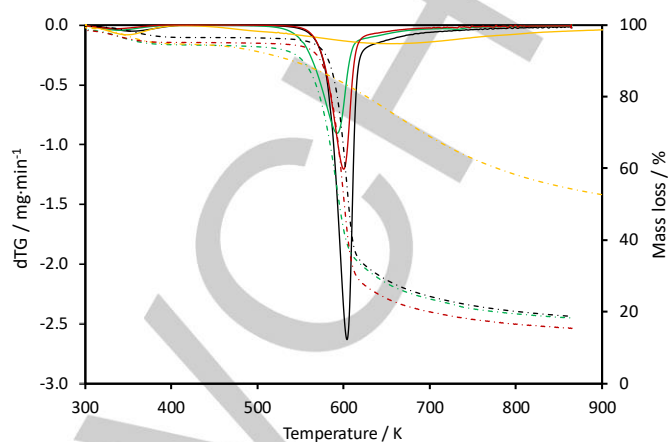


Figure 4. Thermogravimetric results obtained analysing the solid recovered after reaction carried out in monophasic (green) and biphasic (red) configuration. Results compared with the thermal decomposition of pure cellulose (black), and humins (yellow). Data in continuous lines correspond to dTG, whereas broken lines correspond to the mass loss.

The presence of some glucose oligomers in the reaction samples cannot be totally discarded, since these peaks are a bit wider than the peak of pure cellulose, with the maximum slightly displaced to slower temperatures, clear signal of a partial degradation of the crystalline structure. However, the difference is not significant enough (10 K in the case of the monophasic phase) to be considered as relevant. According to the literature, the thermal decomposition of glucose occurs at temperatures a bit higher than its melting point (419 K), being some signals detected up to 513 K, due to the loss of water produced throughout different oligomerization processes that take place during this decomposition, including the cellobiose formation.^[27] According to these results, saccharides decompositions take place from 420 to 610 K, being the temperature directly related to the complexity of their structure (from the monosaccharide to the polymer).

Taking into account to this study, the displacement of the main peak of reaction samples to lower temperatures is suggested as related to a small amount of oligomers, being the peaks obtained in the reactions considered as the envelope curve of the cellulose and these small contributions. This slight difference suggests that, in case of having oligomers, those molecules are closer to the polymer than to the monomer structure. This result is congruent with the absence of oligomers detected in the liquid phase, except the cellobiose. According to these analyses, the absence of humins is corroborated in both cases, and the clear profiles suggest a good correspondence between liquid-phase carbon yield concept and cellulose conversion.

Carbon materials as phase transfer promoters

Once the two-phase configuration has been tested, two main conclusions are obtained, related to a slower kinetics and a poor liquid-liquid mass transfer. Thus, lower conversions are obtained

and 5-HMF is distributed almost 50 % in each solvent, with a low concentration in the MIBK (despite being the only product transferred to the organic phase). Both problems can be solved if the phase transfer is improved, since some steps of the reaction are equilibrium steps (glucose isomerization into fructose, and glucose intermolecular dehydration) and the transfer of HMF can shift these equilibria to the products, enhancing the global cellulose conversion.

In order to improve this transfer, two different carbonaceous materials were tested: carbon nanotubes (CNT) and activated carbon (AC). These two materials are among the most known carbonaceous structures, and were chosen because their different properties in terms of surface area, to compare the role of a mesoporous material (CNT, 277 m²/g) and a microporous one (AC, 1005 m²/g). The use of other inorganic materials, such as alumina or zeolite has been discarded because of their poorer adsorption performance, as well as their surface reactivity. All the characterization is detailed in a previous work.^[28] In both cases, materials were directly used, without introducing any modification in their surface, in order to ensure the absence of any extra catalytic process that could play a role in the results analyses. However, the presence of some functional groups in their surface cannot be completely prevented. According to the literature, CNT presents some weak acid groups, whereas the AC exhibits also some oxygen surface groups.^[28] In good agreement, both materials present a very similar isoelectric point (4.19 and 4.63 for CNT and AC, respectively). It can be expected that these functionalities have a negligible catalytic role in this reaction, since it requires strong acid sites. In order to check this premise, a preliminary reaction in absence of HCl but with the carbon materials was carried out, observing negligible cellulose conversions.

For an initial test, both materials were introduced in 2 % concentration, being this value referred to the initial amount of cellulose. The temporal evolutions of these results are shown in Figure 5 and Figure 6, for the analysis of liquid-phase carbon yield and products' concentration, respectively. According to the analyses of the two experiments carried out with each conditions,

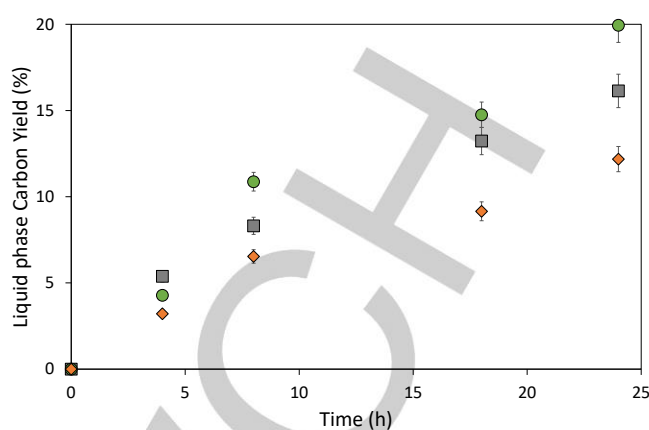


Figure 5: Temporal evolution of liquid phase carbon yield when reaction was carried out in a biphasic system without any mass-transfer agent (■), with CNT (●); and with AC (◆).

the relative errors are always lower than 6 %, as it is plotted in the figures. The expected improvement in the global reaction is clearly observed when using CNT, obtaining higher cellulose conversion (analysed in terms of liquid phase carbon yield) than in absence of any mass-transfer agent with a relative increase higher than 20 % (from 16.5 to 19.95 % without and with CNT, respectively). A relevant catalytic activity of these CNT can be discarded because of the low concentration of functional sites of these materials, much lower than the corresponding to the activated carbons. Thus, this improvement can be caused by the enhancement in the HMF transfer from the aqueous to the organic phase, also promoting the glucose consumption by the equilibrium shift. According to this possibility, the amount of glucose dimmer would also decrease and the role of CNT amount will be lower (once the minimum required to promote all the transfer is reached, an extra amount has not any role in the reaction). In order to identify the key parameter, reactions with different amount of CNT were performed.

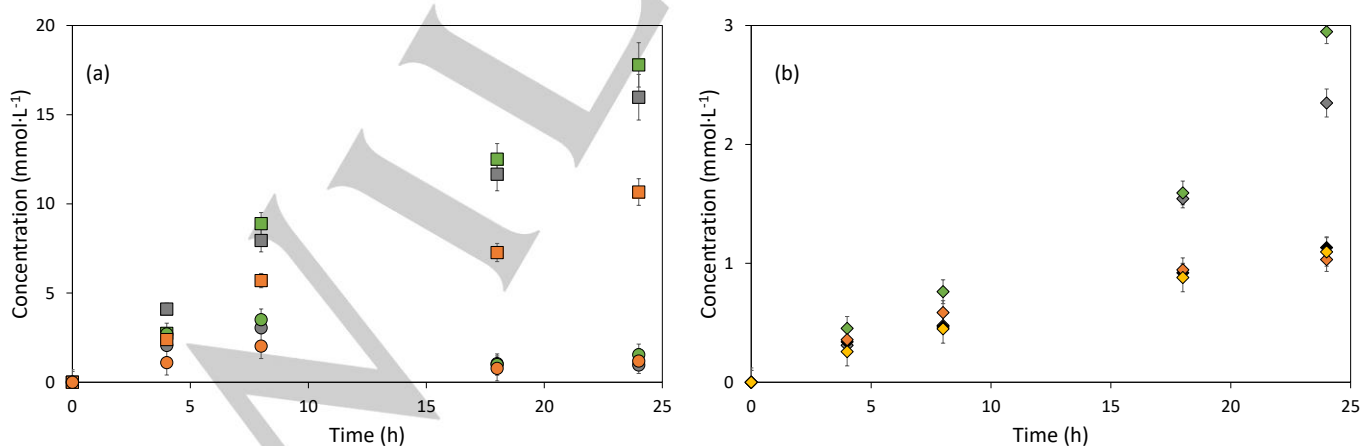


Figure 6: Temporal evolution of (■) cellobiose; (●) glucose; and (◆) 5-HMF when reaction was carried out in a biphasic system without any mass-transfer agent (grey), with CNT (green); and with AC (orange). Data of (a) correspond to aqueous phase; (b) organic phase (light colours) and aqueous phase (dark colours). There is not any signal related to 5-HMF in aqueous phase when using CNT

In the case of active carbon (AC), the performance is clearly poorer, with a final cellulose conversion of 12.18 %. These results suggest a negative role of oxygen sites on the AC surface or a strong adsorption of glucose and cellobiose on the active carbon surface, as it was previously demonstrated in the literature.^[29]

Glucose dimer (cellobiose) and glucose are selectively obtained in the aqueous phase, with both carbonaceous materials, as well as without any mass-transfer agent (Fig. 5). The concentration obtained with CNT is similar than the one without any carbonaceous materials, whereas the amount of cellobiose with the AC is significantly lower at any time. This result is congruent with the suspected strong adsorption of these sugars onto the AC surface. Humins, anhydroglucose, levulinic and formic acid production were prevented. These results suggest that 5-HMF is entirely transferred to the organic phase. This is the case of using CNT, no signals of any 5-HMF were detected in the aqueous phase at any reaction time (distribution coefficient close to infinity). On the contrary, results obtained with AC are even worse than without adding any mass-transfer agent, obtained almost the same concentration in both cases. This result corresponds to a distribution coefficient close to 1.

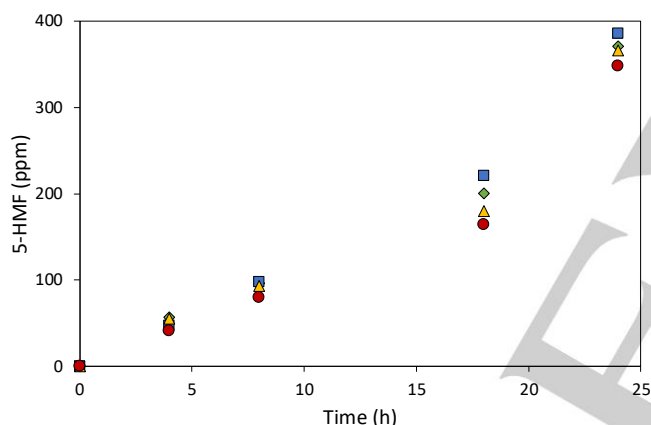


Figure 7. Temporal evolution of 5-HMF concentration obtained as function of the CNT concentration: (●) 0.5 %; (▲) 1 %; (■) 1.5 %; (◆) 2 %.

The infinite distribution coefficient suggests that 2 % of CNT could be too much, in such a way that lower CNT concentrations could be enough to maximize the extraction. Despite the adsorption is more relevant in the case of AC, this cannot be discarded in the case of CNT, since the total final 5-HMF obtained (371 ppm) is lower than the total amount obtained without CNT in the reaction (439 ppm) and, for sure, when using a monophasic system (736 mg). Thus, following experiments were done using decreasing CNT concentration (0.5, 1, and 1.5 %). The main difference expected concerns the 5-HMF concentration, this evolution is plotted in Figure 7. Despite the similar profiles obtained, best results are obtained with 1.5 % of CNT (386 ppm). This result corresponds to a 43.3 % selective conversion of cellulose into HMF (corresponding to a 9 % of total yield of cellulose to HMF), 23 % more than without the mass transfer agent, and a value higher than typical values obtained with comparable conditions (soft temperature and low catalytic loading in a biphasic medium)^[22]. Lower values of HMF concentration were obtained with both, lower and higher concentrations,

requires a deep study of HMF individual extraction to identify if it is only explained in mass-transfer terms or if the reaction global kinetic controls the process.

Kinetics of the phase transfer in presence of carbon materials. Effect of the pH and the presence of glucose

In order to study the extraction of HMF, the time evolution of HMF concentration in aqueous and MIBK phase was analysed for the four CNT concentrations (0.5, 1, 1.5 and 2 %). The evolution of HMF concentration in the organic phase is compared in Figure 8. The evolution obtained when adding AC was also included. In all the cases, the transfer reaches an equilibrium after 300 min. The maximum concentration obtained is higher in presence of the carbonaceous materials, with slight differences as function of the concentration and the material used. Thus, partition coefficient (organic/aqueous concentration under stationary conditions) evolves from 1.09 (absence of any mass-transfer promoter) to 1.23 (1.5 % of CNT). However, main differences are related to the speed at which these equilibriums are reached, since the partition coefficient reached with 0.5, 1 and 2 % of CNT and AC are very similar (from 1.15 to 1.17).

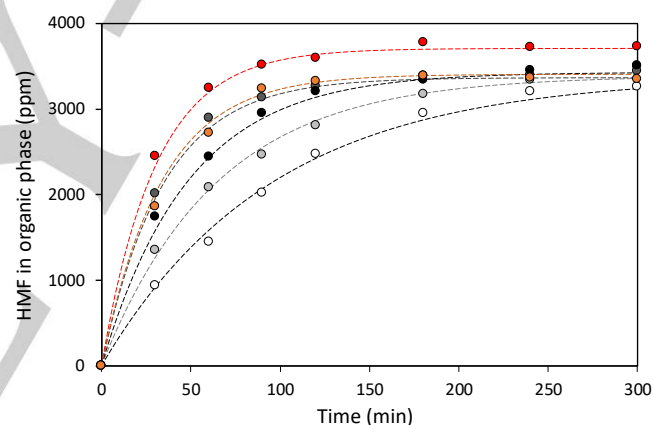


Figure 8. Temporal evolution of 5-HMF concentration in organic phase in the extraction studies. Experimental points correspond to (○) no mass-transfer agent; (●) 0.5 % CNT; (▲) 1 % CNT; (■) 1.5 % CNT; (◆) 2 % CNT; (●) 2 % AC.

The deep analysis of these results requires analysing the kinetic of the process. Considering that all the steps involved in this process only take place in the aqueous medium, the appearance of HMF in the organic one, as well as its faster or lower temporal evolution must be controlled by the transfer between aqueous and organic phase. According to this premise, the modelling of this mass-transfer process was done considering overall mass transport coefficients (K^w and K^o , for the water and organic phase, respectively). Thus, the HMF transport rate ($\text{mol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$) can be calculated as function of the effective transport coefficients ($K^i\cdot a$, being "i" the phase, in min^{-1}) according to the following equations for water (w) and MIBK (o) phase:

$$\frac{dC_{HMF}^w}{dt} = -(K_{HMF}^w \cdot a) \cdot (C_{HMF}^w - C_{HMF}^{w*})$$

$$\frac{dC_{HMF}^o}{dt} = (K_{HMF}^o \cdot a) \cdot (C_{HMF}^{o*} - C_{HMF}^o)$$

In these equations, terms with asterisks correspond to the concentration in each phase under equilibrium conditions. In the experimental fit, these values correspond to stable concentrations obtained after 24 h of extraction, being a particular value for each experiment (HMF concentrations in both phases do not suffer any evolution after 300 min in any case). Considering the principle of mass conservation, these expressions are equal. Thus, both volumetric mass transport coefficients can be related by the partition coefficient, HMF, defined as the ratio between HMF in the organic and aqueous phase, once the equilibrium is reached.

$$K_{HMF}^0 = H_{HMF} \cdot K_{HMF}^w$$

This fact allows studying the whole mass transfer process just analysing the evolution of one phase. In this case, as the HMF is selectively extracted to the organic solvent, this phase was chosen to evaluate this phenomenon. Taking into account that the initial concentration in the organic phase is zero, the integration of the concentration evolution in organic phase is simplified in the following expression:

$$C_{HMF,t}^o = C_{HMF}^{o,*} \left[1 - e^{-((K_{HMF}^0) \cdot t)} \right]$$

Experimental data were fitted according to this model, obtaining good correlation coefficients ($r^2 > 0.92$ in all the cases). The values of volumetric mass-transfer coefficients in the organic phase as function of the CNT percentage are plotted in Figure 9. In all the cases, the carbon balance considering both phases are close to 100 %, discarding any relevant permanent adsorption phenomenon, even in the case of active carbon. Values obtained are in good agreement with the concentration of HMF in the organic phases of reaction mediums, suggesting that extraction is promoted with 1.5 % of CNT. However, the high coefficient observed with the AC (very similar to results of 1 and 1.5 % of CNT) contrasts with its poor behaviour in the reactions.

This apparently incongruent behaviour of AC can be due to two main reasons: a strong dependence of pH, or a negative influence of sugars adsorption. In the first case, results obtained with 200 ppm of HCl in the reaction medium would modify the volumetric transfer coefficients (real conditions in the reaction

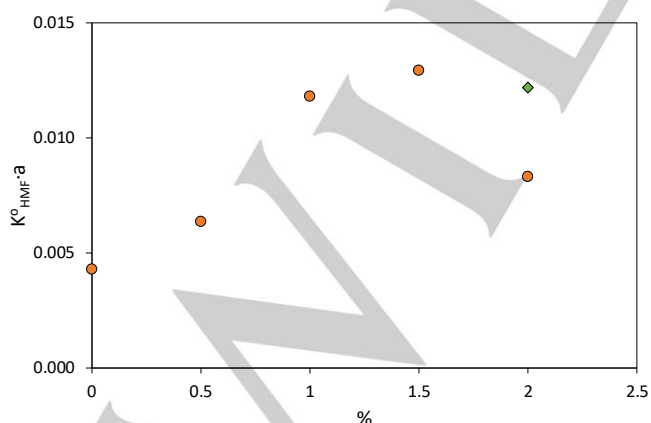


Figure 9. Comparison of volumetric mass transfer coefficients (min^{-1}) as function of the percentage of carbonaceous materials in the interface. Orange symbols (●) correspond to CNT; green one (◆), to AC.

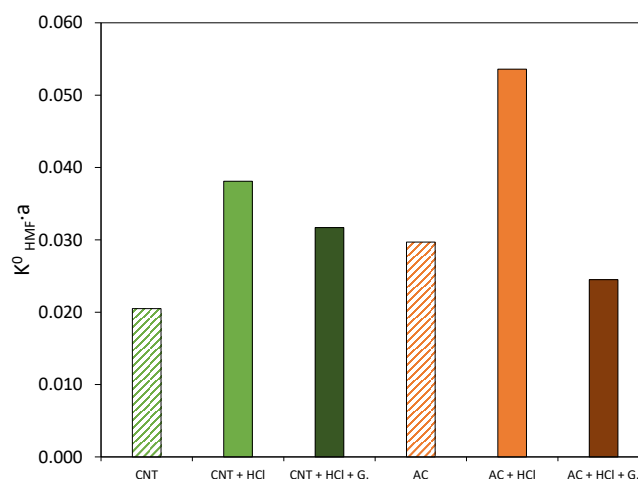


Figure 10. 5-HMD global mass-transfer coefficient values (min^{-1}) obtained with CNT (green) and AC (orange) as function of the extraction conditions: Neutral pH selective extraction of 5-HMF (lined bars); Acid pH selective extraction of 5-HMF (light colours); and acid pH with co-presence of glucose (dark colours).

studied). In the second one, this modification could be checked by studying the HMF transfer when sugars are also presented, evaluating if their adsorption on the AC surface hinders the mass transfer. These two conditions were tested with both, CNT and AC, comparing the final volumetric mass transfer coefficients in the Figure 10.

A clear improvement is observed when working under acid conditions (lined bars), with both CNT and AC. Both coefficients reach values twice higher than those under neutral pH. This improvement is a clear consequence of the positive effect of acid conditions in liquid-liquid extractions.^[30] This result suggests that the protonation of the carbon functional groups increase their phase transfer promotion effect, being this effect more marked in the AC, because of its larger concentration of these sites.

The presence of other compounds in the aqueous phase can modify the mass transfer process, since these molecules can be adsorbed, decreasing the free surface available to the HMF transfer. In order to check this effect, the co-presence of glucose in the extraction medium was analysing, choosing this compound because of being the majority one in the reaction medium. Results indicate that the co-presence of glucose (darkest bars) has a negative effect on both coefficients, suggesting a competitive process between mass transfer and glucose adsorption. This decrease is much less evident in the case of CNT (relative descent of 16.7 %), whereas the K_{HMF}^0 decreases more than 50 % when working with the AC, obtaining a final value very similar to the previous one at neutral pH. This situation is due to the high affinity between sugars and the activated carbon surface, previously mentioned in the literature.^[2] As these conditions are similar to the real one in the reaction medium, this adsorption is proposed as the main cause of the worse behaviour of AC as selective mass-transfer promoters in this reaction, being this negative effect more relevant than the improvement due to the acid conditions. On the contrary, CNT is a good mass-transfer promoter, allowing the transport of 5-HMF to the organic phase fast enough to promote the overall process, preventing the long-

time contact of 5-HMF with acid sites that can produce undesired secondary reactions (humins and acids), and obtaining a 5-HMF productivity 2.7 times higher than the previous one obtained in absence of mass-transfer agent. In addition, all the 5-HMF is extracted to the organic phase, whereas less than 50 % was efficiently extracted with the water/MIBK system.

Conclusions

The use of CNT as mass transfer promoter clearly improves the cellulose transformation of cellulose into 5-HMF in a water-MIBK biphasic system. Considering that the acid conditions required to promote the cellulose hydrolysis are also responsible of the 5-HMF degradation into humins and levulinic acid, the extraction of this compound to an organic phase is needed. A selective extraction is proposed using a water/MIBK system, being the 5-HMF formation rate of this process decreased by the slower L-L mass transfer kinetics. Carbon nanotubes are proposed as promising mass-transfer promoter, enhancing the extraction kinetic more than 3.7 times, mainly under acid conditions. As several equilibria steps are involved in the process, this extraction displace all the reaction, also yielding to an increase in the productivity (270 times higher). The use of AC instead of CNT is discarded, due to the competence between 5-HMF and glucose for the adsorption sites (the first one is reversible, but the second one produces the partial blockage of the AC). With this approach, 5-HMF can be selectively produced from cellulose avoiding use of complex catalyst, toxic solvents or severe conditions.

Experimental Section

Materials

Microcrystalline cellulose (CAS: 9004-34-6), as well as D-(+)-glucose ($\geq 99.5\%$), D-(-)-fructose ($\geq 99\%$), 5-HMF ($\geq 99\%$), formic acid (98%) and levulinic acid (98%) were provided by Sigma Aldrich. Hydrochloric acid (37 %) was purchased from Fisher Chemical. The cellulose was characterized by different techniques, in order to know the main properties that could affect this reaction. Thus, ICP analyses were carried out to identify the atomic bulk composition, using an octapole HP-7500c. The cellulose was dissolved in HNO_3 (1%) and Rh was used as internal standard. The crystallographic structure was determined by XRD using a Philips X'Pert Pro diffractometer, working with the $\text{Cu-K}\alpha$ line, in the range $2\theta = 5\text{-}30^\circ\text{C}$. The crystallinity index was calculated using the Segal equation, where I_c is the intensity of the maximum crystalline peak and I_a is the minimum intensity between two crystalline peaks:

$$CI = \frac{I_c - I_a}{I_c}$$

Two different carbonaceous materials were used as mass transfer agents: carbon nanotubes (CNT) provided by Dropsens; and active carbon (AC) (GC-900, supplied by ChemiVall). These materials were deeply characterized in a previous study.^[28]

Reactions and samples' analyses

Reactions were carried out in a 0.5 L stirred autoclave reactor (Autoclave Engineers EZE seal) equipped with a PID temperature controller and a back-pressure regulator. Reactor was loaded with 350 mL of a biphasic mixture of MIBK and water (0.175 L of water, 0.218 L of MIBK, 1:1 in weight) with 5.83 g of cellulose (50-80 μm) and 200 ppm of HCl as catalyst. The reactor was pressurized to 10 bar with N_2 and heated to the reaction temperature, 413 K. When reaction was performed in presence of the carbonaceous materials, different mass loadings of CNT or AC were added to the system (values detailed in the corresponding section).

Samples were taken from the sampling port, using a 0.45 μm Nylon syringe filter. The aqueous phase was analyzed by HPLC (1200 Series, Agilent) using a refraction index detector (G1362A RI). Method was optimized using a Hi-Plex H Column (Agilent) as stationary phase and 5 mM of H_2SO_4 solution as the mobile one. The organic phase was analysed by capillary GC in a Shimadzu GC-2010 equipped with a FID detector. A 15 m long CP-Sil 5 CB column was used as stationary phase. For both instruments, quantitative responses were determined using standard calibration mixtures. Each sample was analysed twice in the HPLC or GC, as required, obtaining a good reproducibility of these analyses, with relative errors lower than 4 % in all the cases.

The cellulose conversion is calculated in terms of "liquid-phase carbon yield" a concept involving the theoretical cellulose required to obtain all the compounds detected in the liquid phases. This concept only involves the real conversion of cellulose to products of the main route (cellobiose, glucose, 5-HMF, AHG, formic acid and levulinic acid). This magnitude, analysed in carbon terms, is calculated according to the following expression:

$$\eta_c = \frac{[V \cdot \sum(n_i \cdot C_i)]_{\text{aqueous}} + [V \cdot \sum(n_i \cdot C_i)]_{\text{org}}}{0.4421 \cdot \frac{m_{\text{cellulose}}}{MWC}}$$

Where "V" is the volume of each solvent; "C_i", the molar concentration of each compound detected in each liquid phase (water or organic phase); "n_i", the number of carbons in the molecule of "i" compound; "m_{cellulose}" is the mass of cellulose introduced in the reactor at the initial point; "MWC" is the molar mass of cellulose, considered as 162 g·mol⁻¹; and 0.4421 corresponds to the atomic percentage of carbon in this cellulose, according to results obtained by ICP analyses of the raw material (44.21 % of C, 6.2 % H; 49.59 % O).

The yield of 5-HMF is calculated in base of the mass of this compound divided by the mass of cellulose converted, as function of this expression:

$$\Phi_{\text{HMF}} = \frac{C_{\text{HMF,water}} \cdot V_{\text{water}} + C_{\text{HMF,MIBK}} \cdot V_{\text{MIBK}}}{\eta_c \cdot V}$$

Selectivities are calculated as the carbon included in each compound divided by the total amount of carbon present in all the compounds quantified in the liquid phase.

Solids obtained after each reaction were dried and analysed in a TG-DSC instrument (Setaram, Sensys) using α -alumina as inert reference material. 20 mg of samples were treated in a nitrogen flow (20 mL·min⁻¹) with a temperature program of 5 K·min⁻¹, from 298 to 873 K.

Extraction analyses

The mass transfer kinetic as well as adsorption/desorption studies were carried out reproducing the reaction conditions in terms of solvent ratio and HCl concentration. In each experiment, 0.18 g of HMF were dissolved in 25 mL of water. Once the corresponding amount of mass transfer agent was added (same concentrations as those studied in the reaction experiments), 31.25 mL of MIBK were added. The temporal evolution of HMF was analysed by GC (organic phase) and HPLC (aqueous one). In order to identify a possible competitive adsorption of HMF and glucose, similar analyses were carried out with same global mass of organics (0.18 g) and a 1:1 distribution of both compounds in mass terms.

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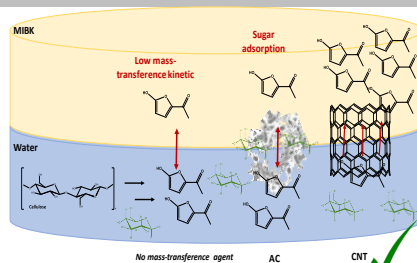
Keywords: Nanotubes • hydrolysis • bioplatfrom • MIBK • green chemistry

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Entry for the Table of Contents

FULL PAPER

Carbon helps 5-HMF to remain safe It is well known that biphasic systems are efficient for avoiding 5-HMF side reactions in cellulose acid hydrolysis. However, L-L mass transfer largely decreases the reaction rate. We demonstrate that the addition of carbon materials (for example CNTs) effectively promotes the interphase mass transfer of the 5-HMF, increasing the overall reaction rate.



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Carbon materials as phase transfer promoters for obtaining 5-hydroxymethylfurfural from cellulose in a biphasic system