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Carbon Materials as Phase-Transfer Promoters for Obtaining 5-Hydroxymethylfurfural from Cellulose in a Biphasic System

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Different carbonaceous materials were tested as mass-transfer promoters for increasing the yield of 5-hydroxymethylfurfural (5-HMF) in biphasic cellulose hydrolysis. The benefits of working with a biphasic system (water/methyl isobutyl ketone) under soft acid conditions were taken as starting point (no humins or levulinic acid production), with slow extraction kinetics as the weakest point of this approach. Carbon nanotubes (CNTs) and activated carbon (AC) were proposed to improve 5-HMF liquid–liquid mass transfer. A kinetic analysis of the extraction process indicated the competition between 5-HMF and glucose adsorption as the main cause of the poor results obtained with AC. In contrast, very promising results were obtained with CNTs, mainly at 1.5 wt% loading, with complete transfer of HMF and a high global mass-transfer coefficient. The use of CNTs improved the amount of 5-HMF in the organic phase by more than 270%.

Introduction

The increasing demand for 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 highly crystalline polymer structure, consisting of thousands of D-glucose molecules.[2] This polymer can be hydrolyzed to glucose sugars, which can be transformed to a huge variety of valuable chemicals, generally known as bio-platform molecules.[3] 5-Hydroxymethylfurfural (5-HMF) is considered to be among the most relevant ones, with many interesting valorization 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 condensation and hydrodeoxygenations steps.[4]

5-HMF production from cellulose requires two main steps, as summarized in Figure 1: (1) hydrolysis of cellulose towards glucose; and (2) glucose dehydration to produce 5-HMF. The hydrolysis can be enzymatically catalyzed.[5] However, the high sensitivity of these technologies, as well as their high cost, limit their 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 the use of mineral acids such as HCl and H_2SO_4 with Brønsted acid sites are widespread.[6,7] Cellulose is an insoluble polymer, which hinders the effective use of heterogeneous catalysts despite the well-known disadvantages of homogeneous catalysts. In fact, most of the previous works proposing solid catalysts report the need of expensive pretreatments of cellulose[8] and the challenge of catalyst fouling caused by humins.[9] Because of these reasons, homogeneous catalysis is nowadays considered as technically more viable, and current works are focused on process optimization by minimizing the use of mineral acids and reducing the reaction temperature.

Once the glucose is obtained, it has to undergo a further dehydration under acidic conditions, which removes three water molecules and produces 5-HMF. This reaction must be performed at softer conditions than the previous hydrolysis to prevent side reactions, such as the decomposition into levulinic and formic acid as well as different glucose and 5-HMF polymerization routes, yielding insoluble and valueless humins.[10] However, these soft conditions also limit the productivity by requiring longer reaction times. Several authors have proposed a previous isomerization of glucose into fructose, reducing humin formation (because most of these undesired products are obtained by oligomerization and side reactions of unreacted glucose) and allowing higher temperatures, resulting in an increased reaction rate.[11,12] This isomerization requires the copresence of a Brønsted acid catalyst (homogeneous; HCl) and a Lewis acid (heterogeneous; e.g., acid zeolites or mesoporous silicates). The production of 5-HMF is strongly enhanced by this route,[13] which lowers the activation energy of the dehydration step by more than 30%, but adsorption usually decreases the carbon balance.[11]

If the whole process, from cellulose to 5-HMF, was performed in a one-pot configuration, the mechanism and mass-transfer limitations would be difficult to control. Thus, this process is mainly studied considering mineral acids (typically HCl). In this case, side products (acids and humins) cannot be pre-

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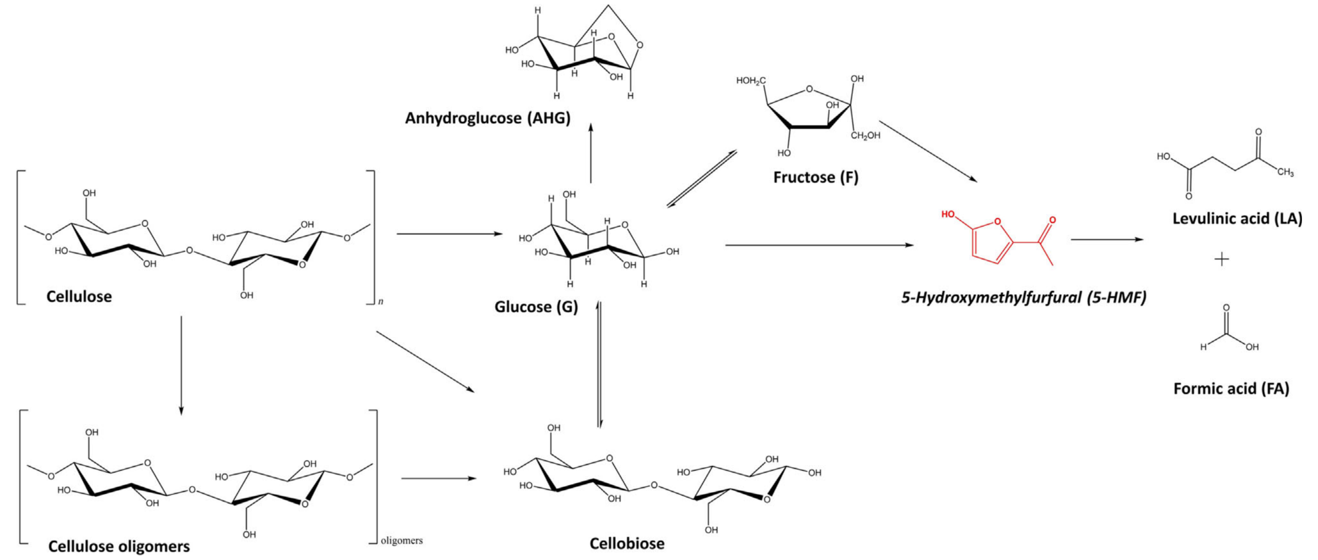

Figure 1. Reaction pathway for cellulose conversion into 5-HMF.

vented because experiments are typically conditioned by the pressure and temperature required in the first step.[10a,14,15] To overcome this drawback, various ionic liquids and polar aprotic organic solvents have been proposed.[16] In all cases, results were limited by the slow kinetics if hydrolysis was performed in any non-aqueous solvent. With these premises, biphasic systems have been proposed,[17] based on the hydrophilic character of all 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 humin polymers in addition to minimizing the need for subsequent purification steps. However, the choice of solvent is a key parameter because the extraction kinetics must be fast enough to prevent the reaction from continuing in the aqueous phase with the 5-HMF that has not been efficiently extracted.

Mass-transfer limitations are the weakest point of these multiphasic reactions. Several works have dealt with this topic, concluding than even under high stirring and with a small disperse-phase droplet size, the liquid–liquid mass-transfer resistance usually controls the overall kinetics.[18] A poor contact hinders 5-HMF transfer despite it being thermodynamically favored. Thus, increasing the interfacial area between organic and aqueous phase is required to promote the intrinsic transport rate.[19]

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.). These kinds of materials tend to adsorb non-hydrophilic molecules in the aqueous phase and desorb them in the organic phase. The equilibrium between these processes depends 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 cellulose upgrading.

The aim of this work is to study the role of carbonaceous materials as mass-transfer promoters in the context of the selective transformation of cellulose into 5-HMF in a biphasic system. In addition to the use of these mass-transfer promoters, the system methyl isobutyl ketone (MIBK)/water applied to the cellulose transformation without any pretreatment and at these conditions is also a novelty in the literature because previous works propose the use of microwaves and ultrasonication to pretreat the cellulose[21] or use complex catalytic and solvent systems.[22,23] MIBK 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 DMSO.[21a,22] Two different types of carbons were tested as mass-transfer agents: active carbon (AC) and carbon nanotubes (CNTs). The amount of material required was optimized with the best one (CNTs), and results are explained in terms of extraction kinetics and equilibrium. The motivations for selecting these materials were the high adsorption capacity of AC and the regular structure and weak surface functionalization of CNTs. Other carbonaceous materials (activated graphite or carbon nanofibers) are supposed to have intermediate behaviors.

Results and Discussion

Performance in the absence of phase-transfer promoters

Trying to optimize 5-HMF production without promoting the formation of side products, this reaction was studied with low acid concentration and a biphasic system (MIBK/water), with the aim of selectively extracting 5-HMF, the only compound with larger solubility in the organic phase than in the aqueous phase. Although MIBK has a relative solubility in water (19 g L^{-1} at reaction conditions), the MIBK/water ratio (1:1 *w*/*w*) guarantees a perfectly defined biphasic system. In addition to allowing us to obtain a selective extraction of the desired compound, this methodology introduces an extra advantage for 5-HMF purification in isolating it as a solid. Despite the scarce studies about this topic, two different alternatives are proposed in the literature, distillation and crystallization.[24] The first one was discarded because of the high boiling point of MIBK (117 °C), whereas crystallization is entirely feasible because of the large difference in freezing points of MIBK (−84 °C) and HMF (30 °C). To analyze if the presence of the biphasic system has a negative effect on the normal activity, results plotted in Figures 2 and 3 are compared with the corresponding ones obtained in a monophasic (aqueous) medium. In this case, reaction was performed by using 0.175 L water as solvent.

Figure 2 shows the temporal evolution of the main compounds involved in the reaction. All results shown are the average value after performing each experiment twice. Experimental errors were estimated in terms of standard deviation and were 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 acid are obtained in equimolar fashion as the two compounds produced by rehydration of 5-HMF. Levulinic acid is more relevant as bio-platform molecule than formic acid, and its production under these conditions can also be relevant because the reaction conditions are soft enough to prevent side reactions involving this molecule. These facts justify that only levulinic acid is plotted in Figure 2 because the concentrations of both reaction products are similar and follow the same trend.

The main product in both the monophasic (empty symbols) and the biphasic system (filled symbols) is the glucose dimer cellobiose, with a continuous increasing trend in the biphasic system and a more stable trend in the monophasic system. Two different reaction steps can produce this compound. On the one hand, this dimer can be a hydrolytic intermediate between cellulose and glucose. On the other hand, this compound is also obtained in reactions feeding glucose, produced by intermolecular dehydration reactions.[25,26] This second route is proposed as the main one in this case because it is largely promoted at temperatures close to the glucose melting point (419 K),[27] and there is no 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 detailed below. This etherification is a reversible reaction, congruent with the profiles obtained, and explains the high amount of dimer observed during all reactions although glucose is consumed in the subsequent steps.

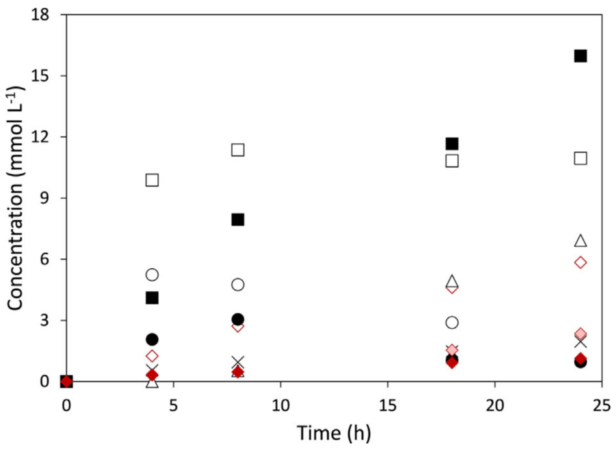

Figure 2. Temporal evolution of main products involved in cellulose hydrolysis (5.83 g) at 413 K with 200 ppm HCl as catalyst. Empty symbols correspond to the aqueous solvent, whereas filled symbols correspond to the biphasic MIBK/water system. Legend: cellobiose (□); glucose (○); 5-HMF (◇); AHG (×);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

Glucose is also relevant, following in both cases the typical behavior of an intermediate, with a maximum concentration of 943 ppm in the monophasic system and 550 ppm in the biphasic system (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 as in the aqueous one, with slower kinetics. This effect is more relevant in the first hydrolytic step (all these steps require water as solvent, but the first one is the most sensitive because it requires more severe conditions). As consequence of the slower kinetics affecting also 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 with just water as solvent. 5-HMF has an increasing profile in both systems, reaching a maximum of 736 ppm (selectivity of 15.6 %) if the reaction is performed in the aqueous phase. However, if the process is performed in a biphasic configuration, 5-HMF is observed in both phases, with a concentration distribution only relevant in the last stages of the reaction, with 296 and 143 ppm in the 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 no solubility limit in the concentration range studied because it was experimentally tested in the laboratory. These data correspond to a 5-HMF yield of 10.26 % in the biphasic system and 11.6 % in the monophasic system.

As to secondary compounds, such as anhydroglucose (AHG) as well as levulinic and formic acid, the desired effect is reached because these compounds are not detected if reaction is performed in a biphasic system, whereas the concentrations of these products reach values of 318 and 804 ppm for AHG and levulinic acid, respectively, after 24 h in the monophasic system. In fact, the selectivity to levulinic acid rises up to 14.8 %, the same value as the desired compound (15 % 5-HMF selectivity at 24 h). Because both maxima correspond to the same time, the presence of this side product is the most relevant drawback of the monophasic system, justifying the use of a biphasic system because the extraction of 5-HMF in MIBK is 100% selective. The low distribution coefficient, however, reduces is productivity to only 55% of the one obtained in the monophasic system. All these results suggest a relevant mass-transfer limitation, justifying the need for promoting mass transfer between both phases.

An accurate analysis of cellulose conversion in these systems is not possible because of the different phases involved. Because cellulose is a solid (whereas all the analyzed compounds 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, resulting by this technique in a glucose conversion lower than the real one. Considering this situation, the evolution of cellulose was analyzed according to the “liquid-phase carbon yield” concept defined in the Experimental Section. Because it is measured considering the liquid phases (water and MIBK), evolution analysis is possible, whereas the conversion calculated by mass difference can also be analyzed at the final point of each reaction.

The temporal evolution of this parameter is depicted in Figure 3. Results suggest a higher glucose conversion in the monophasic system (empty symbols) than in the biphasic one (filled symbols), with the difference most noticeable in the initial 8 h. However, theoretical conversions after 24 h are very close: 18.9 and 16.4%, respectively, 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 hydrolyzing 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). In good agreement with this hypothesis, the biphasic system has the same trend, suggesting the same final point, but with a clearly slower kinetics. These results, congruent with the product profiles obtained, indicate that the biphasic system could be a good option to perform the reaction considering that acidity and thermal conditions (and not the organic phase) are the most probable limiting parameters to obtain a higher conversion.

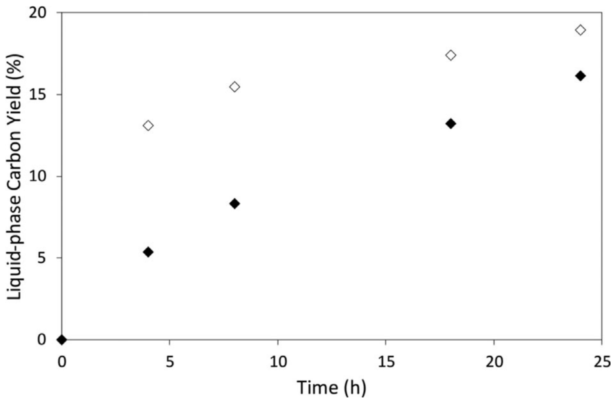

Figure 3. Temporal comparison of liquid-phase carbon yield obtained for the reactions performed in aqueous phase (◇) and with the biphasic MIBK/water system (◆).

To determine whether the liquid-phase carbon yield can be directly related to the cellulose conversion, thermogravimetric analysis (TGA) was performed, 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 can be observed, both profiles after the reaction suggest the presence of cellulose (decomposition temperature at 590–610 K), whereas the weakest humin signal is at 660 K. The lower mass loss obtained with the humins sample compared with the other analyses also suggests the presence of more stable humins deposed 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 ones obtained with the fresh cellulose, disproving the presence of any of these side compounds.

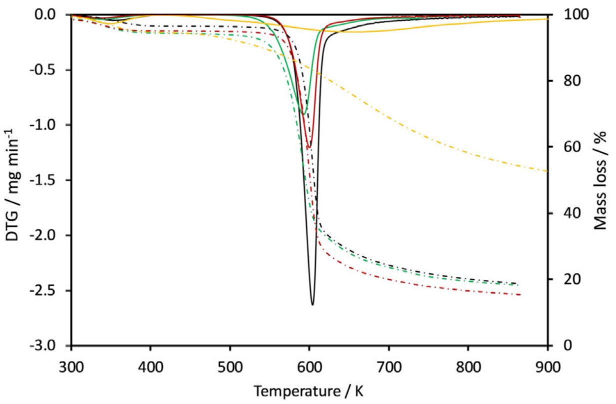

Figure 4. TGA results obtained by analyzing the solid recovered after reactions performed in monophasic (green) and biphasic (red) configuration. Results compared with the thermal decomposition of pure cellulose (black) and humins (yellow). Data in continuous lines correspond to derivative thermogravimetry (DTG), whereas dotted lines correspond to the mass loss.

The presence of some glucose oligomers in the reaction samples cannot be totally discarded because these peaks are a bit wider than the peak of pure cellulose with the maximum slightly displaced to slower temperatures, a clear signal of 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 relevant. According to the literature, the thermal decomposition of glucose occurs at temperatures a bit higher than its melting point (419 K), with some signals detected up to 513 K owing to the loss of water produced through different oligomerization processes occurring during this decomposition, including cellobiose formation.[27] According to these results, saccharide decompositions take place from 420 to 610 K, with the temperature directly related to the complexity of their structure (from monosaccharide to polymer).

Taking this into account, the displacement of the main peak of reaction samples to lower temperatures is suggested to be related to a small amount of oligomers, with the peaks obtained in the reactions considered as the envelope curve of cellulose and these small contributions. This slight difference suggests that, if oligomers are present, 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 for cellobiose. According to these analyses, the absence of humins is corroborated in both cases, and the clear profiles suggest a good correspondence between the liquid-phase carbon yield concept and cellulose conversion.

Carbon materials as phase-transfer promoters

After testing the two-phase configuration, two main conclusions are obtained related to slower kinetics and a poor liquid–liquid mass transfer. Thus, lower conversions are obtained and 5-HMF is distributed to almost 50% in each solvent, with a low concentration in MIBK (despite being the only product transferred to the organic phase). Both problems can be solved if the phase transfer is improved because 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 overall cellulose conversion.

To improve this transfer, two different carbonaceous materials were tested: CNTs and AC. These two materials are among the best-known carbonaceous structures and were chosen because their different properties in terms of surface area to compare the role of a mesoporous (CNTs, 277 $m^2 g^{-1}$) and a microporous material (AC, 1005 $m^2 g^{-1}$). The use of other inorganic materials such as alumina or zeolite has been discarded because of their inferior adsorption performance as well as their surface reactivity. All characterization is detailed in a previous work.[28] In both cases, materials were directly used without introducing any modification in their surface to ensure the absence of any extra catalytic process that could play a role in the results. However, the presence of some functional groups on their surface cannot be completely prevented. According to the literature, CNTs presents some weak acid groups, whereas AC also exhibits some oxygen surface groups.[28] In good agreement, both materials present very similar isoelectric points (4.19 and 4.63 for CNTs and AC, respectively). It can be expected that these functionalities have a negligible catalytic role in this reaction because it requires strong acid sites. To verify this premise, a preliminary reaction in the absence of HCl but with the carbon materials was performed, resulting in negligible cellulose conversion.

For an initial test, both materials were introduced in 2 wt% concentration referring to the initial amount of cellulose. The temporal evolutions of these results are shown in Figures 5 and 6, for the analysis of liquid-phase carbon yield and product concentration, respectively. According to the analysis of the two experiments performed for each condition, the relative errors are always lower than 6%, as shown in Figures 5 and 6.

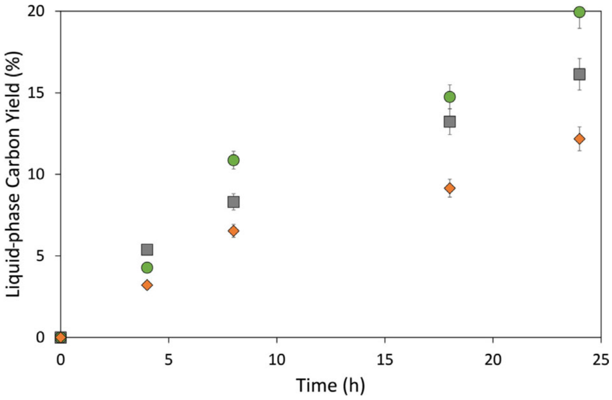

Figure 5. Temporal evolution of liquid-phase carbon yield for reactions performed in a biphasic system without any mass-transfer agent (■), with CNTs (●), and with AC (◆).

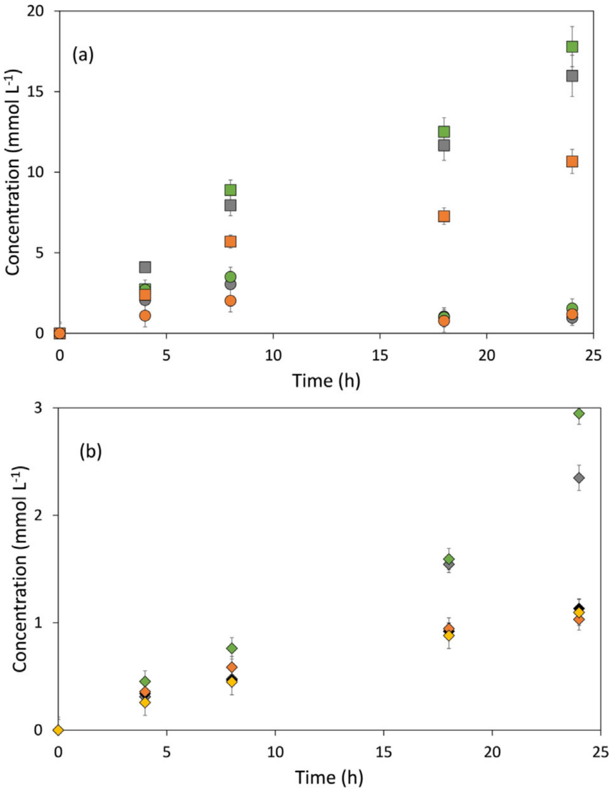

Figure 6. (a) Temporal evolution of cellobiose (■) and glucose (●) obtained in the liquid phase of the biphasic system using no mass-transfer agent (grey), CNTs (green), and AC (orange). (b) Temporal distribution of 5-HMF (◆) between phases. Data correspond to aqueous (grey) and organic phase (black) in absence of any mass-transfer agent; aqueous (orange) and organic phase (yellow) using AC; and organic phase using CNTs (green), with no signal for 5-HMF in aqueous phase using CNTs.

The expected improvement in the overall reaction is clearly observed when using CNTs, resulting in higher cellulose conversion (analyzed in terms of liquid-phase carbon yield) than in the absence of any mass-transfer agent, with a relative increase higher than 20% (from 16.5 to 19.95% without and with CNTs, respectively). A relevant catalytic activity of these CNTs can be discarded because of the low concentration of functional sites of these materials, much lower than for the corresponding AC. Thus, this improvement can be caused by the enhancement in the transfer of 5-HMF from the aqueous to the organic phase, also promoting the glucose consumption by the equilibrium shift. According to this possibility, the amount of glucose dimer also decreases, and the influence of the amount of CNTs is low (once the minimum required to promote the complete transfer is reached, an extra amount has no bearing on the reaction). To identify the key parameters, reactions with different amounts of CNTs were performed.

In the case of 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 AC surface, as previously demonstrated in the literature.[29]

Cellobiose and glucose are selectively obtained in the aqueous phase with both carbonaceous materials as well as without any mass-transfer agent (Figure 5). The concentration obtained with CNTs is similar to the one without any carbonaceous materials, whereas the amount of cellobiose with AC is significantly lower at all times. This result is congruent with the suspected strong adsorption of these sugars onto the AC surface. The production of humins, AHG, and levulinic and formic acid is prevented. These results suggest that 5-HMF is entirely transferred to the organic phase. For the reaction with CNTs, no signals of any 5-HMF are detected in the aqueous phase at any reaction time (distribution coefficient close to infinity). In contrast, results obtained with AC are even worse than without adding any mass-transfer agent, affording almost the same concentration in both cases. This result corresponds to a distribution coefficient close to 1.

The infinite distribution coefficient suggests that 2% CNTs could be too much, in such a way that lower CNT concentrations could be sufficient to maximize the extraction. Although the adsorption is more relevant in the case of AC, this cannot be discarded in the case of CNTs because the total final amount of 5-HMF obtained (371 ppm) is lower than the total amount obtained without CNTs in the reaction (439 ppm) or for using a monophasic system (736 mg). Thus, further experiments were performed by decreasing the 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% CNT (386 ppm). This result corresponds to a 43.3% selective conversion of cellulose into HMF (corresponding to a 9% total yield of 5-HMF from cellulose), 23% more than without the mass-transfer agent and a value higher than typically obtained under comparable conditions (low temperature and low catalytic loading in a biphasic medium).[22] Lower values of 5-HMF concentration were obtained with both lower and higher concentrations, requiring an in-depth study of 5-HMF extraction to identify if it is only explained in mass-transfer terms or if the overall reaction kinetics control the process.

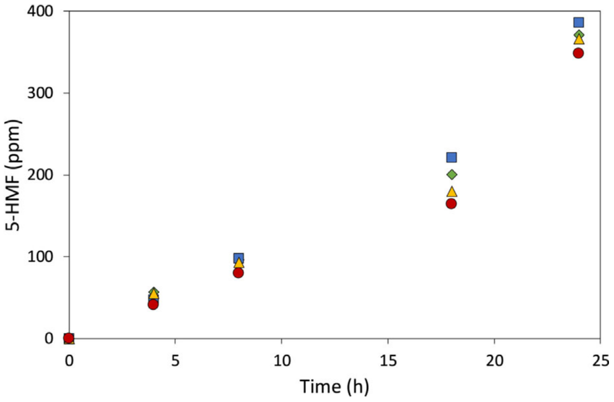

Figure 7. Temporal evolution of 5-HMF concentration obtained as function of the CNT concentration: 0.5 (●), 1 (▲), 1.5 (■), and 2% (◆).

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

To study the extraction of 5-HMF, the time evolution of 5-HMF concentration in aqueous and MIBK phase was analyzed for the four CNT concentrations (0.5, 1, 1.5, and 2%). The evolution of 5-HMF concentration in the organic phase is compared in Figure 8. The evolution obtained upon adding AC was also included. In all 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, the partition coefficient (organic/aqueous concentration under stationary conditions) evolves from 1.09 (absence of any mass-transfer promoter) to 1.23 (1.5% CNTs). However, the main differences are related to the speed at which these equilibriums are reached because the partition coefficients reached with 0.5, 1, and 2% of CNTs and AC are very similar (from 1.15 to 1.17).

The in-depth analysis of these results requires analyzing the kinetics of the process. Considering that all steps involved in this process only take place in the aqueous medium, the appearance of 5-HMF in the organic phase, as well as its faster or

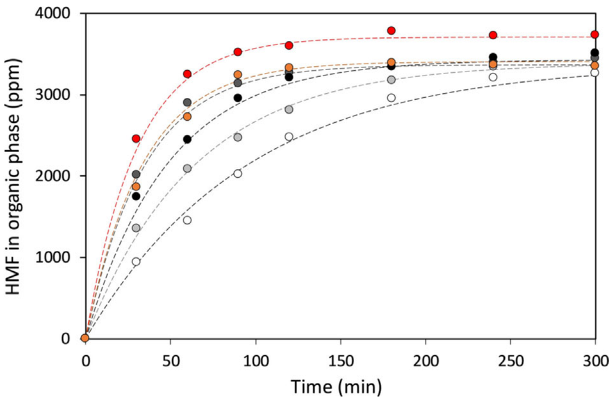

Figure 8. Temporal evolution of 5-HMF concentration in the organic phase in the extraction studies. Experimental points correspond to no mass-transfer agent (○); 0.5% CNTs (●); 1% CNTs (●); 1.5% CNTs (●); 2% CNTs (●); 2% AC (●).

slower 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 5-HMF transport rate [mol L^{-1} min^{-1}] can be calculated as a function of the effective transport coefficients ($K^i \times a$, with a being the effective coefficient and i indicating the phase [min^{-1}]) according to the following equations for water (w) and MIBK (o) phase [Eqs. (1) and (2)]:

$$\frac{dC^w_{HMF}}{dt} = -\left(K^w_{HMF} \times a\right) \times \left(C^w_{HMF} - C^{w*}_{HMF}\right) \tag{1}$$

$$\frac{dC^o_{HMF}}{dt} = \left(K^o_{HMF} \times a\right) \times \left(C^{o,*}_{HMF} - C^o_{HMF}\right) \tag{2}$$

in which C refers to concentration, and 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, as a particular value for each experiment (5-HMF concentrations in both phases do not undergo 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, H_{HMF}, defined as the ratio between 5-HMF in the organic and aqueous phase once the equilibrium is reached [Eq. (3)]:

$$K^o_{HMF} = H_{HMF} \times K^w_{HMF} \tag{3}$$

This fact allows us to study the whole mass-transfer process by just analyzing the evolution of one phase. In this case, because 5-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 the organic phase is simplified in Equation (4):

$$C^o_{HMF,t} = C^{o,*}_{HMF} \times \left\{1 - e^{-\left[\left(K^o_{HMF} \times a\right) \times t\right]}\right\} \tag{4}$$

Experimental data were fitted according to this model, obtaining good correlation coefficients ($R^2 > 0.92$ in all 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 cases, the carbon balances considering both phases are close to 100 %, discarding any relevant permanent adsorption phenomenon even in the case of AC. Values obtained are in good agreement with the concentration of 5-HMF in the organic phases of reaction media, suggesting that extraction is promoted with 1.5 % CNTs. However, the high coefficient observed with AC (very similar to results of 1 and 1.5 % CNTs) contrasts with its poor behavior in the reactions.

This apparently incongruent behavior of AC can be caused by two main reasons: a strong pH dependence or a negative influence of sugar adsorption. In the first case, results obtained with 200 ppm HCl in the reaction medium would modify the volumetric transfer coefficients (real conditions in the reaction studied). In the second case, this modification could be checked by studying the 5-HMF transfer when sugars are also present, evaluating if their adsorption on the AC surface hinders the mass transfer. These two conditions were tested with both CNTs and AC, comparing the final volumetric mass-transfer coefficients in Figure 10.

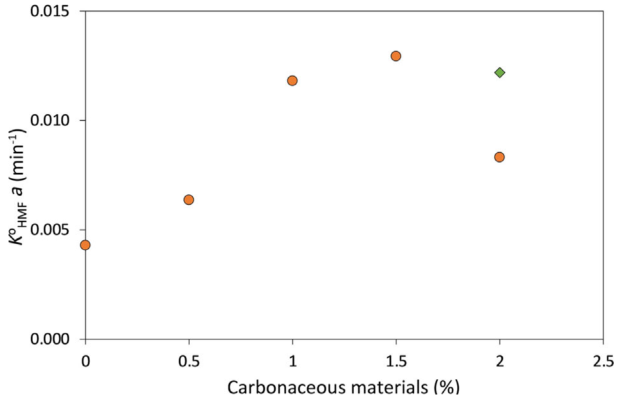

Figure 9. Comparison of volumetric mass-transfer coefficients [min^{-1}] as function of the percentage of carbonaceous materials in the interface. Orange symbols (●) correspond to CNTs; green symbols (◆) to AC.

A clear improvement is observed when working under acidic conditions (striped bars) with both CNTs and AC. Both coefficients reach values twice as high as those under neutral pH. This improvement is a clear consequence of the positive effect of acidic conditions in liquid–liquid extractions.[30] This result suggests that the protonation of the carbon functional groups increases their phase-transfer promotion effect, which is more marked for AC because of its larger concentration of these sites.

The presence of other compounds in the aqueous phase can modify the mass-transfer process because these molecules can be adsorbed, decreasing the free surface available to the

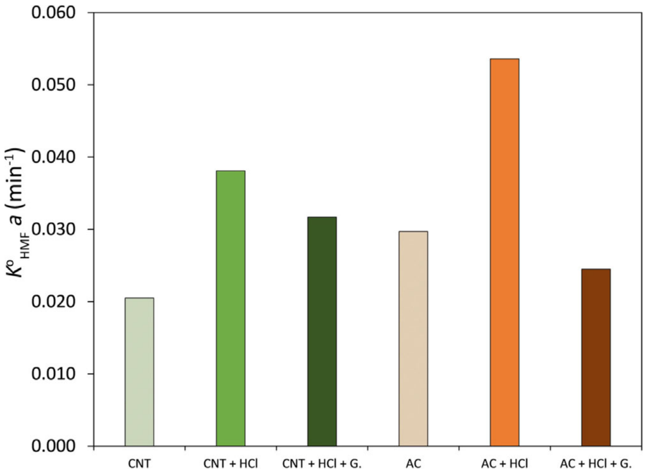

Figure 10. 5-HMF overall mass-transfer coefficient values [min^{-1}] obtained with CNTs (green) and AC (orange) as function of the extraction conditions: neutral pH selective extraction of 5-HMF (striped bars); acidic pH selective extraction of 5-HMF (🟩 and 🟧); and acidic pH with co-presence of glucose (🟩 and 🟫).

5-HMF transfer. To investigate this effect, the co-presence of glucose in the extraction medium was analyzed, chosen because it is the major component 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 CNTs (relative decrease of 16.7 %), whereas $K^{\circ}_{HMF} \times a$ decreases more than 50 % for AC, obtaining a final value very similar to the one at neutral pH. This situation is owing to the high affinity between sugars and the AC surface, as previously mentioned in the literature.[2] Because these conditions are similar to the ones in the real reaction medium, this adsorption is proposed as the main cause of the inferior behavior of AC as selective mass-transfer promoter in this reaction, making this negative effect more relevant than the improvement caused by the acidic conditions. In contrast, CNTs are a good mass-transfer promoter, making 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 one obtained in the absence of mass-transfer agents. In addition, all 5-HMF is extracted to the organic phase, whereas less than 50 % is efficiently extracted with the water/MIBK system.

Conclusions

The use of carbon nanotubes (CNTs) as mass-transfer promoters clearly improves the transformation of cellulose into 5-hydroxymethylfurfural (5-HMF) in a water/methyl isobutyl ketone (MIBK) biphasic system. Considering that the acidic conditions required to promote cellulose hydrolysis are also responsible for 5-HMF degradation into humins and levulinic acid, the extraction of this compound to an organic phase is needed. A selective extraction is proposed by using a water/MIBK system, but the 5-HMF formation rate of this process is decreased by the slower liquid–liquid mass-transfer kinetics. CNTs are proposed as promising mass-transfer promoters, enhancing the extraction kinetics more than 3.7 times, mainly under acidic conditions. Because several equilibrium steps are involved in the process, this extraction also results in an increased productivity (270 times higher). The use of activated carbon (AC) instead of CNTs is discarded owing to the competition between 5-HMF and glucose for the adsorption sites (the first one is reversible, but the second one causes partial blockage of the AC). With this approach, 5-HMF can be selectively produced from cellulose without need for a complex catalyst, toxic solvents, or severe conditions.

Experimental Section

Materials

Microcrystalline cellulose (CAS: 9004-34-6), as well as D-(+)-glucose (≥99.5 %), D-(−)-fructose (≥99 %), 5-HMF (≥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 to determine the main properties that could affect this reaction. Thus, inductively-coupled plasma (ICP) analysis was performed to identify the atomic bulk composition by 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 on a Philiphs X'Pert Pro diffractometer, working the with the CuK_{α} line, in the range $2\theta = 5–30^{\circ}$. The crystallinity index (CI) was calculated by using the Segal equation [Eq. (5)]:

$$CI = \frac{I_c - I_a}{I_c} \qquad (5)$$

in which I_c is the intensity of the maximum crystalline peak and I_a is the minimum intensity between two crystalline peaks. Two different carbonaceous materials were used as mass-transfer agents: CNTs provided by Dropsens and AC (GC-900, supplied by Chemi-Vall). These materials were characterized in depth in a previous study.[28]

Reactions and sample analyses

Reactions were performed in a 0.5 L stirred autoclave reactor (Autoclave Engineers EZE seal) equipped with a proportional-integral-derivative (PID) temperature controller and a back-pressure regulator. The reactor was loaded with a biphasic mixture of MIBK and water (350 mL; 175 mL water and 218 mL MIBK, 1:1 *w/w*) with cellulose (5.83 g, 50–80 μm) and HCl (200 ppm) as catalyst. The reactor was pressurized to 10 bar with N_2 and heated to the reaction temperature, 413 K. If the reaction was performed in the presence of carbonaceous materials, different mass loadings of CNTs or AC were added to the system (values detailed in the corresponding section of the main text).

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

The cellulose conversion is calculated in terms of liquid-phase carbon yield, a concept involving the theoretical cellulose required to obtain all compounds detected in the liquid phase. 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 value, analyzed in carbon terms, is calculated according to Equation (6):

$$\eta_c = \frac{[V \times \sum(n_i \times C_i)]_{aqueous} + [V \times \sum(n_i \times C_i)]_{org}}{0.4421 \times \frac{m_{cellulose}}{M_{cellulose}}} \qquad (6)$$

in which η_c is the liquid-phase carbon yield, 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 compound i, $m_{cellulose}$ the mass of cellulose introduced in the reactor at the initial point, $M_{cellulose}$ the molar mass of cellulose (162 g mol^{-1}), and 0.4421 corresponds to the atomic percentage of carbon in this cellulose, according to results obtained by ICP analysis of the raw material (44.21 % C, 6.2 % H, 49.59 % O).

The yield of 5-HMF is calculated based on the mass of this compound divided by the mass of cellulose converted, as shown in Equation (7):

$$\varphi_{\mathrm{HMF}} = \frac{C_{\mathrm{HMF,water}} \times V_{\mathrm{water}} + C_{\mathrm{HMF,MIBK}} \times V_{\mathrm{MIBK}}}{\eta_{\mathrm{c}} \times V} \qquad (7)$$

where $C_{\mathrm{HMF,water}}$ and $C_{\mathrm{HMF,MIBK}}$ are the concentration of HMF in the water and MIBK phases; V_{water}, V_{MIBK}, and V are the volumes of aqueous phase, MIBK, and the total one, respectively. Selectivities are calculated as the carbon included in each compound divided by the total amount of carbon present in all compounds quantified in the liquid phase.

Solids obtained after each reaction were dried and analyzed with a thermogravimetry–differential scanning calorimetry (TG–DSC) instrument (Setaram, Sensys) by using α-alumina as inert reference material. The samples (20 mg) 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 kinetics as well as adsorption/desorption studies were performed by reproducing the reaction conditions in terms of solvent ratio and HCl concentration. In each experiment, 5-HMF (0.18 g) was dissolved in water (25 mL). Once the corresponding amount of mass-transfer agent was added (same concentrations as those studied in the reaction experiments), MIBK (31.25 mL) was added. The temporal evolution of 5-HMF was analyzed by GC (organic phase) and HPLC (aqueous phase). To identify a possible competitive adsorption of 5-HMF and glucose, similar analyses were performed with the same total mass of organics (0.18 g) and a 1:1 (*w*/*w*) distribution of both compounds.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon nanotubes · cellulose · green chemistry · hydrolysis · methyl isobutyl ketone

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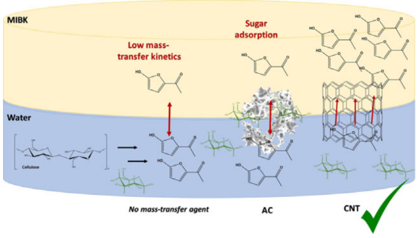
Carbon Materials as Phase-Transfer Promoters for Obtaining 5-Hydroxymethylfurfural from Cellulose in a Biphasic System



Carbon saves 5-HMF: It is well known that biphasic systems are efficient for avoiding side reactions of 5-hydroxymethylfurfural (5-HMF) in cellulose acid hydrolysis. However, liquid–liquid mass transfer largely decreases the reaction rate. The addiction of carbon materials (for example carbon nanotubes, CNTs) effectively promotes the interphase mass transfer of 5-HMF, increasing the overall reaction rate.