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ARTICLE TYPE

Microwave assisted organocatalytic synthesis of 5-hydroxymethyl furfural in a monophasic green solvent system

Hitesh Pawar^a and Arvind Lali^{*a,b}⁵ Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

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Monophasic microwave assisted dehydration of fructose to 5-hydroxymethyl furfural (HMF) catalyzed by *p*-toluene sulphonic acid (PTSA) was studied in non-aqueous organic solvents. Of the three monophasic systems studied (isopropyl alcohol, *N*, *N*-dimethyl formamide and dimethyl sulfoxide), isopropyl alcohol, a preferred green solvent gave the product in highest yield. Use of PTSA as proton source for microwave (2.45 GHz) assisted dehydration of fructose in isopropyl alcohol resulted in >98% fructose conversion with >90% HMF yield in 90s of reaction time. The use of inexpensive and mild acid catalyst PTSA for HMF synthesis with an ecofriendly solvent IPA offers ease of catalyst handling and solvent recovery.

Introduction

Depletion of fossil fuel resources along with significant increase in carbon emissions have necessitated increased focus on development of processes for production of bio-based chemicals and chemical intermediates. Further, sustainability issues, in addition to associated accident and pollution hazards on account of extreme conditions employed in inefficient synthetic procedures, have created a need to move synthetic chemistry towards intensified rapid and highly selective reaction systems. Thus, attempts are being made to develop reaction schemes that are based on non-fossil resources and involve mini-reactors with large throughputs and which are less polluting and consume less energy. Among the existing advanced tools of organic synthesis, microwave reactors provide one of the options for selective and rapid and high throughput processes^{[1]-[6]}.

Non-food lignocellulosic biomass (agriculture, marine and forest) and their co-products provide the most promising alternative renewable feedstock for production of carbon bearing fuel, energy and chemical products^{[7]-[19]}. Of the possible biomass based platform chemicals, 5-hydroxymethyl furfural (HMF) has been listed as one of the more versatile and potential intermediates for production of fuels, bulk chemicals, pharmaceuticals, polymers, fine chemicals etc.^{[10], [11]}. Several reports have been published over the last three decades on designing of effective routes for synthesis of 5-hydroxymethyl furfural^[12].

Procedures reported for the synthesis of HMF from carbohydrate moieties like glucose, fructose and others have consisted of simple acid catalyzed dehydration reaction using organic acids like oxalic acid, levulinic acid, and acetic acid; mineral acids like H₂SO₄^[13], HCl^[14], H₃PO₄^[15] ionic liquids^[16], heteropoly acids^[17], and Lewis acid like AlCl₃^[18] lanthanide chlorides^[19]. Lai and Zhang^[20] studied conversion of fructose to HMF in alcoholic solvents with aqueous HCl as catalyst and

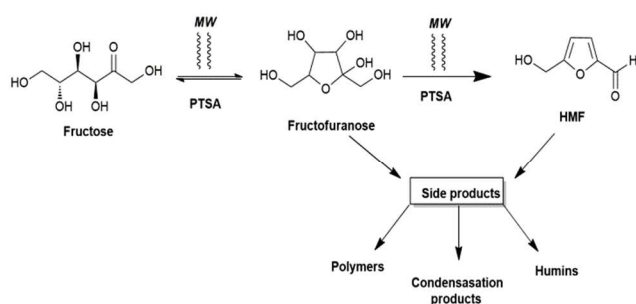
obtained 82% yield in 1h under refluxing conditions. They also studied use of H₂SO₄, H₃PO₄, HCOOH, CH₃COOH, and B(OH)₃ as catalyst with 68% to trace yields. Intensification of the acid catalyzed dehydration of fructose has been attempted by many researchers through use of microwaves with different acid catalysts. Lewis acid catalyst, AlCl₃·6H₂O under microwave heating at 160°C gave 61% yield of HMF within 10min in aqueous tetrahydrofuran^[21]. Typically, the reactions involving aqueous solutions seem to suffer from rehydration reactions of HMF to several unwanted products during the work-up of the reaction mixture aimed at product isolation. De *et al.*^[22] used AlCl₃ as catalyst for fructose dehydration in monophasic system of DMSO, and biphasic system of water and methyl isobutyl ketone. Microwave assisted reaction at 100-140°C was observed to provide the best HMF yield of 71.3 % in 5min in water and MIBK.

Bi *et al.*^[23] reported the advantage of using an inorganic salt like NH₄Cl in isopropyl alcohol over use of mineral acid catalysts in terms of lower corrosiveness. The reaction was however much slower and a yield of 68% was obtained in 12h. Microwave assisted heating was then successfully attempted for enhancing reaction rates and the reaction time of 12h could be reduced to 10min with 92% fructose conversion giving a 37% yield to HMF. Riisager and Hansen^[24] have also reported microwave assisted synthesis of HMF catalyzed by aqueous HCl with reaction time ranging from 1s to 60s at 200°C. Fructose conversion of 52% was possible with a HMF selectivity of 63% in only 1s while 95% conversion could be possible with a much reduced yield of 53% in 60s.

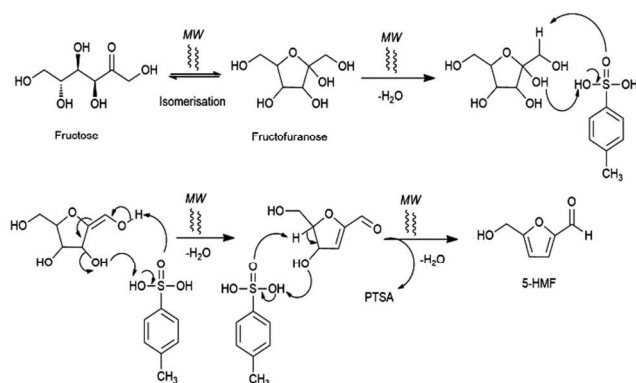
On account of handling and corrosion issues with mineral acids, and relative ineffectiveness of organic acids like acetic and oxalic acids, several workers have attempted use of *p*-toluene sulphonic acid (PTSA) as catalyst for synthesis of HMF in different solvent systems such as water, polyethylene glycol, ionic liquids and supercritical solvent^[25]. Ilgen *et al.*^[26] studied

fructose dehydration in presence of PTSA in choline chloride at 100°C with 67% of HMF yield. Asghari *et al.* [27] reported use of PTSA in supercritical water at 240°C while Moreau *et al.* [28] reported use of PTSA for HMF synthesis in presence of the imidazolium ionic liquid and DMSO at 80°C with a yield of 68 % in 32h.

In the present study, we report a green and efficient microwave assisted dehydration of fructose in non-aqueous solvents in presence of *p*-toluene sulphonic acid (PTSA) as catalyst (Scheme 1). Non-aqueous solvents were used in order to facilitate the dehydration reaction and also for subsequent work up of the reaction mixture by utilization of minimum energy for solvent separation. Monophasic solvents with small but finite solubility for fructose were selected. Thus, isopropyl alcohol (IPA), *n*-butanol, *tert*-butanol (TBA), isoamyl alcohol (IAA), *n*-butyl alcohol (NBA), *N,N*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) were used. Microwave (MW) assisted heating was selected for its proven advantages of short reaction time and higher selectivity. Thus, the complete reaction protocol with respect to reaction time, temperature and PTSA concentration was optimized to obtain high yield of HMF with high conversion of fructose.



Scheme 1 Microwave assisted formation of HMF in presence of PTSA



Scheme 2 Plausible mechanism of MW assisted PTSA catalyzed fructose dehydration reaction

Results and Discussion

Effect of solvent on HMF yield, conversion and selectivity

Dehydration of fructose to HMF was attempted in different low and high boiling monophasic organic solvents. High boiling solvents were selected from the group of previously most studied solvents for fructose dehydration viz. DMF and DMSO. The low boiling solvents were selected from the group of higher alcohols namely IPA, NBA, TBA, and IAA which are considered as green

solvents for synthesis. It was found that of the tested solvents, IPA, DMF and DMSO were remarkable in terms of yield and conversion (Fig.1). The percentage yield of HMF in DMF, DMSO and IPA obtained was 90%, 88% and 85%, respectively with more than 94% fructose conversion. As DMF gave highest yield out of all the tested solvents, and IPA gave highest yield among the tested alcoholic solvents, these two solvents were selected for further study.

Lower yields of about 60% of HMF in IPA (than obtained in this work) has been previously reported and attributed to formation of stable fructofuranose intermediate under the acidic conditions [29]. Although the use of lower alcohols for HMF synthesis in combination with aq. HCl has been reported with formation of etherification products, IPA was considered a better candidate for higher selectivity due to its bulkiness [20]. Use of the mineral acid as catalyst reported in these works makes the process system corrosive, tedious and non-ecofriendly. In the present study an attempt was therefore made to employ an inexpensive and mild acid catalyst PTSA in combination with IPA to provide ease of handling and reduced adverse environmental impact. Further, the present process gave HMF in higher yield (>85%) in MW assisted conditions in short reaction times (maximum 120s). The high yields obtained can be said to be due suppression of both etherification reactions and formation of unstable fructofuranose intermediates in presence of PTSA and IPA under MW radiation. Thus, a combination of MW, PTSA and IPA was observed to favor formation of unstable intermediates that selectively convert into HMF. The plausible mechanism under MW heating in presence of PTSA can be given as in Scheme 2 i.e. via formation of fructofuranose intermediates. On the other hand, higher alcohols also gave HMF yields lower than IPA: TBA (39%); NBA (47%); and IAA (17%) even though the conversion was more than 88% in all three cases.

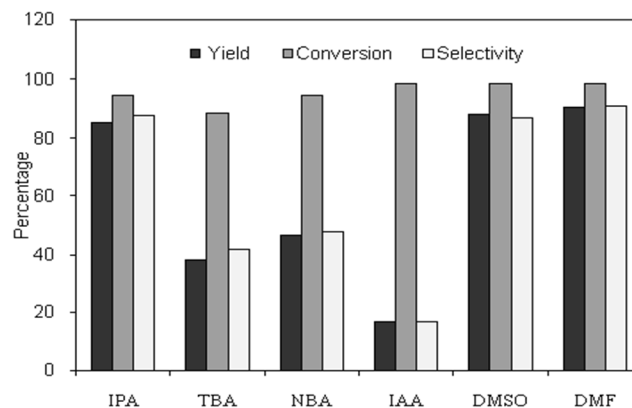


Fig. 1 Effect of different solvents on yield, conversion and selectivity. Reaction condition: PTSA (0.1 g/ml for alcohols and 0.2 g/ml for DMF and DMSO) temperature 120°C, time 120s.

Effect of catalyst concentration

PTSA was selected as the organocatalyst for fructose dehydration for its ease of handling and low corrosiveness compared to previously reported mineral acids. The effect of PTSA concentration on fructose dehydration was studied through runs made with varying concentrations (0-0.2 g/ml) of PTSA in IPA

and DMF as reaction media. The choice of solvent was seen to have a significant effect on HMF yield and fructose conversion. Results, shown in Fig. 2, indicated that IPA was a better solvent system in terms of both yield and conversion despite DMF having a better solubility for fructose.

It was found that there was no fructose conversion and decomposition in absence of catalyst. On increasing PTSA concentration in DMF beyond 0.03 g/ml, HMF yield increased gradually up to 0.10 g/ml and there was negligible effect from 0.10-0.16 g/ml. However, the yield increased remarkably from 0.16 to 0.20 g/ml. While in case of IPA, yield of HMF showed similar trend the requirement of PTSA was 50% less in IPA as compared to DMF for >98% conversion which can be attributed to the formation of a stable complex between PTSA and DMF^[30]. Besides, the existence of DMF in two resonance forms of amide structures can be said to favor hydrogen bonding with the acidic part of PTSA thereby possibly resulting in lower availability of PTSA as a proton source for fructose dehydration. Optimal PTSA concentrations were found to be 0.10 g/ml and 0.20 g/ml in IPA and DMF, respectively for obtaining maximum of HMF yield and fructose conversion. Hence, these PTSA concentrations were used for further study in the two solvents. It may be noted that while the concentrations of PTSA used were higher than typical catalytic amounts, its low cost and good performance coupled with possible recovery and reuse makes PTSA an acceptable process option.

Recovery and reuse of PTSA was attempted by evaporating the solvent from the reaction mixture followed by mixing with water and separating the organic layer for HMF recovery^{[22],[24]}. The water wash layer containing PTSA and water soluble side products was polished on a hydrophobic adsorbent column and then evaporated to obtain PTSA for reuse. However, after the evaporation of water a viscous brown mass was obtained from which it was difficult to isolate the PTSA. While better scheme for recovery and reusability of PTSA can be developed the present process nevertheless proves attractive as it avoids use of stringent reaction conditions e.g. supercritical water and higher temperature ionic liquid and long reaction times. The present system is seen to offer better productivity from these view points under relatively less severe conditions (Table 1).

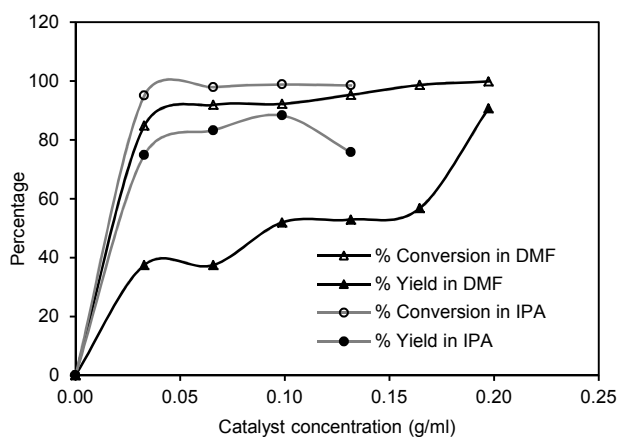


Fig. 2 Effect of PTSA concentration on conversion and yield in IPA and DMF. Reaction conditions: fructose (2.77 mmol), IPA 8ml, temperature 120°C, time 120s.

Table.1 Comparison of present system with previously reported systems using PTSA as catalyst

Entry	Solvent	% Yield	Reaction time	Productivity kg/L/h	Ref.
1	IPA	90	90s	25.20	This work
2	ChCl ^a	67	30m	0.62 ^c	(26)
3	Super critical water	65	120s	0.29	(27)
4	IL ^b and DMSO	68	32h	0.001	(28)

^a Choline chloride, ^bIL ionic liquid, ^c kg/kg of ChCl/h.

Effect of reaction time

As shown in Fig. 3, there was a significant effect of reaction time on fructose conversion and HMF yield in both solvent systems i.e. DMF and IPA. A higher yield of HMF (91%) was obtained only in 90s when IPA was employed, whereas DMF took 120s to give similar yield. It can be seen that while reaction is faster in DMF, the selectivity shown is higher in IPA at yields greater than about 65%. A decrease in HMF yield was seen in both systems at longer reaction time of 150s although conversions were >99% in both solvents. Long reaction times have been reported to favor formation of side products due to decomposition of HMF to humins, levulinic acid, formic acid and other condensation products.^{[11],[31]} Product yield decreased in IPA and DMF at reaction times beyond 90s and 120s, respectively. This was visibly apparent by change in color of the reaction mass to dark brown. It was found that while there was increased formation of side products with increased reaction time there was no formation of levulinic acid in the process under conditions used.

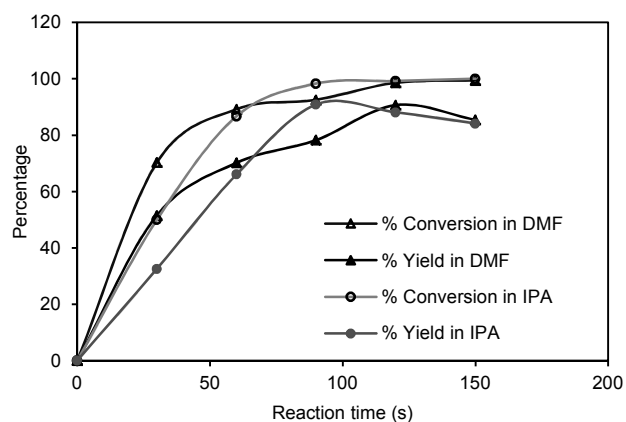


Fig. 3 Effect of reaction time in DMF and IPA on conversion and yield. Reaction conditions: fructose (2.77 mmol), IPA 8ml, PTSA 0.10 g/ml and 0.2 g/ml for IPA and DMSO respectively, temperature 120°C.

Effect of reaction temperature

MW system (Biotage) operating at 2.45GHz frequency was used for the reaction. The reaction temperature in the system was

adjusted by giving temperature set point to MW system which uses appropriate power for quick heating of the reaction mass to the desired temperature measured by an IR temperature sensor. Thus reaction temperature was varied to study the effect on the reaction progress. Temperatures were tested in the range of 90 to 130°C while maintaining the desired substrate and catalyst concentrations. A reaction temperature of 120°C gave ~90% yield to HMF at 100% fructose conversion in both IPA and DMF. The reaction temperature above and below 120°C in both solvents resulted in a decrease in HMF yield. The lowest yield between 30-40% and conversion between 85-90% was observed at 90°C. At higher temperatures even though the conversion was complete the yield to HMF suffered significantly (Fig. 5). The optimum temperature thus was found to be 120°C for the reaction system.

It was generally noted that higher temperatures (>120 °C) and longer reaction times (>120s) resulted in a loss of yield expectedly on account of by-product formation and/or decomposition of HMF (Fig.3 and Fig.4). Sequential conversion of fructose to HMF and its subsequent conversion to other products can be expected to be controlled by intensified short duration reaction on MW system. It was therefore decided to deploy the microwave system in the work. A comparison between the progress of the reaction in MW assisted system with that using a conventionally heated system was also done and is described later below.

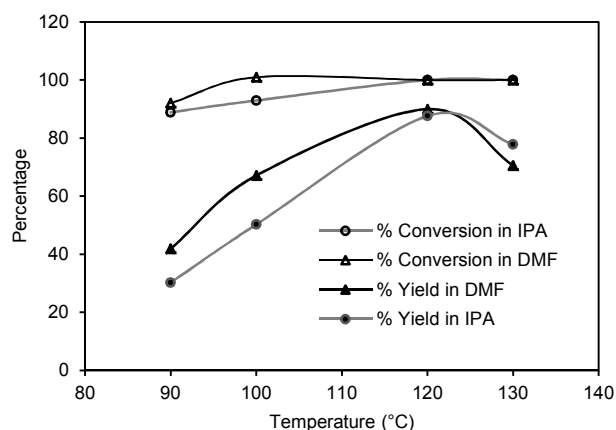


Fig. 4 Effect of reaction temperature in DMF and IPA on conversion and yield. Reaction conditions: fructose (2.77 mmol), IPA 8ml, PTSA 0.10 g/ml and 0.2 g/ml for IPA and DMSO, respectively, Reaction time: IPA system 90s; DMF system 120s.

Effect of fructose concentration

Fructose concentration has remarkable effect on percentage yield and selectivity in the PTSA catalyzed dehydration under MW assisted heating (Fig.5). As mentioned in Scheme 1 during fructose dehydration, side reactions can lead to decrease in yield and selectivity. Varying initial concentration (0.032-0.25 g/ml) of fructose was used to illustrate the effect of substrate concentration for selective fructose dehydration. There was negligible effect of fructose concentration on conversion, which was more than 90% for all concentrations tested. However, it was found that fructose concentration has remarkable effect on HMF yield and

selectivity. The yield and selectivity decreased at fructose concentrations above 0.125 g/ml and below 0.0625 g/ml. There was negligible effect of fructose concentration from 0.0625 to 0.125 g/ml which gave almost same HMF yield (91 % and 90%, respectively).

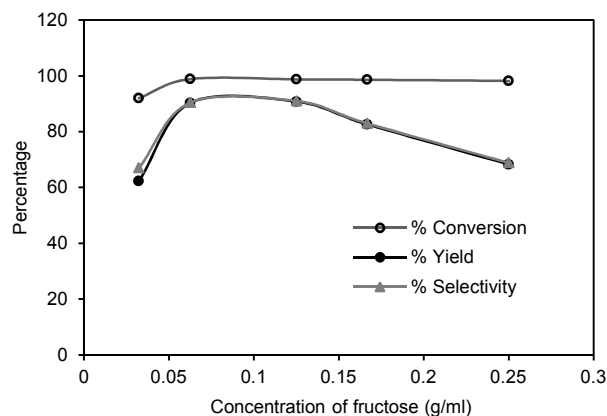


Fig. 5 Effect of fructose concentration on conversion yield and selectivity in IPA. Reaction conditions: Fructose (2.77mmol), PTSA (0.1 g/ml) temperature 120°C, time 90s.

Effect of water content

Water has high solubility for sugars and it is a green solvent too. Thus, use of water or aqueous reaction media provides an excellent platform but is unfriendly to dehydration reactions and aqueous acidic conditions may lead to formation of by-products [22]. On the other hand, use of strictly anhydrous solvents poses practical problems especially in large scale production systems especially when the solvents used have tendency to carry water traces. Thus, in order to evaluate the role of water content for microwave assisted fructose dehydration in presence of acid catalyst PTSA and IPA as reaction medium, fructose dehydration was examined with different concentration of water in IPA. The concentration of externally added water in reaction was varied in the range 4-10% v/v and fructose dehydration was examined under otherwise optimized reaction conditions. Fig 7 indicates the observed influence of water content in reaction medium on HMF yield and fructose conversion.

Both HMF yield and fructose conversion are seen to be strongly affected by water presence, with maximum being obtained with IPA containing moisture in equilibrium with atmospheric air (0.3%). Indeed presence of water is known to lead to formation of side products (Scheme 1) during fructose dehydration as reported in earlier reports [24].

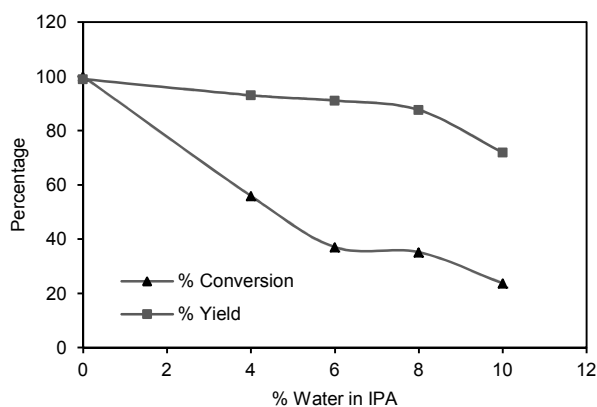


Fig. 6 Influence of initial water content on yield and conversion.

Comparison of microwave assisted versus conventionally heated systems

In order to bring out the significant role microwaves played in intensifying the reaction, synthesis of HMF was carried out using conventional heating under otherwise similar optimized process parameters. It was found that whereas MW assisted reaction resulted in 90% yield of HMF in 90s, conventionally heated reaction could give a maximum of 66% yield in 2h at the same temperature of 120°C (Fig. 7). Use of MW for large scale synthesis suffers from scalability issues and high investment in equipment, and therefore MW assisted reactions can possibly be scaled up only when reaction times are very short resulting in compact less expensive reactor systems. MW assisted heating may be recommended for HMF synthesis for increase in productivity with high yield and selectivity when reaction times are as short as those seen in the present study.

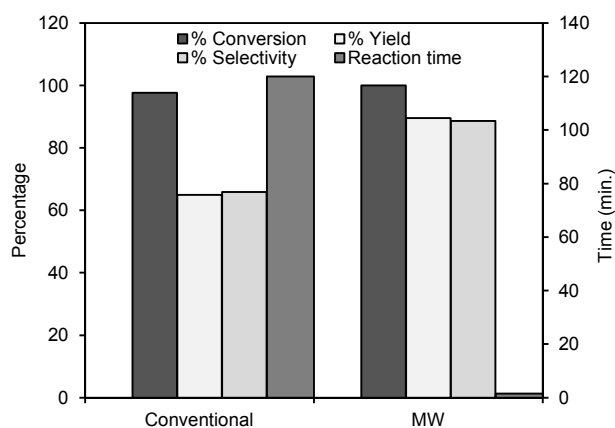


Fig. 7 Comparison of conventional and microwave assisted heating reactions in IPA

Experimental

Materials and Experimental methods

The substrate fructose (98% purity), chemical reagents (*p*-toluene sulphonic acid) and solvents used were of commercially pure grade obtained from local suppliers and were used as such.

Fructose (99%) and 5-hydroxymethyl furfural (99%) standards for HPLC analysis were purchased from Sigma-Aldrich (St. Louis, MO) and used without any purification. MW assisted reactions were performed in 20 mL microwave safe glass pressure vials on a Biotage Initiator 2.5 microwave reactor system operating at a frequency 2.45GHz, with maximum power of 600W.

HPLC analysis

HPLC analysis was performed on an Agilent 1200 series HPLC system equipped with an RI detector and using Bio-Rad aminex HPX-87H, 300mm×7.8mm ion exclusion column. The mobile phase used for analyses was 5mM H₂SO₄ in deionised water as eluent at 60 °C and 0.6 mL/min. Liquid samples were suitably diluted before analysis with deionised water and filtered through a 0.2µm PTFE filter. All values are obtained by tabulating mean of three experiments.

The concentrations of fructose and HMF were quantified from HPLC analysis through use of standards obtained from SIGMA. Fructose conversion (mole %), HMF yield (mole %), and selectivity (mole %) is determined as,

$$\text{Fructose conversion} = \left(1 - \frac{\text{Fructose Conc.}}{\text{Initial Fructose conc.}}\right) \times 100 \%$$

$$\text{HMF Yield} = \left(\frac{\text{HMF Conc.}}{\text{Initial fructose Conc.}}\right) \times 100 \%$$

$$\text{HMF Selectivity} = \left(\frac{\text{HMF yield}}{\text{Fructose conversion}}\right) \times 100 \%$$

General reaction and workup procedure

Fructose dehydration using microwave heating

In a 20 mL microwave tube Fructose (5.5mmole) was suspended in solvent (16mL). Desired amount of PTSA (as monohydrate) was added and then tube was purged with nitrogen before sealing. The reaction mixture was stirred for 2min at room temperature before subjecting to microwave heating. Biotage initiator 2.5 was pre-programmed to heat the vial contents to 120 °C within 5s, maintained for specified time and then cooled rapidly to 50 °C by purging nitrogen and then removed from the microwave cavity to cool further to room temperature. Samples of about 50 mg were withdrawn from the reaction mass and appropriately diluted for injection into HPLC.

For the sake of product isolation and characterization, the reaction mixture was subjected to vacuum distillation (IPA run samples) and the appropriate amount of water was added to the residue and repeatedly extracted with ethyl acetate. The combined organic layer was dried with anhydrous sodium sulfate and filtered. The pale yellow colour ethyl acetate layer was subjected to vacuum distillation to remove solvent giving faint yellow to brown colour oil of HMF. Alternatively, for isolation of PTSA, aqueous layer was polished on a hydrophobic (non-ionic styrene) adsorbent column (5cm X 1cm) for removal of water soluble side products, and then evaporated under vacuum resulting viscous brown mass.

Fructose dehydration using conventional heating

The fructose dehydration was carried out in 20 ml sealed glass tube by heating oil bath. Fructose (5.5 mmoles), solvent (16 mL) and desired amount of PTSA was suspended in tube and purged with nitrogen before sealing. The reaction mixture was stirred for 2min at room temperature and then, heated at 120 °C for 2h. After completion of reaction, samples were analyzed by HPLC. The reaction work up was carried in a similar manner as described for MW assisted synthesis.

HMF characterization

An NMR spectrum of the obtained product in DMSO-d6 was obtained on a Bruker Advance 300 spectrometer (¹H: 300.1 MHz, at 300°K). The spectrum was referenced against the NMR obtained internal standard and chemical shifts are reported in ppm. The functional group characterization was done on a Shimadzu IR Prestige-21 instrument equipped with ATR-FTIR. The mass of obtained HMF was confirmed by GC-MS on Agilent 7890A GC coupled with 7975C inert XL EI/CT MSD triple axis detector. High resolution mass was confirmed on Agilent Q-TOF LC-MS 6520 coupled with Agilent 1200 HPLC.

Characterization of the obtained HMF was as:

¹H NMR: δ_H (300 MHz; DMSO-d6) 4.51, (d, 2H, CH₂), 5.5, (s 1H, OH), 6.5 (s 2H, H-furan ring), 7.4 (s 2H, H-furan ring), 9.5 (s 1H, CHO).

FTIR ν_{max} /cm⁻¹ 1656.85 (CO), 3373.50 (OH), 2924.09 (CH), 2850.79 (CH).

GC-MS: m/z 125.9 (M⁺), 108.9, 96.0, 69.0, 41.1.

Q-TOF LCMS-MS: m/z 127.03792 (M+1), 109.02747, 81.03398, 53.03852.

Conclusions

The sustainability of a reaction system for synthesis of 5-HMF is to be seen from many angles. While higher yield is always desirable, the reaction times, temperatures, overall energy consumption, and ease of downstream processing all play important part in making a process truly friendly. The proposed system uses reaction times of 120s, temperatures of about 120°C, and uses low bp low latent heat solvents for achieving acceptable conversions and yields. This is the first report on microwave assisted monophasic dehydration of fructose that uses a combination of IPA as reaction medium and PTSA as catalyst in a way capable of giving high throughputs in terms of kg/L/h in absence of multiple liquid or solid phases. Reaction conditions were optimized for selection of solvent, catalyst concentrations, temperature and time of reaction to provide maximum yield. A cursory comparison was also made with conventionally heated reaction system and the specific role of microwave assisted heating was demonstrated.

The new developed process gave 90% HMF yield in 90s using IPA, a green solvent. The use of IPA was also seen to facilitate solvent separation and recovery by simple distillation with lower energy consumption on account of lower bp and lower heat of vapourization.

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- ^a DBT-ICT Centre for Energy Biosciences, Institute of Chemical Technology, Matunga, Mumbai 400 019, India
Fax: 91 22 3361 1020; Tel: 91 22 3361 2302;
E-mail: arvindmlali@gmail.com
- ^b Department of Chemical Engineering, Institute of Chemical Technology, Matunga, Mumbai 400 019, India
Fax: 91 22 3361 1020; Tel: 91 22 3361 2302;
E-mail: arvindmlali@gmail.com
- † Electronic Supplementary Information (ESI) available: Product purification procedure, HPLC analysis chromatograms of reaction mass and final products. Product characterization data FTIR, GC-MS, Q-TOF LC-MS MS, H¹NMR. See DOI: 10.1039/b000000x/.
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Graphical abstract

Microwave assisted organocatalytic synthesis of 5-hydroxymethyl furfural in a monophasic green solvent system

Hitesh Pawar^a and Arvind Lali^{*a,b}

^a DBT-ICT Centre for Energy Biosciences, Institute of Chemical Technology, Matunga, Mumbai 400 019, India
Fax: 91 22 3361 1020; Tel: 91 22 3361 2302;
E-mail: arvindmlali@gmail.com

