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HMF synthesis in aqueous and organic media under ultrasonication, microwave irradiation and conventional heating

Naser Esmaeili*, Mohammad Jalal Zohuriaan-Mehr*,†, Hossein Bouhendi*, and Gholam Bagheri-Marandi**

*Biomass Conversion Science and Technology (BCST) Division, Iran Polymer and Petrochemical Institute,
P. O. Box 14965-115, Tehran, Iran
**Department of Chemistry, Karaj Branch, Islamic Azad University, Karaj, Iran

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Abstract−5-Hydroxymethyl furfural (HMF) is known as a noteworthy platform in a biorefinery concept. HMF was prepared via fructose dehydration in aqueous and organic media, using three methods, i.e., conventional heating, ultrasonication and microwave irradiation. Water, methyl isobutyl ketone (MIBK), methyl ethyl ketone and ethyl acetate were used as media for HCl-catalyzed synthesis of HMF. FTIR and ^{1}H-NMR spectroscopies were used for analysis. The synthesis yield and selectivity were investigated to optimize variables such as fructose concentration, catalyst dosage, temperature, irradiation power, solvent, and the reaction atmosphere. It was found that the yield in the organic media was superior to that of the aqueous ones. In addition, nitrogen atmosphere favored higher yield than air, due to lack of HMF oxidation. As conclusion, the highest yields of the conventional, ultrasonicated and microwave-assisted reactions were 87, 53, and 38%, respectively. In the reactions ultrasonically promoted, the reaction time scale was highly reduced from hours to minutes. The yield was varied with treatment times, so that ultrasonication was recognized to be the best approach in terms of yield, while the microwave method was the fastest one. Selectivity varied from 60 to 90% depending the reaction media and promotion method.

Keywords: Hydroxymethyl Furfural, Synthesis, Ultrasonication, Microwave Irradiation, Fructose Dehydration

INTRODUCTION

The world has become increasingly reliant on oil and natural gas resources. Finding an all-inclusive replacement for the resources is a critical issue, due to the population growth and diminishing fossil resources. Biomass has been considered as an excellent candidate for this substitution. Carbohydrates are one of the most important members among all of the biomass types [1].

Carbohydrates can be converted into different treasury chemicals [1-3] by various methods such as dehydration. Among all, furan compounds have a considerable potential for production of the value-added chemicals. 5-Hydroxymethyl furfural (HMF) as a significant platform in the biorefinery concept [4,5], is produced from dehydration of hexoses such as fructose. The announced awakening of the 'sleeping giant' HMF [6] has brought furan compounds and polymers back to the forefront of both fundamental and industrial research.

The first sugar dehydration in aqueous acidic media was reported by Mulder [7], who declared the formation of formic acid and levulinic acid from sucrose. Dull [8] and Kiermayer [9] synthesized HMF for the first time. After that, incredible attention was attained among scientists for the furan derivatives production [10], especially HMF [11-15]. The potential of HMF for converting into many noteworthy molecules used in polymer industry or fuels is very attractive for scientists [16]. For instance, dimethyl furan (DMF), a highly recommended choice for biofuel with 31.5 MJ/L energy content (having higher energy density by 40% than that of bioethanol) [17,18] and furan dicarboxylic acid [14,15] as a replacement for terephthalic acid in production of poly(ethylene terephthalate) for textiles and packaging are two most important HMF derivatives. Furthermore, 2,5-diformylfuran as an important dialdehyde precursor for various pharmaceutical products [2], caprolactam in the production of nylon 6 and caprolactone used for the polycaprolactone production needed in suture surgery tools are some other strategic compounds which are manufactured from HMF. Finally, adipic acid as a monomer in the polyester industry, hexanediol in the role of plastic raw material, levulinic acid as plasticizer and antifreeze ingredient, and many other worthwhile materials which their existence are highly crucial for chemical and polymer industries can be produced from HMF.

HMF had been synthesized from fructose [20] or glucose [21,22] by a dehydration reaction in aqueous media using mineral acids catalyst such as HCl [3,4]. The solubility of the raw materials in the water is noble, but HMF is not stable in the aqueous media, due to involvement in side reactions, e.g., rehydration of HMF to formic acid and levulinic acid [24], oligomerization [25], etc. Meanwhile, usage of other solvents such as DMSO, MEK, MIBK, ionic liquids [26-32] and crown ethers could be beneficial for subsiding the undesirable reaction and improvement of the reaction yield and selectivity. Although higher selectivity was observed by non-aqueous media, the solubility of the carbohydrates into them is lower than that of the aqueous ones [33]. There are diverse parameters which can

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[†] To whom correspondence should be addressed.
E-mail: mjzohuriaan@yahoo.com, bcst.ippi@gmail.com

influence the yield, such as initial raw material concentration, catalyst quantity, temperature, pressure, time and many other factors.

In the present work, HMF was synthesized from fructose in aqueous and organic media by HCl as a catalyst. HMF was produced by conventional heating method and microwave irradiation based on the literature data. To the best of our knowledge, no report has been found about HMF production promoted by ultrasonication, so this promoting approach was also followed in this work. The yield and selectivity of the mentioned three methods have also been compared to each other. The HMF production was detected by thin layer chromatography, separated from the reaction mixture by liquid-liquid extraction, purified by recrystallization, and characterized by FTIR and ^{1}H-NMR.

EXPERIMENTAL

1. Materials

D-fructose (99%, CAS 57-48-7), methyl isobutyl ketone (MIBK, 99%), methyl ethyl ketone (MEK, 99%), ethyl acetate (EtOAc, 99.5%), HCl 37%, hexane, and acetone, all analytical grades, were purchased from Merck. HMF (99%, CAS 67-47-0), as a reference material, was obtained from Aldrich. All materials were used as received without further purification.

2. Synthesis of HMF

Three different methods including conventional heating (T), microwave irradiation (M) and ultrasonic irradiation (U) were used for the synthesis of HMF. The scheme of this work is shown in Table 1. The effects of the concentration of fructose, catalyst, reaction temperature, time and atmosphere on the yield and selectivity were investigated. Aqueous hydrochloric acid (HCl 0.1 M) was used as the catalyst. All syntheses were performed in triplicate and the average yields were reported.

2-1. Conventional Heating Method (Series T)

In this series, the given solvent (50.0 g), fructose and catalyst were loaded into a 250-mL two-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser. In biphasic synthesis, 30.0 g MIBK was used as an extracting solvent. Four parameters including fructose concentration, catalyst, temperature and time were studied to optimize HMF preparation.

2-2. Microwave Irradiation (Series M)

Different amounts of fructose and 10.0 g solvent were charged to a closed glass dish irradiated by an American microwave machine (PMT08E28, produced by PHILCO Co.). In this part, the fructose concentration, catalyst, time and power of the machine were changed to optimize the synthesis of HMF.

2-3. Ultrasonication (Series U)

HMF was ultrasonically synthesized from fructose, HCl and 30.0 g solvent imported into a 50 mL-beaker, placed in an ice bath. The ultrasound frequency of 20 KHz and power 70 W was applied by a German BANDELIN HD 3200 machine. The fructose concentration, catalyst and time were variable to achieve the optimum yield.

3. Extraction, Purification and Characterization

At first, extraction was done by MIBK due to the better partition coefficient of the HMF between MIBK and water compared with that of the other organic solvents. Thus, the mixture of reaction was extracted by MIBK, the solvent was dried to reach the unpurified solid, washing with water and acetone to remove remained fructose and HCl. For obtaining the pure HMF, the solid was then dissolved in MIBK at 50 °C to recrystallize at room temperature for gaining the yellowish precipitation of pure HMF.

A KBr pellet of the HMF powder was used for the primary characterization of the product by an FTIR spectrophotometer (BRUKER, IFS48, Germany). For more investigation, the solution of HMF in $CDCl_3$ was analyzed by ^{1}H-NMR spectroscopy (BRUKER, Ultrashield 300MHz, Germany) using a TMS standard. Melting point of product was measured by a system of B-545 BRUKER (Germany).

RESULTS AND DISCUSSION

1. Spectral Analysis

FTIR spectrum showed the major bands of HMF [34]. Broad alcoholic O-H stretching vibration at 3,400 cm^{-1}, aldehyde C-H at 2,850 and 2,930 cm^{-1}, aldehyde C=O stretching at 1,675 cm^{-1}, aromatic C=C stretching at 1,520 cm^{-1}, furan ring ether asymmetric stretching C-O-C at 1,190 cm^{-1} and alcoholic C-O stretching at 1,025 cm^{-1} were observed. The spectrum is provided in supplementary materials as Fig. S1.

^{1}H-NMR spectrum revealed the HMF structure [35]: alcoholic H (s) 2.7 ppm, CH_2 (s) 4.7 ppm, aromatic CH (d) 6.5 and 7.1 ppm, aldehyde CHO (s) 9.6 ppm. The results are provided in supplementary materials as Figs. S2 and S3.

Table 1. Reaction variables and conditions for HMF synthesis in the present work

Promoting factor of reaction	Reaction media^a	Reaction time range	Fructose conc. range (%)	Catalyst conc. range (%)	Reaction atmosphere	Reaction temp. range (°C)	Power (W)
Thermal (T)	H_2O-MIBK	0.5-3 h	5-50	0.5-10	N_2 or air	40-80	-
	MIBK	0.5-3 h	0.5-10	0.5-10	N_2 or air	50-105	-
	MEK	0.5-3 h	5 or 10	2.5 or 5	N_2 or air	70	-
	EtOAc	0.5-3 h	5 or 10	2.5 or 5	N_2 or air	70	-
Microwave (M)	H_2O	30-90 s	5-50	0.5-10	air	-	800 or 1000
	MIBK	30-90 s	0.5-10	0.5-10	air	-	800 or 1000
Ultrasound (U)	H_2O	3-18 min	5-50	0.5-10	air	-	70
	MIBK	3-18 min	0.5-10	0.5-10	air	-	70

^{a}MIBK=methyl isobutyl ketone, MEK=methyl ethyl ketone, EtOAc=ethyl acetate

2. Effect of Reaction Time on Yield

The yield and selectivity were calculated using the following Eqs. [36]:

$$\text{Yield (\%)} = \frac{\text{Practical weight (g)}}{\text{Theoretical weight (g)}} \times 100\% \qquad (1)$$

$$\text{Selectivity (\%)} = \frac{\text{Weight of purified HMF (g)}}{\text{Practical weight (g)}} \times 100\% \qquad (2)$$

As shown in Fig. 1, for all three different synthesis methods, the yield was growing in the early stages of the reaction, but this increasing was not continued up to the end, and after a definite time the yield started to decrease. This may be generally attributed to three main reasons: (a) hydrolysis of HMF product to formic acid and levulinic acid, (b) self-oligomerization of HMF, and (c) polycondensation of HMF with fructose [37-39].

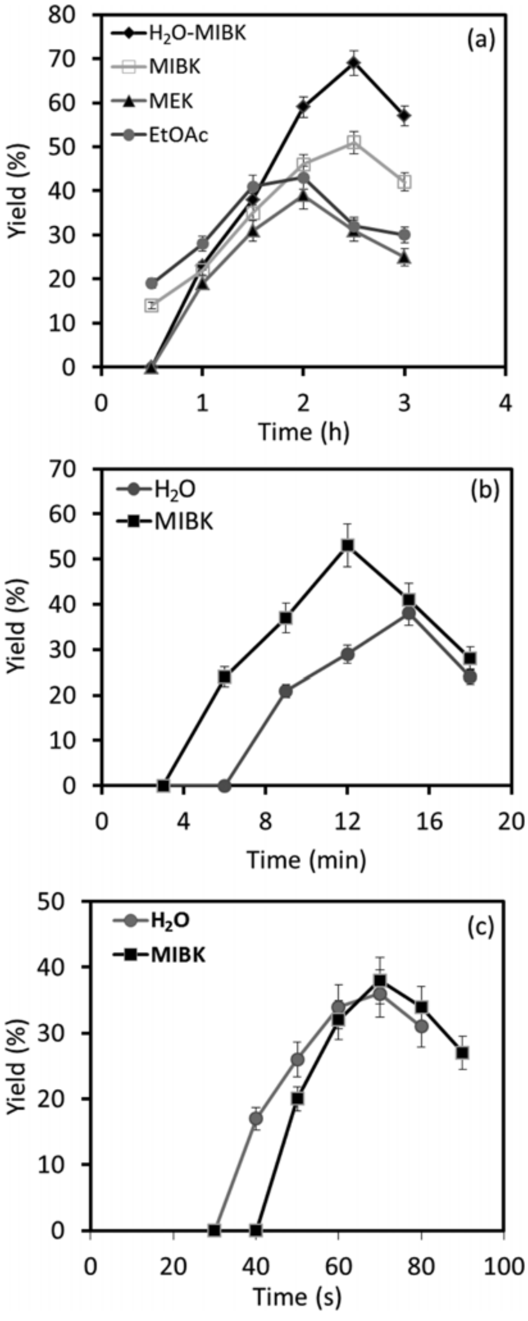

Fig. 1. Effect of reaction time on HMF yield. Fructose 5%, (a) conventional heating, catalyst 2.5% (b) ultrasound irradiation, catalyst 5%, (c) microwave irradiation, catalyst 5%, power 800 W.

As exhibited in Fig. 1(a), for the conventionally promoted reactions by heating, the highest yield was obtained in H_2O-MIBK media. In this biphasic mixture, HMF can be separated in both phases by a partition coefficient, i.e., the ratio of HMF in the organic phase to the aqueous phase. Therefore, by continuous extraction of HMF from the reaction media, higher yield is attained, due to the low instant concentration of HMF in water, and reaction progress toward HMF production [40]. Besides, HMF should be quickly left aqueous medium toward MIBK phase to avoid unfavorable reactions such as hydrolytic degradation [41], because there is no catalyst in the organic phase for involving HMF in unfavorable side reactions. After all, it could be explained why the yield was decreased after 2.5 h. HMF saturation in MIBK was a major consequence of inefficient extraction from water phase. Therefore, the product involved in side reactions led to loss of yield.

As represented in Fig. 1(a), among the used organic solvents of MEK, EtOAc, and MIBK, the latter favored achieving higher yield (the negligible yield of reaction in water is not recorded in the Fig. 1). It can be explained by polarity index of the solvents. Polarity index of MIBK, EtOAc, MEK and water was 4.2, 4.4, 4.7 and 10.2, respectively [42]. As polarity of unwanted byproducts, like levulinic and formic acid, was more than that of HMF itself, lower polarity index of solvent favored higher yield of reaction. Consequently, in the single phase syntheses, MIBK with the least tendency to polar byproducts was recognized to be the best medium for HMF synthesis [43,44].

In the reactions ultrasonically promoted (Fig. 1(b)), the reaction time scale was highly reduced from hours to minutes; however, a similar trend of the yield variation versus time was obvious, due to the aforesaid reasons. In addition, by comparing the media of H_2O and MIBK in Fig. 1(b), the effect of solvent is clearly shown. The higher yield in MIBK can be attributed to inferior side reactions in absence of water [38].

In the microwave-assisted reactions, the time scale was reduced to tens of seconds. Trend of the HMF product yield versus the reaction duration (Fig. 1(c)) was found to be approximately similar to those of thermal and ultrasonic ones (Figs. 1(a) and 1(b)). Similarly, the yield in MIBK medium was higher than that of in water; however, a remarkable phenomenon was observed in aqueous medium. In the fast synthesis of HMF in water (time consumed just 90 s), the mixture gradually changed from orange color to dark brown dense liquid having a peanut odor [45]. So, the yield calculation was impossible (data not given in Fig. 1(c)). This occurrence might be related to an unfavorable caramelization reaction that took place during sugar heating in presence of acid by microwave irradiation. The study of chemical reactions and components participating in the caramelization process is very complicated. Caramelization of fructose is a combination of many reactions such as aldose-ketose isomerization, dehydration, anomeric-cyclic equilibrium [34,46]. Each carbohydrate has its own degradation temperature occurring at lower temperature in acidic media rather than neutral or basic media. Fructose is degraded at 110 °C in neutral conditions; however, the degradation happens in acidic media at lower temperature [34,41]. Furthermore, in the first moments of the reaction, fructose to HMF conversion is noticeable. However, as the concentration of HMF is increased, its hydrolysis causes dramatic decreasing of yield.

The yield decreasing can also be attributed to possible self-oligomerization and condensation reactions [30,37,47]. HMF has some active functional groups for incorporation into the oligomerization reactions. For example, in acidic media, the alcohol group can be transformed into carbocation and then initiates the oligomerization or they can make an ether bridge by H_2O elimination. On the other hand, owing to the presence of alcoholic groups in both of HMF and fructose, they can be condensed to form ether bridge leading to co-oligomeric species like humins [44]. This reaction takes place easily in presence of acidic catalyst, e.g. HCl. Particularly in aqueous media, after a long time reaction, the yield calculation was impossible due to formation of a pitch-like dark residue. Presence of trace amounts of the residues was detected in ^{1}H-NMR spectrum (see Supporting information, Fig. S3).

3. Effect of Reaction Media

Four different solvents were used for HMF synthesis by fructose dehydration. As exhibited in Fig. 2, HMF yield showed considerable dependency on the type of reaction media. Among three different methods of the reaction promotion, conventional thermal method (T), ultrasonication (U), and microwave irradiation (M), the most and the least yields were generally achieved by means of the U and M methods, respectively.

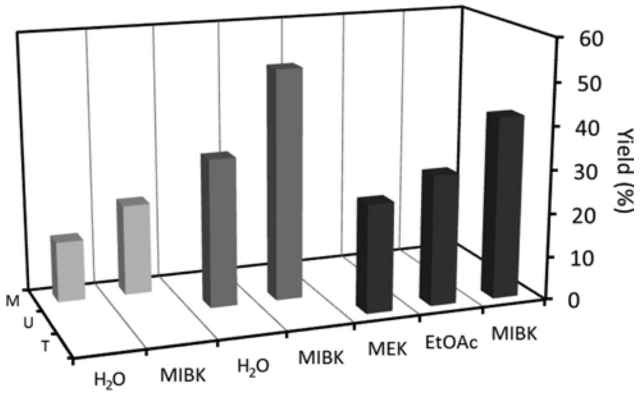

Fig. 2. Effect of solvent types on HMF yield. Fructose 5%. "T" indicates conventional heating (catalyst 2.5%, 2 h). "U" indicates ultrasonication (catalyst 5%, 15 min). "M" indicates microwave irradiation (catalyst 5%, 80 s, 800 W).

In M series, a dark brown viscous mixture with peanut odor was formed, which could be attributed to very fast HMF thermodegradation and fructose caramelization. Since air has not been

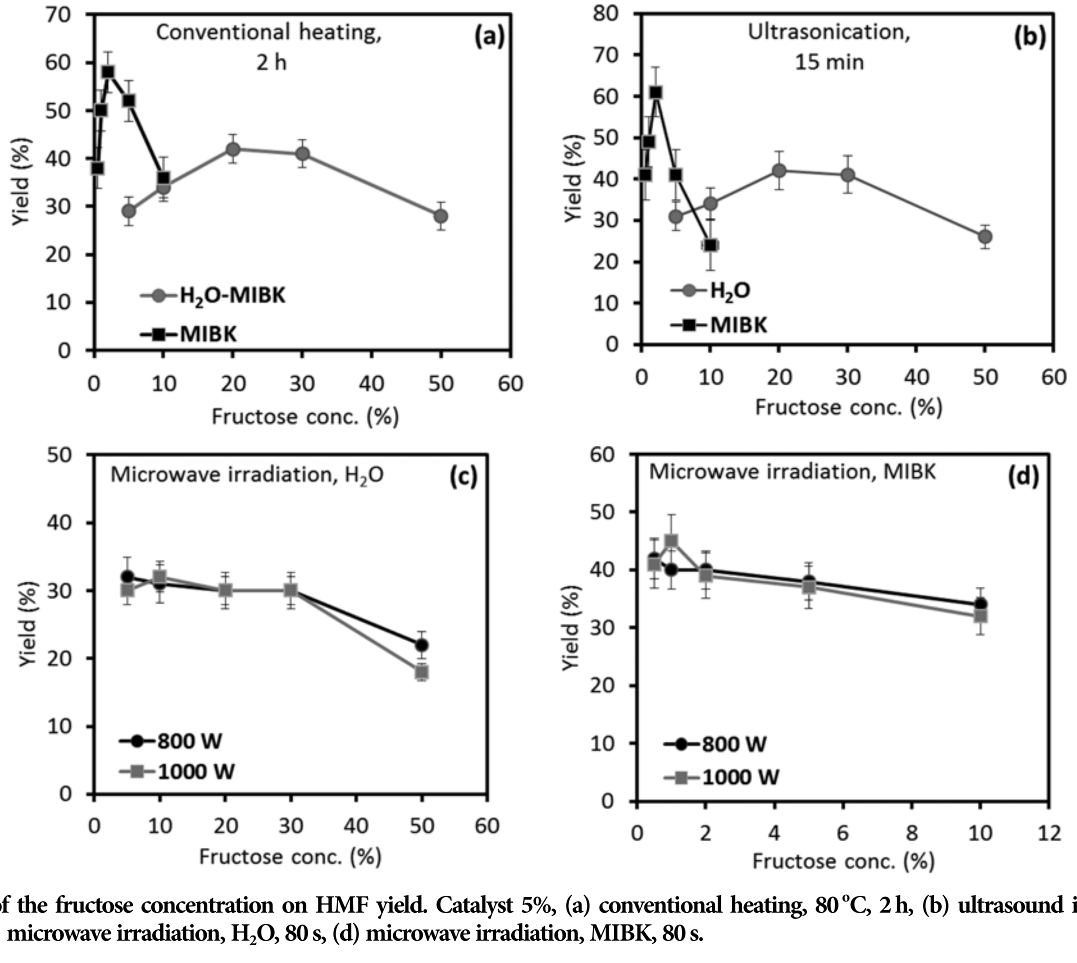

Fig. 3. Effect of the fructose concentration on HMF yield. Catalyst 5%, (a) conventional heating, 80 °C, 2 h, (b) ultrasound irradiation, 15 min, (c) microwave irradiation, H_2O, 80 s, (d) microwave irradiation, MIBK, 80 s.

excluded from the reaction atmosphere, formation of singlet oxygen and its ability to induce various reactions including HMF-oxygen Diels-Alder adducts [48,49] could also be another reason to reduce the yield. These unwanted reactions prevented the yield from rising.

In U series, the reaction duration (several minutes) was much lower than the T series reaction duration (hours). This restricted time was too short to give a chance for progressing destructive reactions such as HMF thermo-degradation and rehydration. Although the M series reaction duration (several seconds) is lower than that of U series, ultra-fast temperature increasing caused fructose caramelization leading to the significant loss of yield.

In all three series of synthesis, MIBK provided higher yield in comparison with the other media (MEK, EtOAc, and H_2O) illustrated in Fig. 2, as explained in section 3.2; these variations were attributed to difference in polarity index of the solvents [42].

4. Effect of Fructose Concentration on Yield

Fig. 3 shows the effect of fructose concentration on the reaction yield. It is obvious from Figs. 3(a) and 3(b) that conventional and ultrasonic methods gave similar yields and trends. However, the latter method resulted in maximum yield in only 15 minutes instead of the 2 h consumed in the conventional method.

High concentration of reactants in reaction medium is generally considered as one of the most desirable features of a feasible manufacturing process. Therefore, high concentration of fructose is essential for the cost-effective manufacture of HMF. The initial loaded fructose had significant effect on HMF yield [44] (Fig. 3). High water solubility of HMF favors synthesis feasibility. Nonetheless, growth of the fructose concentration prepares appropriate medium for unfavorable side reactions such as HMF-fructose polycondensation or fructose caramelization [34]. In contrast to aqueous medium, the used organic solvents with low capability to dissolve fructose diminish production capacity. As shown in Figs. 3(a) and 3(b), yield was dramatically reduced by increasing fructose concentration more than 2%.

According to Fig. 3(a), a maximum was observed in the fructose concentration-yield curve. The increasing fructose value favored dehydration reaction of fructose leading to HMF production. When the fructose content was more than that of the reaction ability to yield HMF, it would be converted into unfavorable side products mentioned before [46]. The effect of fructose concentration on yield of ultrasound synthesis was similar to that of the conventional synthesis (Fig. 3). The similar trend of the curves of Fig. 3(b) originated from similar reasons explained for Fig. 1.

Figs. 3(c) and 3(d) represent the yield of reaction versus fructose concentration in water and MIBK media under microwave irradiation. Again, MIBK played superior role to be a more appropriate medium than water. However, trends were clearly different from those of the two other mentioned methods (Figs. 3(a) and 3(b)). Due to very fast increasing temperature in the microwave promoted reaction, fructose and HMF thermo-degradation and oligomerization was obvious from formation of a viscous mixture having dark brown color and peanut odor. Since air had not been excluded from the reaction atmosphere, the presence of singlet oxygen and its ability to initiate the unfavorable free radical reactions and/or formation of HMF-O_2 Diels-Alder adducts could also be another reason to diminish the yield [48-50]. All of these unwanted reactions prevented the yield from rising. Additionally, for both media in higher fructose concentration, a yield drop was observed. This reduction was much greater in the aqueous medium comparing to MIBK (i.e., yield dropping ~50% in H_2O vs. ~15% in MIBK; Figs. 3(c) and 3(d)).

5. Effect of the Catalyst Quantity on Yield

HCl catalyst quantity had considerable effect on dehydration reaction of fructose to yield HMF (Table 2), so that in the absence of the catalyst, fructose was not converted at all. Small amounts of the catalyst initiated the fructose conversion to HMF up to a certain level, due to well-known dehydration mechanism [51]. However, by catalyst concentration of more than 2.5%, the yield fell due to the foresaid reasons, including fructose and HMF oligomerization and condensation. Although the presence of HCl is essential for the HMF formation, its overload can boost both main and side reactions. So, high dosages of the catalyst caused lower HMF yields [46].

In microwave synthesis, high amount of the catalyst (10%) decreased the yield more significantly in comparison with the other methods (Table 2). This deficiency, as mentioned before, was attributed to caramelization induced by intense microwave irradia-

Table 2. Effect of catalyst concentration on HMF yield. Fructose 5% (For data of each column, standard deviation value is shown in parenthesis)

Catalyst[a] (%)	Yield (%)					
	Conventional heating[b]		Ultrasonication[c]		Microwave irradiation[d]	
	in H_2O-MIBK	in MIBK	in H_2O	in MIBK	in H_2O	in MIBK
0.5	37 (1.3)	38 (2.0)	34 (2.5)	35 (1.6)	30 (2.3)	35 (1.7)
1	49 (1.2)	40 (1.8)	46 (1.4)	44 (2.8)	38 (0.3)	42 (2.5)
2.5	60 (1.8)	39 (1.5)	48 (2.9)	54 (0.9)	34 (0.5)	47 (0.1)
5.0	52 (2.5)	34 (1.8)	41 (0.7)	49 (1.9)	32 (2.6)	40 (1.3)
10	38 (1.9)	28 (1.8)	31 (1.1)	45 (0.6)	18 (2.1)	29 (1.4)

[a] HCl 0.1 M

[b] 80 °C, 2.5 h

[c] 15 min, 70 W

[d] 80 s, 800 W

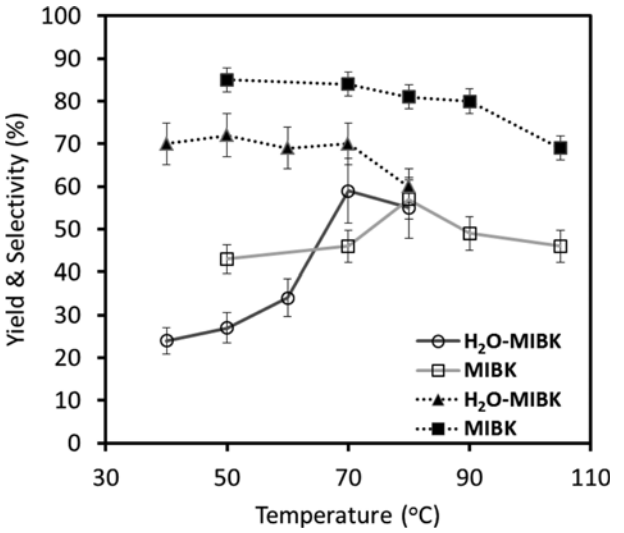

Fig. 4. Effect of temperature on yield and selectivity of HMF synthesized by conventional heating. Fructose 5%, catalyst 2.5%, 2 h. Solid and dotted lines represent yield and selectivity, respectively.

tion during a short time [43].

6. Effect of Temperature on Yield and Selectivity of Thermal Method

The effect of temperature on yield and selectivity of HMF produced from conventional thermal synthesis is presented in Fig. 4. No remarkable changes were observed in selectivity versus temperature either in MIBK or in H_2O-MIBK. Similar observations have also been reported by other researchers [43]. However, MIBK favored higher selectivity rather than H_2O-MIBK (~80% vs. ~70%), due to the aforesaid reasons given based on polarity index differences and possible side reactions happening in presence of water (Section 3.2).

In contrast to the selectivity, the yield of reaction performed in H_2O-MIBK was remarkably increased from ~22 to 60% when temperature rose from 40 to 70 °C. The positive effect of higher temperature on HMF yield increasing has been reported as well [52]. In MIBK medium, the increasing yield was moderate. Smooth decreasing of yield in both media at temperatures more than 70-80 °C could mostly be related to possible thermo-degradation of HMF to form unwanted by-products of levulinic acid and formic acid [52].

7. Effect of Reaction Atmosphere

One of the most probable side reactions that occurred during the HMF formation was the oxidation of the product by the air oxygen [23]. Therefore, oxygen withdrawn by purging N_2 in the atmosphere reduced this unwelcome reaction. This effect was investigated in the conventional thermal reaction (Fig. 5). As is obvious from Fig. 5, both the HMF yield and selectivity were improved by the substitution of air with N_2. Because the HMF oxidation took place in water easily, elimination of oxygen obviously improved yield of the reactions. The yield improvement was more significant in aqueous medium than that of in the organic media.

8. Effect of Microwave Irradiation Power

It was proved before that microwave irradiation produced efficient internal heating by direct coupling microwave energy with solvents and catalysts that can greatly increase rate of reactions [38]. It was expected that the effect of microwave power was similar to the temperature effect on the HMF formation under conventional heating. However, a preliminary study showed that the microwave irradiation power had no significant effects on the yield of HMF synthesized either in water or in MIBK (Table 3). Zhou et al. [39] reported a similar observation. Meanwhile, all the yields (max. 32%) were not considerable due to reasons mentioned in section 3.4.

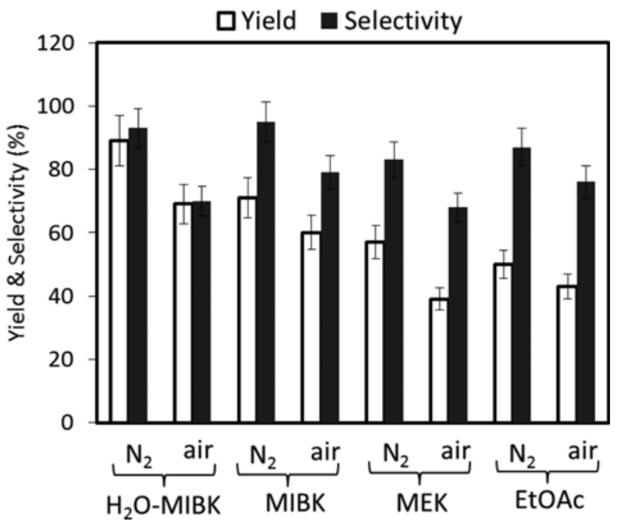

Fig. 5. Effect of the reaction atmosphere and solvents on yield of HMF synthesized by conventional heating. Fructose 10%, catalyst 5%, 2.5 h, 70 °C.

Table 3. Effect of microwave irradiation power on yield of HMF synthesized in water and MIBK media (fructose 5%, catalyst 5%, 80 s). (For data of each column, standard deviation value is shown in parenthesis)

Power (W)	Yield (%)	
	in H_2O	in MIBK
200	22 (2.0)	25 (0.7)
400	29 (1.4)	27 (1.1)
600	28 (2.3)	28 (1.5)
800	30 (0.4)	34 (2.1)
1000	30 (0.5)	32 (1.1)

CONCLUSION

HMF synthesis was comparatively studied in different media under three different promoting conditions: ultrasonication, microwave irradiation and conventional heating. Thee ultrasonicated reaction led to yield of 53% and selectivity of 72% during just 12 min, while the conventional heating method needed 2 h to give a yield of 57% (and selectivity of 81%) in MIBK. Microwave-assisted reactions consumed only tens of seconds to produce HMF, although this highly accelerated reaction led to low yield (38%) and medium selectivity (63%). In all three methods of the reaction promotion, at the early periods of the reaction, yield was increased and then diminished. MIBK and H_2O-MIBK media were recognized to have the highest yield (87%) and selectivity (92%).

SUPPORTING INFORMATION

Additional information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

HMF synthesis in aqueous and organic media under ultrasonication, microwave irradiation and conventional heating

Naser Esmaeili*, **Mohammad Jalal Zohuriaan-Mehr***,†, **Hossein Bouhendi***, **and Gholam Bagheri-Marandi****

*Biomass Conversion Science and Technology (BCST) Division, Iran Polymer and Petrochemical Institute,
P. O. Box 14965-115, Tehran, Iran
**Department of Chemistry, Karaj Branch, Islamic Azad University, Karaj, Iran

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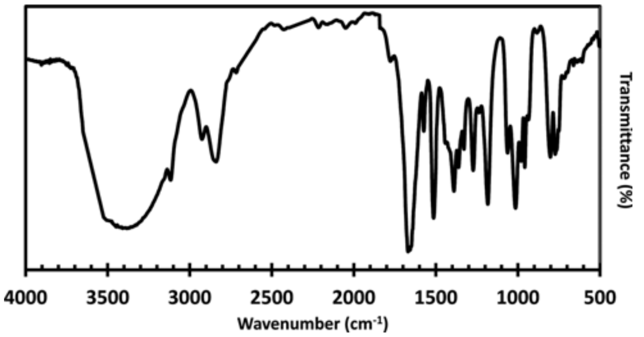

Fig. S1. **FTIR spectrum of HMF synthesized under conventional heating. H_2O-MIBK, fructose 10%, catalyst 5%, 2.5 h, 70 °C, air atmosphere.**

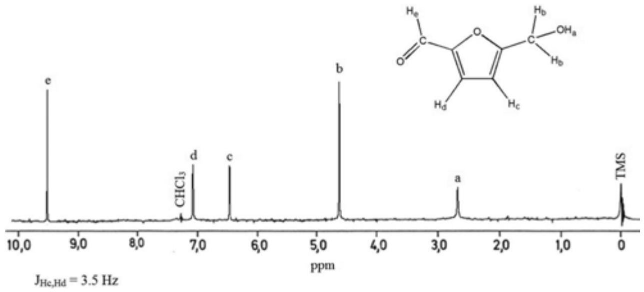

Fig. S2. **^{1}H-NMR spectrum of highly purified HMF sample synthesized under conventional heating. H_2O-MIBK, fructose 10%, catalyst 5%, 2.5 h, 70 °C, air atmosphere.**

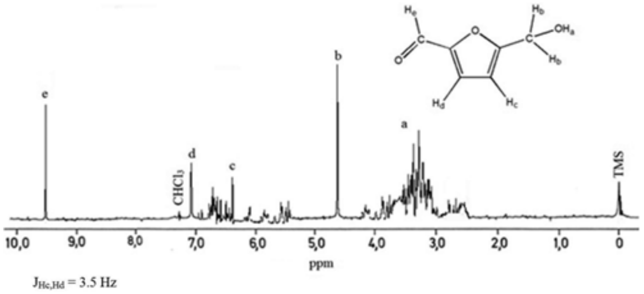

Fig. S3. **^{1}H-NMR spectrum of HMF synthesized by microwave irradiation promotion. MIBK, Fructose 5%, catalyst 5%, 70 s, 800 W, air atmosphere (Note: Peaks of unwanted by-products formed under the microwave irradiation are appeared. The sample was not highly purified).**