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Title: Amberlyst A-70: a surprisingly active catalyst for the MW-assisted dehydration of fructose and inulin to HMF in water

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Keywords: 5-hydroxymethyl-2-furaldehyde; Amberlyst-70; fructose; inulin; microwaves; dehydration in water.

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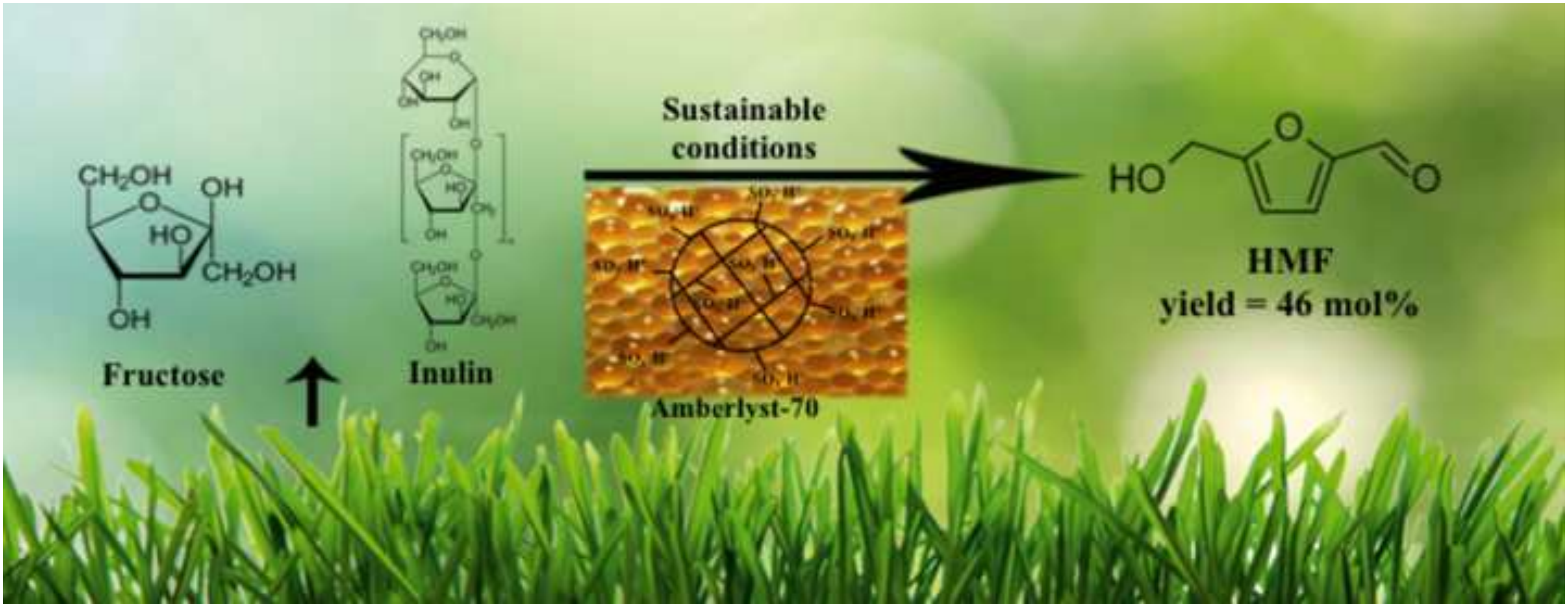
Abstract: 5-Hydroxymethyl-2-furaldehyde (HMF) is a biomass-derived intermediate for the sustainable production of monomers and biofuels. However, most of its syntheses are performed under not environmentally and/or economically green conditions. In this work, the dehydration of fructose/inulin to HMF was optimized, employing aqueous medium, high substrate concentrations (10 and 20 wt%), low loading of commercial acid resin (Amberlyst-70) and microwave heating. The influence of substrate/catalyst ratio, time and temperature on the products yields was investigated. Amberlyst-70 resulted a very active and recyclable system: HMF yields up to 46 mol% were ascertained, the best result up to now reached under these reaction conditions.

Graphical Abstract



Highlights

- The dehydration of fructose and inulin to HMF with resin Amberlyst-70 was studied.
- The reactions were carried out under sustainable conditions in water with MW heating.
- HMF yields up to 46 mol% were achieved with a substrate/catalyst wt/wt ratio of 80.
- High HMF yields were obtained from concentrated fructose/inulin solutions, 10-20 wt%.
- Amberlyst-70 resulted very active, stable and recyclable.

Amberlyst A-70: a surprisingly active catalyst for the MW-assisted dehydration of fructose and inulin to HMF in water

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Abstract

5-Hydroxymethyl-2-furaldehyde (HMF) is a biomass-derived intermediate for the sustainable production of monomers and biofuels. However, most of its syntheses are performed under not environmentally and/or economically green conditions. In this work, the dehydration of fructose/inulin to HMF was optimized, employing aqueous medium, high substrate concentrations (10 and 20 wt%), low loading of commercial acid resin (Amberlyst-70) and microwave heating. The influence of substrate/catalyst ratio, time and temperature on the products yields was investigated. Amberlyst-70 resulted a very active and recyclable system: HMF yields up to 46 mol% were ascertained, the best result up to now reached under these reaction conditions.

Keywords: 5-hydroxymethyl-2-furaldehyde; Amberlyst-70; fructose; inulin; microwaves; dehydration in water.

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1. Introduction

The massive consumption of unsustainable fossil resources has boosted research on renewable resources. Today, biomasses are promising and still underexploited resources used to produce many chemicals and biofuels [1-9]. In particular, 5-hydroxymethyl-2-furaldehyde (HMF) is an attractive platform chemical, due to its potentiality as starting material for the synthesis of many fine-chemicals, biofuels, solvents and monomers [10-11]. The most efficient synthetic route employs fructose as starting substrate, which, under acidic conditions, undergoes dehydration to HMF. However, by-products formation is also promoted, resulting in the formation of levulinic (LA) and formic (FA) acids, originated from HMF rehydration, and humins obtained from HMF polymerization [11-12]. These reactions result particularly favoured in water, thus compelling many researchers to carry out them in other solvents, such as organic media [13-14], ionic liquids [15-16] and biphasic systems [17-18], or removing in continuous water under reduced pressure [19]. Alternatively, some authors report the HMF synthesis in water but in the presence of an activated carbon that adsorbs selectively the product, preventing its side reactions [20].

A wide range of catalysts has been employed for this reaction, from homogeneous (HCl, H_2SO_4, H_3PO_4) to heterogeneous ones, such as zeolites [21], metal phosphates [22], metal salts [23] and acidic resins [24]. The most investigated commercial resins are the styrene-based sulfonic acids type, generally employed in organic media (DMSO, THF, ionic liquids) or in aqueous/organic two-phase systems [13,16,18,24-26]. In this work the resin Amberlyst-70 was employed in the dehydration of fructose and inulin to HMF because is more thermally stable (up to 190°C) than the other commercial styrene-divinylbenzene resins and has higher acid site density (2.55 meq/g) than perfluorinated sulfonic resins, such as Nafion [27,28].

Despite the problems that the HMF synthesis shows in aqueous medium, in this study, in a sustainable perspective, the optimization of the HMF synthesis was performed in water. Microwave heating was adopted, due to its ability to reduce both reaction time and energy consumption and to reach generally higher yield of the target product [29].

To the best of our knowledge, this is the first work that reports HMF synthesis starting from fructose and inulin catalysed by the acid resin Amberlyst-70 carried out in aqueous system under microwave irradiation.

2. Experimental

2.1 Materials

Commercial materials were used as received by suppliers. Details about the purity grade of reagents and properties of Amberlyst-70 are reported in the supplementary information.

2.2 Dehydration reactions

Catalytic dehydration of fructose and inulin to HMF in water was carried out as previously reported [22]. Conversion, yields and selectivities were expressed in mol %. The "unidentified products" include humins, other soluble and insoluble compounds and gases. Their yield (mol%) was determined by the following equation: [(converted fructose mol - HMF mol - FA mol)/starting fructose mol] x 100, being formic acid in equimolar ratio with levulinic acid.

2.3 Analytical instrumentation

The HPLC Perkin Elmer Flexer Isocratic Platform equipped with a column Benson 2000-0 BP-OA (300mm x 7.8 mm) was employed to analyse the liquid samples. A 0.005 M H_2SO_4 aqueous solution was used as mobile phase with a flow-rate of 0.6 ml/min and the column was kept at 60°C.

FT-IR-attenuated total reflection (ATR) was used to characterize the solid by-products and the catalyst. Spectra were recorded in the range of 500-4000 cm^{-1} employing a Perkin Elmer Spectrum Two.

3. Results and discussion

3.1 *HMF synthesis from fructose and inulin*

Commercial resin Amberlyst-70 was employed as catalyst for HMF synthesis from 10 wt% fructose aqueous solution. The adopted substrate concentration is higher than the majority of those reported in the literature for the catalytic conversion of fructose solution, which generally are under 6 wt% [11], but higher loadings are necessary for industrial application, making HMF recovery simpler and cheaper.

A preliminary fructose dehydration experiment was carried out in the absence of catalyst at 150 °C for 15 min but negligible fructose conversion (4.2 mol%) and HMF yield (2.5 mol%) were reached. On the other hand, the results obtained in the catalytic runs performed under the same conditions at different substrate/catalyst weight ratio (R) showed high fructose conversions and appreciable HMF yields, confirming the crucial role of the catalyst. The HPLC chromatograms acquired working with R=20 and R=1.25 are reported, as an example, in the supplementary information (Figures S1 and S2).

Figure 1, near here

With the progressive increase of R from 1.25 to 20, the fructose conversion decreases from 84.1 to 36.1 mol% and also the HMF yield decreases from 26.0 to 7.8 mol%. HMF selectivity shows its maximum when a substrate/catalyst ratio of 5 was employed. It is well known that the fructose dehydration proceeds according to a number of both series and parallel reactions, which markedly affect the products selectivity, depending on their activation. At R values lower than 5, the strong acid condition, due to the high amount of catalyst, activates not only the fructose dehydration to HMF but also the rehydration of HMF to acids and the significant formation of humins, as confirmed by the high formic, levulinic acids and unidentified products yields. On the other hand, for R higher than 5, the amount of catalyst is insufficient to activate the dehydration reaction under the adopted experimental conditions and fructose itself undergoes side reactions, leading to condensation products, as shown by the increase of the unidentified products yield when 5 < R < 20, already reported with niobium phosphate (NbPO) [22]. However, the obtained results evidence a different behaviour of Amberlyst-70 and NbPO towards the rehydration acids. In fact, under identical reaction conditions (R=5, 15 minutes at 150 °C), Amberlyst-70 leads to significant yields of FA and LA, while in the presence of NbPO the acids are formed only in trace. This can be ascribed to the presence on resin surface of strong Brønsted acid sites, responsible for rehydration reaction, which become present on NbPO surface only at temperature higher than 150 °C, generated in-situ by the interaction between Lewis sites and water [22].

The profile of the reaction carried out at 150 °C with R of 5 is reported in Figure 2.

Figure 2, near here

The HMF yield versus run-time data increases until 20 minutes, reaching the maximum value of 25.6 mol%, then, for longer reaction time it remains almost constant, whereas the rehydration acids yields increase. This trend confirms the mechanism of the fructose dehydration. In fact, HMF is the direct product of the reaction but it is unstable under the experimental conditions necessary to its formation and it rehydrates to formic and levulinic acids and undergoes side reactions to humins, whose yields increase during the reaction time.

The influence of higher temperatures (160 and 180 °C) on the fructose dehydration at 20 minutes employing a substrate/catalyst ratio of 5 was also investigated. The achieved results are reported in Table 1, together with those obtained at 150°C.

Table 1, near here

The increase of temperature causes only a slight increase of HMF yield because HMF rehydration reaction and the side reactions become more important. On the basis of these results, under higher temperatures, in order to improve HMF selectivity, the substrate/catalyst ratio was increased up to 80, and the reaction profile is reported in Figure 3.

Figure 3, near here

The obtained results show that the increase of the substrate/catalyst ratio markedly improves HMF selectivity and yield. In fact, comparing the results reported in Figure 3 (180 °C, R=80) with run 3 (180 °C, R=5) after 20 minutes, higher HMF selectivity and yield and lower by-products yields were ascertained working with R=80 (HMF yield= 45.6 mol%, HMF selectivity= 56.9 mol%) than with R=5 (run 3, Table 1). Moreover, the HMF selectivity reported in Figure 3 is about constant up to 20 minutes, concomitantly with the highest HMF yield (45.6 mol%), reached after 20 minutes. Figure 3 shows that extending the reaction time at 25 minutes, the by-products formation becomes important and HMF yield decrease to 32.9 mol%. These results outline that the extension of reaction time beyond the optimal one is detrimental for HMF synthesis because the by-products formation is particularly promoted.

At 180 °C, HMF synthesis (20 minutes with R= 80) was also performed starting from inulin at the same 10 wt% loading and from both substrates at higher loading (20 wt%), together with the blank experiment for both substrates at 10 wt%. The results are summarized in Table 2.

Table 2, near here

The comparison between the blank (run 4) and the catalytic experiment (run 5) highlights that under the adopted conditions the catalyst causes an increase of fructose conversion (80.1 mol%) and HMF yield (45.6 mol%), underlining the fundamental role of the catalyst, although a certain blank catalytic reactivity [30]. Therefore, the best yield to HMF is obtained at high temperature (180 °C) and short reaction time (20 minutes) employing a very high substrate/catalyst ratio (R=80). This result confirms that Brønsted acid sites play a key role in fructose dehydration and a very high substrate/catalyst ratio is sufficient at high temperature. In addition, run 5 was replicated employing a double fructose loading, 20 wt%, in run 6. The obtained results are promising because the achieved HMF yield is comparable to that reached with the 10 wt% substrate loading solution. The data show that at 20 wt% fructose loading a higher substrate conversion is reached with a slight lower HMF selectivity, due to the formation of rehydration acids and unidentified products. The obtained results assume even greater value considering that until now only a few works have investigated the fructose dehydration in water with acidic resins, reaching unsatisfactory results and starting from diluted substrate solutions. A HMF yield around 18 mol% starting from a 6 wt% fructose aqueous solution was reported, carrying out the reaction at 135 °C with Amberlyst-15 as catalyst, due to the high formation of rehydration acids [17]. Using a fructose solution at 2 wt% and the resin Dowex 50wx8-100 with a R= 1 a HMF yield of 34 mol% and a levulinic acid yield of 24 mol% were ascertained [25]. A fructose conversion of 73 mol% and HMF selectivity of 60 mol% were reported working in water with Amberlyst-15 [26]. This yield (43 mol%) is still lower than the value now reached but it requires higher catalyst amount (R= 15) and 3 h of reaction time.

The high HMF yields obtained in the present work are the highest reported in the literature for aqueous system [11], adopting high fructose concentrations (10 and 20 wt%), and above all, a very low catalyst amount, R=80 [3].

When the fructan inulin (97 wt% of fructose and 3 wt% of glucose units) [23] was employed (run 8, Table 2) under the reaction conditions optimized for fructose (180 °C, 20 minutes, R= 80), at the end of the reaction the polysaccharide was completely depolymerized. This is shown by the chromatogram (Figure S3 of the supplementary information), where only the peaks of fructose and glucose, both deriving from inulin hydrolysis, rehydration acids and HMF are present. Comparable fructose units conversion and HMF yield were ascertained starting from both fructose and inulin (compare run 5 with run 8 in Table 2). Moreover, when starting from the second substrate, an about 40 mol% glucose conversion was verified, contributing to unidentified products. Also for inulin the catalytic performances significantly overcome those of the blank run (run 7, Table 2). Run 8 was replicated with a double inulin loading, 20 wt%, in run 9. The same trend already found for fructose was ascertained, thus high yields can be reached employing concentrated-inulin solutions, opening the way to the direct exploitation of inulin-rich biomasses, such as chicory root and *Helianthus tuberosus*.

3.2 Catalyst stability and recyclability

During fructose and inulin dehydrations significant formation of soluble and insoluble humins is ascertained. These last originate from polymerization reactions, which involve HMF, fructose and other components of the reaction mixture [31-32]. In this work, where a Brønsted acid resin was employed, humins deposition on the catalyst surface can determine its deactivation. FT-IR analyses of fresh and spent catalysts (Figure S4 of the supplementary information) showed the presence of humins on the catalyst surface and study the effect of experimental parameters on their formation. The organic material adsorbed on the surface of the spent catalyst can influence its performances during recycling tests. The catalyst obtained from the fructose dehydration at 180 °C for 20 min employing R= 80 (run 5, Table 2) was recovered by filtration and reused in two subsequent recycle experiments under the same conditions of the first cycle. The obtained results are reported in Figure 4.

Figure 4, near here

During these three cycles (1, 2 and 3), only a slight decrease of the catalytic performances is observed, with a negligible increase of unidentified products yield. At the end of the third cycle, the recovered catalyst was washed with acetone and reused again in other three subsequent recycle tests. In fact, this resin is swellable by water/acetone and all the acid sites can be easily accessible [24]. After the washing treatment, the catalyst performances are totally recovered and the trend of the new consecutive three cycles (4, 5 and 6) is similar to that shown during the first three cycles (1, 2 and 3). Finally, after the sixth cycle and the subsequent washing treatment, the recovered catalyst was employed in the last recycle (cycle 7), which confirmed that the simple washing treatment is an efficient reactivation method. This is also confirmed by the comparison of FT-IR spectra between spent and reactivated catalyst after the sixth cycle (Figure S5 of the supplementary information): the spectrum of the reactivated system is very similar to that of the fresh sample, providing again that washing with acetone is a promising reactivation treatment. This is in agreement with the results reported in the literature that have demonstrated the good stability of Amberlyst-70 at 180 °C for 6h [26]. The feasibility of the washing reactivation is particularly important for the acidic resin because, unlike inorganic materials, in this case a thermal reactivation (generally carried out at 500°C) is not feasible, due to its low stability.

4. Conclusions

The dehydration of fructose aqueous solutions to HMF was carried out with the commercial Brønsted acid resin Amberlyst-70, investigating the influence on the reaction profile of substrate/catalyst weight ratio (R), time and temperature. The highest HMF yield (45.6 mol%) is ascertained on 10 wt% fructose solution working at 180°C, with short times (20 min) and very high substrate/catalyst ratio (80). Comparable results can be obtained starting from inulin under the same reaction conditions, thus opening the way to the direct exploitation of raw biomasses rich of fructans. When the substrate concentration was doubled, the HMF yield remained significant, being 42.5 mol% starting from fructose and 41.6 mol% from inulin. Recyclability tests proved that an easy reactivation by washing treatment is possible, showing a negligible loss of activity after seven successive catalytic cycles.

Acknowledgements

The authors thank Rhom & Haas Company for kindly providing Amberlyst-70.

Appendix A. Supplementary data

Supplementary data to this article can be found online at...

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Table 1 Effect of temperature on the fructose dehydration under microwave heating for 20 minutes with a R=5 wt/wt.

Run	**T (°C)**	**Conv. (%mol)**	**HMF (% mol)**		**FA yield (%mol)**	**LA yield (%mol)**	**Unidentified products yield (% mol)**
			Yield	**Select**			
1	150	56.4	25.6	45.4	5.4	5.7	25.4
2	160	67.8	29.4	43.4	10.0	10.9	27.5
3	180	98.7	31.0	31.4	23.7	23.9	43.8

Table 2 Comparison between fructose and inulin as substrate in dehydration reactions (180°C; 20 minutes; R= 80 wt/wt) and respective blank runs* (180°C; 20 minutes).

Run	**Substr. and loading**	**Conv. (%mol)**		**HMF (%mol)**		**FA yield (%mol)**	**LA yield (%mol)**	**Unidentified products yield (% mol)**
		Fruct. units	**Glu. units**	**Yield**	**Select**			
4*	fructose 10 wt%	51.1	**-**	23.6	46.2	trace	trace	27.5
5	fructose 10 wt%	80.1	-	45.6	56.9	2.9	2.4	31.6
6	fructose 20 wt%	94.2	-	42.5	45.1	12.3	6.1	39.4
7*	inulin 10 wt%	54.9	26.7	21.5	39.8	1.7	0.9	30.9
8	inulin 10 wt%	82.4	40.2	43.1	53.1	5.0	2.3	33.0
9	inulin 20 wt%	95.1	45.0	41.6	44.4	14.7	5.8	37.4

[a] Fructose and glucose conversions are calculated considering that inulin is composed of 97 wt% of fructose units and 3 wt% of glucose units.

[b] The yields are calculated on the basis of the total starting C6 units.

[c] HMF selectivity is calculated on the basis of the total converted C6 units.

Caption for figures

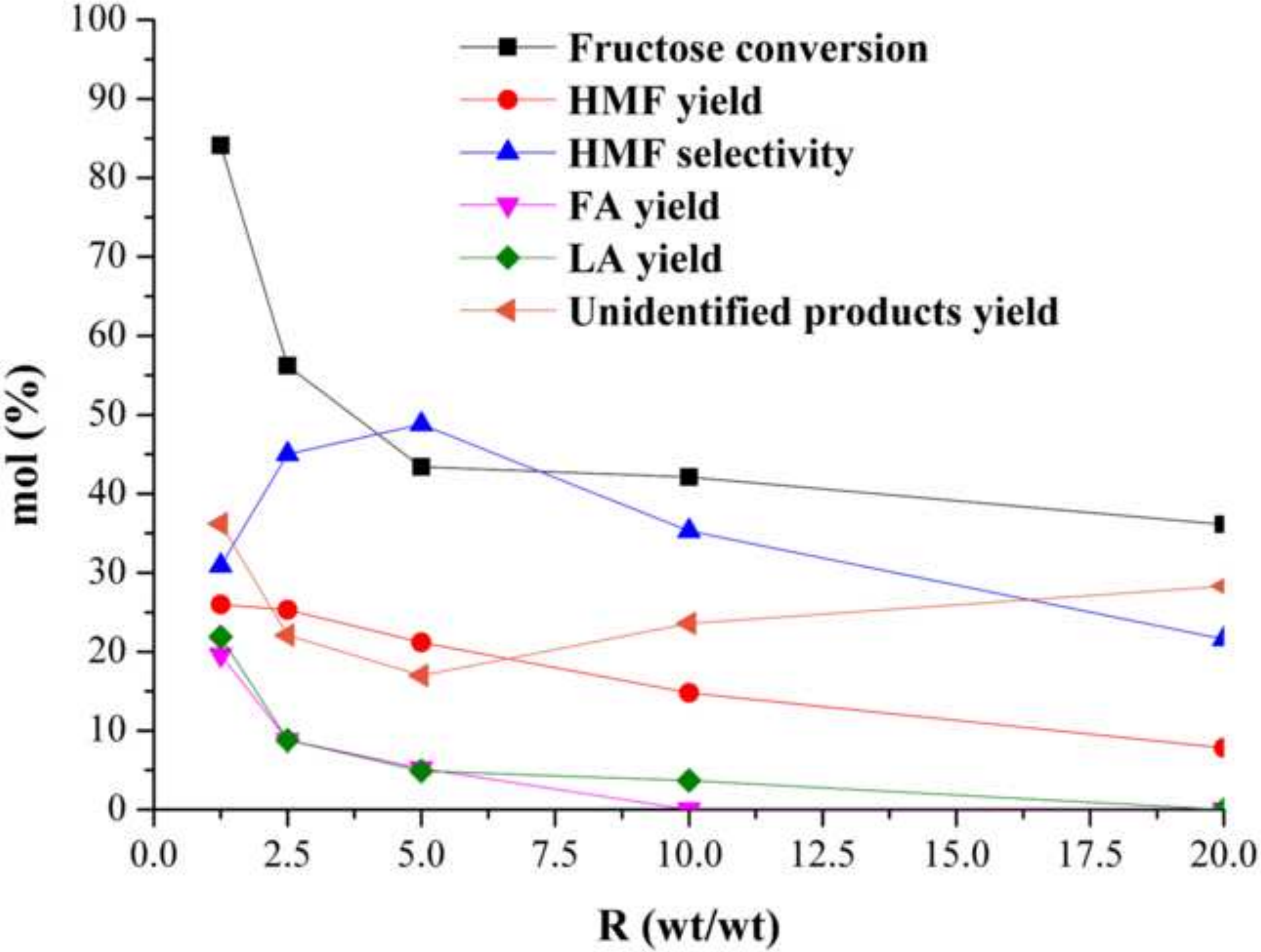
Figure 1: Effect of substrate/catalyst ratio wt/wt (R) on the fructose dehydration under microwave heating at 150°C for 15 minutes.

Figure 2: Profile of fructose dehydration at 150 °C with R=5 wt/wt.

Figure 3: Profile of fructose dehydration at 180 °C with R=80 wt/wt.

Figure 4: Dehydration reaction of fructose in the presence of Amberlyst-70 at 180 °C for 20 minutes with R= 80 wt/wt and six subsequent recycles of the solid catalysts.

Figure 1


Fructose conversion
HMF yield
HMF selectivity
FA yield
LA yield
Unidentified products yield
mol (%)
0
10
20
30
40
50
60
70
80
90
100
R (wt/wt)
0.0
2.5
5.0
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12.5
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Figure 2

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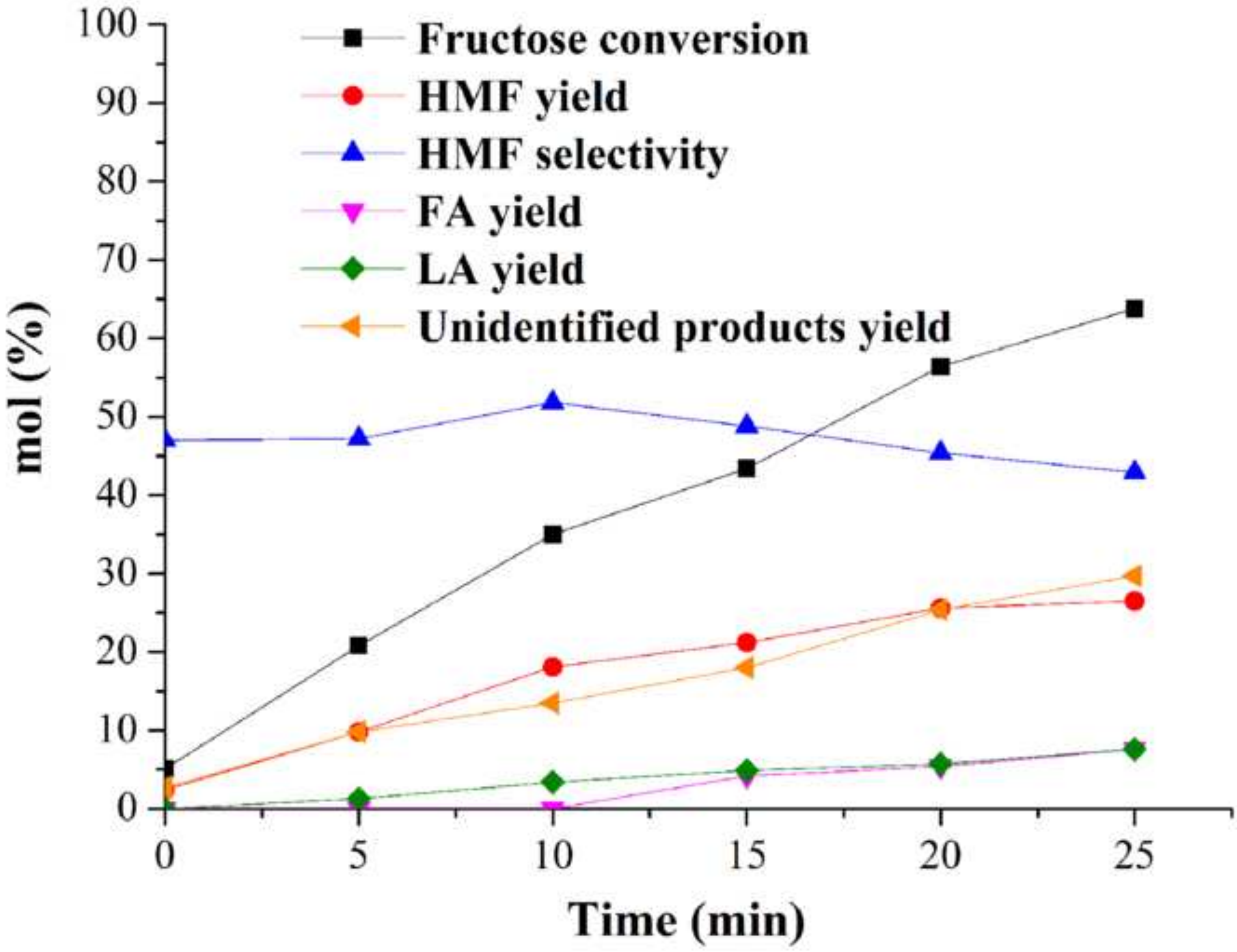

Figure 3

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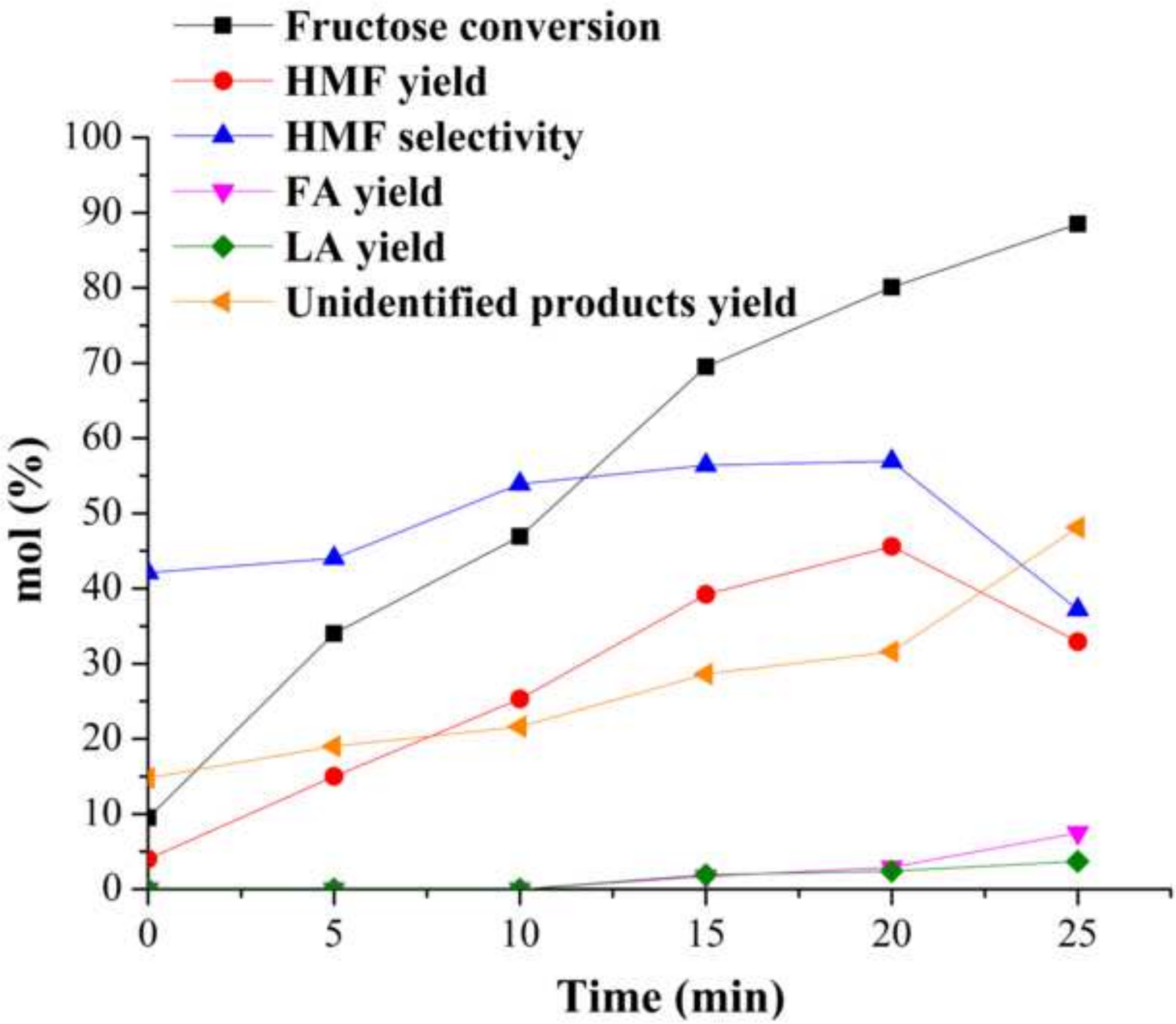

Figure 4

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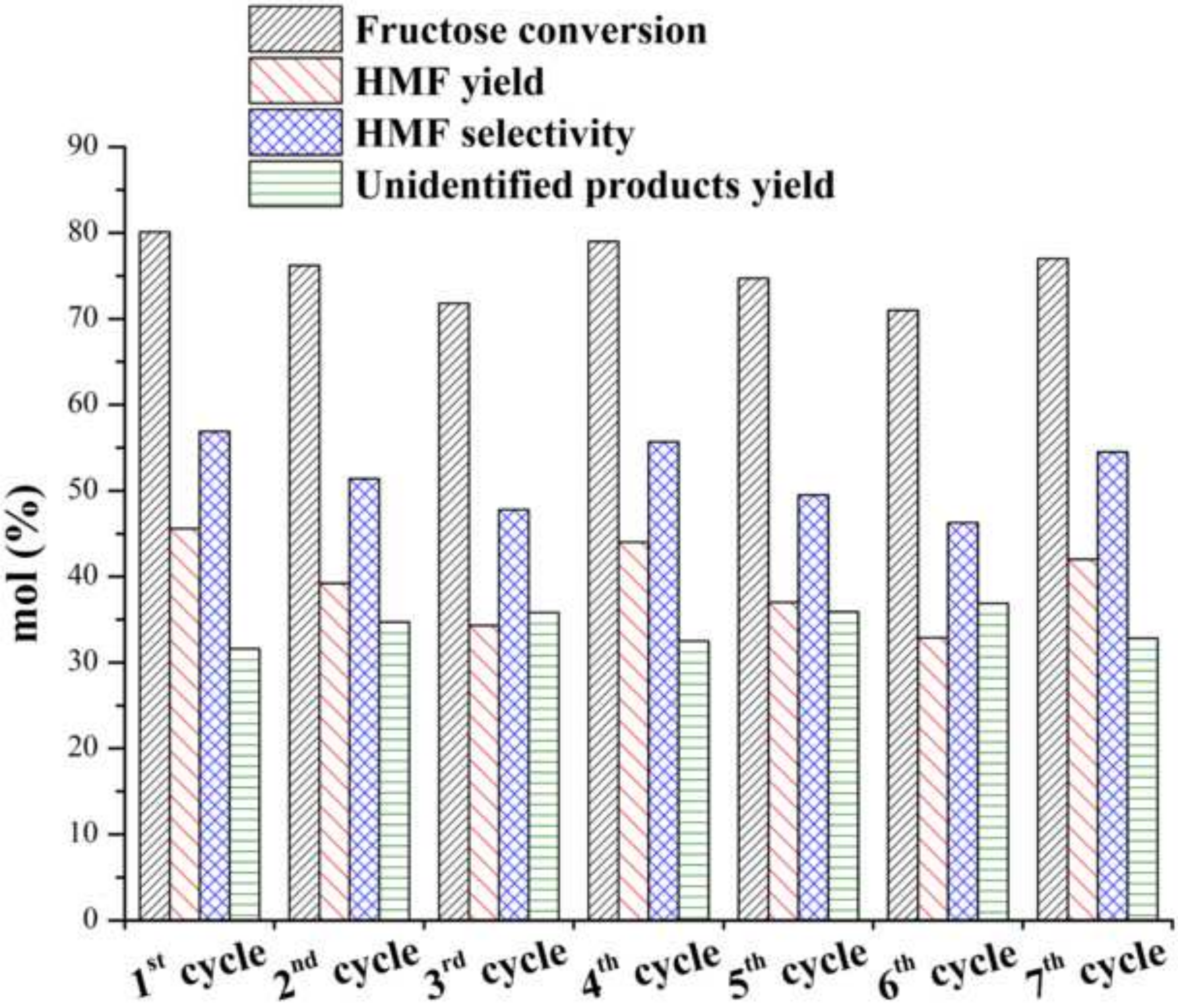

Amberlyst A-70: a surprisingly active catalyst for the MW-assisted dehydration of fructose and inulin to HMF in water

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Supplementary Information

1. Materials

5-hydroxymethyl-2-furaldeyde (98%), formic acid (99.8%) and levulinic acid (98%) were purchased from Sigma-Aldrich and used as received. Fructose was alimentary grade and used without any further purification. Inulin from *Dahlia Tubers* ($[\alpha]_D^{20}$= -37.0 and $M_n \approx 5{,}000$) was purchased from Fluka and used as received. Inulin is composed of 97 wt% of fructose units and 3 wt% of glucose units. Amberlyst-70 (concentration of acid sites: 2.55 meq/g; surface area: 36 m^2/g; particle size: 0.5 mm;

average pore diameter: 22 nm; divinylbenzene content: 8%; T maximum: 190°C) was provided from Rohm and Haas and used as received.

2. Chromatograms of fructose dehydration

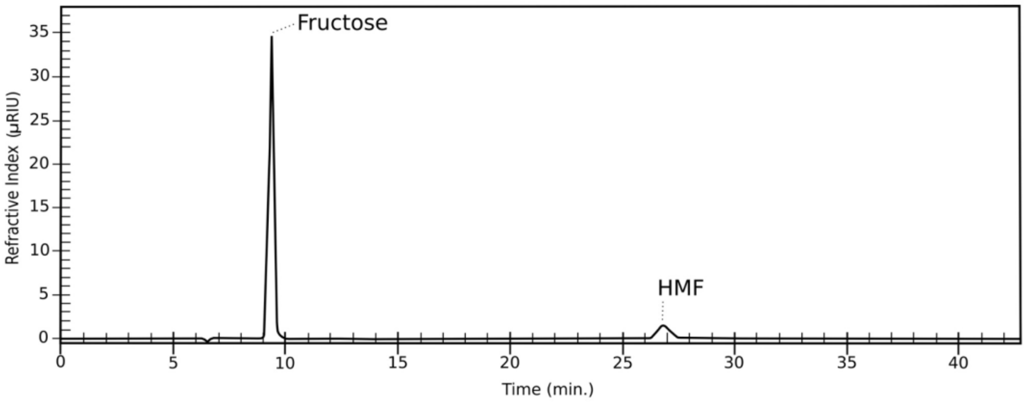

Figure S1: Chromatogram of fructose dehydration with a substrate/catalyst 20 wt/wt ratio

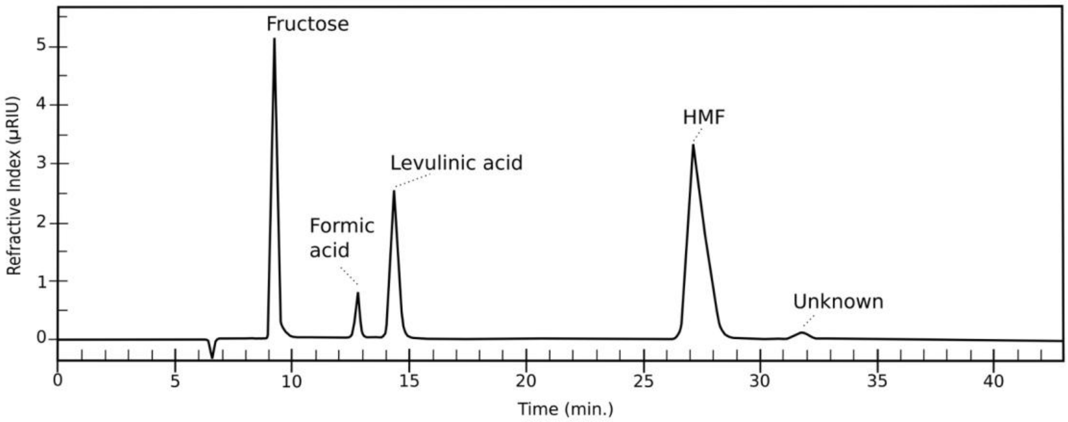

Figure S2: Chromatogram of fructose dehydration with a substrate/catalyst 1.25 wt/wt ratio

3. Chromatogram of inulin dehydration

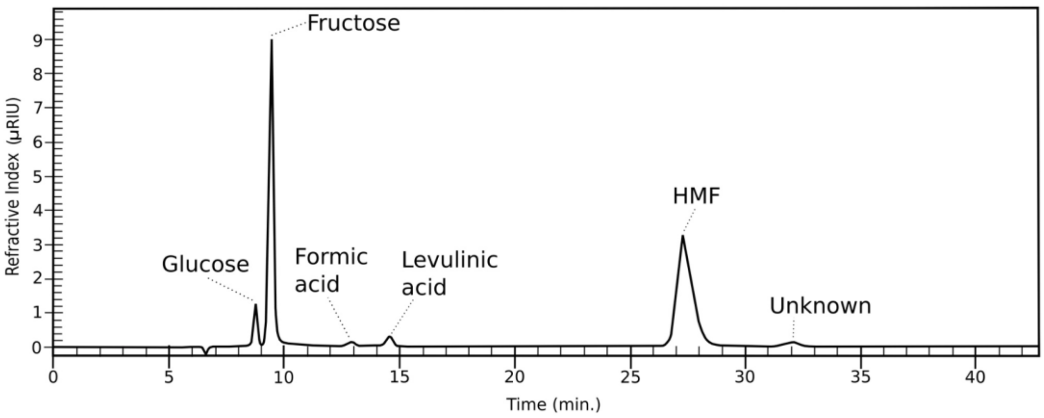

Figure S3: Chromatogram of inulin dehydration with a substrate/catalyst 80 wt/wt ratio.

4. FT-IR spectra of fresh and spent catalysts

In order to verify the presence of humins on the catalyst surface and to investigate the effect of experimental parameters on their formation, FT-IR analyses of fresh and spent catalysts were carried out. The comparison between spent and fresh catalyst spectra is reported in Figure S4, where the influence of temperature and substrate/catalyst ratio were investigated.

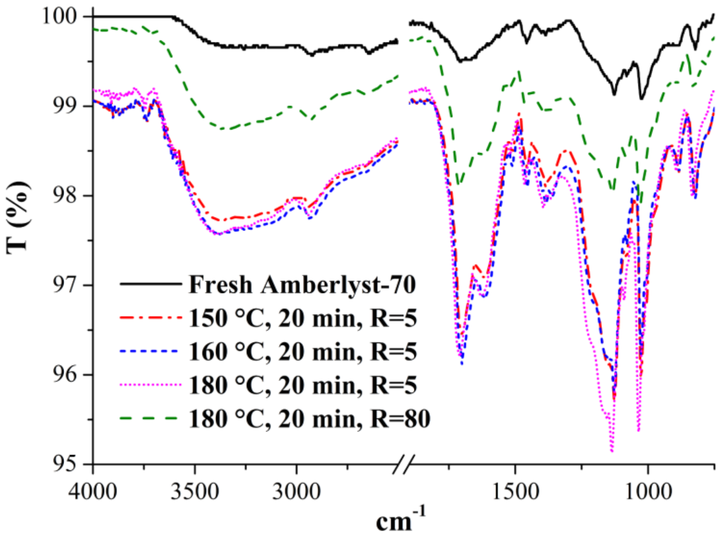

Figure S4: FT-IR spectra of fresh and spent catalysts employed at 150, 160 and 180°C with R = 5 wt/wt and at 180 °C with R = 80 wt/wt, all of them after 20 minutes of reaction.

In all the reported spectra, the always-observed absorptions of humins on the catalyst surface are in agreement with the spectra reported in the literature for the humins obtained during the fructose dehydration [1-5]. In fact, a broad band at around 3300 cm^{-1} due to O-H stretching of hydroxyl or carboxyl groups is observed together with a weak band at 2920 cm^{-1} due to stretching of aliphatic C-H, broad peaks characteristic of C=O stretching of carbonyl, quinone, ester, or carboxyl at 1705 cm^{-1} and at 1664 cm^{-1} and bands at 1279 cm^{-1}, 1189 cm^{-1} and 1022 cm^{-1}, due to C-O stretching of aliphatic alcohols and ethers. Moreover, the presence of furan and/or aromatic rings in the humins structure is shown by bands at 1515 cm^{-1}, characteristic of C=C bond stretching of furan ring, at 1395 cm^{-1}, due to C-O-C stretching of furanyl ether, and bands between 875-750 cm^{-1} ascribed to aromatic/furanic C-H bending out of plane.

Figure S1 shows the FT-IR spectra of spent catalysts employed under different temperature (150, 160 and 180°C) at R = 5 wt/wt and at 180 °C for R = 80 wt/wt, after 20 minutes of reaction. The comparison for R = 5 wt/wt highlights that at increasing temperature the intensities of humins peaks correspondingly increase. In particular, at 180 °C the peaks at 1279 cm^{-1}, 1189 cm^{-1} and 1022 cm^{-1}, due to ethers group, are very intense, being the condensation reactions promoted at higher temperature. When R = 80 wt/wt was employed, the humins characteristic bands have much low intensity, proving that under these experimental conditions the amount of the organic material adsorbed on catalyst surface is scarce, in agreement with the very low catalyst loading.

5. FT-IR spectra of reactivated catalyst

The feasibility of the washing reactivation is also confirmed by the comparison of FT-IR spectra of fresh, spent and reactivated catalysts (Figure S5).

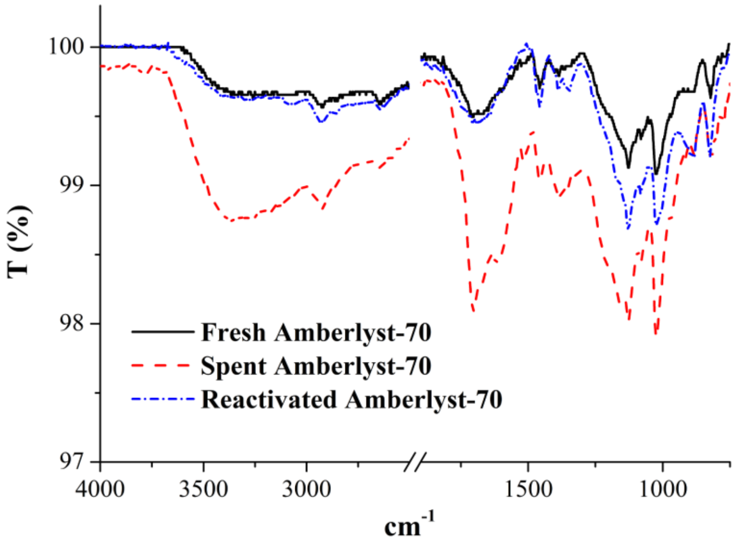

Figure S5: Comparison between FT-IR spectra of fresh catalyst, spent catalyst (180 °C, 20 minutes, R=80 wt/wt) and catalyst after washing reactivation with acetone (after 6th cycle).

The spent one presents the characteristic bands of soluble or insoluble humins, due to hydroxyl (3300 cm^{-1}), carboxyl and carbonyl groups (1705 cm^{-1} and at 1664 cm^{-1}), alcoholic and ether functionality (1279 cm^{-1}, 1189 cm^{-1} and 1022cm^{-1}) and aromatic/furanic ring (1604 cm^{-1}, 1515 cm^{-1}, 1395 cm^{-1}). Instead, the FT-IR spectrum of the reactivated catalyst is very similar to that of the fresh sample, proving that washing with acetone is a promising reactivation treatment.

6. References

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Figure S1

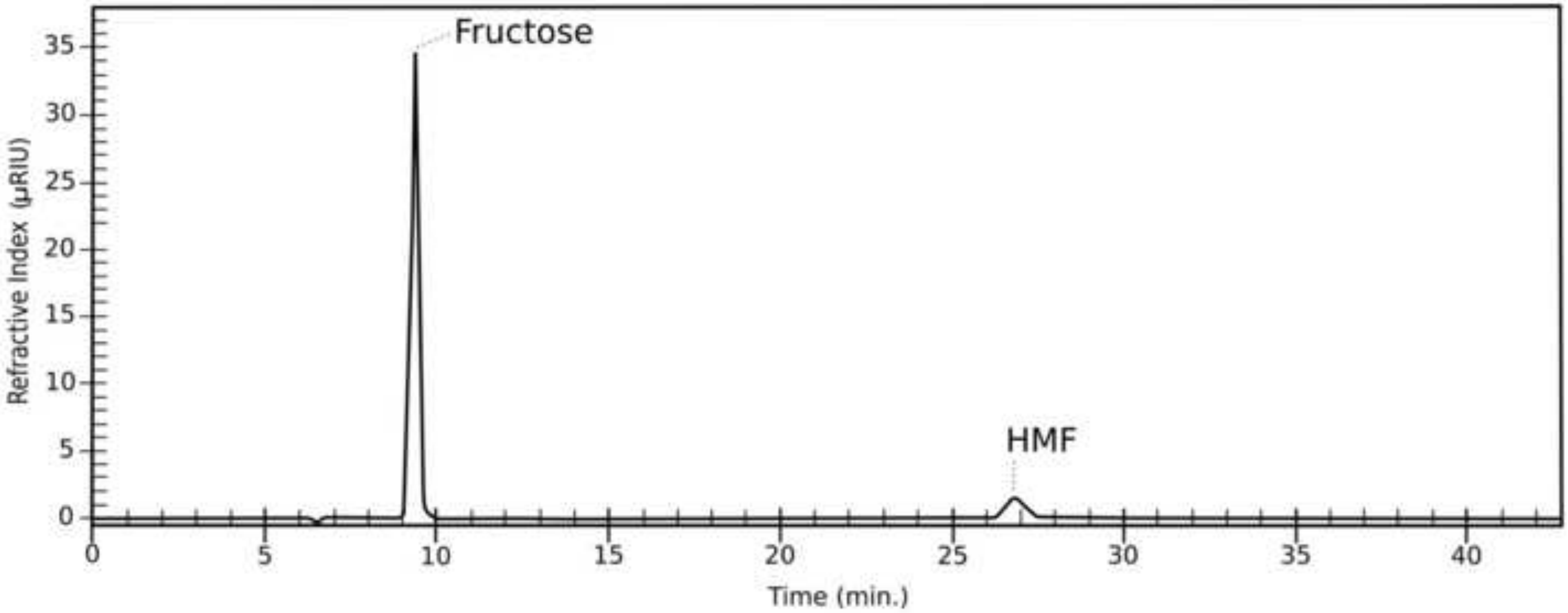

Fructose
HMF
Refractive Index (μRIU)
0
5
10
15
20
25
30
35
0
5
10
15
20
25
30
35
40
Time (min.)

Figure S2

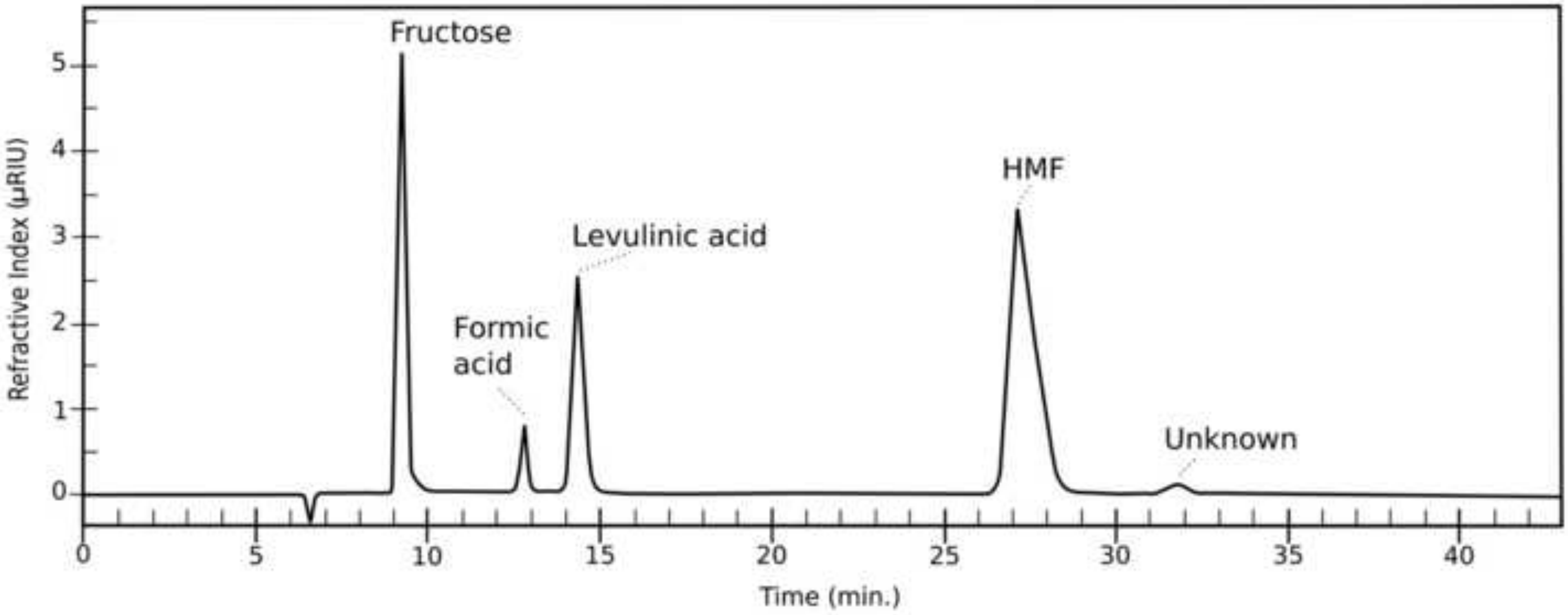

Fructose
Formic acid
Levulinic acid
HMF
Unknown
Refractive Index (µRIU)
0
1
2
3
4
5
Time (min.)
0
5
10
15
20
25
30
35
40

Figure S3

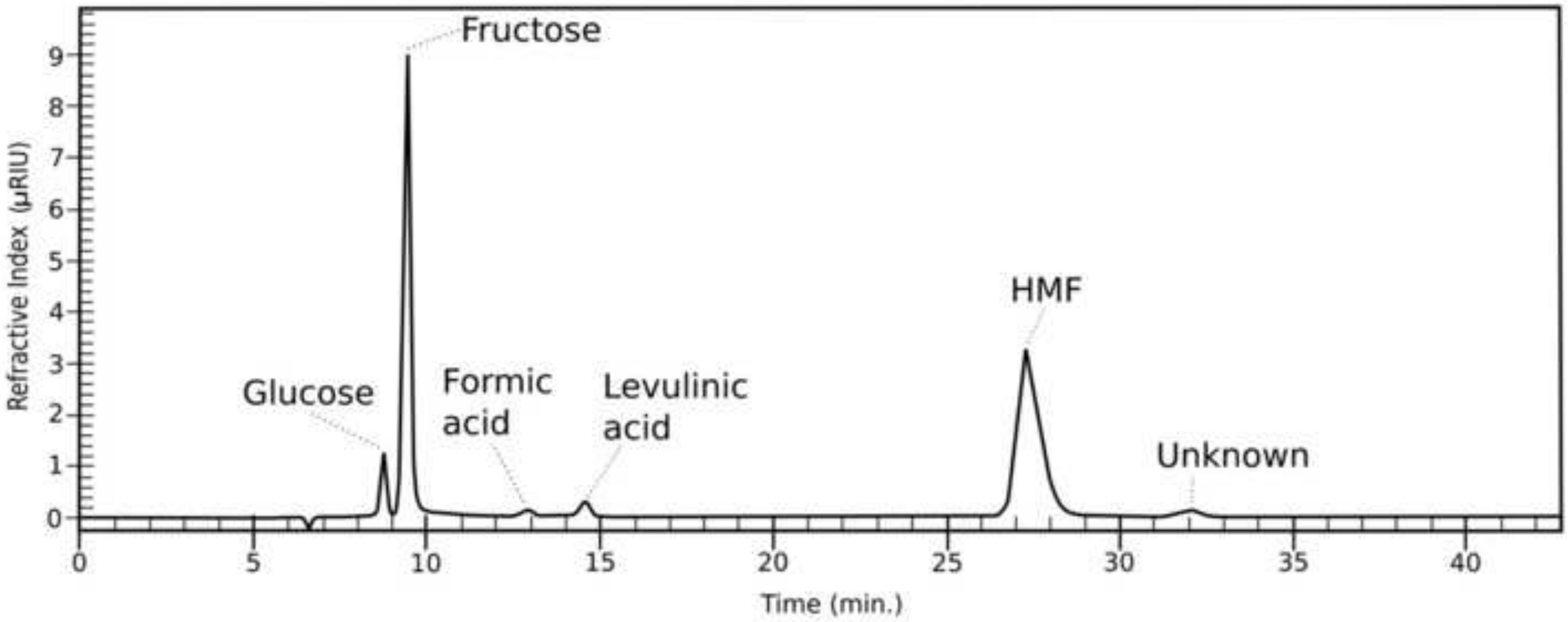
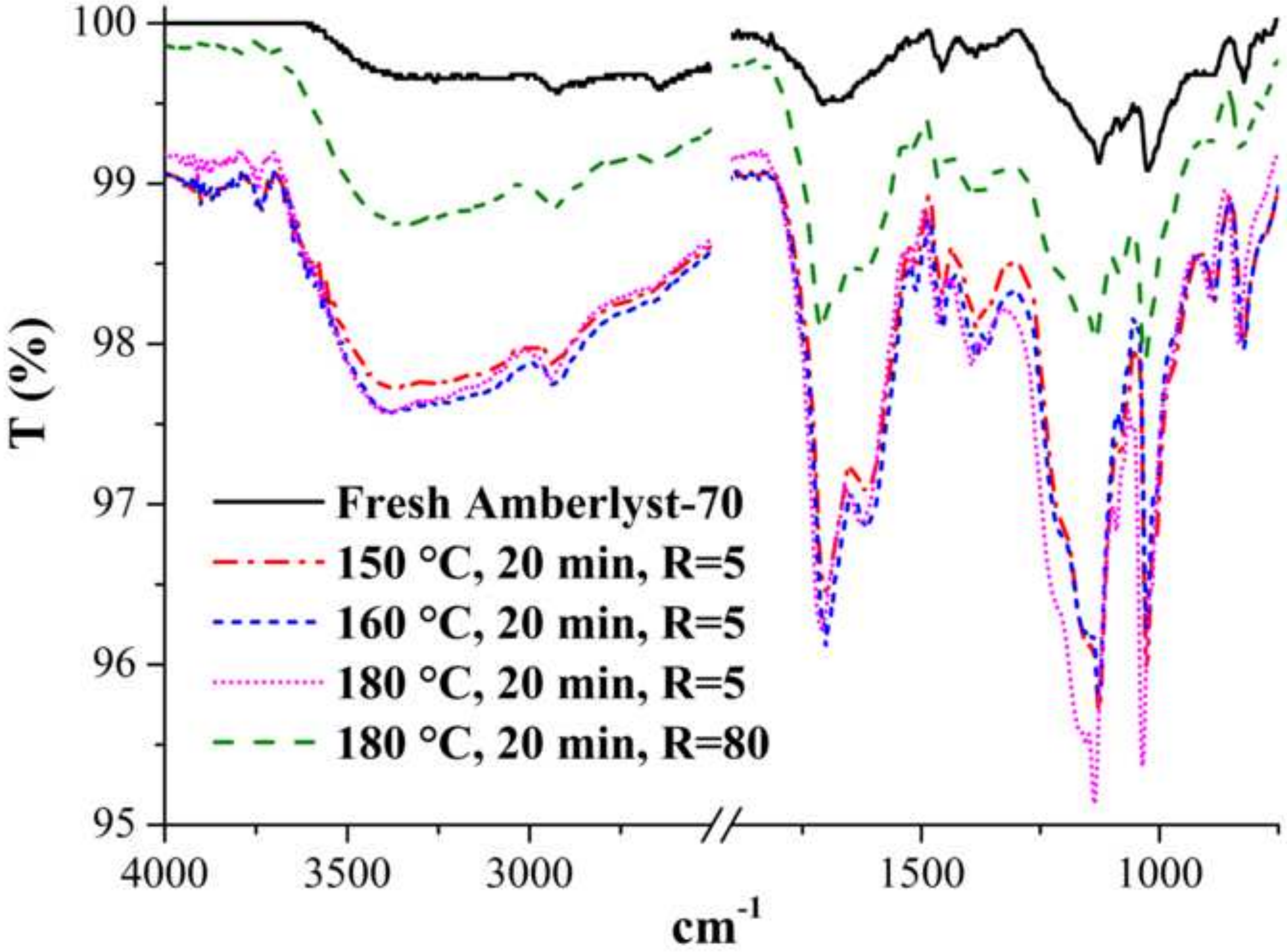

Fructose
Glucose
Formic acid
Levulinic acid
HMF
Unknown
Refractive Index (µRIU)
0
1
2
3
4
5
6
7
8
9
Time (min.)
0
5
10
15
20
25
30
35
40

Figure S4



T (%)
100
99
98
97
96
95
4000
3500
3000
1500
1000
cm^{-1}
Fresh Amberlyst-70
150 °C, 20 min, R=5
160 °C, 20 min, R=5
180 °C, 20 min, R=5
180 °C, 20 min, R=80

Figure S5

Click here to download high resolution image