

Article

Reaction Mechanism of the Microwave-Assisted Synthesis of 5-Hydroxymethylfurfural from Sucrose in Sugar Beet Molasses

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Abstract: 5-hydroxymethylfurfural (HMF) stands out among the chemical products derived from biomass as a building block in the chemical industry. The conventional production of HMF is usually carried out from fructose, glucose, or other monosaccharides as feedstock, but sugar beet molasses, a by-product of the sugar industry containing sucrose (45–55%), is promising. This exploratory study used three aqueous stock solutions and one biphasic system as the sources of sucrose. The dehydration of sucrose to 5-hydroxymethylfurfural was assisted by microwave heating and subcritical water conditions. The maximum yield of HMF was 27.8 mol % for the aqueous solution of synthetic sucrose at 80 min of treatment. Although HMF yield was 7.1 mol % in the aqueous sugar beet molasses solution, it increased 2-fold after clarification (15.1 mol %) and 1.6-fold in the biphasic system (11.4 mol %). These are favorable outcomes since this is an exploratory investigation. The pseudo-first-order model fitted experimental data from the conversion of the sucrose from the stock solutions, and kinetic parameters were estimated and compared. The estimated reaction rate constant showed that inversion of sucrose is faster than fructose dehydration to HMF, but the latter reaction was the rate-determining step only for the biphasic system. The maximum partition coefficient value was four between 40 min and 60 min of reaction, calculated at room temperature. These predictions help investigators to estimate conversions and selectivity when pilot plants need to be simulated.

Keywords: 5-hydroxymethylfurfural; microwave-assisted synthesis; biobased building block; biphasic synthesis



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1. Introduction

Non-renewable, petrochemical sources are raw materials for the vast majority of plastics. The challenge of dealing with non-biodegradable residues of petrochemicals and their impacts on the environment requires urgent attention. Current researchers and technology development institutes focus their attention on viable alternatives of petrochemical-derived materials where biomass and biomass-derived compounds appear to be versatile, renewable, abundant, having fixed carbon, and affordable price.

5-hydroxymethylfurfural (HMF) stands out among the chemical products derived from biomass. The conventional production of HMF is usually from fructose, glucose, or other monosaccharides as feedstock [1–3]. Recently, several studies used alternative raw materials such as sugarcane bagasse and molasses [4–6]. Sugar beet molasse is a by-product of the sugar industry containing sucrose (45–55%), glucose (~1%), fructose (~1%), organic acids, vitamins, and minerals [7–11]. Consequently, it represents one of the most promising alternative biomasses to be used as feedstock for HMF production.

Thermal and thermochemical synthesis of HMF in acidic and alkaline mediums need to be assisted by heterogeneous or homogeneous catalysts to control forward undesirable by-products, such as levulinic acid and formic acid, or other potentially toxic compounds derived from decomposition or polymerization of HMF. Reaction media such as organic solvents [12], biphasic systems [13], and ionic liquids [14] also contribute to ruling reaction pathways and boosting scaling up processes.

Microwave-assisted subcritical water (MASW) technology improves the heat transfer efficiency and reduces the reaction times reaching better conversion rates than conventional technologies [15,16]. As an energy source, microwaves save up to 85-fold energy compared to conventional heating sources [1]. In subcritical conditions, water acts as an acid–base catalyst precursor [4]. MASW may reduce the cost of producing furans from biomass in aqueous media [2] and represent a green alternative for HMF synthesis. On the overall process, this alternative gives a side stream high in organic acids such as levulinic acid (LA), formic acid (FA), glucose (Glc), and, in less proportion, furans including HMF and furfural, to potentially be used as a substrate to other applications such as LA conversion to fuel additives and biopolymers, FA conversion to green H₂, Glc recovery, and HMF and furfural bioconversion into other building blocks, improving the biomass valorization under the biorefinery concept.

In addition to using MASW technology and an available low-cost carbohydrate-rich source, the study of the kinetic parameters and reaction pathways is required to take any low-scale technology to industrial development. Studies of the kinetics of converting fructose, glucose, and polysaccharides into HMF, using strong homogeneous Brønsted acids and heterogeneous catalysts in water, have already been published [17–21]. However, there is no preceding kinetic study of HMF synthesis from molasses sucrose assisted by MASW technology. Therefore, the purpose of this study was (i) to investigate microwave-assisted subcritical water technology to synthesize HMF from the sucrose content in sugar beet molasses and (ii) to study reaction pathways for the conversion of sugar beet molasses to HMF.

2. Results and Discussion

Chemical Reaction Model for the Conversion of Sucrose to HMF

Figures 1 and 2 show the proposed reaction pathway used to fit the model to experimental data of the reactions in water (aqueous solution of sucrose (ASUC), aqueous solution of sugar beet molasses (ASBM), and aqueous solution of clarified sugar beet molasses (ACSBM)) and in the biphasic system (a solution of sugar beet molasses diluted in a mixture of water/MeTHF rate 1:4 (SBM-W/MeTHF)), respectively. The reaction pathway was based on the model proposed by Steinbach et al. [22], where sucrose, glucose, or fructose are converted into HMF and by-products.

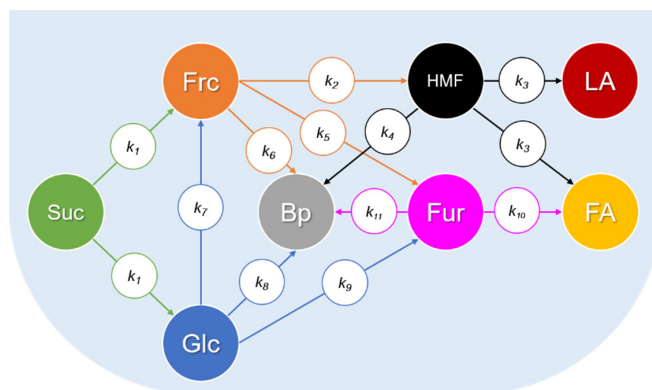


Figure 1. Schematic representation of the reaction network for the dehydration of sucrose (Suc) to 5-hydroxymethylfurfural (HMF) from monophasic stock solutions (ASUC, ASBM, and ACSBM). Reaction products (HMF, Glc (glucose), Frc (fructose), Fur (furfural), LA (lactic acid), FA (formic acid)) and by-products (Bp).

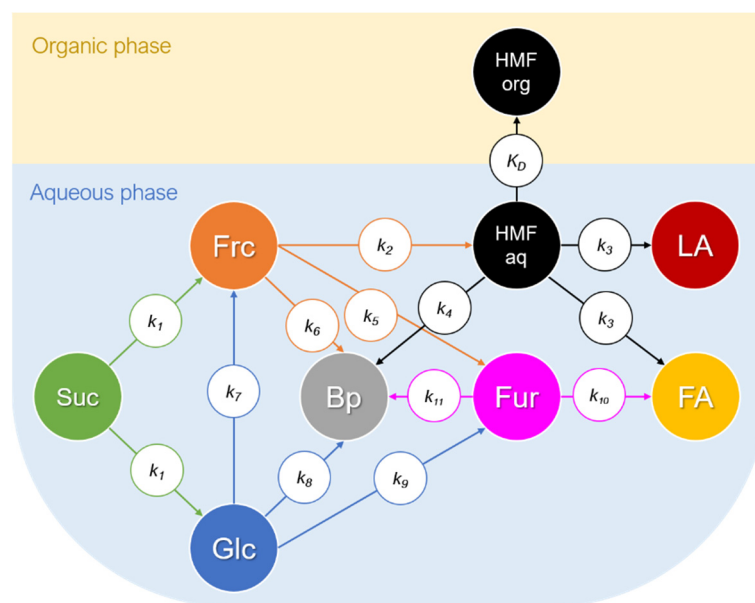
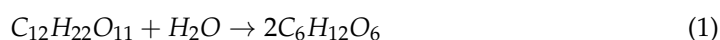


Figure 2. Schematic representation of the reaction network for the dehydration of sucrose (Suc) to 5-hydroxymethylfurfural (HMF) from the biphasic system SBM-W/MeTHF at atmospheric pressure. Reaction products (HMF_{aq} (HMF in aqueous phase), HMF_{org} (HMF in organic phase), Glc (glucose), Frc (fructose), Fur (furfural), LA (lactic acid), FA (formic acid)) and by-products (Bp).

The chemical reaction model begins with sucrose inversion, as shown in Equation (1).



Sucrose inversion is represented as a pseudo-first-order reaction (Equation (2)):

$$R_{Suc} = k[C_{12}H_{22}O_{11}][H_2O][H^+] = k[C_6H_{12}O_6]_{Frc}[C_6H_{12}O_6]_{Glc}[H^+] \quad (2)$$

Subindex *Frc* and *Glc* stand for fructose and glucose, respectively, and *k* is the kinetic rate constant.

Assuming that both concentrations of protons and water in the medium do not change over time, the reaction rate is expressed as in Equation (3):

$$\frac{dSuc}{dt} = R_{Suc} = k[C_{12}H_{22}O_{11}][H_2O][H^+] = -k_1[Suc] \quad (3)$$

where k_1 is the apparent constant rate of sucrose inversion and $[Suc]$ is the sucrose concentration.

Analogous to the sucrose inversion reaction, the proposed model assumes that all reactions follow a pseudo-first-order reaction mathematically represented by the differential equations (Equations (4)–(10)).

$$\frac{dFrc}{dt} = R_{Frc} = k_1[Suc] + k_7[Glc] - k_2[Frc] - k_5[Frc] - k_6[Frc] \quad (4)$$

$$\frac{dGlc}{dt} = R_{Glc} = k_1[Suc] - k_7[Glc] - k_8[Glc] - k_9[Glc] \quad (5)$$

$$\frac{dHMF_{aq}}{dt} = R_{HMF_{aq}} = k_2[Frc] - k_3[HMF] - k_4[HMF] - K_D[HMF] \quad (6)$$

$$\frac{dHMF_{org}}{dt} = R_{HMF_{org}} = K_D[HMF] \quad (7)$$

$$\frac{dFA}{dt} = R_{FA} = k_3[HMF] + k_{10}[Fur] \quad (8)$$

$$\frac{dFur}{dt} = R_{Fur} = k_5[Frc] + k_9[Glc] - k_{10}[Fur] - k_{11}[Fur] \quad (9)$$

$$\frac{dBp}{dt} = R_{Bp} = k_4[HMF] + k_6[Frc] + k_8[Glc] + k_{11}[Fur] \quad (10)$$

k_2 , k_5 , and k_6 are the apparent constant rates of fructose dehydration, fructose decarboxylation, and fructose condensation, respectively; k_7 , k_8 , and k_9 are the apparent constant rates of glucose isomerization, glucose decarboxylation, and glucose condensation, respectively; k_3 and k_4 are the apparent constant rates of HMF rehydration and HMF condensation, respectively, K_D is the partition coefficient of HMF for biphasic reactions, and k_{10} and k_{11} are the apparent constant rates of furfural rehydration and furfural condensation, respectively. Additionally, $[Frc]$, $[Glc]$, $[HMF]$, $[FA]$, $[Fur]$, and $[Bp]$ are the concentrations of fructose, glucose, HMF, FA, and byproducts (including humins and other side reaction products), respectively.

The initial concentrations used to solve the system of differential equations are represented by Equations (11)–(17).

$$[Suc]_0 = C_{Suc,0} \text{ (M)} \quad (11)$$

$$[Frc]_0 = 0 \quad (12)$$

$$[Glc]_0 = 0 \quad (13)$$

$$[HMF]_0 = 0 \quad (14)$$

$$[FA]_0 = 0 \quad (15)$$

$$[Fur]_0 = 0 \quad (16)$$

$$[Bp]_0 = 0 \quad (17)$$

where $C_{Suc,0}$ is the Suc concentration at $t = 0$ (min). The product distribution and sucrose conversion over time for the reactions in water (ASUC, ASBM, and ACSBM) and the biphasic system (SBM-W/MeTHF) are shown in Figure 3. In all cases, sucrose has the higher reaction rate and dehydrates entirely within the time period. A slow reaction rate was observed for ACSBM, suggesting that clarification took away some organic acids or reaction-promoting species present in the raw material (Figure 3C).

Overall, the presence of glucose, fructose, HMF, and all by-products indicates that all experiments reached the subcritical water condition acting as a weak acid–base catalyst, which is in agreement with the observations of Agustina et al. [4]. Microwave radiation provides instantaneous and homogeneous heat, exciting water molecules that favor intermolecular collisions, leading to an increase in the reaction rates [1,5,23,24]. As expected, fructose was completely converted by the end of all experiments due to favorable reaction conditions. On the other hand, glucose behaves as an intermediate in ASBM, ACSBM, and SBM-W/MeTHF (Figure 3B–D). However, in ASUC, Glc stayed at high concentrations for almost all the reaction time (Figure 3A). The absence of any alkaline catalyst to promote the isomerization of glucose to fructose may explain this outcome [20], in agreement with studies for the dehydration of sucrose using sulfuric acid in water [18,22].

The highest yield of HMF reached within all experiments was 27.8 mol % in ASUC (Figure 3A) at 80 min of treatment. Howard et al. reported a lower HMF yield from industrial cane molasses solution performed with similar operational conditions [5]. On the other hand, ASBM had the lowest maximum HMF yield (7.1 mol %) achieved in the current study, although sucrose dehydration was completed (Figure 3B). The low yield could be attributed to the presence of some inhibitors such as amino acids (betaine) and minerals, as reported in the literature [25,26].

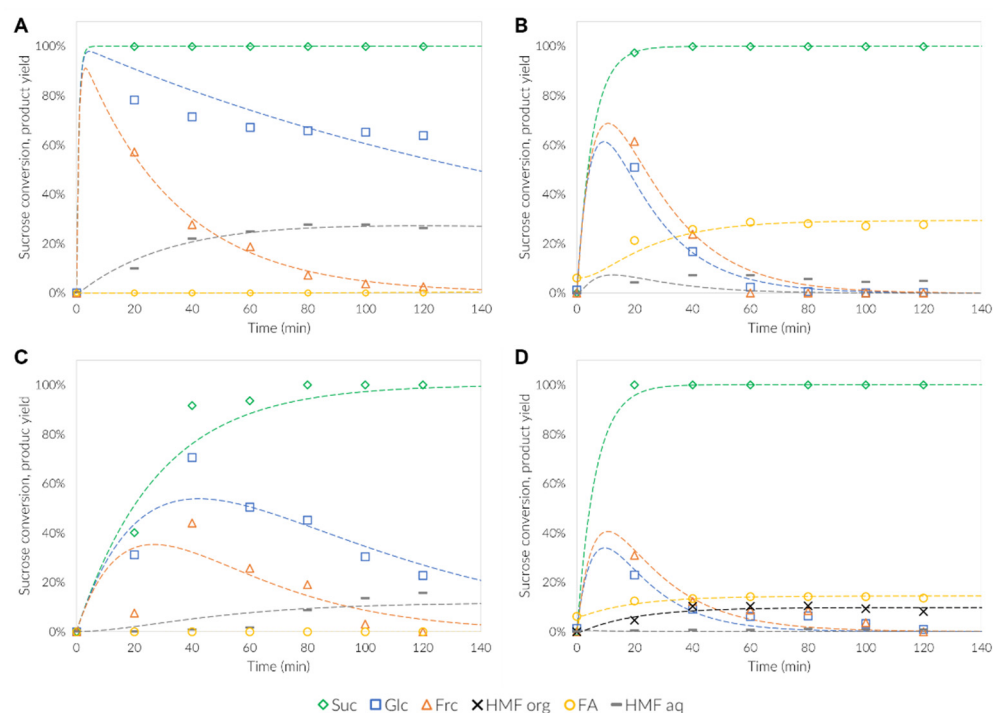


Figure 3. Microwave-assisted dehydration of sucrose (Suc) to 5-hydroxymethylfurfural (HMF) in (A) sucrose solution (ASUC), (B) aqueous sugar beet molasses solution (ASBM), (C) aqueous clarified sugar beet molasses solution (ACSBM), and (D) in biphasic ($H_2O/MeTHF$ 1:4) sugar beet molasses (SBM-W/ $MeTHF$) system. Profile of the conversion of sucrose, the yield of HMF and concentration of products over time: sucrose conversion (green diamond), glucose (blue square), fructose (orange triangle), HMF aq yield (HMF in aqueous phase, gray rectangle), formic acid (yellow circle), and HMF org yield (HMF in organic phase, black crosses).

In our experiments, the presence of FA (28.8 mol %) implies that HMF could be an intermediate, which was produced and rapidly transformed to FA and LA or polymerized into humins (Bp). The presence of humins could be validated because the color of the reaction mixtures changed over 5 min of running, from clear to yellow-brown, due to the formation of a dark-brown solid (humins) or caramelization by-products. By-products and humins are formed by the condensation reactions of products and intermediates [5,27,28]; however, the current study did not quantify them. The impurities in ASBM may negatively affect HMF yield. The treatment of ASBM with Carrez Clarification Reagents to remove nitrogen compounds, along with most of the cations and other impurities (Table 1), partially improved it (Figure 3C).

As mentioned before, amino acids from proteins could react with glucose and fructose through the Maillard reaction [25,29], preventing the primary reaction, which is the dehydration of fructose to HMF, by consuming fructose and glucose. Consequently, the removal of amino acids and K and Ca ions could be the reason for the doubled yield of HMF (15.5 mol %) in ACSBM (Figure 3C). Our results agree with those obtained by Abdilla-Santes et al. [26], who studied the effect of some ions in the dehydration of sucrose from thick juice to HMF.

Table 1. Kinetic constants for the microwave-assisted dehydration of sucrose to HMF in water and a biphasic system.

Reaction	Kinetic Constant	ASUC (Min ⁻¹)	ASBM (Min ⁻¹)	ACSBM (Min ⁻¹)	SBM-W/MeTHF (Min ⁻¹)
Suc → Frc + Glc	k_1	0.5381	0.1935	0.0846	2.6815
Frc → HMF	k_2	0.0100	0.0750	0.0044	0.0054
HMF → LA + FA	k_3	0.0001	0.1107	-	1.4958
HMF → Bp	k_4	0.0014	0.6524	-	0.0187
Frc → Fur	k_5	0.0005	0.0084	0.0002	0.0000
Frc → Bp	k_6	0.0168	0.0030	0.0295	0.0447
Glc → Frc	k_7	-	0.0546	0.0000	0.0000
Glc → Bp	k_8	0.0035	0.0011	0.0145	0.0629
Glc → Fur	k_9	0.0001	-	0.0002	0.0000
Fur → FA	k_{10}	0.0002	0.0005	0.0039	0.0285
Fur → Bp	k_{11}	0.0003	0.2824	0.5106	0.0178
HMF _{aq} → HMF _{org}	K_D	-	-	-	0.4448
	R ² ^a	0.9925	0.9815	0.9059	0.9065

^a Coefficient of determination.

Examining the kinetic constants at the operational temperature in Table 1 revealed that the sucrose inversion to fructose and glucose is by far the fastest reaction in the network, followed by the formation of by-products in ASBM and ACSBM, which is in line with the experimental findings (Figure 3A–C). The kinetic constant for sucrose inversion was exceptionally high in SBM-W/MeTHF, 14-fold faster than in the aqueous solution. Similarly, the kinetic constant for the formation of LA and FA from HMF was also 14-fold faster, preventing the degradation of HMF into by-products. These outcomes are aligned with experimental data plotted in Figure 3D. Several studies have reported the benefits of the use of biphasic systems *in situ* to recover HMF from the reaction mixture using sucrose or monosaccharides as the reactant and methyl isobutyl ketone, 1-butanol, 2-butanol, or dimethyl sulfoxide as the organic solvent [30,31].

We selected MeTHF, a renewable origin solvent with high affinity for HMF, a low boiling point (80.2 °C), polar aproticity, and very low miscibility in water, as the organic solvent in the current study. The product distribution time profile in SBM-W/MeTHF was similar to ASBM. However, HMF yield increased from a maximum value of 7.1 mol % in ASBM to a constant value of 11.4 mol % in the biphasic system. This significant increment in the production of HMF is due to the immediate extraction and stabilization of HMF in the organic phase, as reported in the literature [13,30,31].

Biphasic systems containing an organic extracting phase improve HMF yields by increasing the partitioning of HMF into the extracting phase, as measured by the partition coefficient, K_D [31]. In the current study, the partition coefficient (K_D) was measured from the concentrations of HMF at room temperature at several reaction times. Interestingly, K_D had a maximum value of 4 between 40 min and 60 min of reaction. This value is similar to, or even higher than, other investigations of biphasic systems, although they may have used different solvents [32–34].

3. Materials and Methods

3.1. Materials

Sugar beet molasses obtained from Industria Azucarera Nacional S.A. (IANSAs), Los Angeles, Biobío, Chile, was homogenized manually and stored at 4 °C before use. Sucrose (Suc), HMF, and betaine (trimethylglycine) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Glucose (Glu), fructose (Fru), and levulinic acid (LA) were acquired from Merck KGaA (Darmstadt, Germany). We also obtained sulfuric acid (H₂SO₄) (97%, Merck Millipore, Darmstadt, Germany), formic acid (FA) (98%, Sigma-Aldrich, Steinheim,

Germany), and hydrochloric acid (HCl) (38%, Merck Millipore, Darmstadt, Germany) for the experiments.

3.2. Microwave-Assisted Subcritical Water Experiments

This study investigated the dehydration of the sucrose from four stock solutions: (a) aqueous solution of sucrose (ASUC), (b) aqueous solution of sugar beet molasse (ASBM), (c) aqueous solution of clarified sugar beet molasse (ACSBM), and (d) a solution of sugar beet molasses diluted in a mixture of water/MeTHF rate 1:4 (SBM-W/MeTHF) (summarized in Table 2). HPLC analysis confirmed that the treatment with Carrez Clarification Reagents did not affect the concentration of carbohydrates in ACSBM, but ASBM was 50-fold diluted because of the clarification protocol.

Table 2. Chemical composition of raw sugar beet molasses and stock solutions.

Parameter	Samples			
	Raw Sugar Beet Molasses (SBM)	Sucrose Solution (ASUC)	Sugar Beet Molasses Solution (ASBM)	Clarified Sugar Beet Molasses ^f (ACSBM)
Brix value (%) ^a	81.6	32.4	40.8	3.8
Moisture (wt %)	15.05	n.d.	n.d.	n.d.
pH	6.52	4.19	6.52	6.71
Fat	Traces	-	n.d.	n.d.
Total protein ^b (db wt % ^c)	8.83	-	n.d.	n.d.
Total ash (db wt %)	11.2	-	5.6 ^d	n.d.
Sugars (db wt %)				
Sucrose	53.21	34.2	35.08 ^d	3.15 ^e
Glucose	2.81	-	3.19 ^d	0.27 ^e
Fructose	2.53	-	1.59 ^d	0.14 ^e
Element (db wt %)				
K	10.19	-	5.09 ^d	-
Ca	1.14	-	0.57 ^d	0.007 ^g
S	1.08	-	0.54 ^d	-
Cl	0.88	-	0.44 ^d	0.024 ^g
Na	0.85	-	0.42 ^d	-
Rb	0.12	-	0.06 ^d	0.001 ^g
Fe	0.04	-	0.03 ^d	-
P	0.03	-	0.01 ^d	-

^a Brix value: wt % of dissolved sugar in a liquid solution. ^b Kjeldahl estimation (%Nitrogen \times 6.25). ^c Dry basis weight. ^d Estimation from raw material composition. ^e HPLC quantification. ^f Carrez clarification method, 20-fold dilution of raw sugar beet molasses (SBM). ^g Estimated by the difference with the elemental composition of precipitates from the Carrez clarification method.

All reactions were carried out in a CEM Discover SP reactor in dynamic mode to deliver the energy as a function of the fluid temperature at 300 W, which is the maximum power allowed by the equipment and at 250 psi, to avoid heating limitations. The operating temperature was 170 °C because our previous studies (data not shown) conducted in a range of 150–160 °C achieved low conversion of sucrose to HMF, but higher temperatures (180–190 °C) led to the formation of condensation products such as humins.

3.3. Kinetic Experiments Protocols

For the kinetic experiments, 5 mL of each stock solution described in Table 2 were placed in a 35 mL standard borosilicate glass vial and sealed with a polyether ether ketone (PEEK) snap cap and a PTFE-coated silicone septum. The samples were heated to 170 °C (to ensure subcritical water), held at that constant temperature for 10 to 120 min, and cooled to 30 °C by flowing compressed air into the reactor (over 10 min). Reaction solutions were filtered through a 0.22 μ m hydrophilic syringe filter, transferred to a closed vial, and stored at 4 °C until HPLC analysis.

The experiments carried out in a biphasic system for the in situ extraction of HMF followed a similar experimental protocol than previously described, but instead of pure water, 4 mL of methyl-tetrahydrofuran (MeTHF) was added as the organic phase. These experiments started from 1 mL of SBM at 50 wt % only, non-catalyzed (KBA) or 77.5 mM HCl catalyzed (KBB) media.

3.4. Analytical Procedures

3.4.1. Estimation of Moisture, Brix Value, and Inorganics in Sugar Beet Molasses

Moisture in sugar beet molasses was determined gravimetrically after convection drying at 105 °C for 2 h. Brix values were measured by Leica 10,480 Mark II Ab non-diluted fresh sugar beet molasses (SBM), sucrose solution (ASUC), and clarified sugar beet molasses (ACSBM). The content of inorganic ions in sugar beet molasses was determined by X-ray fluorescence (Bruker S4 Explorer spectrometer, Billerica, MA, USA).

3.4.2. Determination of Sugars, Organic Acids, and HMF in Aqueous Phase

Sucrose, glucose, fructose, levulinic acid, formic acid, and HMF were measured using the High-Performance Liquid Chromatography (HPLC) model YL9100. Sugars and organic acids were detected using a refractive index detector (RID), and HMF was detected with a diode array detector (DAD). A solution of 5 mM of sulfuric acid was used as the mobile phase at 0.6 mL/min. The chromatography column was a Bio-Rad Aminex HPX-87H 300 × 7.8 mm column operating at 35 °C. Before analysis, all samples were diluted at least ten times with deionized water and filtered through a 0.22 µm syringe filter.

3.4.3. Determination of HMF in Organic Phase

Organic phase MeTHF was previously separated by a separating funnel, and contained HMF was measured using gas chromatography (GC) coupled to mass spectrometry (MS) with a Perkin Elmer model Clarus 600 equipped with an Elite 1701 (30 m, 0.25 mm, 0.25 µm) column, with oven operating from 50 °C to 270 °C at 4 °C/min and maintaining 270 °C for 3 min, injector temperature at 290 °C, injection volume of 1 µL, 2 mL/min of carrier gas flow, and split of 20 mL/min. The total analysis time was 58 min, and the solvent delay was 5 min.

3.4.4. Carrez Clarification of Sugar Beet Molasses

The treatment of samples with Carrez Clarification Reagents was quick and straightforward. Five grams of sugar beet molasses was added to 60 mL of deionized water followed by 1 mL of Carrez Reagent I and carefully mixed. Subsequently, 1 mL of Carrez Reagent II was added and remixed. Afterwards, the solution was adjusted to a pH of 7.5–8.0 by adding sodium hydroxide (1 mol/L) to precipitate any excess zinc ions (Zn(OH)₂). The mixture was quantitatively transferred to a 100 mL volumetric flask, and the flask was filled to the mark with deionized water. Subsequently, the solution was centrifuged to separate the insoluble compounds. The clear supernatant was collected and filtered through a 0.22 µm syringe filter and storage at 4° to use later in microwave dehydration reactions and HPLC analysis.

3.5. Data Analysis and Fitting

3.5.1. Substrate Conversion and HMF Yield

The sucrose (*Suc*) conversion (X_{Suc}) and products (Glc, Frc, HMF, FA, and Fur) yield (Y_P) were determined by Equations (18) and (19), respectively:

$$X_{Suc}(\text{mol}\%) = \frac{C_{Suc,0} \times V_{aq} - C_{Suc} \times V_{aq}}{C_{Suc,0} \times V_{aq}} \times 100\% \quad (18)$$

$$Y_P(\text{mol}\%) = \frac{C_P \times V_{aq}}{C_{Suc,0} \times V_{aq}} \times 100\% \quad (19)$$

where $C_{Suc,0}$ (mM) is the sucrose initial concentration and C_{Suc} (mM) is the sucrose concentration at $t = 20, 40, 60, 80, 100,$ and 120 min. V_{aq} represents the volume of water (1 mL).

Analogously, in biphasic experiments, the products (Glc, Frc, HMF, FA, and Fur) yield (Y_{PB}) was calculated using Equation (20).

$$Y_{PB}(\text{mol}\%) = \frac{C_{Paq} \times V_{aq} + C_{Porq} \times V_{org}}{C_{Suc,0} \times V_{aq}} \times 100\% \quad (20)$$

where C_{Paq} (mM) is the molar concentration of HMF in aqueous phase, C_{Porq} (mM) is the molar concentration of HMF in organic phase (MeTHF), V_{aq} is the volume of water (1 mL), and V_{org} is the volume of MeTHF (4 mL).

For the biphasic system, the partition coefficient (K_D) was calculated by Equation (21):

$$K_D = \frac{C_{HMForg}}{C_{HMFaq}} \quad (21)$$

where C_{HMForg} (g/L) is the concentration of HMF in the organic phase, and C_{HMFaq} (g/L) is the concentration in the aqueous phase.

3.5.2. Fitting of Model to Kinetic Data

The fitting of the reaction model to kinetic data from the conversion of the sucrose in ASUC, ASBM, ACSBM, and SBM-W/MeTHF was developed from the basis of the reaction mechanism described by Steinbach et al. [22]. The kinetic parameters were estimated by fitting these models to the experimental data using a non-linear least-squares approach run by the MS Excel software and their Solver optimization algorithm of Runge Kutta of fourth-order in VBA.

4. Conclusions

The current exploratory study analyzed the transformation of sucrose from sugar beet molasses, a by-product of the sugar industry, to HMF by MASW technology.

The pseudo-first-order model adequately fitted experimental data from the sucrose conversion of the stock solutions. The estimated reaction rate constants showed that the inversion of sucrose was faster than fructose dehydration to HMF. However, the latter reaction was the rate-determining step only for the biphasic system addressing the importance of having a biphasic system to maximize HMF recovery. The maximum partition coefficient for HMF reached within 40 min and 60 min of the reaction is in line with fructose increasing yield. Future research should focus on testing other biphasic systems to improve HMF yield and HMF in situ extraction.

Estimated reaction rate constants and space/time yields (not shown in this article) can be used to set reaction conditions and to predict conversions and selectivity of HMF using a continuous reactor at the level of pilot plants.

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