Microwave Assisted Synthesis of 5-hydroxymethylfurfural Using Mild Reaction Conditions

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5-Hydroxymethylfurfural (5-HMF) is an important platform molecules, being a green precursor for a variety of high performance fuels and valuable chemicals. The production of 5-HMF from fructose under microwave-assisted heating conditions by varying different parameters (catalyst, temperature, stirring rate and reaction time) was studied. Microwave assisted synthesis leads to a shorter reaction time (40 min versus 150 min for conventional method) and the energy consumption is lower compared with the conventional method. Homogeneous and heterogeneous catalysts were tested. Although homogeneous catalysis produced the highest conversion of fructose to 5-HMF, ion exchange resins are preferable for industrial development and the best results were obtained for Dowex resin.

Keywords: 5-hydroxymethylfurfural, fructose, heterogeneous catalysts, microwave

The rapid depletion of fossil resources, global warming and environmental pollution has attracted significant efforts for the development of alternative renewable resources to produce valuable organic compounds [1-3]. A number of building blocks obtained from biomass, such as ethanol, furfural, lactic acid, glycerol, levulinic acid, and succinic acid, are already in use or are considered to have a great significance in the near future [4]. Organic compounds made from biomass have similar properties or better than those produced from petroleum. 5-hydroxymethylfurfural (5-HMF) attracted attention of many researchers in recent years. This compound can be a promising intermediate building block due to its chemistry that allows different conversions into chemicals such as biofuels (dimethyl furan), polymer monomers (2,5-furandicarboxyllic acid and 2,5-diformylfuran), adipic acid, levulinic acid, caprolactone and caprolactam, as well as many other more specific molecules, [5-9] including active pharmaceutical components [10,11]. Carbohydrates and lignocellulosic compounds found in biomass are the most abundant renewable resource that can be used as a feedstock for various categories of organic compounds [12-14]. They can be broken down into hexoses that form by further dehydration, different organic compounds as well as 5-hydroxymethylfurfural.

In recent years, heterogeneous and homogeneous acidic catalysts for the dehydration of carbohydrates into 5-HMF were used. Mineral or organic acids [15,16], metal chlorides [17,18], and ionic liquids [19,20] have been used as homogeneous catalysts. Even though, these types of catalysts are inexpensive and can lead to high yields of 5-HMF, they have limited applications at industrial scale due to their toxicity and difficult product separation from the reaction media. Heterogeneous catalysts have several advantages such as ease of product separation, reusability of catalyst, and less corrosiveness that makes them efficient and suitable for industrial processes [21,22]. Some researches investigated the HMF synthesis using solid catalysts such as zeolites and ion-exchange resin [23].

Microwave-assisted organic synthesis has progressively begun to be an attractive heating source leading to improved yields and selectivity and allowing energy savings. The heating assisted by microwave is based on the effect of the microwaves on material molecules by ionic conduction and dipole rotation and an efficient heating requires either polar extraction solvents or polar materials [24].

The degree of originality of this paper is to develop the optimal conditions for microwave assisted synthesis of 5-HMF using feedstock derived from renewable resources. The performance of heterogeneous and homogeneous acidic catalysts, namely HCl and ion exchange solid catalysts was also compared in order to evaluate the replacement of the mineral acid by heterogeneous catalysts.

Experimental part

Materials and methods

Fructose (≥99%), HCl (≥37%, p.a.), 5-hydroxymethylfurfural (5-HMF) (≥ 99%) used as standard for HPLC analysis and methanol (HPLC grade) were purchased from Sigma-Aldrich and used without further purification. Amberlyst, Dowex and Purolite (sulfonated -exchange resin) were purchased from Sigma-Aldrich and they were dried overnight at 60°C. Deionized water was used for the preparation of aqueous solutions.

Dehydration of fructose

The microwave-assisted fructose dehydration was performed using a microwave system (Biotage Initiator). The Biotage reactor (20 mL) was charged with aqueous fructose solution (10 wt. %, 3 mmol), and the required amount of aqueous HCl solution (0.1 N, 0.3 mmol) was added. Experiments using heterogeneous catalysts were carried out in the same procedure using 150 mg of catalyst, 1 mmol of substrate in deionized water. Basic operations for 5-HMF synthesis and separation are presented in figure 1.

On the other hand, the conventional conversion of fructose was carried out in the same reactor as for microwave assisted experiments, using as heating source an oil bath. The conventional reactions were performed in an oil-bath using a heating plate equipped with a temperature controller unit and magnetic stirring. The experiments were carried out at different temperatures (80, 100 and 120°C) and stirring rates (300 and 900 rpm).

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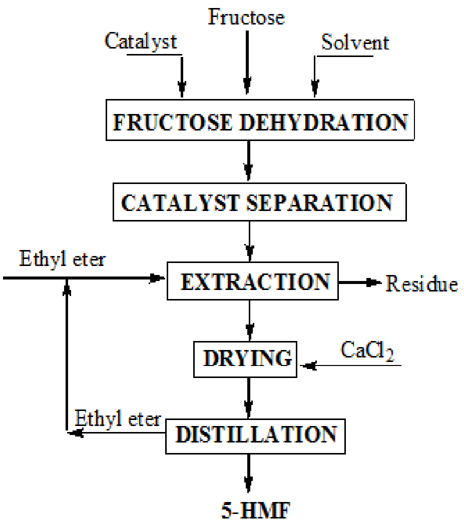

Fig. 1. Basic operations for 5-HMF synthesis and separation

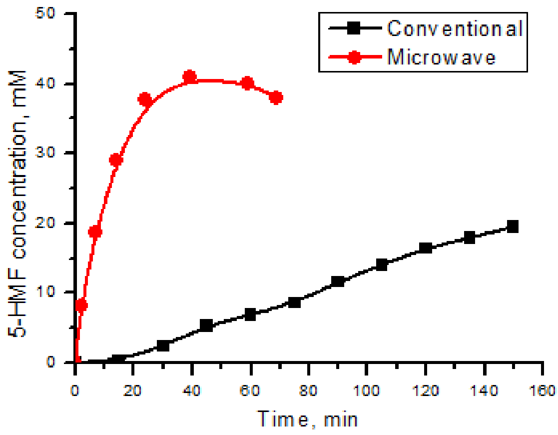

Fig. 2. Influence of heating type on the 5-HMF concentration (temperature: 100°C, catalyst HCl, stirring rate: 900 rpm)

Analytical methods

5-HMF aqueous solutions were filtered through a syringe filter prior to analysis by high performance liquid chromatography (HPLC). The analyses were undertaken using a Jasco HPLC equipped with: UV-2075 detector; PU-2080 plus pump; LG-2080_4 gradient unit; DG-2080_4 degasser; Teknokroma Nucleosil 100 C18 (10 µm, 250×0.4) separation column. Analyses were performed at a flow rate of 0.5 mL/min using water with 2% v/v acetic acid (solvent A) and methanol (solvent B) under the following gradient program: 0-9 min 70% A, 9-18 min 60% A, 18-30 min 50% A, 30-60 min 50% A and then returned to initial condition for a 10 min re-equilibration, with a total run time of 70 min. 5-HMF was identified by comparison of retention times from samples with pure standard compound. HMF concentrations were determined using calibration curves and product yields (%), were calculated.

Results and discussions

Microwave assisted extraction vs. conventional extraction

Microwave assisted synthesis is a promising technology to obtain valuable compounds from biomass. The heating assisted by microwave is based on the effect of the microwaves on material molecules (reagent, solvent or catalyst) by ionic conduction and dipole rotation. Thus, an efficient heating requires either polar extraction solvents or polar materials.

To highlight the effect of microwaves on the 5-HMF concentrations the syntheses were carried out by microwave irradiation and by conventional heating. Figure 2 presents the influence of heating type on the 5-HMF concentration.

As is shown in figure 2, for the same reaction conditions, in the case of microwave assisted synthesis a higher 5-HMF concentration was obtained, the maximmum concentration was 40.93 mM, compared with 19.45 mM for conventional synthesis. Increasing the reaction time leads to an increase in 5-HMF concentration, reaching a maximum after 40 min in the microwave assisted reaction. For conventional heating after 150 min the maximum concentration of 5-HMF has not been reached. However, further increase of the reaction time leads to decreasing the 5-HMF concentration. This behaviour is due to the 5-HMF degradation or condensation reactions with forming of levulinic acid or humins leading to a slightly reduction in final concentration.

Determination of specific power and specific energy

For all experiments carried out by microwave heating, the temperature and power profiles were recorded.

In addition, the specific power and specific energy were calculated for the reactions performed by microwave and conventional heating at 100°C using equations (1) and (2), where P_{sp} is the specific power (W/g fructose), P the power supplied into the system (W), m_f the weight of fructose (g), E_{sp} the specific energy (J/g HMF), t the reaction time (s), and m_{HMF} the weight of 5-HMF obtained from reaction (g). Specific power and specific energy as well as reaction time and 5-HMF concentration for both heating types are summarized in table 1.

$$P_{sp} = \frac{P}{m_f} \qquad (1)$$

$$E_{sp} = \frac{Pt}{m_{HMF}} \qquad (2)$$

As shown in table 1, the reaction performed by microwave heating for 40 min lead to double amount of 5-HMF compared with the reaction carried out by conventional heating for 150 min. In addition, the specific power and specific energy for microwave-assisted reaction are with three orders of magnitude lower than those for conventional heating. In order terms, besides a higher yield with a lower reaction time, an advantage of 5-HMF synthesis from fructose by microwave heating is represented by a low energy required in order to perform the reaction.

Heating type	Reaction time [min]	HMF [mM]	Specific power [W/g fructose]	Specific energy [kJ/g HMF]
Microwave	40	40.95	79.2	0.205×10^4
Conventional	150	19.45	1292.2	0.390×10^7

Table 1
SPECIFIC POWER AND SPECIFIC ENERGY FOR THE REACTIONS PERFORMED BY MICROWAVE AND CONVENTIONAL HEATING AT 100°C USING HCL AS CATALYST

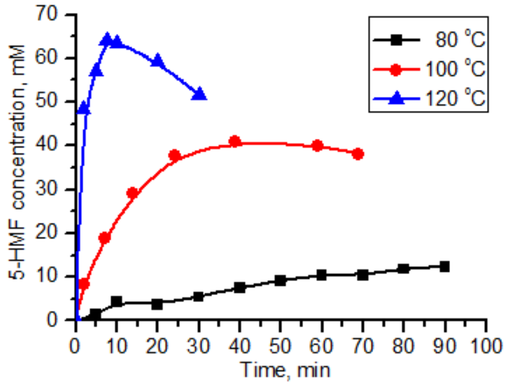

Fig. 3. Influence of temperature on the 5-HMF concentration (microwave irradiation, catalyst HCl, and stirring rate: 900 rpm)

Influence of temperature on fructose conversion to 5-HMF

The reaction temperature is another important parameter for 5-HMF formation. To observe the effect of temperature on the concentration of 5-HMF, the liquid phase dehydration of fructose was studied by varying the reaction temperatures: 80-120°C and in the presence of hydrochloric acid (fig. 3).

Increasing the temperature from 80 to 120 °C, leads to an increase in 5-HMF maximum concentration from 11.84 to 64.23 mM. At higher dehydration temperatures the reaction mixture becomes dark due to the presence of soluble oligomers and insoluble humins are formed. This means that in the presence of HCl, at higher reaction temperatures, formation of humins and oligomerization is predominant among the other side reactions. Since the fructose dehydration is temperature-sensitive, the following experiments were carried out using mild conditions with the reaction temperature of 120°C, at which the formation of side products is at low level.

Influence of stirring rate on the fructose conversion to 5-HMF

The influence of stirring rate (300-900 rpm) on the liquid phase fructose dehydration is shown in figure 4. Depicted results highlight that an increase in the stirring rate from 300 to 900 rpm leads to an increase in 5-HMF concentration. Increasing the stirrer speed allows a better contact between catalyst and fructose and increases the probability of effective collisions, when particles collide with enough energy (activation energy) and correct orientation.

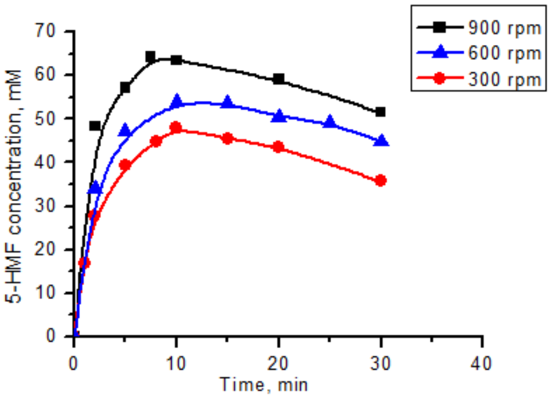

Fig. 4. Influence of stirring rate on the 5-HMF concentration (microwave irradiation, temperature: 120°C, catalyst HCl)

Fructose dehydration using heterogeneous catalysts

The development of a more effective catalyst and process for efficient dehydration of carbohydrates in heterogeneous catalysis is still a challenge even if a series of processes have been studied. The current trend is to work in friendly environments, thus we tried to replace hydrochloric acid with other solid acid catalysts. The advantage of these catalysts is that they can be easily removed by a simple filtration, regenerated and reused after reaction. Several cationic resins were screened as catalysts for the catalytic dehydration of fructose using water as green solvent. The ion exchange resins used were Amberlyst, Purolite and Dowex that contain sulfonic groups. The influence of the catalyst on the 5-HMF concentration for microwave assisted synthesis in the presence of water is presented in figure 5.

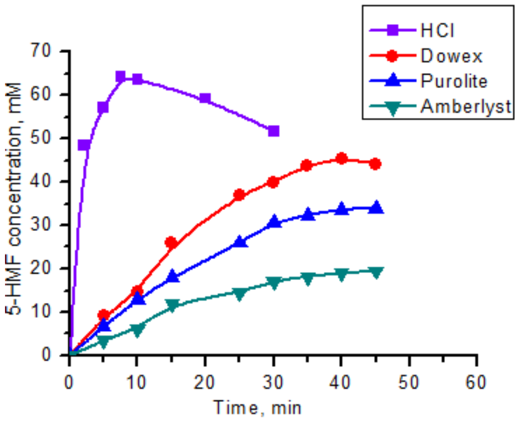

Fig. 5. The influence of the catalyst on the 5-HMF concentration (Reaction conditions: microwave irradiation, temperature: 120°C, stirring rate 900 rpm).

As is shown in figure 5 for the same reaction conditions using hydrochloric acid as a catalyst, higher concentrations of 5-HMF were obtained. This behaviour is due high mobility of the catalyst and fructose molecules in the reaction mixture leading to collisions with substrate molecules. Also, it has been observed that the optimum time of reaction in the case of hydrochloric acid is less than the optimum reaction time for ion exchange resins (10 min and 40 min, respectively). The screening studies revealed that Amberlyst catalyst was less active under the reaction conditions than Purolite and Dowex resins. The lower activity of heterogeneous catalysts is due to the lower active site concetration on the surface of catalysts. Only the surface atoms are active. The catalyst activity can also be reduced by the side-product formation (humins) that can be adsorbed and can block the active centers.

Conclusions

The suitable conditions for the microwave assisted production of 5-HMF from fructose was studied in this paper. A comparative study between conventional and microwave assisted synthesis has been peformed and the microwave irradiation led to an increase of 5-HMF concentration by almost 100% (from 19.45mM to 40.93 mM) and the reaction time was two times shorter. Moreover, the consumption of the specific energy for microwave synthesis is lower compared with conventional method (with 3 magnitude order). To establish the best conditions for microwave assisted fructose dehydration, the influence of several parameters (catalyst, temperature, time, stirring rate) was studied. The highest concentration of 5-HMF was obtained for a temperature of 120°C, stirring rate of 900 rpm and 10 min. Heterogeneous catalysts (ion exchange resins) were screened for fructose dehydration using water as green solvent. The 5-HMF concentrations are lower for solid catalysts than for mineral acid catalyst but considering the other advantages of heterogeneous catalysts, e.g., simple separation, reusability, they can be successfully used for dehydration of fructose. This microwave assisted process proves to be a cost-efficient altenative to the conventional one and, due to this economic advantage, should be employed more often in transformation of biomass into biofuels and valuable bio-based products.

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