Biomass and Bioenergy 117 (2018) 38–43

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: www.elsevier.com/locate/biombioe

Research paper

Microwave assisted synthesis of 5-ethoxymethylfurfural in one pot from D-fructose by using deep eutectic solvent as catalyst under mild condition

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ARTICLE INFO

Keywords:
Biomass
Biofuel
Deep eutectic solvent (DES)
Microwave irradiation
5-Ethoxymethylfurfural
One-pot synthesis

ABSTRACT

5-Ethoxymethylfurfural (EMF), a potential and viable biofuel, was synthesized in one pot from D-fructose by using cheaper and environmentally friendly deep eutectic solvents (DESs) at mild condition. A variety of DESs were synthesized and used under microwave irradiation to get the maximum conversion of fructose and selectivity to EMF. Among various DESs the combination of choline chloride-oxalic acid gave the highest conversion of D-fructose (92%) with yield of EMF (74%) in 3 h at 343 K. A systematic study on effect of different parameters on reaction rate and selectivity was undertaken. Ethyl levulinate (EL) is also formed due to a parallel reaction of D-fructose with ethanol and water generated in-situ coupled with a consecutive reaction of ethanol with EMF. The formation of EL, which is also a fuel additive, was controlled by using lower temperature. DESs are highly reusable and show good activity up to four cycles. All raw materials used in this process are derived from biomass. The process parameters were optimized to get maximum yield of EMF. The process is green.

1. Introduction

The prices of natural gas and oil, which are non-renewable, are greatly influenced by volatile markets as well as are increasing rapidly due to diminishing resources [1,2]. Hence, production of fuel from biomass is a hotly pursued area of research worldwide [3,4]. Carbohydrates are abundant, cheaper, and easily available renewable biomass and can be transformed into various value added chemicals [5]. 5-Hydroxymethyl furfural (HMF), which is particularly obtained by triple dehydration of sugar (hexoses) is a versatile platform molecule for synthesis of a spectrum of important chemicals such as 2,5-dimethylfuran (DMF), 2,5-furandicaboxylic acid (FDCA), 2,5-bis(hydroxylmethyl)furan (BHMF), 5,5′(oxy-bis(methylene))bis-2-furfural (OBMF), 2,5-diformylfuran (DFF), γ-valerolactone (GVL), alkyl levulinates and 5-ethoxymethylfurfural (EMF) [6–8].

EMF is a liquid biofuel having more energy density than ethanol and closer to diesel, and hence it is a potential additive to diesel and gasoline [8–11]. EMF is also used as a flavoring agent in wines and beers [12]. Various reports demonstrated that EMF was directly synthesized from HMF [13–17] or from sugar by one pot strategy [18–22]. High cost and instability of HMF makes it an unfavorable starting material to synthesize EMF. However, EMF can be synthesized from monomers of sugar, namely, glucose and fructose in a single reactor by a two-step process. Firstly, the acid catalyzed triple dehydration of the sugars gives HMF as an intermediate, which is further converted into EMF by etherification with ethanol. Various studies have shown that the yield of EMF from glucose is lower than that from fructose because the former requires one additional step, namely, isomerization of glucose into fructose and therefore the overall yield of EMF decreases [10,23]. Hence, to obtain EMF on large scale, fructose is a better starting material.

In previous reports, EMF was synthesized from fructose by using various homogeneous acid catalysts such as $H_3PW_{12}O_{40}$, $FeCl_3$, $AlCl_3$, $BF_3{\cdot}(Et)_2O$, H_2SO_4, and HCl [19,24–27], heterogeneous acid catalysts (K-10 clay-HPW, graphene oxide, HSM-SO_3H, Fe_3O_4@SiO_2-HPW, sulfated zirconia, Al-MCM-41, $[MIMBS]_3PW_{12}O_{40}$) [18,22,23,27–29], SO_3H functionalized ionic liquid [30], H-beta zeolites [10], and acidic resins (Amberlyst-15, Amberlyst-131) [9]. The use of homogeneous acid is not convenient, because it causes reactor corrosion and also requires neutralization during reaction work-up producing a large amount of waste. The use of heterogeneous acids for this reaction is also not suitable because it requires either harsh reaction condition or long reaction time. Zeolites and resins are good solid catalysts, but costly making the process more expensive for the production of EMF on large scale. The foregoing suggests that there is a need to develop more efficient and economical process for synthesis of EMF. The objective of the current work was therefore to find newer, cheaper and better alternative for conversion of sugar directly into EMF. In this connection

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https://doi.org/10.1016/j.biombioe.2018.07.008
Received 9 July 2016; Received in revised form 29 June 2018; Accepted 10 July 2018

Table 1
Reported processes for conversion of D-fructose into EMF vis-à-vis current work.

#	Catalyst	Solvent	Temp K	T (h)	X_F (%)	Y_{EMF} (%)	ref.
1	H-USY (6) + Amberlyst-15	Ethanol	369	11	83	67	10
2	30 wt% K-10 clay-HPW	Ethanol	373	24	100	61.5	28
3	$FeCl_3$	Ethanol + [Bmim]Cl	393	24	100	40	24
4	HPW	Ethanol	413	2.1	99	64	12
5	cellulose sulfuric acid	Ethanol + DMSO	373	12	95	72.5	21
6	Fe_3O_4@SiO_2-HPW	Ethanol	373	24	100	54.8	22
7	$AlCl_3$	Ethanol	373	11	–	71.2	16
9	Graphene Oxide	Ethanol + DMSO	373	24	100	71	23
10	$AlCl_3{\cdot}6H_2O/BF_3{\cdot}(Et)_2O$	Ethanol	383	5	99	44.3	25
11	HSM-SO_3H	Ethanol	373	24	–	63.1	18
12	$[MIMBS]_3PW_{12}O_{40}$.	Ethanol	383	24	98.1	90.5	29
13	**DES (ChCl-Oxalic acid)**	**Ethanol**	**343**	**3**	**92**	**74**	**This work**

deep eutectic solvents were thought as potential candidates.

Deep eutectic solvents (DESs) are green solvents which can be used as an alternative for ionic liquids because of their exceptional properties like non-toxicity, low flammability, low melting point, low vapor pressure, stability towards moisture and air, high thermal stability, easy biodegradability and recyclability [31–34]. Along with their excellent solvent properties, DESs show good catalytic properties [31,35]. The preparation of DES is simple and starting materials required for their preparation are cheaper and easily available [36]. Many reports have shown their use in various organic transformations [37–39]. It was also found that DESs are good reaction media for HMF synthesis because of their excellent solvation properties which prevent the rehydration of HMF into side products [32,40]. Choline chloride (ChCl) based DESs were made by Abbott et al. [41]. ChCl is much cheaper and easily obtained from biomass or fossil resources. Combination of ChCl with suitable hydrogen bond donors like carboxylic acids, urea, and polyols rapidly forms DESs [32]. The DESs obtained from ChCl and carboxylic acid show excellent solvent properties as well as good acidity [33]. Thus, it was envisaged that DESs should be systematically investigated for the synthesis of EMF from fructose.

In order to make the overall process energy efficient, the use of microwave irradiation was also considered along with the most active DES selected for preparation of EMF in this work. Application of microwave irradiation in intensification of chemical reactions has grown rapidly because it is an efficient, clean and selective technique [42]. As compared to conventional heating, microwave irradiation enhances the rate of reaction substantially at much lower temperature and gives high product yield [43]. Many studies have shown that a long reaction time is a major drawback in one pot synthesis of EMF [27]. The increase in reaction time also increases the formation of side products and results in decrease in selectivity of EMF.

From the foregoing, it was decided to use DESs and microwave irradiation to develop an energy- and time-efficient process for the synthesis of EMF from fructose.

2. Experimental

2.1. Materials

All chemicals such as D-fructose, ethanol, choline chloride, oxalic acid, malonic acid, succinic acid, malic acid, tartaric acid and itaconic acid were procured from S. D. Fine Chemicals Ltd. Mumbai, India.

2.2. Synthesis of DESs

All DESs were synthesized and analyzed according to various reported methods [32,33]. Herein, only a brief synthetic process is given. Before use of ChCl, it was recrystallized from absolute EtOH and dried at 373 K in vacuum oven for 4 h. Also, all dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, malic acid, tartaric acid and itaconic acid were dried at 373 K prior to their use. For synthesis of ChCl-oxalic acid deep eutectic solvent, ChCl and oxalic acid were mixed in 1:1 mol ratio and heated at 373 K for 5 h. The transparent homogeneous liquid so obtained was directly used for EMF synthesis. For the synthesis of various DESs, different dicarboxylic acids were used and the procedure was the same as given above.

2.3. Typical reaction setup and procedure for EMF synthesis

The one pot conversion of D-fructose to EMF was performed under conventional heating as well as under microwave heating.

2.3.1. Conventional heating

The EMF synthesis in conventional heating was performed in a $5 \times 10^{-5}\,m^3$ capacity glass reactor with 5×10^{-2} m internal diameter and four baffles. The reactor was also equipped with a pitched turbine impeller to properly maintain agitation speed. In a typical reaction, D-fructose (2×10^{-3} mol), ethanol (85×10^{-3} mol) and ChCl-oxalic acid (6×10^{-3} mol) was taken in glass reactor and stirred at room temperature until homogeneous solution obtained. The total reaction volume was $6 \times 10^{-6}\,m^3$.Then, the reaction was commenced by heating it in a thermostatic oil bath at desired temperature.

2.3.2. Microwave heating

The EMF synthesis in microwave heating was performed in Discover CEM-SP (1245 model) microwave reactor. The details of set up were well described in our previous reports [42,43]. A typical reaction procedure for one pot conversion of D-fructose into EMF was the same as described for conventional heating. The yield obtained of EMF by using DESs under microwave heating is higher than previous reported methods (Table 1).

2.4. Analysis of reaction mixture

The analysis of collected samples, which mainly contained D-fructose, HMF, EMF and ethyl levulinate, was done on HPLC (Agilent 1260 infinity) by using Hi-plex H column (300 × 7.7 mm) and refractive index (RI) detector. The mobile phase used was $5\,mol\,m^{-3}\,H_2SO_4$ solution with $1 \times 10^{-8}\,m^3s^{-1}$ flow rate. During analysis the temperature of column was maintained at 333 K. The product was confirmed by GC-MS and ^1H NMR.

3. Results and discussion

Scheme 1 depicts the reaction of D-fructose with ethanol leading to HMF which further reacts with ethanol to produce EMF. In the absence of any side reaction, it is a series reaction which should lead to EMF.