Fuel 237 (2019) 263–275

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Direct conversion of furan into levulinate esters via acid catalysis

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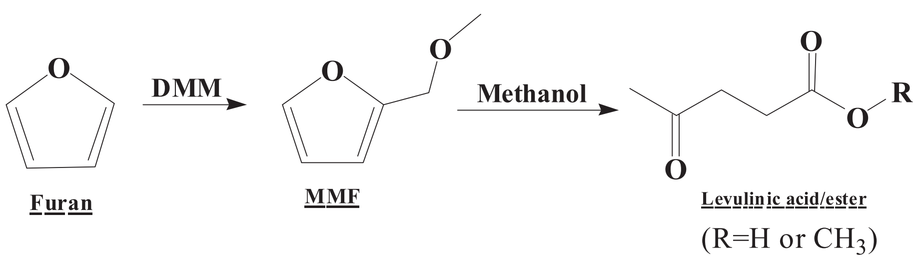
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Furan
Methyl levulinate
Acid-catalysis
Dimethoxymethane/methanol
Mechanism for polymerization

ABSTRACT

This study developed a method for the direct conversion of the biomass-derived furan to the methyl levulinate, a platform molecule, via acid-catalysis in dimethoxymethane/methanol. Dimethoxymethane acted as the electrophile to transform furan into 2-methoxymethyl-furan (the ether of furfuryl alcohol). The following step of acid catalysis converted 2-methoxymethyl-furan to methyl levulinate. No hydrogenation catalyst or hydrogen was used in the process, which was the new reaction route for the conversion of furan to the value-added levulinic acid/ester. Polymerization was the main challenge in this reaction route, which could be suppressed but to some limited extent with methanol as a co-reactant/solvent in the reaction medium. The polymerization of furan and cross-polymerization reactions between dimethoxymethane (the reactant) and methyl levulinate (the targeting product) via Aldol condensation were the important reasons for the decreased production of methyl levulinate. The DRIFTS and TG-MS studies showed that the coke formed from the polymerization of furan contained more aliphatic structure, more carboxylic groups and methyl groups, while the coke from methyl levulinate contained more carbonyl groups and more conjugated π-bonds, projecting the structural difference of furan and methyl levulinate.

1. Introduction

Methyl levulinate is a bio-based platform chemical with versatile applications, including the use as food additive, cosmetic additives, plasticizer, solvents, fuel additives or the feedstock for manufacturing the high value pharmaceutical chemicals [1–5]. Several methods have been developed to produce levulinates from sugars and furans. The most traditional route is the dehydration of the cellulose-derivated glucose to 5-hydroxymethylfurfural (HMF), and the followed conversion of HMF via acid catalysis produces levulinic acid in aqueous

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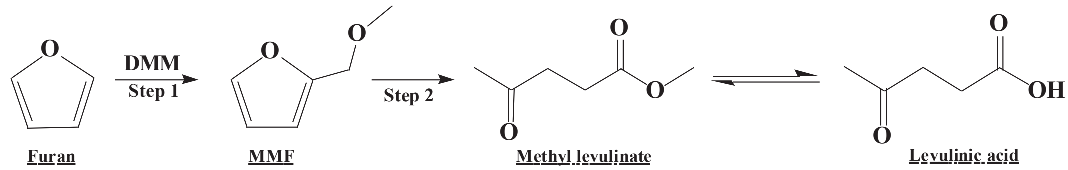
https://doi.org/10.1016/j.fuel.2018.09.148
Received 5 July 2018; Received in revised form 17 September 2018; Accepted 28 September 2018



Scheme 1. Conversion of furan to methyl levulinate and levulinic acid in DMM/Methanol. All the products were detected by GC-MS fragments. Step 1: Electrophilic substitution reaction; Step 2: acid catalysis reaction.

Table 1
Conversion of furan to methyl levulinate (ML) and levulinic acid (LA).[a]

Entry	Key parameters		Yield (%)	
	Reaction medium	Furan conversion	ML	LA
1	DMM	96.5	56.5	2.5
2	DMM/Methanol	97.2	67.9	2.2
3	DMM/Ethanol	97.9	46.3[b]	1.6
4	DMM/H_2O	99.7	15.4	5.8
5	DMM/THF	97.9	53.6	2.0
6	DMM/Toluene	97.6	50.8	1.0
7	DMM/Acetone	96.0	52.5	2.9
8	DMM/DMSO	81.8	31.4	5.0
9	DMM/Guaiacol	78.2	27.5	6.1
10	DMM/Isoeugenol	45.0	7.8	0.0
11	DMM/Ethyl formate	95.1	46.4[b]	2.9
12	DMM/Ethyl acetate	97.2	49.8[b]	1.7
13	DMM/DMF	0.0	0.0	0.0

[a] Other reaction conditions: Furan: 4 g; Reaction temperature: 170 °C; D008 catalyst: 3.4 wt%; Solvent: 56 mL; DMM: solvent = 10: 4; t = 90 min;

medium or levulinate esters in alcohols medium [6–8]. In addition to glucose, xylose could also be converted to levulinates via a one-pot conversion in alcohol medium with the presence of acid catalyst and hydrogenation catalyst [9], or in the presence of an acid catalyst [10].

In addition to the C6 and C5 sugars, the furans can also be potentially used as the feedstock for the production of levulinic acid/ester. For example, the acid catalysis conversion of furfuryl alcohol or HMF in alcohol medium could selectively produce levulinates [11–15]. The acid catalysis of furan, nevertheless, produces benzofuran but not methyl levulinate or levulinic acid [16]. Furan is actually a very important product in catalytic pyrolysis of biomass [17–22], which is mainly used to produce tetrahydrofuran (THF) for the use as solvents, pyrrole or thiophene as value-added chemicals [23–28]. If furan could also be converted to levulinic acid/ester via acid catalysis, there will be a new addition for the application of furan and another alternative route for manufacturing levulinic acid/esters.

Via acid catalysis in alcohol medium, furfuryl alcohol can be selectively converted to methyl levulinate [29–33], while furan cannot. The structural difference between furan and furfuryl alcohol mainly lies

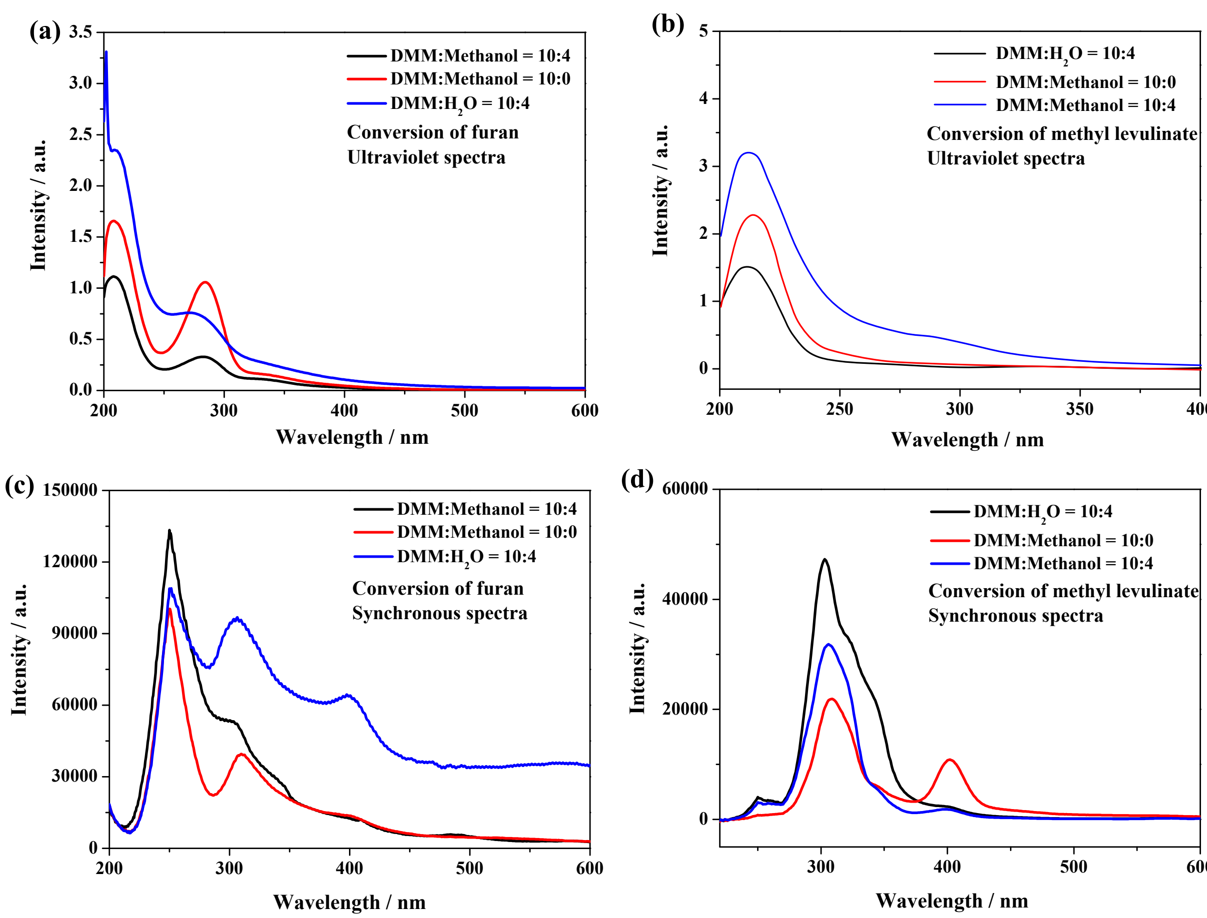


Fig. 1. Ultraviolet spectra and synchronous spectra for the soluble polymers produced from the acid catalysis conversion of furan or methyl levulinate in different co-solvents.