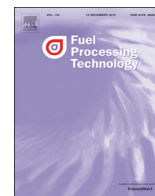




ELSEVIER

Contents lists available at ScienceDirect

## Fuel Processing Technology

journal homepage: [www.elsevier.com/locate/fuproc](http://www.elsevier.com/locate/fuproc)

Research article

## Production of 2-methylfuran from biomass through an integrated biorefinery approach

Inaki Gandarias<sup>a,\*</sup>, Sara García-Fernández<sup>b</sup>, Iker Obregón<sup>a</sup>, Iker Agirrezabal-Telleria<sup>a</sup>, Pedro Luis Arias<sup>a</sup><sup>a</sup> Department of Chemical and Environmental Engineering, School of Engineering, University of the Basque Country (UPV/EHU), Bilbao, Spain<sup>b</sup> Gaiker Technology Centre, Parque Tecnológico de Bizkaia, Edificio 202, 48170 Zamudio, Spain

## ARTICLE INFO

## Keywords:

Hydrogenolysis  
Cu-Co  
Bio-refinery  
Furfural  
Biofuel  
2-methyltetrahydrofuran

## ABSTRACT

Herein we present a high yield 2-methylfuran production process with the required features to be implemented in a future integrated biorefinery. The strategy is based on the right solvent selection, 2-methyltetrahydrofuran, which i) can be used to extract the reactant, furfural, from the aqueous solution obtained after corncob biomass hydrolysis; ii) allows for highly selective 2-methylfuran production from furfural with up to 80% yields and iii) presents suitable biofuel properties in the gasoline range. Using this innovative approach, two energy intensive separation steps are avoided: the initial furfural purification and the final solvent/product complete separation. Further benefits of this process arise from the developed low-cost, selective, and reusable Cu-Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

## 1. Introduction

Furfural (FUR) is considered the main building-block molecule for the upgrading of the hemicellulosic biomass fraction, based on the large variety of products that can be derived from it [1]. Some of these products such as tetrahydrofuran (THF) [2], ethylfurfuryl ether [3], 2-methylfuran (MF) [4, 5], long chain (C-15) hydrocarbons obtained from furanic condensation intermediates [6, 7] and 2-methyltetrahydrofuran (MTHF) [8] meet the requirements to be used as biofuels. Among these compounds, MF is considered as the most promising gasoline bio-additive based on its suitable fuel properties (see Table 1), and its relatively low manufacture cost and CO<sub>2</sub> emissions when produced from FUR [9]. MF has a high octane number (103) [10], higher thermal efficiency than gasoline [11] and it can be directly used in gasoline blends (10 vol%) without loss of fuel economy or detrimental impact on engine gear [9]. Despite all its potential, the use of MF as biofuel is hampered by the lack of a technically and economically feasible production process.

FUR is currently produced from food crop residues and wood wastes using H<sub>2</sub>SO<sub>4</sub> as homogenous catalyst. The hemicellulose fraction of the biomass is first transformed into the corresponding monosaccharides, through a hydrolysis reaction, which are subsequently dehydrated to FUR. In order to avoid acid catalyzed degradation reactions, FUR is continuously extracted from the reactor by steam stripping and further purified from water by a double distillation [15]. Such commercial

processes result in a starting material (FUR) with a market price fluctuating from 2.1 to 1.2 \$·L<sup>-1</sup> in the 2012–2016 period [16]. Taking into account the price of the most used gasoline bio-additive (ethanol), estimated to be around 0.40 \$·L<sup>-1</sup> by 2020 [17], competitive MF prices for biofuel use would require more than three times cheaper FUR. Although commercial FUR production shows very low yield and energy efficiency [15], the required FUR price reduction seems a chimera in the mid-term. Therefore, any proposal to form MF from pure FUR faces an obstacle difficult to overcome: the reactant is significantly more expensive than the target biofuel. This is the case for gas-phase FUR hydrogenation processes [18–22], where the presence of small amounts of water in the feed stream entering the reactor promotes condensation reactions that deactivate the catalyst [23].

A more feasible approach would be to carry out the reaction in liquid phase using a much cheaper feed, *i.e.* the aqueous FUR solution obtained after the steam stripping step. Water, however, is reported to strongly promote furan ring rearrangement to cyclopentanone (CPO) [24] (see Fig. 1), which can be used as raw material for fuel precursors [25, 26]. Besides, FUR and furfuryl alcohol (FOL) polymerization are well-known acid catalyzed reactions [27], that can even be catalyzed by protons coming from water at the used reaction temperatures [28]. As in the case of the gas phase hydrogenation, the surface adsorption of these water-insoluble polymers deactivates the active sites responsible of the FOL hydrogenolysis to MF [29].

These techno-economic evidences support the use of organic

\* Corresponding author at: Department of Chemical and Environmental Engineering, School of Engineering, University of the Basque Country (UPV/EHU), Bilbao, Spain.  
E-mail address: [inaki.gandarias@ehu.eus](mailto:inaki.gandarias@ehu.eus) (I. Gandarias).

<https://doi.org/10.1016/j.fuproc.2018.05.037>

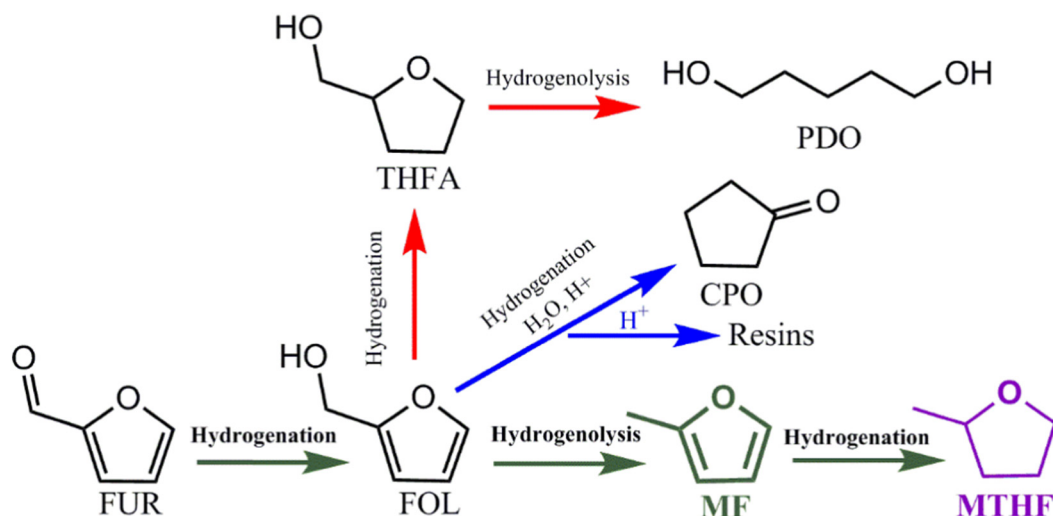
Received 22 March 2018; Received in revised form 14 May 2018; Accepted 31 May 2018  
0378-3820/ © 2018 Published by Elsevier B.V.

**Table 1**

Properties of MF, MTHF, DMF and TOL compared to gasoline and ethanol. Adapted from [10–14].

	RON 95 E10 Gasoline (EN51626-1)	Ethanol	MF	MTHF	DMF	TOL
Boiling T. (K)	309–463	351	337	351	367	384
Vapor P at 20 °C (kPa)	–	5.8	13.9	13.6	–	2.8
Low Heating Value (MJ/L)	30.8	21.1	27.6	28.2	30.1	35.3
RON	> 95	109	103	86	119	121
Distribution Coefficient $K_D^a$	–	–	–	$7.2 \pm 0.4$	$4.9 \pm 0.2$	$4.9 \pm 0.3$

<sup>a</sup> See Supplementary Data for information regarding the experiments for obtaining the distribution coefficients ( $K_D = C_{\text{FUR,extract}} / C_{\text{FUR,raffinate}}$ ).



**Fig. 1.** Reaction scheme for FUR transformation into MF and main routes for by-products formation. Tetrahydrofurfuryl alcohol (THFA); 1,5-pentanediol (PDO).

solvents and liquid phase reaction. The highest reported MF yields (50–80%) in liquid phase were reported using 2-propanol (2-PO) as solvent [30–32]. However, the use of 2-PO entails the same relevant drawback as gas phase processes: FUR needs to be double distilled from water and then diluted in the alcohol. Moreover, as 2-PO has not the required fuel properties, the final 2-PO/MF mixture should be completely separated, which further increases the energy demand and cost of the process.

Under this background, technically and economically viable MF production has to be addressed from an integrated biorefinery approach. Hence, this work presents a holistic process design to produce MF from biomass in high yields while minimizing the separation and purification steps. This process includes, the production of aqueous FUR from corncob biomass, the extraction of FUR from the aqueous phase and its selective conversion into MF.

## 2. Materials and methods

### 2.1. Catalyst synthesis

Monometallic Cu and bimetallic Cu-M catalysts (M = Ni, Co, Fe or Sn) were prepared by wet (co-)impregnation (WI). The support ( $\gamma$ - $\text{Al}_2\text{O}_3$ , Alfa Aesar,  $\geq 99.9\%$ ;  $S_{\text{BET}} = 202 \text{ m}^2/\text{g}$ ;  $V_{\text{pore}} = 0.81 \text{ mL/g}$ ;  $d_p = 77 \text{ \AA}$ ) was impregnated using the calculated amounts of metal precursors, to reach the specified metal loadings, dissolved in deionized water (or methanol in the case of Sn):  $\text{Cu}(\text{NO}_3)_2 \cdot 5/2\text{H}_2\text{O}$  (Alfa Aesar, 98.0%),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich, 99.99%),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Quimivita SA, 98.0%),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Alfa Aesar,  $\geq 98.0\%$ ),  $\text{Sn}(\text{C}_2\text{H}_3\text{O}_2)_2$  (Sigma-Aldrich, 98.0%). The mixture was stirred for 2 h in a rotatory vacuum evaporator at 90 rpm and room temperature (RT). The solvent was removed afterwards at 333 K under vacuum. The samples were further dried overnight at 383 K and subsequently calcined under flowing air in a tubular oven for 4 h at 723 K (heating rate of  $2 \text{ K min}^{-1}$ ). The catalysts were labelled as xCu-yM/ $\gamma$ - $\text{Al}_2\text{O}_3$ , where M is

the promoter metal (Ni, Co, Fe or Sn), x and y refers to Cu and M content respectively in wt%.

Prior to the activity tests, the active metal species were reduced in a tubular furnace for 1 h under pure  $\text{H}_2$  flow ( $100 \text{ mL min}^{-1}$ ) at 723 K ( $10 \text{ K min}^{-1}$  heating rate).

### 2.2. Catalysts characterization

#### 2.2.1. XRD

X-ray diffraction (XRD) patterns of calcined and reduced catalyst samples were obtained with an Xpert-Pro device equipped with a PW3050/60 goniometer and Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) working at 40 mA and 40 kV. The patterns were recorded in a  $2\theta$  range from  $10^\circ$  to  $90^\circ$  with a  $0.026^\circ$  step size. Phase identification was carried out by comparison with the power diffraction files (PDF) using the Xpert-Pro High Score tool, and with the literature data.

#### 2.2.2. ICP-OES

The metal contents of the calcined catalysts were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin-Elmer Optima 2000 instrument. Prior to the analysis, solid samples were digested in a microwave oven with a mixture of  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{HF}$  (3:2:3 in volume ratio). Possible leaching of the catalyst metal species during the activity tests was examined on the same device quantifying the concentration of Cu and Co in the filtrated liquid reaction solution.

#### 2.2.3. TPR

Temperature-programmed reduction (TPR) profiles were obtained using a Micromeritics AutoChem II 2920 instrument equipped with a TCD detector. In order to eliminate water and other impurities from the surface, the calcined samples were heated at 523 K under a He stream for 2 h before the analysis. Subsequently, they were reduced in a stream of 5 vol%  $\text{H}_2/\text{Ar}$  ( $50 \text{ mL min}^{-1}$ ) from 313 K up to 1223 K at a

Download English Version:

<https://daneshyari.com/en/article/6656301>

Download Persian Version:

<https://daneshyari.com/article/6656301>

[Daneshyari.com](https://daneshyari.com)