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Kinetics of dimethylfurane production by dehydration and hydrogenolysis of carbohydrates



 $\rightarrow DMF_{(L)}$

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HIGHLIGHTS

GRAPHICAL ABSTRACT

Dehvdration - Cu/ Al, O,

- Evidences of biomass conversion into compounds with potential for use as fuel.
- Production of DMF by a catalytic heterogeneous one-step process.
- Conversion of fructose into HMF and DMF with a bifunctional catalyst.
- DMF indicated as a product with combustion characteristics comparable to gasoline.

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- $Biomass \longrightarrow Polyssacharides \longrightarrow Monossacarides_{(L)}$
 - Monossacharides_(L.)

ABSTRACT

To produce 2,5-dimethylfurane (DMF), an organic compound with fuel properties, carbohydrates were processed in a slurry reactor, by catalytic dehydration and hydrogenolysis. Fructose dehydration was evaluated with the conversion of fructose at a range of 423-463 K and under a pressure of 34.5 and 51.7 bar of argon in the presence of a γ -Al₂O₃ catalyst. The simultaneous dehydration/hydrogenolysis operation was also carried out with fructose in the presence of a Cu/γ-Al₂O₃ catalyst at 443 K and under 34.5 bar of hydrogen. Experimental data indicated that fructose via dehydration was transformed into 5-hydroximethylfurfural (HMF) and then, via hydrogenolysis into DMF. Model equations, including Langmuir-Hinshelwood's kinetic laws were fitted to the experimental data, providing the quantification of the effects of the operating variables (temperature, pressure, copper wt.% in the catalyst). Dehydration of fructose into HMF via interaction with alumina was represented by the specific rate $k_1 = 3.28 \times 10^{-2}$ $g L^{-1} min^{-1}$, while the specific rate of hydrogenolysis of HMF into DMF on the copper sites was as $k_3 = 2.28 \times 10^{-2} \text{ g L}^{-1} \text{ min}^{-1}$.

HMF(L)

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Hydrogenolyis – \underline{Cu}/Al_2O_3

1. Introduction

The growing need for alternative energy sources has also directed its search to energy production from vegetal materials. Lignocellulosic and starchy biomasses with high contents in glucose and fructose may be transformed into substitutes of petroleum products, such as HMF (5-hydroxymethylfurfural) and DMF (2,5-dimethylfuran). This last one presents emission and combustion characteristics comparable of gasoline (Lower Heating Values: DMF, 33.7 MJ/kg; gasoline, 42.9 MJ/kg) which means that it can be easily adopted with current spark-ignition engine technologies without the need for major modifications. Its employment as fuel in an Otto engine has a performance similar to gasoline [1].

The dehydration of carbohydrates to HMF has been evaluated, and many strategies have been tested to increase the yields [2]. HMF has been obtained via homogeneous acid processes, in aqueous [3,4] and nonaqueous [5] media, with mixture of solvents [6–9], or under subcritical conditions with a heterogeneous catalyst [10]. By reacting fructose with hydrochloric acid, HMF is



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obtained and then via a catalytic hydrogenolysis [11] it may be transformed into DMF. Akien et al. [12] identified several intermediates and different paths for the acid catalyzed conversion of fructose to HMF. In general, it is proposed that fructose is a necessary intermediate in the route to convert glucose to HMF [13].

The acid-catalyzed conversion of HMF produces levulinic and formic acids. Aldol addition and condensation are proposed as reaction steps in the acid-catalyzed growth of humins, that are dark-colored by-products [14]. As an alternative to two-step process, carbohydrates can be dehydroxylated to DMF by the use of a dual catalytic system consisting of both an acid homogeneous process and a heterogeneous one with a metallic catalyst [16,17]. The mechanism of one-step conversion of fructose to DMF indicates that the acid acts as a dehydration agent while metal is hydrogenation catalyst for C=O and C=C bonds [18,19].

The purpose of this work was to evaluate the kinetic behavior of the one-step heterogeneous process of DMF production, in which dehydration and hydrogenolysis were carried out simultaneously in the presence of a heterogeneous bifunctional catalyst.

2. Experimental

2.1. Catalyst formulation

The copper catalysts were prepared using an alumina ($S_p = 208 - m^2 g^{-1}$, $d_p = 85-120 \mu m$, Degussa, Br) as support. The systems were formulated by the incipient wetness impregnation method with Cu $(NO_3)_2 \cdot 3H_2O$ solutions (Merck Chemicals, Br). The catalysts, after slowly dried at 333 K for 24 h, were calcinated at 773 K under an argon flow ($100 \text{ cm}^3 \text{ min}^{-1}$, 5 h) followed by reduction at 509 K under an argon and hydrogen flow (1:1 v/v, $100 \text{ cm}^3 \text{ min}^{-1}$, 3 h). The formulated catalysts were characterized by metal contents determinations (atomic absorption spectrophotometry, A.A.S., Model-CGAA7BC), textural characteristics via BET-method (BET-N₂, ASAP, 2010), surface acidity by TPD of n-butyl amine (DSC Q1000, TA Instruments) and identification of solid phases by X-ray diffraction (XRD, Cu-K source, Siemens D5000).

2.2. Evaluation of the catalysts and processing

The dehydration and hydrogenolysis experiments were carried out in a slurry reactor (Parr Inst., Mod. 4532, USA), where a thermal sensor and external heating provided controlled temperatures in the reactor with an accuracy of ±1 K. Liquid samples were collected from the reactor where a cylindrical porous filter (20 mm \times 5 mm) was placed inside the reactor immersed in the liquid and connected to a pipe which passes through the cover of the reactor. The liquid was transported through the porous filter due to the high pressure inside the reactor.

The residual reactant and the products were analyzed with a high performance liquid chromatograph (HPLC, Pro Star, Varian). The chromatograph was equipped with a refractive index detector (350 RI) coupled to a Biorad Aminex HPX-87H column (300 mm \times 7.8 mm, mobile phase: H₂SO₄ 0.01 mol L⁻¹, 0.60 cm³ - min⁻¹, 323 K) to analyze fructose; a UV detector (PDA 335) coupled to a Varian C18 column (250 mm \times 4.6 mm, mobile phase: aceto-nitrile/water, 5:95 v/v, 1.00 cm³ min⁻¹, 295 K) to analyze HMF at 283 nm; and a UV detector (SPD-20A) coupled to a Phenomenex C18 column reverse phase (150 mm \times 4 mm, mobile phase²: methanol/water, pH 2, 0.70 cm³ min⁻¹, 308 K) to analyze DMF at 222 nm.

The alumina (γ -Al₂O₃, d_p = 85–120 µm, 10.0 g) was evaluated as dehydration catalyst by processing an aqueous solution of fructose (0.50 L, 40.0 g L⁻¹) at 423 K, 443 K, 463 K, under inert gas (Ar) pressures of 34.5 and 51.7 bar, respectively. Fructose was processed by

dehydration and hydrogenolysis employing a copper catalysts ($d_p = 85-120 \ \mu m$) operating in an aqueous solution (0.50 L, 40.0 g L⁻¹) at the presence of Cu/ γ -Al₂O₃ (10.0 g) at 443 K, under hydrogen pressure of 34.5 bar.

3. Results and discussion

Considering the purpose of DMF production from fructose, copper catalysts supported on alumina were formulated to promote dehydration and hydrogenolysis activities attributed to alumina and copper, respectively. To produce DMF from fructose, copper catalysts supported on alumina were prepared in order to promote the respective dehydration and hydrogenolysis. The alumina activity was indicated by the acidity (moderate and strong) of its surface. The desorption activation energies used to indicate the acidity were evaluated employing an organic base (n-butylamine) via TPD analysis (Fig. 1), providing 26.89 kcal/mol for medium acidity and 38.66 values kcal/mol for strong acidity.

The copper/ γ -Al₂O₃ catalysts presented a Cu loading of 1.95, 3.31 and 6.79 wt.%. Their specific surface areas and pore volumes were 208 m² g⁻¹, 0.42 cm³ g⁻¹; 193 m² g⁻¹, 0.37 cm³ g⁻¹; and 178 m² g⁻¹, 0.36 cm³ g⁻¹, respectively. The values were lower than those of the alumina (214 m² g⁻¹, 0.43 cm³ g⁻¹), which may be attributed to a partial blockage of the pore structure of the support by metallic crystallites during the preparation of the catalyst. The copper was identified by XRD with 2 θ 43.6°, 50.8°, while the support γ -Al₂O₃ was identified with XRD with 2 θ 33.1°, 37.2°, 38.9°, 46.0°, 60.2°, 66.4°).

The samples of the reaction media, employing copper/ γ -Al₂O₃ and 40.0 g L⁻¹ of fructose, when analyzed, indicated presences of residual fructose, HMF, DMF, and other acids.

3.1. Dehydration activity of γ -Al₂O₃ catalyst

To evaluate the possibility to transform fructose by heterogeneous dehydration γ -Al₂O₃ was tested as catalyst in operations under inert gas (Ar). HMF and other compounds (melanoidins, humins [14] due to fructose polymerization and HMF by-reactions of aldol addition/condensation were obtained. In acidic water solutions, HMF is decomposed to levulinic acid and formic acid [12]. Its decomposition into levulinic acid and the production of humic acids by polymerization were presented as the most important secondary reactions to reduce the yield of HMF. The surface acidity of alumina, measured by DSC analysis via a TPD employing



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Fig. 1. Temperature programmed desorption by DSC analysis (μ V vs. temperature) of n-butylamine on adsorbent alumina (γ -Al₂O₃). Effect of the linear heating speed.

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