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# Hydrodeoxygenation of furfural-acetone condensation adducts to tridecane over platinum catalysts

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## ABSTRACT

The total hydrodeoxygenation of furfural-acetone condensation adduct ( $F_2A$ ) for obtaining tridecane is studied in this work. Three different Pt catalysts (using alumina, activated carbon, and graphite-MgZr oxide composite as supports) were tested using acetone as solvent (4.5 mmol/L of adduct) in a stirred batch reactor at 493 K and 5.5 MPa. Best results were obtained with Pt/ $Al_2O_3$ , yielding 21.5% of n-tridecane after 24 h reaction time, with carbon balances close to 96%. The performance of the carbon supported catalysts was poorer (both in terms of conversion, tridecane selectivity and carbon mass balance closure) mainly because of the strong adsorption of reactants and reaction intermediates, whereas the MgZr-HSAG also present activity for the undesired cleavage of C–C bonds of the condensation adducts. A kinetic model, considering serial-parallel reaction steps and first order dependence on the organic reactant has been successfully applied for modelling the results obtained with the three catalysts. The dependence of the kinetic constants on the catalyst properties suggest that metal dispersion and the concentration of weak acid sites are the main parameters affecting catalyst performance.

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## 1. Introduction

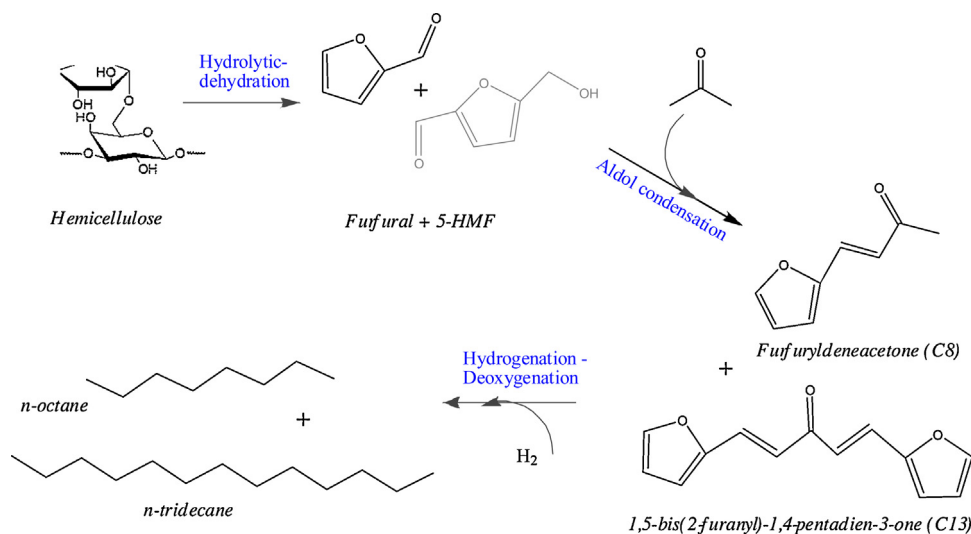
Production of renewable liquid fuels from biomass resources is nowadays of key interest, especially the promising aqueous-phase routes [1]. Among them, the process suggested by *Dumesic and co-workers*, proposing a catalytic process that allows obtaining diesel from biomass, is specially promising, since it does not require high temperatures, improving the global economy of the process [2,3]. The process sequence is summarized in Scheme 1. As it can be observed, it is a sequence of four steps with different catalysts at different reaction conditions: the hydrolysis of the sugar polymers; followed by the dehydration of sugars yielding aldehydes; the condensation of these compounds using a linking molecule (usually acetone); and the total hydrodeoxygenation of these condensation adducts to the final linear hydrocarbons, with similar properties as the mineral diesel.

Considering the promising results of these first studies, the efforts to improve this process have grown exponentially. In good agreement, the mechanism of sugar hydrolysis and dehydration has been deep studied, developing active and selective heterogeneous catalysts that allow optimizing the reaction conditions under the green-chemistry principles [4–6]. In the same way, the

activity of different mixed oxides and other basic catalysts in the aldol condensation of furfural and acetone is the topic of many papers, concluding that Mg-Zr mixed oxide is one of the most promising materials, reaching condensation yields higher than 80% at mild conditions [7,8]. Besides, this material yields higher selectivities to C13, increasing the quality of the resulting drop-in fuel upon hydrogenation of the resulting adducts.

The combustion enthalpy of these condensation adducts is very low because of the high oxygen content, which markedly decreases its quality as fuel and promotes corrosion problems [9]. Hydrodeoxygenation (HDO) is the most effective technology for increasing this combustion enthalpy by hydrogenation of double bonds and removing the oxygen as water at medium pressure and temperature [10]. This reaction was previously applied to oil-derivatives, and the references of applying this process to biomass upgrading have increased in the last ten years [11]. However, the hydrodeoxygenation of the furfural-acetone condensation adducts is much more difficult because of the complexity of the parent molecules, with different functional groups. Different successive steps are required for removing oxygen atoms (ketonic and cyclic ones), to hydrogenate the aliphatic chain and the furan-ring saturations as well as to open these rings. In addition, these steps must take place without breaking the carbon chain. The complexity of these individual reactions is even higher due to steric interactions among the different functional groups. As consequence, a very limited number of studies about the total HDO of these compounds

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**Scheme 1.** General mechanism for biodiesel synthesis from hemicellulosic biomass by dehydration-aldolization-hydrogenation/deoxygenation [3].

have been published [12–14]. Despite of the few references, noble metals (mainly Pt, Pd and Ru) seem to be the optimum catalysts for these reactions. However, each individual step is controlled by different parameters, so the role of acidity and metal dispersion in the global process is not negligible [15]. The reaction conditions must be well defined when these noble metals are used, in order to prevent side-reactions such as decarboxylation and decarbonylation [16] that would decrease the carbon chain length, decreasing the diesel quality.

Previous works of our research group are focused in the hydrodeoxygenation of the first condensation adduct (C8) obtained by the reaction between furfural and acetone. Pt was identified as the most active noble metal, obtaining more than 25% of n-octane after 24 h of reaction [17]. The reaction mechanism, the kinetic and the stability were also studied, identified the role of different morphological and surface catalytic properties in each reaction step. Consequently, different supports were tested concluding that the metal dispersion is the key parameter of this reaction, obtaining good results with supports as different as alumina, active carbon and high surface area graphites [15].

The aim of this paper is to study the hydrodeoxygenation of the second adduct: the C13-condensated (1,5-bis(2-furanyl)-1,4-pentadien-3-one), which presents the highest practical interest. Reaction conditions were chosen considering the best results obtained in the HDO of the first adduct (493 K; 2.0 MPa of H<sub>2</sub> with a total pressure of 5.5 MPa, 24 h) using Pt catalyst. Despite the higher complexity of this molecule, there are same functional groups in both cases, so it could be predicted that main effect of this complexity should be in the reaction time but not in the reaction temperatures. Besides, good results obtained at these conditions could be useful to consider the hydrodeoxygenation of both adducts (real mixture obtained after the condensation step) without any purification. The differences and similarities between the HDO of C8 and C13 condensated adducts are also discussed. Results obtained are used to corroborate the mechanism and the kinetic model, relating the results to the catalytic properties.

## 2. Experimental methodology

### 2.1. Catalytic preparation

Three different catalysts have been tested in this work: Pt/Al<sub>2</sub>O<sub>3</sub>; Pt/AC and Pt/MgZr/HSAG. 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was a commercial sample supplied by BASF. High surface area graphites (HSAG-500)

and active carbons (AC, GF 40) were stocked by Timcal S.A. and Norit, respectively. In order to study the possibility of implement the condensation and hydrodeoxygenation as one-step process, Pt/MgZr/HSAG500 was also prepared, by impregnation of Pt over the MgZr/HSAG prepared by co-precipitation, as it is detailed in previous work [8]. The possibility of carry out the condensation and hydrodeoxygenation steps as on-pot process was previously studied, leading to important economic and technical improvements [18].

Pt-catalysts were prepared by ion exchange, using metal chlorides as precursor (Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>, supplied by Aldrich). The solutions were prepared considering a final metal loading of 1%. The ion exchange was carried out in a rotavapor at 343 K for 24 h, after which the solvent was removed using a vacuum system. Resulting solids were washed, filtered, dried at 373 K and heating in He flow at a temperature rate of 5 K/min until 873 K, holding this temperature during 2 h. All the materials were activated before any characterization or activity test at 473 K for 2 h under flowing hydrogen gas.

### 2.2. Catalysts characterisation

The surface, morphological and physical-chemical properties of all the materials have been determined by N<sub>2</sub> physisorption (surface area, pore volume and diameter), XRD and TEM (metal dispersion), ICP-OES (metal loading) and NH<sub>3</sub>-TPD (acid sites strength and concentration). Details about each procedure and instruments have been reported in our previous works [15,17]. In order to better understand the catalytic activity of each catalyst, main characterisation results are summarised in Section 3.

### 2.3. Reaction studies

Reactions were carried out in a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE Seal) equipped with a PID temperature controller and a back pressure regulator. The reactor was loaded with 0.25 L of a acetone solution of 0.45 g of 1,5-bis(2-furanyl)-1,4-pentadien-3-one (labelled as "A" to better identified it) (Alfa Aesar, 98%). Considering the low aqueous solubility of this compound, acetone was used as solvent. This solvent was chosen taking into account economic reasons as well as the fact that acetone is already presented in the condensation reaction. Preliminary experiments using other solvents, including water and linear alkenes, show very low solubility of the C13 condensation adducts.

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