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Cyclopentanone: A raw material for production of C₁₅ and C₁₇ fuel precursors

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ABSTRACT

The synthesis of diesel or jet fuels intermediates from furfural or 5-hydroxymethylfurfural (HMF) via aqueous aldol-condensation with cyclopentanone was studied. Cyclopentanone is the product of furfural rearrangement in an aqueous system. Since the aldol-condensation reaction is conducted in an aqueous solution all these biomass-derived reactants can be applied as water solutions formed in the processes of their preparation. The aldol condensation of furfural with cyclopentanone is at low concentration of base and molar ratio of reactants 2:1 highly selective and after 40–80 min of reaction at a temperature of 40–100 °C more than 95 mol% yield of 2,5-bis (2-furylmethylidene) cyclopentan-1-one (F₂C) was obtained. When instead of furfural as a reactant HMF was used higher than 98 mol% yield of 2,5-bis (5-hydroxymethyl-2-furylmethylidene) cyclopentan-1-one was achieved. The final products of aldol condensation of furfural and HMF are exclusively corresponding dimers, what enables to obtain after subsequent hydrogenation/hydrodeoxygenation step dialkylcyclopentane type of diesel or jet fuels having C₁₅ or C₁₇ molecules.

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1. Introduction

An increasing demand for transportation fuels has attracted the researchers to develop fuel-grade products from abundant lignocellulosic biomass which can be used in the existing infrastructure without necessity to modify the engine of the vehicle. Because biomass-derived carbohydrates contain an excess of oxygen containing groups the conversion processes of lignocellulosic biomass to fuels must involve various types of reactions [1–3]. Several routes have been described in the literature to convert biomass into gasoline or diesel fuels or their precursors [4–15].

The production of linear or singly branched hydrocarbons for diesel applications (usually C₉–C₁₇) from biomass-derived pentoses and hexoses as a feedstock includes in the first step chemical dehydrogenation into furfural and 5-hydroxymethylfurfural [16–19]. To meet the number of carbon atoms required for diesel-grade products usually two chemical routes have been extensively studied: (i) the route based on the aldol condensation reaction of furfural or 5-hydroxymethylfurfural in the presence of a base catalyst and acetone or an aldehyde as a second reactant, (ii) the acid-catalyzed C–C coupling reactions with furfural, furan, 2-methylfuran or levulinic acid ester as the feedstock [10,20–22].

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The aldol condensation plays an important role in the above mentioned process. It has been studied in homogeneous aqueous or water/alcohol solutions [1] and biphasic systems [3]. Among the homogeneous base catalysts that are active for aldol condensation are sodium and calcium hydroxide. To simplify the process and decrease water streams new solid base catalysts are developing [23–27]. Despite high activity these catalysts are not stable and lose their activity when recycled due to the leaching effect.

An example of effective process integration would be the combination of aldol condensation and hydrogenation of C=C and C=O bonds in the formed condensation product using bifunctional catalysts. Dumesic and coworkers [28] developed the Pd/MgO–ZrO₂ bifunctional catalyst for a single reactor, aqueous phase aldol condensation and hydrogenation of furfural and 5-hydroxymethylfurfural, leading to water-insoluble intermediates that can be converted to liquid alkanes. The simultaneous condensation and hydrogenation of short biomass-derived oxygenates in emulsions stabilized by metallized (Pd, Pt) amphiphilic nanohybrid catalysts described by Resasco and coworkers [29]. The combination of self-condensation and hydrogenation of 2-hexanone was studied in vapor-phase over Pd/CeZrO_x catalyst [30].

The second route for the production of diesel fuel precursors is based on the acid-catalyzed C–C coupling reaction. Huber et al. [20] synthesized C₁₃ oxygenate precursors by the hydroxyalkylation/alkylation reaction of furfural and furan under the catalysis of 72% H₂SO₄. An alternative method described by Corma et al. [10]. The process starts from 2-methylfuran (Sylvan) which is in the first step hydrolyzed to 4-oxopentanal by heating in 24 weight % aqueous sulfuric acid. Subsequently two molecules of 2-methylfuran are hydroalkylated and alkylated with 4-oxopentanal producing a C₁₅ oxygenate (5, 5-bisylvl-2-pentanone) in approximately 73% yield.

In order to overcome the problem connected with the use of corrosive, high concentrated H₂SO₄ as an acid catalyst, Li et al. used solid-acid catalysts [21,22].

Very recently we have demonstrated [31,32], that furfural can be converted in one-step to cyclopentanone with above 75 mol% yields. Therefore, this method provides a cheap raw material not only for the synthesis of polyamides and various specialty chemicals, but potentially also for the production of diesel or jet fuels from fully lignocellulose-derived platform chemicals. Since the rearrangement reaction of furfural to cyclopentanone proceeds in an aqueous medium, the aqueous solution of cyclopentanone e.g. from azeotropic distillation (b.p. 97.85 °C) can be used for the aldol condensation reaction with furfural. In addition, if the aldol condensation process will be integrated with the dehydration of hemicellulose streams, e.g. from the pretreatment of lignocellulosic materials, it is attractive to use for the reaction a diluted aqueous solution of furfural, which can substantially reduce steam consumption for recovery of furfural [15].

In this paper we present the study of preparation of oxygen-containing precursors of diesel or jet fuels having exclusively carbon chain lengths C₁₅ and C₁₇. The synthesis is based on the aldol condensation of biomass-derived reactants, i.e. by the reaction of cyclopentanone with furfural or 5-hydroxymethylfurfural. The effect of various reaction

parameters and solvents on the product yield, selectivity and the kinetics of the aldol condensation reaction were explored.

2. Materials and methods

2.1. Materials

Furfural (99%), furfuryl alcohol (99%), cyclopentanone (99%), 5-hydroxymethylfurfural (99%), furoic acid (99%) were purchased from Sigma–Aldrich. Sodium hydroxide, calcium hydroxide, Na₂CO₃, HCl (37%), tetrahydrofuran and toluene were purchased from Mikrochem (Slovakia). Furfural was purified by vacuum distillation and stored in a refrigerator at –15 °C.

The self-condensation product of cyclopentanone, 2-cyclopentylidene-cyclopentan-1-one (CC) was prepared according to Ref. [33]. The dimeric product of cross-condensation of furfural–cyclopentanone, 2,5-bis (2-furylmethylidene) cyclopentan-1-one (F₂C) was prepared by Ref. [34]. The product of cross-condensation of furfural with 2-cyclopentylidene-cyclopentan-1-one, i.e. 2-cyclopentylidene-5-(2-furylmethylidene) cyclopentan-1-one (FCC) was prepared using a similar procedure as described in Ref. [34]. The purity of all products was verified by NMR analysis (Supplementary information), and the products were used as the standard compounds for calibration.

2.2. Aldol condensation

The reactions were carried out in the batch mode in 50 and 250 mL three-neck glass reactors at atmospheric pressure under nitrogen atmosphere. Furfural and cyclopentanone (molar ratio was usually kept at 2:1) and cyclopentanol as the internal standard were dissolved in deionized water and the mixture was heated to the temperatures ranging from 20 to 80 °C. Into the homogeneous solution was injected an aqueous solution of the corresponding hydroxide and the mixture was vigorously stirred. The experiments at 100 and 130 °C were performed in a 50 mL stainless steel vessel. Inside the vessel was a capsule with the volume of 0.7 mL made of Teflon. The vessel was purged with nitrogen, closed and then in a vertical position carefully placed into a pre-heated oil bath. The vessel was mounted on a swinging device that could oscillate in a large diameter of circles. During the heating of vessel to the desired temperature (usually it lasted 5–8 min) the vessel was located in a vertical position, i.e. both reagents placed in the capsule were separated from the aqueous phase. After switching on the swinging device the reactants were mixed with the basic solution and the reaction started. In specified time intervals the vessel was withdrawn from the oil bath and then quickly cooled down to ambient temperature with water. The total volume of the solutions in the aldol condensation experiments was about 25 and 100 mL, respectively. The resulting solid/liquid mixtures were neutralized by an aqueous solution of HCl to pH ~6.5, weighed, filtered and washed several times with an excess of water to remove the base and unreacted organics. The obtained solid yellow-colored product was dried in vacuum, weighed and stored in dark under nitrogen.

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