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Selective synthesis of biogasoline precursor from renewable platform molecules at ambient temperature

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Abstract

The condensation of the dilute platform biochemical from the renewable lignocellulosic cellulose depolymerization for high quality energy production has attracted increasing attention currently. In this study, we propose an efficient process for biogasoline precursor production from the furfural and ethyl levulinate through the Aldol reaction at the ambient temperature. The results show that the furfural and ethyl levulinate can be efficiently condensed with the catalyst of commercial alkalis. Under the optimized condition, 78% of the product isolated yield can be obtained in the presence of KOH. Furthermore, the final product analysis using FT-IR, GPC, ^{1}H-NMR, ^{13}C-NMR and elemental analysis demonstrates that it mainly composes of 3-(furan-2-yl(hydroxy)methyl)-4-oxopentanoate acid, an excellent precursor for C9 branched hydrocarbon of gasoline. Moreover, the investigation shows that the product distribution of this Aldol process is high temperature dependent, higher temperature resulting in the recondensation of the product, hence decreasing the C9 gasoline precursor selectivity.

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Keywords: Furfural; ethyl levulinate; Aldol condensation; biogasline precusor; Carbon chain propagation

1. Introduction

Lignocellulosic cellulose is the unique carbon-containing renewable energy on the globe, so it has long been considered as the most promising alternative for the fossil fuel in the high quality biofuel and value-added biochemical production[1]. However, it should be noticed that most of the biochemical from

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the biomass selective depolymerization, such as synthesis gas, furfural, 5-hydroxylmethylfurfural (HMF) and levulinic acid usually has an effective carbon chain length of less than six, which cannot be used for high quality biofuel directly. The carbon length of crude oil from biomass pyrolysis and that of phenolic monomer from lignin degradation are in the range of biogasoline and biodiesel. However, these products are generally highly acidic, viscous and species complex. Therefore, a series of upgradation technologies (such as esterification, hydrogenation and hydrodeoxygenation) [2, 3] are necessary. Furthermore, the upgrade fuel is still complex on the product species and ingredient uncontrollable. In contrast, the carbon chain propagation of the platform chemicals from biomass selective degradation is more attractive. Fischer-Tropsch synthesis, alkylation, Diels-Alder polymerization, and Aldol condensation following by hydrodeoxygenation are efficient and robust processes for this issue [4]. In especially, the Aldol condensation of the ketonic chemicals has attracted increasing attention because of its mild condition, cost-effective catalyst, and handily achievable feedstock (for example, the ketonic biochemical furfural, HMF and LA can be easily obtained from the carbohydrate depolymerization).

In 2005, Huber and the coauthors first reported a catalytic process for the conversion of biomass-derived carbohydrates to liquid alkanes (C7–C15), where Aldol reaction was used for the increase of the carbon chain length.[5] Inspired by this work, many efforts are devoted for the selective production of the high quality biofuel from the biomass derived platform molecule. For example, their further investigation showed that 94% of the product yield can be obtained from the Aldol condensation of furfural and acetone with NaOH aqueous[6]. They also claimed a four step integrated process for jet and diesel fuel range alkanes (C8–C13) generation from the waste hemicellulose-derived aqueous solutions, in which, the Aldol reaction of furfural and acetone is the key step for carbon chain increase [7]. They also claimed an experimental studies and techno-economic analysis of a catalytic process for the conversion of whole biomass into drop-in aviation fuels with maximal carbon yields, and C7-C31 hydrocarbon could be obtained through the carbon chain extension by Aldol process in tetrahydrofuran (THF)/H_2O [8]. Corma *et al* had reported an efficient process for high-quality diesel production from the biomass waste as well. The obtained furfural from the hemicellulose hydrolysis was first ring cleaved to 4-oxopentanal which was further condensed with the furfural catalyzed by acid to give a highly branched C15 precursor. After the HDO process, a high quality diesel could be obtained [9]. Recently, Zhang and his group had also done a great quantity of work in the condensation of biochemical to the bio-jet fuel [10]. As described above, many current processes use acetone as the ketonic reagent, which is generally originated from the fossil fuel. Otherwise, the product selectivity is still improvable due to the simultaneous condensation of ketonic reagent with 1 and 2 equivalent of the furfural. Furthermore, most of the reported product has an effective carbon of more than C13, indicating that it cannot be used for a gasoline precursor. Moreover, the biochemical concentration from biomass is generally less than 3-5 wt%, so the efficient condensation of the dilute solution is highly desired. In this study, we propose an efficient process for the selective synthesis of C9 gasoline precursor from the low concentration biochemical of furfural and ethyl levulinate through the temperature control in the presence of the commercial catalysts.

2. Material and method

2.1 Materials

Furfural, ethyl levulinate and THF (HPLC grade) were purchased from Acros (Belgium) and used without further purification. KOH, NaOH, Et_3N, Na_2CO_3, CH_3COONa, HCl (36 wt%) and other reagents used in this study were all provided by Guanghua Sci-Tech Co., Ltd. (Guangzhou, China). All of the reagents are analytic grade and directly used.