An integrated process for diesel range precursors from biomass: Furfural extraction, furfural to 2-methylfuran and condensation to fuels

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Abstract: An integrated process scheme was developed including furfural exraction, catalytic transfer hydrogenolysis of furfural to 2-methylfuran with 2-pentanol, and condensation of 2-methylfuran and/or 2-pentanone. Herein, we focused on the conversion of furfural to 2-methylfuran over two different Cu-ZnO catalysts in the presence of 2-pentanol as H_2 donor.

Keywords: Furfural conversion, Transfer hydrogenolysis, Diesel range biofuel

1. Introduction

Falling fossil fuel reserves and growing atmospheric CO_2 emissions have made the development of renewable biofuels a global priority.[1] A possible source of renewable biomass is residual agriculture waste that is increasingly recognized attractive for biofuels. While furfural is one of the leading chemicals from biomass, furfural (FFA) production is mostly based on hemicellulose derived sugars as the feedstock. The extraction of FFA after chemical treatment of hemicellulose has been conducted by using different solvents including methyl isobutyl ketone, toluene, methanol, ethanol, 2-pentanol, etc. Among these solvents, alcohols would be a good candidate because they can be used in further chemical transformation so that the separation of FFA from alcohols is unnecessary. Additionally, the use of alcohols as the reaction solvent can prevent the easy polymerization of reactive FFA leading to a low carbon balance. Due to this intrinsic problem, the hydrogenation of FFA has been conducted with cyclopentyl methyl ether[2] and other alcohols. In this work we selected 2-pentanol as a reaction solvent in the hydrodeoxygeantion of pure FFA to 2-methylfuran (2-MF) since it can be formed as a side product. Herein, the extraction of FFA from an aqueous FFA solution with 2-pentanol and the transfer hydrogenolysis of FFA in presence of 2-pentanol were demonstrated. Also, the transfer hydrogenation product was condensed to produce fuels range precursors via self-condensation and/or cross-condensation of 2-methylfuran and 2-pentanone.

2. Experimental

For extracting FFA from aqueous solution, 5 wt% FFA in water was prepared as a model according to the report that the average FFA content in biomass is 5 wt%.[3] When 2-pentanol was added in an equivalent amount to the FFA solution, the recovery was estimated to be 90% in the first cycle. The complete recovery was achieved through repeated cycles, indicating the good extraction efficiency of 2-pentanol. Hence, the FFA solution in 2-pentanol with the same FFA concentration (5 wt%) was used as a reaction feed for transfer hydrogenolysis of FFA over Cu-ZnO (30:70) in a continuous fixed-bed reactor under N_2 flow. The major products were 2-methylfuran and 2-pentanone, while 2-pentanol and furfuryl alcohol (FOL) were produced in minor quantities.

3. Results and discussion

The main step involved in the integrated process is transformation of FFA to 2-MF. Conventionally the conversion of FFA to 2-MF was carried out with external hydrogen. Interestingly, our work focused on a novel method i.e., transfer hydrogenolysis. In this process the required hydrogen is generated from 2-pentanol and transferred to FFA over a catalyst surface. After successful extraction of FFA using 2-pentanol as a solvent, transfer hydrogenolysis of FFA in 2-pentanol was studied over Cu-ZnO (30:70). The catalytic performance of Cu-ZnO (30:70) at 235 °C for 20 h is shown in Fig. 1. In the beginning hours of reaction, the measured FFA conversion was 90 %, however, the conversion increased with time and stabilized near 95 % until the end of the reaction. These results clearly demonstrated the stability of Cu-ZnO over transfer hydrogenolysis. The yield of 2-MF was 70% at starting hours but it was elevated up to 80% during the course of the reaction. In the case of FOL, the yield above 10 % was noticed at early hours but it decreased with time to below 5%. The reaction solvent, 2-pentanol, was transformed to 2-pentanone with > 65% conversion and 100% selectivity. The overall carbon balance was nearly 85%, which is much higher than the FFA hydrogenation in presence of external hydrogen (65%). In other words, the transfer hydrogenolysis of FFA in 2-pentanol improves the carbon balance.

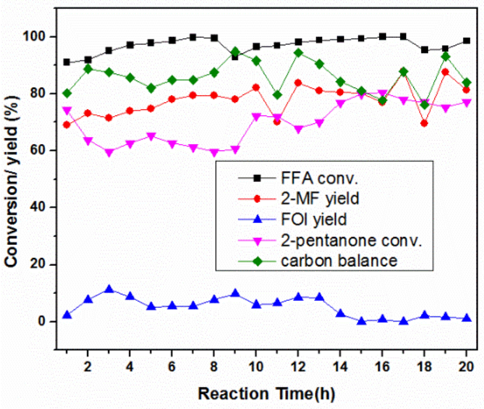

Figure 1. Time on stream study in transfer hydrogenolysis of FFA to 2-MF over Cu-ZnO (30:70).

The final product mixture composed of 2-MF, 2-pentanone, and 2-pentanol with minor amount of FOL will be transformed to diesel range precursors in the subsequent condensation step.

4. Conclusions

In summary, FFA extraction and transfer hydrogenolysis of FFA to 2-MF was carried out very successfully using 2-petanol as a solvent as well as hydrogen donor. 2-Pentanone produced from 2-pentanol can be utilized in the condensation of 2-MF for further upgrading to biofuels. Hence, our proposed process scheme would pave the way towards producing diesel range precursors and it is applicable for biofuels synthesis at an industrial scale.

References

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