An Integrated Synthesis of Jet-fuel Precursors from Carbohydrates *via* Dehydration Followed by Aldol Condensation

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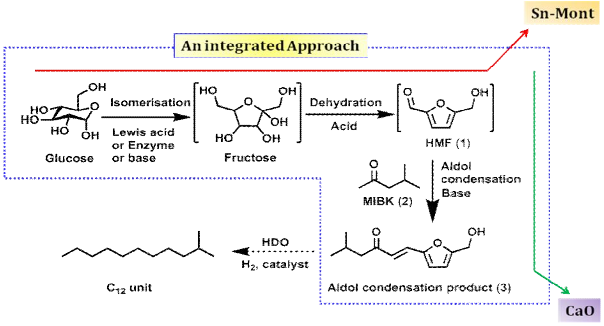
Abstract: We have investigated a new integrated approach for the production of jet-fuel range precursor from carbohydrates *via* dehydration followed by aldol condensation. A satisfactorily yield (42%) of HMF was achieved from dehydration of carbohydrates (e.g. fructose, glucose and sucrose) in methylisobutylketone (MIBK): H_2O: DMSO (8:1.5:0.5; *v*/*v*/*v*) biphasic solvent system over Sn-Mont catalyst. In the next integrated step, aldol condensation of in-situ formed HMF and MIBK (organic phase) was performed over CaO to achieve utmost 32% yield of aldol condensation product.

Keywords: Dehydration, aldol condensation, jet-fuel precursor.

1. Introduction

HMF is not an easy to extract from aqueous phase, since the distribution coefficient between the organic and the aqueous phase is not favorable. [1] However, this problem has been overcome by the use of organic solvent such as MIBK (methyl isobutyl ketone), which has been reported to be efficient extraction solvent. [2] It has been used as an extracting solvent to increase the selectivity towards furfural in the dehydration of xylose or its oligomers. [3] From a process intensification point of view, it is preferable if MIBK can be directly used as the HMF extraction solvent as well as carbonyl compound for aldol condensation with extracted HMF. Furthermore, the branched structure of MIBK also renders it as a potential feedstock for the direct synthesis of branched alkanes. [4] More importantly, these branched alkanes have low freezing points and can be blended into jet fuel without hydroisomerization.

Importantly, production of jet fuel precursors (liquid branched alkane precursors) directly from carbohydrate is not yet reported. As shown in Scheme 1, jet fuel production from carbohydrates requires three steps as follows (i) dehydration of carbohydrates to HMF, (ii) aldol condensation of HMF with MIBK and (iii) hydrodeoxygenation (HDO) of aldol condensation product. On the basis of this background, we report here an integrated conversion of carbohydrates into jet fuel precursor. This strategy involves the dehydration of carbohydrates over Sn-Mont catalyst in a biphasic solvent system involving MIBK: H_2O: DMSO (8:1.5:0.5; v/v/v) followed by aldol condensation of in-situ formed HMF with MIBK (solvent) over CaO catalyst. In this strategy MIBK works as solvent for product extraction as well as a reactant (carbonyl compound) for aldol condensation with HMF. In order to establish this integrated approach, initially we have meticulously found out suitable catalysts and reaction conditions for separate glucose dehydration and aldol condensation reaction.



Scheme 1. Process for the production of jet-fuel precursor from carbohydrates

2. Experimental (or Theoretical)

Mixture of carbohydrate, water, DMSO, MIBK and Sn-Mont was heated at 170 °C for 12 h. Mixture was quickly cooled to room temperature and filtered to separate the catalyst (Sn-Mont). Into mother liquor containing in-situ formed HMF, CaO was added and continued to react at 80 °C for 12 h.

3. Results and discussion

Dehydration of glucose and aldol condensation between crude HMF and MIBK was accomplished in single pot integrated process. The reactions flow-chart of glucose dehydration and aldol condensation is presented in Fig. 1. In a pressure reactor glucose was dissolved in H_2O + DMSO (1.5 mL + 0.5 mL) then MIBK (8 mL) and Sn-Mont (0.2 g) were added. This biphasic reaction mixture was stirred and heated at 170 ^{o}C for 12h, to give 42% total yield of HMF in both the organic and aqueous phases. Subsequently, reaction was quickly cooled to ambient temperature and filtered to separate the catalyst (Sn-Mont) and then the resultant biphasic filtrate was reloaded into the same reactor and treated with CaO (0.15 g) at 80 ^{o}C for 12h. After that upper organic phase was pipetted out and evaporated under reduced pressure to afford aldol condensation product (3) in 32% yield. Interestingly, evaporated MIBK was collected upto 80% (6.3 mL) of its initial volume (8 mL) which could be reused for this reaction.

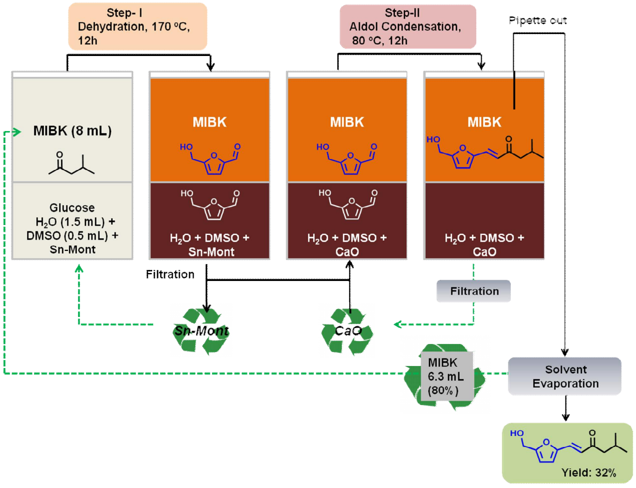


Figure 1. Schematic presentation of reaction flow-chart of integrated conversion of glucose to aldol condensation product.

4. Conclusions

In the first step of integrated approach, carbohydrates were dehydrated to HMF over Sn-Mont catalyst. Importantly, Sn-Mont having combination of Lewis and Brønsted acid sites facilitates the dehydration of carbohydrates to HMF in biphasic solvent system (MIBK: H_2O: DMSO; 8: 1.5: 0.5; *v*/*v*/*v*). Interestingly, intrinsic stability of Sn-Mont doesn't leave acidity into reaction mixture which could avoid the neutralization of basic catalyst used for next step (aldol condensation). In a second step, MIBK was condensed with in- situ generated HMF over CaO to form aldol condensation product. In biphasic solvent system, MIBK (organic phase) turns out to be important as reactant as well as product extraction phase. In addition to that, MIBK could be recovered upto 80% of its initial volume and could be reused.

References

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