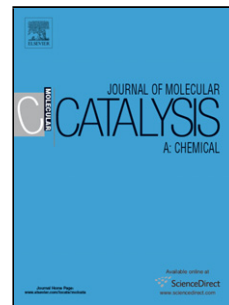


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**Effect of hydrogen donor on liquid phase catalytic transfer hydrogenation
of furfural over a Ru/RuO₂/C catalyst**

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ABSTRACT

The effect of alcohol hydrogen donor on methyl furan production through catalytic transfer hydrogenation of furfural in the liquid phase has been investigated over a mildly calcined Ru/C catalyst in the temperature range of 110-200 °C. It has been found that several parameters contribute to furfural hydrogenolysis, including alcohol dehydrogenation activity, solvent properties, as well as side reactions such as etherification between the intermediate, furfuryl alcohol, and the hydrogen donor. Methyl furan yield increases from 0 to 68% at 180 °C following the order of 2-methyl-2-butanol < tert-butanol < ethanol < 1-propanol ~ 1-butanol < 2-propanol < 2-butanol ~ 2-pentanol, which correlates well with the alcohol dehydrogenation activity. In ethanol, 1-propanol, 2-propanol and 2-pentanol, furfuryl alcohol hydrogenolysis to methyl furan is significantly retarded at low temperatures due to furfuryl alcohol etherification with the corresponding alcohol solvent. We find that methyl furan yield decreases with increasing alcohol polarity. An optimum methyl furan yield of 76% is attained after 10 h of reaction at 180 °C, using 2-butanol and 2-pentanol as hydrogen donors. This is the highest reported yield in the liquid phase at temperatures below 200 °C.

Keywords

Ruthenium; furfural; catalytic transfer hydrogenation; hydrogen donor; alcohol; solvent effects; methyl furan

1. INTRODUCTION

Declining availability of petroleum reserves and emerging environmental concerns have generated interest in developing economically efficient and environmental friendly technologies to transform lignocellulosic biomass into fuels and chemicals. Biomass derived furfural is considered as a potential platform for biofuels and chemicals and thus, its upgrade has recently gained interest [1]. Catalytic hydrogenolysis of furfural to methyl furan (MF) is attractive because MF has excellent energy density, boiling point, research octane number and potential use for chemicals (e.g., toluene) [2-4]. Furfural hydrogenolysis in the liquid phase with high-pressure H₂ has been studied over a variety of mono- and bi-metallic catalysts on various supports [5-14], but the MF yield has generally been low (Figure 1).

We have recently reported a MF yield of 61% over a Ru/RuO₂/C catalyst using 2-propanol as hydrogen donor and solvent in a process termed catalytic transfer hydrogenation (CTH) [12]. The approach combines in situ hydrogen generation from the alcohol to carry out the hydrogenolysis of furfural and overcomes multiple challenges in using high pressure external hydrogen, such as compression cost, complex trickle bed reactor design, safety, transportation, and storage. Evidence was provided that the effective catalyst is a combination of Ru and RuO₂ and can fully be regenerated. The reaction network has been postulated (Figure 2). In particular, it has been found that furfural is initially hydrogenated to furfuryl alcohol (FA) that then undergoes hydrogenolysis to MF. FA can dimerize or be etherified with 2-propanol.

Understanding solvent effects and developing correlative descriptors, such as solvent polarity, in single overall reactions, such as hydrogenation of C=C, on metal sites with external H₂, are emerging [15, 16]. There is also descent understanding in the hydrogenation of C=O from an alcohol as a hydrogen donor via interhydride transfer (Meerwein-Ponndorf-Verley (MPV) reaction) on Lewis acid catalysts; for this class of reactions, it is well

established that secondary alcohols are more effective than primary alcohols [17-19]. For example, Bui et al. [20] found that the production of γ -valerolactone from furfural is enhanced using secondary alcohols as hydrogen donors, rather than primary alcohols, having alkyl chains longer than C₄. It has been proposed that suitable CTH solvents possess intermediate polarity and neither acidic nor basic properties [1]. In particular, a polar solvent enhances adsorption of a non-polar reactant and vice versa [16].

Despite the progress in understanding solvent effects, little is known about the *effect of reacting solvents in tandem reactions*, such as hydrogenolysis of furans using alcohols. This cascade of reactions entails first hydrogenation of the C=O on a metal or possibly on Lewis acid sites via the MPV reaction, dehydration and hydrogenation (hydrogenolysis) of –CH₂OH to CH₃ on Lewis and metal sites, as well as side reactions. Appropriate selection of a reacting solvent is critical in order to suppress side reactions, such as ring hydrogenation of reactant and products, etherification, and overalkylation [21].

Here we study the effect of alcohol as a reacting solvent on the production of MF through CTH of furfural in the liquid phase over a Ru/RuO₂/C catalyst. We compare primary, secondary, and tertiary alcohols over a range of temperatures and correlate performance with solvent polarity and dehydrogenation and etherification propensity of the hydrogen donors.

2. EXPERIMENTAL

Catalytic transfer hydrogenation of furfural has been carried out in a Parr batch reactor using the following alcohols as hydrogen donors: ethanol (Sigma Aldrich), n-propanol (Sigma Aldrich), n-butanol (Sigma Aldrich), 2-propanol (Sigma Aldrich), 2-butanol (Sigma Aldrich), 2-pentanol (Sigma Aldrich), 2-methyl-2-butanol (Sigma Aldrich) and tert-butanol (Sigma Aldrich). Briefly, in a typical experiment, 24 mL of an alcohol solution of furfural (1 wt %) and 0.1 g of Ru/RuO₂/C catalyst were added to the reactor, sealed under N₂ pressure

(2.04 MPa) and heated in a temperature-controlled oil bath. The reaction was stopped at desired times, the reactor was cool down in an ice bath and the suspension was collected, filtered, stored in sealed vials and analysed using both gas chromatography (GC, Agilent 7890A) and gas chromatography–mass spectrometry (GC/MS, Shimadzu QP2010 Plus). The catalyst used was 5 wt.% Ru/C (Sigma-Aldrich), which, prior to each experiment, was treated for 3 h at 300 °C in H₂ flow of 40 cc/min followed by mild oxidation for 3 h at 130 °C in 5%O₂/He flow of 40 cc/min. Details of methods can be found in the supporting information (Section S1).

3. RESULTS AND DISCUSSION

3.1 Catalyst characterization

The fresh and spent Ru/RuO₂/C catalysts were characterized using XRD, TEM, H₂-TPR, XPS and EXAFS spectroscopy [12, 21, 22]. The metal dispersion was measured employing CO chemisorption over the fresh reduced Ru/C catalyst. It has been found the Ru metal dispersion is 46% with 220 μmol/g of CO uptake at 298 K, indicating that the Ru metal is highly dispersed on the carbon support. The size of the Ru metal particles measured by TEM was in the range of 3-5 nm. H₂-TPR, XPS and EXAFS spectroscopy studies [12, 22], showed that mild oxidation treatment at 130 °C generates a partially oxidized ruthenium surface (sub-oxide layer on ruthenium metals) on the fresh Ru/RuO₂/C catalyst. H₂-TPR results over the spent catalyst clearly showed that during CTH of furfural, using 2-propanol as hydrogen donor, the Ru oxide is being partially reduced, resulting in partial catalyst deactivation and a slight decrease of MF yield [12]. Similar results have been obtained for the CTH of 5-hydroxymethylfurfural using the same hydrogen donor, where it was demonstrated that the ruthenium oxide species are easily reduced *in-situ* during reaction [22].

3.2 Effect of hydrogen donor on furfural conversion and product distribution

The effect of hydrogen donor on performance was investigated at 180 °C (Figure 3). Furfural conversion depends strongly on the alcohol and increases from 13 to 92% following the order: tert-butanol < 2-methyl-2-butanol < 1-butanol < ethanol < 1-propanol < 2-butanol < 2-propanol < 2-pentanol. The main hydrogenolysis products are FA and MF. The yield of the former is low. The yield of the latter varies strongly (from 0 to 68%) with alcohol in the order of 2-methyl-2-butanol < tert-butanol < ethanol < 1-propanol ~ 1-butanol < 2-propanol < 2-butanol < 2-pentanol. As expected, tertiary alcohols are totally inactive for furfural hydrogenolysis, due to their negligible dehydrogenation [23, 24]. Although, formation of FA in liquid phase furfural hydrogenation has been reported, only a few studies have reported MF production using high-pressure molecular hydrogen, with a maximum yield typically lower than 50% [5-7, 12, 14, 25-27] (Figure 1). By comparison, our MF yield is higher than any previous work.

Furfural decarbonylation to furan (FU) is slow (yield <8%) [28, 29] and ring hydrogenation occurs only in 1- and 2-butanol (THFA's yield is 12 and 7%, respectively) and is negligible (<0.5%) in other alcohols (Figure 3). Our results are in agreement with previous studies (selectivities <10-15%).[5-7] Furan,2-(2-furanylmethyl)-5-methyl (compound 2; Figure 2) forms in all alcohols, with yields lower than 8%.

We have previously found that etherification between the FA and the alcohol solvent leading to 2-(isopropoxyl)methyl furan (compound **1**; Figure 2) is an important reaction competing with hydrogenolysis [12]. Etherification is enhanced at short reaction times and/or low temperatures and reverses at longer reaction times and/or higher temperatures to FA and 2-propanol, with the FA converted eventually to MF. Here, we find interesting differences in etherification with other alcohols: the ether yield is negligible with 1- and 2-butanol and low (~2%) in 2-pentanol but significant in other alcohols (as high as 20-25%). Shorter chain alcohols favor the etherification reaction with FA indicative of steric effects.

Figure 4A correlates the furfural hydrogenolysis with the alcohol dehydrogenation. Interestingly, furfural hydrogenolysis increases with increasing alcohol dehydrogenation, with 2-butanol and 2-pentanol exhibiting optimum MF yields. Our results provide evidence that alcohol dehydrogenation is a key step in MF production. Secondary alcohols are better than primary alcohols consistent with previous hydrogenation studies of acetophenone under H_2 pressure [30] and of mesityl oxide to allylic alcohol [31]. The improved hydrogenation ability of secondary alcohols has previously been attributed to the highest reduction potential of the corresponding ketones [30] or the smaller electron-releasing inductive effect of one alkyl group compared to two alkyl groups [32].

Solvent properties, such as polarity, could affect solvent-reactant interactions and consequently, furfural hydrogenolysis. Polarity can be expressed with various parameters, including dipole moment μ , dielectric constant ϵ , polarity/polarizability π^* , as well as the Kosower's Z and Dimroth-Reichardt's $E_T(30)$ scales, which are based on the charge-transfer absorption spectra of 1-ethyl-4-carbomethoxypyridinium iodide and the spectrum of pyridinium N-phenol betaine, respectively [30, 33, 34]. The furfural hydrogenolysis is correlated with solvent polarity (the dielectric constant and the solvatochromic parameters $E_T(30)$ and π^*) in Figures 4B and S1. Clearly, MF yield decreases with increasing alcohol polarity, possibly due to increased furfural-alcohol interaction that in turn retards furfural adsorption on the catalyst. A similar trend was observed in acetophenone hydrogenation [30].

3.3 Effect of reaction temperature on product distribution

Catalytic Transfer Hydrogenation (CTH) of furfural

The effect of reaction temperature was investigated in the range of 110-200 °C in 2-propanol [12], 2-butanol, and 2-pentanol (Figure 5, S2, and S3). It was found that although furfural conversion is within experimental error, product distribution varies with alcohol. Below 160 °C, the MF yield is higher using 2-butanol followed by 2-pentanol and then 2-propanol, whereas at higher temperatures, the yield to MF is comparable in the two larger

alcohols, with the MF yield reaching 69% at 195 °C (Figure 5A). 2-propanol results in lower MF yield in the entire temperature range, reaching 50% at 195 °C.

The yield of FA and FU vs. temperature is similar in all alcohols. The THFA yield is enhanced in 2-butanol, reaching a maximum of 10% at 165 °C, and is low in 2-propanol and completely suppressed in 2-pentanol.

Among the three secondary alcohols, FA etherification with the corresponding alcohol is suppressed in 2-butanol and is enhanced in 2-propanol (Figure 5B). In 2-propanol, the ether yield goes through a maximum of 32% at 170 °C. Little is known about the effect of molecular structure of alcohols on etherification in Lewis acid catalyzed chemistry to provide insights into the observed trends, with a few studies only correlating the carbon cation stability with the production of alkene during dehydration [24]. We believe that the maximum in the ether yield corresponds to the etherification reaction transition from kinetically controlled at lower temperatures (below the maximum) to equilibrium-limited at high temperatures (above the maximum). Higher temperatures lead to de-etherification to FA and the alcohol solvent, a trait of exothermic reactions. The temperature of this maximum shifts to 140 °C and the maximum yield decreases to 20% in 2-pentanol. This provides support that the etherification equilibrium constant may be lower for 2-pentanol than for 2-propanol.

Results of Figures 5A and B imply that FA hydrogenolysis to MF is strongly influenced from the FA etherification. Hydrogenolysis is also affected from the FA dimerization, with the dimer (compound 2) yield varying inversely to that of MF. However, the effect of dimerization is lower compared to that of etherification, due to the low dimer yields (<8%) in the whole temperature range (Figures S2 and S3).

Alcohol Product Distribution

Next we turn to the reactivity and product distribution of the alcohols. For all hydrogen donors examined, it was found that alcohol dehydrogenation is faster than alcohol

self-etherification or dehydration to the corresponding alkene and supplies the necessary hydrogen to drive furfural hydrogenolysis (Figure S4A, S5A and Ref.[12]). Comparison of ketone yield vs. temperature under CTH of furfural shows that the alcohol dehydrogenation at any temperature increases in the following order: 2-propanol < 2-butanol < 2-pentanol (Figure 5C), with the exception of a narrow temperature range of 120-140 °C, where 2-butanol and 2-pentanol exhibit similar activity. Figures 5A and 5C show that although the rate of 2-pentanol dehydrogenation is higher than that of 2-butanol, MF production is not higher in 2-pentanol, providing evidence that the hydrogen donor ability is not the only parameter affecting hydrogenolysis. Below 140 °C, 2-pentanol etherification with FA is favored over FA hydrogenolysis, leading eventually to lower MF yield compared to 2-butanol (Figure 5A and B). Above 140 °C, the etherification reaction reverses to 2-pentanol and FA, followed by hydrogenolysis of FA to MF, and the MF yield is similar to that in 2-butanol. FA etherification with 2-propanol reverses at higher temperatures and the rate of 2-propanol dehydrogenation is lower compared to other alcohols, leading to lower MF production in the entire temperature range examined.

Figure 5 clearly indicates that there is a complex interplay between reactions. Furfural hydrogenolysis to MF is affected from the propensity of the alcohol to dehydrogenate and to etherify with FA in a nonlinear temperature-dependent manner. At low temperatures, FA etherification is dominant and strongly limits MF production. At high temperatures, on the other hand, FA etherification reverses due to equilibrium limitations, and the alcohol dehydrogenation activity determines MF yield. In the case of 2-butanol, which is not etherified with FA, MF production strongly correlates with the alcohol dehydrogenation.

Optimum results have been obtained after 10 h of reaction at 180 °C, using 2-butanol and 2-pentanol, where furfural conversion is almost complete and MF yield reaches 76% (Figure 6). This is the highest yield reported to date. Combined with in situ hydrogen

generation, our process addresses several challenges from using external H₂ and can generate MF from all renewable feedstock.

Neat Alcohol Conversion

The reactions of neat secondary alcohols (2-propanol, Figure S6; 2-butanol, Figure S4B; and 2-pentanol, Figure S5B) have been investigated to determine the reactivity of alcohols in neat conditions and understand the effect of furans on it. Results show that alcohol dehydrogenation dominates at all temperatures, whereas self-etherification and dehydration to alkene, followed by its hydrogenation to alkane, occur to a smaller extent at high temperatures. Interestingly, the ketone yield is significantly lower when alcohols are converted during CTH of furfural (Figure 5C) compared to that from the neat alcohol. Density functional theory (DFT) plane wave calculations (VASP) show that the adsorption energy (in eV) varies as follows: furfural (-2.4) > furfuryl alcohol (-1.8) > methylfuran (-1.6) > furan (-1.6) > 2-butanone (-1.17) > 2-butanol (-1.13) > acetone (-1.1) > IPA (-1.0). Our DFT results suggested that alcohol and furfural compete for active sites, resulting in lower rates of alcohol dehydrogenation during CTH of furfural compared to neat conditions. Dehydrogenation activity on the Ru/C catalyst follows the order 2-butanol < 2-propanol < 2-pentanol (Figure S7), which, as discussed above, is different from the activity-order observed in CTH of furfural (Figure 5C). The presence of furfural not only retards significantly the alcohol dehydrogenation, but also affects the activity-order compared to neat alcohols.

CONCLUSIONS

We have studied the effect of alcohol as solvent and hydrogen donor in the catalytic transfer of hydrogen (CTH) of furfural to produce methyl furan (MF) over a Ru/RuO₂/C catalyst. Our results show several interesting findings:

1. The Ru/RuO₂/C catalyst is capable of complete furfural conversion and high MF yield using a range of primary and secondary alcohols, enabling MF production from renewable sources (e.g., butanol or ethanol).
2. Secondary alcohols are more effective in CTH, similarly to hydrogenation of model compounds. MF yield increases from 0 to 68% at 180 °C following the order of 2-methyl-2-butanol < tert-butanol < ethanol < 1-propanol ~ 1-butanol < 2-propanol < 2-butanol ~ 2-pentanol. We report the highest MF yield of 76% ever using 2-butanol and 2-pentanol as reacting solvents.
3. We have found that the MF yield is controlled from a complex interplay of reactions, including the etherification of the alcohol solvent with furfuryl alcohol (an intermediate in hydrogenolysis of furfural to MF), the dehydrogenation propensity of the alcohol, and the ability of furfuryl alcohol to dimerize. Etherification controls the concentration of furfuryl alcohol and dominates at low temperatures and short times and possibly reduces the dimerization byproduct. Importantly, the etherification reverses at longer times and/or higher temperatures to increase the MF yield.
4. Solvent polarity correlates well with the hydrogenolysis activity as happens in single hydrogenation reactions, indicative of the importance of solvent-reactant interactions. Specifically, we have shown that MF yield increases with increasing alcohol dehydrogenation activity and decreasing alcohol polarity.
5. In neat alcohols, alcohol dehydrogenation dominates at all temperatures; self-etherification and dehydration to alkene, followed by hydrogenation to alkane, also occur at high temperatures. The competitive adsorption of furans and alcohols, consistent with DFT results, and solvent-reactant interactions reduce the dehydrogenation ability of alcohols during hydrogenolysis of furans compared to neat alcohols and reverse the

reactivity order of alcohol dehydrogenation. The additional side channels of hydrogen donors (self-etherification and dehydration) are also suppressed by the furans.

Overall, our results demonstrate that CTH in reacting solvents can be very effective in the upgrade of furans but process and catalyst optimization requires understanding of the complex interplay of the main and side reactions.

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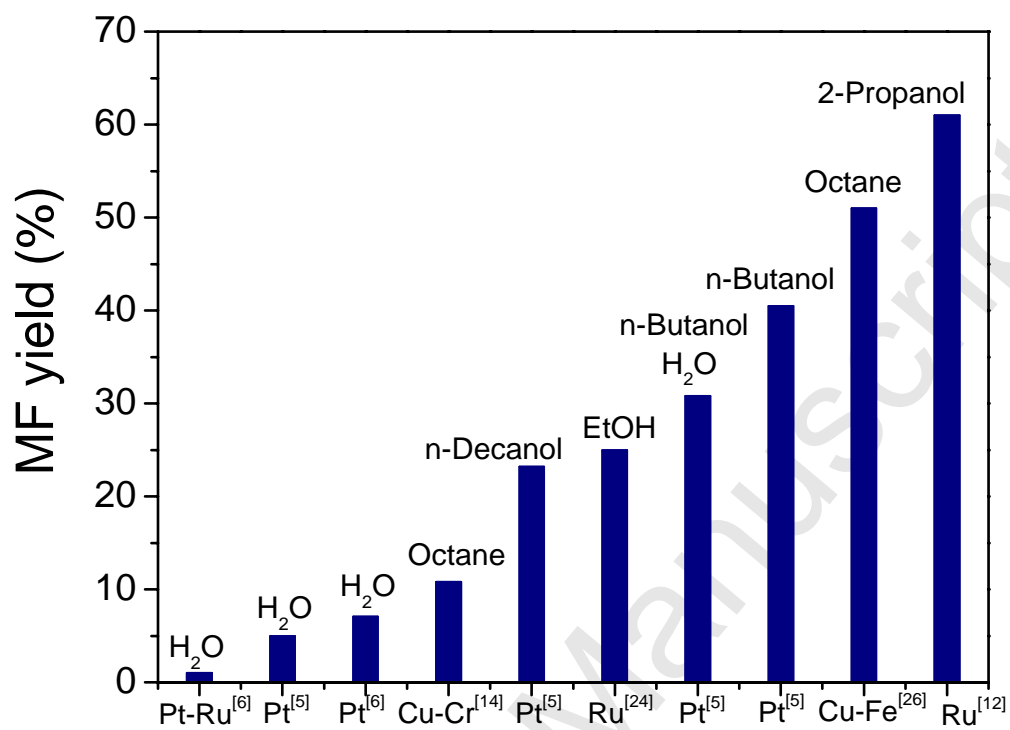


Figure 1. Literature reported methyl furan (MF) yield for an almost complete furfural conversion using different catalysts and solvents.

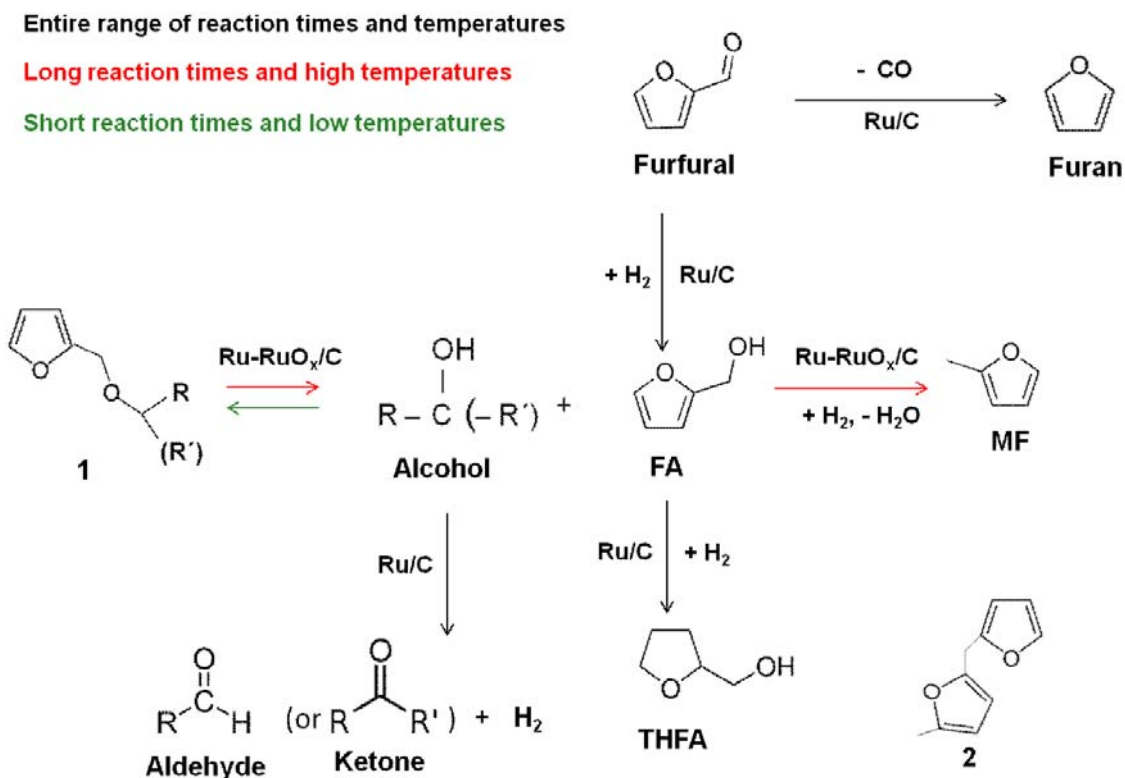


Figure 2. Proposed reaction network in furfural hydrogenolysis on Ru/RuO₂/C in various alcohols. Compounds: Furfural (F); 2-methyl furan (MF); Furfuryl alcohol (FA); Furan (FU); Tetrahydrofurfuryl alcohol (THFA); Ether of FA and alcohol solvent (1); Furan, 2-(2-furanylmethyl)-5-methyl (2).

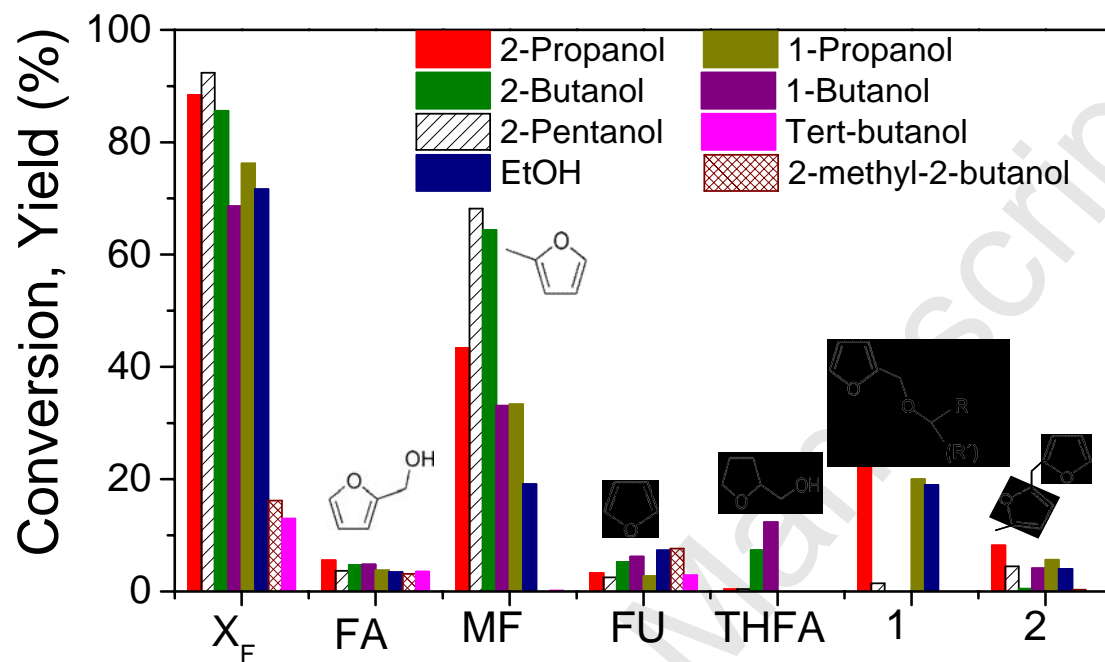


Figure 3. Furfural conversion and product yield using various alcohols as hydrogen donors. [Furfural (F); 2-methyl furan (MF); Furfuryl alcohol (FA); Furan (FU); Tetrahydrofurfuryl alcohol (THFA); ether of FA and alcohol (1); Furan, 2-(2-furanylmethyl)-5-methyl (2)]. Experimental conditions: 1 wt.% furfural in alcohol solution; $C_{cat}=4.1 \text{ g L}^{-1}$; 2.04 MPa N_2 , reaction temperature of 180 °C and reaction time of 5 h.

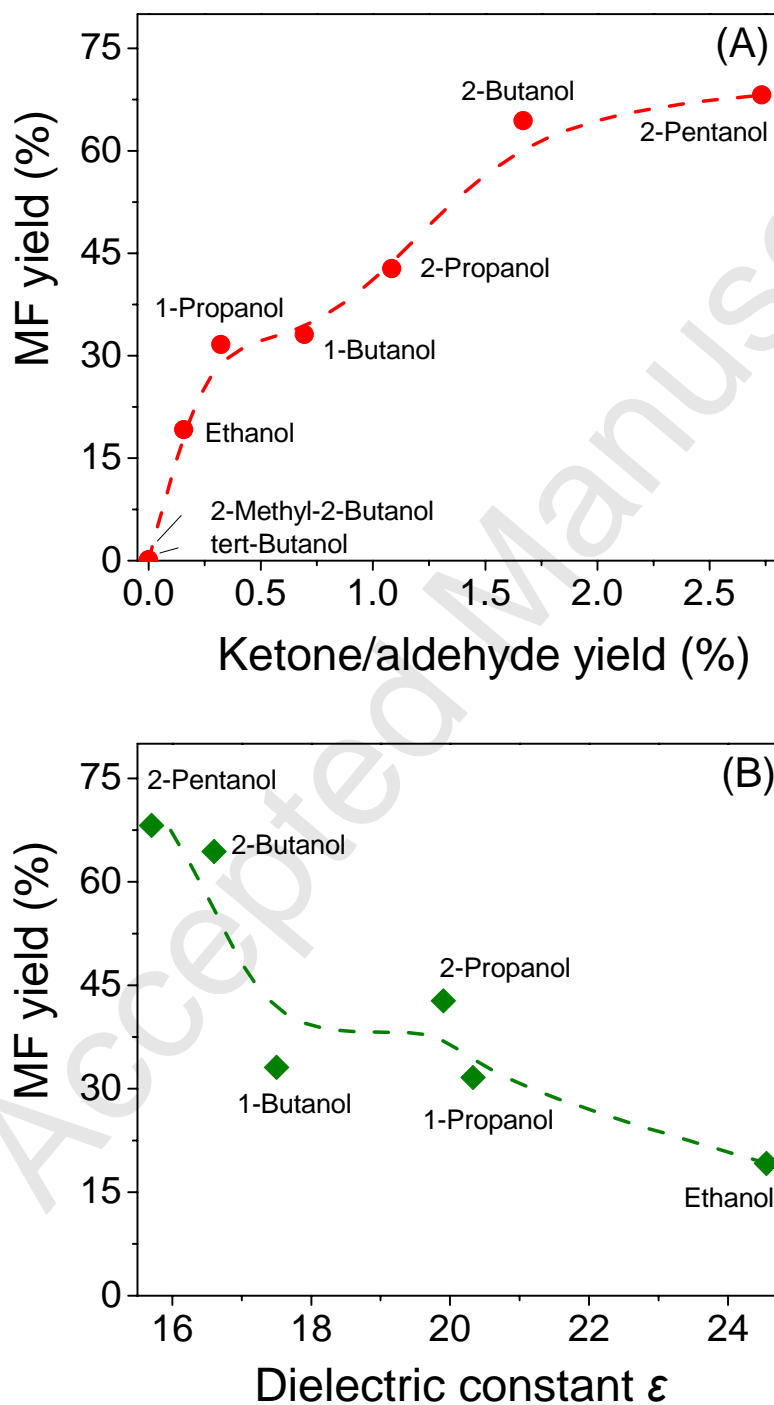


Figure 4. MF yield as a function of the (A) ketone/aldehyde yield and (B) dielectric constant of the alcohol. Experimental conditions as in Figure 3.

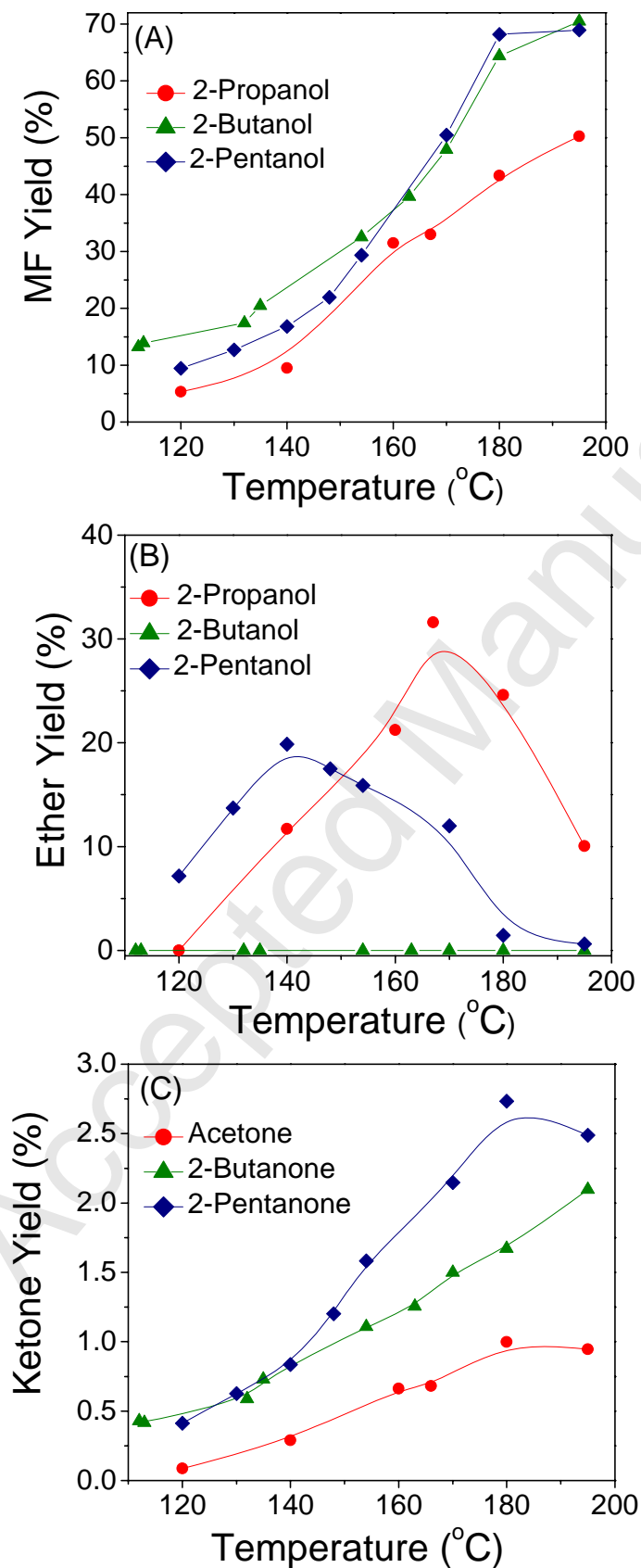


Figure 5. Effect of reaction temperature on (A) 2-methylfuran, (B) ether and (C) ketone yield using 2-propanol, 2-butanol, and 2-pentanol as hydrogen donors [Furfural (F); 2-methyl furan (MF); Furfuryl alcohol (FA); Furan (FU); Tetrahydrofurfuryl alcohol (THFA); ether of FA with alcohol (1); Furan, 2-(2-furanylmethyl)-5-methyl (2)]. Experimental conditions: 1 wt.% Furfural in alcohol solution; $C_{cat}=4.1 \text{ g L}^{-1}$; 2.04 MPa N_2 and reaction time of 5 h.

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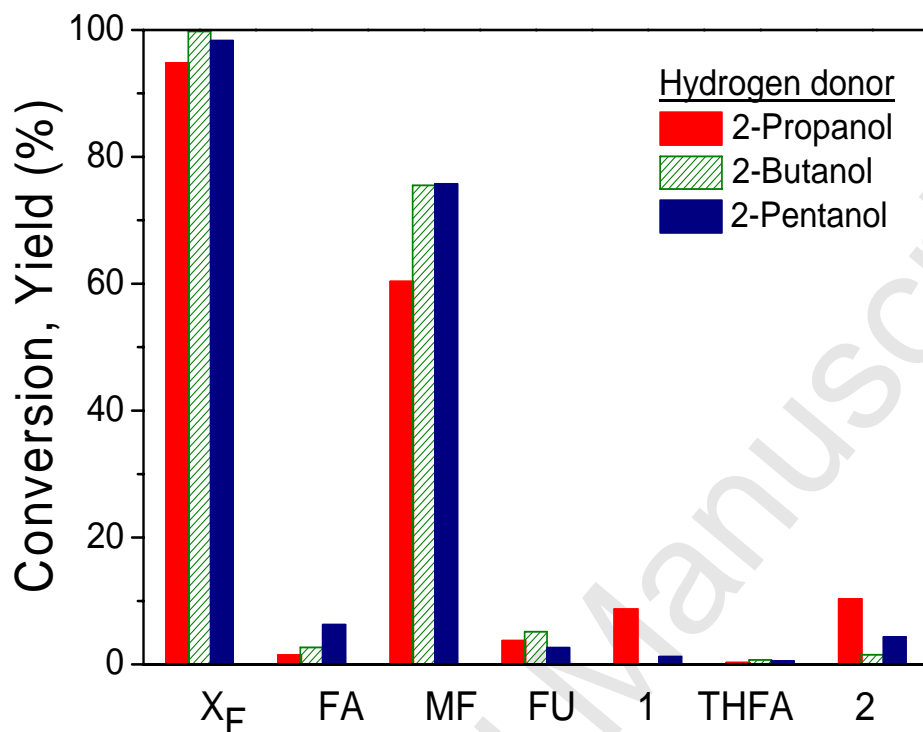
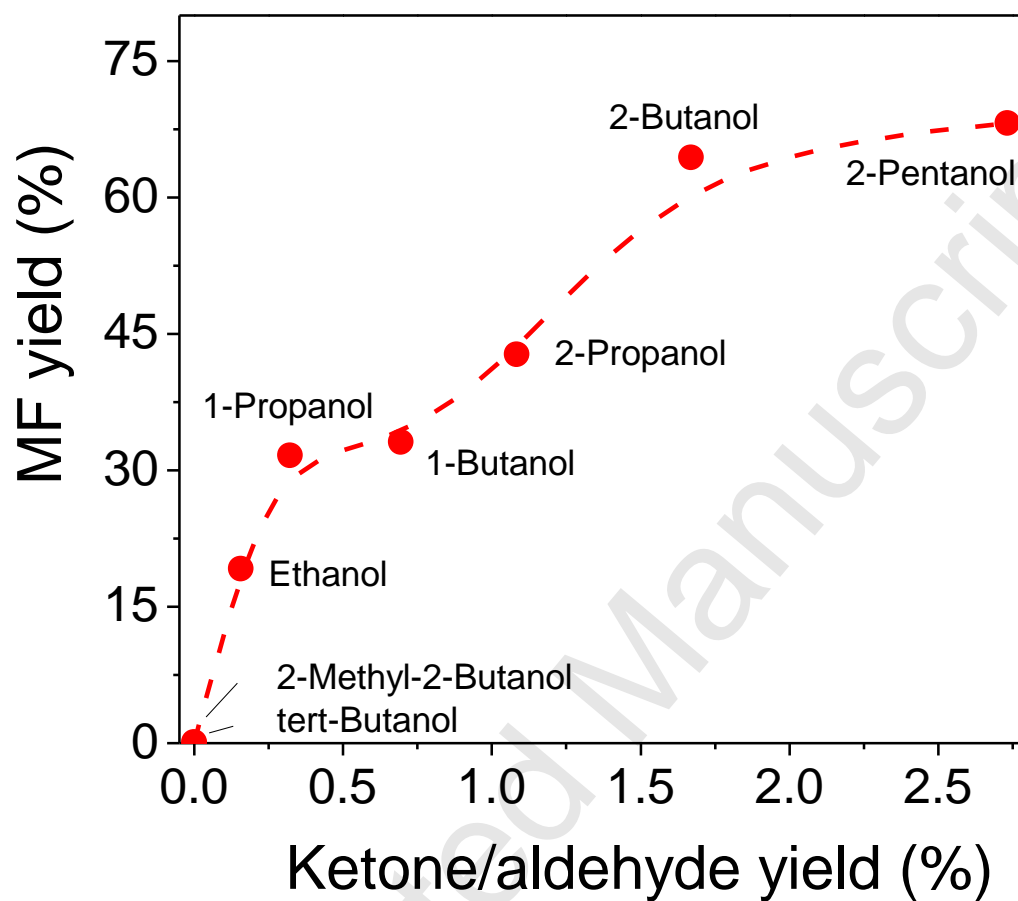


Figure 6. Furfural conversion (X_F) and product yield for the indicated hydrogen donors. Experimental conditions: 1 wt.% furfural in alcohol solution; $C_{cat}=4.1 \text{ g L}^{-1}$; 2.04 MPa N_2 , reaction temperature of 180 °C and reaction time of 10 h.

Highlights:

- Catalytic transfer hydrogenation of furfural toward methyl furan was demonstrated.
- Secondary alcohols are more effective among a range of hydrogen donors.
- An optimum methyl furan yield of 76% was achieved using 2-butanol and 2-pentanol.
- Methyl furan yield increases with increasing alcohol dehydrogenation activity.
- Methyl furan yield increases with decreasing alcohol polarity.

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Methyl furan yield increases with increasing the alcohol dehydrogenation activity.