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Evaluation of carbohydrates and lignocellulosic biomass from different wood species as raw material for the synthesis of 5-bromomethyfurfural

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ABSTRACT

The influence of different parameters on the conversion of carbohydrates and biomass into the potential biofuel intermediate 5-bromomethylfurfural (BMF) has been studied. Our optimized conditions avoid the use of lithium salt additives, making this method cheaper and environmentally more benign compared to previously reported methods. Different wood species and their potential as a raw material in BMF and furfural production have also been evaluated. In addition, we report a very simple and efficient procedure for conversion of 5-hydroxymethylfurfural (HMF) into BMF or 5-chloromethylfurfural (CMF).

1. Introduction

Depletion of oil reserves, increasing CO_2 emissions, and rising prices of gasoline and diesel make the development of new biofuels an extremely important task. Most of currently produced biofuels are based on edible raw materials and large-scale production, for example, ethanol production from corn, is competing with the food industry and has already led to an increase of food prices.[1] Current focus in this area is, however, directed toward using non-edible lignocellulosic raw materials like wood and straw. Also various types of cellulose-containing wastes including old paper, cotton clothes, and sawdust can be converted to fuel.

Currently, bioethanol is the most widely used biofuel. However, during the production of bioethanol one third of the carbon content of the starting material is expelled in the fermentation process, making this a rather inefficient process. It has also been noted that the heat of combustion of ethanol is considerably lower than that of gasoline and diesel fuel.[2] Therefore intense research has concentrated on furanic compounds like 5-hydroxymehtylfurfural[3,4] (HMF, **1**), 5-chloromethylfurfural[5–9] (CMF, **3**), 5-bromomethylfurfural[10–13] (BMF, **2**), and levulinic acid[14] (LA, **5**, Fig. 1). None of the mentioned compounds can be used directly as biofuel and must be converted to corresponding alkyl ethers or other suitable derivatives. For example 5-ethoxymethylfurfural (EMF, **4**) and ethyl levulinate (EL, **6**) are considered to be promising biodiesel candidates.[15,16]

Our goal is to contribute to the development of a new biofuel and the current study concerns several aspects of biofuel production: evaluation of different biomass samples and carbohydrates as starting materials, and development of improved procedures for the preparation of BMF and EMF.

2. Results and discussion

Inspired by recent progress in this field we started off by optimizing the conditions for the conversion of glucose/cellulose into BMF (**2**) (Scheme 1). The results from this study are summarized in Table 1.

Hydrobromic acid was chosen as an acidic reagent because it has several advantages compared to hydrochloric acid: it is a stable, stronger acid, can be easily distilled, and is non-volatile.

The choice of the solvent is an important factor when producing biofuel and several parameters must be evaluated. We have found that the most suitable solvent is 1,2-dichloroethane (DCE) (entries 5–14). We also looked for environmentally friendlier solvent which does not contain halogens and tested toluene (entries 1 and 2) and cycloalkanes (entries 3 and 4). However, toluene was found to react partially under these reaction conditions yielding benzyl bromide. Cycloalkanes are not suitable because of low solubility

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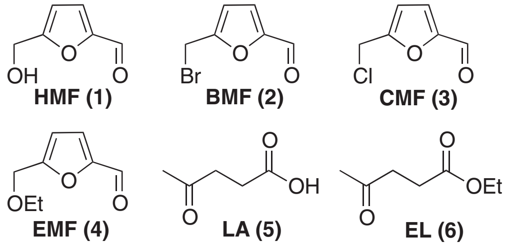
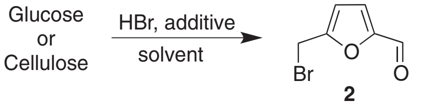


Figure 1. Chemicals readily available from lignocellulosic biomass.



Scheme 1. Synthesis of BMF (**2**).

of BMF (**2**) in them. Ether type solvents (THF, Me-THF, 1,4-dioxane, 1,2-dimethoxyethane, MTBE, Et_2O) were rapidly hydrolyzed or hydrobrominated in the presence of concentrated hydrobromic acid.

Optimal temperature was found to be 65 °C, below this temperature the reaction is slow or does not happen at all, and higher temperatures lead to slightly lower yields of BMF (entries 5 vs 9 and entries 8 vs 10). At 80 °C the difference in yield for reactions conducted for 3 or 24 h was only 4% (entries 9 and 11), indicating that most of the product is formed during the first 3 h.

Table 1
Optimization of carbohydrate conversion to BMF[a]

Entry	Substrate	Solvent	Temp (°C)	Additive	Yield[b] (%)
1	Glucose	Toluene	65	LiBr	47
2	Cellulose	Toluene	65	LiBr	44
3	Glucose	Cyclohexane	80	LiBr	20
4	Glucose	Methylcyclohexane	100	LiBr	7
5	Glucose	DCE	65	LiBr	64
6	Glucose	DCE	65	LiBr	53[d]
7	Glucose	DCE	65	LiBr	60[e]
8	Cellulose	DCE	65	LiBr	59
9	Glucose	DCE	80	LiBr	59
10	Cellulose	DCE	80	LiBr	51
11	Glucose	DCE	80	LiBr	55[c]
12	Glucose	DCE	65	—	54
13	Cellulose	DCE	65	—	48
14	Aspen	DCE	65	—	41

[a] Conditions: HBr, additive, solvent, 24 h; substrate loading is 1%.
[b] Yield of isolated product.
[c] Reaction time 3 h.
[d] 10% Substrate loading.
[e] Continuous extraction.

The best reaction conditions (entry 5) were successfully tested on 10% substrate loading (entry 6). Continuous extraction gave no improvement compared to manual extraction (entries 7 vs 5).

The use of LiBr as an additive in this reaction is problematic due to the cost of lithium compounds and difficulties associated with its regeneration. Therefore, it would be highly desirable to reduce the amount of LiBr used, or preferentially, to eliminate it completely. Therefore we studied the influence of the concentration of LiBr using our optimized reaction conditions (entries 12–14). We were pleased to discover that the decrease in the yield of BMF (**2**) in the absence of LiBr is only 10%, thus making the procedure much more suitable for industrial applications.

To the best of our knowledge we have completed the first evaluation of different wood species as a source of raw material for the production of BMF (**2**) (Table 2). Wood species chosen for this study (Quaking aspen, Silver birch, Black alder, Scots Pine, and Norway Spruce) are common in Northern Europe. It is assumed that dry wood in average contain 40% of cellulose, 20% of hemicellulose, and 40% of lignin, however cellulose content significantly varies in different species. Also not only cellulose is converted to BMF, but all C_6 carbohydrates (hexoses), while all C_5 carbohydrates are converted to furfural. Due to the variation of hexose and pentose content in different species we provide both mass and percent yields. Percent yields are calculated based on hexose and pentose content in given wood species. According to our observations the best wood was aspen because of high mass and percent yields of both BMF (**2**) and furfural. It was also the best from technological point of view, because of the easiness of phase separation during extraction. Pine and spruce gave also good mass yields of BMF, however these species are known to have higher content of cellulose, thus making percent yields from these species less than that of birch. Birch and alder were creating considerable difficulties during extraction, producing hardly separable emulsions.

Conversion of aspen to BMF and furfural was also performed on 10 g scale with 5% substrate loading. In this experiment products were separated by distillation to give 2.159 g (35% yield) of BMF and 0.366 g (28% yield) of furfural. It should be noted that the increase of substrate loading from 1% to 5% led to formation of emulsion during extraction. This was probably the cause for lower BMF yield.

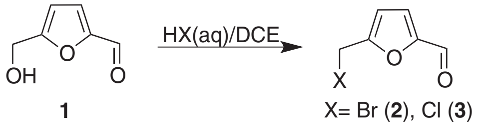
Yields of BMF from glucose and cellulose under the same conditions are higher than yields from wood (compare Table 1, entries 5 and 8 with Table 2), however the difference between pure cellulose and wood is only 3–10%, which is a very good result.

Addressing significant community interest and recent advances in conversion of sugars and biomass to HMF (**1**), we have also developed a simple and very efficient method for conversion of HMF (**1**) to CMF (**3**) and BMF (**2**) (Scheme 2). Current methods[20,21] for making compounds **1** and **2** are complicated, requiring the use of solutions of gaseous hydrogen halides in organic solvents or other reagents like PCl_3, PBr_3, $SOCl_2$ etc. It is known that HMF (**1**) is sensitive to acidic conditions, and undergoes decomposition

Table 2
Conversion of different wood species[a]

	Hexose content[b] (%)	BMF yield[c]		Pentose content[b] (%)	Furfural yield[c]	
		(mg)	(%)		(mg)	(%)
Aspen,[18] *Populus tremula*	53	237	55	18	34	35
Birch,[17] *Betula pendula*	43	197	56	28	42	29
Alder,[18] *Alnus glutinosa*	48	197	50	24	30	25
Pine,[17] *Pinus sylvestris*	56	232	51	9	9	20
Spruce,[17] *Picea abies*	58	230	49	9	15	33

[a] Conditions: HBr, LiBr, DCE, 65 °C, 24 h; 700 mg of wood shavings.
[b] Adopted from Refs. 17,18.
[c] Yield of isolated product.



Scheme 2. Conversion of HMF (**1**) to halomethylfurfurals.

Table 3
Conversion of HMF (**1**) to BMF (**2**) or CMF (**3**)

Conditions	Product	Yield[a] (%)
HBr (aq)/DCE, 24 h, rt	BMF	92
HBr (aq)/DCE, 1 h, 65 °C	BMF	94
HCl (aq)/DCE, 24 h, rt	CMF	86
HCl (aq)/DCE, 4 h, 65 °C	CMF	79

[a] Yield of isolated product.

Table 4
Optimization of EMF (**4**) synthesis

Entry	Solvent	Conditions	Yield[a] of **4** (%)	Content[b] of **6** (%)	Yield[a] of **7** (%)
1	96% EtOH	3 h, reflux	99	20	–
2	96% EtOH	1 h, reflux, $CaCO_3$	95	9	–
3	Abs EtOH	3 h, reflux	dec	–	–
4	Abs EtOH	1 d, rt, $CaCO_3$	50[c]	3	30[c]
5	Abs EtOH	5 h, 80 °C, $CaCO_3$	64[c]	5	29[c]

[a] Yield of isolated product.
[b] Determined by ^{1}H NMR.
[c] Purified by column chromatography.

with the formation of levulinic acid or polymerization depending on the conditions used.[19] This issue was resolved by using a biphasic acid/DCE reaction mixture which affords the corresponding halomethylfurfurals in excellent yields (Table 3).

As CMF (**3**) and BMF (**2**) cannot be used directly as fuels, we have also studied their conversion to EMF (**4**) (Table 4). Using the literature procedure[10] we managed to obtain crude oil in up to 99% yield (Table 4, entry 1). However, analysis showed the product to be a mixture of EMF (**4**) and EL (**6**) (up to 20%) which was not separable by column chromatography. An attempt to use $CaCO_3$ as a base in absolute ethanol (Table 4, entries 4 and 5) resulted in a mixture of EMF (**4**), EL (**6**), and EMF diethyl acetal (**7**) (Scheme 3). Similar difficulties during conversion of HMF (**1**) to EMF (**4**) in ethanol were also recently reported by others.[15,22] Conversion of BMF (**2**) with 96% ethanol in the presence of $CaCO_3$ worked better, holding the levels of EL (**6**) below 10% (Table 4, entry 2). We have found that additional wash of this mixture with NaOH (aq) furnishes pure EMF (**4**), thus providing a method for obtaining EMF (**4**) in a pure form.

We have demonstrated a procedure for transformation of cellulose to EMF, which does not require chromatography and purification of intermediate BMF, thus making the whole process more suitable for industrial application. Cellulose is converted to BMF using optimized conditions (Table 1, entry 8) and organic extracts are evaporated to yield crude BMF as black oil, which was then mixed with $CaCO_3$ and EtOH (96%) and refluxed for 1 h. Subsequent evaporation, extraction, and washing with NaOH gave pure EMF in 40% yield from cellulose.

3. Conclusion

Carbohydrates and wood of different species have been evaluated as a raw material for making 5-bromomethylfurfural (BMF, **2**). Individual carbohydrates (glucose, cellulose) generally gave better yields compared to wood, although the difference was not significant. The Quaking aspen gave highest yields of BMF and furfural among the wood species. The impact of several reaction parameters on the conversion of carbohydrates to BMF (**2**) has also been studied. Optimized procedure allows direct conversion of carbohydrates and raw wood biomass to BMF in good yields, substrate loadings as high as 10% are allowed. Also LiBr additive can be eliminated from the process, which is advantageous compared to the current methods. A mild and efficient method for the conversion of HMF (**1**) to halomethylfurfurals is reported. And finally, a procedure for converting BMF (**2**) to a perspective biodiesel candidate EMF (**4**) is reported.

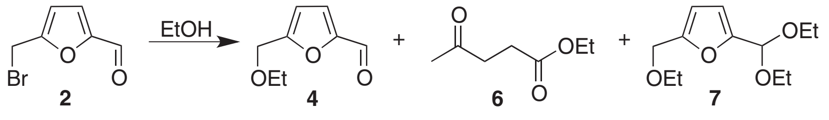
4. Experimental section

4.1. General methods

All reagents and solvents (except absolute ethanol) were obtained from commercial sources and used without further purification. Absolute ethanol was obtained by drying commercial 96% ethanol over CaH_2 (boiling 2 h with reflux, then distillation) and was stored under inert atmosphere. NMR spectroscopy was performed on a Bruker AVANCE II 400 MHz spectrometer using residual solvent peak ($CDCl_3$, 7.27 ppm for ^{1}H and 77.0 for ^{13}C NMR spectra) as internal standard. Infrared spectra were measured on a Shimadzu IRAffinity-1 FTIR spectrometer, using ATR module with ZnSe crystal. Melting points were determined on a Gallenkamp melting point apparatus. Reactions were monitored by thin-layer chromatography (TLC) and visualized by UV light or with $KMnO_4$ solution. Reaction products were purified by flash chromatography using silica gel 60 (0.040–0.063 mm, 230–400 mesh ASTM). Wood shavings were dried in drying oven at 105 °C until constant mass is achieved (20 h).

4.2. Typical procedure for conversion of wood to 5-bromomethylfurfural (2)

Dry aspen shavings (700 mg) and anhydrous LiBr (7 g) were mixed with HBr (aq, 48%, 70 mL) and 1,2-dichloroethane (70 mL), and then heated on the oil bath at 65 °C. After 1 h organic layer was separated and acidic fraction was extracted with 1,2-dichloroethane (2 × 70 mL). Organic fractions were combined and dried with Na_2SO_4. A fresh 1,2-dichloroethane (70 mL) was added to the acidic fraction and flask was placed again on the oil bath. Procedure was repeated after 1 and 2 h. Then reaction mixture was left to stir with heating overnight. On the next day (24 h), organic layer was separated and acidic residue extracted with 1,2-dichloroethane (3 × 70 mL). All organic fractions were combined and evaporated. Residue was subjected to column chromatography (eluent CH_2Cl_2) resulting in **2** (237 mg, 55%) as yellowish crystals and furfural (34 mg, 35%). **2**: mp 58.3–60.0 °C. FTIR (ATR): 3113, 3032, 2970, 2924, 2854, 1667, 1520, 1392, 1277, 1219, 1196, 1115, 1018, 968, 810, 772, 698, 655, 563. ^{1}H NMR (400 MHz, $CDCl_3$): δ



Scheme 3. Synthesis of EMF (**4**).

9.61 (s, 1H), 7.19 (d, J = 3.6 Hz, 1H), 6.58 (d, J = 3.6 Hz, 1H), 4.48 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 156.1, 152.7, 121.7, 112.0, 21.5 ppm. Furfural: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 (s, 1H), 7.68 (m, 1H), 7.24 (dd, J = 3.6, 0.7 Hz, 1H), 6.59 (dd, J = 3.6, 1.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.8, 152.9, 148.0, 120.9, 112.5 ppm.

4.2.1. Conversion of wood to 5-bromomethylfurfural (2), 10 g scale

According to typical procedure described above, dry aspen shavings (10 g) and anhydrous LiBr (20 g) were mixed with HBr (aq, 48%, 200 mL) and 1,2-dichloroethane (200 mL), and then heated on the oil bath at 65 °C. Solvent replacement and extraction with 1,2-dichloroethane (2 × 200 mL) were performed after 1, 2, 3, and 24 h. All organic fractions were combined and evaporated. Crude oil was filtered through the plug of silica (eluent CH_2Cl_2) and evaporated. Residue (2.566 g) was distilled with Kugelrohr apparatus to give **2** (2.159 g, 35%) as yellowish crystals and furfural (0.366 g, 28%) as colorless oil.

4.2.2. Conversion of glucose into 5-bromomethylfurfural (2)

According to typical procedure described above, glucose (721 mg) gave crude product that after purification with column chromatography and drying under vacuum resulted in **2** (482 mg, 64%) as yellowish crystals.

4.2.3. Conversion of cellulose into 5-bromomethylfurfural (2)

According to typical procedure described above, cellulose (700 mg, 5% water by mass) gave crude product that after purification with column chromatography and drying under vacuum resulted in **2** (452 mg, 59%) as yellowish crystals.

4.3. Conversion of 5-hydroxymethylfurfural (1) into 5-bromomethylfurfural (2)

4.3.1. Method a

Compound **1** (252 mg, 2 mmol) was dissolved in 1,2-dichloroethane (7 mL), then HBr (aq, 48%, 7 mL) was added. Biphasic reaction mixture was stirred at rt for 24 h, then organic layer was separated, and acidic fraction was extracted with CH_2Cl_2 (3 × 20 mL). Organic fractions were combined, dried with Na_2SO_4, and evaporated. Residue was purified by filtering through short silica gel column (eluent CH_2Cl_2) yielding after drying under vacuum **2** (348 mg, 92%) as yellowish crystals.

4.3.2. Method b

Compound **1** (252 mg, 2 mmol) was dissolved in 1,2-dichloroethane (7 mL), then HBr (aq, 48%, 7 mL) was added. Biphasic reaction mixture was heated for 1 h at 65 °C, then organic layer was separated and acidic fraction was extracted with CH_2Cl_2 (3 × 20 mL). Organic fractions were combined, dried with Na_2SO_4, and evaporated, yielding after drying under vacuum **2** (355 mg, 94%) as black crystals.

4.4. Conversion of 5-hydroxymethylfurfural (1) into 5-chloromethylfurfural (3)

4.4.1. Method a

Compound **1** (252 mg, 2 mmol) was dissolved in CH_2Cl_2 (10 mL), then HCl (aq, 37%, 5 mL) was added. Biphasic reaction mixture was stirred at rt for 24 h, then organic layer was separated, and acidic fraction was extracted with CH_2Cl_2 (3 × 20 mL). Organic fractions were combined, dried with Na_2SO_4, and evaporated. Residue was purified by filtering through short silica gel column (eluent CH_2Cl_2) yielding after drying under vacuum **3** (0.249 g, 86%) as yellowish crystals. mp 37.8–38.6 °C. FTIR (ATR): 3117, 3024, 2970, 2854, 1667, 1524, 1396, 1265, 1184, 1142, 1022, 980, 814, 772, 714, 687, 606. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (s, 1H), 7.19 (d, J = 3.6 Hz, 1H), 6.58 (d, J = 3.6 Hz, 1H), 4.60 (s, 2H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 156.0, 152.8, 121.6, 111.9, 36.4 ppm.

4.4.2. Method b

Compound **1** (252 mg, 2 mmol) was dissolved in CH_2Cl_2 (10 mL), then HCl (aq, 37%, 5 mL) was added. Biphasic reaction mixture was heated for 4 h at 65 °C, then organic layer was separated, and acidic fraction was extracted with CH_2Cl_2 (3 × 20 mL). Organic fractions were combined, dried with Na_2SO_4, and evaporated. Residue was purified by filtering through short silica gel column (eluent CH_2Cl_2) yielding after drying under vacuum **3** (229 mg, 79%) as yellowish crystals.

4.5. 5-Ethoxymethylfurfural (4)

Compound **2** (500 mg, 2.65 mmol) and $CaCO_3$ (265 mg, 2.65 mmol) were stirred in ethanol (10 mL) until dissolution of **2**. Then reaction mixture was placed on the oil bath and refluxed for 1 h. After this reaction mixture was cooled down, evaporated to the small volume and partitioned between Et_2O (30 mL) and water (30 mL). Water fraction was additionally extracted with Et_2O (3 × 30 mL). Organic fractions were combined and dried with Na_2SO_4, then volatiles were removed to give crude **4** (387 mg, 95%) as yellowish oil. Analysis showed that crude product contained also 9% of **6**. To obtain pure **4**, the crude oil was dissolved in Et_2O (15 mL) mixed with NaOH (1 M, 10 mL) in separation funnel. Then organic layer was separated and aqueous layer washed with ethyl ether (1 × 10 mL). Organic layers were combined, dried with Na_2SO_4. Then volatiles were removed to furnish **4** (301 mg, 74%) as pale yellow oil. FTIR (ATR): 3121, 2978, 2870, 1674, 1520, 1346, 1277, 1192, 1092, 1018, 968, 945, 806, 756. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.59 (s, 1H), 7.19 (d, J = 3.5 Hz, 1H), 6.50 (d, J = 3.5 Hz, 1H), 4.50 (s, 2H), 3.56 (q, J = 7.1 Hz), 1.21 (t, J = 7.1 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.6, 158.7, 152.5, 121.8, 110.9, 66.5, 64.7, 15.0 ppm.

4.5.1. Conversion of cellulose into 5-ethoxymethylfurfural (4)

According to typical procedure Section 4.2, cellulose (700 mg, contains 5% water by mass) gave crude BMF product (574 mg, black oil, contains 7% 1,2-dichloroethane) which was mixed with $CaCO_3$ (300 mg, 3.0 mmol) and ethanol (10 mL). Then reaction mixture was placed on the oil bath and refluxed for 1 h. After this reaction mixture was cooled down, evaporated to the small volume and partitioned between Et_2O (15 mL) and water (15 mL). Water fraction was additionally extracted with Et_2O (3 × 15 mL). Organic fractions were combined and dried with Na_2SO_4, volatiles were removed to give crude **4** (363 mg, contains 6% ethyl levulinate) as brownish oil. To obtain pure **4**, the crude oil was dissolved in Et_2O (15 mL) and mixed with NaOH (1 M, 10 mL) in separation funnel. Organic layer was separated and aqueous layer washed with ethyl ether (1 × 15 mL). Organic layers were combined and dried with Na_2SO_4. The removal of volatiles afforded pure **4** (251 mg, 40% from cellulose) as yellowish oil.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2013.04.002.

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