Valorisation of humins-extracted 5-Methoxymethylfurfural: towards high added value furanics via continuous flow catatalytic hydrogenation

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Abstract

The formation of humins is one drawback of biomass valorization (e.g. hemicellulosic fraction) towards platform chemicals and fuels. Furanic compounds including 5-hydroxymethylfurfural and 5-methoxymethylfurfural can be extracted from humins and valorized. Unlike HMF, reactions with MMF have not been widely studied. In this work, 5-methoxymethylfurfural (MMF) was extracted from humins aiming to its hydrogenation in continuous flow. Based on success from literature studies with HMF hydrogenation, 5% Ru/C and 5% Pd/C catalysts were employed and both have demonstrated excellent conversion of MMF towards hydrogenation products (100%), with an interesting selectivity switch depending on reaction conditions. Ru-based catalyst were more prone to deactivation as compared to Pd catalysts, extremely stable after a few hours on stream under the investigated reaction conditions. A reaction mechanism was proposed for MMF hydrogenation.

1. Introduction

Biomass has proven to be one of the most promising routes toward sustainability within the chemical industry [1-3]. As a renewable resource, the environmental benefits of using biomass over petroleum to obtain platform chemicals are substantial. Yet, there are still many challenges on this path to a more bio-based chemical industry [4]. One of the challenges is the inevitable formation of humins during the acid-catalyzed hydrolysis of biomass-derived sugars [5]. Humins comprise a polymeric network of furanic derivatives containing sugar-derived moieties rather complicated to work with due to their complex structure, which is still being investigated and not fully understood [6-7].

Nevertheless, humins have tremendous potential to be valorized to a range of valuable chemicals and fuels due to the presence of the aforementioned furanics in its composition [7-9].

Furanics have been recently highlighted for their use as excellent platform molecules [10]. From internal studies, we identified two extractible furanics of high interest from humins: 5-hydroxymethylfurfural (HMF) and 5-methoxymethylfurfural (MMF). Both of these compounds are formed during the acid dehydration of biomass (C-6 sugars) [11]. MMF is formed when methanol is used in the dehydration process, whereas HMF is formed when water is present [12]. Generally, MMF is believed to be more stable than HMF as the process with methanol generates less side products [13].

While plenty of experimental work has been done with HMF valorization [13-21], MMF has been virtually untouched, with no studies available of humins-derived MMF. Catalytic hydrogenation reactions have been a common approach to transform HMF into high-added value compounds including dimethylfuran (DMF), a potential biofuel [15].

A summary of HMF hydrogenation results and reaction conditions reported in literature is shown in Table 1. Overall, most sources have reported relatively good conversion of HMF in their hydrogenation experiments. Some conditions that have led to better conversions include the use of carbon supported Ru as a catalyst, reaction temperatures above 150 °C and the use of alcohol as a solvent to additionally enable a transfer hydrogenation step.

With regards to hydrogen, overly high pressures were not generally needed to achieve excellent conversions although these did not have any detrimental effect in the reported systems. Importantly, the large majority of these reactions were performed 1) in batch conditions 2) at moderate to high temperatures (over 150ºC) and 3) required longer reaction times to achieve relevant DMF yields (typically over 70%).

Based on preceding studies, the present work was aimed to valorize industrial humins via extraction/separation/purification of MMF in view of its further selective hydrogenation to high added value products under continuous flow conditions.

Table 1. Literature studies of HMF hydrogenation.

Reaction Type	**Catalyst**	**Conversion (%)**	**Reaction Conditions** *T* (°C)	*P* (bar)	**Time**	**Solvent**	**HMF Conc.**	**Product**[a]	**Ref.**
Batch	Ru/C	100	60	50	0.6 h	H_2O	5.6 mmol	DHMF	[13]
Flow	Pd/Fe_2O_3	100	180	25	0.4 h	IPA	0.12 M	DHMF, DMF	[14]
Batch	5% Ru/C	43	150	6.9	1 h	H_2O	39.7 mM	DHMF	[15]
Batch	5% Ru/C	82	150	6.9	1 h	H_2O	39.7 mM	DHMF, DHMTHF, MFA, DMF	[15]
Batch	CuZn	95	120	70	3 h	EtOH	---	DHMF	[16]
Batch	Ru/C	100	200	20	2 h	THF	2.5 wt%	DMF	[17]
Batch	Cu-Ru/C	100	220	6.8	10 h	1-BOH	2.5 g	DMF	[10]
Batch	Ru/C	100	190	20	6 h	IPA	1.2 wt%	DMF, BHMF, MFA, MF	[19]
Batch	10 wt% Pt/C	100	180	33	0.5 h	1-Propanol	1 wt%	DMF, DMTHF, 2-hexanone	[20]
Flow	10 wt% Pt/C	83.4	180	33	0.5 h	1-Propanol	1 wt%	DMF, other	[20]
Batch	1 wt% Ru/C	55	150	20	1 h	2-BOH	0.08 M	DMF	[21]

[a]Legend: HMF, 2,5-hydroxymethylfurfural; MF, 5-methylfurfural; 1-BOH, 1-butanol; 2HAO, 2-hexanol; FA, furfurylalcohol; DHMF, 2,5-bis(hydroxymethyl)furan; MFA, 5-methylfurfurylalcohol; DMF, 2,5-dimethylfuran; DHMTHF, 2,5-bis(hydroxymethyl)tetrahydrofuran; MTHFA, 5-methyltetrahydrofurfurylalcohol; DMTHF, 2,5-dimethyltetrahydrofuran.

2. Experimental Methods

2.1 Chemicals and Materials

Hexanes (95%), ethyl acetate (99.9%) and silica gel (60, 63-200) were purchased from Panreac. The catalysts (5% Ru/C and 5% Pd/C CatCarts™) were purchased from ThalesNano©. Humins were kindly provided by Avantium Chemicals, The Netherlands in the framework of the HUGS MSCA-ITN project.

2.2 Extraction of MMF from Humins

MMF was separated and purified from humins using column chromatography. Humins were first dissolved in ethyl acetate and then adsorbed onto silica gel through rotary evaporation. The resulting powder was dry loaded and run through a column packed with a 3:1 mixture hexane:ethyl acetate. The procedure was repeated several times in order to achieve an employable quantity of reactant. MMF is the first compound to pass through the column and its presence and purity was confirmed using mass spectrometry (MS).

2.3 Hydrogenation Reactions

The hydrogenation reactions of MMF were carried out in a ThalesNano© H-Cube Mini Plus™. In a typical experiment, 0.20 g of MMF were dissolved in 20 mL of ethyl acetate (1 % w/v MMF solution) that was continuously fed at a flow rate of 0.3 mL/min. After flushing the system with methanol and then ethyl acetate (room temperature, 0.1 mL/min, 1 h), the reaction conditions were initiated (50-100ºC, different hydrogen pressures). Once the system was stable with the desired reaction conditions, MMF was pumped through. Sampling began at the moment the entire system was filled with the feed solution based on the system dead volume and feed flow rate (typically after 20 mins). After the reaction was complete, both the system and catalyst were washed thoroughly with ethyl acetate while still at the reaction conditions and the system was subsequently rinsed with methanol. The collected samples were filtered with a 0.45 μm syringe membrane filter and analyzed by gas chromatography-mass spectrometry (GCMS).

2.4 Analysis of Products.

Reaction products were analyzed in an Agilent 7820A gas chromatograph (60 mL min^{-1} N_2 carrier flow, 20 psi column top head pressure) using a flame ionization detector (FID). A capillary column HP-5ms Ultra Inert (30 m × 250 μm × 0.25 μm) was employed. To calculate the molar amount of product generated, the peak areas were used to work out the experimental reagent to product ratio that was then compared to the expected reagent to product ratio. Conversions and selectivities were calculated using these molar quantities. In addition, the products were identified by GC-MS with an Agilent 5977B High Efficiency Source (HES).

3. Results and Discussion

Commercial carbon supported Ru and Pd catalysts (5 to 10% metal, 30 mm CatCart® https://thalesnano.com/products/catcarts-and-compatible-systems-for-safe-catalysthandling/) were both used for the continuous flow hydrogenation of MMF. A 5%Ru/C catalyst was firstly employed to explore the effect of hydrogen pressure on MMF conversion experiments due to previous success cases reported in literature for HMF (Table 1).

The hydrogen pressure was adjusted between 0 to 100 bar in order to see the effect on the conversion of MMF (Figure 1). As expected, MMF conversion essentially topped out at a pressure (30 bar) and did not considerably improve upon exceeding such high pressure. Runs in the absence of hydrogen did not provide any conversion in the systems. These results are in good agreement with previous reports for hydrogen pressure effect studies in HMF hydrogenation [13]. The conversion declined rapidly with time on stream (from quantitative to ca. 20-25%), remaining stable at ca. 20-25% for longer reaction runs (typically 5-10 h). These results indicate a rapid deactivation of 5%Ru/C and a poor stability of the system (significant Ru leaching observed, >50 ppm into solution) under the investigated relatively high flow conditions. Reducing flow rates to 0.1 mL/min could stabilize the conversion in the systems to ca. 45-50% even after extended reaction runs (3 h and over).

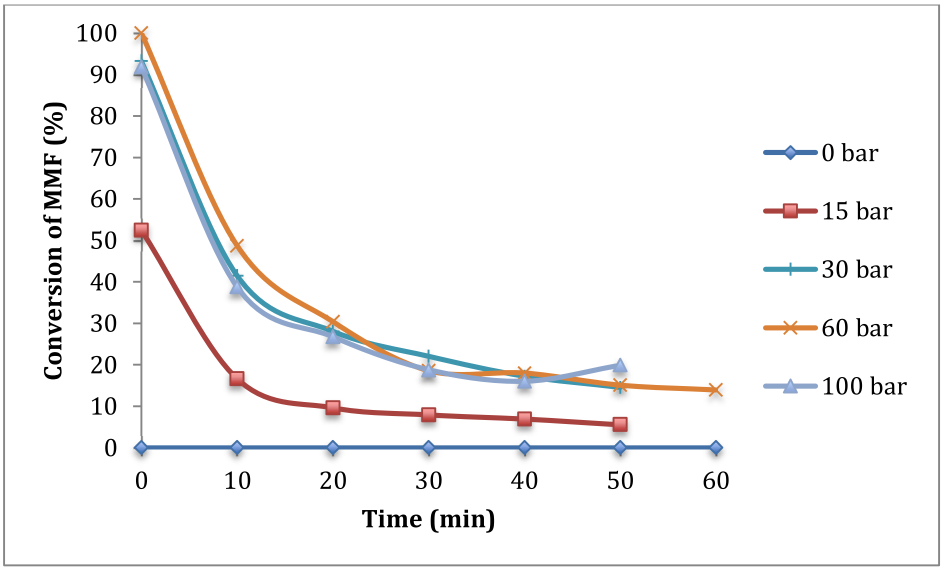
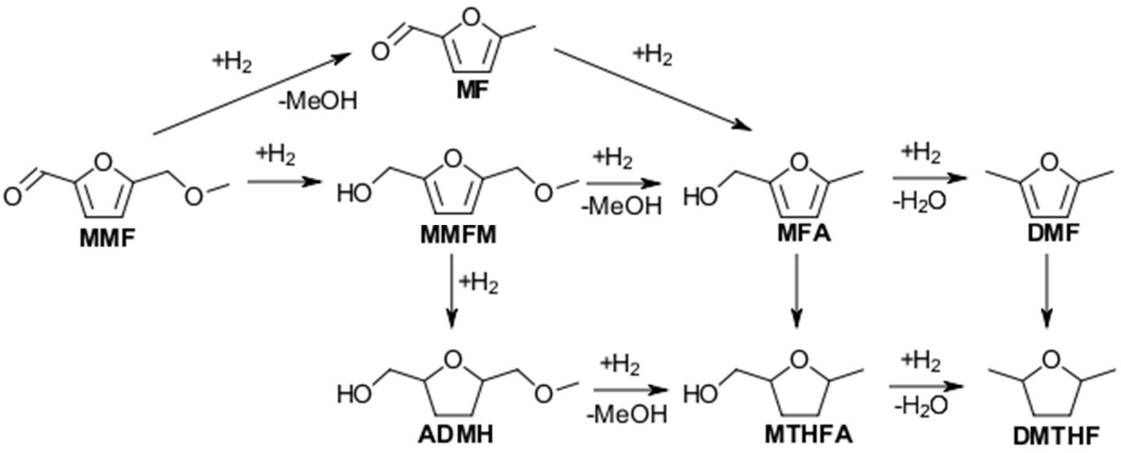


Figure 1. Effect of hydrogen pressure on conversion of MMF. Reaction conditions: 100 °C, 0.3 mL/min feed flow rate, 1% w/v MMF in ethyl acetate, 5% Ru/C catalyst.

Two main products could be observed under the investigated reaction conditions: 5-(methoxymethyl)-2-furyl]methanol (MMFM) and 5-methyltedtrahydrofurfuryl alcohol (MTHFA). As shown in Scheme 1, the formation of MMFM is considered to be one of the first hydrogenation steps [13]. The second compound, MTHFA, is the further hydrogenation product that occurs upon ring hydrogenation.



Scheme 1. Reaction scheme of MMF hydrogenation MMF (adapted from the HMF hydrogenation scheme in ref. 13) Legend: MMF, 5-methoxymethylfurfural; MF, 5-methylfurfural; MMFM, [5-(methoxymethyl)-2-furyl]methanol; ADMH, ; MTHFA, 5-methyltetradhydrofurfuryl alcohol; DMF, 2,5-dimethylfuran; DMTHF, 2,5-dimethyltetrahydrofuran

Product distribution from MMF hydrogenation reactions at different hydrogen pressures is shown in Table 2. The presence of MTHFA only at initial time-zero samples also makes evident that the catalyst activity decreases quickly mostly due to metal leaching (almost no coking observed, results not shown).

Table 2. Product distribution of pressure study reactions run with 5% Ru/C catalyst.

Hydrogen Pressure (bar)	MMFM Yield (%)			MTHFA Yield (%)		
	0 min	10 min	30 min	0 min	10 min	30 min
0	-	-	-	-	-	-
15	52	17	8	-	-	-
30	76	42	22	17	-	-
60	62	49	19	38	-	-
100	33	39	19	59	-	-

Having optimized the pressure conditions with 5% Ru/C catalyst, another catalyst was tested to compare activity, along with a blank reaction (without catalyst, Figure 2). As expected, no conversion was observed in the absence of catalyst. Unexpectedly, complete MMF conversion and full product selectivity to MTHFA was obtained for the Pd catalyst (Figure 2), as well as an exceptional stability with no apparent catalyst deactivation under the investigated conditions for extended runs (typically 2-4 h).

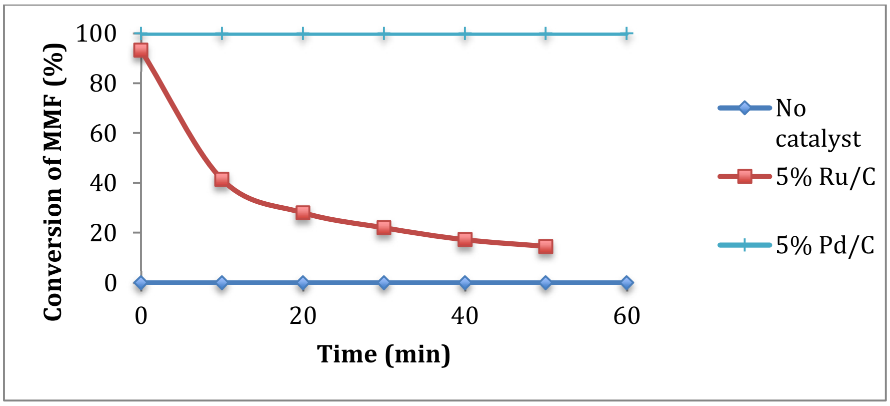


Figure 2. Comparison of MMF conversion from hydrogenation reaction performed with no catalyst, 5% Ru/C, and 5% Pd/C. Reaction conditions: 100 ºC, 30 bar, 0.3 mL/min feed flow rate, 1% w/v MMF in ethyl acetate.

As shown in Figure 3, the product distribution was remarkably different between Ru and Pd, with Pd offering an unprecedented stability and further ring hydrogenation under otherwise identical continuous flow conditions. A selectivity switch was therefore possible by changing the catalytic system under continuous flow under the investigated conditions.

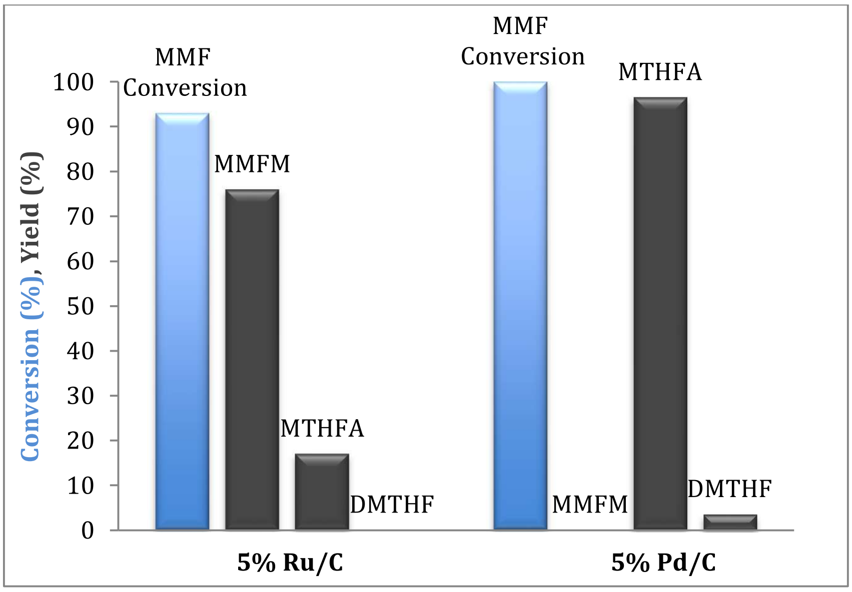


Figure 3. MMF conversion and hydrogenated product distribution for the 5% Ru/C and 5% Pd/C.

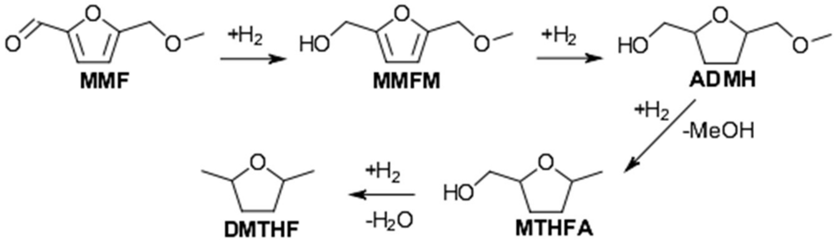
To gain a better insight into the hydrogenation pathway of MMF, two reactions were performed with the Pd catalyst at lower temperatures of 50 °C and 75 °C (Table 3). The two main hydrogenation products formed were still MMFM and MTHFA. However, small amounts of intermediates were also detected, namely DMTHF.

Table 3. Summary of initial MMF conversion and product yields at different conditions

Catalyst				Yield (%)		
	T (°C)	H_2 P (bar)	Conversion (%)	MMFM	MTHFA	DMTHF
5% Ru/C	100	15	52	52	-	-
5% Ru/C	100	30	93	76	17	-
5% Ru/C	100	60	100	62	38	-
5% Ru/C	100	100	92	33	59	-
5% Ru/C	100	-	-	-	-	-
5% Pd/C	50	30	100	-	96	3
5% Pd/C	75	30	100	-	93	7
5% Pd/C	100	30	100	-	97	3
No catalyst	100	30	-	-	-	-

The main product even at lower reaction temperatures was still MTHFA, as shown in Table 3. However, trace amounts of ADMH were also detected (yield < 1%) in the product samples of the 50 °C reaction, suggesting that it is a highly reactive intermediate under the investigated flow reaction conditions.

As a result, the hydrogenation pathway of MMF appears to favor ring dehydration first before decarboxylation of the methoxy group. Scheme 2 shows the MMF hydrogenation mechanism we have observed in these experiments. Similar results were observed in the conversion of HMF under hydrogen pressure, rather than other H-donor sources [22].



Scheme 2. Proposed mechanism for MMF hydrogenation

4. Conclusions

In this work, we have demonstrated successful and efficient hydrogenation of MMF under continuous flow conditions. The two catalysts tested, 5% Ru/C and 5% Pd/C, both facilitated MMF hydrogenation. An optimum conversion (>93%) could be achieved for a milder H_2 pressure of 30 bar for both systems, despite a rapid catalytic deactivation was observed for the Ru catalyst with high selectivity to MMFM. Alternatively, 5% Pd/C provided further hydrogenation/demethoxylation to MTHFA and 100% conversion with no catalytic deactivation within times tested (typically 2-4 h on stream). A reaction mechanism was then proposed for MMF hydrogenation which favors 1) carbonyl-to-hydroxyl hydrogenation and 2) ring hydrogenation followed by demethoxylation.

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