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Furfural to Cyclopentanone – a Search for Putative Oligomeric By-products

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We report here on the reductive rearrangement of biomass-derived furfural to cyclopentanone, a promising non-fossil feedstock for fuels and chemicals. An underreported aspect of this reaction is the inevitable formation of heavy byproducts. To mitigate its formation, process condition such as, solvent, catalyst, temperature, acidity, and feed concentration were varied to unravel the chemistry and improve the reaction performance. Water medium was confirmed to play a crucial role, as organic solvents were unable to deliver cyclopentanone or heavy by products. Copper-based catalyst showed the highest selectivity for ring-rearrangement, reaching 50 mol% under the conditions investigated. The main factor influencing the yields of cyclopentanone (CPO), and promote oligomer formation, are the feed concentration and the pH, as high feed concentrations and high acidity facilitate the self-polymerization of furfuryl alcohol (FALC). This was confirmed by dedicated experiments using FALC and the hydroxypentenone intermediate as feed. The concentration challenge could be mitigated by slowly dosing the feed, which increased the desired product yields by 4–12 mol%. Nevertheless, most oligomers appeared to fall in the range of common liquid fuels and could be converted to diesel by hydrodeoxygenation.

Introduction

The growing awareness of climate change has encouraged industry to explore the use of renewable and biobased feedstocks.[1–4] One promising platform chemical is furfural (FUR),[5–9] which can be readily derived from lignocellulose, one of the most abundant biomass resources on earth.[5,6,10] Product derivatives of furfural can be applied in different sectors such as fuel, plastics, solvents, inks, dies and adhesives, among others.[5,11,12] For instance, furfural can be converted to tetrahydrofuran (THF)[11] as solvent, to 1,4-butanediol as monomer for biodegradable polyesters,[13] to tetrahydrofurfuryl alcohol (THFALC)[14] for coatings and to 2-methylfuran[15] as a fuel or flavouring agent.

Besides the products mentioned above, another derivative was discovered by Piancatelli et al.[16] in 1976. Furfural was shown to undergo a reductive rearrangement to 4-hydroxy-2-cyclopentenone (4-HCP), which is an intermediate in cyclopentanone (CPO) and cyclopentanol (CPA) production. CPO can be used as an intermediate for rubber adhesives, synthetic resins and pharmaceuticals. In addition, the cyclic ketone has gathered considerable attention of researchers and the aviation industry alike as CPO has potential applications in the synthesis of bio jet using aldol condensation reactions.[17–18]

The conversion of FUR to CPO requires a hydrogenation catalyst and H_2 atmosphere, elevated temperature and an acidic aqueous medium. It is also generally recognized to proceed through the series of intermediates illustrated in Figure 1, namely via furfuryl alcohol, 4-hydroxy-cyclopentanone, 2-cyclopentenone, cyclopentanone and finally cyclopentanol.[19–21] Extensive research has been conducted towards catalyst formulation and reaction conditions. Hronec et al.[22] investigated the performances of Pt, Pd, Ru, CoMnCr and Raney Ni and reported 81 mol% yield of CPO and CPA. Dohade et al.[19] studied the use of cobalt- platinum alloys and reported CPO yields of 75 mol%. Tian[23] et al. investigated the relation between availability of Ni sites against CPO selectivity. Yang et al.[24] combined both Ni and Cu in bimetallic catalyst(s)

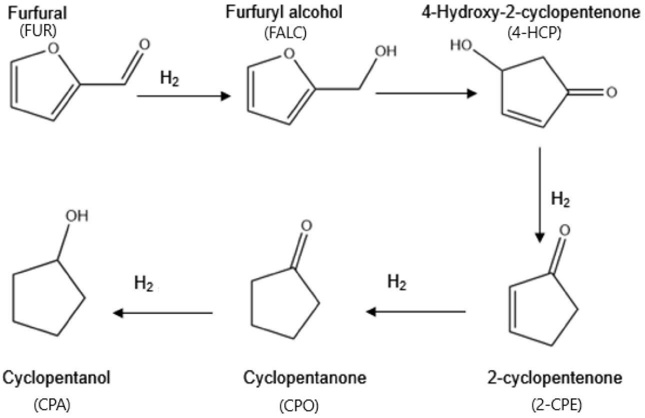

Figure 1. Proposed reaction intermediates for the catalytic reductive rearrangement of furfural to cyclopentanone.

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resulting in 65 mol% CPO/CPA selectivity. Jianhua et al.[25] reported a yield of 62 mol% of CPO with CuZnAl catalyst. Mironenko et al.[26] synthesized bimetallic catalyst using Pd and Ru which delivered selectivities of CPA of around 77 mol%. Zhu et al.[27] investigated the bimetallic ratios of Cu- and Ni-containing hydrotalcites and reported yield of 96 mol% CPO. Another study with bimetallic catalysts performed by Li Y et al.[28] used Co–Ni combinations resulting in subsequent CPO yields of 53 mol%. Fang et al.[29] studied metal-organic frameworks (MOF) using mRu/MIL-101 catalyst and reported yields higher than 96 mol% towards CPO.

Thus, there appears to be a wide variety of hydrogenation catalysts. However, much less attention has been devoted to the hydrothermal stability of the catalyst, i.e., of the support as well as the active metals. Many of the catalysts proposed so far are expected to deactivate by support degradation and metal sintering or leaching under prolonged operation.[30]

Another parameter of importance is the solvent. Organic solvents lead to ring-hydrogenated products and do not allow the desired ring-rearrangement reaction. Jia et al.[31] and Dohade et al.[19] investigated the role of solvent and concluded that water plays a crucial role in the rearrangement reaction. However its exact interaction leading to the rearrangement remains unclear.

Most importantly, however, the selectivities reported so far should be taken with caution because they seem to be based on measured low-Mw products, without consideration of oligomeric by-products that are expected but neither reported nor eluted to by incomplete mass balances. One critical intermediate is furfuryl alcohol (FALC), for it is prone to self-polymerization under acidic conditions.[32–35] This undesired side-reaction cannot be negated and forced researchers to use dilute systems ($\leq$5 wt% furfural in water). Nevertheless, the literature pays little to no attention to these oligomers. The selectivities reported seem to be based on low molecular weight products, e.g., CPO/CPA, ring hydrogenated products, without reporting that the furfural conversion exceeds the products observed and, thereby, likely overestimating the yields and selectivities.

This work aims to investigate the formation of unreported heavy product. To this end, we have focused on closing our mass balance, providing evidence, characterisation and quantification of heavy products, investigating their origin by spiking various reaction intermediates, and investigating the impact of process parameters on their formation during the (reductive) rearrangement.

Materials and Methods

Materials

Furfural (99%), Furfuryl Alcohol (98%), Cyclopentanone (99%), Cyclopentanol (99%), Phosphoric Acid (99.999%), were purchased from Sigma Aldrich. Intermediate 4-hydroxy-2-cyclopentenone was obtained from BLDPharm. Platinum, ruthenium and palladium catalysts were acquired from sigma Aldrich. Nickel, Copper and Cobalt catalysts were provided by Shell.

Catalytic conversion of furfural and its intermediates

The catalytic hydrogenation was performed in a 45 mL stainless steel autoclave equipped with a magnetic stirrer, a pressure gauge and automated temperature control. Both nitrogen and hydrogen cylinders were attached to the reactor's pressure gauge. Before each experiment, the oxidic catalyst (0.10 grams) was reduced in the reactor at 200 °C, 40 bar H_2 for 1 hour under dry conditions. In a typical hydrogenation experiment, furfural (1 gram, 10.4 mmol) was dissolved into 20 mL of demineralized water that was optionally buffered to the desired pH with H_3PO_4. The solution was added to the reactor accommodating the reduced catalyst. The reactor was sealed and purged three times with nitrogen to remove most of the air, flushed three times with hydrogen, pressurised with hydrogen to 80 bar and heated to the desired temperature. Temperature and pressure profiles were logged using Picolog software. Reaction time was set to start when the liquid temperature reached the "target temperature – 5 °C", which typically took 10–15 min. After the desired reaction time, the reactor was indirectly cooled down by employing cooling water after which the gas was released. Samples were collected at the start and end of each experiment and subsequently analysed.

The so-called batch dosing experiments were performed by loading the 45 mL reactor with an 0.5 wt% aqueous acidic solution of furfuryl alcohol (2 mmol), without hydrogenation catalyst. Once loaded, the reactor was purged with nitrogen for three times, pressurised to 40 bar N_2 at room temperature, and heated up to the desired reaction temperature of 160 °C in around 15 minutes. Reaction time was set to start when the liquid temperature reached the "target temperature – 5 °C". Once the desired reaction time was reached, the reactor was cooled down to room temperature in around 15 minutes, depressurised, opened, loaded with a new dose of 2 mmol pure furfuryl alcohol, purged, repressurised and run for another period. Depending on the experiment, the dosing was repeated for "n" number of doses. Samples were taken before and after each dose and analysed accordingly.

Analysis and calculations

Reaction products were analysed using a GC 7890A MS 5975C by Agilent Technologies with auto sampler and flame ionization detector (FID). The GC column was an Agilent VF-1701 ms. The column temperature was initially kept at 45 °C for 10 minutes, and then increased at a rate of 3 °C per minute to 280 °C.

Conversion, selectivity and yield were determined according to equations 1 and 2. The mole balance was determined by summing all products and unconverted furfural according to eq. 2. The missing moles were then subject of dedicated investigation, by searching for gaseous products with gas sampling and searching for heavy products by Gel permeation chromatography.

$$\mathit{Conversion}\ (\mathit{mol}\ \%) = \frac{\mathit{mole\ furfural\ converted}}{\mathit{mole\ furfural\ loaded}} \times 100 \tag{1}$$

$$\mathit{Selectivity}\ (\mathit{mol}\ \%) = \frac{\mathit{mole\ formed\ product}}{\mathit{mole\ furfural\ loaded}} \times 100 \tag{2}$$

Oligomeric products were analysed using an Agilent 1260 Infinity Gel Permeation Chromatography (GPC). The machine was equipped with a UV detector running at 254 nm, a refractive index detector and a 3 GPC PLgel 3 m MIXED–E column. The column was operated at 40 °C and a pure tetrahydrofuran mobile phase. The mobile phase flowrate was constant at 1 mL/min. Molecular weight distributions were calibrated using polystyrene solutions having molecular weights ranging from 162 to 27810 g/mol.

Validation of prior art

Previous literature has reported a wide range of metal catalysts over a large window of operating conditions. Initial trials to reproduce these results proved to be deceiving. High selectivity towards ring-hydrogenated products and pentanols were dominant with Pt and Ru catalysts (not reported here), with poor selectivity towards ring-rearranged products if any.

We also found incomplete mass balances, which was typically not reported in the literature. Hence, we revisited catalysts and operating window to validate prior art.

Influence of catalyst

We used catalysts based on Co, Ni and Cu. Figure 2 reveals that the catalysts with the highest activity for CPO/CPA formation are based on Cu. In particular, Cu (60 wt%) supported on zirconium oxide displayed the best performance, with a cumulative yield of CPO + CPA of 50 mol%. Ring-hydrogenated products accounted for 10 mol%, while the remaining 40 mol% remained unaccounted for. CPO + CPA yields obtained with Ni and Co catalysts were 30 and 12 mol% respectively under used experimental conditions. The main products observed by using Ni catalyst are THFALC, showing high activity for ring-hydrogenation whilst keeping the furanic ring still intact. Cobalt based catalysts however show a wider variety of ring-hydrogenated products ranging from THFALC, to 2,3-dihydro-5-methylfuran, pentanediol and cyclopentanediols.

Furthermore, the mole balance of the reactions can be directly derived from Figure 2. The overall mole balance varies between 38–85 mol%. As the reactors gas phase did not account for any light fraction, the missing mass could be attributed to the formation of heavier products, observed visually by the liquids change in colour and as deposition inside the reactor and will be quantified in a later section.

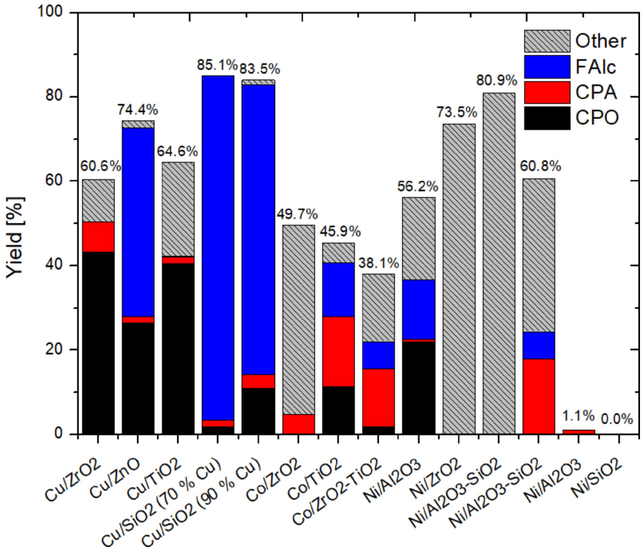

Figure 2. Experimental data for reductive rearrangement using batch reactions, 5 wt% furfural in water with pH 3.5, 160 °C, 80 bar H_2 at 20 C, for 60 minutes.

Importantly, catalysts supported on SiO_2 and Al_2O_3 appeared to be relatively unstable during experiments, as the inside of the reactor was coated with the hydrogenation metal. SiO_2 and Al_2O_3 are indeed known to rehydrate to $Si(OH)_4$ and $AlO(OH)$, respectively, when run in water at high temperature.[30] The other supports appeared to survive such short runs, which is obviously no guarantee that they will survive thousands of hours of operation.

Influence of solvent

We investigate the role of solvent by conducting reactions in aqueous, protic and aprotic organic medium using Cu/ZrO_2 (60 wt% Cu) as catalyst. As can be observed from Figure 3, organic solvents, both protic and non-protic, did not pursue the reaction beyond furfuryl alcohol (FALC) and some minor ring-hydrogenated products such as dihydro-methyl furan and tetrahydrofuran that were included in “other”. In contrast, reactions performed in aqueous medium showed the formation of CPO, CPA, some ring-hydrogenation products and humins. Notably, the cumulative GCMS-measurable products from the water experiments did not surpass 50 mol%. Examination of the gas phase within the reactor revealed an absence of any light products, which led us to attribute the missing moles to humins. The mole balance was eventually closed by analysis and quantification of the humins, as discussed later in this work. Interestingly, no heavy products were observed in organic solvents.

Given the pivotal role of water in the reductive rearrangement reaction and its apparent involvement in facilitating humin formation, all subsequent catalytic assessments were undertaken under aqueous conditions with complete feed

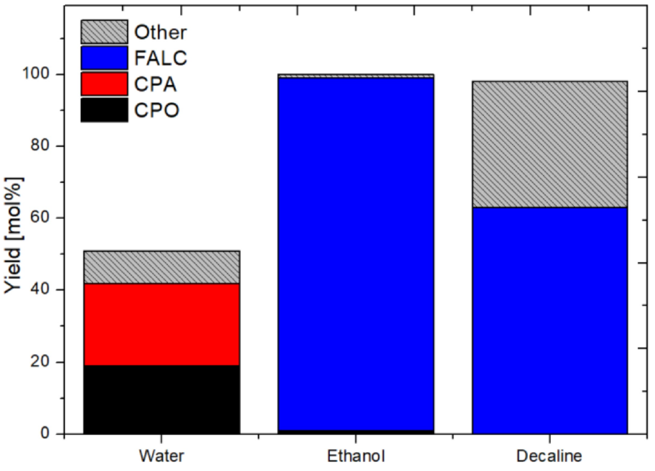

Figure 3. The role of solvent on the conversion of furfural (0.5 wt% Cu/ZrO_2 at 160 °C, 80 bar H_2 for 120 min, 5 wt% FUR in various media, Demineralized water at pH 6.8).

conversion. This approach aims to elucidate the competition between rearrangement and oligomer formation.

Influence of temperature

Temperature effects were investigated and reported in Figure 4. Moving from 140 to 180 °C increases the CPO and CPA yield and shift the ratio towards CPA as ketone hydrogenation is promoted. Indeed, the cumulative selectivity towards ring-rearranged products increase from 39 mol% at 140 °C, to 41 mol% at 160 °C and 53 mol% at 180 °C. Meanwhile, the formation of ring-hydrogenated products such as tetrahydrofuran, dihydro-5-methylfuran, and tetrahydro-2-methylfuran, or of ring-rearranged intermediates, e.g., 2-cyclopente-1-one, appears to be suppressed with increasing temperature. Similarly, elevated temperature seem to depress the putative formation of oligomeric products evidenced by the improved mole balance. The shift is related to presence of parallel side-reactions that have a lower activation energy than the desired ring-rearrangement.

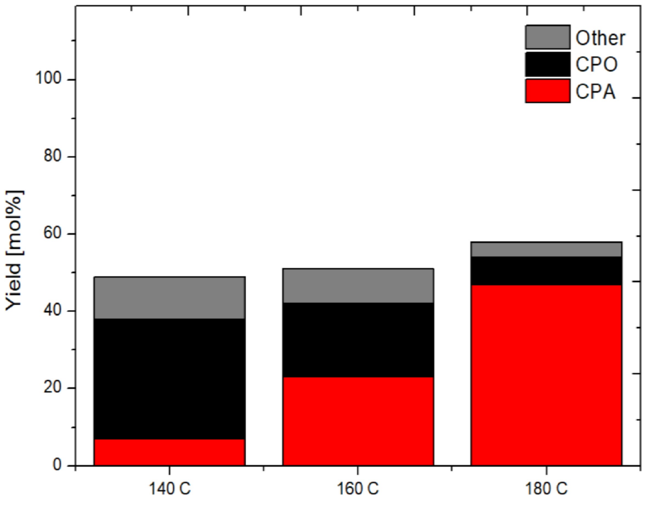

Figure 4. The influence of temperature on the reductive rearrangement of furfural (0.5 wt% CuO/ZrO_2, 80 bar H_2 at 20 °C, 120 min, 5 wt% FUR in demineralized water (pH = 6.8)).

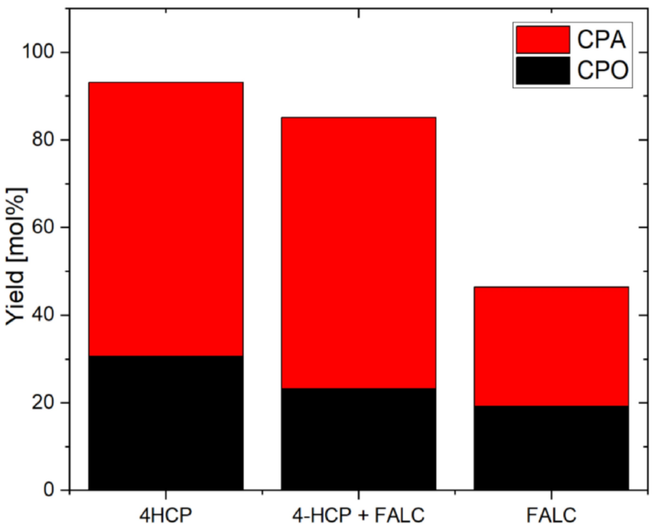

Figure 5. Reactivity of putative reaction intermediates of reductive rearrangement of furfural (160 °C, 80 bar H_2, 2 wt%, 1 hour, H_2O pH 3.5 (H_3PO_4), 0.5 wt% CuO/ZrO_2).

Oligomer study

Reactivity of putative intermediates

Different intermediates were used as feed to identify the source of oligomers. As depicted in Figure 1, the overall reaction consists out of the hydrogenation of FUR to FALC, the rearrangement of FALC to 4-HCP and finally a last hydrogenation of 4-HCP to CPO/CPA. Therefore, experiments were performed using FALC and secondly 4-HCP as feed. The product distribution and mole balances are reported in Figure 5.

In reactions starting from FALC, the mole balance reached 46 mol%, which is close to the mole balance obtained from furfural (Figure 4). Vast amounts of oligomers could be seen on the stirrer and inside the reactor after the experiment. Changing feed from FALC to 4-HCP increased the yields of CPO and CPA, pushing the mole balance to 93 mol%. Investigating the behaviour further, 4-HCP was cofed together with FALC in equimolar ratio and led to an the intermediate result depicted in Figure 5. Overall, the FALC intermediate appears to be the main cause for the oligomerization reaction.

Influence of pH

Acidity was found to also play a key role in the competitive formation of CPO/CPA and oligomers. Both rearrangement and oligomerization are indeed expected to be catalysed by acid. Reactions were performed with FALC as reagent instead of FUR under nitrogen atmosphere without hydrogenation catalyst to purely investigate the competition between the two parallel and acid-catalyzed reactions, the oligomerization of FALC and its rearrangement to 4-HCP. The rearranged products were analysed using GCMS, and the identification of 4-HCP was confirmed by ^1H- and ^{13}C-NMR (see SI). All reactions were studied at full FALC conversion where the mole balance is identical to the 4-HCP yield.

The FALC self-oligomerization appears to be strongly pH dependent as can be observed in Figure 6. The lower the pH, the lower the yield towards 4-HCP and the more visible liquid discoloration and oligomer deposition on reaction equipment. It is worth noting that the rearrangement and oligomerization reactions, when starting from FALC, only occur in acidic conditions. Reactions performed at a pH of 10.5 by addition of NaOH, did not show any conversion under similar reaction conditions.

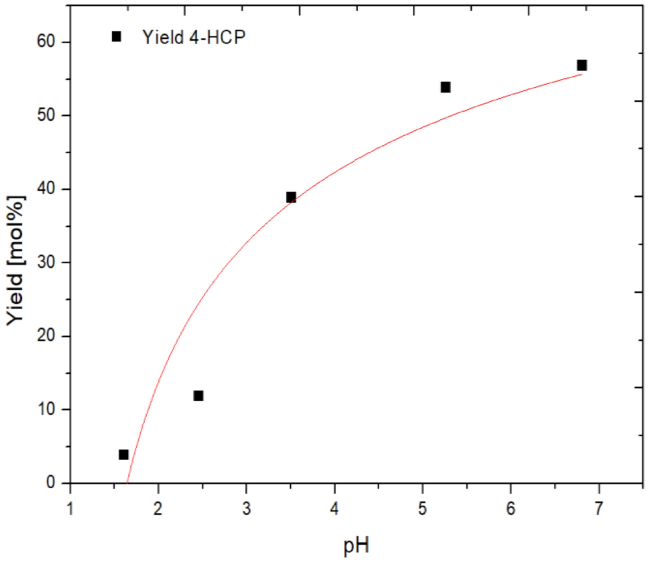

Figure 6. The influence of pH on the product distribution FALC rearrangement to 4-HCP (2 wt% FALC in water at varying pH, 160 °C, 40 bar N_2, 60 min).

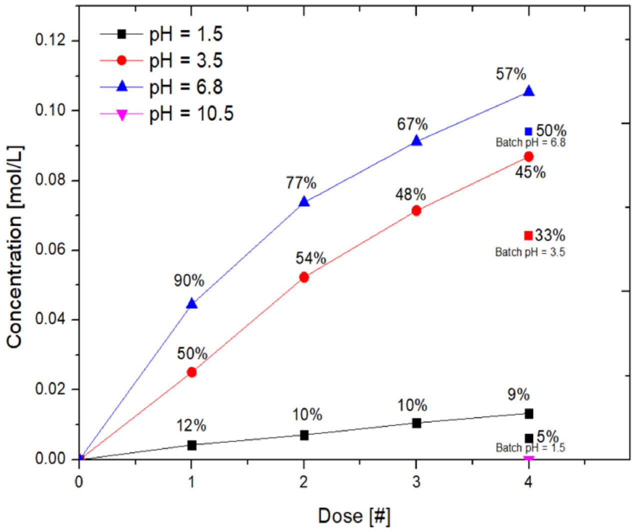

Figure 7. Batch-dosing experiments mimicking the workings of a CSTR. After each dose the cumulative 4-HCP selectivity was determined. Reactions were performed in a stainless-steel autoclave, aqueous phase, pH control using H_3PO_4, 0.5 wt% FALC per dose, 160 °C, nitrogen atmosphere of 40 bar.

The influence of FALC concentration

The self-polymerization of FALC is expected to be favoured by high FALC concentration. In fact, this is likely the reason why the literature is using highly diluted condition, typically <5 wt% of furfural in aqueous solutions. However, the recovery of a very diluted product is not economically attractive.[36] The industrial practice to mitigate such challenges is to dose the reactant to a continuous stirred tank reactor (CSTR) slowly enough to react it away without significant accumulation in the reactor. We have mimicked the CSTR operation by applying the feed in a few small doses (cold batch-dosing experiments) rather than the whole at once. As done above, we used FALC as feed and run it at three different pH in absence of hydrogenation catalyst and hydrogen atmosphere.

Figure 7 shows the results of cumulative selectivity of four consecutive doses of 0.5 wt% FALC to 4-HCP intermediate. What can be observed is, firstly, the negative influence of low pH on selectivity. This trend corresponds to the observed behaviour as described before (Figure 6). The highest selectivities were obtained using slightly acidic water with a pH of 6.8 where a 4-HCP yield of 90 mol% is achieved in the first dose of 0.5 wt%, which is already significantly higher than the yield of ~40 mol% observed at higher FALC concentrations (Figure 6). Expectedly, increasing the number of dosages resulted in a further increase of the 4-HCP concentration. However, the increase in 4-HCP concentration is lower than the increase in feed dosing, which indicates a steady drop in cumulative selectivity. This drop appears more severe at low pH, as indicated by a drop of 10%, 17% and 24% when going from two to four doses at pH 1.5, 3.5 and 6.8, respectively. This drop in selectivity with increasing number of doses is most likely due to an increase in humin formation, which suggests that fresh FALC in not only lost by reacting with itself but also by alkylating existing humins.

Finally, the final selectivity observed after four doses remained higher than after feeding the same amount of FALC (2 wt%) in a single dose, i.e., by 80%, 36% and 14% at pH 1.5, 3.5 and 6.8, respectively. This further confirms the potential benefit of CSTR operation at industrial scale.

It should be mentioned that the interval between doses, reaction time, has been varied for the various pH to correct for the decrease in yield and reaction rate observed upon increasing the medium pH. Doses performed at pH 1.5 and 3.5 have only 10 minutes of reaction time, where for experiments performed at pH 6.8 use 60 minutes.

Oligomer distribution

Besides the relative oligomer quantification (1 − yield 4-HCP = oligomers), the distribution was also analysed using GPC. Independent of pH, the distribution of water-soluble oligomers (>200 g/mol, twice the molecular weight of FALC) appears to remain approximately constant and falls mainly in the GPC-apparent molecular weight measured for diesel fuel (130–230 g/mol), Figure 8. The components observed at lower molecular weight are monomeric species that were properly analysed by GCMS and, thereby, fall outside the present discussion.

More humins were also deposited on the stirrer and reactor wall. These were "washed" with acetone and analysed by GPC, Figure 9. These water-insoluble humins contain components with higher molecular weight that fall in the range of "Vacuum Gas Oil" (VGO, 250–1000 g/mol) and even "Vacuum Residue" (VR, >1000 g/mol), particularly at the lowest pH of 1.5.

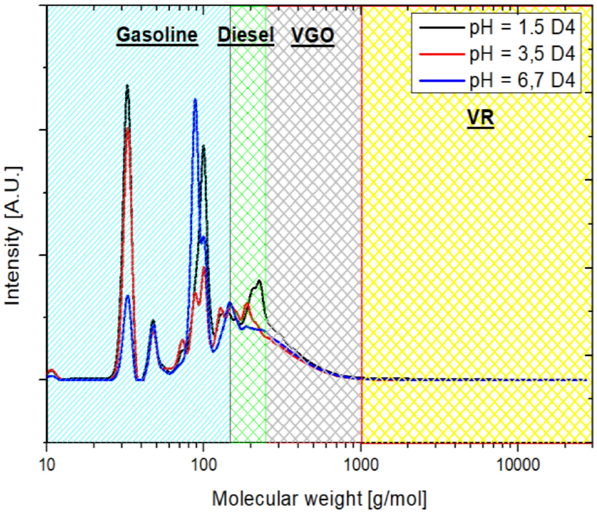

Figure 8. Distribution of water soluble furanic oligomers at various pH determined by GPC.

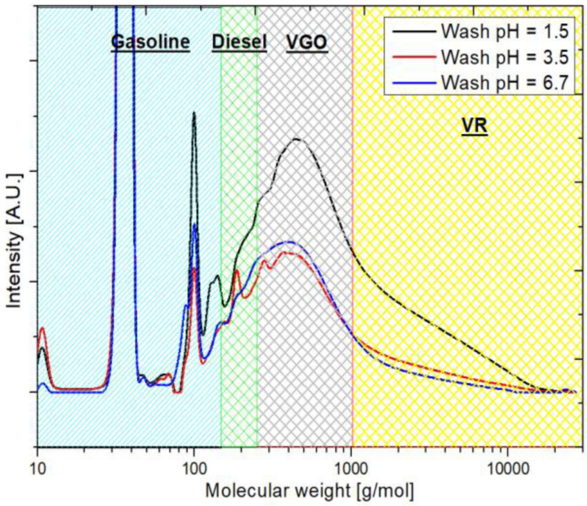

Figure 9. The molecular weight distribution of the acetone wash of the deposited oligomer inside of the autoclave reactor.

Closing the mole balance

Since we could not detect gaseous products, it felt reasonable to assume that the gap in mole balance would be due to the formation of oligomers. Quantifying the oligomers appeared to be challenging, however. Two methods were used for that purpose. The first method made use of a combination of GCMS, GPC and UV-VIS observing a negative correlation between 4-HCP yield (GC-MS) and GPC/UV-VIS peak area. Using this first method, mole balances could be closed between 90–105 mol%, Figure 10. Although high mole balances were determined, they do not close the mole balance quantitatively, but makes it credible that the oligomers are responsible for the gap.

A more quantitative approach was based on GPC using lignin as a model compound for calibrating the GPC. According to Figure 10, GPC would close the mole balances to about 80–95 mol%, with a possible outlier at 67 mol%. Despites their respective inaccuracies, both methods converge in closing most of the gap in mole balance by including the oligomers.

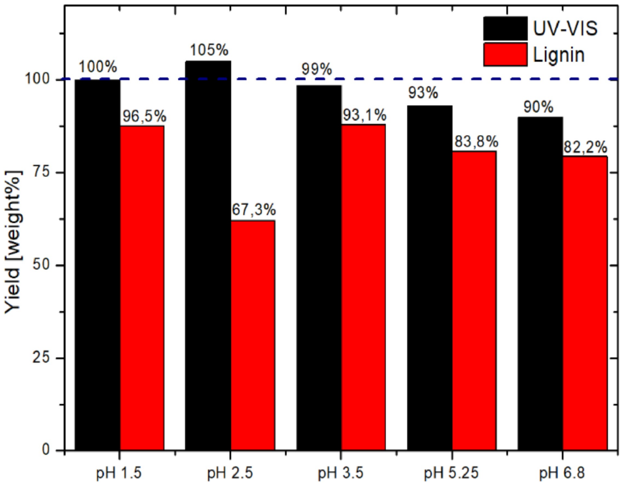

Figure 10. Closing the mole balance of rearrangement of FALC to 4-HCP by quantifying the humins with UV-VIS and with GPC (2 wt% FALC in water at varying pH, 160 °C, 40 bar N_2, 60 min, The GPC was calibrated with lignin).

Oligomer valorisation

The oligomer study is summarized in Figure 11, based on the dosing experiments. As can be observed, there is a clear relation between the medium acidity and the product distribution. pH of 6.8 delivers the lightest product slate, with highest yield of 4-HCP, a sizable fraction of oligomers in the gasoline, diesel and VGO range that could be upgraded to distillate fuels.[35] This results in an overall yield in potential fuel precursor of 88 mol% according to peak integration of GPC spectra (including 4-HCP,

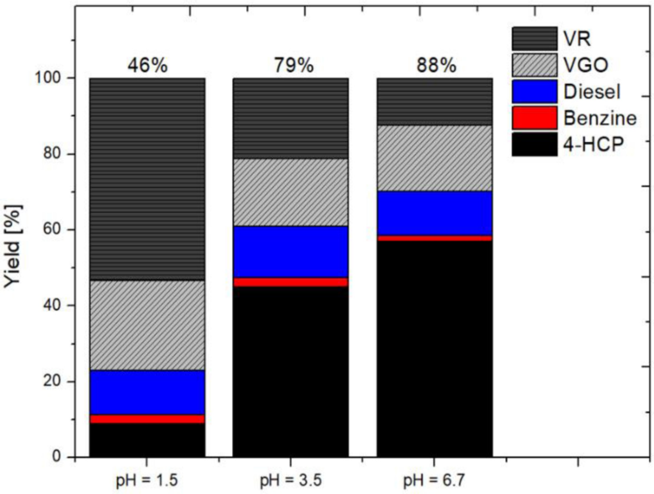

Figure 11. Investigation of the oligomer distribution by GPC assigning peak area to liquid fuel weight ranges of FALC to 4-HCP and oligomer experiments described in the dosing experiments.

gasoline, diesel and VGO). In contrast, the overall fuel yields for pH 3.5 and 1.5 were 79 and 46 mol%, respectively.

Control over the oligomerization could result in an alternative valorisation pathway for the synthesis of renewable fuels.[35]

Mechanistic insight

Although no in-depth mechanistic investigation was performed, the experiments reported here are providing insight into the reaction pathways with the competition of FALC rearrangement and oligomerization. No significant new mechanistic insight was obtained, but our findings and literature review allowed for the completion of the mechanism best described by Piancatelli et al.,[16] filling in some blanks whilst largely validating prior art. these findings, both experimentally and reviewed from literature, are compiled in Figure 12.

Although a clear consensus is not reached on the exact reaction pathways that occurs in aqueous media, the rearrangement of FALC towards 4-HCP reported here is best described by the work performed in 1976 by Piancatelli et al.[16,19,21]

The reaction pathway starts from FUR (I), hydrogenation to FALC (II), protonation and dehydration to the furfuryl carbocation (III). Once this carbocationic species is formed, it can react along two paths, the undesired oligomerization (XIII)[33] and the desired rearrangement (step IV forming XI). The large abundance of water favours the desired nucleophilic addition that leads to the rearrangement via 4π conrotory cyclization (IV–VII). Following a deprotonation, the intermediate 4-HCP is formed (VIII). It is further hydrogenated to CPO and CPA in step IX till XI–XII.

It must be stressed that the rearrangement reaction only occurs under acidic conditions.

Isotope labelling experiments from Yang and al[24] using water and O-labeled water (H2O^{18}) as solvent revealed a slight kinetic isotope effect with of 1.089 ± 0.011 that suggests that the water-O is involved in the reaction. Using NMR, Yang et al. also observed an abundance of 95% of ^{18}O-isotope in the keto-oxygen of CPO, which led them to conclude that the oxygen of CPO comes from water and not from furfural. However, they also show significant O-exchange between CPO and water, which could equally explain the ^{18}O-enrichment observed. Alternatively, we explain here the ^{18}O enrichment by the keto-enol equilibrium of VIII that makes both oxygen chemically identical, Figure 12. This would hypothetically lead to an 50/50 distribution of original furanic oxygen and isotopic oxygen. This completes the reaction pathway proposed by Piancatelli and is further confirmed by the formation of cyclopentadiol intermediate that we observed.

During the catalytic conversion of FUR, large quantities of undesired humins are formed, but the exact chain initiation and propagation remains unclear.

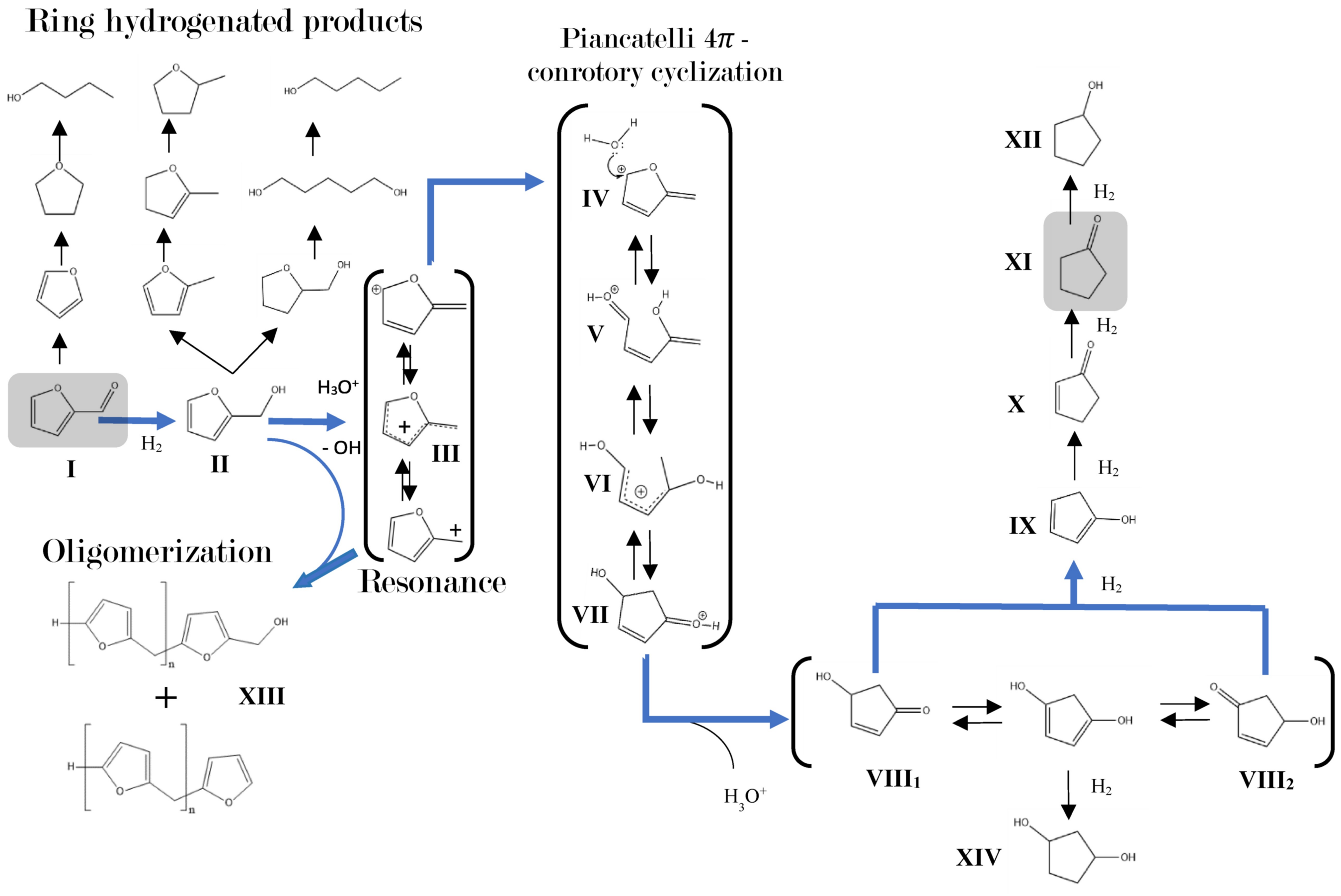

Figure 12. The mechanism for the reductive rearrangement of Furfural to Cyclopentanone based on work from Piancatelli et al.[16]

Arguably, the carbocation (tetrahydrofuran-2-yl)-methylium (species III in figure 12) is alkylating another FALC monomer at position 2 or 5 to form the dimeric species XIII in Figure 12. The dimers can then be alkylated by another furfuryl cation (III) to form a trimer. Alternatively, the dimer that contains a $HOCH_2$-group can be dehydrated to the corresponding cation and alkylate another furanic species, being FALC or another FALC oligomer.

The competition between rearrangement versus oligomerization therefore finds its nature here: as soon as the furfuryl carbocation (III) is formed, it can undergo rearrangement to IV or oligomerization to XIII. Interestingly, such FALC oligomers can be converted to diesel distillate by hydrodeoxygenation.[35]

Conclusions

Upon validation of prior art, copper-based catalysts using aqueous conditions showed the highest selectivity in converting furfural to CPO/CPA, with yields of up to 50 mol% (with 5 wt% furfural in water at pH 3.5, 160 °C and 80 bar H_2).

The rearrangement reaction is accompanied by the competitive acid-catalyzed oligomerization of FALC to form oligomers, a reaction that is rarely reported in the literature, but was proven and quantified by means of GPC analysis. By varying parameters such as temperature, solvent and pH, some degree of control over the oligomer formation was achieved. Most dominantly were the effects of concentration and pH, when running the reaction in CSTR mode, i.e., by slowly dosing the FALC into the reactor whilst fine tuning pH conditions. By operating under these conditions, oligomer formation could be mitigated and rearrangement yield could be improved by 80%, 36% and 14% at pH 1.5, 3.5 and 6.8 as compared to single dose batch experiments.

However, oligomeric products appeared to not be fully useless as a significant fraction falls still in the desired distillate range and should therefore be considered as valuable fuel precursors.

A detailed reaction scheme is proposed to account for the desired reaction as well as the competing ring-hydrogenation and oligomerization reactions.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Bio jet fuel · Furfural · Cyclopentanone · Biomass · Oligomers · Humins

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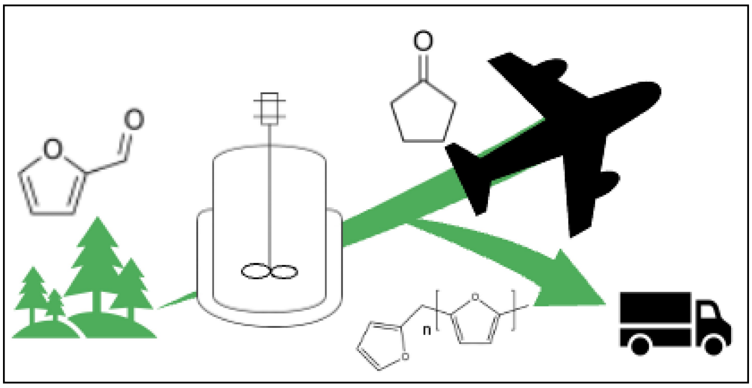

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Furfural to Cyclopentanone – a Search for Putative Oligomeric By-products

The reductive rearrangement of Furfural to Cyclopentanone, a renewable chemical with bio jet applications, is accompanied by the undesired formation of oligomeric by-products. Although initially deemed unwanted, upon thorough analysis, these heavier side products exhibit promising potential for conversion into liquid hydrocarbon fuels.