



# Furanic jet fuels – Water-free aldol condensation of furfural and cyclopentanone

R. Baldenhofer, A. Smet, J.-P. Lange, S.R.A. Kersten, M.P. Ruiz\*

Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Drienerlolaan 5, 7522, NB, Enschede, the Netherlands

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## ABSTRACT

A method for the water-free, large-scale synthesis of bio-jet fuel precursors, distinct from traditional fossil-based sources, is introduced. This approach involves the aldol condensation of furfural with cyclopentanone, producing C<sub>10</sub>-C<sub>15</sub> fuel precursors eligible for further hydrodeoxygenation to high-performance diesel and jet fuel hydrocarbons. In the context of process integration, aldol condensation reactions were conducted under water-free conditions, utilizing excess furfural as the solvent. Evaluation of various commercial catalysts confirmed the feasibility of running in excess furfural. Both basic and acidic catalysts demonstrated significant activity, with CaO and amorphous silica-alumina achieving  $\geq 80$  mol% conversion of cyclopentanone and yielding  $\geq 80$  mol% selectivity towards the desired fuel components within 5 h of reaction. However, an overlooked aspect is the notable formation of undesired heavy side products. Observations indicated that the high furfural concentration, combined with the use of strong acidic catalysts, were the primary cause of heavy side product formation. The strong base catalyst, CaO, significantly reduced the formation of these oligomers, but did not appear to stop it completely. Interestingly, water content did not appear to play a major role in byproduct selectivity. To further suppress the formation of oligomers, the use of process-owned intermediates as solvents is proposed.

## 1. Introduction

The aviation industry is an integral part of the global transportation network, connecting people and goods across the world. However, the environmental impact of traditional jet fuels, primarily derived from fossil sources, has come under intense scrutiny due to their significant contribution to greenhouse gas emissions [1–3]. Consequently, renewable alternatives have emerged [4].

These liquid hydrocarbon fuels must adhere to several important characteristics, to be eligible as replacement and blend in jet fuels. First, and foremost, the energy density. Jet fuels need to present a high energy density, both on volume and weight basis (35 MJ/L and 43 MJ/kg), to allow the plane to transport freight or passengers over long distances [5]. Additionally, jet fuels need to have low freezing point (below  $-47$  °C), to enable safe operation at high altitude, and need to present sufficiently high flash point (above 40 °C) to enable safe distribution and filling on the ground [6].

Furfural (FUR), a key derivative of lignocellulosic biomass, represents an abundant and renewable feedstock for the production of advanced biofuels [7–11]. It can be readily produced from

lignocellulosic biomass via a conventional acid digestion process, but ongoing research has proven improved performance by biomass fractionation followed by biphasic dehydration of the extracted xylose or by xylose extraction and dehydration [7,8,10–15].

Its potential as a sustainable source of jet and diesel fuel has gathered considerable attention from researchers and the aviation industry alike. Different pathways in the upgrading of FUR to bio jet are known, which all are based on C-C coupling followed by deep hydrogenation [7,10,11]. Examples already exist in literature such as the alkylation of FUR and methyl-furan [16,17] or the aldol condensation of FUR with different ketones [18–21].

The aqueous phase aldol condensation of FUR with various ketones has garnered significant attention, particularly due to its notable versatility and mild operating conditions, e.g. room temperature and alkaline conditions [18,19,22–26].

An aldol reaction of particular interest is that of FUR with cyclopentanone (CPO), a cyclic ketone which can be derived from FUR [27–29]. Their coupling results in hydrocarbons with high energy densities and low freezing points after hydrotreatment, desirable for jet and diesel applications, Fig. 1 [5].

\* Corresponding author.

E-mail address: [m.p.ruizramiro@utwente.nl](mailto:m.p.ruizramiro@utwente.nl) (M.P. Ruiz).

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The implementation of furanic bio jet is however, still in its infancy. Operational constraints are encountered during the aqueous phase aldol condensation such as complexities related to product and homogeneous catalyst separation, the precipitation of poorly soluble aldol adducts leading to reactor and equipment fouling, the generation of substantial alkaline wastewater streams, equipment corrosion and pH swings, considering that the production of the CPO is performed under acidic conditions and the subsequent aldol condensation under highly alkaline conditions [27]. This has forced researchers to explore alternative operational pathways.

To circumvent aqueous phase downsides, with in particular the reactor and equipment fouling caused by poor product solubility, water can be substituted for organic solvents. Further research into intensification have led to the proposal of running the reaction under “solventless conditions”, e.g. running the reaction in excess FUR, which acts as the solvent and reactant, using a variety of heterogeneous catalysts [20,30–32]. But little attention was devoted to the potential formation of heavy side products, which is notorious for acidic hydrothermal conditions [27,33].

This work investigates the aldol condensation under water-free conditions. Several catalysts were evaluated with a focus on minimizing the formation of heavy byproducts. Additionally, a novel solvent approach was explored, leading to an integrated process design that utilizes process-owned solvents from hydrogenated aldol adducts. This approach both minimizes heavy byproduct formation and reduces the need for excessive separation steps.

## 2. Materials and methods

### 2.1. Materials

**Reactants:** Cyclopentanone ( $\geq 99\%$ ), furfural ( $\geq 99\%$ ) were supplied by Sigma Aldrich. **Catalysts:** Pd/C (5 wt% loading, Hydrogenation catalysts), CaO ( $\geq 99.9\%$ , aldol), MgAl-Hydrotalcite (HT, aldol) (quality level 100, aldol), Hydroxyapatite (HAP) ( $\geq 99.8\%$ , aldol) were supplied by Sigma Aldrich. NaOH pellets ( $\geq 99\%$ ) by Riedel de Haën and Al<sub>2</sub>O<sub>3</sub> (catalyst support, high surface area) was supplied by Alfa Aesar. MG20, MG30 and MG70 (solid base aldol catalysts) were supplied by Sasol. Alumina Powder, Zeolite-Y and ASA-5545 Powder as aldol catalysts were provided by Shell. **Solvents:** Technical grade ethanol (100%) and acetone (99.5%) were supplied by Boom, ethyl acetate ( $\geq 99.5\%$ ), acetone for analysis ( $\geq 99.8\%$ ), THF for analysis ( $\geq 99.9\%$ ) were obtained via Sigma Aldrich.

### 2.2. The aldol condensation reaction

The catalytic conversion of FUR and CPO to aldol adducts were performed in 15- and 45-mL stainless steel autoclaves equipped with a magnetic stirrer, pressure gauge and automated temperature control. In case of the 45 mL autoclave, both nitrogen and hydrogen cylinders were attached to the reactor’s pressure gauge.

Before each experiment, catalysts were conditioned at 200 °C for 30 min at 8–10 bars N<sub>2</sub> in the autoclave under dry conditions. A desirable amount and stoichiometry of FUR and CPO was added to the reactor containing the conditioned catalyst. The reactor was sealed and purged three times with nitrogen to remove most of the air. The pressure was increased to 40 bar using N<sub>2</sub> and heated to the desired temperature. Temperature and pressure were logged using Picolog software. Reaction time was set to start when the liquid temperature reached the “target temperature – 5 °C”. After the desired reaction time, the reactor was cooled down and the gas was released. Samples were collected at the start and end of each experiment and subsequently analysed. In addition, glass reflux condenser setups were employed to allow product sampling and run under similar conditions unless specified otherwise.

### 2.3. Hydrogenation of aldol adducts

The hydrogenation of the aldol adducts was carried out in a 200 mL stainless steel autoclave. The autoclave is equipped with a gas connection for N<sub>2</sub> and H<sub>2</sub>, a pressure sensor, thermocouples, and a stirrer. A H<sub>2</sub> gas buffer vessel ensures operation under constant pressure.

The autoclave was typically loaded with 80 mL of solvent (decalin or ethanol), 0.25 g catalyst (Pd/C) and 60 g of aldol adducts (wet). The reactor was sealed and purged three times with nitrogen to remove the air. The pressure was increased to 50 bar using H<sub>2</sub> and heated to 160 °C. After the desired reaction time, the reactor was cooled down and the gas was released. Samples were collected before the closing of the reactor, and end of each experiment and subsequently analysed using GCMS. The hydrogenated oxygenates were concentrated by boiling the solvent using a lab scale distillation setup, operated under vacuum conditions.

### 2.4. Analysis

Reaction products were identified and quantified using a GC 7890A MS 5975C by Agilent Technologies equipped with auto sampler, flame ionization detector (FID) and an Agilent VF-1701 ms GC column. The column temperature was initially kept at 45 °C for 10 min, and then increased at a rate of 3 °C per minute to 280 °C. Conversion, selectivity and yield were determined according to equations I, II and III. Equipment was calibrated for CPO, FUR and trimeric aldol adducts in desired concentration regimes.

$$\text{Conversion (\%)} = \left(1 - \frac{\text{mole CPO end}}{\text{mole CPO loaded}}\right) * 100 \quad \text{(I)}$$

$$\text{Selectivity (\%)} = \left(\frac{\text{mole CPO in product}}{\text{mole CPO loaded} - \text{mole CPO end}}\right) * 100 \quad \text{(II)}$$

$$\text{Yield (\%)} = \left(\frac{\text{mole CPO products}}{\text{mole CPO loaded}}\right) * 100 \quad \text{(III)}$$

Oligomeric products were analysed using an Agilent 1260 Infinity Gel Permeation Chromatography (GPC). The machine was equipped

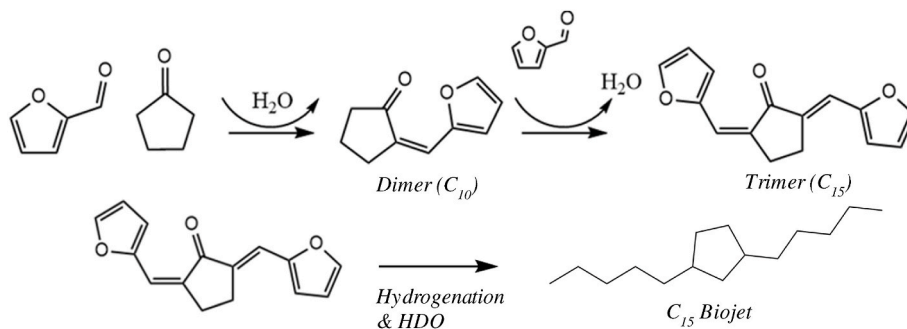


Fig. 1. Synthesis of Diesel and Jet fuel precursors via the aldol condensation of FUR and CPO.

with a UV detector running at 254 nm and with a refractive index detector. The column was a 3 GPC PLgel 3m MIXED-E. 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 27.810 g/mol.

### 3. Results and discussion

To substantiate the existing knowledge regarding operations in organic solvents, our initial focus was on confirming prior art concerning running reactions in organic solvents using heterogeneous catalysts. An in-depth examination of byproduct formation was conducted, leading to the development of a novel methodology to address this issue on an industrial scale.

#### 3.1. The solventless aldol condensation

Transitioning from aqueous phase settings, homogeneous catalysts and water were replaced with a heterogeneous catalyst, utilizing FUR as the solvent. Prior literature has documented an extensive array of (complex) solid acid and base type catalysts across a broad spectrum of operational parameters. The process began with the screening of commercial catalysts to validate prior art. The basic catalysts encompassed commercial alumina's doped with MgO obtained from Sasol. These catalysts varied in doping (w/w), resulting in 20, 30 and 70 wt% MgO with similar BET surface areas (MG20 294 m<sup>2</sup>/g, MG30 301 m<sup>2</sup>/g, MG70 189 m<sup>2</sup>/g). CaO, reportedly a good aldol catalyst, was also investigated (BET 12 m<sup>2</sup>/g) 31.

Acid catalysts were obtained from Shell ( $\gamma$ -Alumina; 300 m<sup>2</sup>/g, Zeolite - USY 930 m<sup>2</sup>/g and amorphous silica-alumina ASA with 55:45 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio 500 m<sup>2</sup>/g).

The experiments confirmed the activity of solid acid and base catalysts Fig. 2; which is an interesting observation, as aqueous phase aldol condensation appeared to only be active under alkaline conditions.

Fig. 2 shows the selectivity to trimeric aldol adduct versus the CPO conversion after a batch reaction performed for 5 h at 150 °C.

CaO performed best under investigated conditions, obtaining X<sub>cpo</sub>  $\geq$ 95 mol%, Strimer  $\sim$ 95 mol% (on CPO) and with a CPO yield of  $\geq$ 95 mol%. Although showing great promise, CaO appeared to have significant downside as it deposited onto the reactor wall and stirrer under

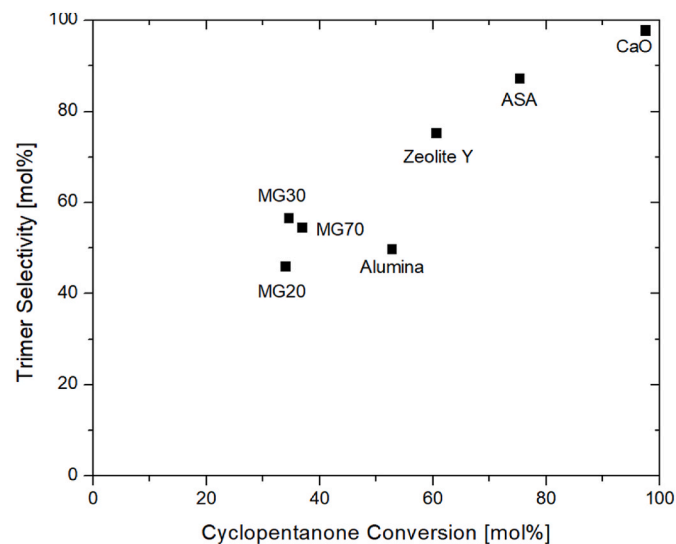


Fig. 2. Cyclopentanone conversion and trimer selectivity for the catalyst screening, reaction conditions: 40 bar N<sub>2</sub>, 150 °C and 3050 rpm. Cyclopentanone (4.09 wt%), furfural (94.22 wt%) and catalyst (1.71 wt%), 5 h.

stoichiometric ratios of FUR and CPO, Figs. SI–1, leading to complex cleaning procedures. This deposition likely originates from the hydration of CaO to Ca(OH)<sub>2</sub>, as water is produced during the reaction. Although all screened catalysts were utilized in powder form, only CaO was observed to not remain well-suspended.

Next to CaO, solid acids Alumina, Zeolite and ASA still showed relatively high activity, reaching 50–80 mol% CPO conversion, but having variable selectivity towards the trimer adducts, ranging from 50 to 85 mol% with the balance being the dimeric (C10) intermediate.

The doped MgO alumina's (MG-series) demonstrated a marginal improvement in activity as the level of MgO doping increased. Nevertheless, their performance remained inferior to that of the solid acids, achieving only 30–40 mol% CPO conversion alongside a similarly low trimeric adduct selectivity of roughly 50 mol%. The performance at similar conversion level is discussed in a later section.

As Fig. 2 strongly indicated the superior performance of both base CaO and the acidic ASA, these were investigated further. Conversion profiles using both CaO and the ASA showed a first order dependency in CPO (Figs. SI–2) where the reaction proceeded through the dimeric intermediate, finding  $\geq$ 95 % CPO conversion after 7.5 h for ASA (Fig. 3) and only 1.5 h using CaO (Fig. 4).

A notable decrease in yield to 80 % was observed when using ASA, in contrast to CaO, which maintained a yield of  $\geq$ 95 mol% throughout. This slight reduction in yield suggests the potential formation of undesired side products.

Besides conversion, selectivity also appeared to be catalyst dependent, Fig. 5. CaO showed dominant selectivity towards the trimeric adducts even at lower CPO conversion, in contrast to the acidic ASA, indicating a faster conversion of dimeric adducts. By conducting the reaction at various temperatures, an Arrhenius plot, Figs. SI–3, was constructed enabling the determination of the overall activation energy to be 82 kJ/mol for the ASA, in line with aqueous phase reports of FUR with Acetone [34].

#### 3.2. The drawbacks of "solventless" operation

On further inspection, large deposits of heavy products were observed in the reactor and identified by GPC in the liquid product, reaching  $\geq$ 20.000 g/mol, Fig. 6. The culprit was identified to be FUR. FUR is notorious for forming heavy products (humins) under acidic conditions.

the formation of oligomeric species here results in the deposition of

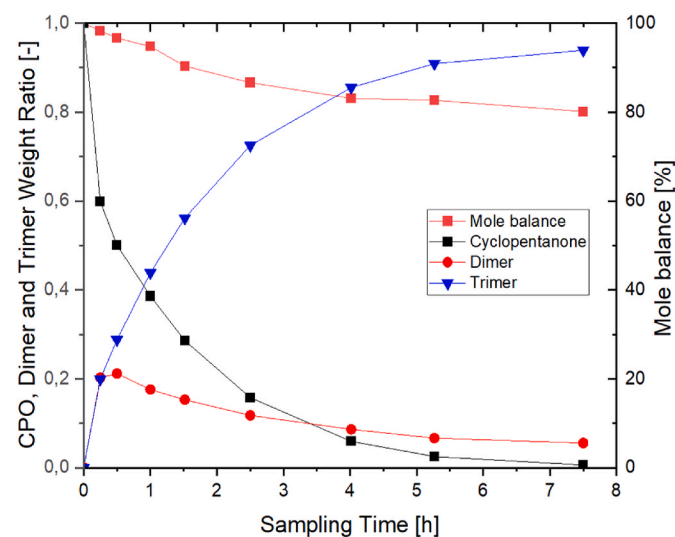


Fig. 3. Weight ratios and yields at 170 °C, reaction conditions: ambient atmosphere, 1000 rpm, Cyclopentanone (4.1 wt%), furfural (94.2 wt%) and catalyst ASA-5545 (1.7 wt%).

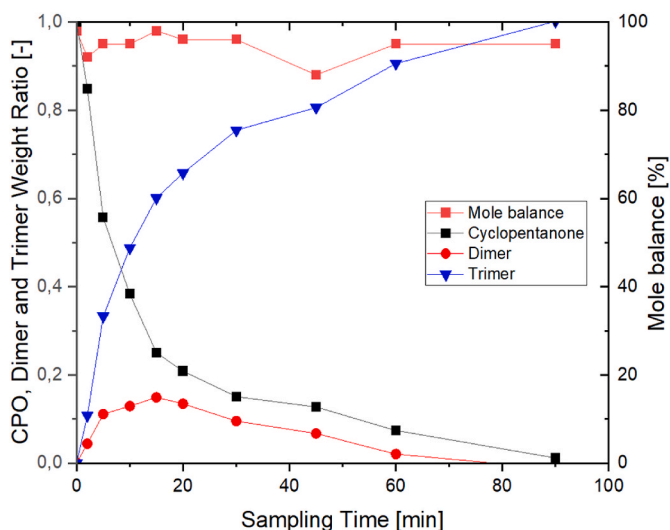


Fig. 4. Weight ratios and yields at 170 °C, reaction conditions: ambient atmosphere, 1000 rpm, Cyclopentanone (4.4 wt%), furfural (95.5 wt%) and catalyst CaO (0.1 wt%).

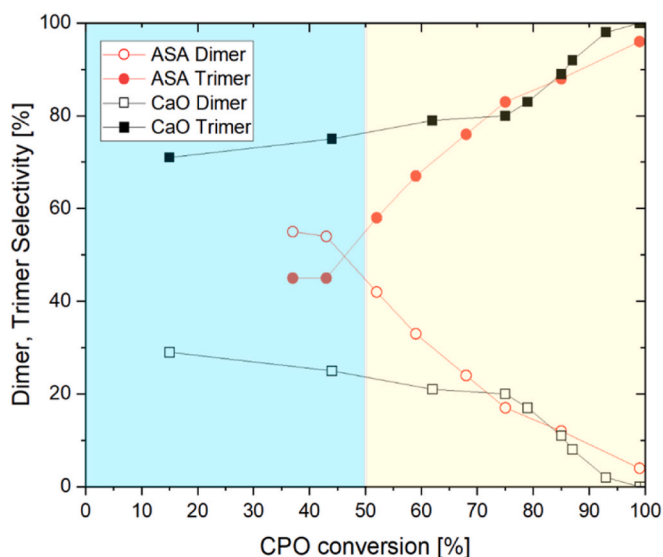


Fig. 5. Conversion versus selectivity profile comparing strong acid and base performance.

material inside reactors, blocking equipment, complicating separation, covering catalyst leading to deactivation and, most importantly, decreasing in desired product yield. Operating at varying temperatures appeared to somewhat limit oligomer formation, lowering the Mw, but did not completely mitigate it, Fig. 6. This also resulted in a slowdown of CPO conversion, as shown in Figs. SI-3 (Arrhenius plot). Consequently, longer residence times were required, which led to additional oligomer formation.

To better understand the formation of heavy side products during water-free operation, the effects of conversion (e.g., water production), catalyst, and solvent conditions were investigated. The aim was to reduce and/or control the mass distribution of these products. The evolution of heavy products was monitored by peak integration of the GPC.

To investigate if the oligomerization depended on catalyst (e.g. acid or base), the reactions were performed using base catalyst using MG70, acidic ASA-5545, without catalyst (blank) and extended with another

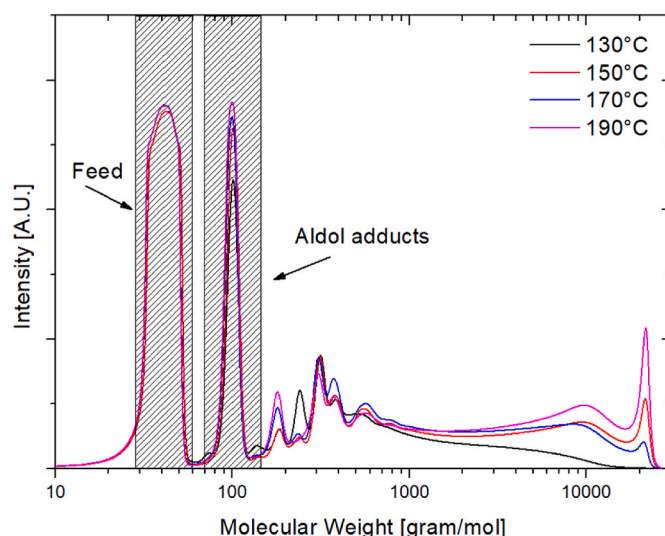


Fig. 6. GPC results for the aldol condensation in a solventless environment performed in excess furfural for 5h at different temperatures using ASA-5545 as catalyst.

basic catalyst CaO, Fig. 7.

Base-type catalysts CaO and MG70 showed significantly lower formation than the acid catalyst and even to the blank reaction, even at higher levels of conversion (CaO). This can be seen in the modest increase in GPC area of heavy products vs. the GPC area of trimer during the reaction, as illustrated in, Fig. 8.

Interestingly, the MgO and ASA catalysts show a linear increase of oligomers with increasing aldol product, which suggests that the two reactions proceed in parallel with similar reaction order for the reactants. But CaO behaves differently by showing only an initial formation of oligomers that stabilizes while the aldol trimers keep being formed.

The higher tendency of acid catalysts to form oligomers under excess FUR conditions, is hypothesized to find its origin in the protonation of the aldehyde group resulting in the formation of an active carbocation species [27,33]. Basic catalysts are expected to neutralize existing acids and acidic groups hence mitigating heavy formation but might lead to

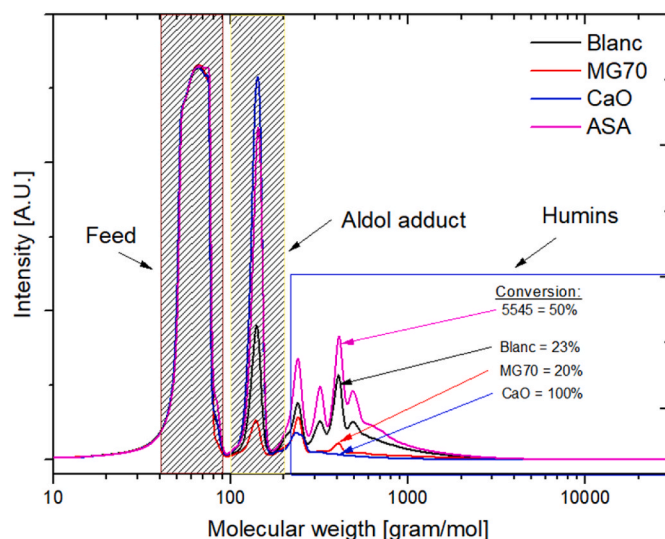


Fig. 7. The formation of heavy products during the aldol condensation of furfural and cyclopentanone under solventless (excess furfural) condition using different catalysts. Reflux condenser setup, 120 min, 5 wt% CPO in Furfural, 160 °C.

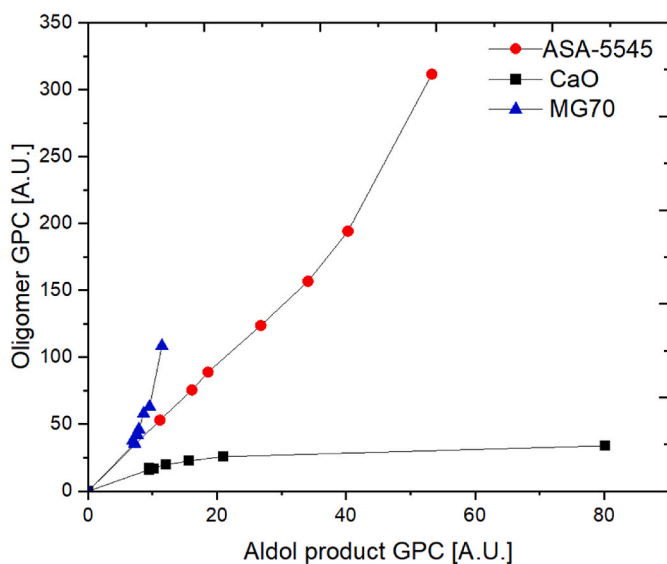


Fig. 8. Oligomer versus aldol adduct selectivity monitored over time as determined by peak integration of GPC. (go to 0 aldol product and label the lines, without legend).

catalyst neutralization resulting in their observed lower activity.

An intriguing observation is that doped MgO-alumina exhibits the highest oligomer formation as a function of conversion. Despite the presence of basic MgO groups, the significant tendency for oligomerization may be attributed to the alumina carrier which could still be acidic.

Given the chemical similarity of the aldol adducts to their FUR and CPO reactants, additional experiments were conducted to investigate the stability of the dimeric and trimeric products. Saturated solutions of aldol adduct in excess FUR were tested (without CPO) using acidic ASA, revealing a constant concentration profile, Figs. SI-4. This indicated the inertness and stability of the adducts under the experimental conditions used.

Furthermore, FUR can be oxidized in the presence of atmospheric oxygen. To determine whether initial FUR oligomers in the feed could enhance oligomerization, FUR was purified through distillation and compared to non-distilled feed (see Figs. SI-5). Since little to no difference was observed, it is expected that the primary oligomerization occurs during the reaction at elevated temperatures (catalyst) and is not significantly influenced by the initial feed composition.

Additionally, to determine whether oligomerization is dependent on H<sub>2</sub>O produced during the reaction, a reaction with FUR saturated with H<sub>2</sub>O was compared to a reaction with distilled FUR. The results showed no significant deviations between the two, indicating that primary oligomerization is not strongly dependent on H<sub>2</sub>O content, Figs. SI-5.

Comparing catalyst performance after a 2-h reaction performed in glass equipment, the oligomers formed for both acid and base catalysts, initially seemed to remain largely within the "valuable" Vacuum Gas Oil (VGO) range (Mw < 1000 g/mol), potentially making them amenable for valorisation through thermal and/or catalytic cracking, Fig. 7 [35]. However, with prolonged residence times using acid or blank (no catalyst) conditions, considerable additional growth in their molecular weight was observed similar to Fig. 6.

### 3.3. An integrated solvent approach

While the use of a CaO catalyst effectively mitigated significant oligomer formation, other catalysts still generated substantial byproducts. In industrial operations, which typically run continuously for thousands of hours, even minimal oligomer deposition could trigger additional alkylation and growth, presenting significant operational

challenges. This highlights the need for further catalyst optimization and/or a shift away from excess FUR operation to ensure efficient and reliable operation. One approach could be the use of alternative inert organic solvents. Since the heavy formation of byproducts is likely attributable to the high concentration of FUR, it could be promising to lower the furfural concentration back to its stoichiometric ratio and compensate it by adding a solvent. This report details the use of process-owned solvents, specifically the hydrogenated aldol trimer and/or the final hydrocarbon product, which eliminates the need for costly product-solvent separation.

The hydrogenation of the trimeric aldol adducts results in the production of 2,5-Bis [(tetrahydro - 2 - furanyl) methyl] cyclopentanone or saturated oxygenates for short (SO). This hydrogenation has been adjusted from Wang et al., as outlined in the method section, using a stainless steel 200 mL autoclave operated under constant H<sub>2</sub> pressure.

The hydrogenated trimeric adducts still contained partially hydrogenated products. While the trimeric feed had an *m/z* ratio of 240, analysis using GC-MS showed product *m/z* ratios ranging from 244 to 252, as shown in Figs. SI-6. 85 mol% consisted of fully hydrogenated products of 250–252 g/mol while roughly 10 mol% (yield ≥90 mol%) remained in 248 *m/z*, Fig. 9A and B.

The aldol condensation was conducted with CPO and FUR dissolved at ~5 and 10 wt%, i.e. in the stoichiometric molar ratios of 2:1. The ASA catalyst was utilized to observe the anticipated reduction in oligomerization.

Experiments showed a notable drop in reaction rate. Even after 24 h, only 60 mol% of CPO was converted with a yield closure of 80 mol%, Fig. 10.

An important observation worth noting is the absence of significant oligomerization during SO conditions, observed both in the liquid phase and as deposit inside the reactor, Fig. 11. Although heavy products appear between Mw 100–1000, a proper identification is challenged by the presence of SO component that elute in the same Mw range.

Nonetheless, FUR conversion exceeded CPO conversion (Fig. 10), still suggesting the occurrence of side reactions.

Although proper oligomer identification was challenged, the entire observed product distribution appeared to have an Mw < 2000. This

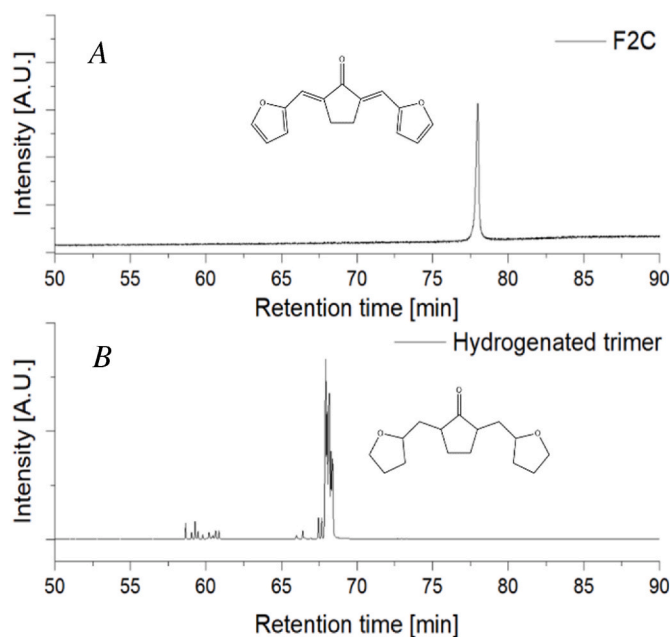
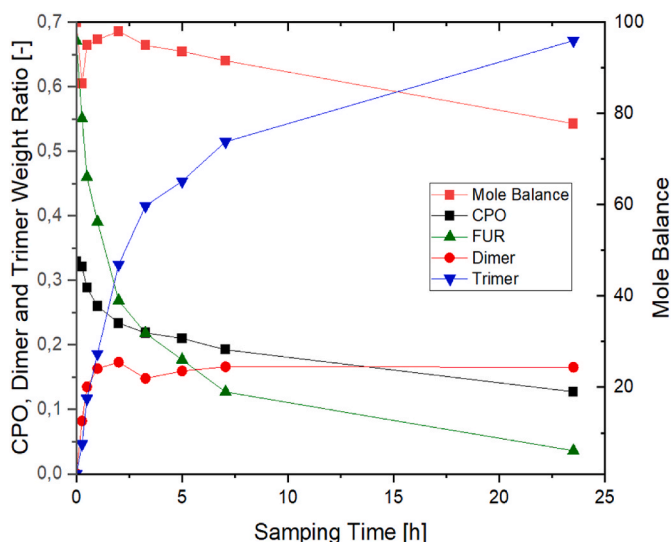
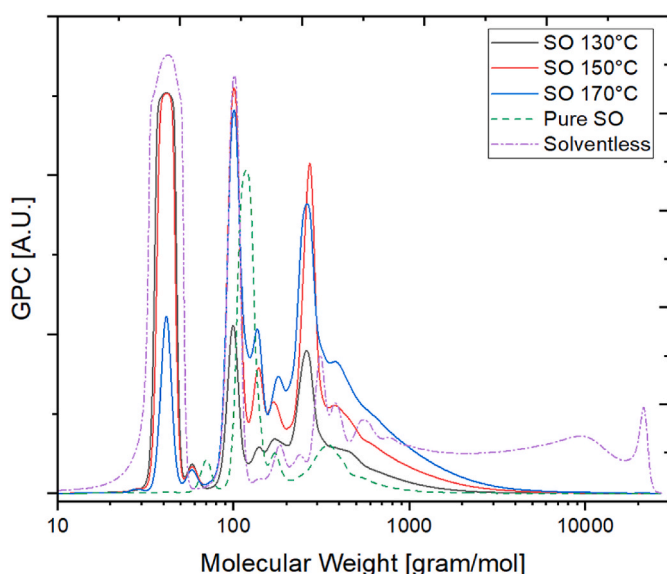


Fig. 9. The hydrogenation of trimeric aldol adducts. A) The aldol feed. B) The hydrogenated product distribution performed using EtOH. Performed using a 200 mL stainless steel autoclave, ~30 gr. Aldol adducts, 80 mL solvent, 0.20 gr Pd/C 160 °C, 50 bar H<sub>2</sub> constant pressure.



**Fig. 10.** Reaction profile of the aldol condensation performed in saturated oxygenated product obtained via hydrogenation of the aldol adduct. Cyclopentanone (5.36 wt%), furfural (10.04 wt%), ASA-5545 catalyst (2.08 wt%), 170 °C, 40 bar initial N<sub>2</sub>.



**Fig. 11.** Reaction profile of the aldol condensation performed in saturated oxygenated product obtained via hydrogenation of the aldol adduct. Cyclopentanone (5.36 wt%), furfural (10.04 wt%), ASA-catalyst (2.08 wt%), 170 °C, 40 bar initial N<sub>2</sub>.

indicated that the heavy products formed remain within the valuable diesel and VGO range, making them eligible for further valorisation even at extended residence times of 24 h. Additionally, a distinct lower product peak ( $\sim M_w = 100$ ) was observed at lower temperatures, resulting from reduced conversion. This observation signifies a clear difference between the SO ( $SO-M_w < 2000$ ) and Excess FUR operation ( $FUR-M_w < 20,000$ ), Fig. 11.

The reduction in the formation of heavies is expected to be largely due to the significant decrease in FUR concentration. This exploration signifies the feasibility of conducting the reaction in different solvent conditions, at decreased FUR concentrations.

Running the reaction using CaO, achieved  $\geq 90$  mol% CPO conversion after 4 h only with a yield of  $\geq 90$  mol%, Figs. SI-7.

### 3.4. Process concept

These results led us to develop a new process concept with the aim to minimize heavy formation whilst simultaneously avoid complex solvent separation and purification and is illustrated in Fig. 12.

Fig. 12 illustrates two operational strategies. The first strategy runs the aldol reaction in excess of FUR (R1). The excess FUR is removed by distillation and the aldol adduct, which is solid at room temperature is dissolved by a process-owned solvent (stream B), prior to reaching the reboiler of the column.

The advantage of this mode of operation is the excess FUR, which can push selectivity towards trimeric adducts and allow short residence time. An important downside is the large excess of FUR that could result in the formation of heavy byproducts and will need significant distillation duty and recycle stream.

The second mode of operation utilizes the process-owned solvents of SO or the hydrocarbon product of (R3), by directly feeding it to the aldol reactor (R1), via stream (C). This circumvents the requirements of a cosolvent in stream (A) as compared to the excess FUR operation. Reactants could be dosed to R1 stoichiometrically or in slight excess of FUR as desired which offers significantly more operating flexibility and includes advantages such as lower heating duties and distillation resistance [36]. It is important to highlight that under both solvent operating conditions, no precipitation of aldol adducts was observed, indicating good solubility. This represents a significant advantage over aqueous phase operations, where one of the major challenges is the precipitation of products.

## 4. Conclusion

Transitioning from aqueous environments to solvent-free conditions necessitated the use of a heterogeneous catalyst. Following validation of prior art, various acidic and basic catalysts were considered. Among them, CaO demonstrated exceptional performance, achieving  $X_{cpo} > 95$  mol% with a yield and trimer selectivity of  $\geq 95$  mol%.

While all catalysts exhibited activity for aldol coupling under solventless conditions, a notable drawback was the formation of heavy side products, ranging up to a  $M_w$  of 30,000 g/mol. However, by managing residence times, temperature and operating at lower conversion rates, mass distributions could be maintained within the valuable VGO range, rendering heavy side products suitable for valorisation. In addition, water content did not appear to play a crucial role in oligomer selectivity.

Despite initial observations suggesting that base-type catalysts exhibited significantly less tendency towards oligomerization, a comparison at similar conversion levels revealed inconsistencies, complicating the catalyst selection process. Nevertheless, strong bases, CaO, appeared to be the most suitable choice under the investigated catalysts.

To address the challenge of mitigating oligomer formation, a novel solvent approach was proposed. An integrated process design suggested utilizing process-owned intermediates as solvents to reduce FUR concentration, thereby mitigating the formation of heavy byproducts without requiring excessive separation processes. Experiments demonstrated the feasibility of running aldol condensation reactions under these conditions, validating the process concept. However, they also indicated a strong need for further optimization of both the catalyst and solvent system.

### CRedit authorship contribution statement

**R. Baldenhofer:** Writing – original draft, Investigation, Formal analysis. **A. Smet:** Investigation. **J.-P. Lange:** Writing – review & editing, Supervision, Investigation, Conceptualization. **S.R.A. Kersten:** Writing – review & editing, Supervision, Resources, Methodology, Investigation, Funding acquisition, Conceptualization. **M.P. Ruiz:** Writing – review & editing, Supervision, Project administration,

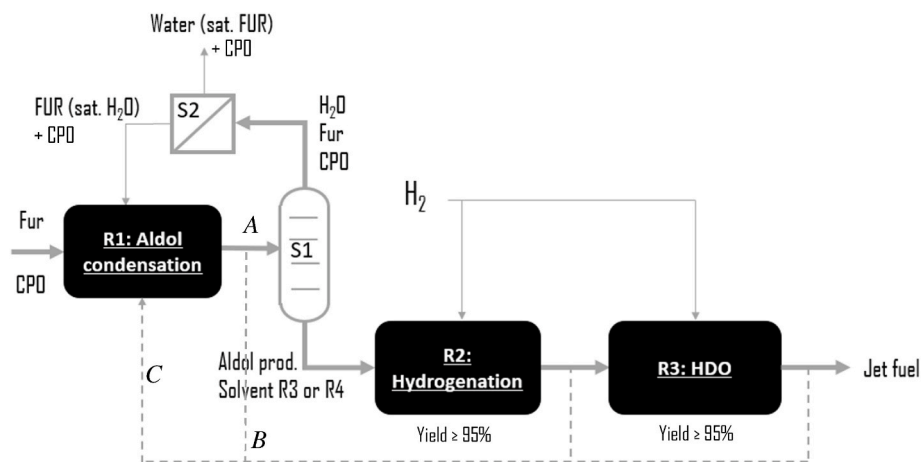


Fig. 12. Proposed process design for running solventless aldol condensation (e.g. excess FUR), or by employing process owned-solvents. Reaction conditions R2: 100–180 °C, Pd/C, 40 bar H<sub>2</sub>. Reaction conditions R3: 250–400 °C, HDO catalyst, 40 bar H<sub>2</sub>.

Investigation, Funding acquisition, Conceptualization.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biombioe.2024.107410>.

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