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Synthesis of jet-fuel precursors from renewable biomass through aldol condensation of cyclopentanone and furfural on base catalysts

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ABSTRACT

Furfural condensation with cyclopentanone has been studied over calcium oxide as a catalyst exploring the influence of temperature, cyclopentanone to furfural ratio, furfural purity, and the effect of a stabilizer. This research delves into the synthesis of aviation fuels from renewable biomass through aldol condensation, focusing on the reaction kinetics. The comprehensive study assesses the previously mentioned factors to optimize the conditions for maximum yield and selectivity towards the desired product. X-ray diffraction (XRD) and scanning electron microscopy (SEM) revealed significant changes in the catalyst structure after the reaction, influencing its efficiency. The preferred conditions were determined to be the furfural to catalyst mass ratio of 10:1, cyclopentanone to furfural molar ratio of 15:1, stirring speed above 800 rpm and temperature of 130 °C, resulting in high catalytic activity. Furthermore, it was found that addition of a stabilizer enhanced the reaction rate and selectivity towards the desired products, which could be due to changes in the acidity of the reaction media. This study lays the groundwork for further exploration into the production of sustainable jet fuels from the aldol condensation of smaller biomass-derived compounds, highlighting the importance of the reaction conditions to achieve high conversion, product yield and selectivity.

1. Introduction

The development of green chemistry and the decrease of fossil resources have motivated industries to search for renewable, carbon-based feedstocks. Biomass has proved to be the only carbon source that can replace petroleum and also to reduce pollution [1,2]. Lignocellulose-rich biomass, including waste from crops, pulp and paper, as well as marine algae, stands out as a promising candidate due to its status as a non-competitive waste product in the human food chain [2,3]. Lignocellulose, the primary component of forest residues and agricultural waste [4], is cost-effective and abundantly available worldwide. Lignocellulosic biomass primarily comprises three different biopolymers in varying proportions: 35–50 % cellulose, 15–25 % hemicellulose, and 20–30 % lignin [2]. Lignocellulosic biomass has attracted the interest of researchers as it is an abundant and renewable feedstock that can be used to obtain biomaterials with various applications, from adhesives to biofuels [5,6].

One of the most versatile products obtained industrially from lignocellulosic biomass is furfural, as it is used as a building block for high-value products [7]. An attractive application of furfural is the production of larger molecules through aldol condensation with an aldehyde or ketone, which can then be further utilized to produce biofuels such as diesel and aviation fuels [8], which are needed to reduce the impact of fossil fuels.

For aldol condensation of furfural (FF), acetone is regularly used as a linking molecule between two FF molecules. This reaction has been extensively studied in the literature with both homogeneous catalysts such as hydroxides and heterogeneous catalysts, namely oxides/mixed oxides [9].

The issue at hand revolves around acetone, which is derived from

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petroleum as a by-product of the cumene process generating phenol from benzene. Consequently, the current approach is not completely sustainable. An environmentally friendlier alternative would involve acetone-butanol-ethanol (ABE) fermentation. However, this method faces a challenge in terms of low selectivity since the primary goal of this reaction is to achieve a high butanol yield [10].

Additionally, using acetone only allows formation of products with the carbon chain length of 8 (one FF condensed to one molecule of acetone) and C13 (two FF molecules condensed to one molecule of acetone). The closer the chain length is to 15 carbons, the better the quality of the jet fuel, as higher density, lower freezing point, and a higher heating value are elevated [11].

For synthesis of longer carbon chains molecules, the idea came up to substitute acetone with another reagent. The use of cyclopentanone (CP) proved to be a good alternative for several reasons. First, as discussed above, it can be produced in an environmentally friendly way by for example hydrogenation of FF [12]. Second, CP has two carbon atoms with protons in the α-position, which makes it a good candidate as a binding molecule in an aldol condensation reaction. Third, the inductive effect of the side carbon atoms helps to enhance the aldol condensation and minimize the reverse reaction. Lastly, it is possible to obtain longer chains and therefore a better-quality fuel from CP compared to acetone [9].

Current research is, therefore, turning to the aldol condensation of FF and its derivatives with CP because with the use of this linking molecule, the product can then be considered fully renewable as both reactants are derived from biomass [9].

In the literature several studies report aldehydes/ketones aldol condensation, using homogeneous and heterogeneous catalysts in a solvent or solventless conditions operating in batch or continuous fixed bed reactors [13,14].

CaO reported as a base catalyst for aldol condensation can be derived from an eco-friendly source - marble. The latter is a naturally occurring mineral, thus using it as a catalyst aligns with the principles of green chemistry by utilizing abundant and renewable resources. Marble is a widely available material, and extracting CaO from it can be a cost-effective industrially attractive alternative compared to more traditional catalysts. Moreover, unique properties of CaO derived from marble may offer enhanced catalytic activity, as a specific crystalline structure or impurities present in marble derived CaO could lead to improved performance in the aldol condensation reaction, resulting in higher yields and selectivity.

The aldol condensation reactions in general can be catalysed by acids or bases [3,15] through different reaction mechanisms giving, however, the identical product. In both cases, the aldol condensation can be separated into two steps: the aldol condensation reaction followed by dehydration. In the literature (11), basic catalysis for aldol condensation between FF and CP is more thoroughly investigated. Its reaction network can be consulted in Scheme 1.

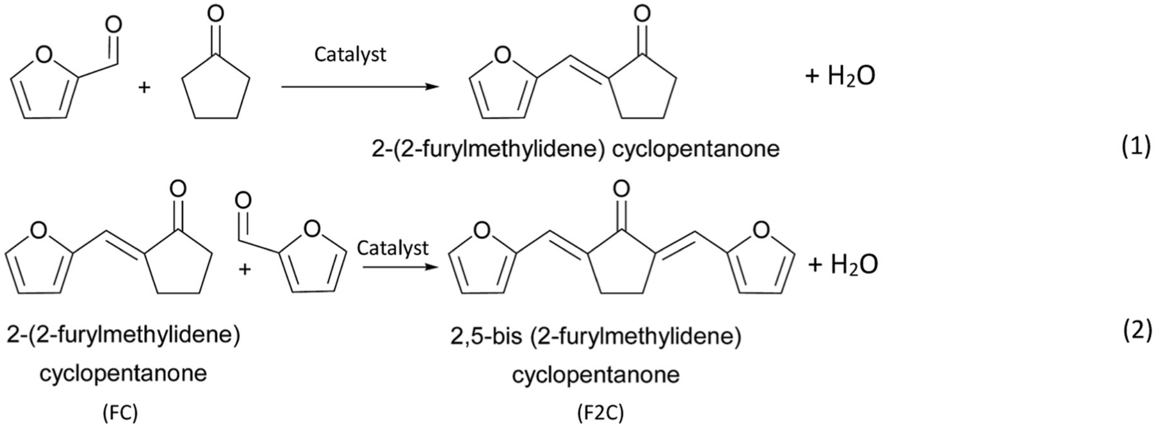
According to the reaction mechanism proposed by Hronec et al. [10] the main products are the self-condensation products of CP (CC) and (CCC), the cross-condensation product (FCC) of FF with the (CC), the monomeric product 2-(2-furylmethylidene) cyclopentan-1- one (FC) and the dimeric product (F2C) of FF with CP. The self-condensation products CC and CCC as well as the cross-condensation product FCC are not mentioned in Scheme 1 for simplicity. The aldol condensation of furfural and CP has many applications and in the last years particularly intriguing was synthesis of 1,3-dipentylcyclopentane (C15) fuel precursors[15]. The two main products obtained from the reaction between FF and CP are 2-(2-furylmethylidene) cyclopentanone (C10 (FC)) and its isomers, as well as 2,5-bis(2-furylmethylidene) cyclopentanone (C15 (F2C)) and its isomers [16].

Aldol condensation has attracted a lot of interest for the production of high-quality fuels on a large scale because it can occur under relatively mild conditions, such as operating at temperatures below 180°C [13]. The ultimate goal is to produce fuels characterized by high density, a low freezing point, and the maximum achievable heating value, making the pursuit of C15 derivatives particularly significant [11].

An overview of the reaction conditions and the yields of FC and F2C products is presented in Table 1 illustrating that high yield of F2C can be

Table 1
Overview of the literature data on aldol condensation of CP with FF.

Catalyst	Conditions	Conversion (%)	Yield (%)	Reference
Nafion; Amberlyst−15; Amberlyst−36;	60 °C, 6 h; 1.92 g (20 mmol) FF, 5.04 g (60 mmol) CP, 0.40 g catalyst.	74;59;56;	F_2C - 38, FC - 24; F_2C - 28, FC - 26; F_2C - 20, FC - 20;	[4]
Mg–Zr mixed oxides	equimolar ratio of both reactants (5 % of organics in water), 30 °C, 0.5 g of catalyst	98;	F_2C - 34, FC - 32;	[9]
NaOH	25°C 100 ml H_2O, 1.68 g CP; molar ratio of CP:FF 1:2; molar ratio of CP: NaOH 0.75	100;	F_2C – 98;	[15]
KF/ γ -Al_2O_3	60°C, 2 h; 1.92 g FF, 0.84 g CP (FF: CP molar ratio2: 1), 0.2 g catalyst and 40 ml ethanol	100;	F_2C – 95;	[17]



Scheme 1. A simplified reaction network for the aldol condensation of FF and CP.

obtained depending on the catalyst and reaction conditions.

According to our knowledge FF-CP aldol condensation reaction has never been done over CaO from marble as a catalyst. The aim of this study was to investigate the effect of the ratio of CP to FF and the reaction temperature. The purity of FF was identified during this study as a vital factor affecting these parameters, with impurities, such as humins, potentially blocking the catalyst surface over time. During the course of this work it was noticed that distilled FF itself is stable for just one day, thereafter changes in colour are becoming apparent. Purification of FF before each reaction can increase conversion of the reagents as reported for acetone condensation[18]. Moreover, because FF is not stable with time under exposure to air and sunlight forming humins, a stabilizer could be added to prevent their formation. Subsequently the effect of stabilizer was also studied in this work for the first time in the FF-CP aldol condensation.

2. Experimental

2.1. Materials

Furfural (99 %), cyclopentanone (≥99 %), ethanol (99 %) were purchased from Sigma-Aldrich. CaO from marble with the grain size between 3 and 20 μm was ordered from Merck (97 %). The stabilizer, 2,6-di-tert-butyl-4-methylphenol (Sigma-Aldrich, 99 %), was selected as it is commonly used for its antioxidant properties, in order to prevent free radical-mediated oxidation in fuels, oils, and other materials. For certain experiments FF was purified by vacuum distillation in a rotary evaporator and stored in a fridge at 5 °C under an inert gas to prevent re-oxidation. An inert gas used to flush FF and the batch reactor was argon (99.999 %) supplied by Woikoski (Argon N50). Aldol condensation products FC (100 %) and F2C (100 %) for calibration were prepared by Laboratory of Thermochemical Processes Unit, IMDEA Energy Institute, Spain, according to the procedure reported in [19]. The products were characterized by ^{13}C and ^{1}H NMR spectroscopy (Supporting Information, Fig. S1).

2.2. Catalytic tests

The catalyst was calcined at 600 ∘C with a ramp 4 °C/min for 4 h, then it was cooled down to 250 °C and held at this temperature.

All the aldol condensation reactions were carried out in a 300 ml stirred batch reactor for 6 h under an inert atmosphere of Ar (5 bar). Stirring speeds were varied in the range of 400–900 to study external mass transfer limitations. CP and FF were mixed with the following molar ratios 10:1, 15:1, 20:1 (with FF being the limiting reactant) and then heated up to the desired temperature (130–150 ∘C) with the ramp of 10 ∘C/min. The samples were periodically taken from the reactor at desired time intervals and diluted with ethanol. Products of the reaction were analysed by gas chromatography using an Agilent 6890 N gas chromatograph equipped with an Agilent 7683 autosampler, using DB-1 column (Agilent 122–103E) (30.0 m × 250 μm × 0.50 μm). As a carrier gas helium was used with a flow rate of 1.7 ml/min. The temperature program for GC analysis was: 60 °C (2 min), 10 °C/min to 280 °C (10 min). GC-MS analysis was done using an Agilent 6890 N gas chromatograph with an Agilent technologies 5973 Network mass selective detector, using DB-1 column (30.0 m × 250 μm × 0.50 μm) to identify the main reaction products. The temperature program for GC analysis was: 60 °C (25 min), 3 °C/min to 135 °C (10 min) and 15 °C/min to 300 °C (1 min). The equations used to determine the catalytic activity, product yield, and selectivity can be found in the supplementary material.

2.3. Catalyst characterization

CaO was characterized by X-ray diffraction (XRD), N_2-physisorption (BET), temperature-programmed desorption of CO_2 (CO_2-TPD) and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX).

Crystalline structures of the fresh and spent CaO were determined by powder X-ray diffraction (XRD), recorded with Panalytical Aeris Research Edition diffractometer in Bragg-Brentano geometry using Cu $K_{\alpha1,\alpha2}$ radiation (Kα1 = 1.540598 Å, Kα2 = 1.544426 Å) and equipped with PIXcel1D detector. The samples were prepared on a standard back-loaded sample holder and rotated 60 rpm during the data collection. The data were recorded with 0.022° (2θ) step size while 1/2° divergence slit and 13 mm mask were used. HighScore Plus [20] was used for data analysis together with PDF4+ database [21].

The concentration of basic sites was determined through Temperature Programmed Desorption of CO_2 (CO_2-TPD) using Microtrac Belcat II equipped with a TC-detector and a zeolitic water trap (13x molecular sieves, Sigma-Aldrich). Initially, around 200 mg of the catalyst was dried at 300°C for 60 min under a flow of high-purity helium (AGA, 99.996 %). Subsequently, the catalyst was cooled to 50°C. Following this, CO_2 was adsorbed on the catalyst surface for 60 min and then flushed from the surface at 50°C for another 60 min. Finally, the temperature was gradually increased to 750°C at a rate of 10°C per min.

SEM analysis was performed to obtain information about the morphological structure of CaO. This analysis was carried out with a Zeiss Leo Gemini 1530 Scanning Electron Microscope, which was outfitted with a Thermo Scientific UltraDry Silicon Drift Detector (SDD).

For the evaluation of textural properties, the Micromeritics 3Flex-3500 instrument was employed. To prepare the catalyst samples, moisture was eliminated, and the samples weighing 0.15 g underwent ex-situ degassing under vacuum (0.1 mbar) conditions at 280 °C for 18 h. Subsequently, a sample was pre-treated in the physisorption equipment under vacuum at 280 °C for 2 h. This was followed by liquid nitrogen adsorption at −196 °C. The specific surface area was calculated using the BET method, while the pore size distribution was determined utilizing the NL-DFT method.

The potential leaching of metals from the catalyst into the liquid phase was explored through analysis of the filtrated liquid sample after the reaction on an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Optima 5300 DV). Methanol was eliminated from the product mixture by purging it with nitrogen. Subsequently, 3.6 ml of hydrochloric acid (65 %, Sigma Aldrich) and 1.2 ml of nitric acid (70 %, Sigma Aldrich) were introduced to the product to attain an optimal concentration for the analytical equipment. The resulting solution was transferred to a 100 ml volumetric flask, with meticulous rinsing of the beaker walls using an in-situ prepared aqua regia. The solution was then diluted with distilled water to achieve a final volume of 100 ml. After the preparation and the measurement, the discrepancies in metal concentrations between the two different media could be detected.

3. Results and discussion

3.1. Characterization results

3.1.1. XRD results

Two crystalline phases were observed for each of the samples, indicating some changes during reaction. The diffractograms of both catalysts presented in Fig. 1 show peaks corresponding to calcium hydroxide ($Ca(OH)_2$, PDF-4+ 00–044–1481). In addition to this phase, calcium oxide (CaO, PDF-4+ 01–082–1690) is found only in the sample of the fresh catalyst, but not in the spent catalyst. On the other hand, calcium carbonate ($CaCO_3$, PDF-4+ 01–083–4612) is present in the spent catalyst, but not in the fresh catalyst, suggesting that $CaCO_3$ is formed during the catalytic reaction, probably by carbonation of calcium hydroxide generated from water released in the reaction media and CaO surface [22].

It is worth noting that since the spent catalyst has not been in the oven, it is logical not to find any CaO and that it is entirely in the form of $Ca(OH)_2$ because of the humidity in the air. This means that after

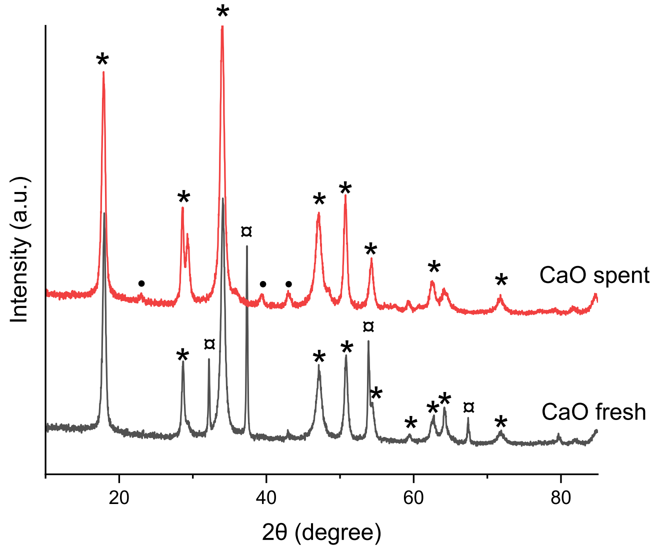


Fig. 1. Diffractograms of the fresh and spent CaO. Peaks corresponding to CaO (¤), $Ca(OH)_2$(*) and to $CaCO_3$(●). The spent catalyst corresponds to the reaction with the following conditions: mass ratio of FF:cat = 10:1, molar ratio of CP:FF = 10:1, reaction temperature = 130°C, stirring speed = 900 rpm.

calcination at 600 °C, CaO can be recovered. To obtain CaO from $CaCO_3$, which was formed during the reaction, by release of CO_2, the catalyst must be calcined at temperature above 900 °C [23]. If the spent catalyst was calcined at 600 °C to study the reuse of the catalyst, a loss of activity of the catalyst would be expected due to formation of $CaCO_3$.

3.1.2. Coupled SEM-EDX analysis

From SEM images of CaO (Fig. 2), it can be seen that the particles exhibit irregular agglomerated shapes with the particle size varying in the range of 1–7 µm.

EDX analysis (see supporting information Fig. S3) indicated that the purity of CaO is 95.24 %. MgO (1.59 %), Al_2O_3 (1.26 %), SiO_2 (0.76 %) and Cl (1.15 %) were also found in the powder.

Because MgO in principle can also be a catalyst of aldol condensation, a separate experiment was conducted to check the influence of magnesia. The conversion level of MgO was three fold lower after 2 h than for CaO. Subsequently, considering a low concentration of MgO as an impurity in CaO, the impact of magnesia as a catalyst can be neglected.

3.1.3. N_2-physisorption

The adsorption-desorption isotherms of the fresh and spent catalysts are shown in Fig. 3. According to the data the fresh CaO is not porous at all exhibiting rather low surface area which is associated with the fact that the sample is in the form of hydroxide under the pretreatment and measurement conditions. The spent catalysts possess some interparticle porosity (the surface area of 32 m^2/g) obviously originated from a decrease in the particle size (as can be seen from the broader XRD signals for the spent catalysts, Fig. 1) after the decomposition of the initial sample (mainly calcium hydroxide) into calcium oxide during the activation stage, which can be associated with the leaching of the material as observed with ICP-OES.

3.1.4. ICP-OES

Leaching of metals (Ca, Mg, Al) from the catalyst into the liquid phase was around 8.7 % of the mass of the catalyst used for the reaction.

3.2. Thermodynamic analysis

3.2.1. Methods

Enthalpy (ΔH_r^0) and Gibbs free energy (ΔG_r^0) at standard conditions were calculated by a thermodynamic approach reported in literature [24], starting from the standard enthalpy (ΔH_f^0) and Gibbs free energy

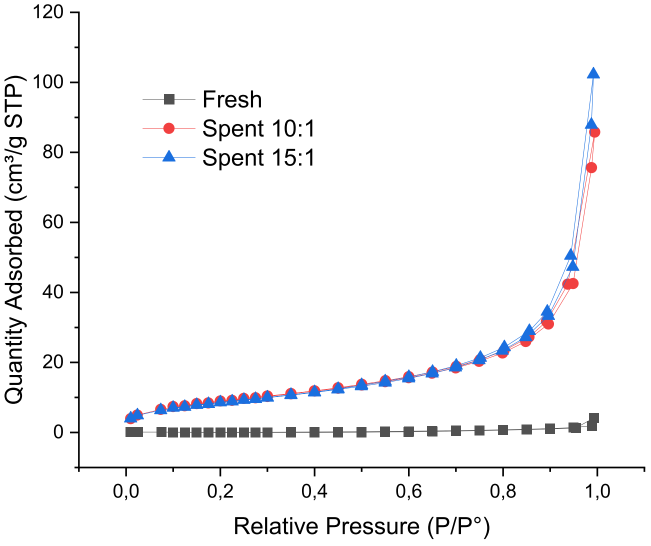


Fig. 3. Nitrogen adsorption-desorption isotherms for the fresh and spent CaO. Spent CaO samples were recovered after reactions with the following conditions: mass ratio of FF:cat = 10:1, molar ratio of CP:FF = 15:1, 20:1, reaction temperature = 130°C, stirring speed = 900 rpm.

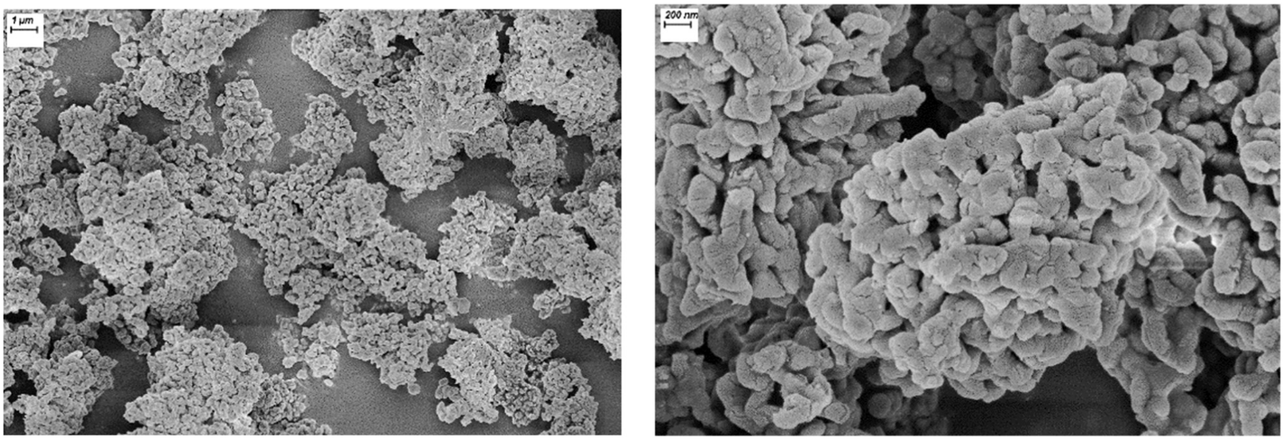


Fig. 2. SEM images of CaO at different magnification.

(ΔG_f^0) of formation from the elements retrieved from CHEMCAD database [25] using the Joback approach [26–28]. Equations can be found in Supplementary material.

3.2.2. *Results of thermodynamic analysis*

The calculated enthalpy and Gibbs free energy formation for each component (i) are reported in Table 2. The stoichiometric matrix was built based on the reaction scheme (Scheme 1).

Starting from these values, the enthalpy and Gibbs free energy for each reaction (j) at standard conditions, equilibrium constants at standard conditions (K_j^0), enthalpy and Gibbs free energy at different temperatures and pressure were calculated. A temperature range was investigated ($T_{\min} = 323K$, $T_{\max} = 423K$). The results of the calculations are reported in Table 3 and Fig. S4.

As revealed, both reactions are spontaneous without thermodynamic limitations.

3.3. *Catalytic results*

3.3.1. *Leaching of the catalyst*

A hot filtration test was done to understand if there is leaching of the catalyst during the reaction. The catalyst was filtered from the reaction mixture after 2 h of reaction using vacuum filtration. Fig. 4 shows that after removal of the catalyst, conversion of FF still increased but at a slower rate than with the solid CaO, hinting at dissolution of CaO in accordance with ICP-OES results, and therefore a certain contribution of the homogeneous catalytic reaction. A comparison with the conversion at 4 h using solid CaO is also displayed in Fig. 4 (red circle). Complete conversion of FF can be observed for the reaction without filtration of the catalyst, while ca. 90 % was reached after 6 h when CaO was filtered after 2 h. Based on the slopes in conversion-time profiles the potential contribution of the homogeneous reaction can be in the range of 30 %.

3.3.2. *Stirring speed*

To study influence of the stirring speed on aldol condensation reaction three reactions were done with different stirring speeds, namely 400, 800, and 900 rpm with the molar ratio of CP to FF – 15:1 using distilled FF as a feedstock and the mass ratio of FF to catalyst of 10:1. The apparent rate constants calculated from the pseudo first order kinetics as a function of the stirring speed are presented in Table 4, illustrating that the rate constants at 800 and 900 rpm are rather close to each other while at 400 rpm the mass transfer limitations are clearly present. Fig. S5 illustrates changes of the FF conversion with the reaction time.

For the reactions with the stirring speed 800 and 900 rpm there was almost no difference between conversion after 6 h of the reaction, with the respective values of 96 % and 100 %. At the same time the reaction with the stirring speed 400 rpm only reached 70 % after 6 h (Fig. S5). Thus, the stirring speed of 900 rpm was used in kinetic experiments.

3.3.3. *Influence of furfural purity and CP:FF ratio*

To study influence of the FF purity two types of reactions were performed with three different molar ratios of CP to FF – 10:1, 15:1, 20:1 and a constant mass ratio of FF to CaO of 10:1 with and without distillation of FF. Fig. 5 illustrates changes in the undistilled FF conversion with the reaction time.

Table 2

Enthalpy and Gibbs free energy formation for each component (i) and stoichiometric matrix for component i for reaction j. Notation: The reactions 1 and 2 are shown in Scheme 1.

Component	ΔH_f^0 [kJ/mol]	ΔG_f^0 [kJ/mol]	i/j	1	2
furfural	−147.85	−57.12	**1**	−1	−1
cyclopentanone	−195.10	−87.11	**2**	−1	0
2-(2-furylmethylidene) cyclopentanone	−213.55	−28.35	**3**	+1	−1
H_2O	−241.83	−228.44	**4**	+1	+1
2,5-bis (2-furylmethylidene) cyclopentanone	−223.69	30.41	**5**	0	+1

Table 3

Enthalpy and Gibbs free energy at standard conditions, equilibrium constants at standard conditions (K_j^0).

ΔH_r^0 [kJ/mol]	ΔG_r^0 [kJ/mol]	K_j^0
−112	−113	$5.24 \cdot 10^{19}$
−104	−113	$5.24 \cdot 10^{19}$

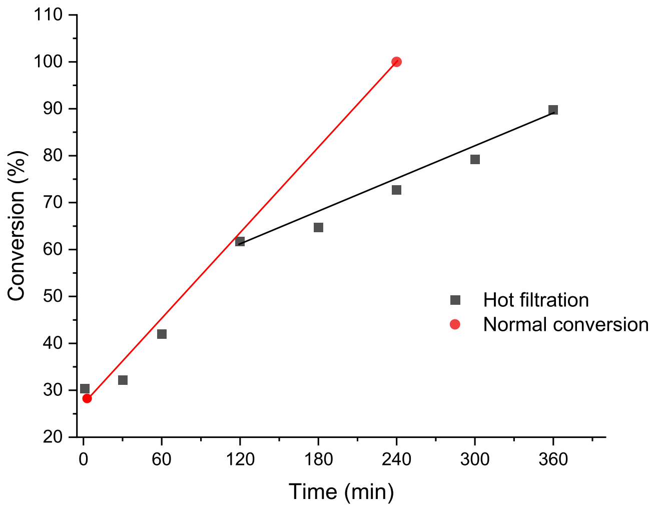


Fig. 4. Conversion of FF in aldol condensation reactions with CP with and without filtration of the catalyst after 2 h of the experiment. Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF = 15:1, reaction temperature = 130 °C, stirring speed = 900 rpm.

Table 4

Apparent rate constants depending on the stirring speed at the following conditions: molar ratio of CP:FF 15:1, mass ratio FF:cat 10:1, reaction temperature = 130°C.

Stirring speed (rpm)	Rate constant ($\min^{-1}$)
400	0.00298
800	0.01858
900	0.02116

After 360 min of the reaction, FF conversion of more than 60 % was observed. The best results were achieved at the ratio of CP to FF 20:1 when conversion of FF after 360 min of the reaction reached almost 80 %. At the same time conversion of FF in the experiments with the ratio of CP to FF 10:1 and 15:1 was 75 % and 70 % respectively.

The first product formed (Fig. 6a) with undistilled FF was an intermediate product hydroxylated FC with the molecular mass of 180 g/mol, also visible in the chromatogram (Fig. S6). This product was also mentioned as a potential intermediate in FF-CP aldol condensation but not observed experimentally over Mg-Zr catalyst presumably because of a high reaction rate [9]. In the case of undistilled FF, the reaction rate is slower. The yield of the hydroxylated intermediate reached a maximum of 10 % reacting further to FC.

The yields of FC were in the range of 40–45 % for all the experiments (Fig. 6b), which can be related to formation of humins, as almost no generation of F2C was visible despite high conversion.

At the same time, selectivity to the main product reached 60 % for the reaction with the ratio of CP to FF 15:1 and 55 % and 50 % for the ratios 20:1 and 10:1 accordingly (Fig. 7). Overall, the low yields of FC

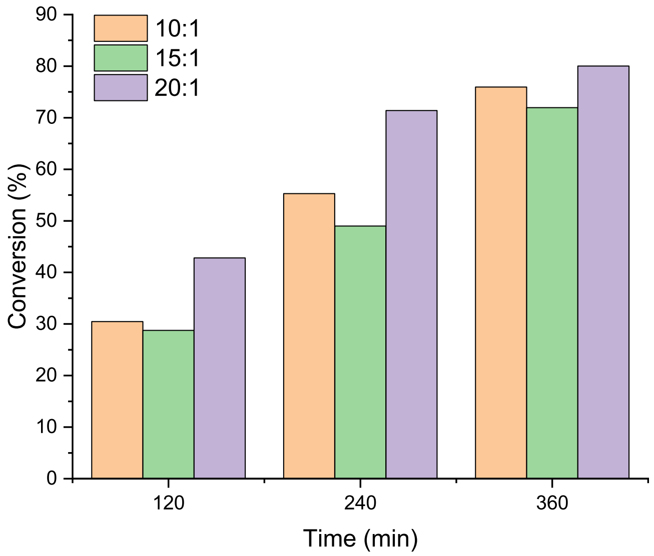


Fig. 5. Conversion of undistilled FF at different FF to CP ratios. Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF = 10:1, 15:1, 20:1, reaction temperature = 130 °C, stirring speed = 900 rpm.

and F2C can be explained by slow reaction rates with undistilled FF.

Analogous experiments as described above were also performed with distilled FF using three different molar ratios of CP to FF – 10:1, 15:1, 20:1 and a constant mass ratio of FF to CaO – 10:1. Conversion of distilled FF as a function of time in the aldol condensation with CP is given in Fig. 10.

It can be seen from Fig. 8 that the CP to FF ratio of 15:1 resulted in the highest conversion of FF 93 % after 4 h of the reaction, while for 20:1 and 10:1 ratios only 87 % and 67 % FF conversion was achieved, respectively. At the moment, the reason behind higher activity with CP to FF ratio of 15 is unclear. It should be, however, noted, that in the current work the amount of cyclopentanone was always fixed, while the concentration of furfural was varied. Subsequently different ratios between cyclopentanone and furfural imply different concentrations of furfural, which can have a strong impact on generation of side products that can be formed.

In any case, the conversion levels in Fig. 8 are clearly higher than those obtained with undistilled FF (Fig. 5). The same correlation could be observed in [18] for the reaction of aldol condensation of FF with acetone over MgAl mixed oxide catalysts. Four experiments were performed using FF previously distilled at different time intervals. A significant difference was observed when using freshly distilled FF and FF as received, with FF conversion changing from 2.1 % to 44.9 %, respectively.

The yields of FC and F2C products (Fig. 9) displayed analogous dependence after 4 h of the reaction. The FC yield for the ratio of CP to FF 15:1 was 66 % after 4 h with the F2C yield of 7 %. After 6 h the yields decreased due to formation of other products. For the ratio of CP to FF of 20:1 the highest yield was 65 % for FC and 5 % for F2C after 6 h of the reaction. A lower excess of CP (CP to FF ratio of 10:1) gave the lowest FC yield (54 %) and the highest F2C yield (11 %) after 6 h, as expected. Obviously F2C formation was enhanced with a higher initial FF

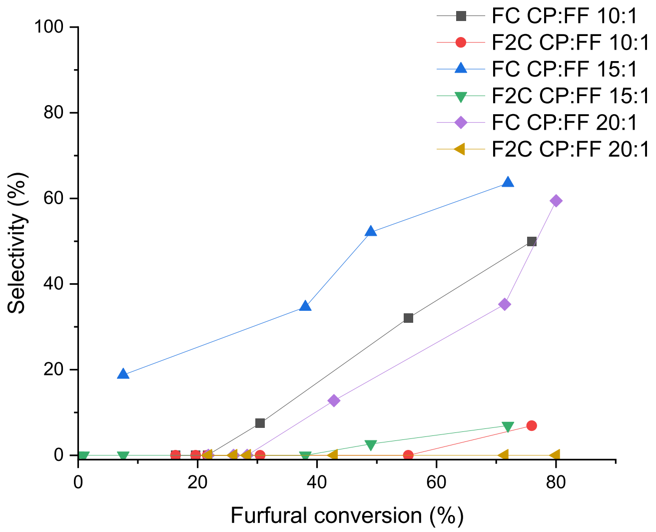
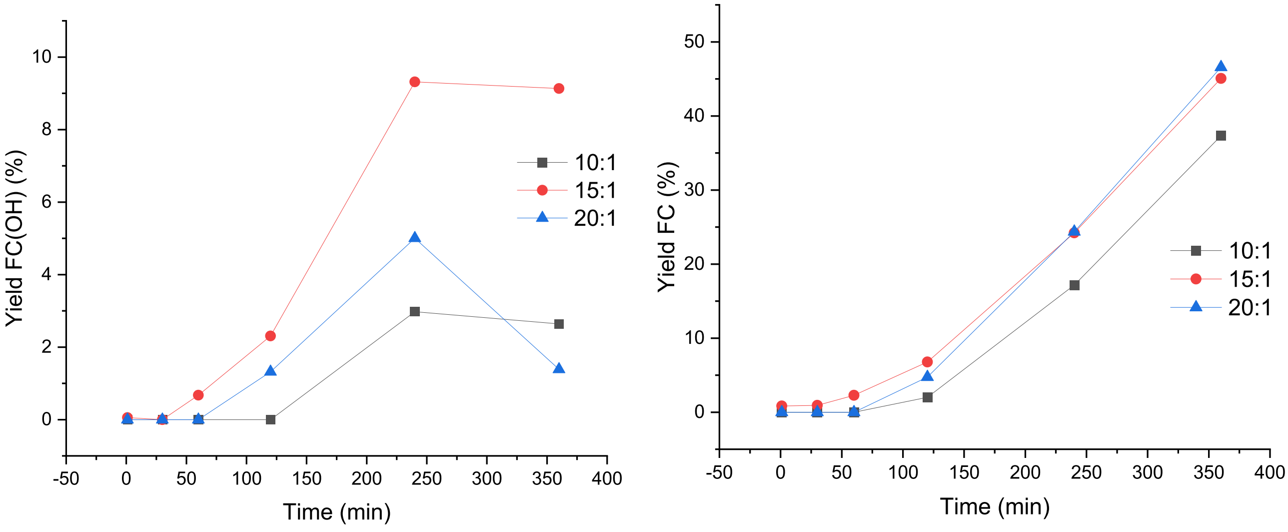


Fig. 7. Dependence of selectivity to FC and F2C on FFL conversion using undistilled FF with CP over CaO. Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF = 10:1, 15:1, 20:1, reaction temperature = 130 °C, stirring speed = 900 rpm.



(a)

(b)

Fig. 6. Variation of the product yields (a) FC(OH) and (b) FC at different FF to CP ratios using undistilled FF with CP over CaO. Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF = 10:1, 15:1, 20:1, reaction temperature = 130 °C, stirring speed = 900 rpm.

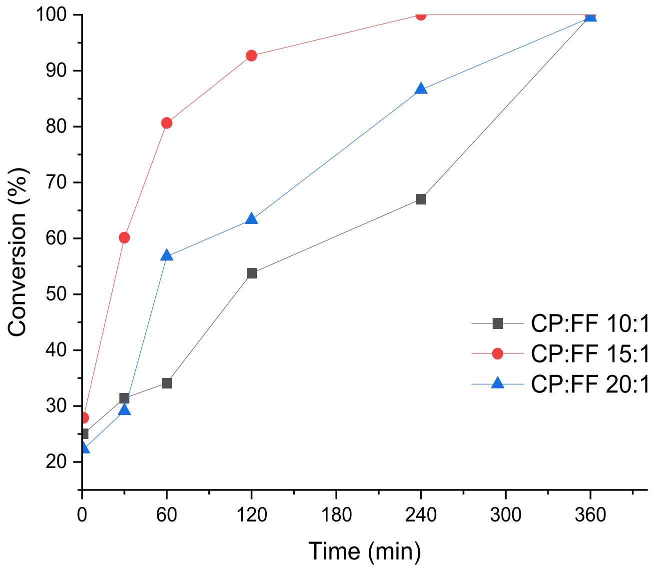


Fig. 8. The effect of the FF to CP ratio on the distilled FF conversion with CaO as a catalyst. Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF = 10:1, 15:1, 20:1, reaction temperature = 130 °C, stirring speed = 900 rpm.

concentration. Similar results have been reported for aldol condensation with acetone and also with CP [9,14,29]. A summary of the results with FF of different purity is given in Table 5.

It can be seen from the experimental data (Fig. 10) that the reactions with CP to FF ratios of 15:1 and 20:1 are rather selective (67 %) to FC product. This selectivity decreases for the 15:1 ratio after 100 % conversion. At the same time for the 10:1 ratio the lowest selectivity to FC product (52 %) and the highest selectivity to F2C product (10 %) were obtained, as could be expected, in the presence of a higher initial amount of FF.

3.3.4. Influence of the stabilizer

The influence of the stabilizer (2,6-di-tert-butyl-4-methylphenol) was studied by comparing aldol condensation reactions of purified FF with CP with or without a stabilizer. The experiments were performed with the mass ratio FF:cat = 10:1, molar ratio CP:FF =10:1, T = 130 °C.

From Fig. 11 it can be clearly seen that in the aldol condensation of distilled FF with CP, the stabilizer significantly enhanced the reaction rate more than 6 fold, acting as an acid homogeneous catalyst analogously to [4], when a solid acid, Amberlyst 15, was used as a catalyst. For the same reactions but with differently pretreated FF the best results were achieved with FF in the presence of the added stabilizer. High conversion of FF (97 %) was achieved already after 2 h of the reaction (Fig. 11) and selectivity to both desired products was 74 % to FC and 25 % to F2C (Fig. 12) while without a stabilizer for undistilled FF selectivity of ca. 50 % to FC and 10 % to F2C was reached. This difference can be explained by an increase of FF acidity under different

Table 5
Results of aldol condensation reactions with undistilled and distilled FF and CP after 6 h of the reaction at: molar ratio of CP:FF 15:1, mass ratio FF:cat 10:1, reaction temperature = 130 °C, stirring speed = 900 rpm.

Feed	Conversion (%)	Yield FC(OH) (%)	Yield FC (%)	Yield F2C (%)
Undistilled FF	72	9	45	5
Distilled FF	100	0	57	6

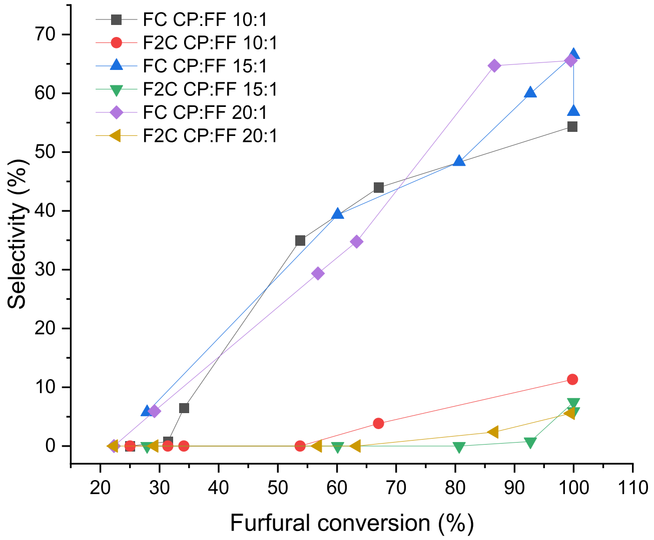


Fig. 10. Dependence of selectivity to FC and F2C on FF conversion in the aldol condensation of distilled FF with CP over CaO. Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF = 10:1, 15:1, 20:1, reaction temperature = 130 °C, stirring speed = 900 rpm.

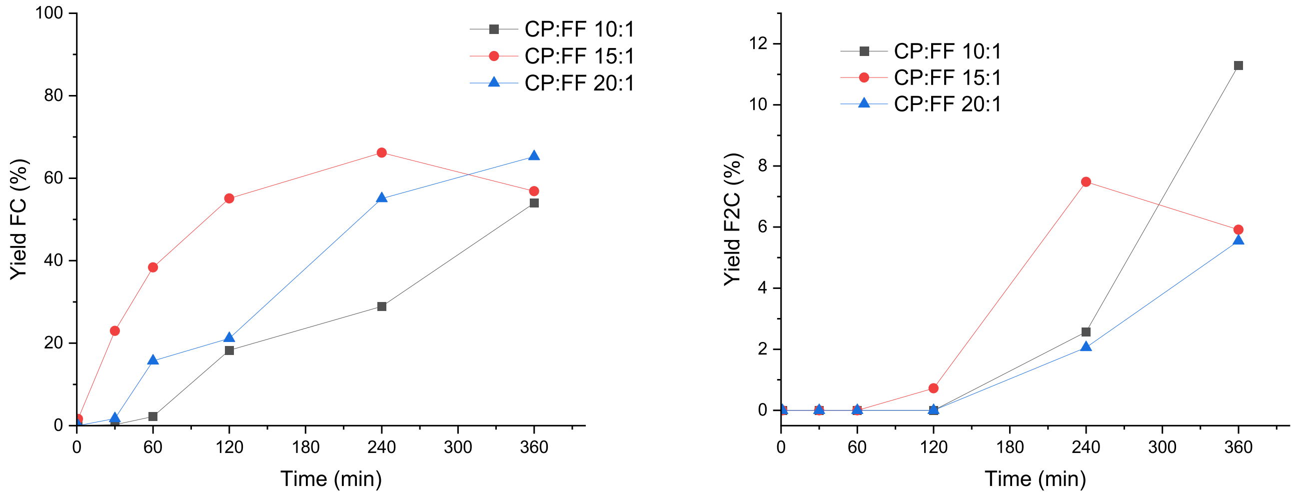


Fig. 9. Dependence of the product yield on the CP:FF ratio over CaO with distilled FF. Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF = 10:1, 15:1, 20:1, reaction temperature = 130 °C, stirring speed = 900 rpm.

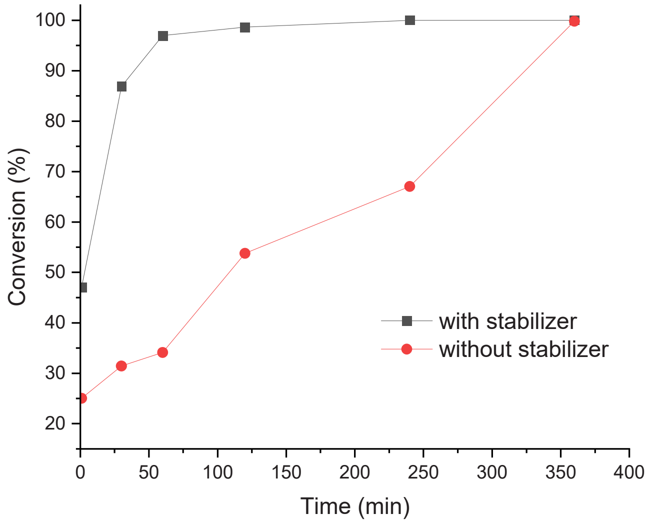


Fig. 11. Conversion of distilled FF in the presence of added stabilizer (2,6-di-tert-butyl-4-methylphenol). Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF = 15:1, reaction temperature = 130 °C, stirring speed = 900 rpm.

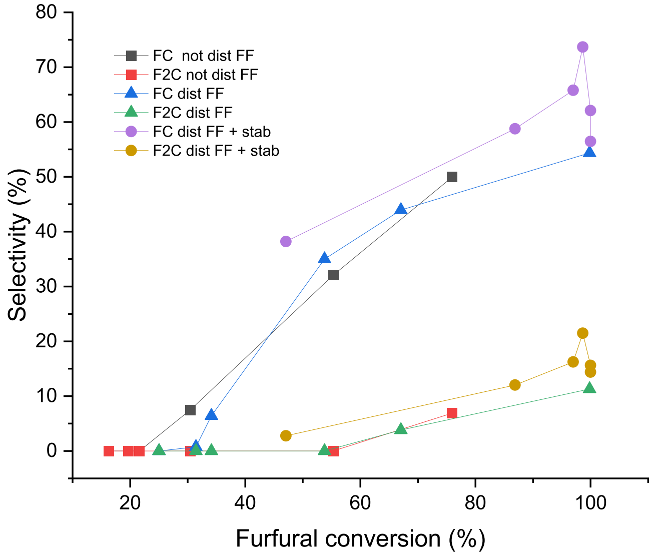


Fig. 12. Dependence of selectivity on FF conversion in the aldol condensation of differently pretreated FF with CP over CaO. Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF =10:1, T = 130 °C, stirring speed = 900 rpm.

storage conditions as reported in [4,18] where freshly distilled FF was stored under inert atmosphere (Ar) in a closed container in a dark place thereby decreasing the influence of light and oxygen from air.

3.3.5. Influence of the reaction temperature

The influence of temperature on the reaction was studied at three different temperatures, namely 110, 130, 150 °C with the molar ratio of CP to FF of 15:1 and the mass ratio of FF to cat of 10:1. Fig. 13a illustrates changes in FF conversion with the reaction time. The best result was obtained at the highest temperature as expected. Complete conversion was obtained at 150 °C after already 2 h resulting, however, in numerous side products such as 1′-hydroxy-[1,1′-bi(cyclopentan)]-2-one (CC(OH)), [1,1′-bi(cyclopentylidene)]-2-one (CC) and the tetramer of two FC(OH) molecules (Fig. S7).

Analogous behaviour was also discussed in [30] reporting aldol condensation of FF with acetone. Effect of temperature on conversion in aldol condensation reaction was also studied in [9]. While temperature did not result in significant changes in conversion, its impact on selectivity at the same conversion level was quite profound.

The activation energy calculated from the experimental data (Fig. 13b) is 43 kJ/mol, in line for FF-CP aldol condensation reaction using binary water–ethanol mixtures as a solvent [8] where for the ratios of ethanol-water 1:1 – 1:2 the activation energy was 22.8 – 49.4 kJ/mol.

The highest product yields were obtained at the highest temperature of 150 °C after 2 h being 74 % FC and 9 % F2C, while during the subsequent 4 h the yields decreased to 45 % and 6 %, respectively. On the other hand, the product yields for the reaction at 130 °C reached a maximum (66 %) for FC and 7 % for F2C after 4 h, decreasing thereafter to 57 % and 6 %, respectively (Fig. 14). The total mass balance decreased after prolonged times to 69 % due to formation of heavy products, which were not visible in the GC.

The reaction at the highest studied temperature was highly selective to products during the first two h with selectivity to FC and F2C products reaching 75 % and 9 %, respectively, while during the next 4 h it decreased to 45 % and 6 %. Selectivity to FC at a lower temperature (130 °C) was 70 % during 4 h decreasing after 100 % conversion of FF to 55 % due to further reactions (Fig. 15).

4. Conclusions

In this study aldol condensation of furfural (FF) with cyclopentanone (CP) over CaO catalyst was investigated. The catalytic experiments showed that the stirring speed, purity of furfural, CP:FF ratio, and the reaction temperature significantly influenced the aldol condensation reaction. The best conditions for FF conversion and the product yield among the tested ones were identified, with the FF:cat mass ratio of 10:1 and a CP:FF molar ratio of 15:1 at 130 °C being particularly effective. Higher stirring speeds of 800 and 900 rpm enhanced the reaction rate and FF conversion, while mass transfer limitations were clearly present at insufficient stirring speed. The high purity of FF and addition of the stabilizer (2,6-di-tert-butyl-4-methylphenol) significantly improved the reaction rate and selectivity to the desired products.

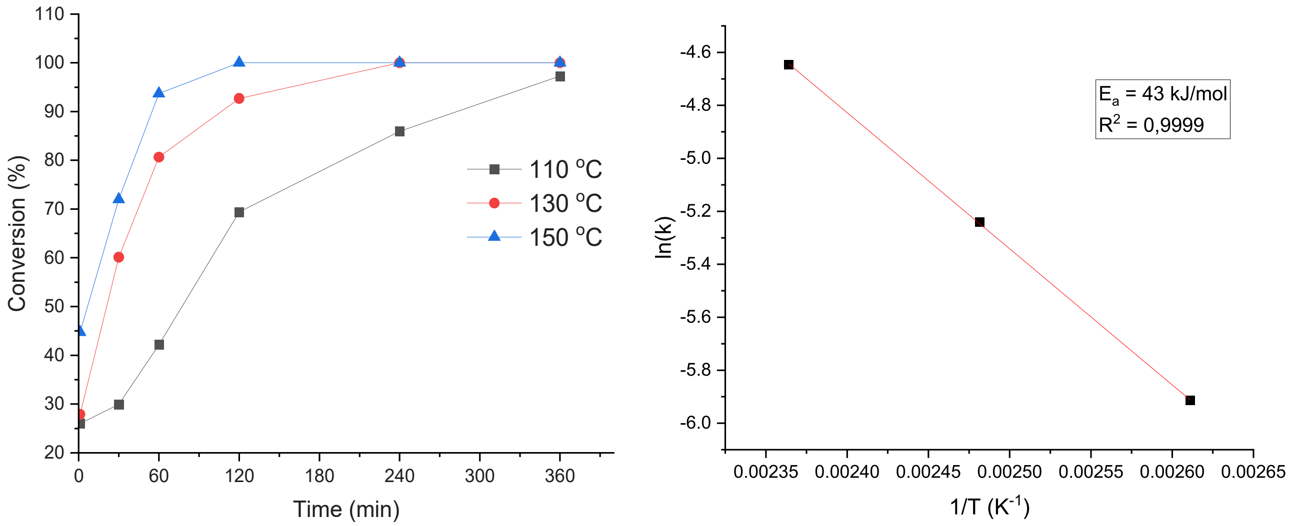
The influence of reaction temperature was also notable, with higher temperatures leading not only to complete FF conversion but also to formation of the side products. The activation energy for the reaction was determined to be 43 kJ/mol, which is within the expected range for this type of reaction.

This study provides valuable insights into the synthesis of precursors of jet-fuels from renewable biomass using the aldol condensation of CP and FF with base catalysts. Future research could focus on exploring alternative catalysts and reaction conditions to further enhance efficiency and selectivity of the process. In particular, different types of catalysts, such as hydrotalcites, ceria and metal organic frameworks are explored by the authors for the aldol condensation of cyclopentanone and furfural.

Additionally, investigating the mechanism of catalyst deactivation and strategies for catalyst regeneration could provide avenues for improving sustainability and cost-effectiveness of the process.

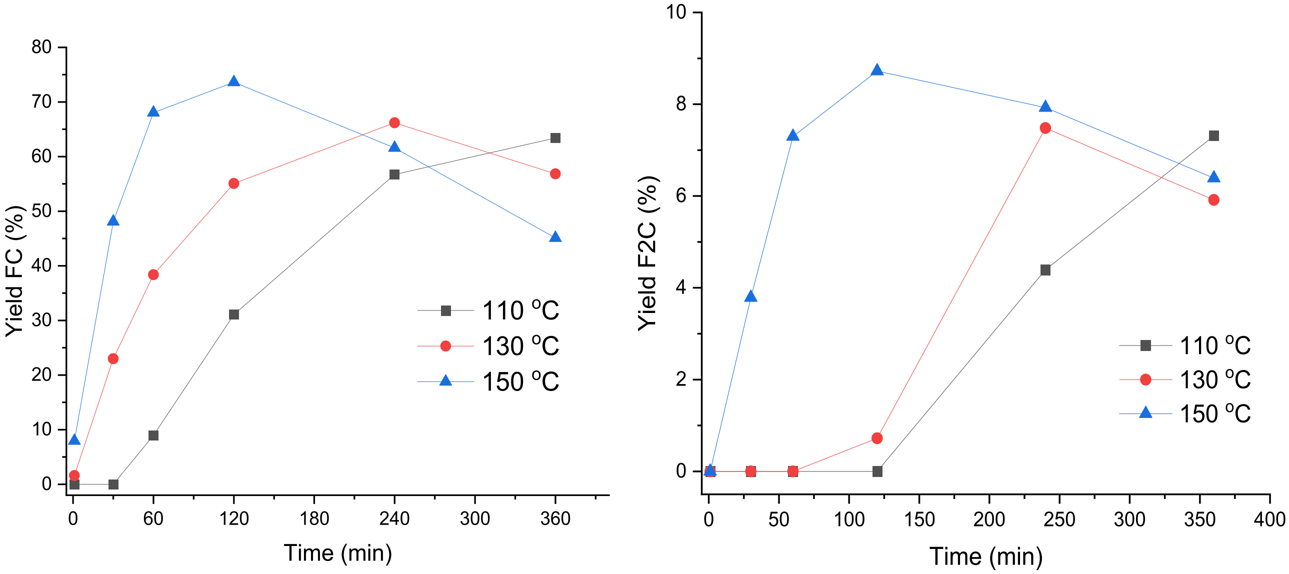
CRediT authorship contribution statement

Mark Martinez-Klimov: Methodology, Investigation, Data curation. **Nataliya Shcherban:** Methodology, Investigation. **Dmitry Yu. Murzin:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Olha Yevdokimova:** Writing – original draft, Investigation, Data curation. **Kari Eränen:** Project administration, Methodology. **Elena Giner:** Investigation. **Jennifer Cueto:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Roman Weydisch:** Investigation. **Päivi Mäki-Arvela:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Vincenzo Russo:** Investigation. **Mika Lastusaari:** Investigation. **Anssi Peuronen:** Investigation.



(a) (b)

Fig. 13. Condensation of CP with FF: (a) effect of temperature on conversion of distilled FF, (b) determination of activation energy based on the Arrhenius equation. Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF =15:1, T = 110, 130, 150 °C, stirring speed = 900 rpm.



(a) (b)

Fig. 14. Effect of temperature on the yield of a) FC and b) F2C Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF =15:1, T = 110, 130, 150 °C, stirring speed = 900 rpm.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

List of symbols

K_j^0Equilibrium constant at standard conditions for reaction j

n Moles, mol

P Pressure, bar

P^0Standard pressure, bar

RIdeal gas constant, J/K/mol

TAbsolute temperature, K

T^0Absolute standard temperature, K

Greek symbols

ΔG_f^0Gibbs free energy of formation at standard conditions, J/mol

ΔG_r^0Gibbs free energy of reaction at standard conditions, J/mol

$\Delta G_{r,j}^{\Phi}$Gibbs free energy of reaction at 1_{bar} and a chosen temperature, J/mol

ΔH_f^0Enthalpy of formation at standard conditions, J/mol

ΔH_r^0Enthalpy of reaction at standard conditions, J/mol

$\nu_{i,j}$Stochiometric matrix composed by i components and j reactions -

Data Availability

Data will be made available on request.

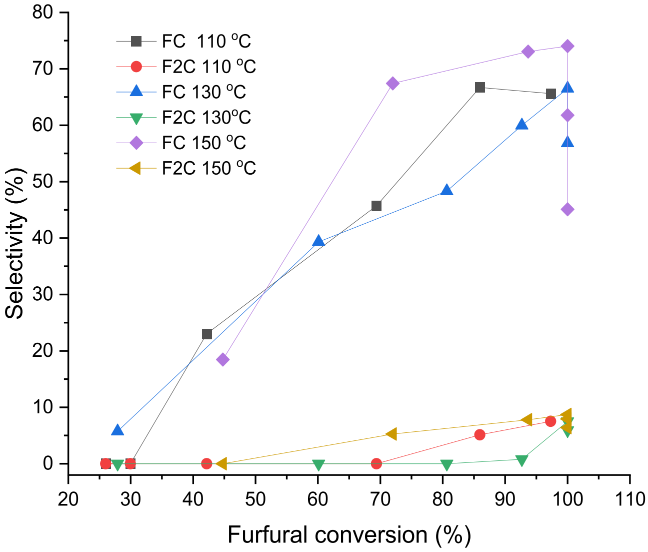


Fig. 15. Dependence of selectivity to different products in distilled FF condensation with CP at different temperatures. Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF =15:1, T = 110, 130, 150°C, stirring speed = 900 rpm.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2024.114962.

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