

# Catalytic Upgrade of Pyrolysis Vapors: Bio-Fuels Production from Acetic Acid on Ru/TiO<sub>2</sub> Catalyst

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The valorization of waste biomass is a resource for the current energy transition and a pillar of circular economy. In particular, the short-term evolution of the mobility sector requires a suitable green liquid fuel, especially for aviation and shipping market. Pyrolysis is a promising technology to convert lignocellulosic biomass into valuable fuels and chemicals, but several negative features of bio-oil (poor stability, acidity, coking tendency, high oxygen content) limit both its direct use and its upgrading processes. These negative factors are mainly caused by the presence of C<sub>2</sub>-C<sub>4</sub> oxygenates in bio-oil (aldehydes, ketones, acids). A possible solution to improve bio-oil quality is the addition of a catalytic upgrading stage, aiming to convert these detrimental light oxygenates from the vapor-phase. C-C coupling reactions - like ketonization and aldol condensation - can increase the C-chain length of bio-oil species while reducing the overall O/C ratio. Catalysis is necessary to improve the kinetics (rate and selectivity) of these processes. In this work, acetic acid chain-growth reactions are studied on TiO<sub>2</sub> and Ru/TiO<sub>2</sub> catalysts, proving relevant performances in promoting not only ketonization but also secondary growth reactions with the formation of C<sub>8</sub>+ species.

## 1. Introduction

The current energy transition is asking for a lower dependence on fossil fuels and novel technologies based on sustainable energy sources are under investigation. In this context, a possible route is the employment of 2<sup>nd</sup>-generation biomasses, which would allow to valorize waste according to the principles of circular economy while abating the net CO<sub>2</sub> production. In particular, liquid bio-fuels are expected to play a critical role in the short-term decarbonization of those sectors of mobility which are more difficult to be electrified, that are aviation and shipping. For instance, the IEA (2021) predicts an increase of bio-fuels global demand of 28% over 2021-2026, including 4.1×10<sup>9</sup> liters/year of jet-fuels.

Among the investigated biomass conversion routes pyrolysis is a thermochemical process where solid biomass is heated in the absence of oxygen and three distinct streams of products are produced: a gaseous stream (rich in light species as CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>), a liquid stream referred to as bio-oil (a complex mixture of oxygenated hydrocarbons) and char, a solid carbon-rich residual. However, bio-oil has some negative features which limit both its direct use as fuel and its upgrading processes: poor stability, high acidity, coking tendency, high O<sub>2</sub>-content (around 35 wt%). These negative factors are mainly caused by the presence of C<sub>2</sub>-C<sub>4</sub> oxygenates (aldehydes, ketones, acids). A possible solution to improve bio-oil quality is the development of a catalytic upgrading stage of pyrolysis vapors (Catalytic Vapor Upgrading, CVU), aiming to convert these detrimental light oxygenates into useful products. A possible CVU route involves C-C coupling processes, where C<sub>2</sub>-C<sub>4</sub> oxygenates are converted to higher species via chain-growth reactions, thus increasing the carbon-chain length while reducing the overall O/C ratio.

In particular, two important chemical routes of oxygenates C-C coupling are being investigated: ketonization of carboxylic acids and aldol condensation of aldehydes/ketones, as reviewed by Gürbüz et al. (2010). During ketonization, two carboxylic acids react to form a ketone, with elimination a molecule of CO<sub>2</sub> and a molecule of H<sub>2</sub>O Eq(1).

The most promising catalysts are Ce, Zr, Ti oxides, where acid-base functionality plays a key role (Kumar et al., 2018). Gaertner et al. (2009) investigated the ketonization of carboxylic acids over CeO<sub>2</sub>/ZrO<sub>2</sub>; they found that also esterifications can play a role and developed a macro-kinetic scheme for hexanoic acid ketonization. In the case of aldol condensations of carbonyl compounds, bifunctional catalysts are preferred, with metal particles (e.g., Pd, Pt, Ru, Cu) supported on metal oxides (e.g., CeO<sub>2</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, MgO). Indeed, in the presence of H<sub>2</sub> co-feed the metal sites are expected to favor the hydrogenation of unsaturated intermediates that are formed according to aldol condensation mechanism. This is expected to mitigate C-poisoning and catalyst deactivation (Wang et al., 2016). Indeed, light oxygenates are widely known for their marked coking tendency (Ochoa et al., 2020) and this opens new challenges in terms of catalyst formulation.

In this work, as a first step in the study of catalytic upgrading processes of pyrolysis vapors, the reactivity of acetic acid (chosen as model C2 oxygenate) in chain-growth reactions over TiO<sub>2</sub> and Ru/TiO<sub>2</sub> catalysts was investigated in a micro packed-bed reactor. Aim of this study was the analysis and rationalization of the behavior of TiO<sub>2</sub>-based catalytic materials in ketonization reaction under different conditions. Besides, the reacting system was pushed to more severe conditions (i.e., high temperature and high conversion) in order to promote the production of species in the fuel-range. For this purpose, an experimental set-up and an analytical methodology suitable for the detailed speciation of complex products mixtures were developed.

## 2. Materials and methods

### 2.1 Catalyst preparation and characterization

Experiments were performed on TiO<sub>2</sub> and 1.2 wt% Ru/TiO<sub>2</sub> catalytic powders. A commercial anatase TiO<sub>2</sub> powder (DT-51D, Tronox) was employed, after calcination at 400°C for 3h. The 1.2 wt% Ru/TiO<sub>2</sub> catalyst was obtained via incipient wetness impregnation, using an aqueous solution of RuCl<sub>3</sub> salt. The metal content was verified by ICP-MS analysis. After the impregnation, Ru/TiO<sub>2</sub> powders were calcined at 400°C for 3h. Both TiO<sub>2</sub> and 1.2 wt% Ru/TiO<sub>2</sub> catalysts were sieved (140–200 mesh) to obtain the desired particles size for the kinetic investigation in the micro packed-bed reactor. Prior to testing, the catalyst was pre-reduced in flowing H<sub>2</sub> in the packed-bed reactor at 400°C for 1h, following a 10°C/min temperature ramp.

BET-surface area of powders was determined via N<sub>2</sub> adsorption/desorption (Tristar Micrometrics 3000) and the crystalline structure of TiO<sub>2</sub> was analyzed by XRD (Bruker D8 Advanced diffractometer).

### 2.2 Lab-scale apparatus for catalytic activity tests

C-C coupling experiments were carried out in a micro fixed-bed reactor, consisting of a quartz tube (with 9 mm ID), where the TiO<sub>2</sub> and 1.2 wt% Ru/TiO<sub>2</sub> catalysts were tested in powder form and without dilution. The catalyst load amounted to 300 mg, corresponding to a bed height of 8 mm. A column of quartz grains (20-35 mesh) was loaded above the catalytic bed to obtain uniform flow distribution and pre-heating of the inlet stream. An additional bed of quartz grains was placed below to hold the catalytic bed. The reactor was placed inside a vertical tubular electric oven (Carbolite), whose heating was controlled by a K-thermocouple placed in the catalytic bed. Mass flow controllers (Brooks) were employed to supply feed gases, while acetic acid was fed by bubbling a stream of He into a saturator, which was maintained at 35°C. The composition of inlet feed and outlet products mixture was measured with an online GC (Agilent 6890), equipped with TCD detectors, a Molecular Sieve and a PlotU capillary columns. Nitrogen was used as internal standard for the quantitative analysis of mixture composition. Additionally, offline measurements in a GC-MS instrument (Agilent 6890, 5973 MSD) were performed to identify the chemical structure of unknown species found in products mixture. For this purpose, a syringe was used to sample the vapor products mixture at the outlet of the reactor.

All C-C coupling experiments were run at atmospheric pressure and high dilution (with >95% He and N<sub>2</sub>), aiming to keep the bed isothermal. The standard acetic acid ketonization test over TiO<sub>2</sub> catalyst was performed with a Gas Hourly Space Velocity (GHSV) of 20,000 NL/h/kg<sub>cat</sub>, feeding 3% acetic acid and 10% N<sub>2</sub> in He. The effect of inlet acetic acid concentration (in the range of 1.5-3.6%) and of H<sub>2</sub> co-feed (0-20%) were then explored. Tests were performed under steady state conditions at different temperatures in the range of 225-400°C, by keeping the catalyst at the desired temperature for 1 h while monitoring the outlet composition by online GC. High temperature performances of TiO<sub>2</sub> were then further investigated and compared with Ru/TiO<sub>2</sub>: in this case, the catalytic activity was monitored along 4h of Time on Stream (ToS) at constant temperature (400°C) while analyzing the composition of products mixture.

### 3. Results

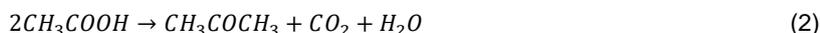
#### 3.1 Catalyst characterization

Morphological analyses performed on calcined TiO<sub>2</sub> powders revealed a BET surface area of 75 m<sup>2</sup>/g and a pore volume of 0.38 cm<sup>3</sup>/g, with a pore size distribution centered on pore diameters of 9 and 13 nm. The addition of ruthenium in Ru/TiO<sub>2</sub> caused a partial decrease of pore volume (0.31 cm<sup>3</sup>/g), and a moderate decrease of surface area (68 m<sup>2</sup>/g). These results show that the TiO<sub>2</sub> and Ru/TiO<sub>2</sub> catalysts compared in the present work share similar morphological properties.

The crystalline structure of TiO<sub>2</sub> support was analyzed via XRD and, as expected, the anatase phase of the original commercial TiO<sub>2</sub> was maintained after the calcination procedure at 400°C. It was also verified via XRD analysis that anatase phase remained unaltered after the addition of Ru.

#### 3.2 Acetic acid ketonization on TiO<sub>2</sub>: low temperature vs high temperature investigation

Experiments of acetic acid ketonization were performed on TiO<sub>2</sub> with standard GHSV at varying inlet acid concentration, in a low temperature range. The results are presented in Figure 1, where acetic acid conversion and product molar flowrates are plotted against reaction temperature. Acetic acid conversion was seen starting from 235°C, and it increased with temperature together with acetone, CO<sub>2</sub> and H<sub>2</sub>O production according to the ketonization reaction stoichiometry Eq(2).



The outlet molar flowrates of products were insensitive to inlet acetic acid concentration throughout the entire temperature range (thus both in differential and integral regimes). Consistently, the conversion of acetic acid decreased with increasing acid concentration in the feed.

On purpose, the preliminary ketonization runs were stopped when acetic acid conversion reached 50% (in the 262-288°C range), aiming to preserve the catalyst stability and to maximize the selectivity of the ketonization route. Indeed, the multiple repetitions of standard ketonization tests on the same TiO<sub>2</sub> showed reproducible results, thus proving that the catalyst was not subjected to deactivation when tested under these operating conditions. Moreover, the closure of atomic balances proved that acetic acid ketonization was the only active route in this temperature range and that the possible formation of surface carbon-deposits was negligible.

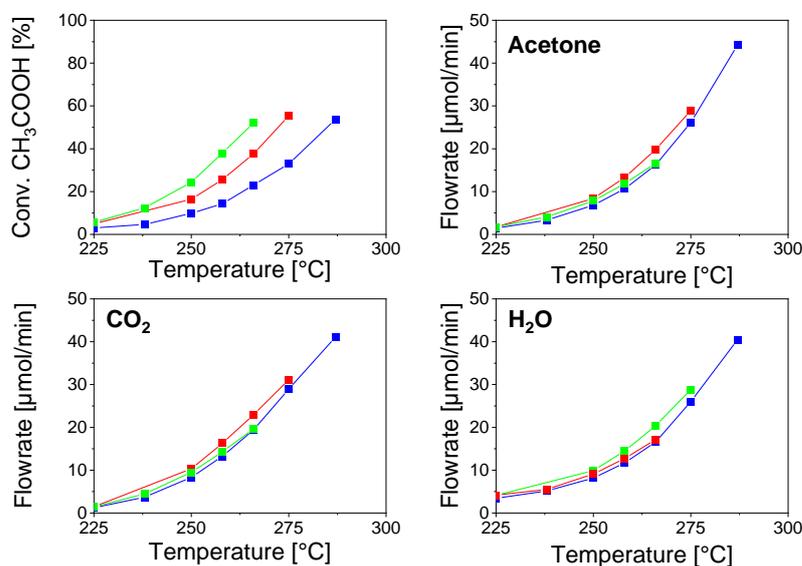


Figure 1: Experimental results of acetic acid ketonization on TiO<sub>2</sub>: effect of inlet acid concentration. GHSV = 20,000 NL/h/kg<sub>cat</sub> (total flowrate = 4470 μmol/min). Feed composition: CH<sub>3</sub>COOH=1.5%, N<sub>2</sub>=10% in He, green symbols; CH<sub>3</sub>COOH=2.4%, N<sub>2</sub>=10% in He, red symbols; CH<sub>3</sub>COOH=3.6%, N<sub>2</sub>=10% in He, blue symbols.

High temperature performances of TiO<sub>2</sub> were then investigated, by extending the analysis to 400°C and complete acetic acid conversion. For this purpose, 20% H<sub>2</sub> was added in the feed, in order to hinder possible coking phenomena. Figure 2 compares the results of two experiments run with and without H<sub>2</sub> co-feed (blue and red symbols, respectively) at standard acid concentration and GHSV. It was observed that, in the low temperature region (below 275°C), acetone production and thus the ketonization reaction rate was not affected

by the presence of H<sub>2</sub> in the reacting mixture. The reactivity at higher temperatures was then investigated in the presence of H<sub>2</sub> (blue symbols). Acetic acid conversion grew with temperature and achieved 100% at 325°C: consistently, also CO<sub>2</sub> production progressively increased until reaching a plateau value, while at variance acetone passed through a maximum value at 325°C and then decreased at higher temperatures. Notably, the carbon-balance to ketonization products (i.e., considering acetone and CO<sub>2</sub> only) declined above 275°C, and this indicates that ketonization alone could not explain high temperature conversion of acetic acid. For this reason, the high temperature reactivity of TiO<sub>2</sub> catalyst was further investigated, and analytical improvements were developed to fully identify and quantify the formed products.

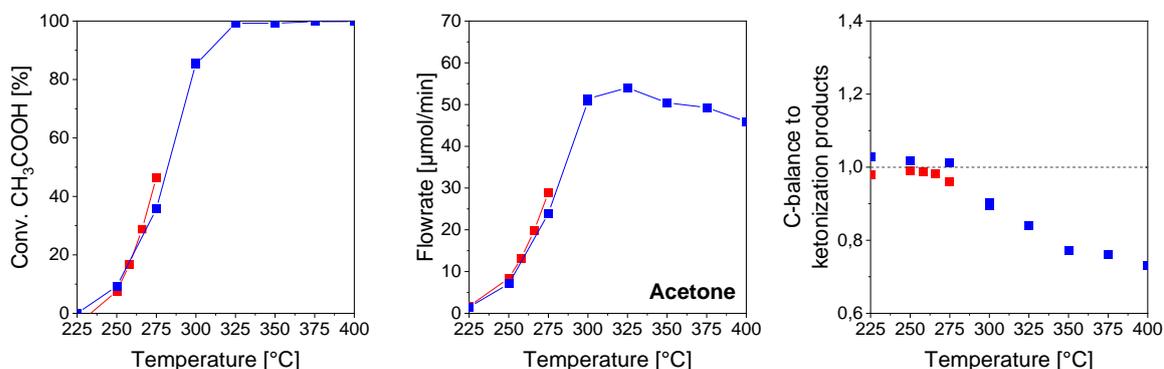


Figure 2: Experimental results of acetic acid ketonization on TiO<sub>2</sub>: effect of H<sub>2</sub> co-feed. GHSV = 20,000 NL/h/kg<sub>cat</sub> (total flowrate = 4470 μmol/min). Feed composition: CH<sub>3</sub>COOH=3%, N<sub>2</sub>=10% in He, red symbols; CH<sub>3</sub>COOH=3%, N<sub>2</sub>=10%, H<sub>2</sub>=20% in He, blue symbols.

### 3.3 Acetic acid ketonization at high temperature: TiO<sub>2</sub> vs Ru/TiO<sub>2</sub>

The study of high temperature performances of TiO<sub>2</sub> required the improvement of the experimental set-up, since outlet mixtures of highly complex chemical nature were obtained. A different analytical methodology was developed in order to successfully fulfil the qualitative and quantitative speciation of outlet mixture. In particular a combined analytical methodology was used, where online analysis in GC were coupled with offline analysis in GC-MS, via syringe sampling of vapor products mixture as explained in 2.2. Accordingly, GC-MS measurements allowed the qualitative analysis of the reaction products, whereas online analysis GC were used for the quantification of species concentration.

High temperature performances of TiO<sub>2</sub> were investigated by analyzing the catalyst activity at 400°C for 4h while monitoring the evolution of product distribution. Carbon selectivities to all detected products were measured at the beginning (4 min) and at the end of the test (4 h) and shown in Figure 3a and 3b, respectively. This test was performed with 20% H<sub>2</sub> co-feed aiming to hinder possible catalyst deactivation phenomena, which are well documented in literature (Wang et al., 2016).

In the case of the bare TiO<sub>2</sub> sample, conversion of acetic acid was complete throughout the entire experiment, but changes in product distribution were observed. At the beginning of the test (Figure 3a), besides ketonization products, other species were identified: CO, CH<sub>4</sub>, C3 hydrocarbons (propylene, propanal), C6 (e.g., mesityl oxide, methyl isobutyl ketone), C8 (e.g., dimethylphenol) and C9 (e.g., mesitylene). The presence of heavy species indicates the activation of secondary chain-growth reactions, where acetone (produced by the acetic acid ketonization) played a crucial role. With time on stream (Figure 3b), these reaction routes were inhibited, such that selectivity to the ketonization product acetone increased. The detailed detection of outlet mixture composition allowed to close C-balance at the beginning of the test (compare Figure 2 and Figure 3c); however, upon increasing the time on stream, C-balances significantly decrease (from 1.03 to 0.88), suggesting the onset of carbon deposition on the surface.

The same test was repeated with Ru/TiO<sub>2</sub> to investigate the effect of the presence of the metal phase. Also in this case, complete acetic acid conversion was found with ToS and at the beginning of the experiment (Figure 3a), a considerable share of C-selectivity was covered by heavy species, similarly to TiO<sub>2</sub> experiment. The speciation of outlet mixture indicated the presence of the same compounds, with mesityl oxide and methyl isobutyl ketone, dimethylphenol and mesitylene accounting for the greatest share of C6, C8 and C9 species, respectively. Differently from what observed in Figure 2, H<sub>2</sub> co-feed played a role in this high-temperature experiment with Ru: indeed formed products exhibited a higher level of hydrogenation (e.g., > methyl isobutyl and < mesityl oxide than over TiO<sub>2</sub>). An increased production of CH<sub>4</sub> was also observed, due to the activation of methanation routes by Ru. Also in this case, after 4 h (Figure 3b) secondary chain-growth reactions slowed

down, as proved by the increased selectivity to acetone at the expense of heavier C6-C9 species. Differently from  $\text{TiO}_2$ , C-balance remained constant (0.96) throughout the entire test, which apparently excludes coking.

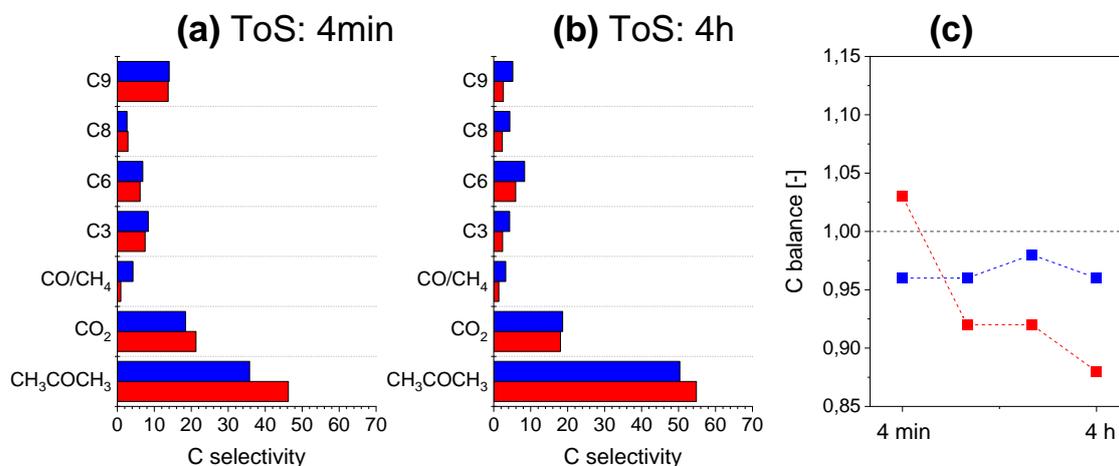


Figure 3: Experimental results of acetic acid ketonization at 400°C: C-selectivities after 4min ToS (a), C-selectivities after 4h ToS (b) and dynamic trend of C-balance (c). GHSV = 20,000 NL/h/kg<sub>cat</sub>. Feed composition: CH<sub>3</sub>COOH=3%, H<sub>2</sub>=20%, N<sub>2</sub>=10%, He diluent. Red = TiO<sub>2</sub>. Blue = Ru/TiO<sub>2</sub>.

#### 4. Discussion

Anatase TiO<sub>2</sub> proved relevant performances in the promotion of acetic acid ketonization. Wang and Iglesia (2017) demonstrated that the active sites for ketonization are acid-base Ti-O pairs, where the kinetically relevant step is the C-C coupling between an intermediate hydroxy enolate and an acid molecule co-adsorbed in a vicinal acid-base pair. Experiments in the micro fixed-bed reactor here presented clearly showed that the concentration of acetic acid in the gas-phase does not influence ketonization reaction rate, so that acetone production was not affected by acid concentration in the feed. Consistently, acetic acid conversion diminishes with the increase of its inlet concentration, since the net moles consumption remains unchanged even if more acid is fed in the reactor. These findings reveal a zeroth order dependence of acetic acid ketonization, as also found by Pham et al. (2014). It was also proved that the addition of excess H<sub>2</sub> co-feed did not affect catalyst performances in the low temperature region.

High temperature performances of TiO<sub>2</sub> were then investigated by analyzing the catalyst activity at 400°C for 4h while monitoring the product distribution. It turned out that at the beginning of the test (ToS = 4min), besides ketonization products, heavy C6-C9 species were detected among products as well as traces of CH<sub>4</sub>, CO, propylene and propanal. Indeed, the successful combination of online GC analysis for species quantification and offline GC-MS analyses for species identification, allowed to recognize and quantify a great variety of products species, ranging from light gases (e.g., CH<sub>4</sub>, CO) to jet fuel-like compounds (i.e., C8+). The chemical pathways responsible for the conversion of acetic acid to valuable C8+ compounds were then identified; acetone, the primary ketonization product, plays here a crucial role. C6 mesityl oxide and methyl isobutyl oxide were detected, and these are respectively the unsaturated and the saturated products of acetone aldol condensation (2C<sub>3</sub>→C<sub>6</sub>). The subsequent aldol condensation between mesityl oxide and another acetone originates a linear C<sub>9</sub> species, 2,4-dimethylhepta-2,4-dien-6-one (C<sub>3</sub>+C<sub>6</sub>→linear C<sub>9</sub>). This species was however not detected in the reaction products, possibly because it undergoes an intramolecular 1,6 aldol condensation to mesitylene (linear C<sub>9</sub>→cyclic C<sub>9</sub>), as suggested by Lippert et al. (1991). In fact, mesitylene accounts for the whole C<sub>9</sub> selectivity in the reaction mixture. Moreover, C<sub>8</sub> dimethyl-phenol was observed (accounting for 2% of carbon-selectivity), as well as traces of deoxygenated C<sub>7</sub> and C<sub>10</sub> compounds (dimethyl-pentadiene and tetramethyl-cyclohexadiene, respectively). Even if further efforts and dedicated experiments are needed to identify the whole reaction network, the detailed speciation of outlet mixture proved that TiO<sub>2</sub> is able to promote not only ketonization reaction but also secondary-chain growth pathways, leading to the production of oxygenated and deoxygenated heavy species, which represent interesting compounds for the synthesis of biomass-derived jet-fuels. However, it was found that secondary-chain growth reactions were significantly hindered with time on stream: the decreasing trend of C-balance indicates that carbon deposits were formed on the surface and catalyst deactivation was in progress.

The addition of ruthenium to the catalyst formulation as well as the co-feed of 20% H<sub>2</sub> in the feed did not significantly affect the speciation at 400°C for low ToS. As in the case of TiO<sub>2</sub>, the product distribution included

