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Research Article

Toward Catalytic Ketonization of Volatile Fatty Acids Extracted from Fermented Wastewater by Adsorption

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ABSTRACT: Volatile fatty acids (VFA) produced by fermentation of organic-rich wastewater streams can, after efficient recovery from the dilute fermentation broth, serve as a circular source of carbon and be catalytically upgraded into various valuable platform molecules. Waste-derived VFA, that is, a mixture of acetic, propionic, and butyric acids, can thus be converted into mixed ketones, which in turn are valuable intermediates for light aromatics synthesis. Here, an integrated process is presented for the recovery and in-line catalytic conversion of VFA extracted from a fermentation broth by adsorption on a nonfunctionalized resin adsorbent. Gas-phase ketonization of the VFA was studied with and without co-fed water, which is inevitably coextracted from the broth, over TiO_2 anatase catalysts to assess catalyst performance, including stability as a function of time on stream. While VFA conversion over bare TiO_2 at 375 °C proceeded at 90% conversion with 100% selectivity to ketones, the presence of water in the feed resulted in an activity drop to 40%. Catalyst stability toward water could be greatly improved by dispersing the titania on a hydrophobic carbon support. The carbon-supported catalyst showed superior performance in the presence of excess water, providing a quantitative yield toward ketones at 400 °C. The approach thus allows coupling of VFA recovery from a fermentation broth with successful catalytic upgrading to mixed ketones, thus providing a novel route for the production of value-added products from waste streams.

KEYWORDS: ketonization, carboxylic acids, titanium dioxide, circular chemistry, fermented wastewater
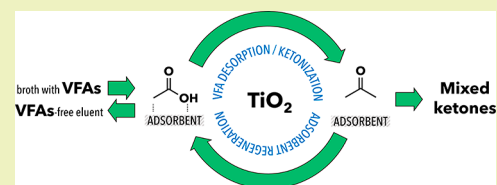
INTRODUCTION

Wastewater streams can serve as a feedstock for the production of value-added chemicals, thus simultaneously minimizing the amount of waste and contributing to a circular carbon economy by closing carbon loops. This approach is also attractive from an economical point of view, as such streams are generated in large volumes and typically have a negative market value. One particularly attractive strategy is the fermentation of organic-rich waste streams, for example, those produced by agriculture[1] or by the dairy or[2] pulp and paper industries.[3] Such waste streams can be used for the fermentative production of short-chain carboxylic acids (mainly acetic, propionic, and butyric acid), the so-called volatile fatty acids (VFA).[4,5] Nowadays, about 90% of these short-chain carboxylic acids are produced via chemical routes that use petrochemical feedstock (e.g., carboxylation of methanol or ethylene, oxidation of butyraldehyde, or ethylene hydroformylation) and have a negative environmental impact.[5] For example, the emissions of carbon dioxide from the petrochemical production of HAc have been reported to be 3.3 t CO_2 eq/t.[5] The global potential VFA production capacity from dairy industry wastewater alone was estimated at 9.15 Mt acetate, 5.39 Mt butyrate, and 6.47 Mt propionate.[5] Another potential source of renewable carbon is food waste, a major component (22−54%) of municipal solid wastes.[4] According to the Food and Agriculture Organization (FAO), one-third of global food production is wasted along the food supply chain.

In 2012, approximately 89 Mt of food wastes were produced in the European Union.[6] Most of these food wastes are currently incinerated for energy recovery (with concomitant GHG emission) or worse, disposed of in a landfill with null recovery of resources.[7] Thus, these values show that a significant fraction of VFA demand can be potentially covered by utilizing waste streams as the feedstock.

The composition and yield of VFA strongly depend on process parameters and operational factors, such as temperature, pH, retention time, additives, organic loading rate, and substrate, and can be optimized toward the production of specific short-chain acid compositions.[4,5] These short-chain carboxylic acids have a broad range of applications and serve as solvents, food additives, and raw materials for production of chemicals (e.g., esters and vinyl acetate).[5,8] Recently, waste-derived VFA have been attracting more widespread interest as a potential renewable carbon source for the production of bioplastics[9−12] and biohydrogen.[11,13,14] Alternatively, VFA could be converted by catalytic ketonization[15,16] to mixed ketones, which are valuable platform chemicals and can be

used as precursors for fuel components, lubricants, or alkylated aromatics.[17−22] For example, we recently showed that VFA-derived ketone mixtures can be efficiently converted to light aromatics by zeolite catalysis.[23]

Catalytic ketonization involves the coupling reaction of two carboxylic acids to give a ketone and carbon dioxide and water as byproducts, with a resulting atom efficiency of ketone formation of 65%. Ketonization of small carboxylic acids has received considerable attention, often in the context of studies aimed at the upgrading of biooils.[15,16,24−42] Amphoteric (reducible) metal oxides, such as TiO_2,[24−31] CeO_2,[27,32−39] and ZrO_2,[29−31,35−42] have been extensively studied and became the benchmark of ketonization catalysis, but also zeolites[43] have been used as solid catalysts. Ketonization reactions are typically run in the gas phase[26−30,33−39,42] at elevated temperatures (>300 °C), but liquid-phase reactions have also been reported.[24,32,41] For example, Pham et al.[24] observed high activity and selectivity to ketone using a hydrophobic $Ru/TiO_2/C$ catalyst in the aqueous-phase ketonization of acetic acid. Wang and Iglesia[26] reported on kinetic studies in the gas-phase ketonization of acetic acid over TiO_2 polymorphs (anatase and rutile), showing that ketonization turnover rates are higher on anatase TiO_2. Most studies focused, however, on the ketonization of pure, single carboxylic acids only, with only a limited number of studies being available on carboxylic acid mixtures[30,33,34] or the application of real feeds (such as pyrolysis oil[44]). Nonetheless, the development of new, more sustainable value chains requires insights into how different steps in the route affect each other, for example, by the study of integration of separation and conversion technology with all its associated challenges. Indeed, to the best of our knowledge, the connection between fermentative VFA production, separation, and subsequent product diversification by ketonization of the mixed carboxylic acids obtained has not yet been reported.

The composition of VFA produced from wastewater varies depending on the substrate, type of microbial culture, and process parameters, yet the most common acids produced are acetic, propionic, and butyric acids. The fermented waste streams typically have very low VFA concentrations (around 1 wt %), too dilute for efficient and industrially relevant further direct conversion. The broth also contains significant amounts of ions of various salts, such as Na^+, K^+, $H_2PO_4^-/HPO_4^{2-}$, Cl^-, and SO_4^{2-} (Table S1),[45,46] which might poison a solid catalyst. Besides, water is known to inhibit the ketonization reaction.[24,28,39,41] Finally, other short-chain oxygenated compounds, such as the lactic acid or even alcohols and aldehydes,[47] which can be coproduced during fermentation, are also anticipated to influence catalyst performance. López-Nieto et al. suggested, for example, that the presence of such oxygenated compounds can favor aldol condensation reactions instead of ketonization over a metal oxide catalyst at low temperatures (<300 °C).[48,49] Taken together, this makes the direct conversion in the broth undesirable and requires the VFA to be (selectively) recovered and concentrated prior to further conversion. Several extraction techniques have been proposed in the literature for VFA separation from dilute aqueous solutions, including liquid−liquid extraction and adsorption on an affinity agent.[5,45,50−52] Excitingly, Reyhani-tash et al.[52] very recently observed that a nonfunctionalized polystyrene−divinylbenzene (PS−DVB) resin adsorbent allows for very efficient VFA extraction from such dilute and complex solutions, through hydrophobic and hydrogen

bond−π interactions. This adsorbent also proved highly stable during several VFA adsorption−desorption cycles and, importantly, showed exceptional selectivity toward VFA extraction. This allows for extraction of the VFA only, with neither the lactic acid or inorganic salt impurities in the feed being coextracted.[52,53] Moreover, the use of temperature-profiled desorption enabled fractionation of VFA. The achieved concentration of butyric acid was as high as 91 wt % with the initial concentration in the feed being as low as 0.25 wt %.[46,52] Using such a PS−DVB adsorbent, a process scheme depicted in Figure 1 could then be envisaged for stepwise extraction and catalytic conversion of VFA to mixed ketones.
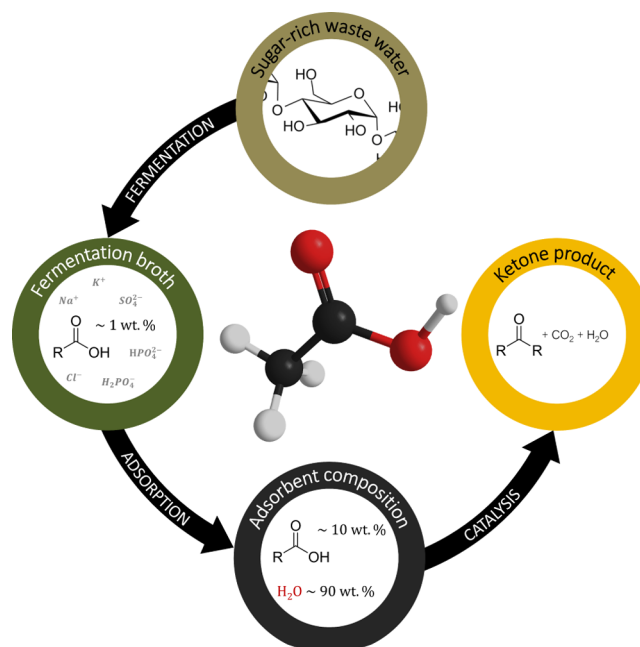

Figure 1. Schematic overview of the process for the production of mixed ketones via integrated VFA production from wastewater streams, separation, and catalytic conversion.

While the resin is highly selective for extraction of VFA over other (in)organics, water itself is significantly coadsorbed as well. Indeed, a weight loading of 10 wt % of VFA of the resin is obtained, with the remaining ~90 wt % on the resin consisting of coadsorbed water.[52] While a small amount of water might be beneficial for the process,[54,55] such an excess amount of water is expected to be detrimental for downstream ketonization because of the active site blockage by competitive adsorption.[24,28,39,41] To reduce the water amount, the adsorbent can be subjected to a drying step at 70 °C prior to desorption, making use of the low-temperature waste heat available at any facility.[46] Such a pretreatment step would allow for the removal of up to 80 wt % of water, thus increasing the VFA/water molar ratio from 0.02 to 0.1. While this is a considerable reduction, it would still leave a significant amount of excess water on the resin. Liberation of the (wet) extracted acids by thermal desorption to the gas phase is subsequently required to allow in-line catalytic upgrading by ketonization over a catalyst to a mixture of ketones, provided that this stoichiometric excess of water (wrt the moles of VFA) can be dealt with. Mitigation of water inhibition has been studied in liquid-phase ketonization,[24,41,56] but hardly in the gas phase.

Here, we report on VFA mixture ketonization over TiO_2 catalysts and the effect of coextracted water present in the feed on catalytic performance. Furthermore, results are presented on the integrated recovery/gas-phase ketonization of VFA mixtures extracted from a model solution representing fermented wastewater extracted by adsorption on the non-functionalized PS−DVB resin-based adsorbent (Lewatit VP OC 1064 MD PH, Lenntech). By thermal treatment, the acids were liberated and directly converted over a TiO_2 ketonization catalyst to yield a mixture of ketones with high selectivity. Additionally, we show that dispersing the TiO_2 on a hydrophobic carbon support greatly improves the tolerance of the catalyst against water inhibition.

■ RESULTS AND DISCUSSION

First, the gas-phase continuous-flow ketonization of a synthetic VFA mixture, mimicking the gas-phase composition expected upon desorption from a resin adsorbent used for VFA extraction, was studied in a conventional fixed bed reactor to investigate catalyst performance with time on stream. TiO_2 was selected as the prototypical ketonization catalyst[24−31] and synthesized via a sol−gel method as reported elsewhere.[57] A self-synthesized TiO_2 (pure anatase, Figure S2) was chosen rather than commonly used commercial TiO_2 P25, an anatase/rutile mixture, to allow for a fair performance comparison with the hydrophobized titania, which is phase-pure anatase as detailed below. The prepared TiO_2 catalyst material possessed a BET surface area of 80 m^2/g, as measured with N_2 physisorption, which is slightly lower than previously reported (97 m^2/g) (Table S2). Figure 2a illustrates the results of the ketonization of a VFA mixture consisting of acetic (HAc), propionic (HPr), and butyric (HBu) acids over TiO_2 as a function of time on stream. At 375 °C, conversion of the acids was around 90%, showing full selectivity toward ketones (no byproducts were detected at a closed mass balance; CO_2 and H_2O liberated upon ketone formation were not quantified); only a slight sign of deactivation was seen over time, with conversion decreasing from 92 to 89% over 3.5 h on stream. Both the expected symmetric ketones [acetone (HAc/HAc), 3-pentanone (HPr/HPr), and 4-heptanone (HBu/HBu)] produced via homoketonization, together with the non-symmetric ketones [2-butanone (HAc/HPr), 2-pentanone (HAc/HBu), and 3-hexanone (HPr/HBu)] formed via cross-ketonization were all observed. The isomeric 2- and 3-pentanones could not be tracked separately because of the overlapping peak in the GC chromatogram. The distribution of products (Figure 3) was found to be close to binomial, in agreement with the previous results observed for unbranched acids, suggesting that the difference in the length of the alkyl chain influences the extent of adsorption on the catalyst surface only slightly.[30,34,36] The reactivity of carboxylic acids is known to decrease slightly with increasing carbon chain length; thus, the selectivity of VFA ketonization marginally shifted toward the symmetric ketones of acids with shorter chains. However, only traces of acetone were detected (~0.1%), in line with the binomial distribution dictated by the low fraction of HAc in the VFA mixture.

Given that during the VFA extraction from the fermentation broth considerable amounts of water are coextracted and expected to codesorb with the VFA, the effect of excess water on ketonization activity was assessed as a function of time on stream (Figure 2a). The reaction was performed at the same space velocity of the acids, with the VFA feed mixture now
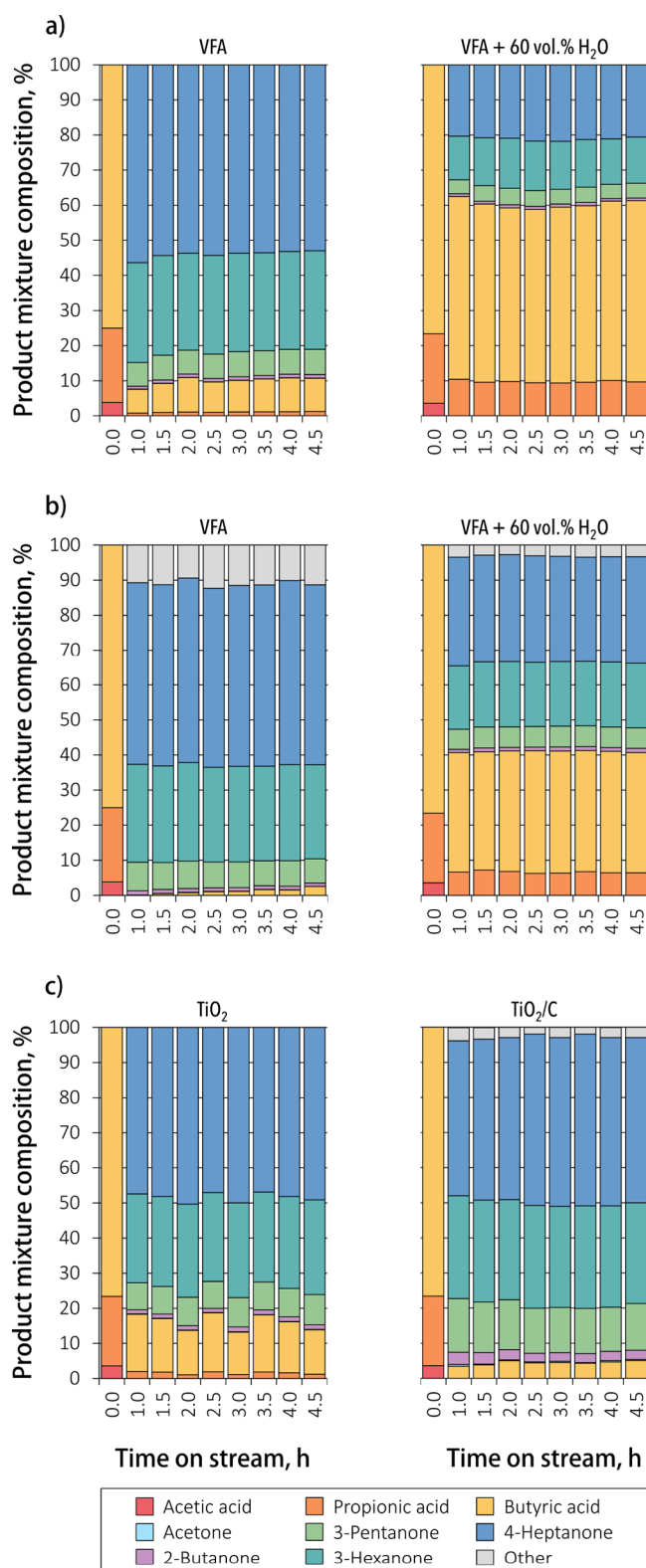

Figure 2. Composition of the reaction mixture of VFA and VFA + 60 vol % H_2O mixture over (a) TiO_2 and (b) TiO_2/C at 375 °C. (c) Composition of the reaction mixture of the VFA + 60 vol % water mixture at 400 °C (WHSV = 3.6 h^{-1}).

containing 60 vol % of water, corresponding to the gas-phase composition expected upon VFA desorption from a resin mildly dried at 70 °C. As anticipated, the presence of water leading to a considerable drop in activity was observed, with
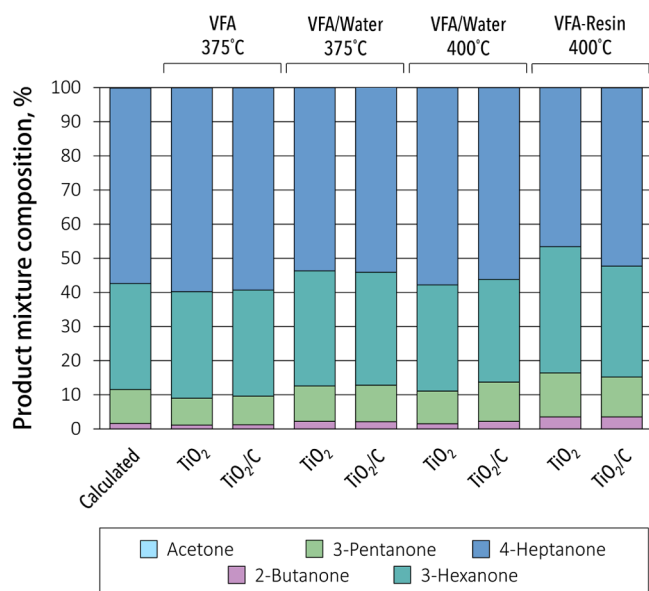
Figure 3. Distribution of the ketone products; calculated indicates the statistically expected distribution given the initial ratio of acids used.

the ketone yield dropping from ∼90 to ∼40%, and the corresponding average ketone formation rate decreased from 38.3 to 16.8 mmol·$(h·g_{cat})^{-1}$. This decrease in activity is nevertheless considered reversible.[28] Water only affected activity, as selectivity stayed almost the same, with no significant changes in the product distribution (Figure 3).

The catalyst stability against water inhibition could be improved by dispersion of the catalyst on a hydrophobic carbon support, as was previously reported for the liquid-phase ketonization.[24,41] The carbon-supported titania was prepared using the method similar to the method described by Pham et al.,[24] who used this approach for the aqueous-phase ketonization of acetic acid. The synthesized TiO_2 on the carbon material was characterized by N_2 physisorption experiments (Table S2), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Impregnation of the activated carbon with titanium dioxide resulted in a decrease of the surface area and pore volume, expected because of the micropore blockage by titania.[24,58] XRD (Figure S2) showed the synthesized carbon-supported titania to be pure anatase. The XRD pattern of carbon-supported TiO_2 showed, however, a significant shift. The peak position of the (101) plane shifted from $2\theta = 29.5°$ for TiO_2 to $2\theta = 29.8$ for TiO_2/C, with the corresponding d-spacing values of 3.52 and 3.48 Å, respectively. The d-spacing change indicates a lattice distortion induced by TiO_2−support interactions via support species diffusion into the oxide microstructure or due to rearrangement of the oxide atoms at the interface with the support.[24] The TEM images, shown in Figure S2, suggest that TiO_2 is well distributed over the carbon support.

The synthesized TiO_2/C catalyst was then tested in the VFA ketonization reaction with the same TiO_2 loading. The results illustrated in Figure 2b showed that TiO_2/C has a higher activity than TiO_2 with the pure (water-free) VFA feed; this increase in VFA conversion came at the expense of some olefin production, however, as the unwanted side reaction (included in others in Figure 2b). The formation of olefins has been previously reported over TiO_2 catalysts (P25 and pure anatase) as a secondary conversion pathway, with the ketone/olefin

selectivity increasing with the surface area of tested titanias.[31] Two reaction pathways for conversion of ketones to olefins were proposed in the literature. Baylon et al.[59] proposed secondary (cross) aldol condensation to diketone alcohol followed by decomposition to the corresponding iso-olefin and acid; the acid, in turn, can undergo further ketonization. Oliver-Tomas et al.[31] suggested the formation of olefins via secondary reduction of ketones to alcohols followed by subsequent dehydration to the olefin. The hydrogen source for this reduction is assumed to come from cyclization of the ketone condensation product. In the VFA ketonization over TiO_2/C in the presence of water (Figure 2b), such consecutive olefin formation reactions were suppressed, as was again the overall activity of the catalyst. Total ketone yield decreased from ∼90 to ∼60% (and the average ketone production rate dropped from 35.2 to 22.7 mmol·$(h·g_{cat})^{-1}$), which is nevertheless considerably better than the 40% yield seen for unsupported TiO_2 (Figure 2a). The distribution of ketone products (Figure 3) was found to be comparable for both titania materials, implying no (or only weak) interactions of the acid carbon chains with the functional groups of the carbon support, that is, no significant differences in competitive adsorption. In contrast, Da Silva et al.[60] reported that the adsorption capacity of acetic, propionic, and butyric acids on activated carbon increased as a function of chain length. To further improve the catalytic conversion, the temperature was increased to 400 °C (Figure 2c), leading to almost complete conversion (>95%) of the VFA in the presence of 60 vol % of water when the TiO_2/C catalyst was used. The average ketone formation rate at 400 °C was 31.5 and 37.3 mmol·$(h·g_{cat})^{-1}$ for TiO_2 and TiO_2/C, respectively. Furthermore, olefin production at this temperature was still very minor, at the same level as at 375 °C (Figure 2b), indicating strong suppression of consecutive reactions to olefins by the water, ultimately resulting in higher selectivity toward ketones.

The continuous flow catalytic reactions, thus, show that a (wet) VFA mixture can be selectively converted over TiO_2 catalysts to a mixture of ketones, with negligible deactivation over time. Furthermore, water inhibition can be dealt with by catalyst hydrophobization and adjustment of the reaction temperature. We then moved to the batchwise integrated desorption/ketonization reaction of VFA adsorbed on the PS−DVB resin (Lewatit VP OC 1064 MD PH, Lenntech). The polymeric resin was saturated with VFA using a model solution by a procedure reported elsewhere.[52] The model solution representing fermented wastewater comprised of the acid mixture (acetic, propionic, butyric, and lactic acids; 1 wt % in total) and mineral salts (KCl, Na_2SO_4, and Na_2HPO_4). Prior to desorption, the resin was dried at 70 °C under a flow of nitrogen to reduce the water content. Analysis of the liquid collected after this drying step showed that about 80% of total water amount had been removed from the resin, as expected; however, up to 40% of the extracted VFA were removed as well. Such loss of VFA during drying can be minimized, however, as reported by van Beek,[53] by adjusting the temperature ramp and flow parameters to selectively remove only the water. After drying, a desorption step at 165 °C led to the liberation of the adsorbed acids, which were subsequently fed over a fixed bed reactor with (carbon-supported) TiO_2 at 400 °C (Figure S1b). Because the acids have different boiling points and affinities for the adsorbent, the composition of the gas phase upon desorption may change over time, thus potentially affecting the final product distribution. Reyhanitash

et al.[46,52] reported on the fast breakthrough of acetic acid compared to propionic and butyric acids, the latter two having a stronger affinity for the resin. The reaction products were collected in a liquid nitrogen cold trap until VFA desorption from the resin was complete and subsequently quantified. The results (Figure 4) clearly demonstrated that recovered VFA
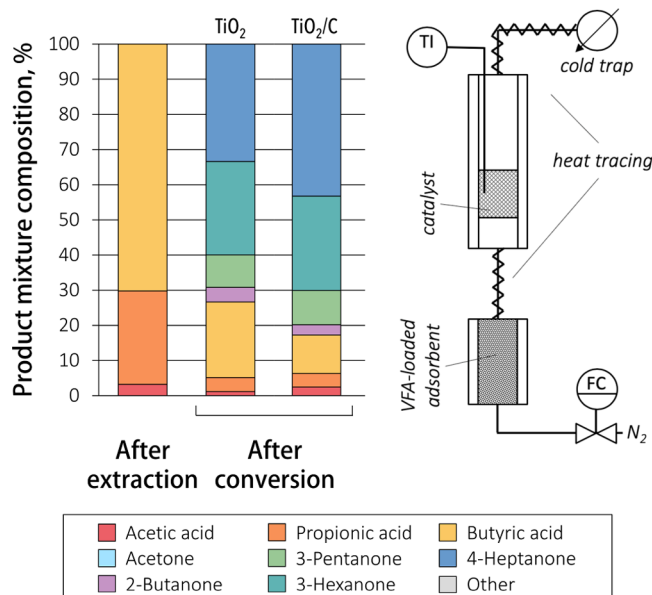

Figure 4. Composition of the reaction mixture after batchwise adsorbent desorption from the PS−DVB resin and in-line ketonization at 165 and 400 °C, respectively.

could be cleanly converted to ketones also in this "batch" desorption mode, with the carbon-supported catalyst again showing improved performance in the presence of water. The amount of acetone in the collected product mixture was below the detection limit because of the necessary dilution with ethanol. No olefinic products were detected this time in the product mixture. The distribution of ketone products obtained over carbon-supported TiO_2 was similar to the continuous flow reactions again following a binomial distribution. These results suggest comparable desorption of VFA from the adsorbent. However, for bare TiO_2, a slightly different distribution of ketones was observed, with the formation of more 3-hexanone. The origin of this phenomenon is not yet clear and requires additional work.

CONCLUSIONS

In conclusion, the ketonization of a VFA mixture extracted from a model fermentation broth by adsorption on a PS−DVB-based resin is thus demonstrated. The catalytic performance studied with increasing time on stream showed that over both TiO_2 and TiO_2/C, the VFA ketonization reaction proceeded at high selectivity toward ketones and with good stability over time. The presence of coextracted water resulted in a considerable drop in activity because of competitive adsorption and active site blockage. The effect of water, however, was found to be beneficial for the suppression of consecutive formation of olefins. In order to enhance hydrostability, dispersing TiO_2 over a hydrophobic carbon support significantly improved stability in water and allowed the selective and efficient conversion of the extracted VFA. Overall, the results show that waste-derived VFA extracted by

adsorption on a PS−DVB resin could be successfully converted to ketones offering a promising route for the production of ketones and other valuable circular platform chemicals.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c03220.

Catalyst synthesis, characterization, and testing details; XRD analysis; physisorption data; and VFA composition in model solution and on resin (PDF)

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