

Primary Alcohols, Aldehydes and Ester Transformations into Ketones over Oxide Catalysts

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Abstract

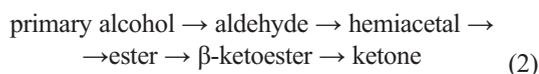
This paper presents the suitability of the unpopular bimolecular reaction of primary alcohol condensation to ketones as the management method for waste or excessive materials containing primary alcohols, aldehydes and esters. This method simultaneously allows winning non symmetric or long-chain ketones.

Keywords: ketones, alcohols, esters, heterogeneous catalysis, waste prevention

Ketonization of primary alcohols and their derivatives in gas phase over heterogeneous catalysts is an alternative in relation to processes provided in liquid phase and other methods of obtaining ketones. Typical primary alcohol conversions (dehydrogenation, dehydration) in gas phase at the heterogeneous catalysts presence are widely discussed in professional writings. However, over some catalysts, there occurs bimolecular condensation of forming aldehydes to esters and ketones containing $2n-1$ carbon atoms in chains. Reactions over these kinds of catalysts are proceeded according to the general equation:



It is possible to provide a reactions progress in accordance with the following sequence [1]:

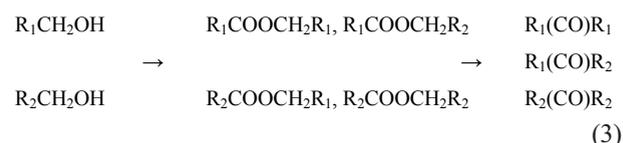


...although other mechanisms with aldol participation [2] or intermediate form of carboxylic acid [3] are also considered.

So, one may treat the carboxylic acid condensations into ketones [4-7] as a relational group of transformations. Besides, these transformation catalysts are ascribed numerous functions [8].

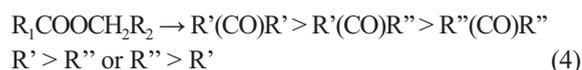
The course of primary alcohol bimolecular condensation sequences allows the use of aldehydes, esters and their mixtures as the raw materials.

On using a mixture of two various primary alcohols and/or aldehydes at lower temperatures, the products may consist of four esters, and at higher temperatures of three ketones:



...in the ratio $\frac{1}{4} : \frac{1}{2} : \frac{1}{4}$, resulting from the reaction probability. Application of both sides of the same carbon chain lengths esters as raw materials results in ketone symmetry. When the raw material is ester with bilateral different numbers of carbon atoms, i.e. in both chains, three ketones in another ratio are formed:

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Such ester transformations run simultaneously: through β -ketoesters and also with partial thermal decomposition of esters to aldehydes (via retro-Tishchenko reaction) and their secondary condensation. Both transformations contribute changes depending on temperature and contact time. Their increase favours the pathway via thermal decomposition of esters [9].

Early discussions concerning this reaction group over heterogeneous catalysts appeared in the 1940s [10]. Since then, a number of papers have been published. However, contrary to widely documented transformations of secondary alcohols, this problem has been scarcely described in literature. Russian and Japanese scientists' papers [11-14] have largely contributed towards this field development and only recently has this domain been increasingly detected. There may be a number of reasons for this phenomenon, like its relation with several technological processes. Besides, promotion of environmental protection as well as waste material utilization has revealed the advisability of this ketone synthesis method.

On methanol production from CO/H₂, higher alcohols are formed incidentally, while in higher alcohols' purposeful formation, oxygenates accompany expected products [15-18]. So, CO and vapour conversion reaction conditions (WGS) [19] for comparative analyzes seem quite advisable [20]. On the other hand, an unstable fuel situation causes the Fisher-Tropsch synthesis renaissance and in the process primary alcohols ketonization is significant [21]. The FT process always appears to yield (in addition to olefins and paraffins) oxygenated products such as alcohols, aldehydes, carboxylic acids and ketones. As these oxygenated products are predominantly linear, it could be of commercial interest to develop suitable catalysts and operating conditions to maximize their selectivity [22-24].

The research aimed at explaining primary alcohol ketonization in the presence of heterogeneous catalysts are of great importance for homologous reaction studies like alkylation of hydroxyarenes with alcohols, hydrogen transfer reaction, decarboxylation reactions, dimerisation of alcohols or Tishchenko reaction as ester synthesis.

On hydroxyarenes alkylation with primary alcohols [25, 26], side reaction of alcohols - bimolecular condensation to ketones - is observed [27, 28]. This transformation's competitive direction refers especially to the alkylation process when carried out with higher alcohols. Ketone catalysts may be also efficient catalysts of hydroxyarenes C-alkylation with alcohols. They seem to reveal *ortho*-directional properties in relation to the hydroxyl group [29].

Catalytic hydrogen transfer reduction over metal oxide catalysts is known as a very selective method for carbonyl group reduction [30, 31]. Another related process is the variant of decarboxylation reactions [32] - this simple, single-step, solvent-free method can be used in the preparation of many types of aldehydes. A known route to higher alcohol synthesis is by the self-condensation of primary or

secondary alcohols with itself or another alcohol [33, 34]. This process is called the Guerbet reaction.

Primary alcohol transformation directions (aldehyde, ester or ketone) depend on a catalyst condition and composition and due to its fixed formula, it also depends on the reaction kinetics (reaction agent load and structure) [35, 36]. Contact time reduction connected with the catalyst formula partial change allows transformation orientation towards ester [37]. This idea of primary alcohol transformation into ester fraction is convergent with contemporary methods applied in new production lines like Sasol Chemical Industries installation of ethyl acetate production [38, 39]. Kvaerner Process Technology Ltd. (KPT) method requires only one material - ethanol and the process eliminates the necessity of acetic acid formation in ethyl acetate production.

Apart from the above practical and cognitive aspects, the presented ketonization method has significant ecological ones. The ketonization process over the heterogeneous catalysts gives new possibilities of waste management of materials containing primary alcohols, aldehydes or esters [40]. As ketonization-susceptible materials undergoing high temperature processes with oxide heterogeneous catalysts include secondary alcohols as well as carboxylic acids, the composition of waste organic fractions which may undergo ketonization may vary largely. Such fractions may also contain hydrocarbons not susceptible to transformations in ketonization conditions, as well as ketones which hardly undergo secondary condensations in these terms.

From a technical point of view, this transformation method is very characteristic for its simplicity. It proceeds continuously, using raw materials only, without any additional substances. Transformations carried out over heterogeneous catalysts correspond to pursuits for an improvement of index of atom numbers derived from a raw material to a final product [41]. The use of materials mixture is an alternative method to obtain required non-symmetric ketones including aromatic-aliphatic ones [42, 43]. As ketone mixtures are of significant importance in their application, ketones mixtures derivation from multicomponent waste fractions seems advisable and at least not obstructive.

Both temperature and load are crucial steering parameters in the case of primary alcohols and their ketonization derivatives. The use of material inertial diluent is possible, but the procedure seems proper in the case of high-molecular materials. Small water content in the material has not been found to influence the process, but such a dependence cannot be ruled out, providing a longer observation period. The material conversion assessment can be obstructed by the apparent conversion drop, which is often observed at higher temperatures and takes place due to the invertibility of some reaction stages (e.g. Tishchenko and hydrogen transfer reactions).

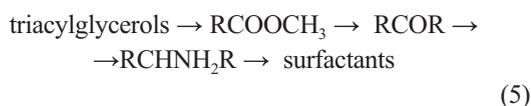
Attempts at alcohol fraction waste management are the example of applying the discussed ketonization method. Such fractions are formed during the process of cyclohexanone production (Cyclopol Process) in the Nitrogen Plant in Tarnów and the one in Puławy. They result from the

cyclohexane oxidation to cyclohexanone and contain mainly primary alcohols and aldehydes. Research has proven that neither multicomponentality of the fractions nor the variability of their composition hinder ketonization process implementation as primary alcohols susceptibility to ketonization is not dependent on the carbon chain length and aldehydes undergo condensation with similar efficiency. Other fraction components do not affect the process in any negative way. For example, such a waste fraction containing mainly: *n*-pentanol and isopentanol (ca 50%), *n*-propanol, *n*-butanol, cyclopentanol, cyclohexanol, valeric aldehyde, caproic aldehyde, and small amounts of normal and cyclic saturated and unsaturated hydrocarbons C₅ to C₇ as well as dialkyl and cyclic ketones underwent the transformation in a continuous manner over Zr-Mg-Y-O catalyst in a typical flow installation under atmospheric pressure, at 420°C and with a 1h⁻¹ load. The process resulted in a fraction of the total ketones content, about 58% of which contained mainly nonanone-5, heptanone-4, octanone-4, cyclohexanone and others [44]. A similar high ketone yield was found on using the Sn-Ce-Rh-O catalyst [45].

Another example of ketonization method application is isobutyraldehyde management as OXO synthesis excess product in "Kędzierzyn" Nitrogen Plant. Isobutyraldehyde can be the material for winning isopropyl group ketones. This compound group is characterized by its attractive smell. Although isobutyraldehyde ketonization, similar to that of primary iso-alcohols, is less intensive than alcohols and normal aldehyde ketonization, the mixture of isobutyraldehyde and normal alcohol gives ketones satisfactory yield [46].

On caprolactam industrial production both in the Nitrogen Plant in Tarnów and the Nitrogen Plant in Puławy, the waste fractions containing a mixture of monocarboxylic acids C₁-C₆ are formed. Out of these mixtures, C₄-C₆ acid fractions can be separated. The fractions include over 60% of valeric acid and over 12% of butyric and caproic acids each. This fraction and normal alcohol mixture continuous ketonization can be an effective way of waste management. The processing performed in the temperature range of 300-480°C may result in fractions containing symmetrical and non-symmetrical ketones with a high total yield [47].

The discussed ketonization method may result in two long carbon chain ketone formations [48]. These ketones, after reductive amination, may be the source of gemini-type surfactants, characteristic for their high surface activity which gives the possibility of spreading their usage, thus relieving the environment. Presented conversion from triacylglycerols to amines with two long chains proceeds according to the scheme:



Stages of fat esterification and transesterification as well as reductive amination of ketones have already been technologically mastered. Long-chain ketones can be processed in several ways into surfactants of gemini-type.

For this purpose, carbohydrates can be used. Together with proteins and fats, they consist of a basic group of natural compounds forming renewable organic material. Up to now, only a small part of carbohydrates have been used as chemical industry material [49]. Amines with two long chain ketones react easily with oxidized sugars, e.g. gluconic or lactobionic acid, producing stable amides - very good nonionic detergents [50].

The mixed methyl ester fractions resulting from non-erucic rapeseed oil transesterification can be a rich source due to contemporary trends of vegetable oils increasing production. Also, ester fractions being the products of technical oils transesterification can be regarded as waste materials. Utilization of waste technical oils like vegetable oil and animal fats is a problem both for the environmental load and industrial value [51-53]. Another example of taking advantage of ketonization methods are transformations of materials being esters fractions obtained in IHOS "Blachownia" as a result of waste fat transesterifications. Ketonization of methyl ester fractions obtained from a non-erucic rapeseed oil allowed winning mainly ketone fraction containing at least 56% of pentatriacontanone-18 (C₁₇H₃₅COC₁₇H₃₅) [54]. A mixture of methyl esters of fatty acids, diluted with methanol or toluene, was converted at atmospheric pressure in the temperature range of 330-420°C and with a load of 0.5-3h⁻¹ over mentioned oxide catalysts. The ketonization of butyl esters fraction derived from animal fats, in the process similar conditions, enabled winning fractions of symmetric and non symmetric ketones of similar yield [55].

Conclusions

Waste technical fats can provide a raw material basis for the production of amphiphilic-type compounds. The concept concerns utilization of harmful, extensive and renewable raw material resource. The discussed method consists of making use of bimolecular condensation of primary alcohols and their derivatives to ketones in gas phase over oxide catalysts. The method allows transformation of other waste or excessive materials containing this group of organic compounds. The examples can be the results of transformation into ketones: mixtures of monocarboxylic acids, isobutyraldehyde and alcohol or ester fractions.

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