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# Oil Industry Waste as a Basis for Synthesis of New Type Surfactants

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## Abstract

This work presents a concept of waste technical fats processing into surfactants of gemini type based on the utilization of methyl esters of long chain fatty acids. The method of such esters ketonization has been elaborated upon. Ketones obtained in this way can be processed using reductive amination. Long chain amines can be used for the production of nonionic surfactants in the condensation with aldoses and hydrogenation or in condensation with oxidized sugars.

**Keywords:** renewable raw materials, waste technical fats, saccharide surfactants, fatty acid methyl esters, long chain ketones, iron catalyst, tin catalyst

## Introduction

Highly efficient surfactants, defined in literature as gemini surfactants [1-5], were obtained only in the 1990s. These compounds consist of two identical lipophilic chains and two identical hydrophilic groups. The presence of two hydrophilic groups is not indispensable to ensure high efficiency. One group of large volume is enough, and similarly the presence of a spacer between the lipophilic chains is not crucial, as it was assumed at the beginning [4, 5]. It is believed that in the near future surfactants of gemini type will become surfactants of a higher generation [6-9] because they possess unique features. They are characterized by an increased surface activity. They form micelles at a very low critical micellar concentration and are highly efficient for the reduction of surface tension of oil-water contact phase. In this respect they are much better than conventional surfactants. For this reason they are interesting both on theoretical and practical levels. The increase in mass surfactant efficiency enables the reduction of their usage, and thus, reduces environmental pollution.

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A basis for the synthesis of surfactants of gemini type can provide long chain amines obtained via symmetrical two-long chain ketones after their reductive amination with ammonia or methylamine over copper-chrome or nickel catalysts [10]. The ketones can be prepared from cheap, waste technical fats, renewable and independent of petrochemical sources. The Institute of Heavy Organic Synthesis (IHOS) "Blachownia" in Kedzierzyn-Kozle produces a fraction of methyl esters of fatty acids during technical fats processing [11, 12]. Animal and vegetable waste technical fats constitute a mixture of free fatty acids processed to methyl esters in the esterification and acylglycerols processed to methyl esters in transesterification.

Global production of fats and oils from natural, renewable sources is estimated to amount to a hundred million tons annually [11]; thus, if we assume that one tenth of them will be recycled and waste fats, it is a considerable renewable material base. This is a crucial issue. Cases of perturbation connected with amassing of the extensive fat wastes are already known [12]. Oil industry activity is connected with the formation of waste technical fats [13]. It should be assumed that the difference between the size of fats production and their usage (and

thus, the amount of wastes, such as agricultural products - vegetable oils and animal fats) will increase, among others as a result of animal farms progress, consumption, and at the same time higher market demands. This is why the utilization of fats is a problem concerning both environmental protection and their market value. Therefore, the ketonization of fatty acids esters should be consistent with the strategy of eco-development [14]. Used oils or redundant fats should be utilized but, in fact, they are often disposed to the sewage system or to soil. Another factor is that Poland is one of the largest producers of rape seed in Europe, and that position is currently insecure. This is connected with the intentional issue of production of rape seed oil unfit for non-consumption purposes. In many countries, including Poland, intense research in this field is carried out. In this sense fats material base is, or can be, much larger. Vast literature of this subject deals with attempts to utilize fats of various origin, among others, sunflower, rapeseed and other oils, animal waste fats, used vegetable oils, vegetable post-refining fatty acids from oil mills, beef tallow, pyrolytic oils from straw and stalk of the rapeseed plants in order to implement them in various ways, as bio-fuels, biodegradable lubricants, and surface active agents such as sulfated and ethoxylated fatty alcohols and others [15-23].

## Methods

Our Department of Catalysis elaborated a method of aliphatic esters ketonization in the gas phase over a heterogeneous catalyst as tin-ceric-rhodium oxide [24] or iron oxide [25, 26]. This method is suitable for the production of long chain esters [27]. It enables the application of a diluent (e.g. n-hexane), which does not participate in the reaction but enables the processing of post reaction mixture. The obtained mixtures of ketones from methyl esters fractions are an appropriate substrate for preparation of amines with two long carbon chains. Direct amination of methyl esters of higher fatty acids does not lead to the required amines.

The ketonization of methyl esters fractions obtained in IHOS "Blachownia" as a result of non-erucic rapeseed oil transesterification allowed obtaining mainly ketone fraction (containing at least 56% of $C_{17}H_{35}COC_{17}H_{35}$, i.e. pentatriacontanone-18) [28, 29].

Long chain ketones can be processed in several ways into surfactants of gemini type. For this purpose carbohydrates can be used. They are, together with proteins and fats, a basic group of natural compounds forming over 95% of the renewable organic material. Up to now only a small part of carbohydrates are used as a material in the chemical industry [30-33]. Amines with two long chain ketones react easily with oxidized sugars, e.g. gluconic or lactobionic acid, producing stable amides, which are very good nonionic detergents. Amines can also be combined with reductive sugars in a reaction resulting in aminoglycosides, which can be stabilized by catalytic hydrogenation or acylation. Ketones can also be subjected to a direct reaction with reduced aminosaccharides (e.g. aminosorbitol), and the resultant product hydrogenated. Another method of obtaining surfactants from long chain ketones is Knovenagel reaction of ketone with malonylnitrile. The reduction of nitrile groups and double bonds leads to obtaining diamines, which can be subjected to all the reactions mentioned also in the case of the former monoamine. Monoamine obtained from ketone can react with acrylonitrile, introducing two nitrile groups which can be hydrogenated to amine groups and again to obtain a whole range of surfactants of gemini type, using reductive sugars or acids obtained from sugars as substrates.

All the described processes are simple addition reactions, which proceed quantitatively almost without by-products. The fact that two basic substrates of the concept - fats and sugars - are renewable natural resources is critical. Surfactants with the application of sugar substrates [34] are characterized by very good application features and a low impact on natural environment.

Long chain amines can also be condensed with ethylene oxide or propylene oxide [35], which leads to non-ionic surfactants.

## Summary

The increasing importance of environmental issues has resulted in the search for natural resources and biodegrading products. Waste technical fats can provide a raw material basis for the production of surfactants of gemini type.

Presented conversion from triacylglycerols to amines with two long chains proceeds according to the scheme:

triacylglycerols -> $RCOOCH_3$ -» RCOR -> $RCHNH_2R$ -» -» surfactants

Stages of fat esterification and transesterification and reductive amination of ketones have already been technologically mastered. The synthesis of surfactants of gemini type with the participation of hydrocarbons is the subject of intense research. Experiments carried out by the authors provide the complementing element of the above sequence - they concern the ketonization of fatty acids esters.

The concept concerns the utilization of harmful, extensive and renewable raw material resource, i.e. waste technical fats. During the reaction of esters ketonization no harmful by-products are formed, and the obtained ketones can constitute a basis for biodegrading and efficient, and thus less harmful to the natural environment, surfactants.

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