Methods for Transforming Residual Glycerin into an Additive: A Review

Lívia Firmani Silva.

Undergraduate Chemical Engineering, Federal Technological University of Paraná, Campo Mourão, Brazil, liviafirmanis@outlook.com.

Abstract. The world is facing a growing need to adopt sustainable choices, due to concerns about the depletion of natural resources and the environmental impact caused by the use of fossil fuels. Reducing consumption and dependence on these fuels is one of the main solutions to mitigate the effects of climate change and promote environmental preservation. In this context, biofuels have emerged as a promising alternative. Over the years, various types of biofuels have been created, developed and are currently being used, including biodiesel from biomass, which can replace petroleum diesel in whole or in part. This extensive market for biodiesel has brought with it a surplus of its coproduct, glycerol, which represents 1/10 of the final volume of the reaction. Although it has well-established applications in various sectors around the world, the surplus on the market calls for new routes for using it in a sustainable and viable way. This article reviews promising techniques for transforming glycerol into fuel additives, so that this product can return to the fuel cycle and be valued economically and environmentally. Among the possible routes are glycerol acetalization/ketalization, catalytic etherification, esterification, and other ways of recovering this product are briefly presented, including its purification and its use as a renewable energy source. This repurposing of glycerol brings improvements directly linked to the flow properties of the fuels evaluated. And this is just as important as finding and developing mechanisms to do this in a cheap, simple way that can be scaled up to industrial sectors.

Keywords. Additive, biodiesel, glycerol/glycerin, sustainable, fuel.

1. Introduction

The significant increase in the population, economic growth and industrialization are reflected in the global demand for energy, which will rise by 53% by 2030. This dependence on energy is reflected in a 6% increase in demand between 2022 and 2028 for oil and, consequently, fossil fuels. The challenges of providing energy globally in a sustainable way reflect these trends [1]. Global warming is caused by the significant release of CO_2 into the environment, which proves the need for incentives for the use of biofuels and their valorization [2]. Concern about greenhouse gas emissions and air pollution has sparked a worldwide need for renewable energy sources and sustainable alternatives to fossil fuels. And as an attractive option, especially for the transportation sector, conventional diesel fuel is increasingly being replaced by biodiesel [3]. Its commercialization will continue to expand, in addition to demand, there is an increase in accessible raw materials, government support and better technologies [2].

The use of biodiesel goes beyond replacing fossil fuels. Its use represents an improvement in waste management, as biomass is one of the reagents for its production, providing a useful destination for waste oils and fats [1].

The main way of obtaining biodiesel is through the transesterification reaction, where triglycerides (from fats or vegetable oils) react with an alcohol, usually methanol, together with the aid of a catalyst and give rise to fatty acid methyl esters, commonly known as biodiesel [1]. This reaction is responsible for generating glycerin as a co-product, representing 10% of the total volume produced [3]. Glycerin has many applications in the cosmetic, pharmaceutical, and food industries, among others. Although there is a destination for glycerin, its surplus on the market has led to the need for new ways to use it. In 2015, global production amounted to 300.000 m^3 and is expected to grow by 3,5% per year until 2025 (reaching approximately 425.000 m^3). In this way, glycerol represents a major bottleneck in the biodiesel production chain, which poses the challenge of new routes for its sustainable conversion to value-added products [4].

One of the direct uses of glycerol is its combustion to produce renewable steam, work, heat and electricity. However, crude glycerol from transesterification has some unfavorable properties and its combustion can generate toxic pollutants. On the other hand, transforming glycerol into an additive for biodiesel itself has been a promising approach, as it can improve the fuel's physical and chemical properties, increasing its efficiency [5].

The additives obtained from glycerol are capable of mitigating particulate matter, unburned hydrocarbons, carbon monoxide and unregulated emissions in internal combustion engines, as well as improving the cold flow properties of biodiesel [5].

This paper focuses on briefly presenting some of the current routes used to transform glycerol into an additive. It shows how this biodiesel co-product can be valorized in terms of energy content and how to clean up the combustion process in the fuel cycle.

2. Methodology

The ability to valorize crude glycerol improves the economy and carbon footprint of the biodiesel industry [6]. Current studies on the transformation of crude glycerol into an oxygenated additive will be presented below, with the main focus on the economic valorization of this co-product.

2.1 Acetals and ketals of glycerol

One of the chemical routes for obtaining fuel additives is described by the reaction of glycerol with an aldehyde organic function in the presence of an acid catalyst, which results in compounds called acetals, and the reaction is known as acetalization. For example, when the reaction occurs between glycerol and fomaldehyde, the product is known as formal glycerol, as shown in Figure 1 [3].

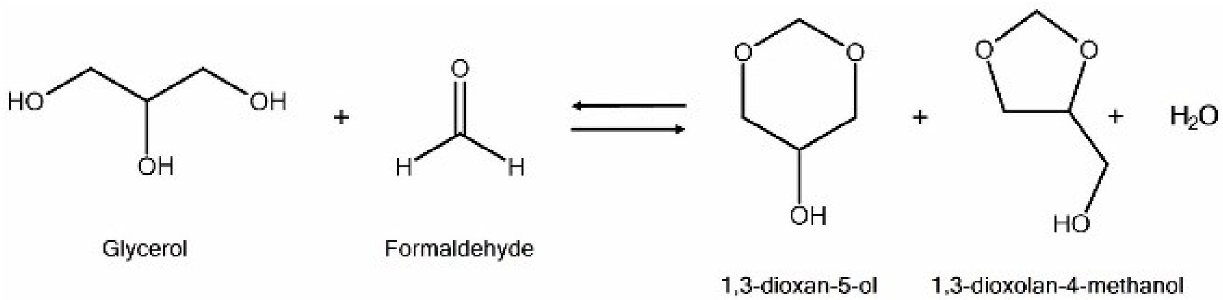

Figure 1 – Glycerol acetalization

Another similar way of converting glycerol into an additive is by reacting glycerol with a ketone function, known as ketalization, and its product is called ketal. Figure 2 shows the reaction of glycerol and acetone, with the products being the molecule known as solketal and its isomer, 2,2-dimethyl-1,3-diozan-5-ol. This is thermodynamically less stable as it has a methyl group in the axial position of the ring [3], [7].

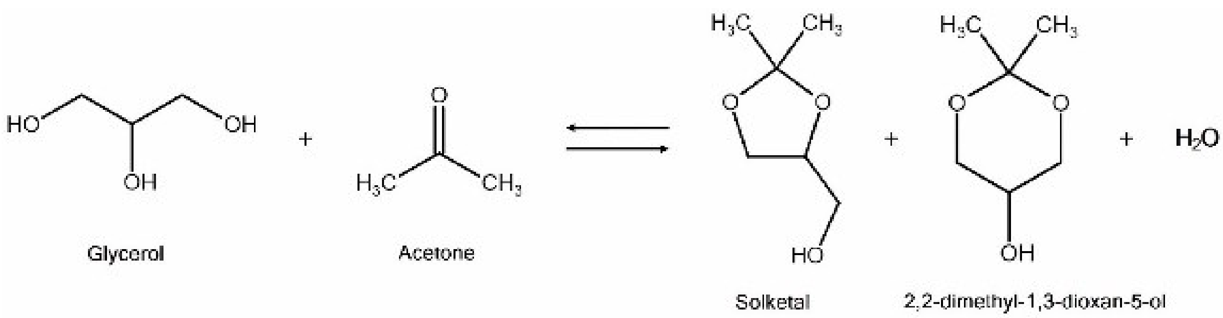

Figure 2 – Glycerol ketalization

Solketal is used as a fuel additive because it reduces gum formation and improves the oxidation stability of gasoline [5]. It also has other applications, such as as a solvent for the production of pesticides and pharmaceutical formulations and its use in the synthesis of polyester resins, polyglycerols and plasticizers [7].

Most of the studies on this subject are on a laboratory scale, evaluating the different catalysts, their stability, activities and selectivities [7]. A study by da Silva et al. showed a conversion of almost 99% and a selectivity for solketal of 97%, with a molar ratio of glycerol to acetone of 1:16, using room temperature and the $Sn_2SiW_{12}O_{40}$ catalyst [8]. Miao et al. showed a conversion of glycerol of 91%

with mesostructured titanium phosphates, with a selectivity for solketal of 94% at 50 ° C with 4 hours of reaction. The catalyst stands out because it can be reused for 10 reaction cycles without losing its activity [9].

A characteristic of acetalization/cetalization is the production of this mixture of five- and six-membered cyclic isomers. These reactions are considered simple, as they are carried out under mild conditions and at atmospheric pressure with the help of acid catalysts and high selectivity for the products. There are several studies that show the efficiency of this process and how these additives have had a positive influence on the fuel, such as reducing the clogging point of the cold filter, reducing the emission of particulate matter, non-combustible hydrocarbons and other pollutants [3].

2.2 Glycerol ethers

Ethers have been explored since the 1930s and their use encompasses a wide variety of products; in addition to additives, they can be used to produce food flavoring agents, surfactants and solvents [3].

The catalytic etherification reaction is a major strategy for improving glycerol. Generally, olefins and alcohols are used with an acid catalyst to obtain di- and tri-tert-butyl ethers of glycerol, creating additives with high potential. The reaction can be carried out with both homogeneous and heterogeneous catalysts, so studies focus on heterogeneous acid catalysts, as they have greater reusability after the reaction and contribute to the sustainability of the process [10].

Studies generally use olefins such as isobutene and tert-butyl alcohol to produce the additive [11]. However, Aimaretti et al. carried out the reaction with isobutylene olefin and other types such as those from FCC (Fluid Catalytic Cracking). Another study analyzed glycerol impurities in the reaction using Amberlyst 15 and showed that the conversion of crude glycerol was low compared to refined glycerol [12].

Ethers can be used to improve cold flow properties and reduce fuel viscosity and density, providing better engine activity, as well as reducing volatile organic emissions [11], [13].

2.3 Glycerol esters (acetates)

The reaction of glycerol with carboxylic acids represents another possibility for converting glycerol and changing its final destination. Monoacetin, diacetin, and triacetin are the three products of this reaction, and triacetin in particular is used as an additive because it has good solubility in hydrocarbons and is able to improve the cold flow of fuel or increase the octane rating [3].

The production of glycerol acetates, or acetines, is done through the esterification reaction in the presence or absence of a homogeneous/heterogeneous catalyst with acetic acid, as shown in Figure 3. This route is used to produce acetates commercially, as its yield is high in a short reaction time, as well as considering the economic viability of the reagents. There are some challenges to the process, such as separating the reaction products. The difficulty arises in the use of distillation for separation, as the compounds have similar boiling points. Another disadvantage is the lower selectivity of the desirable product, triacetin, due to the fact that it also has water as a product and this negatively affects the thermodynamic equilibrium. This can be solved by adding acetic anhydride, but it makes the process more expensive [5].

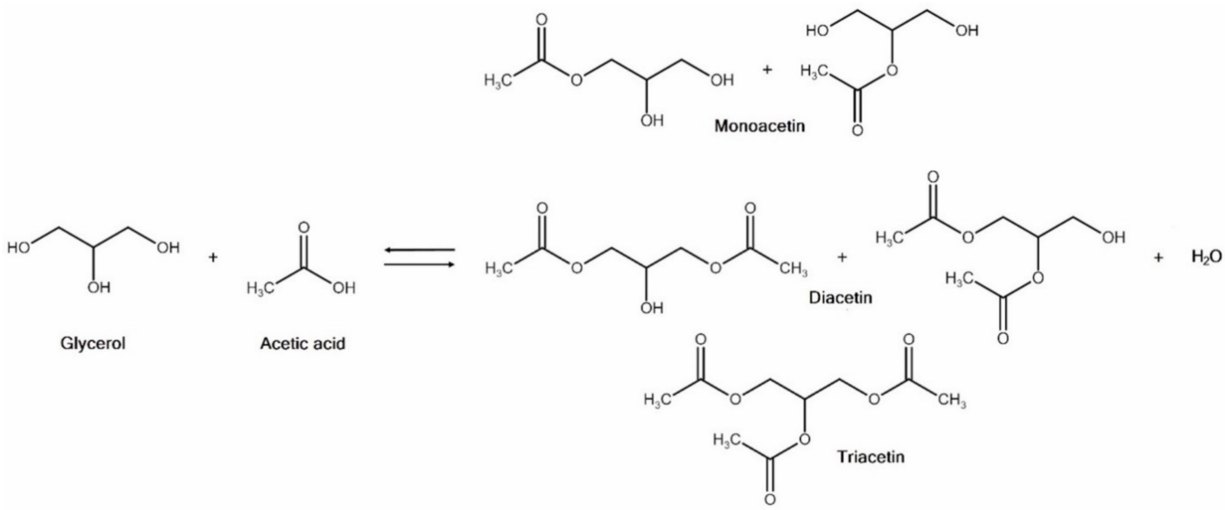

Figure 3 – Glycerol esterification

Studies on this route focus on the development and improvement of heterogeneous catalysts for industrial use, since they are reusable, focusing on high stability, selectivity and sustainability [14].

There is a 2016 patent by Puche [15], which describes the process of producing triacetin and fatty acid alkyl esters and their use as cold flow improvers for diesel and octane enhancers for gasoline.

2.4 Other ways

In addition to processing into additives, technologies are used commercially to purify crude glycerol, such as vacuum distillation and ion exchange adsorption, which are responsible for achieving purities of > 95% glycerol. Another way is chemical treatment, involving acidification to convert the soap present into free fatty acids and the precipitation of valuable by-products. However, the use of chemical and physical processes can be more effective, being able to further refine the glycerol in several stages. This technology is still under development and its advantage is that it can be customized, differentiating the stages, operating conditions and reagents to optimize the purification process [6].

One of the studies was responsible for evaluating the environmental sustainability of the physical-chemical purification process of crude glycerol using three acids (H_3PO_4, H_2SO_4 and HCl), compared to incineration, which is the alternative used to dispose of crude glycerol when purification is not an economically viable option. The results showed that treatment with the three acids had savings in relation to the impact of climate change, considering that the process depends on the composition of the crude glycerol, as well as saving on the amount of waste, but there is still a need for studies on the global scale of the process [6].

Another study shows a different route for the valorization of glycerol, presenting its use as a raw material to generate renewable energy and dispensing with refining processes for residual glycerol. Glycerol can be used as a carbon source in fermentation, generating alcohol and hydrogen, in decomposition together with biomass to produce biogas, in use as an additive for biomass gasification to produce synthesis gas, in addition to liquefaction to convert biomass into bio-oil, among others [16].

3. Results and discussion

The use of residual glycerol from the biodiesel industry to produce additives is a great example of how this co-product of transesterification can be valorized, with great potential to promote a sustainable and environmentally conscious economy. This way of using glycerol contributes to energy efficiency and represents development and innovation in the industry.

Various processes and reactions are used to produce these fuel additives, the change between the types of products lies in their chemical compounds and the main ones are acetals, ethers and acetates. But they all generally serve the same functions, depending only on which fuel is added: they can improve cold flow for bio-diesel; boost octane for gasoline; and reduce particulate matter for diesel. The amount to be added is limited to small concentrations, as it needs to meet the standard for usable fuel and follow the 'drop-in' fuel specifications.

The interesting thing about the additives presented is that they can be produced from low-cost, readily available raw materials such as acetone, formaldehyde and acetic acid.

In the literature, acetals/ketals are widely available, with solketal being the most prominent compound and a product of glycerol and acetone. Ethers, on the other hand, are the most investigated type of glycerol additive and among the three products of their reaction, di-tert-butyl is the target to be achieved. Acetates/acetins come from glycerol and acetic acid and, like ethers, have a compound of greater interest: triacetin.

Based on the studies presented in this paper, glycerol-derived additives have the potential to enhance fuel properties, including octane rating, pour point, and plugging point.

Even though there are a variety of studies on glycerol-derived additives, there is still a need to evaluate, for example, their use in higher concentrations and increase the range of possible applications for these products.

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