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Potential applications of crude glycerol in polymer technology–Current state and perspectives

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ABSTRACT

The increasing use of bio-based fuels and fuel additives, among them biodiesel, causes significant surplus of crude glycerol on the market which creates new challenges in terms of its sustainable utilization. A lot of ways for the incorporation of this by-product into different branches of industry requires purification by expensive and complicated processes. Therefore, researchers are seeking for applications of untreated crude glycerol. Among the possibilities, much attention is drawn to the polymer chemistry and technology. This branch of industry is one of the biggest consumers of glycerol after food, pharmaceutical and personal care applications sectors, and probably the biggest one that does not require complicated purification of glycerol resulting from biodiesel technology. Crude glycerol can be applied in the number of processes such as fermentation, oxidation, esterification and transesterification, biomass liquefaction, oligomerization and polymerization, carboxylation, glycerolysis, hydrogenolysis, dehydration or dihydroxylation. This paper summarizes the use of glycerol in polymer technology and the attempts of crude glycerol incorporation into this field reported in literature.

Contents

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1. Introduction

Glycerol or according to IUPAC nomenclature, propan-1,2,3-triol, contains three hydroxyl groups, which are responsible for its hygroscopic character and solubility in water [1,2]. It is a colorless, odorless, viscous liquid soluble in different polar liquids, such as methanol, ethanol, isopropanol, ethylene glycol, phenol or pyridine and insoluble in fatty oils, in higher alcohols, hydrocarbons and chlorinated solvents such as hexane, benzene and chloroform [3,4]. Glycerol backbone is the main component of all lipids, known as triglycerides, which are constituents of animal fats and vegetable oils [5].

Traditional applications of glycerol include its incorporation into food industry, production of pharmaceuticals and personal care products, anti-freezers, botanical extracts, e-cigarette liquids, explosives and many other processes as an intermediate compound [6]. In pharmaceutical industry glycerol is applied in medical grade nitroglycerin production, which is used to widen the blood vessels. Glycerin is also useful in production of syrups, creams and balsams. In cosmetics it is used as demulcent and anti-inflammatory agent. In food industry, glycerol is applied as moisturizing agent in baking, solvent for dyes and flavoring agents. High purity glycerol is added to animal feed [7].

Traditionally, glycerol was produced through saponification of triglycerides, during soap production [8]. Synthetically it may be produced from propylene, by various routes. Because of the global emphasis on biodiesel production (where glycerol is a by-product), most of the old methods of glycerol production are no longer economically beneficial on an industrial scale. However, crude glycerol (biodiesel by-product) contains various impurities, such as methanol, water, soaps, free fatty acids (FFA) or fatty acids methyl esters (FAME) [7]. Glycerol is a crucial compound for different branches of chemical industry, so the development of economically beneficial methods of its purification is very important [9]. Nowadays, different techniques of glycerol refining are known, such as filtration, microfiltration, ultrafiltration, ion exchange or adsorption. Compilation of these techniques may result in high purity of final product [10].

Despite the low price of glycerol, its purification is an expensive process, especially for small and average companies [11], therefore researchers seek for different possibilities to incorporate crude glycerol, optionally with a very simple purification step, into various branches of industry. Nowadays, very popular trend is related to the use of crude glycerol into polymer technology as a substitute for pure glycerol, commonly used in production of plastics. The aim of the presented contribution is to review and summarize, reported in the literature attempts of crude glycerol utilization in polymer technology.

2. Biodiesel production

Provisions of the Kyoto Protocol on the climate change are important elements of the package of tools necessary to reduce greenhouse gases emission. One way to reduce the excessive emission of CO_2 is the use of energy and raw materials from renewable resources. Having this in mind, the chemical industry became focused on environmentally friendly efforts, and intensive development of technologies based on ecological materials has started. Nowadays, increasingly more information on renewable materials of natural origin is available. This applies especially to oils, which are biodegradable and are a source of new materials for oleochemicals industry. The incorporation of bio-based oils as feedstock for industrial production is crucial not only from the ecological point of view; it is also an economic issue because of unstable prices and decreasing reserves of crude oil and fossil gas.

The development of biofuels market in European Union is determined mainly by the strategic decisions of EU in the field of energetic policy, which is connected with establishments related to the reduction of greenhouse gases and decreasing of their environmental impact. According to the Directive 2009/28/WE, which promotes the use of renewable energy and replaces the Directives 2001/77/WE and 2003/30/WE, until 2020 in each country in European Union, the share of biofuels in the transport sector should reach 10% [12].

In 2008 Parliament of European Union voted down Climate Package 3x20, according to which, in 2020 carbon dioxide emission has to be reduced by 20% comparing to 1990. Simultaneously, the share of energy from renewable resources has to increase from 8.5% then to 20% and energy consumption needs to be reduced by 20%. This 20% share of renewable energy is related to the level of whole EU and has to be regulated at the national level in terms of individual energetic potential [13].

Under these circumstances, in recent years there has been a rapid increase of the production of lubricants and biofuels, especially biodiesel, from renewable plant-based materials.

Biodiesel, composed of fatty acid methyl esters, is produced *via* transesterification of triglycerides contained in fats with alkyl alcohol (most often methanol) in the presence of proper catalysts. Scheme of the process is presented in the Fig. 1. This reaction results in two-phase product. Upper phase, contains main product – biodiesel, while bottom phase consists of glycerol (from 30 to 60%), water, soaps, free fatty acids, their esters, methanol and catalyst. In smaller amounts there are also present peptides, lecithin, proteins and phospholipids [14,15]. Production of biodiesel is based on the esterification of fatty acids originated mainly from vegetable oils [16]. The type of used oil is determined by the type of the crops most popular in specific region. In North and Middle Europe, by far the most popular oil used in biodiesel production, is rapeseed oil, while in North America it is soybean oil, whose