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Production of diacylglycerols by esterification of oleic acid with glycerol catalyzed by diatomite loaded SO_4^{2-}/TiO_2

Zhen Zhang[a,b], Huihua Huang[a,**], Xiang Ma[c], Guanghui Li[b], Yong Wang[b,*], Guo Sun[b], Yinglai Teng[b], Rian Yan[b], Ning Zhang[b], AiJun Li[b]

[a] College of Food Science and Engineering, South China University of Technology, 381 Wushan Road, Guangzhou 510641, China
[b] Guangdong Saskatchewan Oil seed Joint Laboratory, Department of Food Science and Engineering, Jinan University, Guangzhou 510632, China
[c] Research School of Chemistry, The Australian National University, Canberra, ACT 2612, Australia

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ABSTRACT

A new and efficient technique is described for the production of diacylglycerols (DAGs) by the esterification of oleic acid with glycerol catalyzed by diatomite-loaded SO_4^{2-}/TiO_2. DAGs show some potential health benefits compared to triacylglycerols, and also can be used to produce the novel industrial plasticizer epoxy fatty acid methyl ester in material science. Diatomite-loaded SO_4^{2-}/TiO_2 catalyst was prepared and characterized, and the selected conditions for the synthesis of DAGs were determined to be: reaction time = 6.0 h, temperature = 210 °C, catalyst loading = 0.1% of the oleic acid weight, and mass ratio of oleic acid to glycerol = 2:1. Under these conditions, DAGs yield reached 59.6% with a purity of 69.6% after a one-stage molecular distillation. Diatomite-loaded SO_4^{2-}/TiO_2 as a solid catalyst could be recycled and reused with high catalytic efficiency. Under the same conditions, diatomite-loaded SO_4^{2-}/TiO_2 showed a better catalytic performance than the commercial solid acid SO_4^{2-}/ZrO_2-Al_2O_3. Based on this, a two-step reaction method for the production of DAGs was performed and provided a yield similar to the one-step method (58.3% vs. 59.6%), but with a shorter reaction time (4 h vs. 6 h). It is concluded that a two-step reaction method could be a better alternative to the one-step production of DAGs in the presence of diatomite-loaded SO_4^{2-}/TiO_2.

Introduction

Diacylglycerols (DAGs) are from edible oils and widely used as emulsifiers in food and pharmaceutical industries due to their beneficial physiochemical properties and nutritional values [1–3]. Recently, DAGs have been used for the production of hydroxylated epoxy esters, which represent a new category of safe plasticizers for the polymer industry [4].

Catalytic production methods of DAGs can be classified into chemical and enzymatic approaches, and the products of these reactions are purified through high-vacuum distillation. Enzymatic reactions usually occur under mild conditions [5,6]. For instance, Watanabe et al. [7] reported an effective lipase-catalyzed esterification, with the highest DAGs content being ~70%. However, drawbacks of enzymatic approaches include limitations inherent to the equipment used, long reaction time, and high cost enzymes [8]. Chemical methods including esterification and glycerolysis are commonly utilized in the production of DAGs. It has been reported that DAGs could be produced through the continuous chemical glycerolysis of fats and oils at high temperatures (220–250 °C) using inorganic alkaline catalysts in a nitrogen gas atmosphere [9]. Solid acids such as zeolites, resins of the type Naftion-M, zirconium sulfate on silica, and Amberlyst-15, have been reported to catalyze the esterification of oleic acid [10]. Alternatively, sulfated titania (SO_4^{2-}/TiO_2) is also a capable solid acid catalyst for esterification [11]. As solid-catalysts can be easily separated by filtration from the reaction system and be recycled with no corrosive effects on the reaction equipment and little

Abbreviations: MAG, monoacylglycerol; DAG, diacylglycerol; TAG, triacylglycerol; FFA, free fatty acid; TFA, trans-fatty acids; GC, gas chromatography; X-RD, X-ray diffraction; IR, infrared spectroscopy; SEM, scanning electron microscope; FAME, fatty acid methyl ester.

* Corresponding author.
** Corresponding author at. Department of Food Science and Engineering, College of Science and Engineering, Jinan University, 601 Huangpu Ave West, Guangzhou 510632, China. Fax: +86 20 85226630.
E-mail addresses: fehhuang@scut.edu.cn (H. Huang), twyong@jnu.edu.cn (Y. Wang).

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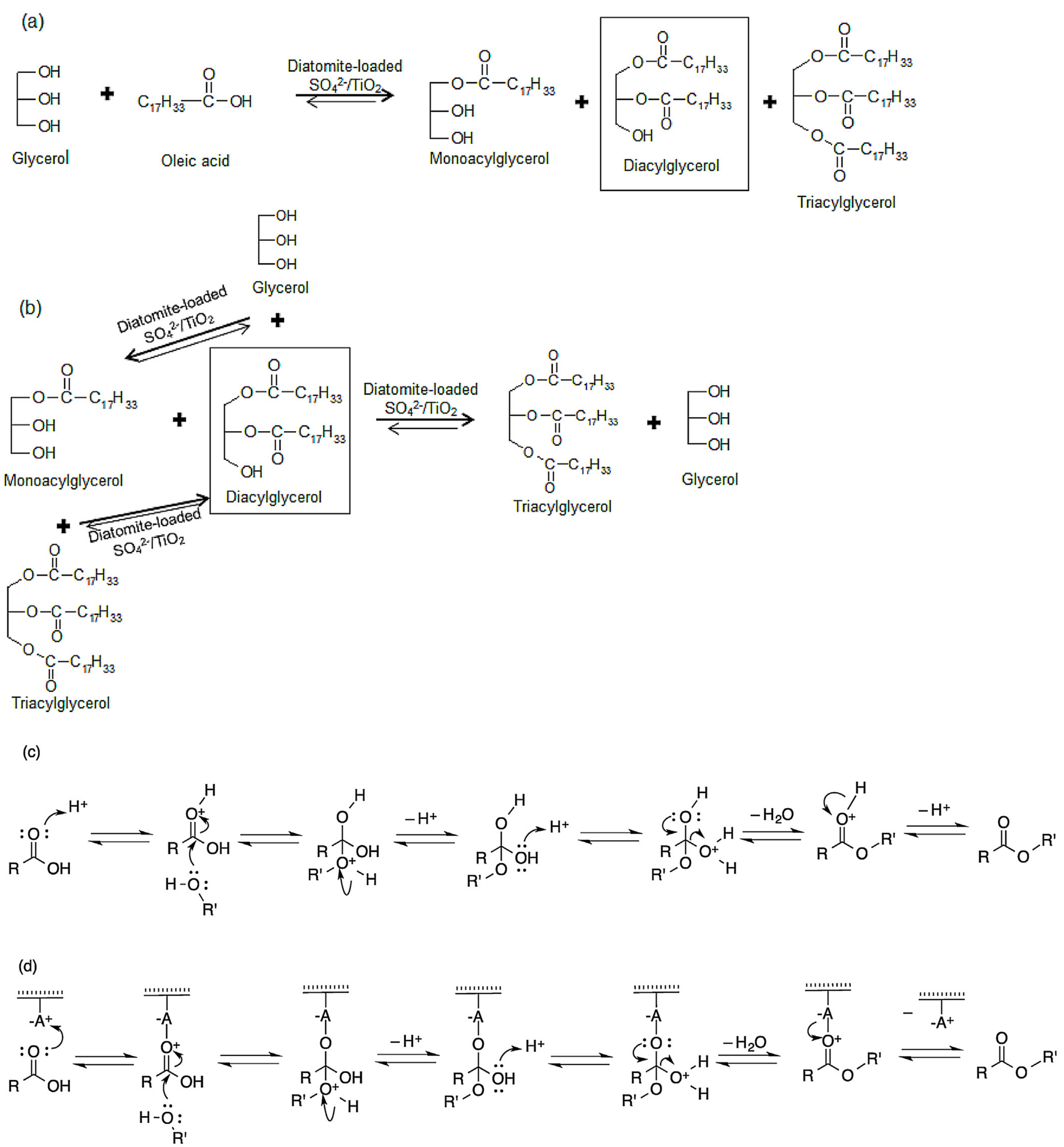
environmental pollution, in recent years they become very attractive for both research and industrial applications [12].

With the rapid development and commercialization of biodiesel, the co-product, glycerol is currently produced in a huge amount, which makes the price of glycerol to decline very sharply. Consequently, it is of potential economic benefits to convert low-cost glycerol into value-added chemicals or materials [13]. As a result, a variety of catalytic processes have been developed for the valorization of glycerol, by hydrogenolysis, reforming, etherification, esterification, oxidation, dehydration, and so on [14–16].

The reaction route of production of DAGs by esterification is proposed in Scheme 1a, and the side reaction of glycerolysis and transestrification of acylglycerols is given in Scheme 1b. Sulfated titania (SO_4^{2-}/TiO_2), the solid acid, shows both Brönsted acid and Lewis acid activity when catalyzing [11] and the mechanisms of catalysis for both activities are clarified in Scheme 1c and d



(c) Brönsted acid sites; (d) Lewis acid sites.

Scheme 1. (a) Production of acylglycerols by esterification of oleic acid with glycerol. (b) Glycerolysis and transesterification of acylglycerols as side reaction. (c) Esterification reaction pathway over Brönsted acid sites (H+). (d) Esterification reaction pathway over Lewis acid sites (A+).

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