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Improved synthesis of carbonated vegetable oils using microwaves

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HIGHLIGHTS

- Reaction proceeded faster when microwaves were used.
- Reaction times using microwaves were ca. 1/4–1/3 of reaction times with conventional heating.
- Addition of water favors the reaction.
- Selectivity towards cyclocarbonates was improved by using microwaves.

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ABSTRACT

Carbonated vegetable oils were synthesized from epoxidized oils and CO_2 using microwave heating with tetrabutyl ammonium bromide as catalyst. The reaction proceeded faster when microwaves were used; reaction times using microwaves were ca. 1/4–1/3 of reaction times required using conventional heating under similar reaction conditions. Other important finding was that the addition of water favors the reaction. Besides, selectivity towards the cyclocarbonate was improved by using microwaves because of the lower reaction time required. Conversions of ca. 90% were obtained at 70 h and 40 h with conventional and microwave heating, respectively.

1. Introduction

Cyclocarbonates are used in several industrial applications such as insecticides, fungicides, herbicides and intermediates for drugs, but their major use is the production of thermoset polymers [1] and non-isocyanate polyurethanes (NIPUs) also known as green polyurethanes [2]. This last application contributes to lowering CO_2 atmospheric emissions, which has a tremendous environmental impact; besides, it eliminates the use of the very toxic and dangerous di-isocyanates customarily used in the synthesis of polyurethanes. Carbonates can be obtained from carbon monoxide or carbon dioxide; the first one involves numerous synthetic pathways, the most used are the phosgenation [3] and the oxidative carbonylation of alcohols [4]. Carbon dioxide reacts with alcohols to produce linear carbonates such as dimethyl carbonate [5], with ammonia to form urea which reacts with alcohols to give also linear carbonates [6], and with cyclic ethers to produce directly cyclic carbonates which can be transform to linear carbonates by transcarbonation [7].

Tetrabutylammonium bromide (TBABr) is the most used catalyst for the production of cyclocarbonates, such as ethylene carbonate, from epoxides, but it requires high pressures and a large CO_2 excess [8]. The proposed mechanism for the formation of cyclocarbonates from epoxides and CO_2, using TBABr as catalyst, is shown in Fig. 1 [9].

Carbonated soybean oil has been synthesized from epoxidized soybean oil and CO_2. Wilkes et al. [10] synthesized carbonated soybean oil at 110 °C, with 94% conversion, in 70 h (atmospheric pressure) using tetrabutylammonium bromide (TBABr) as catalyst. Doll and Erhan [11] lowered the reaction time to 20 h by using supercritical CO_2 (94% conversion at 100 °C); they also achieved 100% conversion in 40 h and improved further the process removing the catalyst by simply heating the reaction system at 190 °C, without the need of organic solvent extraction; at this temperature the catalyst breakdowns but the carbonated oil is stable. Li et al. [12] studied a catalytic system made of $SnCl_4{\cdot}5H_2O$ and TBABr, which required 20 h and 1 MPa.

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