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A cleaner approach for biodegradable lubricants production by enzymatic glycerolysis of castor oil and kinetic analysis

Shangde Sun [a, b, *], Gaoshang Wang [a, b], Ping Wang [a, b]

[a] Provincal Key Laboratory for Transformation and Utilization of Cereal Resource, Henan University of Technology, Lianhua Road, Zhengzhou 450001, Henan Province, PR China

[b] Lipid Technology and Engineering, School of Food Science and Engineering, Henan University of Technology, Lianhua Road, Zhengzhou 450001, Henan Province, PR China

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ABSTRACT

Monoricinolein (MRO) and diricinolein (DRO) were renewable and biodegradable lubricants. In this paper, MRO and DRO were prepared by the novel cleaner enzymatic glycerolysis of castor oil (CO) in solvent-free system. Three commercial immobilized lipases (Novozym 435, Lipozyme RM IM and Lipozyme TL IM) were screened and compared, and Novozym 435 showed the best catalysis performance among the tested lipases. Effects of reaction variables (reaction pressure, reaction time, temperature, enzyme load, substrate ratio and water content) on the enzymatic glycerolysis of CO were investigated. High conversion of CO (92.48 ± 1.02%) and the maximum bio lubricants yields (54.47 ± 0.58% MRO and 38.01 ± 0.50% DRO) were achieved under the following conditions: enzyme load 5% (w/w, based on the total mass), CO/glycerol ratio at 1:6, 90 °C, and 3 h. The activation energies (Ea) for CO conversion and the formation of MRO and DRO were calculated as 33.75 kJ/mol, 22.26 kJ/mol and 24.37 kJ/mol, respectively, and the process showed high selectivity toward the formation of MRO. Reaction kinetic agreed with the ping-pong Bi-Bi mechanism with the inhibition of CO, and the kinetic values (V_{max}, K'_m and K_{IA}) were 0.0946 mol/(L·min), 1.6704 mol/L, and 0.89 mol/L, respectively.

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1. Introduction

Lubricants had been become the basic need for mechanical industries. However, most lubricants (>90%) are from crude petroleum (Mang, 2007), which are non-renewable and toxic to the environment. Hence, there is a need to identify a suitable alternative to petro based lubricants. Due to the renewable and environmental degradation, vegetable oil based lubricants had been considered as an alternative to petro based lubricants (Kleinaitė et al., 2014; Panchal et al., 2017; Singh et al., 2017; Syahir et al., 2017).

Monoricinolein (MRO) and diricinolein (DRO) are natural minor constituents in castor oil, which can be used as vegetable oil based lubricants (Guo et al., 2017; Hajar and Vahabzadeh, 2016; Saboya et al., 2017; Singh, 2011). However, in nature, the contents of MRO and DRO are very low (<5%). Therefore, the preparation of MRO and DRO from vegetable oil has attracted more attention. According to those previous reports, MRO and DRO can be prepared by lipase-catalyzed esterification (Turner et al., 2006) and methanolysis of triricinolein (Turner et al., 2003; Echeverri et al., 2015), which firstly required ricinoleic acid preparation from CO and methanol as reaction substrate. Compared with these approaches, glycerolysis of CO is an efficient and economical method to prepare MRO and DRO. However, there is no available information using enzymatic glycerolysis of CO to prepare these biodegradable lubricants.

Industrially, glycerolysis of natural oil and fats usually employed inorganic basic catalysts. And, high temperatures (220–260 °C) were also used in the process, which resulted in poor product quality (Luo et al., 2015), such as, dark color and burnt taste. In

Abbreviation: PG, Partial glycerides; MRO, Monoricinolein; DRO, Diricinolein; TAG, Triglyceride; FFA, Free fatty acid; CO, Castor oil; GC, Gas chromatography.

* Corresponding author. Lipid Technology and Engineering, School of Food Science and Engineering, Henan University of Technology, Lianhua Road, Zhengzhou 450001, Henan Province, PR China.

E-mail address: sunshangde@hotmail.com (S. Sun).

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order to overcome these issues, in the work, a novel cleaner approach for CO-based biolubricants production was developed by the enzymatic glycerolysis of CO in solvent-free system. Enzyme screening was compared and evaluated. Effects of reaction variables (reaction pressure, reaction time, temperature, enzyme load, substrate ratio and water content) on the glycerolysis were studied. Thermodynamic and reaction kinetic were also investigated.

2. Material and methods

2.1. Materials

Castor oil (CO) was purchased from Aladdin (Shanghai, China). Glycerol (≥99.0%) with 0.45% water content was purchased from Tianjin Kermel Chemical Reagent Co. Ltd. (Tianjin, China). Immobilized lipases: Novozym 435 (from *Candida antaratica*), Lipozyme RM IM (from *Rhizomucor miehei*), and Lipozyme TL IM (from *Thermomyces lanuginose*) were obtained from Novozymes A/S (Bagsvaerd, Denmark). For GC analysis, derivatizing MSTFA (N-methyl-N-(trimethylsiyl) trifluoroacetamide) and GC grade trilaurin were purchased from Sigma-Aldrich (St. Louis, MO., USA). Pyridine and *n*-heptane were HPLC grade.

2.2. Enzymatic glycerolysis of CO

Reaction mixtures consisted of CO and glycerol in different molar ratios were premixed in 100 mL three-necked glass flacks by magnetic stirrer at 300 rpm, and heated to reaction temperature using oil bath. And then the immobilized lipases were added. Aliquot fractions (0.10 mL) were periodically withdrawn from reaction system.

2.3. Determination of monoricinolein (MRO), diricinolein (DRO) and triglyceride (TAG) by GC

Reactants and products were analyzed and identified according to ASTM D6584 and the previous report (Dias et al., 2012). MSTFA (250 μL) and trilaurin (100 μL, 32 mg/mL) were added into the withdrawn samples. After mixed for 20 min, the samples were silylated, and 8 mL *n*-heptane was added. Finally, samples were dried using anhydrous sodium sulfate, and filtered using a microfilter (0.45 μm) before analysis.

Sample analysis was performed by GC Agilent 7890B with automatic on-column injector and a flame ionization detector (FID). The conditions were as follows: DB-1ht (30 m × 0.25 mm, 0.1 μm film thickness), injection volume of 1 μL, N_2 (carrier gas) 4.41 mL/min; split/splitless injector with split injection mode, split ratio of 40:1 at 350 °C. The detector temperature was 380 °C. Oven temperature was set at 50 °C and hold at 50 °C for 1min, then increased at 15 °C/min to 180 °C, and then increased at 7 °C/min to 230 °C, finally increased at 30 °C/min to 360 °C and maintained at 360 °C for 10min. The results were expressed in moles. The calculation for TAG conversion, MRO, DRO, and free fatty acid (FFA) yields were as follows:

$$\text{TAG conversion}(\%) = \frac{n_{MRO} + 2 \times (n_{DRO} - n_{DRO_0}) + n_{FFA}}{3 \times n_{TAG} + 2 \times n_{DRO} + n_{MRO} + n_{FFA}} \times 100 \quad (1)$$

$$\text{MRO yield}(\%) = \frac{n_{MRO}}{3 \times n_{TAG} + 2 \times n_{DRO} + n_{MRO} + n_{FFA}} \times 100 \quad (2)$$

$$\text{DRO yield}(\%) = \frac{2 \times (n_{DRO} - n_{DRO_0})}{3 \times n_{TAG} + 2 \times n_{DRO} + n_{MRO} + n_{FFA}} \times 100 \quad (3)$$

$$\text{FFA yield}(\%) = \frac{n_{FFA}}{3 \times n_{TAG} + 2 \times n_{DRO} + n_{MRO} + n_{FFA}} \times 100 \quad (4)$$

where n_{TAG}, n_{DRO}, n_{MRO}, and n_{FFA} are the contents of TAG, DRO, MRO, and FFA in the samples, respectively; n_{DRO_0} is the initial diricinolein content of the material.

3. Results and discussion

3.1. Enzyme screening

Three kind of commercial immobilized lipases were employed and compared for the glycerolysis of CO (Fig. 1). Among the tested lipases, Novozym 435 showed the best catalytic performance for the glycerolysis. TAG conversion reached 91.36 ± 1.60% using Novozym 435 as catalyst at 6 h, which was higher than those of Lipozyme TL IM (5.24 ± 1.00%) and Lipozyme RM IM (3.67 ± 1.00%). These results were ascribed to the good tolerability of Novozym 435 in the glycerolysis system. Similar results can also be found in other reaction systems, such as ethanol, methanol, and *t*-butanol (Rosa et al., 2009).

3.2. Effect of reaction system pressure

To evaluate the effect of reaction system pressure on the glycerolysis reaction, experiments were carried out at atmosphere or vacuum pressure under the following conditions: enzyme load of 5% (based on total substrate mass), molar ratio of glycerol to CO of 6:1, and reaction temperature of 90 °C. The results were presented in Fig. 2. There was no significant difference of initial reaction rates, TAG conversions and MRO yields in both systems, which indicated that reaction system pressure has minor influence on the

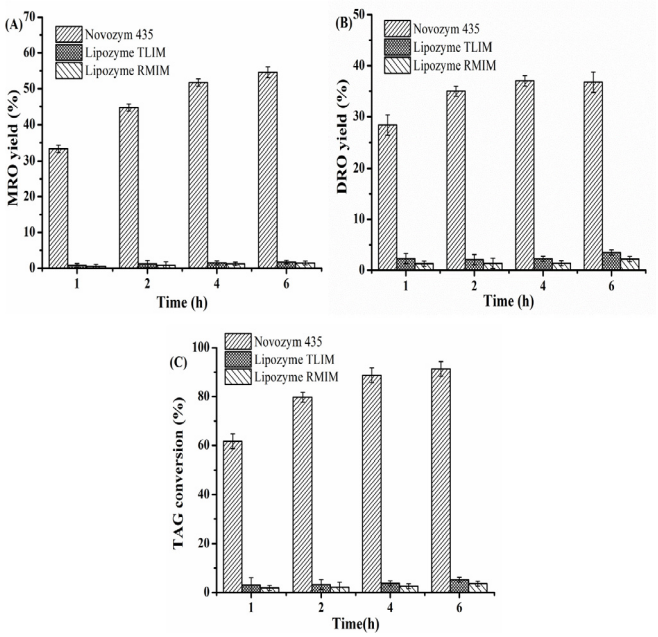

Fig. 1. Effect of enzyme on the glycerolysis of castor oil: (A) MRO yield, (B) DRO yield, (C) TAG conversion. Reaction conditions: atmospheric pressure, 6:1 molar ratio of glycerol to castor oil, enzyme load 5% (w/w, relative to the weight of total substrates) and 90 °C.

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