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Research paper

Catalytic cracking of wax esters extracted from *Euglena gracilis* for hydrocarbon fuel production

Iori Shimada[a,*], Yoshitaka Nakamura[b], Shin Kato[a], Ryohei Mori[b], Haruhisa Ohta[c], Kengo Suzuki[c], Toru Takatsuka[d]

[a] *Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan*
[b] *Graduate School of Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan*
[c] *Research & Development Department, euglena Co., Ltd., 75-1 Ono, Tsurumi-ku, Yokohama, Kanagawa 230-0046, Japan*
[d] *Technology Development Unit, Chiyoda Corporation, 4-6-2 Minatomirai, Nishi-ku, Yokohama, Kanagawa 220-8765, Japan*

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ABSTRACT

Wax esters (WEs) synthesized by *Euglena gracilis* are potential sources for alternative fuels because of their high productivity, recent success in mass cultivation, and low energy consumption in extraction. In this study, deoxygenation of *Euglena* WE and conversion to hydrocarbons in a catalytic cracking process under a hydrogen-free atmosphere was investigated using a residue fluid catalytic cracking equilibrium catalyst with enhanced hydrogen-transfer activity. The deoxygenation of *Euglena* WE proceeded more rapidly with higher H_2O selectivity than that of saturated triglycerides. This is because initial β-elimination of WEs produces saturated fatty acids and higher olefins; the higher olefins rapidly release hydrogen species during cracking, cyclization and aromatization, and the hydrogen species accelerate hydrodeoxygenation of the saturated fatty acids. Furthermore, the cracking of *Euglena* WE produced large amounts of paraffins and olefins instead of aromatics. Therefore, *Euglena* WE was confirmed to be a preferable feedstock for the catalytic cracking process for hydrocarbon fuel production.

1. Introduction

Microalgae have attracted wide attention because they exhibit high growth rates on sites that are unsuitable for agriculture, thus avoiding undesirable competition with food crops. They produce various nutrients and can be used in various applications such as supplements, drugs, and cosmetics. In addition, they are known to produce and store lipids with much higher productivity than conventional plant crops [1]. Therefore, microalgae-derived renewable fuels are expected as potential sources to replace fossil fuels and development of their efficient conversion technology is necessary.

Euglena gracilis is one of such promising microalgae and mass cultivation of it in an open pond has been achieved recently [2]. *Euglena gracilis* synthesizes wax esters (WEs) from paramylon, a *Euglena* specific polysaccharides, when it is brought from aerobic to anaerobic conditions [3], and the lipid yields can reach 50% of cellular dry weight [3,4]. WEs are esters composed of saturated fatty acids and fatty alcohols. The accumulation of WEs is unique to *Euglena* because most other microalgae store lipids as triglycerides (TGs), which are esters composed of glycerol and saturated or unsaturated fatty acids. *Euglena* is also unique in that it has a simple cell structure without cell walls, and therefore accumulated WEs can be extracted easily without requiring energy-consuming disruption of tough cell walls [5,6].

To use WEs as transportation fuels, they can be converted to biodiesel (fatty acid methyl esters; FAMEs) by a transesterification process [7,8]. However, the biodiesel is an oxygen-containing fuel, whose heat value is low and thermal and oxidation stabilities are poor. To improve the heat value and stabilities, deoxygenation of WEs and their conversion to hydrocarbons are important. The deoxygenation of WEs is usually performed using a hydrotreating process [9], but using pressurized hydrogen atmosphere incurs high operation costs. These are common problems with the utilization of TGs as transportation fuels.

In contrast, a fluid catalytic cracking (FCC) process can convert TGs to hydrocarbons under a hydrogen-free atmosphere [10–14]. FCC process is one of the major oil refining technologies that processes feedstocks such as heavy gas oil, vacuum gas oil and atmospheric residue. Typical FCC catalysts consist of zeolite (ultra-stable Y (USY) partly exchanged with rare earth (RE) ions), filler (kaolin clay) and matrix (meso- and macroporous silica or alumina) [15]. The heavy oil feedstocks are converted to high-octane gasoline blend, light olefins

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[*] Corresponding author.
E-mail address: iori@shinshu-u.ac.jp (I. Shimada).

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(propylene and butene), heavy liquid hydrocarbons (light cycle oil; LCO), and coke during cracking, isomerization, cyclization and hydrogen transfer reactions on the acid sites of the USY zeolite. The coke deposited on the catalysts are burned off in the regenerator and the regenerated catalysts are re-used continuously. In addition to these reactions, deoxygenation reaction proceeds in TG cracking and produces H_2O, CO_2 and CO. In particular, we recently found that enhancing the hydrogen-transfer activity in the FCC process is effective for removing oxygens in TGs as H_2O [16]. The formation of H_2O rather than CO_2 and CO is an efficient reaction because all the carbon resources contained in TGs can be converted to hydrocarbons without carbon loss. Therefore, the FCC with enhanced hydrogen-transfer activity is considered to be a promising process for alternative fuel production. However, the catalytic cracking of WEs has, insofar as we are aware, not been reported. In this study, we therefore investigated the deoxygenation of WEs in a catalytic cracking process and compared their reaction with that of TGs.

2. Materials and methods

2.1. Materials

An equilibrium catalyst (E-cat), which was obtained from a commercial residue FCC (RFCC) unit, was used for all the catalytic cracking experiments. The RFCC E-cat is known to exhibit strong hydrogen transfer activity because its hydrothermal stability in the reactor-regenerator cycle was enhanced by the high RE loading on the USY zeolite. The effect of RE loading on the catalyst stability and hydrogen transfer activity has been discussed in the literature [17–20].

The *Euglena* WE, which was extracted from *Euglena gracilis*, was purified and supplied by euglena Co., Ltd. The composition of fatty acids and fatty alcohols of the *Euglena* WE was analyzed using the method reported by Inui et al. [4] and Ichihara and Fukubayashi [21]. WEs were converted to FAMEs and fatty alcohols, which were analyzed using a gas chromatography (GC) system (GC-390B, GL Sciences Inc., Tokyo, Japan) equipped with a flame ionization detector (FID) using He as a carrier gas. The packed columns used for fractionating FAMEs and fatty alcohols were a 3 m-length Unisole 3000 coated on Uniport C 80/100 (GL Sciences Inc.) and a 1 m-length PEG-HT coated on Uniport HP 60/80 (GL Sciences Inc.), respectively. As shown in Table 1, the *Euglena* WE mainly consisted of myristyl myristate. In addition, coconut oil (Kaneda Shoji Co., Ltd., Tokyo, Japan) and sunflower oil (Wako Pure Chemical Industries, Ltd., Osaka, Japan) were also used as reactants. Both coconut and sunflower oil consist of TGs, but their fatty acid composition is different. Coconut oil consists mainly of saturated C_{12} and C_{14} fatty acids (46.9 mol% and 15.7 mol%, respectively), whereas sunflower oil consists mainly of C_{18} unsaturated fatty acids (88.5 mol %). The detailed fatty acid compositions of the two plant oils were reported previously [16].

2.2. Catalytic activity tests

Catalytic activity tests were conducted in a fixed-bed microactivity test reactor, details of which were given in a previous publication [22]. In each trial, E-cat (1.9–5.3 g) was placed in the reactor, which was maintained at 470 °C. The feedstock (*Euglena* WE, coconut oil and sunflower oil) was fed into the reactor using a microfeeder while being heated electrically in a preheating line. The feed injection time was 75 s and the weight hourly space velocity (WHSV) was varied between 12 and 33 h^{-1}. For these conditions, the weight ratio of the catalyst to the oil (cat/oil) was in the range of 1.5–4.0. N_2 gas was added during feed injection at 19 mL min^{-1}. After each test, the catalyst was stripped by purging with N_2 gas at 5 mL min^{-1} for 15 min. During the reaction and stripping stages, the liquid products were collected in a cold trap with two receiving vessels connected in series and maintained at 0 and -15 °C, respectively. Simultaneously, the gaseous products were collected in a gas burette by displacement of a saturated NaCl solution. For all experiments, a mass balance across the collected products was found to be in the range of 92–104 wt% of the process inputs.

The amounts of H_2, N_2, CO_2 and CO in the gaseous products were determined using a GC system (GC-8A, Shimadzu Corp., Kyoto, Japan) equipped with a packed column (SHINCARBON-ST 50/80, Shinwa Chemical Industries, Ltd., Kyoto, Japan) and a thermal conductivity detector (TCD) with Ar as the carrier gas. Hydrocarbons and oxygenates were analyzed with another GC system (GC-2014, Shimadzu Corp.) fitted with a capillary column (BP1, SGE Analytical Science Pty. Ltd., Victoria, Australia) and FID with He as the carrier gas. Biphenyl (99.5%, Sigma-Aldrich Co., St. Louis, MO, USA) was used as the internal standard in the GC-FID assay. Quantification of the hydrocarbons and oxygenates was based on the effective carbon number theory [23]. The amount of coke deposited on the catalyst was determined from the difference between the mass of the reactor before and after testing. Three hydrocarbon fractions were defined based on carbon number or boiling point thresholds: gaseous hydrocarbons ($C_1 - C_4$); gasoline (C_5 – 216 °C) and LCO (216 °C –). In addition, jet fuel fraction was defined as carbon number range of $C_{10} - C_{15}$.

3. Results

3.1. Reaction products of WE cracking

The reaction product yields from the catalytic cracking of *Euglena* WE are shown in Fig. 1 and compared with those from coconut oil (saturated TG) and sunflower oil (unsaturated TG), which were

Table 1
Fatty acid and fatty alcohol compositions of *Euglena* WE used in this study.

Fatty acid [carbon number:double bond]	Composition [mol%]	Fatty alcohol [carbon number:double bond]	Composition [mol%]
Capric acid [10:0]	Trace	Capric alcohol [10:0]	Trace
Undecanoic acid [11:0]	Trace	Undecyl alcohol [11:0]	Trace
Lauric acid [12:0]	8.1	Lauryl alcohol [12:0]	5.6
Tridecanoic acid [13:0]	9.3	Tridecyl alcohol [13:0]	10.6
Myristic acid [14:0]	57.8	Myristyl alcohol [14:0]	50.9
Pentadecanoic acid [15:0]	2.5	Pentadecyl alcohol [15:0]	7.3
Palmitic acid [16:0]	9.3	Palmityl alcohol [16:0]	20.9
Palmitoleic acid [16:1]	1.6	Heptadecyl alcohol [17:0]	0.7
Heptadecanoic acid [17:0]	Trace	Stearyl alcohol [18:0]	1.5
Stearic acid [18:0]	1.9	Oleyl alcohol [18:1]	2.5
Oleic acid [18:1]	4.6		
Linoleic acid [18:2]	1.5		
Eicosadienoic acid [20:2]	1.2		
Eicosatrienoic acid [20:3]	1.1		
Eicosatetraenoic acid [20:4]	1.0		