Spent coffee ground as source for hydrocarbon fuels

Peter Döhlert [a], Maik Weidauer [a], Stephan Enthaler [a,b,*]

[a] *Technische Universität Berlin, Department of Chemistry, Cluster of Excellence "Unifying Concepts in Catalysis", Straße des 17. Juni 135/C2, D–10623 Berlin, Germany*
[b] *Universität Hamburg, Department of Chemistry, Martin-Luther-King-Platz 6, D–20146 Hamburg, Germany*

ARTICLE INFO

ABSTRACT

The conversion of triglycerides (coffee oil) obtained from spent coffee ground to produce hydrocarbon fuel (diesel) was studied. In more detail, a catalytic hydrodeoxygenation of the coffee oil was performed applying polymethylhydrosiloxane (PMHS) as cheap reductant under mild reaction conditions. However, along with the hydrocarbons significant amounts of PMHS-waste are generated, since only ~1.7% of the PMHS is required for the reduction process. Based on that, in a subsequent depolymerization step the PMHS-waste was converted to methyltrifluorosilane and difluoromethylsilane, which can be applied as building blocks for the production of new silicones, with boron trifluoride diethyl etherate (BF_3OEt_2) as depolymerization reagent.

© 2015 Science Press and Dalian Institute of Chemical Physics. All rights reserved.

1. Introduction

The most important challenge for the future is to secure an adequate supply of energy. Current feedstocks are based primarily on fossil resources which causes a manifold of problems. The confirmed reserves of fossil resources are gradually decreasing, and their depletion is merely a matter of time [1]. Additionally, the negative impact of today's consumer society on the environment and natural resources, namely the emission of greenhouse gases associated with global warming, is evident. The fundamental influence of the greenhouse effect on future generations and the depletion of fossil resources are the subjects of recent controversies. Owing to these problems, one of the most decisive issues for current society must address to the development of a more sustainable society [2]. An alternative for crude oil reserves can be the application of renewable resources [3]. For instance biodiesel (fatty acid esters) produced from natural lipids (e.g., rapeseed oil, palm oil, soybean oil) by transesterification has been established as eco-friendly fuel [4]. In order to completely substitute the fossil fuels by renewable resources various ecological, economic and social issues (e.g. competition for land and uses) will arise [5]. A suitable supportive approach towards biodiesel can be the conversion of waste products (e.g. waste natural oils) [6]. In this regard, the use of spent coffee ground has been reported as potential source for biodiesel and other chemicals, since every year ~8 million tonnes of coffee are produced [7]. In more detail, coffee beans typically contains an average of 15 wt% of lipids, which can be easily extracted and via transesterification with methanol or ethanol converted to the corresponding fatty acid ester (fatty acid methyl ester-FAME or fatty acid ethyl ester-FAEE) [8]. Based on the amount of produced coffee (up to 1.3 billion liters), biodiesel could replace fossil fuels [9]. However, the efficient collection of the waste products is still a challenging target. Moreover, fuels containing fatty acid alkyl esters (FAAEs) have several drawbacks, e.g., low fluidity, high oxygen content, poor thermal oxidation stability [10]. Based on that, the transformation of the triglycerides or fatty acid alkyl ester towards hydrocarbons (diesel) via hydrodeoxygenation can be an option [11]. Recently, several methods have been reported to convert ester functions to hydrocarbons. For instance Fu and coworkers demonstrated the conversion of defined triglycerides as well as fatty acid methyl esters to hydrocarbons applying tris(pentafluorophenyl)borane as catalyst under mild reaction conditions (Scheme 1) [12]. In more detail, as reducing reagent an excess of polymethylhydrosiloxane (PMHS, R[OSiMeH]$_n$OR, 9-18 equiv.), an abundant, cheap, low-toxic, air and moisture stable product from silicone industry was applied [13]. However, along with the desired hydrocarbons significant amounts of silicon-waste is produced, since only ~1.7% of the PMHS is employed for the reduction process [14]. For instance the production of 1 g octadecane from tristearin resulted in the formation of ~1.5 g PMHS-waste, which reduces the sustainability of the protocol. In this regard, depolymerization methods can be valuable to convert the silicon-waste to useful commodities, therefore increasing the sustainability of the hydrodeoxygenation protocol. Recently, we established several methods for the recycling of poly(dimethylsiloxanes) waste [15,16]. For instance applying boron trifluoride diethyl etherate (BF_3OEt_2) as depolymerization

---
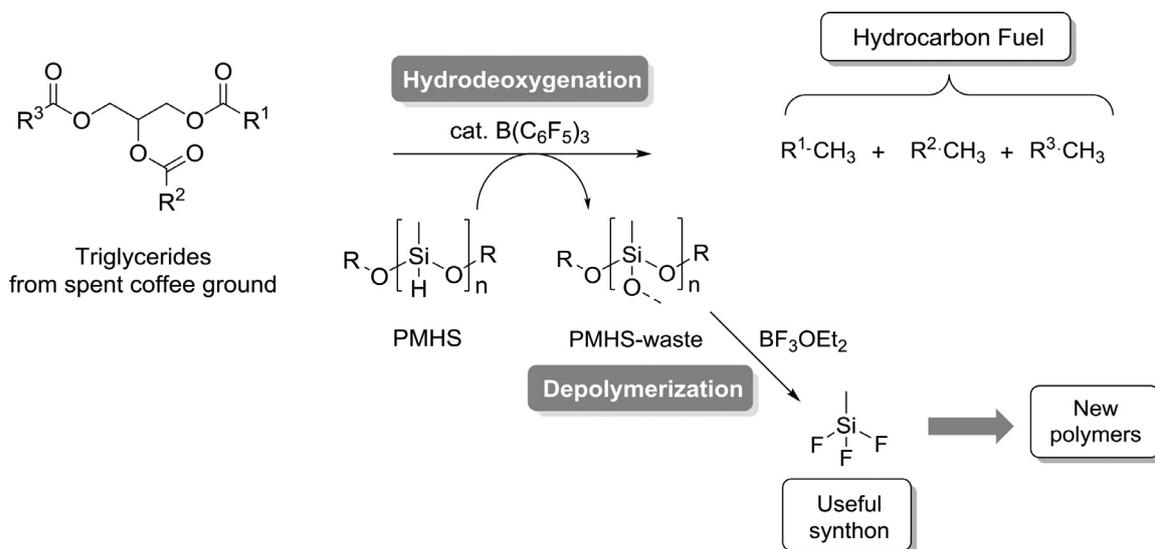
Scheme 1. Hydrodeoxygenation of triglycerides and subsequent depolymerization of produced PMHS-waste.

reagent the end-of-life poly(dimethylsiloxanes) are converted to difluorodimethylsilane and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane, which are useful synthons for new silicones by simple reaction with water and a base [15,16]. A transfer of this concept to the depolymerization of PMHS-waste will produce difluoromethylsilane ($MeSiF_2H$) or methyltrifluorosilane ($MeSiF_3$) as potential building blocks for new polymers or co-polymers and allows overall a recycling of the [MeSi]-unit [13d,17].

Based on that, we present herein the hydrodeoxygenation of triglycerides and fatty acid ethyl esters obtained from spent coffee ground with PMHS as reductant to produce hydrocarbons and a subsequent depolymerization of the PMHS-waste to generate synthons for silicon chemistry.

2. Experimental

2.1. Reagents

Coffee beans (Caffé Crema, 100% Arabica) were received from Tchibo GmbH. Coffee Pads (Senseo Classic, mixture of Arabica and Robusta) were received from Douwe Egberts Senseo. Cyclohexane, dichloromethane, poly(methylhydrosiloxane), tris(pentafluorophenyl)borane, boron trifluoride diethyl etherate were received from Sigma Aldrich, TCI and ABCR in their highest purity and used without further purification steps. Dichloromethane for hydrodeoxygenation was dried using standard techniques and was stored over molecular sieves under an atmosphere of dinitrogen.

2.2. Products analysis

^{1}H, ^{13}C{^{1}H}, ^{19}F and ^{29}Si{^{1}H} NMR spectra were recorded on a Bruker Avance II 200 MHz (^{1}H: 200.13 MHz; ^{13}C: 50.32 MHz; ^{19}F: 188.31 MHz; ^{29}Si: 39.71 MHz) or Bruker Avance II 400 (^{1}H: 400 MHz; ^{13}C: 101 MHz) using the proton signals of the deuterated solvents or standards as reference. GC-MS measurements were carried out on a Shimadzu GC-2010 gas chromatograph (30 m Rxi-5ms column, 40–300 °C) linked with a Shimadzu GCMA-QP 2010 Plus mass spectrometer.

2.3. Procedure for the extraction of triglycerides (coffee oil) from spent coffee ground (Tchibo)

The coffee (Caffé Crema, 100% Arabica, Tchibo GmbH) was brewed with a Saeco Intelia. Noteworthy, the coffee beans were grinded and the coffee ground was collected by the Saeco Intelia. The coffee ground was dried in an oven for 12 h at 60 °C. Afterwards the coffee ground (11 g) was placed in a Soxhlet extractor and extracted with cyclohexane (100 mL) at reflux conditions. After 2 h the system was cooled to room temperature. The defatted coffee ground was dried and was weighed (9.1 g). The solvent of the extract was removed in vacuum (91 mL of the cyclohexane were recovered) and the residue was dissolved in dichloromethane (50 mL); residues of water were removed in a separatory funnel and the clear solution was dried with sodium sulfate. After filtration of the sodium sulfate the solvent was removed to obtain an orange–brown coffee oil **1a** (1.89 g). ^{1}H NMR (400 MHz, CDCl$_3$, 25°C) δ = 5.29–5.47 (m, C*H*=C*H*, C*H*–O), 4.11–4.39 (m, CHC*H*$_2$O), 2.80–2.83 (m), 2.34–2.43 (m), 2.04–2.14 (m), 1.67–1.72 (m), 1.25–1.44 (m), 0.89–0.97 (m) ppm. ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 25°C) δ = 178.9, 173.31, 173.29, 172.9, 130.2, 130.0, 129.97, 129.7, 129.30, 128.10, 128.07, 127.91, 127.90, 68.9, 65.1, 62.1, 34.2, 34.1, 34.0, 33.9, 32.0, 31.5, 29.8, 29.73, 29.70, 29.64, 29.55, 29.51, 29.48, 29.39, 29.37, 29.35, 29.30, 29.23, 29.15, 29.11, 29.07, 27.21, 26.93, 25.6, 24.9, 24.7, 22.6, 14.13, 14.08 ppm.

2.4. Procedure for the extraction of triglycerides (coffee oil) from spent coffee (Senseo)

The experiment was performed in analogy to procedure 2.3 extracting the coffee oil from spent coffee pads (Senseo) (29.7 g) by placing the coffee pads in a flask and refluxing with cyclohexane. An orange–brown coffee oil **1b** was obtained (1.9 g). ^{1}H NMR (400 MHz, CDCl$_3$, 25°C) δ = 5.17–5.35 (m, CH=CH, CH–O), 4.06–4.25 (m, CHCH$_2$O), 2.68–2.71 (m), 2.21–2.28 (m), 1.91–2.00 (m), 1.49–1.61 (m), 1.15–1.31 (m), 0.78–0.84 (m) ppm. ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 25°C) δ = 173.29, 173.24, 172.8, 130.2, 130.0, 129.98, 129.7, 128.10, 127.9, 68.9, 62.1, 34.2, 34.1, 34.0, 31.9, 31.5, 29.8, 29.72, 29.68, 29.64, 29.55, 29.50, 29.38, 29.37, 29.35, 29.29, 29.21, 29.19, 29.14, 29.10, 29.06, 27.21, 26.93, 25.6, 24.9, 22.7, 22.6, 14.13, 14.08 ppm.

2.5. Transesterification of the triglycerides from spent coffee ground (Tchibo)–Fatty acid ethyl esters

The coffee oil **1a** (1.0 g from procedure 2.3) was dissolved in ethanol (10 mL) and H$_2$SO$_4$ (0.1 g) was added at room temperature. The mixture was stirred for 12 h at room temperature. The solvent was removed in vacuum and the residue was dissolved in cyclohexane (10 mL) and washed with water (10 mL), brine (10 mL) and dried with sodium sulfate. After filtration the solvent was removed to yield

دانلود مقاله

daneshyari
دانـشیـاری

✔ امکان دانلود نسخه تمام متن مقالات انگلیسی

✔ امکان دانلود نسخه ترجمه شده مقالات

✔ پذیرش سفارش ترجمه تخصصی

✔ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله

✔ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب

✔ دانلود فوری مقاله پس از پرداخت آنلاین

✔ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات