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Synthesis of Biodiesel without Formation of Free Glycerol

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Abstract—A new approach to the synthesis of biodiesel has been developed on the basis of alcoholysis of a triglyceride in combination with acetalization of glycerol with lower carbonyl compounds or acetals derived therefrom. A model synthesis of biodiesel not involving free glycerol has been accomplished using rapeseed oil and acid catalysts, as well as without a catalyst under generation of ethanol supercritical fluid; in the latter case, monoalkyl glycerol ethers are formed in addition to the expected cyclic ketals.

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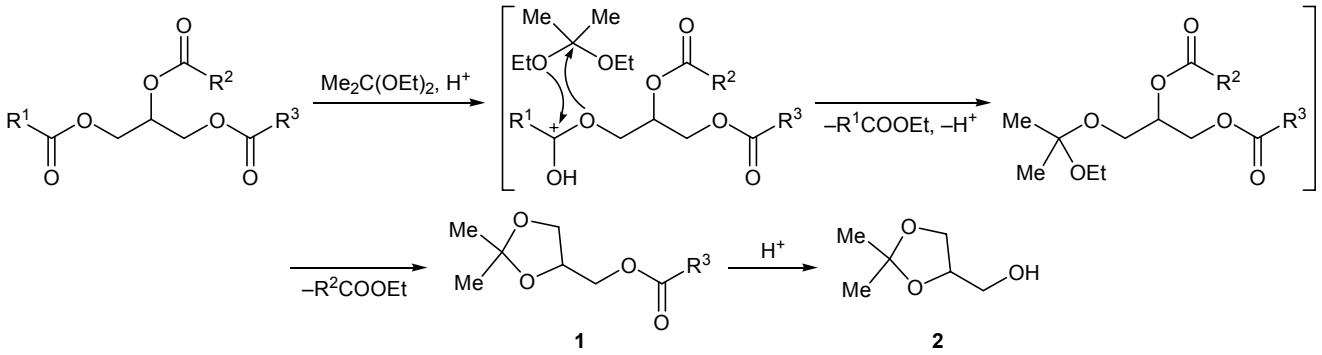
Modern biodiesel production by alkaline alcoholysis of vegetable triglycerides involves the problem of utilization of glycerol formed as by-product. Its subsequent use in organic synthesis to obtain dihydroxyacetone, acrylic acid derivatives, etc., requires refinement which is associated with additional expenditures, so that the efficiency of the main production is reduced. Therefore, many biodiesel manufacturers consider crude biodiesel glycerol as waste material. Taking into account the above stated, it seems reasonable to search for new approaches to the synthesis of biodiesel without formation of free glycerol.

A probable version is a combined process including alcoholysis of triglyceride and ketalization of glycerol. Cyclic ketals resulting from condensation of glycerol with lower carbonyl compounds (such as acetone, ethyl methyl ketone, acetaldehyde, etc.) have recently been found to possess a variety of properties which make it possible to consider them a new liquid biofuel. The addition of cyclic ketals to alcohol-containing gasoline increases the octane number and enhances the phase stability [1], reduces diesel exhaust opacity [2], inhibits thermooxidative degradation [3], and promotes defrosting effect [4]. Thus, a combined alcoholysis–ketalization process should ensure complete utilization of the intrinsic potential of triglyceride in the synthesis of a binary fuel composition. Implementation of this process requires only replacement of alkaline catalyst (commonly used in the synthesis of biodiesel) by acid one. In this article we describe a model synthesis in the presence of sulfuric acid, *p*-toluenesulfonic acid, and a polymeric sulfonic acid cation exchanger in the H form (Amberlyst 15). Lower carbonyl compounds (acetone, acetaldehyde, and butyraldehyde) and the corresponding diethyl acetals were used for the ketalization. The latter ensured the absence of water and free fatty acids in the reaction mixture.

The conversion of triglyceride (rapeseed oil) in the reaction with acetone diethyl acetal and ethanol at a ratio of 1 : 2 : 10 was considerably faster than the alcoholysis in the absence of ketal, which required several times longer time (about 40 h). This suggests that the cyclic ketal is formed directly from the triglyceride and that the entering alkenyl fragment promotes elimination of the acyl group. The combined alcoholysis–ketalization process is synchronous, and no free glycerol is formed. This interpretation is consistent with intermediate formation of 4-(acyloxymethyl)-2,2-dimethyl-1,3-dioxolane (**1**) which is then transformed into final 2,2-dimethyl-1,3-dioxolan-4-ylmethanol (**2**) (Scheme 1).

The combined process with participation of aldehydes or acetals derived therefrom is characterized by a different ratio of isomeric five- and six-membered cyclic acetals **3** and **4** as compared to the acetalization of free glycerol. For example, the ratio **3**/**4** changes

Scheme 1.



R^1, R^2, R^3 = long-chain alkyl.

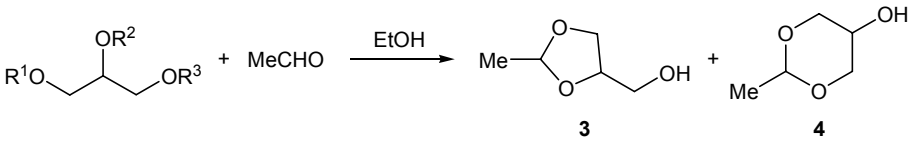
from 83:17 (from glycerol) to 68:32 (from triglyceride), which is naturally related to more facile removal of the acyl groups from positions *1* and *3* of the triglyceride (Scheme 2).

Conditions ensuring generation of ethanol supercritical fluid provide additional possibilities of the combined process. Under these conditions, the reaction time is shortened to a few minutes, the amount of alcohol is reduced, and no catalyst is necessary. In the system triglyceride–acetone–ethanol (1:2:4) at 350°C and a pressure of ~300 bar, the conversion of triglyceride attained 75% in 30 min. The reaction mixture was homogeneous, and it contained the expected fatty acid ethyl esters (biodiesel) and dioxolane **2**, as well as some glycerol derivatives which were detected by GC/MS, in particular dioxolane **3**, 3-ethoxypropane-1,2-diol (**5**), 3-isopropoxypropane-1,2-diol (**6**), 2,3-epoxypropan-1-ol, and bis(hydroxymethyl)dioxane (Scheme 3). The formation of this set of products indicates a more complex transformation sequence, including exchange redox interaction between ethanol and acetone with generation of an isopropyl alcohol–acetaldehyde couple which then participates in the process.

EXPERIMENTAL

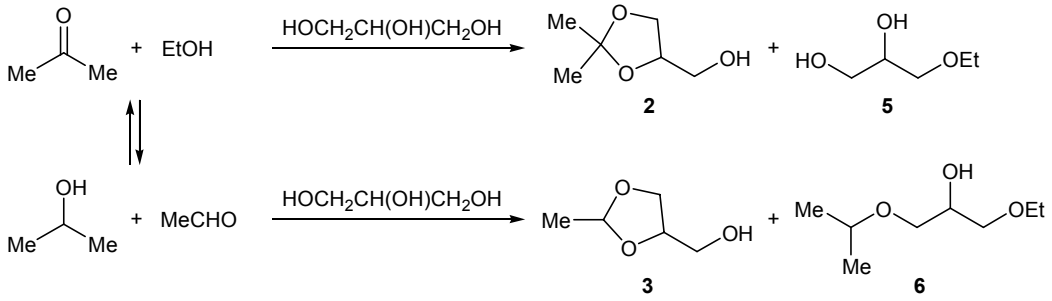
The ^{1}H NMR spectra were recorded on a Bruker Avance 500 spectrometer from solutions in $CDCl_3$ using tetramethylsilane as internal standard. GC/MS analyses were obtained on a Trace-1310 gas chromatograph coupled with an ISQ mass-selective detector (TR-5MS quartz capillary column, 15 m × 0.32 mm, stationary phase 5% phenyl polysilphenylene-siloxane, film thickness 0.25 μm; oven temperature programming from 40 to 290°C at a rate of 15 deg/min and 5 min at the final temperature; injector and interface temperature 250°C; carrier gas helium; sample volume

Scheme 2.



$R^1 = R^2 = R^3$ = H or R^1, R^2, R^3 = long-chain acyl.

Scheme 3.



1 μL, split ratio 1:40; electron impact, 70 eV); the chromatograms were recorded by the total ion current (scan range 30–450 a.m.u.). The components were identified using NIST-2011 database taking into account general rules of fragmentation of organic compounds under electron impact. A 5-μL sample was withdrawn and diluted with 200 μL of chloroform, the mixture was shaken, and 1 μL was injected into the chromatograph. The reaction mixtures were also analyzed by TLC on Silufol UV-254 plates using hexane–diethyl ether (1:1) as eluent and by ^{1}H NMR. A continuous flow setup [5] was used to perform alcoholysis of rapeseed oil in ethanol supercritical fluid.

Commercially available rapeseed oil was used as model triglyceride. Ethanol was distilled over calcium hydride. Acetone, acetaldehyde, and butyraldehyde diethyl acetals were prepared by heating the corresponding carbonyl compounds in excess ethanol under reflux in the presence of 0.1 wt % of concentrated sulfuric acid and molecular sieves with a water capacity of 16–18%.

A reference sample of acetal formed by the reaction of acetaldehyde with glycerol (a mixture of isomers **3** and **4**) was synthesized according to the procedure described in [6]; bp 78–79°C (5 mm). ^{1}H NMR spectrum, δ, ppm: 1.21 d and 1.28 d (CH_3 in **4**, J = 5.4 Hz), 1.32 d and 1.37 d (CH_3 in **3**, J = 4.7 Hz), (3H, CH_3), 2.60 br.s (1H, OH), 3.58 m and 3.65 m (2H, C**H**$_2$OH), 3.80 d.d and 3.81 d.d (2H, CH_2, J = 11.9, 8.0 Hz), 4.15 m and 4.20 m (1H, CH), 4.55 q and 4.69 q (1H, CH in **4**, J = 5.4 Hz), 5.02 q and 5.10 q (1H, CH in **3**, J = 4.7 Hz).

A reference sample of dioxolane **1** was prepared by transesterification of rapeseed oil with an equivalent amount of dioxolane **2** in the presence of sodium hydroxide (1 wt %) under stirring at 80°C. The progress of the reaction was monitored by TLC. The target product was separated from glycerol, residual triglyceride, and dioxolane **2** by preparative TLC and was identified by ^{1}H NMR. ^{1}H NMR spectrum, δ, ppm: 0.92 m [3H, C**H**$_3$(CH$_2$)$_n$], 1.32 m (CH_2), 1.36 s (3H, CH_3), 1.42 s (3H, CH_3), 1.63 m (2H, CH_2), 2.02–2.07 m (4H, CH_2), 2.33 t (2H, CH_2CO, J = 7.2 Hz), 4.16 d.d (1H, CH, J = 5.9, 12.0 Hz), 4.30 d.d (1H, CH, J = 4.4, 12.0 Hz).

Acid-catalyzed alcoholysis of triglyceride. A mixture of 9 g (0.01 mol) of rapeseed oil, 30 mL of ethanol, and 0.1 g of concentrated sulfuric acid or 0.5 g of Amberlyst 15 was heated for 38–40 h under reflux with stirring until almost complete conversion of the initial triglyceride (TLC). The mixture was neutralized with calcium oxide or ion exchanger was filtered off. Excess alcohol was removed on a rotary evaporator, and the residue was analyzed by GC/MS. It contained fatty acid (stearic, oleic, palmitic, linoleic, etc.) ethyl esters. The product was then used as a reference sample of biodiesel.

Combined alcoholysis of rapeseed oil with acetaldehyde diethyl acetal. The procedure was the same as above. The product isolated by vacuum distillation (bp 78–79°C/5 mm) was analyzed by ^{1}H NMR. Its spectral parameters corresponded to reference mixture **3**/**4** (see above) with the difference that the fraction of **4** was 32% against 17% in the reference sample.

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