An Efficient Method for the Transformation of High Fatty Acid Containing Vegetable Oils to Biodiesel Fuels

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(Received August 7, 2008; CL-080766; E-mail: kotail@mail.chemres.hu)

Transesterification of fatty acid containing used or nonfood type vegetable oils with methanol in the presence of partially hydrated calcium oxide has been performed. The calcium soaps formed are treated with sulfuric acid without separation from the ester phase, and the free acids formed are immediately converted to ester with the excess of methanol and the sulfuric acid (as catalyst).

Biodiesel fuels based on vegetable oils have an increasing importance to satisfy the demand for renewable energy or sources.[1] However, their production from nonfood quality vegetable oils with high fatty acid contents (up to 15 wt %) is not economical. This is due to the high alkaline catalyst (KOH and NaOMe) consumption and to the formation of surface active soaps interfering with the catalyst removal by aqueous washing.[2]

In the process presented here, CaO has been used for the neutralization of the fatty acids as well for catalysing the transesterification process at reflux temperature. CaO is a cheap industrial alkaline chemical, and its soaps are insoluble in water and are not surface active agents. The calcium soaps formed are dispersed/dissolved in the ester phase containing the residual methanol from the transesterification. They react with the sulfuric acid then the fatty acids formed are transformed to esters in a H_2SO_4-catalysed reaction.

$$\mathrm{Ca(OOC{-}R)_2 + H_2SO_4 = CaSO_4 + 2R{-}COOH} \qquad (1)$$

$$\mathrm{R{-}COOH + MeOH = R{-}COOMe + H_2O} \qquad (2)$$

The efficiency of the transesterification process strongly depends on the amount of the CaO and H_2O used. The results are given in Table 1.

As it can be seen from Table 1, partial slaking and methanol excess have increased the conversion. The optimal yield was observed at $CaO:H_2O = 1:1$ molar ratio because of $Ca(OH)_2$ formation. The increased amount of CaO is needed to retain the free fatty acids in Ca soap form. The sequence of the reagent addition can also affect the conversion because of the dissolution rate of the solid CaO catalyst precursor. The amount of the dissolved calcium soaps varied between 1–3% (expressed as CaO).[5] In order to decrease the ash content of the ester phase and transform the fatty acid content into esters, a slight excess of the concentrated sulfuric acid toward the used CaO was added and the mixture was refluxed for 3 h. The sulfuric acid has multiple roles in this system: 1) it forms calcium sulphate and releases fatty acids, 2) catalyzes the reaction between the fatty acid formed and the residual methanol from the transesterification step, 3) destroys the thermally and chemically sensitive polyunsaturated compounds which could cause deposits in the engine.[6]

Table 1. Degree of transesterification (HPLC-MS)[3] with partially slaked calcium oxide[4]

CaO[a]	H_2O[a]	MeOH[a]	t/h	ME[b]	TG[b]	DG[b]
1.4	1.4	20	1	17	56	27
1.4	1.4	30	1	42	46	12
2.1	0.7	20	1	90	9	1
2.1	1.4	20	1	55	34	11
2.1	2.1	20	1	19	59	22
4.2	1.4	40	1	100	—	—

[a]Starting material is 100 g vegetable oil (6.7% free acid content), the amount of solid CaO, H_2O, and MeOH are given in grams. [b]ME, TG, and DG means the amount of methyl ester, triglycerides, and diglycerides in wt %, respectively. Monoglycerides could not be detected.

Since the optimal transesterifications were performed at twofold excess of methanol, the residual methanol content ensures a large methanol excess in the esterification reaction of the liberated fatty acids.

Anhydrous $CaSO_4$ formed in reaction (1) promotes the esterification reaction with binding of the H_2O formed in reaction (2) and shifts the esterification equilibrium. Calcium sulphate has two hydrated forms, calcium sulfate hemihydrate ($CaSO_4 \cdot 0.5H_2O$) and dihydrate ($CaSO_4 \cdot 2H_2O$). Instead of the presence of 2 equiv water formed, the IR spectrum of the hydrated calcium sulphate isolated from the reaction mixture (Figure 1) shows only one OH deformation band ($\nu_d = 1605\,\mathrm{cm^{-1}}$), and the intensity area (2:1) of the symmetric and asymmetric O–H stretchings (ν_{as} and $\nu_s = 3600$ and $3550\,\mathrm{cm^{-1}}$, resp.) shows the presence of the hemihydrate exclusively.[7] $CaSO_4 \cdot 2H_2O$

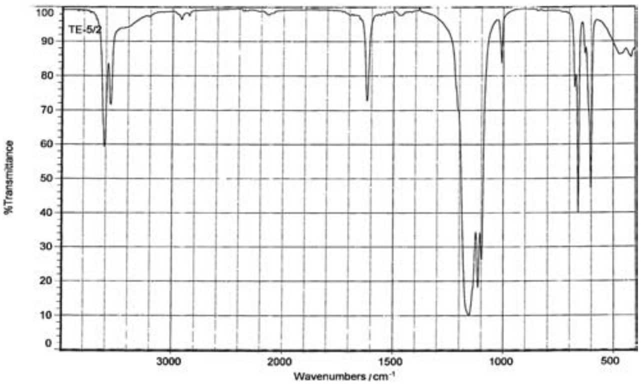

Figure 1. IR spectrum of hydrated calcium sulphate hemihydrate formed in the calcium soaps–methanol-concentrated sulphuric acid system.

Table 2. Deacidification of biodiesel products with MCO_3 ($M = Fe$ and Ca) powders

Deaciding agent and amount in g[10]		Time /h	Acid number mg KOH/g	Ash content /wt %
—			3.18	0
Ca	1	1	2.97	0
Ca	1	2	2.95	0
Ca	2	1	2.95	0.36
Ca	3	1	2.77	0.39
Ca	4	1	2.70	0.48
Fe	1	1	3.06	0
Fe	2	2	2.95	0
Fe	2	1	3.03	0
Fe	2	2	2.86	0

Table 3. Main parameters of biodiesel fuels formed in a combined ion-exchange and vacuum distillation process

Parameter	IE[a]	VD[a]
Ester content/% (v/v)	>99	>99
Carboxylic acid/carboxylate	<1	<1
Glycerides	ND[a]	ND[a]
Ash content	ND[a]	ND[a]
Acid number	1.25	1.24
Boiling point/°C		
Starting	327	327
End	353	352
Conradson number	0.39	0.30
Density (15 °C)/kg dm^{-3}	0.885	0.8852
Viscosity (20 °C)/mm^2 s^{-1}	6.81	6.61
Viscosity (40 °C)/mm^2 s^{-1}	4.37	4.41
Sulfur content/mg kg^{-1}	110	43
Cetan index	47.0	47.3
Cold filter plugging point/°C	−5	−8

[a] IE: ion exchange, VD: vacuum distillation; ND: not detectable.

which could bind all of the water formed in reaction (2) was not formed at all. Although water binding of the calcium sulphate hemihydrate is a well-known process (plaster of paris), organic materials can affect its setting.[8] In our case they can completely inhibit the setting process. The solid $CaSO_4 \cdot 0.5H_2O$ formed can be used as a sulfur fertilizer for high sulfur-demanding oily plants. The sulfur uptake of oily plants is extremely high, e.g. this value for rape is 100–200 kg of SO_3/ha/year.[9] Since the most efficient sulfur fertilization form is the sulphate ion, the sparingly soluble $CaSO_4 \cdot 2H_2O$ formed in the soil via hydration (solubility is 0.200 g/100 mL of water[8]) becomes an appropriate sulfur source (SO_3 content of $CaSO_4 \cdot 0.5H_2O$ is 55%). In this way the only incombustible residue of the present technology could be turned into a useful materal. The calcium soaps separated from the glycerol phase can be recycled to the ester phase before adding the sulfuric acid. Destroying the thermally and chemically sensitive polyunsaturated compounds with sulfuric acid, however, leads to the formation of some acidic by-products (acid number is 3.18 mg KOH/g oil).[6]

It is essential to remove these acids from the ester phase. As a common way, filtering the ester phase through carbonate type mineral granulates such as calcium carbonate (calcite) or iron carbonate (siderite) proved to be only slightly efficient; however, the ash content increased in the case of calcium carbonate (Table 2). It can be attributed to the formation of some soluble oleophilic calcium compounds. Using Varion ADA resin[11] column or vacuum fractional distillation (15 Hgmm) provided acceptable quality of the products. The main parameters are given in Table 3. The lack of ash content (Table 3) shows the complete elimination of the calcium-based catalyst with this method. Table 3 shows that the product obtained meets with the requirements of the national standards and can be mixed as blend components to various commercial diesel fuels.

References and Notes

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4 In a typical experiment 100 g of vegetable oil, a given amount of water and methanol were added to the catalyst, then the mixture was refluxed for 1 h. The catalyst was dissolved in the reaction mixture after 15 min.

5 Soap-containing oils were mixed with hexane, ignited by open flame and the carbon-containing ash was calcined at 1000 °C for 2 h.

6 It has been concluded from the iodine number (depending on the amount of the polyunsaturated compounds) and the acid/carboxylate content of the oils before and after the sulfuric acid treatment.

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10 One hundred g of vegetable oils was treated with a given amount of carbonate mineral powder (100 mesh) for a determined time. The ash content was determined gravimetrically after ashing the sample.

11 Trimethylammonium-type slightly crosslinked styrene–divinylbenzene macroporous ion exchanger in OH-form.

Published on the web (Advance View) September 13, 2008; doi:10.1246/cl.2008.1076