

# Preparation of Rapeseed Oil Esters of Lower Aliphatic Alcohols

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**ABSTRACT:** Rapeseed oil esters with lower aliphatic alcohols (C<sub>1</sub>–C<sub>4</sub>) were prepared in simple batch mode using an alkali (KOH) or acid (H<sub>2</sub>SO<sub>4</sub>) catalyst. The transesterification reaction conditions were optimized in order to obtain high yields of esters of the quality defined by standards for biodiesel fuels and for a short reaction time. Under these conditions it was possible to prepare only the methyl and ethyl esters catalyzed by KOH. Propyl and butyl esters were obtained only under acid catalysis conditions. The reaction catalyzed by H<sub>2</sub>SO<sub>4</sub> was successfully accelerated using slightly higher catalyst concentrations at the boiling points of the alcohols used. The branched-chain alcohols reacted more slowly than their linear homologs, while *t*-butanol did not react at all. It was also possible to transesterify rapeseed oil using a mixture of alcohols characteristic of the end products of some fermentation processes (e.g., the acetone–butanol fermentation). A simple calculation was made which showed that, because of the higher price of longer-chain alcohols and because of the more intensive energy input during production the esters of these alcohols, they are economically unfavorable as biodiesel fuels when compared with the methyl ester.

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Pure and filtered plant oils (e.g., rapeseed, soybean, sunflower, peanut) or even animal fats can be applied as fuel substitutes for rugged indirect injection diesel engines, as has been known since the first use of tractors (1) or for special engines like the Duotherm diesel engine designed by the company Elsbett (Hilpoltstein, Germany) (2). The use of plant oils as a fuel for modern direct injection diesel engines, however, is accompanied by several problems. Due to increased carbonization and formation of resins during combustion of triglycerides in the engine, formation of sediments at injectors, valves, and pistons takes place, followed by component failure and engine damage. Additionally, both the injector and the hydraulic system must be adjusted for the new fuel because of the up to 10 times higher viscosity of plant oils compared to diesel fuel. Furthermore, a dilution of the engine oil

with plant oil takes place, causing more frequent engine oil changes. Nonmodified diesel engines can run only for up to a few hundred hours on plant oil without damage (3).

The problems of high viscosity can be overcome by blending diesel fuel with plant oil up to 25% (4). The resulting viscosity is low enough to avoid special adaptations to the engine. However, the problems of carbonization and resulting engine troubles cannot be completely avoided. The high viscosity of plant oil can also be reduced by blending with alcohols, whereby microemulsions are formed (5,6). It was, however, reported that difficulties in the achievement of stable microemulsions at low temperatures are present (7). Furthermore, the triglycerides present still lead to carbonization.

Transesterification of plant oils using simple, short-chain alcohols is, however, a successful method for their use as fuels (8). The monoesters formed are of smaller molecular weight than triglycerides yielding viscosities in the range of diesel fuel. Additionally, carbonization can be almost completely eliminated by separation of the glycerine formed during purification. Transesterification is currently the most widely used method for the application of plant oils and alcohols as biofuel. Methyl and ethyl esters of plant oils are widely used as diesel fuel substitutes, while fatty acid alkyl esters in general are valuable intermediates in oleochemistry (9).

A variety of transesterification methods using different reactants, catalysts, and reaction conditions are described in the literature (7,9–12). Regarding production of biofuel, many of the processes developed are unsuitable because the yields are too low or because the technical effort and resulting process costs are too high (7). These processes are used therefore only when high product prices can be achieved. For production of low-cost product biodiesel, only the processes at atmospheric pressure based on the use of alkali catalysts (especially alkali hydroxides) are suitable, because the reaction times are short, the reaction conditions are gentle, and the prices of catalysts used are low, whereby KOH is more suitable than NaOH because the glycerine phase is separated more rapidly when KOH is used (7). Alkali alcoholates can also be successfully used as catalysts; however, there are no reports about their use during production of biodiesel on a large scale, probably because of their high prices compared to alkali hydroxides, toxicity, and complicated handling.

Acid catalysts such as mineral acids, *p*-toluenesulfonic acid or boron trifluoride can also catalyze the transesterifica-

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tion reaction (7,12). The advantage of acid catalysis lies in the fact that any free fatty acids present in oil can also be esterified (7). The disadvantage is that higher reaction temperatures and pressures are necessary (13), and more expensive materials must be used in construction.

The aim of the work presented here was to investigate the possibilities for transesterification of rapeseed oil by lower ( $C_1$ – $C_4$ ) aliphatic alcohols. The alcohols were applied either alone or as mixtures characteristically obtained from fermentation processes (e.g., the acetone–butanol fermentation). Both alkali and acid catalysis of the reaction were tested, whereby as alkali catalyst KOH and as acid catalyst  $H_2SO_4$  were used. The decision to use these catalysts was governed by their low price and therefore by their potential suitability for large-scale use. Furthermore, efforts were also made to produce different esters with a minimum of time and material expenditures, i.e., to define the reaction conditions which might be acceptable for the production of biofuel on a large scale. In this context, the alcohol-to-oil ratios were kept as low as possible in order to reduce the alcohol recirculation losses which appear during large-scale operation. Also, efforts were made to obtain high transesterification degrees within short reaction times.

## EXPERIMENTAL PROCEDURES

**Materials.** Rapeseed oil used for transesterification reactions originated from the company Ölmühle Bruck (Bruck an der Leitha, Austria). Alcohols used (methanol, ethanol, *n*-propanol, *i*-propanol, *n*-butanol, *i*-butanol, *t*-butanol) were of p.a. quality (Merck, Darmstadt, Germany). Catalysts used, KOH and  $H_2SO_4$ , as well as the drying agent,  $Na_2SO_4$ , were also of p.a. quality (Merck).

**Methods.** The aim was to investigate the preparation of rapeseed oil esters with methanol, ethanol, *n*-propanol, *i*-propanol, *n*-butanol, *i*-butanol, and *t*-butanol using potassium hydroxide or sulfuric acid as catalyst. The preparation of the esters took place in a 2-L spherical glass flask, equipped with a back-flow condenser, a thermometer, and a sample port. The flask was immersed in an oil bath on a magnetic stirrer with heating plate. For alkali-catalyzed reactions, the catalyst (KOH) was dissolved in alcohol, and the mixture was added to the oil at reaction temperature immediately before starting the reaction. For acid-catalyzed reactions, the catalyst ( $H_2SO_4$ ) was added to the oil–alcohol mixture at reaction temperature immediately before starting the reaction.

As expected, the KOH-catalyzed preparation of the methyl esters was quite simple—it was possible to conduct the transesterification reaction by stirring the mixture at room temperature. The glycerine phase separated out together with excess methanol immediately after reaction completion, since both compounds are of the polar nature. The two-phase system obtained was then separated by decantation, and the esters obtained were worked and dried as described below.

After terminating the other transesterification reactions by adding water, the reaction mixtures were transferred into a

second spherical glass flask, cooled if necessary, and the excess alcohol was evaporated off using a rotary vacuum evaporator. The mixtures were then transferred into a decanter where the aqueous glycerine phases were separated. The esters obtained were then washed with three or four portions of distilled water. The emulsions present were consecutively separated by a centrifuge at 2,000 rpm. Finally, the esters were dried over  $Na_2SO_4$  and filtered.

In order to achieve complete transesterification and to shift the reaction equilibrium to the product side, the alcohols were added in excess. Since the reactivities of the alcohols investigated are different, the excess of alcohol used was different from alcohol to alcohol. Also the reaction temperatures were adjusted as necessary.

Determination of the degree of transesterification during and after the reaction was conducted using the thin-layer chromatography method described previously (14). Glycerine content (free and total glycerine) was determined chemically using AOCS Official Method Ca 14-56 (15). The kinetics of the transesterification reaction between rapeseed oil and *n*-butanol was performed by analyzing the free glycerine.

Calculation of the alcohol costs in the biodiesel sale price was performed with the following equations, using ratios to adjust the methyl ester price as a first approximation:

Alcohol costs in the sale price of biodiesel at fixed biodiesel price (Eq. 1):

$$ACbd = \frac{mF \times Ma \times Pw}{Me \times Pbd} \quad (\%) \quad [1]$$

Alcohol costs in the sale price of biodiesel at fixed energy price:

$$ACe = \frac{mF \times Ma \times Pw \times Cm}{Me \times Ce \times Pbd} \quad (\%) \quad [2]$$

where  $mF$  = molar fraction of the alcohol in the ester molecule (%),  $Ma$  = molecular weight of the alcohol (g/mol),  $Pw$  = weight price of the alcohol (U.S. cents/kg),  $Me$  = molecular weight of the ester considered (g/mol),  $Pbd$  = weight price of the methyl ester (U.S. cents/kg),  $Cm$  = combustion value of the methyl ester (MJ/kg),  $Ce$  = combustion value of the ester considered (MJ/kg).

## RESULTS AND DISCUSSION

**Rapeseed oil methyl ester.** Rapeseed oil methyl ester is already widely produced on an industrial scale. Low-pressure processes are applied for the production of methyl esters which are used as diesel fuel substitutes, while high-pressure processes are used for the production of methyl esters which serve as raw materials for the production of fatty alcohols (12).

Although the technology for production of rapeseed oil methyl ester is well known, this reaction was used here as a standard, and it served for the comparison with the industrially produced ester which meets national standards. This en-

abled also a comparative assessment of the conditions for production of esters of other alcohols regarding the alcohol-to-oil ratio used, type and quantity of catalyst applied, reaction temperature, duration of the reaction, and purity of the end product. During the experiments using higher alcohols, attempts were made to keep the conditions for production of higher esters similar to the conditions for production of methyl ester where possible.

Experiment 1 yielded results as presented in Table 1. During the following experiment (Experiment 2, Table 1), an attempt was made to reduce the quantity of catalyst; however, after 2 h it was found that the degree of transesterification had reached only 91.4%. Prolonging the reaction time by 2 h did not result in significant improvement. Also, an increase in the alcohol/oil stoichiometric ratio during the following experiment (Experiment 3) did not improve the degree of transesterification after 2 h of reaction duration significantly. Only after increasing the reaction temperature to 45°C for a further 2 h was it possible to achieve nearly complete transesterification. Similar results were also obtained when the alcohol/oil stoichiometric ratio was further increased (Experiment 4). It was therefore concluded that the optimal conditions for the preparation of rapeseed oil methyl ester are similar to the conditions applied during Experiment 5 (Table 1).

*Rapeseed oil ethyl ester.* In general, an increased temperature was necessary for the preparation of rapeseed oil ethyl ester. As shown in Experiment 6, when using lower alcohol/oil ratios and lower catalyst quantities, it was not possible to complete the reaction even after several hours of re-

action. The reaction ran quite fast in initial phase when the catalyst quantity was increased, but 4 h were necessary to approach completion (Experiment 7, Table 1). Since glyceride traces were still detected in the reaction mixture during this experiment, the alcohol/oil ratio was increased, leading to an improved, faster reaction (Experiment 8). The best results were, however, only achieved under conditions applied during Experiment 9.

*Rapeseed oil n-propyl ester.* Transesterification of the rapeseed oil by *n*-propanol using alkali catalyst was attempted, but without success even after several hours of heating at the boiling temperature of *n*-propanol (Experiment 10, Table 1). An acidic catalyst (sulfuric acid) was therefore applied in Experiment 11, and the transesterification reaction ran well. It was not even necessary to use boiling temperature.

*Rapeseed oil i-propyl ester.* Since *i*-propanol is a branched-chain alcohol and therefore of lower activity, we did not even attempt to prepare its ester by the alkali catalysis. The acid catalysis took longer than for *n*-propanol (Experiment 12, Table 1) probably because of both steric interferences and lower boiling temperature of *i*-propanol.

*Rapeseed oil n-butyl ester.* Although the literature data (11) show that *n*-butanol esters of fatty acids can reasonably be produced only when acid catalyst is used, an initial attempt using an alkali catalyst (KOH) was performed. As expected, it was not possible to achieve a high degree of transesterification within 5 h (Experiment 13, Table 1). A series of different reaction conditions (Experiments 14–19, Table 1) using H<sub>2</sub>SO<sub>4</sub> as catalyst were conducted in order to optimize condi-

**TABLE 1**  
Overview of the Transesterification Experiments on Rapeseed Oil Using C<sub>1</sub>–C<sub>4</sub> Alcohols

Experiment	Alcohol	Molar ratio <sup>a</sup>	Catalyst	Catalyst quantity <sup>b</sup> (%)	Reaction temp. (°C)	Reaction time (h)	Degree of transesterification (%)
1	Methanol	4.5:1.0	KOH	1.0	Room temp.	2	98.2
2	Methanol	4.8:1.0	KOH	0.5	Room temp.	2	91.4
3	Methanol	6.0:1.0	KOH	0.5	Room t. + 45°	2 + 2	96.9
4	Methanol	9.0:1.0	KOH	0.5	Room t. + 45°	2 + 2	97.6
5	Methanol	6.0:1.0	KOH	1.0	Room temp.	3	98.6
6	Ethanol	4.8:1.0	KOH	0.5	60	5	84.4
7	Ethanol	4.5:1.0	KOH	1.0	60	4	97.1
8	Ethanol	6.0:1.0	KOH	1.0	60	3	97.2
9	Ethanol	6.0:1.0	KOH	1.5	65	3	98.5
10	<i>n</i> -Propanol	9.0:1.0	KOH	2.0	97	5	64.4
11	<i>n</i> -Propanol	9.0:1.0	H <sub>2</sub> SO <sub>4</sub>	1.5	90	3	98.6
12	<i>i</i> -Propanol	9.0:1.0	H <sub>2</sub> SO <sub>4</sub>	1.5	84	4	97.6
13	<i>n</i> -Butanol	6.0:1.0	KOH	2.0	117	5	15.4
14	<i>n</i> -Butanol	9.0:1.0	H <sub>2</sub> SO <sub>4</sub>	0.5	117	3	83.5
15	<i>n</i> -Butanol	6.0:1.0	H <sub>2</sub> SO <sub>4</sub>	1.5	117	5	96.4
16	<i>n</i> -Butanol	9.0:1.0	H <sub>2</sub> SO <sub>4</sub>	1.0	117	3–4	96.0
17	<i>n</i> -Butanol	15.0:1.0	H <sub>2</sub> SO <sub>4</sub>	1.0	117	3	96.0
18	<i>n</i> -Butanol	9.0:1.0	H <sub>2</sub> SO <sub>4</sub>	2.0	117	3	96.5
19	<i>n</i> -Butanol	9.0:1.0	H <sub>2</sub> SO <sub>4</sub>	1.5	117	3	97.5
20	<i>i</i> -Butanol	9.0:1.0	H <sub>2</sub> SO <sub>4</sub>	1.5	99	4–5	96.7
21	6:1 BE <sup>c</sup>	9.0:1.0	H <sub>2</sub> SO <sub>4</sub>	1.5	78–110	4	97.0
22	3:6:1 IBE <sup>d</sup>	9.0:1.0	H <sub>2</sub> SO <sub>4</sub>	1.5	78–110	4	94.4

<sup>a</sup>Molar ratio of alcohol to oil.

<sup>b</sup>Percentage of the catalyst used calculated on the basis of the weight of oil used.

<sup>c</sup>The 6:1 weight ratio of *n*-butanol to ethanol.

<sup>d</sup>The 3:6:1 weight ratio of *i*-propanol, *n*-butanol, and ethanol.

tions for preparation of this ester. It was concluded that the conditions as applied during the Experiment 19 were the most appropriate.

**Rapeseed oil *i*-butyl ester.** The experimental conditions used in Experiment 18 for *n*-butyl ester were also successfully applied for the preparation of the *i*-butyl ester (Experiment 20). However, the reaction time had to be prolonged because the branched-chain alcohol reacted more slowly.

**Rapeseed oil *t*-butyl ester.** An attempt was made to produce *t*-butyl ester, but it was concluded that no reaction between *t*-butanol and glycerides takes place under any of the experimental conditions applied. Even a large excess of alcohol and/or catalyst did not contribute to attainment of any considerable degrees of transesterification. An attempt to produce *t*-butyl ester from the rapeseed oil methyl ester was also unsuccessful. The difficulties in preparation of *t*-butyl ester are also described in the literature (14).

**Transesterification of rapeseed oil using 6:1 *n*-butanol/ethanol mixture.** The acetone/butanol fermentation yields a solvent mixture consisting of acetone, *n*-butanol, and ethanol in an approximate weight ratio 3:6:1 (16). After removal of acetone, the alcohols could be used for transesterification in order to obtain a diesel fuel substitute. Experiment 21 (Table 1) showed that the mixed ester can be prepared under conditions characterized by gentle heating to avoid the evaporation of ethanol.

**Transesterification of rapeseed oil using 3:6:1 *i*-propanol/*n*-butanol/ethanol mixture.** A variant of the acetone/butanol fermentation, the so-called isopropanol/butanol fermentation, yields *i*-propanol instead of acetone, whereby in an additional metabolic step acetone is reduced to *i*-propanol (17). Experiment 22 showed that such an alcohol mixture can be used for transesterification of rapeseed oil in the same way as the mixture used in Experiment 21.

**Reaction kinetics of rapeseed oil transesterification by *n*-butanol.** These investigations showed that an increase in either reaction temperature or catalyst concentration or both improves the rate of transesterification reaction (Fig. 1). A degree of transesterification greater than 60% was achieved after 30 min using 1.5% H<sub>2</sub>SO<sub>4</sub> as catalyst at 117°C, while 1% H<sub>2</sub>SO<sub>4</sub> at the same temperature yielded only 45% *n*-butyl ester for this time. The reaction rate using 1.5% catalyst was actually slower than with 1% catalyst later in the reaction and after 4 h of reaction time *n*-butyl ester yields were similar (99.5% using 1.5% H<sub>2</sub>SO<sub>4</sub> vs. 99.0% using 1% H<sub>2</sub>SO<sub>4</sub>). The reaction rates using lower catalyst concentrations and/or lower temperatures were higher later in the reaction, but final *n*-butyl ester yields after 4 h of reaction duration were significantly lower (93.4% using 0.5% H<sub>2</sub>SO<sub>4</sub> at 100°C vs. 96.0% using 1% H<sub>2</sub>SO<sub>4</sub> at 110°C, Fig. 1). The ratio *n*-butanol-to-rapeseed oil was kept at 3.0 during these experiments, since higher ratios did not contribute to significant improvements (Experiment 17, Table 1).

Initial experiments demonstrated that rapid and complete transesterification of rapeseed oil can be achieved with methanol or with ethanol at higher temperatures when using

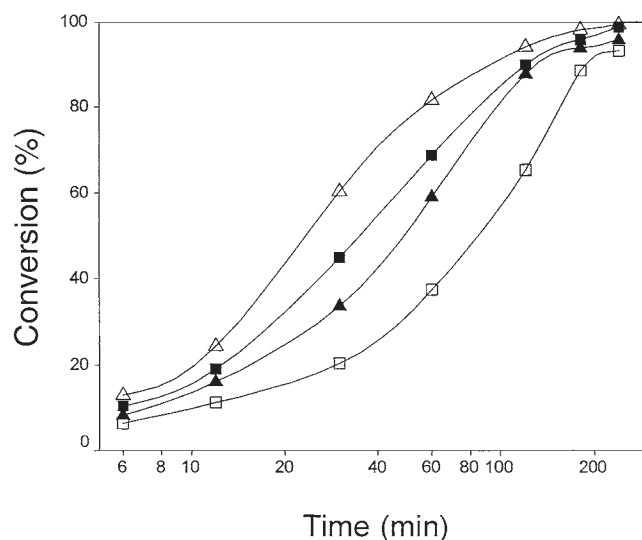


FIG. 1. Time plots of the transesterification patterns of rapeseed oil with *n*-butanol (molar ratio 1:3) at different temperatures and with different catalyst (H<sub>2</sub>SO<sub>4</sub>) concentrations. (□) 100°C, 0.8% H<sub>2</sub>SO<sub>4</sub>; (▲) 110°C, 1.0% H<sub>2</sub>SO<sub>4</sub>; (■) 117°C, 1.0% H<sub>2</sub>SO<sub>4</sub>; (△) 117°C, 1.5% H<sub>2</sub>SO<sub>4</sub>.

KOH as catalyst. The reaction temperature has to be increased, and higher alcohol-to-oil stoichiometric ratios are necessary in order to achieve the acceptable yields from transesterification when using ethanol. As can be seen in Table 1, by using KOH as catalyst it was not possible to prepare higher monoesters like propyl or butyl ester within a reaction time comparable to the reaction time necessary for the production of methyl ester, and with a comparable degree of transesterification.

The Hess Law states that the transesterification reaction occurs because alkyl esters are energetically more stable than triglycerides, whereby the stability of alkyl esters increases when the molecular weight of the alcohol used decreases. Since during transesterification both the energy gradient between reactants and products and the steric mobility of the alcohol used are of importance, intensified reaction conditions have to be applied during transesterification using longer-chain primary alcohols. Branched-chain alcohols are even less reactive because of steric interferences, while *t*-butanol did not react at all under the conditions applied.

The mechanisms of alkali- and acid-catalyzed reactions are different. The alkali-catalyzed reactions are based on an

TABLE 2  
Retail Prices of Technical Quality Alcohols in Austria (mid-1996)<sup>a</sup>

Alcohol	Molecular weight (g/mol)	Price (U.S. cents/kg)	Molprice (U.S. cents/mol)
Methanol	32.04	29.90	0.96
Ethanol	46.07	81.28	3.74
<i>n</i> -Propanol	60.10	121.45	7.30
<i>i</i> -Propanol	60.10	77.54	4.66
<i>n</i> -Butanol	74.12	79.41	5.89

<sup>a</sup>Alcohol prices obtained from distributors of chemicals in Austria. The prices are recalculated on the U.S. currency in the ratio 100 U.S. cents = 10.704 Austrian schilling (exchange rate mid-1996).

**TABLE 3**  
**Alcohol Input Costs for Production of Biodiesel<sup>a</sup>**

Ester	Molecular weight (g/mol)	Combustion value		Molar fraction of alcohol in the ester molecule (%)	Alcohol costs in the biodiesel sale price <sup>b</sup> (%)	
		(MJ/kg)	(MJ/kmol)		Fixed biodiesel price <sup>c</sup>	Fixed energy price <sup>d</sup>
Methyl	355.4	39.83	14,156	8.7	0.50	0.50
Ethyl	369.4	40.03	14,787	12.2	2.64	2.63
<i>n</i> -Propyl	383.4	40.12	15,382	15.4	6.44	6.22
<i>i</i> -Propyl	383.4	40.34	15,466	15.4	4.11	3.95
<i>n</i> -Butyl	397.4	40.52	16,103	18.4	5.82	5.73

<sup>a</sup>Alcohol price basis as shown in Table 2.

<sup>b</sup>A sale price of U.S. cents 46.71 per kg of methyl ester was assumed.

<sup>c</sup>Calculation under assumption that no changes of the sale price (U.S. cents 46.71 per kg of methyl ester) are achievable when other alcohols are used for transesterification.

<sup>d</sup>Calculation under assumption that increased combustion value of the esters of higher alcohols can be paid.

addition–elimination mechanism, while the acid-catalyzed transesterification reactions are characterized by two consecutive substitutions. The alkali-catalyzed reactions are of higher rate, while the acid-catalyzed reactions can be significantly accelerated by increasing temperature. The reaction rate by both mechanisms depends on the nucleophilicity of the attacking reagent, on the polarization of the carbonyl group involved, and on the difficulty for removal of the substituted group.

During the experiments described, the optimized catalyst concentrations were 1.0% for reactions catalyzed by KOH and 1.5% for reactions catalyzed by H<sub>2</sub>SO<sub>4</sub>, calculated on the basis of the weight of the oil used. These catalyst concentrations are in the range of the concentrations used by other authors (10,18). Higher catalyst concentrations did not result in significant improvements. Attempts were also made to conduct the reaction using 0.1% acid catalyst as described in the literature (11), but under these conditions it was not possible to get any significant yield.

Since it was not possible to obtain the yields of propyl and butyl esters comparable to the yield of methyl ester by using KOH as catalyst even at boiling temperatures of the alcohols used, acid catalysis by H<sub>2</sub>SO<sub>4</sub> was applied. The relatively slow acid-catalyzed reaction was successfully accelerated by conducting reactions at elevated temperatures, whereby reactions at the boiling temperatures of the alcohols yielded the best results. This fact can be assessed as unfavorable from the technical point of view since the energy input during acid-catalyzed production of esters at elevated temperatures would be considerably higher. A further disadvantage of sulfuric acid is its corrosive action on stainless-steel equipment at elevated temperatures. On the other hand, free fatty acids are not converted to salts when using acid catalyst, as occurs during reaction using alkali catalyst; therefore both the purification steps are easier and the yield of ester is higher. Further disadvantages of the KOH-catalyzed process are that anhydrous conditions are required and the glycerine phase separates only after removal of excess alcohol.

The retail prices of some technical-quality alcohols in Austria (mid-1996) are presented in Table 2. By using these prices and assuming that the esters of alcohols considered are used as biodiesel, the alcohol input costs for longer-chain al-

cohols during production of biodiesel are presented in Table 3. The prices of higher alcohols are considerably higher than the methanol price, and additionally the molar fraction of alcohol in the ester molecule increases as the carbon chain becomes longer (Table 3), thus leading to the situation that when using higher alcohols for biodiesel production the alcohol input costs become increasingly more significant, thereby making the product even more expensive. The higher production costs caused by higher reaction temperatures required were not included; however, these additional costs probably cannot be justified by the limited improvement in cold-weather properties and combustion values of higher esters. The use of propyl or butyl esters as biodiesel is therefore probably uneconomic. These esters are, however, valuable compounds for a variety of other purposes, such as in lubricant compositions (19) or in drying compositions used in agricultural industry (20). As pure esters they are also widely used in cosmetic industry.

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