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Alkylguanidines as catalysts for the transesterification of rapeseed oil

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Abstract

The transesterification of rapeseed oil with methanol has been studied in the presence of eight substituted cyclic and acyclic guanidines and compared with unsubstituted guanidine. The catalytic activity of the guanidines depends mainly on their intrinsic base strength. With a long alkyl chain on the guanidine, no lipophilic effect is observed. The best catalyst found is commercial 1,5,7-triazabicyclo[4.4.0]dec-5-ene which, when used at 1 mol%, produces a 90% yield of methyl esters with 1 h of reaction time.

Keywords: Alkylguanidines; Transesterification; Vegetable oils

1. Introduction

The transesterification of vegetable oils is an acid or base-catalyzed reaction where a triglyceride reacts with an alcohol producing glycerine and a mixture of fatty acid esters [1]. For a long time this process has been the best method for preparing fatty acid esters [2] which, together with the related alcohols, represent the basic oleochemical intermediates for further synthesis. Vegetable oils also have potential as substitutes for diesel fuel [2–7]. However, their direct use is problematic because of their high viscosity, low volatility, incomplete combustion and possible acrolein formation (due to thermal decomposition of glycerine) [6,7]. Several methods have been evaluated for reducing the high viscosity [8–10] and transesterification with methanol or ethanol seems to be the best method, as these esters can be combusted in a diesel engine without modifications [4,11].

Several inorganic compounds have been used as catalysts for transesterification of vegetable oils with methanol [4,5,12]. Sodium methoxide is the most active catalyst but requires the total absence of water which makes it inappropriate for typical vegetable oil industries [13]. Sodium or potassium hydroxides or carbonates give high yields but normally produce some water in the system. The presence of water in the alcohol/oil mixture may cause hydrolysis, forming soaps and emulsions in the alkaline medium [14]. It is, therefore, necessary to control the system rigorously in order to obtain methyl esters with the necessary purity, including a final purification step (washing, filtration, distillation, etc.) which compromises the

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yields of fatty esters [11].

Guanidines are strong bases which may be used as catalysts for alkylation and elimination reactions [15,16], Michael type additions [17], nitroalkane addition to α,β-unsaturated compounds [18,19], etherifications and esterifications [20], etc. We found that guanidines are also active as base catalysts for the transesterification of vegetable oils [12,21,22]. They produce methyl [12] or ethyl esters [22] in good yields when used in 5 mol%. No formation of soaps or emulsions is observed, even if the reactions are not complete. In this paper we present our results on the transesterification of rapeseed oil with methanol using alkyl-substituted cyclic and acyclic guanidines which show a higher activity and may be used in lower mole-percentages.

2. Experimental

2.1. Guanidines

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, Fluka, >98%), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, Fluka, >98%), 1,1,3,3-tetramethylguanidine (TMG, Aldrich, 99%) and 1,3-diphenylguanidine (DPG, Aldrich, 97%) were used as purchased. Guanidine (G) was prepared by the reaction of guanidine hydrochloride (Aldrich, 99%) with equimolar amounts of sodium methoxide in methanol [12].

1,3-Dicyclohexyl-2-(n-octyl)guanidine (DCOG): A 100 ml two-necked flask equipped with a reflux condenser and a nitrogen inlet tube was charged with 20 ml of dry *tert*-butanol, 2.06 g (10 mmol) of 1,3-dicyclohexylcarbodiimide (Aldrich, 99%) and 2.58 g (20 mmol) of n-octylamine. The mixture was stirred under a nitrogen atmosphere at 100°C for 19 h. The solvent was evaporated and the product was distilled at 172°C/0.1 Torr. The yield was 3.05 g (91.0%). Elemental analysis: Calc.: C 75.2%, H 12.7%, N 12.3%; Found: C 75.0%, H 12.7%, N 12.3%.

1,1,2,3,3-Pentamethylguanidine (PMG) was prepared by a modification of the method of Sennyey et al. [20]: A 250 ml two-necked flask was charged with 50 ml of dry 1,2-dichloroethane and 4.65 g (40 mmol) of tetramethylurea. Oxalyl chloride (5.65 ml, 64.8 mmol) was added at room temperature and the solution was heated for 2 h at 60°C. The solvent was removed under vacuum, the residual yellow solid was solubilized in 20 ml of dry acetonitrile and a solution of 11.0 g of methylamine (354.8 mmol) in 30 ml of dry acetonitrile was added dropwise at 0°C. The reaction mixture was allowed to warm slowly to room temperature, stirred overnight and then refluxed for 1 h. The solvent was evaporated under reduced pressure and the residue was treated with 30% aqueous NaOH. The organic layer was extracted with ether, dried with anhydrous magnesium sulfate and the solvent was evaporated. Distillation of the residue at 100°C/20 Torr yielded 3.22 g (62.3%) of PMG. Elemental analysis: Calc. C 55.8%, H 11.7%, N 32.5%; Found C 55.5%, H 12.0%, N 31.9%.

2-n-Octyl-1,1,3,3-tetramethylguanidine (TMOG): A 250 ml two-necked flask was charged with 50 ml of dry 1,2-dichloroethane and 4.65 g (40 mmol) of tetramethylurea. Oxalyl chloride (5.65 ml, 64.8 mmol) was added at room temperature and the solution was heated for 2.5 h at 60°C. The solvent was removed under vacuum, the residual yellow solid was solubilized in 30 ml of dry acetonitrile and 5.16 g (40.6 mmol) of n-octylamine in 20 ml of dry acetonitrile was added dropwise at 0°C. The reaction mixture was allowed to warm slowly to room temperature and was then refluxed for 15 h. The solvent was evaporated under reduced pressure and the residue was treated with 30% aqueous NaOH. The organic layer was extracted with ether, dried with anhydrous magnesium sulfate and the solvent was evaporated. Distillation of the residue at 110°C/5 Torr yielded 7.72g (90.6%) of TMOG. Elemental analysis: Calc. C 68.7%, H 12.8%, N 18.5%; Found C 68.8%, H 12.5%, N 18.7%.

1,2-Dicyclohexyl-3-piperidylguanidine (DCPG): A 100 ml two-necked flask equipped with a reflux condenser and a nitrogen inlet tube was charged with 10 ml of dry *tert*-butanol, 1.03

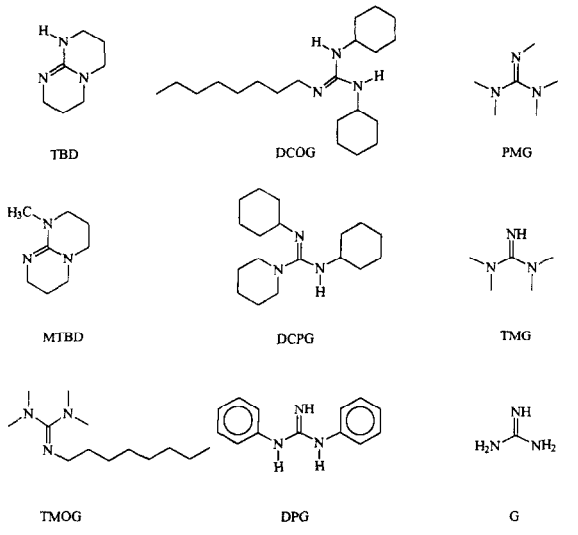

Fig. 1. Molecular structures of the guanidines.

g (5 mmol) of 1,3-dicyclohexylcarbodiimide (Aldrich, 99%) and 0.85 g (10 mmol) of piperidine. The mixture was stirred under nitrogen atmosphere at 100°C for 19 h. The solvent was evaporated and the product was distilled at 200°C/0.1 Torr. The yield was 1.17 g (78.5%). Elemental analysis: Calc.: C 74.1%, H 11.3%, N 14.4%; Found: C 74.0%, H 11.3%, N 14.4%.

The molecular structures of the guanidines are shown in Fig. 1.

2.2. *Transesterification*

A 100 ml two-necked flask was charged with 8.00 g (27.2 mmol, calculated from the average molecular weight of the fatty acid methyl esters) of rapeseed oil (UNICO, France), 2.00 g (62.5 mmol) of methanol (Merck, 99%) and, typically, 1 mol% of a guanidine. The mixture was refluxed at 70°C and the reaction was monitored by ^{1}H-NMR spectrometry (Bruker, 300 MHz). Normally, 1.5 ml of the reaction mixture was removed every 30 min. The mixture was washed three times with 2.0 ml of a saturated aqueous NaCl solution, the organic phase was separated by decantation, dried with anhydrous magnesium sulfate and submitted to NMR analysis in $CDCl_3$ using TMS as internal standard. The conversion of the rapeseed oil to a mixture of methyl esters was determined by the ratio of the signals at 3.68 ppm (methoxy groups of methyl esters) and 2.30 ppm (α-carbon CH_2 groups of all fatty acid derivatives). The conversion was confirmed by the refractive index of the products at 30°C which depends linearly on the methyl ester content between 1.4698 (0% esters) and 1.4520 (100% esters).

For analysis, the rapeseed oil was completely transesterified by the reaction of 4.00 g of the oil with 4.00 g of methanol and 0.20 g (5% w/w) of TBD at 70°C for 1 h. The methyl esters were dissolved in dry diethyl ether and analysed in a HP-5890 II gas chromatograph equipped with an HP-1 (dimethylsiloxane) capillary column and a flame ionization detector. The oven temperature was raised by 2°C · min^{-1} from 150°C to 270°C giving a total analysis time of 60 min. For quantification, the same response factor was assumed for all methyl esters. The identity of the peaks was verified by analysis in a HP-5890 II gas chromatograph coupled to a mass detector (HP-5970B) at 70 eV, using the same column.

3. Results

The gas chromatographic analysis of the rapeseed oil is shown in Table 1. The average molecular weight of the methyl esters is 293.9 g · mol^{-1}. Determination of the saponification index [23] confirmed this value.

All reactions were performed at 70°C, the temperature at which methanol refluxes and which gives the best conversion rates. Fig. 2 shows the

Table 1
Composition of rapeseed oil and retention time of the resulting methyl esters

t_R (min)	Component	Content (%)
20.8	methyl palmitate (C16:0-OMe)	6.5
27.5	methyl linoleate (C18:2-OMe)	15.6
27.6	methyl linolenate (C18:3-OMe)	8.8
27.9	methyl oleate (C18:1-OMe)	62.2
28.1	methyl oleate (*trans*-isomer)	4.7
29.1	methyl stereate (C18:0-OMe)	1.5
36.2	methyl eicosenoate (C20:1-OMe)	0.3
37.5	methyl eicosanoate (C20:0-OMe)	0.4

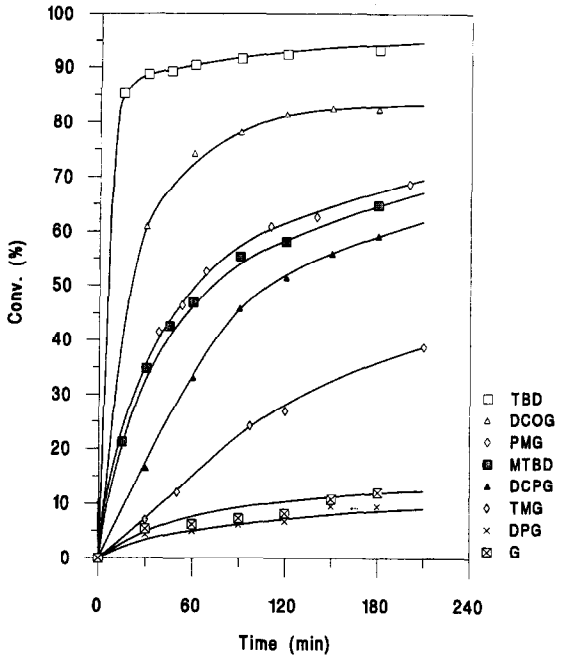

Fig. 2. Conversion of rapeseed oil as a function of time. Conditions: 1 mol% of guanidine, 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 70°C.

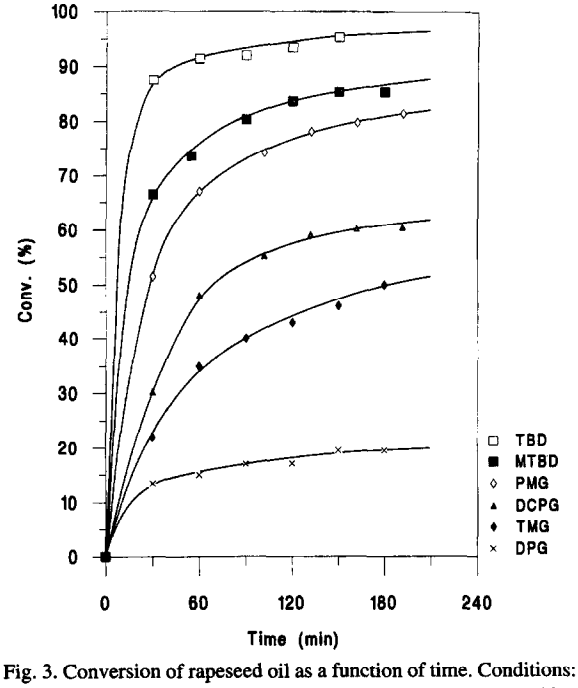

Fig. 3. Conversion of rapeseed oil as a function of time. Conditions: 2 mol% of guanidine, 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 70°C.

time dependence of the conversion of rapeseed oil using several guanidines, at 1 mol%, as catalyst.

With 2 mol% of guanidine, the initial rates of transesterification are similar to those observed with 1 mol%, but the conversions of rapeseed oil, observed with longer reaction times, are higher as shown in Fig. 3. The less efficient guanidines show another strong increase of conversion, if the quantity of the catalyst is increased to 3 mol% (Table 2).

4. Discussion

The transesterification process is a sequence of three consecutive and reversible reactions transforming the triglyceride into a diglyceride, a monoglyceride and, finally, into glycerine and the alkyl esters [2]. If an excess of alcohol is used, glycerine is formed in appreciable amounts and separates from the oil phase, thus improving the yield of the methyl esters. Even so, the reaction can only be completed if a large excess of alcohol (alcohol/triglyceride molar ratio, >30:1) is used. In these experiments, an alcohol/triglyceride molar ratio of 6.86 was used, which is in the range of industrial transesterification processes but gives only a maximum conversion of approximately 98% [2].

The yield obtained with 1 mol% of the most active guanidine (TBD, 93.8% after 3 h) is close to that observed with 1 mol% of NaOH (98.7%) under the same conditions. This smaller activity can be compensated by a higher concentration of the catalyst; with 2 mol% of TBD, the yield increases to 96.0% after 3 h. Furthermore, a sig-

Table 2
Conversion of rapeseed oil in 1 h for different mol% of catalyst

	Conversion (%)		
Catalyst	1 mol%	2 mol%	3 mol%
TBD	90	91	93
DCOG	74	80	92
PMG	49	67	90
TMOG	20	66	87
DCPG	33	48	70
TMG	15	35	55
G	5	15	23

nificant advantage to using the TBD catalyst is a clean transesterification process, even if unrefined oils are used, with an easy phase separation of the glycerine, as the guanidinium salts of the fatty acids, present in small amounts in the oil, are soluble in the reaction mixture and do not form soaps or emulsions [12,22].

The other guanidines studied are less active than TBD, as show in Fig. 2. This reduced activity is due to a lower base strength which decreases when the guanidinium cation is less symmetric (e.g. TMG), is not planar for steric reasons (e.g. MTBD) or has no substituents with a positive inductive effect (e.g. DPG, G). The activity order of the catalysts TBD > MTBD > PMG > TMG corresponds to their relative base strengths reported by Schwesinger [24]. DCOG, DCPG and TMOG are, to the best of our knowledge, described here for the first time and no values for their relative base strength are available.

We first believed that the high activity of DCOG was due to the n-octyl substituent acting as a lipophilic group. This assumption, however, was not correct as PMG and TMOG show the same activity when used with 2 or 3 mol% (Table 2). The high activity of DCOG is, therefore, due to its high base strength, which was observed earlier for the symmetric 1,2,3-trimethylguanidine [25]. MTBD and PMG show intermediate activities when used at 1 mol%. When used at 2 mol% (Fig. 3) their activity increases significantly, with advantage for MTBD, reaching more than 80% conversion after 3 h. DCPG and TMG are less active, not giving good results even at 3 mol% (Table 2). DPG and G give only low conversions as no substituents with a positive inductive effect are present.

5. Conclusions

Guanidines with a high intrinsic base strength may be used for the transesterification of vegetable oils. Their activity cannot be improved by substitution with a long-chain alkyl group. Studies are under way on the heterogenization of several of the guanidines in organic polymers.

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