FATTY ACID METHYL ESTERS SYNTHESIS FROM TRIGLYCERIDES OVER HETEROGENEOUS CATALYSTS IN PRESENCE OF MICROWAVES

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ABSTRACT

Fatty acids methyl esters (FAME) have been prepared both under conventional heating and microwave irradiation. Catalytic tests have been carried out in two phase system in presence of barium hydroxide mono-hydrate at different temperatures and pressures. Relative to conventional heating microwaves irradiation has been proved to be a faster method for trans-esterification reactions (alcoholysis of triglycerides with methanol) leading to high activity and yields of fatty acid methyl esters.

A comparison of catalytic tests performed under microwaves either with NaOH in homogeneous phase or $Ba(OH)_2$ H_2O in heterogeneous phase lead to similar results but with an easier catalyst separation and recycling in the case of barium hydroxide catalyst.

INTRODUCTION

The trans-esterification of natural triglycerides (eg oils and fats) is employed to obtain fatty acid methyl esters (FAME) which are key reagents in the chemical industry [1-4]. The FAME are the raw materials for the production of long chain carboxylic acids, detergents, alternative fuels for diesel engines (BioDiesel) and mono and diglycerides [5], employed as additives for foods, cosmetics and pharmaceuticals [5-7].

Several processes are currently employed for homogeneous catalytic trans-esterification, but these reactions suffer from the production of by-products. This reduces selectivity, increases dramatically the time of separation of the FAME and glycerine products.

To reduce the separation time of the products and to obtain a negligible amounts of by-products, it is necessary to use basic heterogeneous catalysts such as ZnO-Al_2O_3/$ZnAl_2O_4$ but under conventional heating for increasing the reaction rate it is necessary to operate at high temperatures and pressures [8]. These severe operating conditions are highly energy demanding. When reaction is carried out under microwaves, the separation time is very short and the quantity of by-products is reduced drastically.

In the present work catalysts, which consisted of hydroxides such as $Ba(OH)_2$-H_2O have been prepared and tested for trans-esterification reactions both under conventional heating (CH) and in presence of microwaves (MW).

EXPERIMENTAL

All tests under microwave irradiation have been conducted with Milestone Ethos 1600 oven working at 2,450 GHz with a power up to 1000 W.

All trans-esterification reactions have been carried out without the use of solvents in laboratory glass reactors. Stirring was performed with a magnetic stirrer rotating at 650 rpm when tests were performed under pressure or with a mechanical stirring when working at atmospheric pressure. Stirring was unable to emulsify and disperse the methanol in oil, it was solely used to equalise the temperature medium.

Catalytic tests have been carried out in presence of microwaves using barium hydroxide mono-hydrate (Aldrich 98%), methanol (99.8% Aldrich and commercial rape seed oil.

Tests were conducted with the ratio methanol / rape seed oil ratio of 9/1, 18/1 and 30/1 which are definitely higher than the stoichiometric one of 3/1.

The products were analysed by FID gas chromatograph (HP 5890) equipped with HP1 column (l:10m, ϕ: 053, 2.65 μ film) using helium (12ml/min) as carrier gas. Sample of 3μl was analysed with the following heating program: $T_{initial}$ = 75°C, heating rate of 16°C/min till 140°C, 4°C/min till 240°C (1 min), 12°C/min till 300°C and finally 5 min at 300°C before cooling.

RESULTS AND DISCUSSION

To study the action of microwaves on the trans-esterification reaction of rape seed oil using methyl alcohol, runs have been carried out at different pressures and with different quantities of catalyst. Once the reaction was completed the mass was cooled at room temperature and separated by sedimentation (48 hours). The excess of methanol was removed by evaporation under vacuum at room temperature and the rest was washed with distilled water.
At the end of the process three phases are observed:

- light liquid phase: pure FAME (free of barium)
- heavy liquid phase: glycerine (containing small amounts of barium)
- solid phase: catalyst

When the product obtained after reaction is not washed several times with distilled water the resulting FAME and glycerine contain *ca.*0.06% and 0.25% of barium respectively which can be eliminated completely using diluted sulphuric acid solution.

The fatty acids methyl esters (FAME) and the glycerine were recovered and analysed by gas chromatography and volumetric analysis and by periodic acid titration to determine the glycerine and monoglycerides quantities.
Table 1 lists the catalytic conversion of rape seed oil into BioDiesel over barium hydroxide catalyst.

Table I. BioDiesel formation catalysed by barium hydroxide system

Time (min)	$Ba(OH)_2.H_2O$ (w %)	Conversion into FAME (%)	Temperature (°C)	Pressure (atm.)
10	1.5	99	103	3.5
15	0.5	97-98	Under reflux	1
15	1.5	99-100	Under reflux	1

In order to evidence the effect of microwave heating and for a sake of comparison with traditional operating conditions, other tests have been carried out with the same catalyst using conventional heating system and at similar operating conditions. The results obtained are reported in Table II.

Table II. Comparison of the trans-esterification tests of Rape seed Oil (RO) with methyl alcohol carried out under microwave irradiation (MW) and Conventional Heating (CH) to obtain BioDiesel

Run	RO/MeOH (mol.)	catalyst % (w/w)	Reaction time (min)	T (°C)	P (bar)	Heating mode	FAME % (w/w)
A1	1/9	1.5	10	103	3.5	MW	99
A2	1/9	0.5	17	60-65	1	MW	97
A3	1/9	1.5	15	60	1	MW	98
B	1/18	-	60	60	1	CH	81

Catalysts $Ba(OH)_2.H_2O$

A: at laboratory scale in one step, A1 under pressure, A2 and A3, at 1 atm.

B: in one step, at atmospheric pressure at laboratory scale and from reference [9,10]

Referring to the tests carried out in presence of barium hydroxide mono-hydrate it can be observed (Table II) that, if compared to CH tests, MW lead to a higher yields of FAME (81% vs. 98%) and relative to conventional heating microwaves irradiation has been proved to be a faster method for trans-esterification reactions (alcoholysis of triglycerides with methanol) needing a shorter reaction time and preventing products degradation and with a lower energy consumption.

For RO trans-esterification reaction, in order to compare the performance of heterogeneous catalysts with those used in homogeneous phase (hydroxides or methylates of alkaline metals) several tests were performed using NaOH and under similar operating conditions previously used in presence of barium oxide catalyst. Typical results are reported in Table III.

Table III. Homogeneous phase trans-esterification of Rape seed Oil (RO) with methyl alcohol carried out under microwave irradiation (MW) and Conventional Heating (CH)

Run	RO/MeOH (mol.)	Catalyst % (w/w)	Reaction time (min)	T (°C)	P (bar)	Heating mode	FAME % (w/w)
A	1/9	0.1	6.5	103	3.5	MW	98.5
B	1/9	0.3	90	65	1	CH	93.8
C	1/18	0.3	70	65	1	CH	99.4
D	1/30	0.1	21	103	3.5	CH	98.0

Catalyst NaOH (J. T. Baker 98.6%)

A: in one step, under pressure (laboratory scale)

B: in one step, atmospheric pressure (industrial scale)

C (at atmospheric pressure) and D (under pressure): in one step, at laboratory scale

Comparing the runs carried out in heterogeneous phase (Table I and II) with those performed in homogeneous phase (Table III) both under conventional heating or under microwave it can be observed that when heterogeneous $Ba(OH)_2$ H_2O catalyst is employed it can be observed that:

- under conventional heating, if compared to the test with NaOH in homogeneous phase, a difference of yields of FAME (***Y***) is observed (run B Table II ***Y*** = 81% *vs.* run C Table III ***Y***= 99.4%).

- on the contrary when microwave heating is employed similar results can be obtained either in presence of barium or sodium hydroxides (run A1 Table II ***Y*** = 99% *vs.* run A Table III ***Y***= 98.5%) but with an easy catalyst separation and recycling for barium hydroxide catalyst.

CONCLUSIONS

Microwave irradiation helps the synthesis of methyl esters (BioDiesel) and the high conversion of triglycerides in few minutes.

The stirring process doesn't appear to be so notable under MW irradiation as it is with conventional heating.

The energy needed for the trans-esterification under microwave irradiation is very low (*ca.* 0,0156 kW/kg of biodiesel)

A setting up of new catalysts such $Ba(OH)_2$ H_2O, which can prevent soap formation and be easily separated and recycled at the end of the trans-esterification reaction has been investigated.

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