

Study on Alumina Supported Heterogeneous Catalysts for Biodiesel Production

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In this work four heterogeneous catalysts were studied first by preparing a γ -alumina catalytic support then by impregnating with acidic and base compounds to gain certain properties needed to catalyze vegetable oils conversion to biodiesel. The resulted new catalytic properties allowed us to simultaneously conduct esterification and transesterification reaction in a single step when waste cooking oils with a high free fatty acid content were converted to biodiesel. The prepared catalysts were thermally and chemically stable and exhibited good catalytic activity when tested in (trans)esterification reactions to yield biodiesel. The effects of catalyst loading, methanol/oil molar ratio and reaction time on biodiesel yield along with catalyst reusability were investigated. The highest biodiesel yield reached was 88.10% at 65°C reaction temperature, 15:1 methanol/oil molar ratio, 5% catalyst loading and 4 h reaction time.

Keywords: heterogeneous catalyst; γ -alumina, biodiesel; oil conversion, green process

Biofuels along with hydro, wind or solar energy should be considered by now important pieces in any national energy mechanism that develops economic and security strategies. Among biofuels biodiesel is the second most used and produced biofuel by a technology that, in more than 70% of industrial processes, uses fresh oil as feedstock and homogeneous catalyzed transesterification reaction to convert this conflictual feedstock to biodiesel [1-7]. Heterogeneous catalysts can transform this conventional technology into a more sustainable process: second generation fatty acid enriched feedstock can be converted, improved separation and non-toxic products purification can be realized and important energy costs can be reduced [2,5,8-11].

Versatility, thermal stability and chemical stability are key characteristics of an efficient catalytic support to design a heterogeneous catalyst for transesterification reaction to convert vegetable oils to biodiesel. Activated carbon was extensively studied lately, because of its variety of sources like biomass residues, e.g., agricultural and forestry wastes, algal biomass, and because of its numerous functional groups that help binding different key chemical species. Easy to prepare, usually by slow pyrolysis, activated carbon ensures a relatively high specific surface area and a well developed porosity in applications that require an enhanced selectivity [12-17]. Alumina, commonly in form of γ -Al₂O₃, is also an extremely versatile catalytic support due to its Al-O network that easily allows chemical binding of specific chemical compounds to catalyze specific chemical reactions. These catalytic supports are then used to build catalysts by different

methods like impregnation method or precipitation [12]. Various metallic oxides (ZnO, CaO or MgO) were successfully used to catalyze alkali transesterification and various acidic catalysts were studied in vegetable oils conversion to biodiesel, using fresh or waste oils as feedstock [18-24].

In this work heterogeneous catalysts were prepared and tested in a laboratory scale biodiesel production. Catalyst preparing involved the use of a catalytic support, also synthesized in this work, and adding onto it base and acidic compounds for the particularly properties needed to convert oils to biodiesel in a single step reaction [6].

Experimental part

Materials

The following materials have been used in experimental research: Al₂(SO₄)₃ and NH₃ solution for γ -alumina catalytic support preparation; KOH, Mg(NO₃)₂ · 6H₂O, Ca(CH₃COO)₂ · H₂O, (NH₄)₆Mo₇O₂₄ · 4H₂O, Mn(NO₃)₂ · 6H₂O for catalysts preparation; phenophtalein, Hannus Reagent, Na₂S₂O₃, KI, HCl, NaOH, ethyl ether, ethanol, starch indicator solution for feedstock analysis; methanol (99%), fresh sun flower, palm waste cooking oil (PWCO), rapeseed waste cooking oil (RWCO), fresh palm oil (FPO) and fresh rapeseed oil (FRO) for biodiesel production. Prior to catalyst testing in methanolysis reaction, the vegetable oils used as feedstock were analyzed (table 1).

Equipment and procedure

Catalytic support preparation

Catalyst preparation started with catalytic support synthesis according to a pre-established protocol

Vegetable oil	Acid value (mgKOH/g)	Iodine value (gIodine/cg)	Saponification value (mgKOH/g)	FFA (%)
Fresh sun flower oil	0.05	128.00	193.00	-
PWCO	7.13	65.30	201.85	5.45
RWCO	9.09	98.00	199.59	4.31
FRO	0.91	63.19	187.14	0.45

Table 1
CHARACTERISTIC PARAMETERS OF
VEGETABLE OILS

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Catalyst	Symbol	Impregnation solution	Mass (g)	Moles	Catalyst yield (g)
KOH/ γ -Al ₂ O ₃	C _I	KOH	3.00	0.0536	14.48
CaO/MgO- γ -Al ₂ O ₃	C _{II}	Mg(NO ₃) ₂ ·6H ₂ O	36.80	0.1435	51.60
		Ca(CH ₃ COO) ₂ ·H ₂ O	12.50	0.0710	27.73
Mo/CaO-MgO- γ -Al ₂ O ₃	C _{III}	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	1.05	0.0008	10.08
Mn-Mo/CaO-MgO- γ -Al ₂ O ₃	C _{IV}	Mn(NO ₃) ₂ ·6H ₂ O	3.11	0.0108	10.01

Table 2
CHEMICAL COMPOUNDS
USED FOR C_I-C_{IV} CATALYST
SYNTHESIS

operations: 200 g of 21% Al₂(SO₄)₃ solution was added in a three neck flask and heated to 40°C. Then, the solution pH was brought up to 9.5 value by adding 12.5% ammonia solution under continuous stirring until an alumina gel was formed. The gel was further matured turning into hydrogel, which was left under stirring at 40°C for 40-50 min to stabilize its structure. After filtrating and washing the precipitate was again filtered using a blue pH paper, then mixed at 80°C for 1 h to concentrate. The resulted material was then extruded at 100-120°C and further thermally activated by calcination at 550°C.

Supported catalyst preparation

Catalytic support preparation was followed by the building of the final catalyst, step by step, using impregnation method, with the purpose to obtain complex and multiple properties that targeted the capability to catalyse trans(esterification) reaction to convert vegetable oils characterized by a high free fatty acid (FFA) content. For all catalysts the preparation procedure aimed at ensuring both base and acidic catalytic properties (table 2). Operating protocol was the same for all four prepared catalysts and was the impregnation method used by Farooq et al. [6]. γ -Alumina support in powder form and solid chemical compounds were mixed with distilled water then with acidic or base solutions of different concentrations and kept under stirring for 3-4 h at 250 rpm and 25°C. The mixtures were then heated at 70°C for water evaporation and dried at 110 °C for 12 h. The final catalyst synthesis step, *i.e.*, calcination, necessary to activate the catalyst, was performed for 3 h at 500°C for C_I catalyst and for 5 h at 700°C for C_{II}-C_{IV} catalysts (table 2).

C_I (KOH/ γ -Al₂O₃) catalyst preparation sought to obtain both potassium hydroxide (KOH) binding onto alumina (γ -Al₂O₃) catalytic support and base properties, able to catalyse transesterification reaction. In this procedure alumina (0.0980 moles) was added in KOH solution (0.0536 moles dissolved in distilled water) and the resulted mixture was kept under stirring at 250 rpm and 25°C for 4 h, heated at 70°C, dried at 110 °C for 12 h and then activated by calcination at 500 °C for 3 h, yielding 14.48 g of C_I catalyst.

C_{II} (CaO/MgO- γ -Al₂O₃) catalyst preparation targeted increased base properties by adding CaO and MgO onto catalytic support. First MgO/ γ -Al₂O₃ was prepared by adding γ -Al₂O₃ solution (0.0980 moles alumina dissolved in distilled water) to magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O) solution (0.1435 moles), stirred at 300 rpm and 25°C for 3 h, heated at 70°C, dried at 110°C for 12 h and then activated by calcination at 550 °C for 5 h, obtaining 51.60 g of catalyst. Further, MgO/ γ -Al₂O₃ (0.0704 moles) was added in calcium acetate monohydrate (Ca(CH₃COO)₂·H₂O) solution (0.0710 moles dissolved in distilled water), kept under stirring at 250 rpm and 25°C for 3 h, heated at 70°C, dried at 110°C for 12 h and then activated by calcination at 700°C for 5 h, resulting in 27.73 g of C_{II} catalyst.

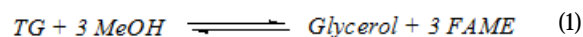
C_{III} (Mo/CaO-MgO- γ -Al₂O₃) catalyst preparation aimed at gaining a new structure of base and acidic active centres by adding metallic (metal oxides) compounds. In this procedure ammonium molybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O (0.0008 moles) was added in CaO/MgO- γ -Al₂O₃ solution (0.0576 moles dissolved in distilled water) stirred at 250 rpm and 25°C for 3 h, heated at 70°C, dried at 110°C for 12 h and then activated by calcination at 700°C for 5 h, yielding 10.08 g of C_{III} catalyst.

C_{IV} (Mn-Mo/CaO-MgO- γ -Al₂O₃) catalyst was similarly prepared using Mo/CaO-MgO- γ -Al₂O₃ as catalytic support by adding manganese nitrate hexahydrate (Mn(NO₃)₂·6H₂O) (0.0108 moles) in Mo/CaO-MgO- γ -Al₂O₃ (0.0325 moles), stirred at 250 rpm and 25°C for 3 h, heated at 70°C, dried at 110°C for 12 h and then activated by calcination at 700 °C for 5 h, obtaining 10.01 g of C_{IV} catalyst.

Supported catalyst testing

The synthesized catalysts were tested in transesterification reactions, *e.g.*, eq. 1, where triglycerides (TG) were converted to glycerol and fatty acid methyl esters (FAME). Vegetable oils were pre-heated at 50°C for 0.5 h in order to reach rapidly the transesterification reaction temperature. Catalyst activation for reaction was performed initially by adding pre-established amounts of methanol and catalyst into a 100 mL three neck flask under stirring at 250 rpm for 0.5 h at 50 °C. The preheated oil was then fed in reactor and the reaction was performed at reflux at 650 rpm and 65 °C. After completion of the reaction, the mixture was filtered and the catalyst was recovered for further reutilisation. The reaction products were separated by centrifugation and then purified and prepared for characterization. Methanol/oil molar ratio ($R_1=12-21/1$), catalyst/oil mass ratio ($R_2=1-7\%$) and reaction time ($\delta=2-5$ h) were selected as synthesis process independent parameters (factors).

Four methanolysis reactions were carried out using KOH homogeneous catalyst (C₀) only to compare the results. C₀ catalyst was used to catalyze the transesterification reactions that were conducted in similar conditions as in commercial biodiesel synthesis.



Biodiesel analysis

Biodiesel analysis is required to close the entire process cycle and it is according to different forms of standards (ASTM-for United States, EN-for European Union or other specific national standards). While a GC method can provide determination of residual free methanol or the presence of residual monoacylglycerols, diacylglycerols and triacylglycerols, a GC-MS method is more suitable in determination of FAME, a method that implies the use of a polar GC column to determine the fatty acid coupled to a MS detector to identify a targeted specific compound.

Exp.	Oil	Cat.	R ₁	R ₂ (%)	τ (h)	Y (%)	Exp.	Oil	Cat.	R ₁	R ₂ (%)	τ (h)	Y (%)
1	FPO	C ₀	15/1	1	1	94.0	24	RWCO	C _{IV}	15/1	5	2	58.3
2	PWCO	C ₀	15/1	1	4	62.1	25		C _{IV}	15/1	5	3	82.9
3		C _I	15/1	5	4	72.6	26		C _{IV}	15/1	5	5	86.0
5		C _{II}	15/1	5	4	75.9	26		PWCO	C _{III}	12/1	5	4
6		C _{III}	15/1	5	4	80.2	28	C _{III}		21/1	5	4	81.1
7	C _{IV}	15/1	5	4	84.8	29	C _{IV}	12/1		5	4	72.3	
8	FRO	C ₀	15/1	1	1	93.3	30	C _{IV}		21/1	5	4	85.2
9	RWCO	C ₀	15/1	1	4	68.1	31	RWCO	C _{III}	12/1	5	4	75.0
10		C _I	15/1	5	4	77.8	32		C _{III}	21/1	5	4	86.6
12		C _{II}	15/1	5	4	80.2	33		C _{IV}	12/1	5	4	78.2
13		C _{III}	15/1	5	4	85.5	34		C _{IV}	21/1	5	4	88.9
14	PWCO	C _{IV}	15/1	5	4	88.1	35	PWCO	C _{III}	15/1	1	4	16.7
15		C _{III}	15/1	5	4	44.5	36		C _{III}	15/1	3	4	68.9
16		C _{III}	15/1	5	3	72.1	37		C _{III}	15/1	5	4	80.2
17		C _{III}	15/1	5	5	81.3	38		C _{III}	15/1	7	4	77.1
18	PWCO	C _{IV}	15/1	5	2	47.2	39	PWCO	C _{IV}	15/1	1	4	17.9
19		C _{IV}	15/1	5	3	73.7	40		C _{IV}	15/1	3	4	73.2
20		C _{IV}	15/1	5	5	82.3	41		C _{IV}	15/1	7	4	82.9
21		C _{III}	15/1	5	2	41.2	42		RWCO	C _{III}	15/1	1	4
22	RWCO	C _{III}	15/1	5	3	78.3	43	C _{III}		15/1	3	4	66.3
23		C _{III}	15/1	5	5	87.2	44	C _{III}		15/1	7	4	83.2
24	RWCO	C _{IV}	15/1	5	2	58.3	45	C _{IV}		15/1	1	4	28.9
25		C _{IV}	15/1	5	3	82.9	46	C _{IV}	15/1	3	4	77.2	
26		C _{IV}	15/1	5	5	86.0	47	C _{IV}	15/1	7	4	85.7	

Table 3
FAME YIELD DEPENDING
ON PROCESS FACTORS
FOR DIFFERENT OIL AND
CATALYST TYPES

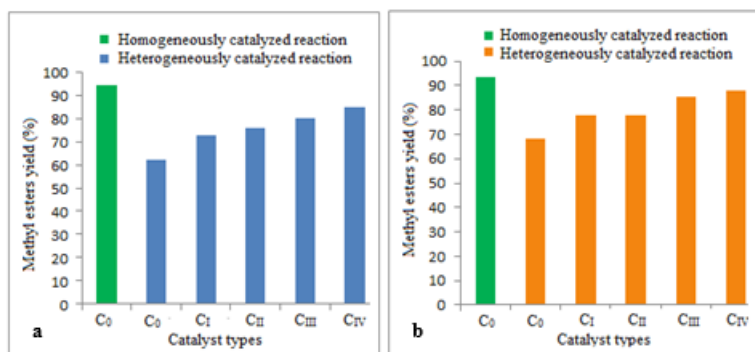


Fig. 1. Catalysts testing in homogeneous and heterogeneous catalysis for PWCO (a) and RWCO (b): comparison between KOH and C₀-C_{IV} catalysts

Results and discussions

Supported catalyst testing

Four types of vegetable oils (FPO, FRO, PWCO and RWCO) were converted to biodiesel and five types of catalysts were tested (one homogeneous catalyst (C₀) and four heterogeneous catalysts (C_I-C_{IV})). The values of FAME yield (Y) for different oil and catalyst types as well as for various levels of process factors, *i.e.*, methanol/oil molar ratio (R₁=12-21/1), catalyst/oil mass ratio (R₂=1-7%) and reaction time (τ=2-5 h), are summarized in table 3. Tabulated data reveal higher FAME yields when catalysts became more complex with base as well as acidic properties and also for higher values of R₁ and R₂.

The results showed significant differences between KOH and the heterogeneous catalysts. As expected the homogeneously catalyzed reaction had the highest FAME yields (94% and 93.3% for both fresh oils, *i.e.*, FPO and FRO), whereas multiple heterogeneously catalyzed reactions yielded over 85% FAME. Reactions using C₀ (KOH catalyst) when WCO was used yielded lower FAME percents, due to a high base concentration. Similarly the C_I and C_{II} catalysts showed lower methyl esters yield, due to feedstock high fatty acid concentration, while C_{III}-C_{IV}, with stronger acidic properties, catalyzed reaction that yielded over 85% methyl esters, being able to catalyze both esterification and transesterification reactions (fig. 1), thus

adding Mo and Mn the reaction dynamics were enhanced, higher methyl ester yields being obtained in these reactions.

Biodiesel analysis

The method for purification of products used in this work implied methyl esters and glycerol distillation using rotary evaporator equipment then analysing samples using GC-MS method. Types and concentrations of FAME produced in exp. 23 (C_{III} catalyst, R₁=15/1, R₂=5%, τ=5 h, Y=87.2) and 47 (C_{IV} catalyst, R₁=15/1, R₂=7%, τ=4 h, Y=85.7) are shown in figs. 2 and 3 and tables 4 and 5, respectively. Seven significant peaks were identified in exp. 23, with methyl oleate and methyl linoleate as major components, whereas eleven significant peaks were highlighted in exp. 47, with same methyl oleate and methyl linoleate as major components.

Influence of catalyst loading on methyl esters yield

Heterogeneously catalyzed transesterification reactions use in generally 3-10% catalyst loading to obtain maximum feedstock conversion. This relatively higher amount of catalyst used compared with that of 1% in homogeneously catalyzed reaction can be compensated by a high re-runs reaction number that can be performed by solid catalysts. For this study 1, 3, 5, 7% catalyst loadings were used. Conversions closed to 100% can not be attained unless the exact amount of base (or acid in case of esterification) is

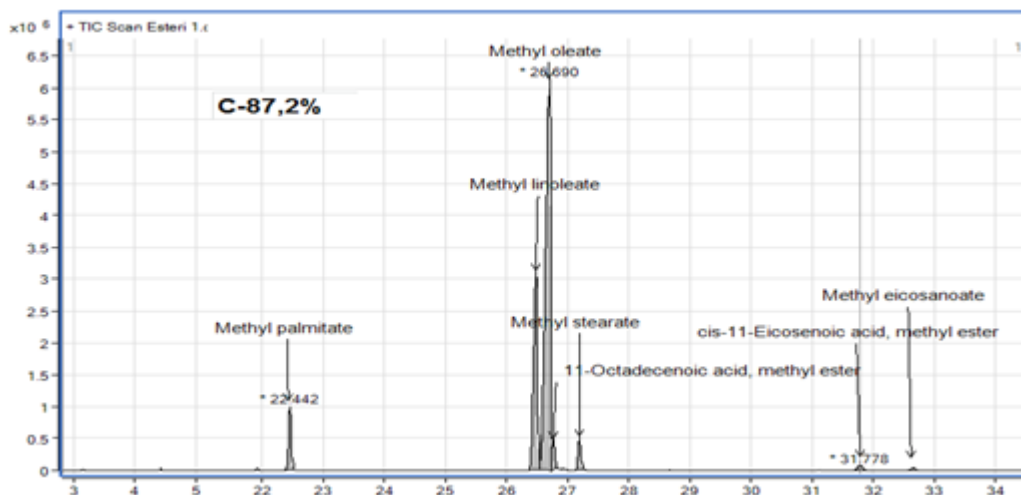


Fig. 2. GC-MS analysis of FAME produced in exp. 23 (C_{III} catalyst, $R_1=15/1$, $R_2=5\%$, $\tau=5$ h)

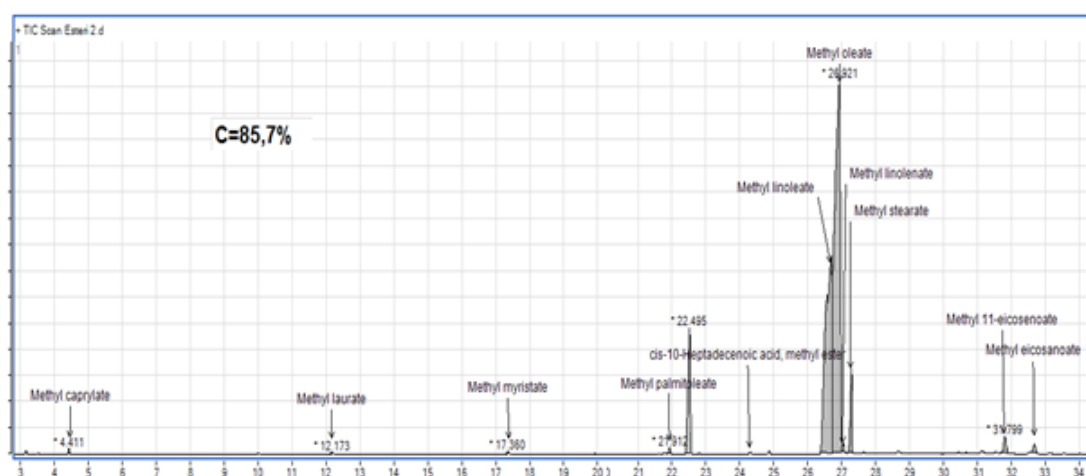


Fig. 3. GC-MS analysis of FAME produced in exp. 47 (C_{IV} catalyst, $R_1=15/1$, $R_2=7\%$, $\tau=4$ h)

present and active, so the problem became ensuring this specific amount, assuming that reactants have access to all catalyst active centres during the reaction. 1% and 3% were considered lower loadings in this protocol, 5% catalyst loading provided enough base concentration to reach high

conversion, while 7% appeared to inhibit instead of catalyse. Thus the maximum yield was reached by using 5% catalyst loading, the other reaction conditions being 65°C reaction temperature, 15/1 methanol/oil ratio and 4 h reaction time (fig. 4).

Peak	Compound	RT	Area	Area %	Height	Area sum %
1	Methyl palmitate	22.442	3388076	10.05	1006180	6.12
2	Methyl oleate	26.475	14523220	43.09	3120221	26.24
3	Methyl linoleate	26.69	33704686	100	6151994	60.89
4	Methyl stearate	26.753	1354542	4.02	519914	2.45
5	11-Octadecenoic acid,methyl ester	27.183	1716624	5.09	537029	3.1
6	cis-11-Eicosenoic acid,methyl ester	31.778	448663	1.33	82661	0.81
7	Methyl eicosanoate	32.648	219828	0.65	43903	0.4

Table 4
FAME TYPES IDENTIFIED IN
EXP. 23

Peak	Compound	RT	Area	Area %	Height	Area sum %
1	Methyl caprylate	4.411				0.14
2	Methyl laurate	12.173	278081	0.18	86034	0.09
3	Methyl myristate	17.36	392300	0.25	120318	0.13
4	Methyl palmitoleate	21.912	848901	0.54	254201	0.28
5	cis-10-Heptadecenoic acid, methyl ester	22.495	21238342	13.58	4785936	7.12
6	Methyl linoleate	26.675	101669659	65.03	7571129	34.09
7	Methyl oleate	26.921	156345284	100	14229274	52.43
8	Methyl linolenate	27.031	847302	0.54	308798	0.28
9	Methyl stearate	27.267	11021765	7.05	3183109	3.7
10	Methyl 11-eicosenoate	31.799	3592567	2.3	641630	1.2
11	Methyl eicosanoate	32.665	1600152	1.02	324915	0.54

Table 5
FAME TYPES
IDENTIFIED IN EXP. 47

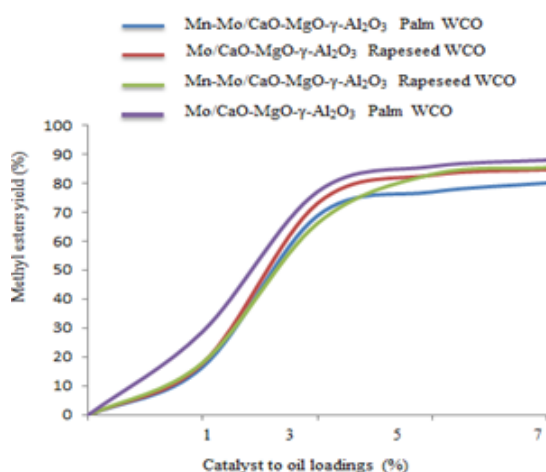


Fig. 4. Methyl esters yield vs. catalyst loadings

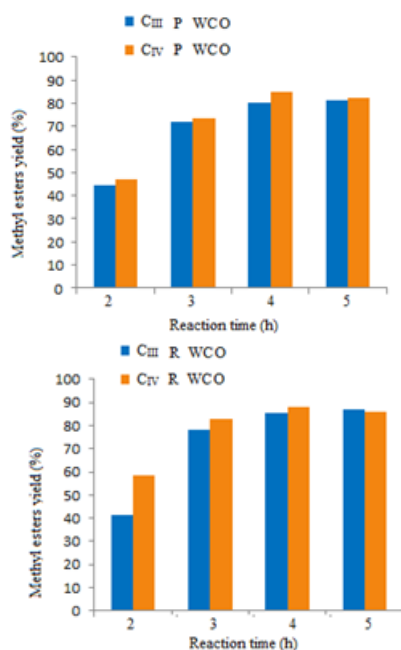


Fig. 5. Methyl esters yield vs. reaction time

Influence of reaction time on methyl esters yield

Time is an important reaction parameter that can define the commercial viability for industrial processes. In this study transesterification reactions were conducted following a certain conditions set, while only reaction time was varying between 2-5 h. The non-varying parameters were 65°C reaction temperature, 15/1 methanol/oil ratio and 5% catalyst loading.

As shown in figure 5 the highest methyl ester yield was reached for 4 h reaction time. The experiments with 5 h reaction time (e.g., exp. no. 20, exp. no. 26) showed a negligible increased variation and for this reason we considered 4 h to be the optimum reaction time in this experiment.

Influence of methanol/oil ratio on methyl esters yield

Methanolysis reaction to convert vegetable oil to biodiesel is a reversible reaction (eq. (1)). 3 moles of methanol react with 1 mol of triglycerol resulting in FAME and glycerol. To shift the reaction toward the desired product in commercial biodiesel process, 6/1 or even 10/1 methanol/oil ratios are widely used. Heterogeneously catalyzed transesterification reaction on the other hand is a much slower reaction, implying adsorption, diffusion, reaction, desorption thus methanol/oil molar ratios like 12/1, 15/1 or higher are needed to shift the equilibrium reaction.

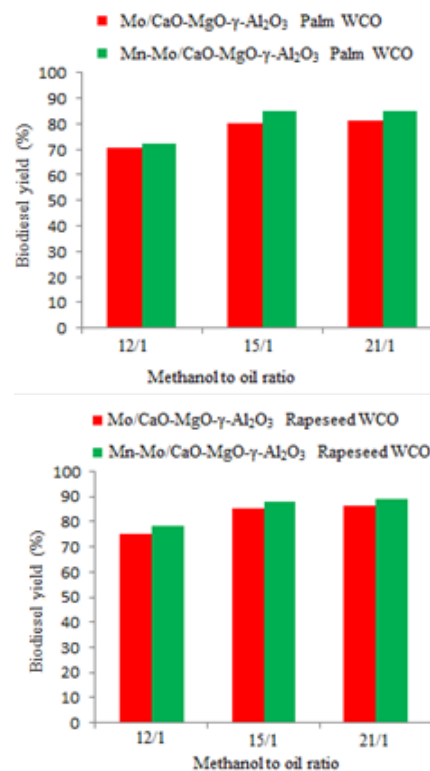


Fig. 6. Methyl esters yield vs. MeOH/oil ratio

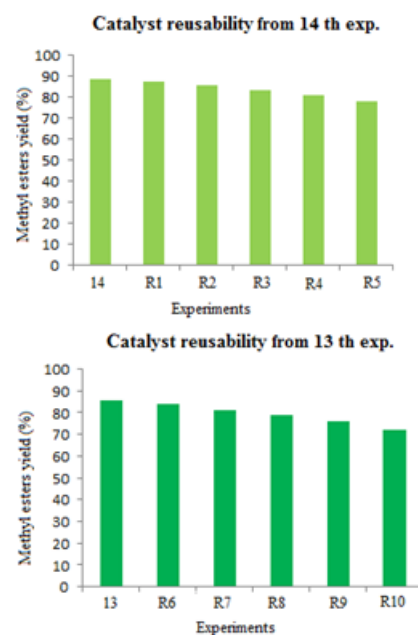


Fig. 7. Dynamic of methyl esters yield with re-runs

For this study we selected 12/1, 15/1 and 21/1 methanol/oil molar ratios at 65°C, the other reaction conditions remaining 5% catalyst loading and 4 h reaction time. Figure 6 shows that the highest biodiesel yields were reached at 15/1 methanol/oil molar ratio, with small but negligible increased variation at 21/1 molar ratio, so we considered 15/1 to be the optimum molar ratio for alcohol use.

Catalyst reusability

Reusability of a heterogeneous catalyst can make the difference while choosing the process catalysis type. Using and re-using a catalyst in multiple cycles can drastically reduce the process total costs. In this work catalysts selected for re-run were the ones that helped reach the highest methyl ester yield and re-used in multiple reaction. After every batch they were filtered and hydrothermally treated and then re-used in a consecutive reaction. Figure

7 shows the variation of methyl ester yield with catalyst reusability as a result of catalysts chemical stability. Catalysts used in experiment 13 and experiment 14 were selected for re-runs (R1-R5 for exp. 14 and R6-R10 for exp. 13).

Conclusions

In this work four heterogeneous catalysts were designed and studied by testing their catalytic activity in transesterification reaction to convert vegetable oils to biodiesel. Using only KOH as catalyst, low methyl ester yields were reached due to the high fatty acid WCO oils content. An alumina catalytic support was used then to develop a heterogeneous catalyst with acidic and base properties able to catalyze fatty acid enriched oils conversion. Stronger acidic and base properties were obtained by adding in multiple steps CaO, MgO or metals like Mn and Mo, compounds that determined the designed catalysts to become chemically and thermally stable and capable to be re-used in multiple reactions.

The influence of process factors in terms of time reaction, catalyst loading and methanol/oil molar ratio on methyl ester yield and catalyst reusability was studied in order to obtain the optimum conditions in which the catalysts can reach their maximum catalytic potential. The highest methyl ester yield was reached at 65°C, 15/1 methanol/oil ratio, 5% catalyst to oil loading and 4 h reaction time.

We consider that using such catalysts the biodiesel production can become sustainable by converting this second generation feedstock type and by reducing the product separation and purification costs.

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