

Transesterification of Glycerol Triacetate with Methanol on Acid and Base Catalysts

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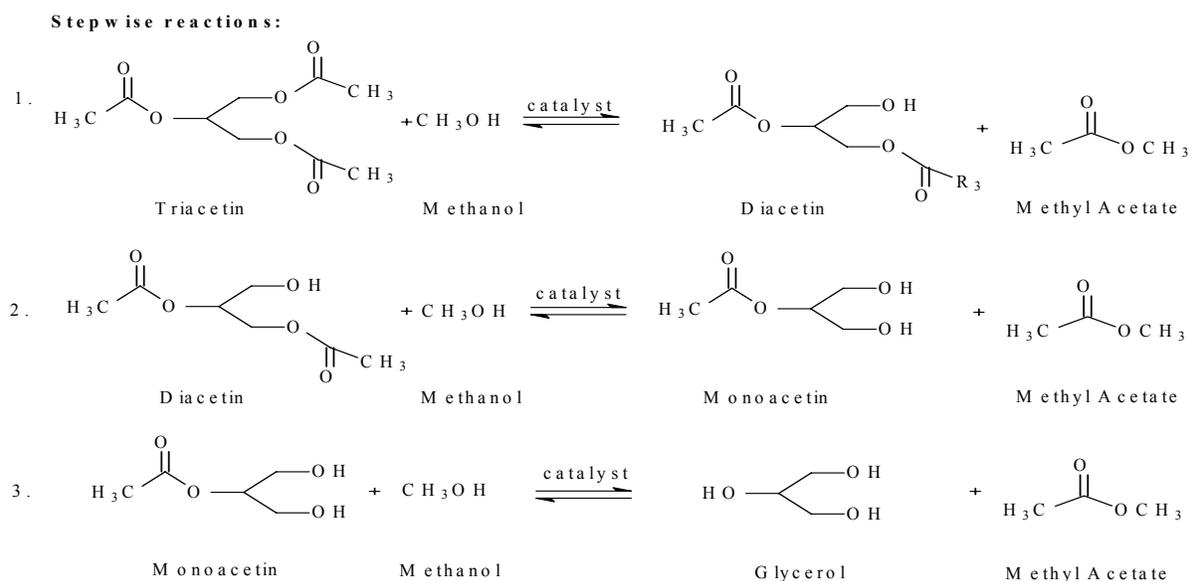
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Introduction

There is much interest in the conversion of fats and vegetable oils to biodiesel due to its desirable environmental, renewable and biodegradable properties. A major problem of the conventional industrial process, which uses homogenous base catalysts (NaOH or KOH), is that the reaction does not tolerate the presence of water or free fatty acids. In addition to the need of a high quality feedstock, the catalyst cannot be recovered. The homogeneous acid catalyzed process is not practical due to corrosion and environmental problems. The use of solid catalysts has the potential to reduce environmental and process costs.

Triglycerides are the major components of oils and fats. The transesterification reaction of a triglyceride (TG) consists of three consecutive and reversible reactions which can be catalyzed by acids or bases. The overall reaction requires 3 mol of alcohol per 1 mol of TG to produce 1 mol of glycerol and 3 mol of ester. Biodiesel is the resulting mixture of ester products obtained from the transesterification of TGs contained in vegetable oils and fats. Scheme 1 shows the transesterification reaction of glycerol triacetate (triacetin) with methanol, a model compound for larger triglyceride molecules.

Scheme 1



Triacetin is a clear oily liquid with a b.p of 258°C and presents good solubility in alcohols. This small molecule can be used as a model compound for larger TG molecules without the drawback of analysis difficulties. The results obtained from the transesterification of triacetin with methanol cannot be directly extrapolated to real oils and fats. However, they do give an idea of the activity of the different catalyst materials on the transesterification reaction.

The purpose of this research was to investigate the catalytic activities and selectivities of different types of catalyst materials for the transesterification reaction of triacetin. Transesterification of triacetin was carried out using methanol to produce methyl acetate and glycerol at 60°C in the presence of a variety of solid and liquid catalysts. The solid acid catalysts used were, Amberlyst-15, supported phosphoric acid, sulphated zirconia, tungstated zirconia, zeolite H β and, ETS-10 (H). The solid base catalysts used were MgO, and ETS-10 (Na). These results were compared to reactions using H₂SO₄ and NaOH.

Experimental

ETS-10 (Na) and ETS-10 (H) were obtained from Engelhard (Iselin, NJ). Magnesium Electron Inc. (MEI, Manchester, UK) provided the sulphated zirconia (SZ) and tungstated zirconia (WZ). The supported phosphoric acid C-131 (PAC) was obtained from Süd-chemie. Amberlyst-15 and MgO were purchased from Sigma Aldrich. Zeolite H β was purchased from Zeolyst International (PA). Sodium hydroxide (98.9%) and sulfuric acid (96.4%) were purchased from Fisher. Triacetin (99%), a mixture of diacetins (4 %wt glycerol, 45 %wt diacetin, 26 %wt monoacetin and 25 %wt triacetin), glycerol (99%), and anhydrous methanol (99%) were purchased from Across Organics.

Elemental analysis, BET surface area, NH₃ and CO₂ TPD/TCD, and powder XRD were employed to characterize the solid catalysts. These solid catalysts were calcined prior to reaction except for Amberlyst-15 which was dried at 90°C under vacuum. An initial molar ratio of 6:1 (methanol: triacetin) was used for all reaction experiments. Prior to reaction, a sample of the reactant mixture was analyzed in order to obtain initial concentrations. To carry out the reactions, an amount of 0.04 g of catalyst (except H₂SO₄ and NaOH) was quickly added to 1.96 g of the mixture methanol/triacetin contained in a 50 ml Erlenmeyer. A 4080 Innova Shaker set at 120 rpm and 60 °C (with an accuracy of ± 0.4 °C) was used to control mixing and temperature. Seven identical sibling samples were prepared for each catalyst and they were quenched at 15 minutes intervals during the first hour, at 4 hours and 8 hours of reaction to measure reactant and product concentrations. To separate the catalysts from the reactant mixtures, samples were centrifuged prior to analysis. Reaction samples were analyzed using HP 6890 gas chromatograph system combined with a HP 5973 mass selective detector. The collection and analysis of data was carried out using a HP chemstation software. An Alltech Econo-Cap EC-WAX fused silica capillary column (30 m x 0.25 mm x 25 μ m) was used for analyte separation. UHP helium was used as the carrier gas. The injector and detector temperatures were set to 255°C and 280°C, respectively. For sample analysis, one microliter of the reaction mixture was injected into the column using the splitless mode option. The oven

temperature program started at 45°C for 4 min, then it ramped up the temperature at 50°C/min to 180°C and, finally this temperature was held for 14 min.

Results and Discussion

Table 1 summarizes results for the catalysts characterization after their respective calcination or dehydration. Even though ammonia could potentially adsorb in both acid and base sites [1], NH₃-TPD can be used to obtain an estimate of the amount and distribution of sites on a solid acid catalyst. XRD experiments showed that sulfated and tungstated zirconia have the typical active tetragonal structure [2].

Table 1

Catalysts characterization results after calcination or dehydration.

Catalyst	Pretreatment Temperature (°C)	Pretreatment Time (h)	Parameter			
			S _{BET} (m ² /g)	Elemental analysis	TPD (μmol/g)	XRD structure
ACIDS						
Amberlyst-15	90	3 (under vacuum)	40	-	^b	NA
PAC	300	2	2.9	66.2 wt% P ₂ O ₅	1903	-
WZ	700	2	91	13.42 wt% W	112 ^c	Tetragonal ZrO ₂
SZ	600	2	137	1.73 wt % S	202 ^c	Tetragonal ZrO ₂
ETS-10 (H)	250	2	434	-	1044 ^c	NA
Zeolite Hβ	500	2	620 ^a	300 ^a	136 ^c	-
H ₂ SO ₄	NA	NA	NA	(SiO ₂ /Al ₂ O ₃) 96.4% H ₂ SO ₄	NA	NA
BASES						
ETS-10 (Na)	500	2	224	6.14 wt% Na 5.22 wt% K	-	-
MgO	600	2	1.5	99.9 wt% MgO	50 ^d	-
NaOH	NA	NA	NA	99 wt% NaOH	NA	NA

a Data obtained from supplier

b acidity of 4.7 eq/kg (obtained from supplier)

c NH₃ TPD

d CO₂ TPD

To determine the effect of catalyst activity on methyl acetate formation, reactions were carried out during an 8 h period -longer times would be impractical from an industrial point of view-. A 6:1 (methanol: triacetin) initial molar ratio is commonly used in industrial reactions when using homogeneous base catalysts. Triglyceride to alcohol initial molar ratio can greatly affect the reaction yield [3]. High conversions can be achieved by homogeneous catalysts at relatively mild temperatures (40 to 65 °C) [4]. For comparison reasons, an initial molar ratio of 6:1 (triacetin: methanol), and a temperature of 60°C were chosen.

Catalyst weight % load is commonly used for comparing among solid catalysts because it is another variable affecting the yield of the reaction. In this study, the solid catalyst load was 2 wt% of the overall reaction mixture. For liquid catalysts, a more reasonable loading (for comparison with the solid catalysts) was achieved by using 0.05 wt% of sulfuric acid (equivalent to 2 wt% of Amberlyst-15) and 0.025 wt% of sodium hydroxide (equivalent to 2 wt% of ETS-10 (Na)) since these are not supported catalysts.

Not surprisingly, higher activities were observed when using base catalysts (fig.1). Catalyst activities among bases varied as follows: NaOH > ETS-10 (Na) > MgO. Catalyst activity decreased in the order of H₂SO₄ > Amberlyst-15 > SZ > WZ > zeolite H β = ETS-10 (H) > PAC among the acids. Amberlyst-15, which has macroporous structure, showed the highest activity among solid acids. ETS-10 (Na) has the highest activity among solid bases. This result is in agreement with results obtained for the TGs present in vegetable oils [4]. In spite of the high BET surface area of zeolite H β , this catalyst presented fairly low activity. Since zeolite H β has a pore size of 7 Å, this may have limited the formation of the reaction intermediates over its acid sites.

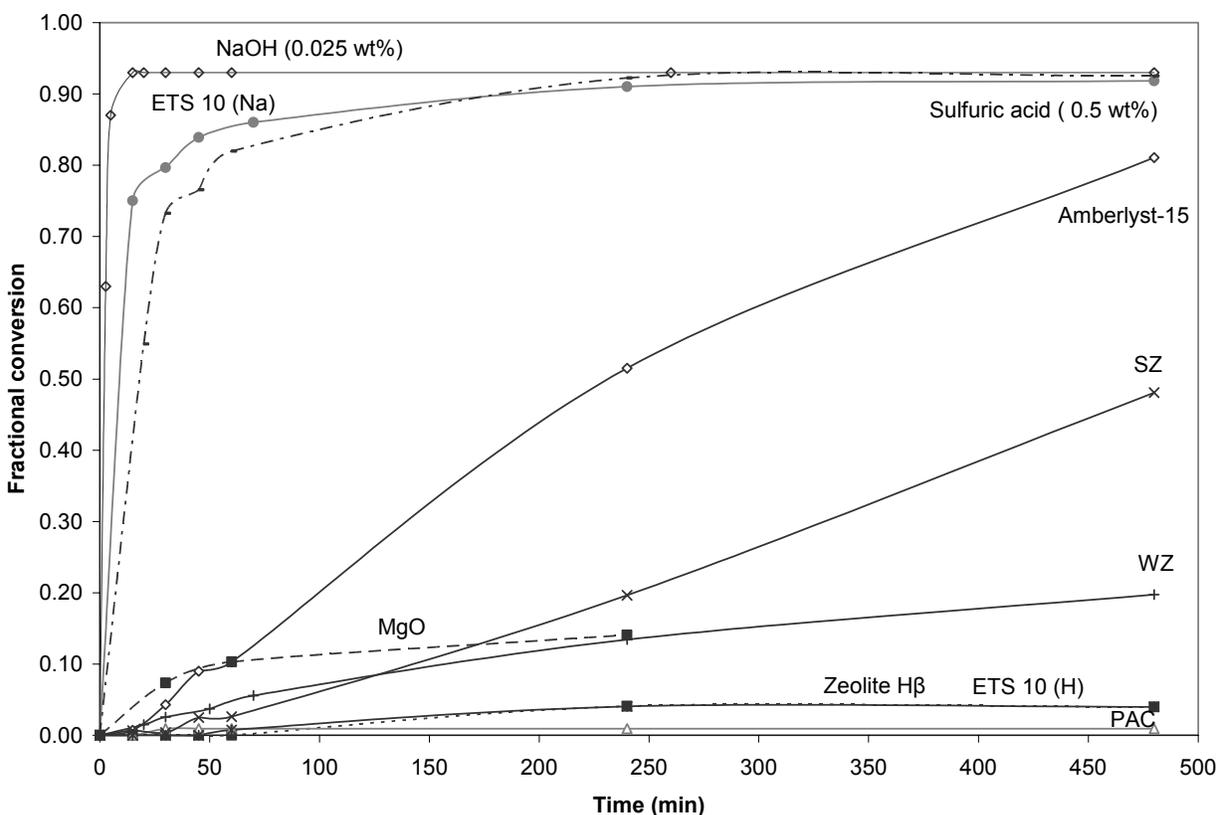


Fig. 1. Triacetin conversion over acid and base catalysts at 60°C.

The experimental equilibrium conversion of triacetin was 93%. Triacetin conversion was calculated using the following equation:

$$\text{Molar conversion (\%)} = \frac{C_{Ti} - C_{Tf}}{C_{Ti}} \times 100 \quad (1)$$

Where C_{Ti} and C_{Tf} are the initial and final molar concentration of triacetin, respectively. Selectivities to diglycerides, monoglycerides and glycerol were calculated using the following equations:

$$\text{Diglyceride selectivity (\%)} = \frac{C_{di}}{C_{di} + C_{mono} + C_{gly}} \times 100 \quad (2)$$

$$\text{Monoglyceride selectivity (\%)} = \frac{C_{mono}}{C_{di} + C_{mono} + C_{gly}} \times 100 \quad (3)$$

$$\text{Glycerol selectivity (\%)} = \frac{C_{gly}}{C_{di} + C_{mono} + C_{gly}} \times 100 \quad (4)$$

Where C_{di} , C_{mono} and C_{gly} are the molar concentrations (at 8 h) of the diglycerides, monoglycerides and glycerol, respectively. Table 2 shows the initial rate, conversion and selectivities for the different catalyst in the transesterification reaction. Initial rate information for H_2SO_4 , ETS-10 (Na), NaOH is not yet available (these reactions exceeded 5% conversion in just a few seconds).

Table 2

Initial rates of reaction, conversions and selectivities to diacetin, monoacetin and glycerol in the triacetin transesterification with methanol on acid and base catalysts after 8 h of reaction at 60°C.

Catalyst	Initial rate of reaction (mol min ⁻¹ g _{cat} ⁻¹)	Conversion %	Diacetin %	Monoacetin %	Glycerol %
Without	0	0	0	0	0
Amberlyst-15	2.34E-4	81	13	24	63
PAC	~0	<1	100	0	0
WZ	8.8E-5	20	86	14	0
SZ	1.0E-4	54	37	25	38
ETS-10 (H)	~0	<1	76	24	0
Zeolite H β	~0	<1	80	20	0
H ₂ SO ₄	-	93	3	10	87
ETS-10 (Na)	-	92	8	22	70
MgO	1.12E-4	14	91	9	0
NaOH	-	93	6	16	78

Without a catalyst, no appreciable conversion was observed at the temperature and pressure used. However, it has been reported that above methanol supercritical conditions (239°C and 8.1 MPa) the transesterification reaction of TGs can substantially proceed in the absence of catalysts [5]. The energy and safety requirements limit the use of this process.

Conclusions

In general, base catalysts exhibited higher reactivities than acid catalysts. External and internal mass transfer limitations are of major importance for the transesterification reaction. Microporosity could severely limit catalyst materials, such as zeolites, when dealing with large species. Reactions experiments indicated that homogeneous catalysts were apparently more active than their respective heterogeneous counterparts. However, Amberlyst-15, sulphated zirconia and ETS-10 (Na) showed reasonable good activities at this moderate temperature, indicating that they could be good alternatives to the homogeneous catalysts without the drawbacks of corrosion, difficulty in handling, and cost. Future studies have to be focused in determining the deactivation (if any) of these active catalyst materials (for reusability purposes) and their applicability to the transesterification of the TGs presents in vegetable oils and fats.

Acknowledgments

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