Esterification of glycerol with acetic acid for improved production of triacetin using toluene as an entrainer

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In the recent years, biodiesel has gained significant attention in Europe and US as clean and sustainable transportation fuel. Glycerol is inevitably produced by 10 wt% in total biodiesel production. Only a part of it is consumed after expensive purification by traditional industries. Thus, the rapid increase in biodiesel production has resulted in a large surplus of low value glycerol in the market. Therefore, intensive efforts are taken to valorize raw glycerol to chemical intermediates, mostly using catalytic processes, such as hydrogenolysis to propanediol, dehydration to acrolein, oxidation to ethylene glycol, acetylation or esterification.
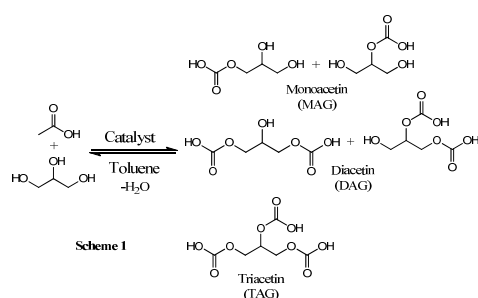

Fig. 1 – Products of glycerol acetylation with acetic acid.

Glycerol acetylation leads to useful chemicals such as glycerol monoacetate and diacetate that have applications in cryogenics and polymers (Figure 1). Glycerol triacetate can act as cold flow improver and viscosity reducer for biodiesel, anti-knock additive and octane booster for gasoline as an alternative for commercial alkyl ethers (MTBE and ETBE) [1]. Acetylation can be carried out with acetic anhydride or acetic acid, with the latter being much cheaper. Glycerol esterification with acetic acid is usually performed using homogenous catalysts like sulphuric acid, paratoluene sulphonic acid, etc., however, these catalysts are hazardous, corrosive and not eco-friendly. Therefore it is desired to replace these mineral acids by strong solid acid catalysts such as sulphated mesoporous silica, heteropolyacids [2], or acidic ion exchange resins like Amberlyst-15 [3]. In general, the selectivity for triacetin on supported heteropolyacids is 19-32% [2] while for Amberlyst-15 it reaches 44% [3]. However, single-pass transformation with high triacetin selectivity is impossible, as the reaction comprises a series of consecutive esterification steps forming various intermediates, and each of them is ruled by chemical equilibrium due to the formation of water as an unavoidable by-product.

In the present work, a modified Dean Stark apparatus and toluene as an entrainer were used to remove the water formed in the reaction through azeotropic distillation process and to drive the reaction equilibrium towards the product side. Several acidic materials like silica (S11), silica-alumina (SA40) and alumina (A12) supported heteropoly acid (STA = silicotungstic acid, TPA = tungstophosphoric acid, PMA = phosphomolybdic acid) and ion exchange resins like Amberlyst-15 (A15) and Amberlyst-70 (A70) were used as catalysts. The reaction was run in a 250 ml round bottom flask at 105 °C with an initial glycerol/acetic acid molar ratio of 1: 6 and a catalyst load of 5 wt% with respect to glycerol. Product analysis was carried out after derivatization with trimethyl silyl chloride in pyridine by means of an offline GC (HP 5890) equipped with a CP-Sil 13 CB column (25 m × 0.32 mm) and a FID. Two internal standards were used to evelute volumetric change in the reactor and to ensure high analytical accuracy.

Organic and inorganic catalysts were studied with physico-chemical methods to evaluate the specific amount of acid sites as well as textural and structural properties (BET, XRD, and others).

Tab. 1 – BET surface area and acidic properties of catalysts

Catalysts	S.A. (m²/g)	B.A. (μmol/g)	L.A. (μmol/g)
S11	244	0.0	0.0
STA/S11	206	274.5	24.3
TPA/S11	206	154.9	31.1
PMA/S11	229	82.0	105.8
SA40	520	82.0	237.1
STA/SA40	350	145.9	278.5
TPA/SA40	341	150.4	289.8
PMA/SA40	377	222.6	231.5
A12	303	0.0	171.5
STA/A12	228	40.6	280.7
TPA/A12	267	38.3	297.7
PMA/A12	228	65.4	168.7
A15	53	4.7 eq./kg	-
A70	36	2.55 eq./kg	-

(S.A. = Surface areas, B.A. = Bronsted acidity and L.A. = Lewis acidity).

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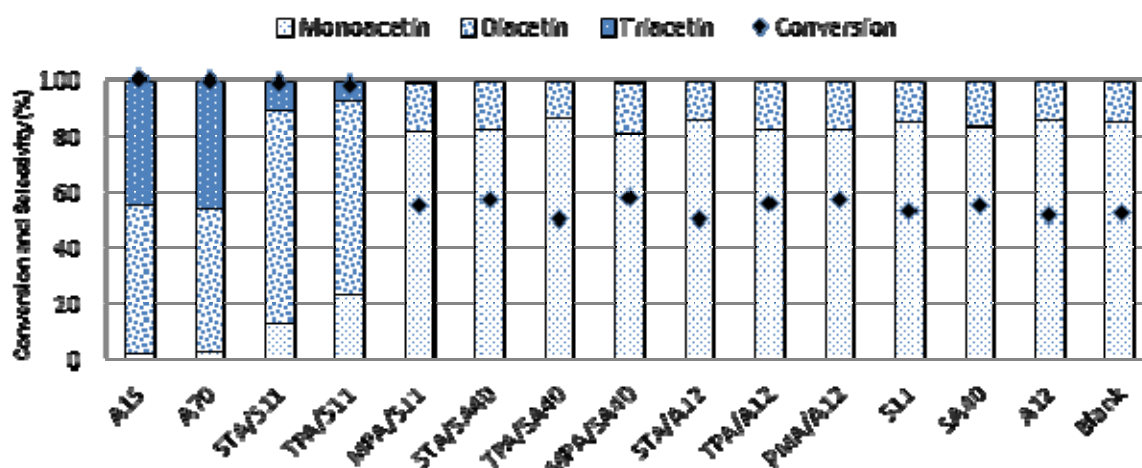
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Fig. 2 – Esterification of glycerol with acetic acid using toluene as an entrainer (reaction conditions: glycerol 10 g, acetic acid 39.16 g, toluene 60 g, catalyst 0.5 g, 105 °C, run time 4 h).

Organic catalysts A70, A15 and supported inorganic catalysts STA/S11 and TPA/S11 showed highest activity (~100% conversion within 4 h) compared to all other catalyst. Other supported heteropolyacids showed nearly ~50% conversion, as shown in Fig. 1. This is only a slight improvement compared to a blank test without catalyst. Hence, these catalysts were used to study the product selectivity with time.

Tab. 2 – Esterification of glycerol with acetic acid using toluene as entrainer after 10 h and 24 h.

Catalyst	t (h)	X (%)	Selectivity			
			MAG	DAG	TAG	DT*
A15	10	100	0	12.3	83.9	3.8
	24	100	0	0	95.3	4.7
A70	10	100	0	7.5	87.6	4.9
	24	100	0	0	94.1	5.9
STA/S11	10	100	1.0	55.5	35.8	7.7
	24	100	0	16.6	71.4	12.0
TPA/S11	10	100	4.9	71.3	21.8	2.0
	24	100	0	21.3	67.5	11.2

DT* = Diglycerol tetraacetate, X = conversion, t = time.

As expected, an increase in triacetin selectivity was observed with time. The formation of the new by-product diglycerol tetraacetate (DT) was observed at prolonged run time and high conversion. With commercial Amberlyst-70 and Amberlyst-15, the maximum selectivity for triacetin reached 87.6% and 83.9% at complete glycerol conversion, respectively, after 10 h. By extending the runs to 24 h, the triacetin selectivity reached 94.1% and 95.3%, as shown in Table 1. In these runs, the esterification rate was so high that also the second intermediate diacetin was completely converted.

The silica supported silicotungstic and tungstophosphoric acids reached selectivity to TAG of 71.4% and 67.4% at complete conversion after 24 h (cf. Table 2). Their specific activity (per catalyst mass) is slightly less than that of the Amberlyst materials.

First results from solids characterization revealed that the efficiency of the organic catalysts is mainly ruled by their specific acidity and thermal stability. Though Amberlyst-70 is less acidic, it outperforms Amberlyst-15 due to higher stability.

Regarding the inorganic catalysts, the activity correlates little to BET surface area and acidity, but the stabilization of the heteropolyacid (Keggin structure) is crucial for effective catalysts.

Acknowledgements

References

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