

# Purification of glycerol from a real process and kinetic modelling of its conversion to triacetin with Amberlyst 36.

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## Highlights

- Crude glycerol (30-50 wt.%) was purified physio-chemically to 74.3 wt.%.
- Resins achieve 25.8-30.1% triacetin yield compared to 11.2–17.6% by zeolites.
- Amberlyst 36 shows stability attaining constant yields of ~27% over 4 recycles.
- Kinetic models to be developed after proving lack of external and internal mass transfer limitations.

## 1. Introduction

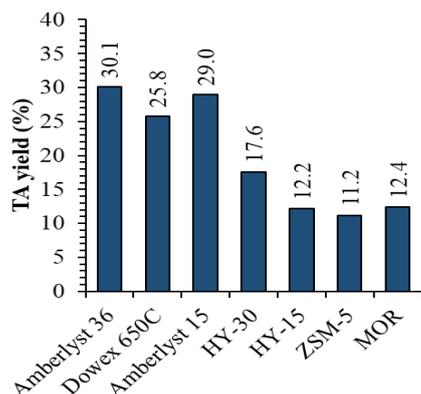
As a replacement to fossil fuels, biodiesel has gained global attention, from whose production approximately 10 wt.% of crude glycerol (Gly) is generated as by-product<sup>[1]</sup>. Gly purity varies between 30–60 wt.%, with impurities such as ash, matter organic non-glycerol (MONG) and water. Crude Gly is an attractive feedstock due to its excess availability and low cost; however, it requires purification before conversion to further products since the impurities can lead to catalyst deactivation<sup>[1]</sup>. A route to valorize Gly is *via* esterification with acetic acid (AA) to produce triacetin (TA), a fuel additive<sup>[2]</sup>. It is an acid-catalyzed reaction consisting of three steps in equilibrium, in which the intermediates monoacetin (MA), diacetin (DA) and by-product water are generated. Due to thermodynamic limitations, excess molar ratio (MR) of AA to Gly (4:1-12:1) and moderate temperatures (80-120°C) are required to attain a high TA yield<sup>[2]</sup>. Various catalysts have been tested, including commercial acidic resins (Amberlyst series) and zeolites<sup>[2]</sup> and different kinetic models have been tested using the power-law, Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley Rideal (ER) approaches<sup>[3]</sup>. However, current research uses pure Gly as a feedstock and thus there is a gap in investigating the reaction using purified crude Gly attained from a real transesterification process. Therefore, this study aims to present the purification of crude Gly and its subsequent conversion to TA in the presence of Amberlyst 36. A detailed kinetic model will be developed that is industrially relevant to be used for scale-up studies.

## 2. Methods

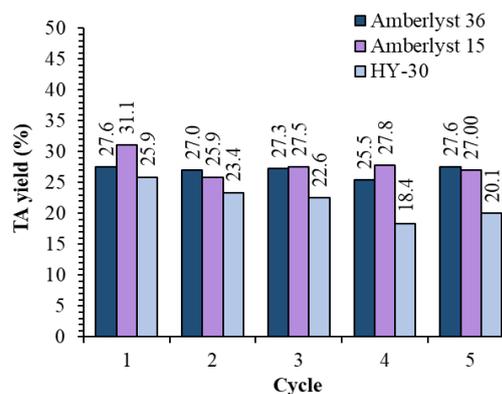
Crude Gly was provided by Argent Energy from a biodiesel plant in Motherwell, UK. It was purified physio-chemically by saponification, acidification, vacuum filtration, neutralization, anti-solvent treatment, evaporation and activated carbon treatment<sup>[1]</sup> and characterized according to the British standard BS 5711-3:1979<sup>[4]</sup>. Ash and water content were determined by burning in a furnace and Karl-Fischer titration (Metrohm 899 coulometer), respectively. MONG content was calculated based on mass balances. Esterification reactions were performed in a batch setup consisting of a reaction flask, thermostat, air condenser, heating plate, a dry block, and a magnetic stirrer. Gly and the catalyst are placed together in a separate flask to AA. Once both flasks are heated to the required temperature, AA is then directly added to the Gly flask to start the reaction. Periodic samples were collected using a syringe and diluted using an IPA solution with 5 g L<sup>-1</sup> of propylene glycol as internal standard. The analysis was done by GC-FID with a DB-WAX 123-7012 column. Screening of commercial resins and zeolites was first performed using pure Gly (99.5 wt%). Recyclability experiments over 5 cycles using purified Gly (~74.0 wt.%) as feedstock were performed for selected catalysts. Lastly, data from experiments in which T (100-130°C), MR (6-12) and catalyst loading (2.5-7.5 wt% of Gly) were collected to develop the model. Using Aspen Custom Modeler, the developed models will be evaluated.

## 3. Results and discussion

The purified Gly attained is 74.3 wt.% pure including 9.8 wt.% of ash, 6.1 wt.% of water and 9.8 wt.% of MONG. The catalyst screening results (Figure 1) illustrate that resins attain higher TA yields (25.8–30.1%) as opposed to zeolites (11.2–17.6%). This is because the HY zeolites have lower acidity (0.063–0.478 mmol g<sup>-1</sup>) and smaller pore size (4–18 nm)<sup>[5]</sup> compared to resins (4.2–5.4 mmol g<sup>-1</sup>, 24–30 nm). Amberlyst 15, Amberlyst 36 and HY-30 were further tested for recyclability, as shown in Figure 2. The resins showed a relatively stable performance attaining a TA yield of ~27%, however HY-30 showed an activity decline of 20%. The smaller pore size of HY-30 could have prevented any blockage due to impurities from being cleared out during the washing process causing deactivation. Thus, Amberlyst 36 was selected for the kinetic study as it can operate up to 150°C as opposed to Amberlyst 15 (120°C).



**Figure 1.** Catalyst screening (pure Gly, 120°C, MR = 9, catalyst = 5 wt.% of Gly, 400 rpm,  $t_{\text{rxn}}$  = 7 h)



**Figure 2.** Catalyst recycling (purified gly, 120°C, MR = 12, catalyst = 5 wt.% of Gly, 400 rpm,  $t_{\text{rxn}}$  = 7 h)

For the kinetic study, external and internal mass transfer limitations were investigated by stirring speed experiments (100–800 rpm) and Weisz-prater (WP) criterion, respectively. Varying the stirring speed led to no changes in Gly conversion indicating the lack of external mass transfer limitations. Internal mass transfer limitations are also negligible as the WP criterion is <1 ( $\eta=0.49$ ). Regarding operating conditions, increasing the temperature and MR aided in achieving higher TA yield as expected by pushing the equilibrium. Increasing catalyst loading also caused positive effects due to the increase in active sites. Finally, based on the results of a set of 16 kinetic runs varying T, MR and catalyst loading, power-law, dual-site LHHW and single-site ER models will be developed assuming that the surface reactions are the rate determining steps. The incorporation of catalyst deactivation due to salts blockage and water poisoning will also be investigated.

#### 4. Conclusions

For the first time, the conversion of Gly purified from a real biodiesel process is investigated. Using physio-chemical techniques, crude Gly was purified to a purity of 74.3 wt.%. Based on an initial catalyst screening and recyclability studies of commercial resins and zeolites, Amberlyst 36 showed the best performance attaining a stable TA yield of ~27% after 7 h at 120°C, MR of 12 and catalyst loading of 5 wt.% of Gly. The use of Amberlyst 36 showed that external and internal mass transfer limitations are negligible when investigating the effect of stirring speed and the WP criterion, respectively. With the available experimental data, a model to describe the intrinsic kinetics of the reaction will be developed with the possible consideration of deactivation. The obtained kinetic model is of relevance to subsequent reactor design and process modelling.

#### References

- [1] T. Attarbach, M.D. Kingsley, V. Spallina, Fuel, 340 (2023) 127485.
- [2] P. Mukhopadhyay, R. Chakraborty, S. Singh, Environ. Chem. Lett., 20 (2022) 1193–1224.
- [3] A. Sandid, V. Spallina, J. Esteban, Fuel Process. Technol., 253 (2024) 108008.
- [4] British Standards Institution, BS 5711-3:1979, 1979.
- [5] R. Zhang, S. Xu, D. Raja, N.B. Khusni, J. Liu, J. Zhang, S. Abdulridha, H. Xiang, S. Jiang, Y. Guan, Y. Jiao, X. Fan, Microporous Mesoporous Mater., 278 (2019) 297–306.

**Keywords** Glycerol; purification; esterification; kinetic models.