From Batch to Continuous Flow Esterification of Glycerol using Heteropoly acids supported on K-10 catalysts

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Introduction

With increasing energy demand and dwindling global supplies of conventional fossil fuels, it is imperative to develop renewable alternatives for fuels and chemicals. One of the potential alternatives is the bio-refinery concept, where biodiesel produced could serve as a potential replacement of petroleum based fuels. A major disadvantage of biodiesel comes in the form of a waste byproduct, glycerol, which accounts for 10 wt% of all biodiesel production. In order to enhance economic viability of biodiesel and promote a circular economy it is essential to add value to glycerol feedstock [1,2]. One pathway of glycerol valorization is through an esterification process using renewable acetic acid. Glycerol esters have a wide range of potential applications, both diacetin and triacetin are effective as an oxygenated fuel additives, improving the combustion and fuel economy of the biodiesel, whilst also decreasing harmful emissions. Typically, esterification process requires stoichiometric use of mineral acids or $AlCl_3$ as catalyst. Such catalysts are hazardous, corrosive and non-renewable. With increased importance placed on green chemistry, catalysts need to be safe, non-corrosive and recyclable. In previous work Bronsted-acidic ionic liquids have been shown to be effective catalysts for this reaction [3]. In this work, it has been shown that Tungstophosphoric acid (DTP) supported on K-10 montmorillonite acidic clay is an efficient and reusable catalyst for this reaction. Using 20 wt% DTP/K-10 a combined selectivity of di- and triacetin of 98.7 % was obtained. The process was also performed under continuous flow conditions using a packed-bed reactor.

Materials and Methods

Tungstophosphoric acid (DTP) was supported on K-10 using a wet impregnation method. Loadings of 5, 10, 20 and 20 wt% DTP on K-10 were prepared in two steps. Firstly the required amount of DTP was dissolved in 1 ml of methanol, which was then added in small amounts to the required amount of K-10 clay, which has been dried in an oven overnight at 120°C. This was then mixed until dried, before more DTP/methanol was added. Secondly the prepared catalyst underwent calcination in a furnace. Esterification of glycerol with acetic acid was conducted in a glass reactor. In a typical experiment, the reactor was charged with DTP/K-10 (10 wt%), glycerol (5 g) and acetic acid (32.42 g) and stirred using a magnetic stirrer at 110℃. The reactions were monitored by taking regular samples and analyzed using gas-chromatography. Continuous flow reactions were performed using a packed-column consisting of 3 g of catalyst mixed with glass beads. A 1:10 molar ratio of glycerol to acetic acid was pumped through the column under different flow rates and different temperatures to observe the effect on the product distribution.

Results and Discussion

Table 1 summarizes the results of the esterification of glycerol with acetic acid using a range of DTP/K-10 catalysts giving the product selectivity to glycerol esters and the conversion of glycerol after 2 hours.

(a)

Catalyst	Glycerol Conv. / %	Acetin Selectivity / % Mono	Di	Tri
K-10	**95.2**	**32.9**	**57.6**	**9.6**
5 wt% DTP/K-10	**97.3**	**26.4**	**61.8**	**11.7**
10 wt% DTP/K-10	**97.9**	**23.8**	**62.5**	**13.7**
20 wt% DTP/K-10	**99.6**	**5.9**	**64.0**	**30.0**
30 wt% DTP/K-10	**99.5**	**4.9**	**60.8**	**34.3**
DTP[a]	**100**	**2.4**	**45.7**	**51.9**

(b)

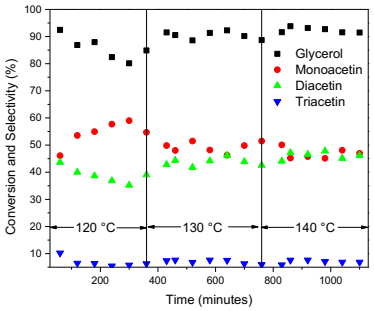

Figure 1 (a) Batch process for Glycerol esterification using DTP/K-10 at 110 ºC (b) Continuous flow process for glycerol esterification using DTP/K-10 under different temperatures.

From the batch process (figure 1(a)) we can see that glycerol conversion for all heteropolyacids loadings is greater than 97 % after 2 hours of reaction using 10 wt% of catalyst. It can be noted than loading K-10 with DTP results in an increase in the activity of the catalyst. A 10 wt% loading of DTP results in an increase in the selectivity of triacetin from 9.6 % shown by neat K-10 to 11.7 %. Doubling the loading of DTP from 10 to 20 wt% results in an increase of greater than double in the selectivity of triacetin from 13.7 % to 30.0 %. This effect is not as pronounced at higher loadings, with an increase in DTP loading to 30 wt% yielding only a 4.3 % increase in triacetin. The greatest selectivity to triacetin (51.9 %) is observed with unsupported DTP; however issues with reusability limit the use of this as a catalyst in the reaction. The reaction was also performed in continuous flow using 20 wt% DTP/K-10 catalyst. A range of flow rates from 0.5 ml/min to 0.1 ml/min were screened with highest conversion and selectivity to di and triacetin observed with a flow rate of 0.1 ml/min. Figure 1(b) shows the effect of temperature on the reaction conversion and product selectivity for the continuous flow process. As the reaction temperature is increased the conversion of glycerol increases and the amount of diacetin also increases.

Significance

Esterification of glycerol with acetic acid produces acetins, in which di- and triacetins are commercially important fuel additives. In this study, glycerol esterification was studied using the heteropolyacid DTP supported on K-10 clay as catalysts. Amongst all the catalysts tested, 20 wt% DTP/K-10 showed the highest activity and selectivity to di- and triacetin.

References

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