



From residual to useful oil: Revalorization of glycerine from the biodiesel synthesis

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ARTICLE INFO

Article history:

Received 15 September 2008

Received in revised form 28 January 2009

Accepted 29 January 2009

Available online 9 March 2009

Keywords:

Glycerol

Triacetin

Biofuels

Reactive distillation

ABSTRACT

The reaction kinetics for the synthesis of glycerol triacetate (triacetin) from glycerol and acetic acid has been studied in the frame of revalorization of residual glycerol in biodiesel production. The reaction has taken place in a stirred reactor at a pressure of 1070 kPa. No external catalyst has been added because the reaction performs better by using as catalyst an excess of acetic acid. Kinetic parameters were obtained at 120 and 160 °C and a model of three reactions with monoacetin, diacetin and triacetin formation was proposed with a good agreement with the experimental results. Arrhenius constants were determined for the involved reactions.

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1. Introduction

The EU is supporting biofuels with the aim of reducing greenhouse gas emissions, boosting the decarbonisation of transport fuels, diversifying fuel supply sources, offering new income opportunities in rural areas and developing long-term replacement for non-renewable fossil fuels (European Commission, 2006). The combustibles from fossil origin represent the 88% of the primary energy consumed in the planet. The fossil fuel resources are becoming more and more difficult to extract and process, there is a strong dependence of the energy supply on the events in the main producer countries. Moreover, the Asian industrialization and growth requires more energy, leading to higher prices for the oil (www.wtrg.com/prices.htm). With the nowadays context of high oil prices, the development of sustainable energetic sources for the transportation is a priority. At the beginning diesel was used mainly for slow engines, but nowadays, the improvement of the diesel engines with performances similar to gasoline and lower fuel consumption has led to usage up to 75% of the diesel production for regular cars surpassing the 18% used for the agriculture. The higher demand this product in EU obliges to import large amounts thus increasing its price. This situation has a direct repercussion on food prices since increases production and transportation costs. The EU aim at mixing 5.75% of biocombustibles in the gasoline and diesel until 2010 (O'Driscoll, 2007). Similar measures have been taken by USA, Canada, Australia or Japan.

On the other hand, there is the globalization in which the products are generated on one side of the world and sold on the other. The use of edible oil to produce biodiesel can lead to a diminution of the oil available as food for persons and farm animals. Another problem is a large surplus of glycerol. A 25% molar of the output stream is the by-product glycerol (10% in weight) which is unavoidable as it is generated by the main reaction. The biodiesel fuel is obtained by transesterification of seed oils, animal fats or recycled oils with methanol or ethanol and the glycerol market is already saturated. Some millions of tons of biodiesel with the associated glycerol are being produced in EU. Glycerol can be used in some applications as emulsifier, softener agent, stabiliser, wetting agent for bakery products, ice creams, tobacco, lotions and other mouthwashes, etc. and, of course, countless pharmaceutical and cosmetic applications, these last increasing in the last years.

Nowadays, a large number of biodiesel producers are incinerating glycerine (O'Driscoll, 2007), but since glycerine is becoming an abundant and cheap natural resource, many new technologies related to its further processing have been appearing. Some of these technologies both already and potential industrialized are introduced in Pagliaro et al. (2007). An efficient way to convert glycerine to food grade triacetin would be a plausible way to revalorize the glycerine because it could be used at least as animal food. There are several industrial synthesis alternatives; one of them is by reaction of glycerine and acetic acid. The triacetin is a transparent oil, combustible and of bitter taste that occurs naturally as oil from cod-liver oil, butter, and other fats (Grant, 1972). Triacetin is reported to function as a cosmetic biocide, plasticizer, and solvent in cosmetic formulations. It is a commonly used carrier for flavours and fragrances (Ogawa et al., 1992), and was affirmed as a

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generally recognized, as safe human food ingredient by the Food and Drug Administration. More information on its properties and toxicity was presented in the Final Report on the Safety Assessment of Triacetin (Andersen, 2003).

The conversion of glycerine to triacetin is a process that exists but that should increase its performance to be able to treat big quantities of glycerine in the most environmental friendly way. Nakamori (1952) found that the quantity of triacetin generated was very small in front of the diacetin and monoacetin formed. There are some studies in the literature searching for catalysts for the reaction of glycerine and acetic acid, for instance Lu and Ma (1991) get 87% triacetin using acidic ion exchange resin and MgSO_4 at room temperature for 72 h. Yang and Lu (1996) use $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$, referring the best activity of the catalyst at 450 °C and Wu et al. (2007) get a yield of 93.6% at a reaction temperature of 130 °C with the same catalyst. Hou et al. (1998) use aminosulfonic acid with a yield higher than 90%, Zhang (1999) determine the optimal conditions for the ratio glycerol/acetic acid/catalyst ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}/\text{C}$) obtaining over 96% yield. Zhang and Yuan (2001) use phosphotungstic acid as the catalyst and with the optimum reaction conditions of mass ratio of catalyst to reactant 3.8%, reaction temperature 135–155 °C and reaction time of 7 h, get up to 84.6%. For Ding et al. (2003), using $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as catalyst, the product yield and purity reached >98% and >99%, respectively. Dong and Guo (2003) use solid sulfated $\text{Fe}_2\text{O}_3/\text{TiO}_2$, easily recovered and reused. Melero et al. (2007) obtain the best performances (up to 90% of glycerol conversion) using sulfonic acids and 4 h of reaction, Liu et al. (2007) use p-toluenesulfonic acid/C reaching a product yield of 92%, Li et al. (2007) use ionic liquids ($[\text{HSO}_3\text{-pmim}][\text{PTSA}]$) and the optimum conditions were obtained at a glycerol/acetic acid ratio of 1:8, catalyst amount 10.5% the total weight of reactants, reaction time 6 h and reaction temperature 120 °C. There are also several patents such as Bremus et al. (1981), Gawrikow et al. (1982), Pechenev et al. (1995), Mitsuya and Ogawa (1996) and Mhaskar et al. (2002). Some of the strategies to favour the formation of triacetin using the Le Chatelier Law are: to use a large excess of acetic acid, eliminate the water by reaction with acetic anhydride generating acetic acid or eliminate the water by simple distillation.

In this context, the aim of this work was to try out the reaction without any catalyst and to determine the kinetics of this reaction to develop the study, in a next work, of a reactive distillation process to obtaining triacetin from glycerol, and removing water at the top of the column.

2. Methods

The reactives used in the experiments are glycerol (PS) of 99% purity (GC) from Panreac (ref. 151339.1212), glacial acetic acid (Reag. Ph. Eur.) PA-ACS-ISO of 99.7% purity (GC) from Panreac (ref. 131008.1611) and triacetin of 99% purity from Aldrich (ref. 525073). Monoacetin and diacetin are not available as pure products in the market.

Gas chromatography has been used because provides good results in the triacetin analysis (Lu, 1991; Ogawa et al., 1988; Ogawa et al., 1992; Uematsu et al., 1997). The gas chromatograph used for the determinations is a HP 7890A with automatic injection and FID detector, with a column HP-5 Part. No. 19091 J-413, the injector and detector working at 310 and 300 °C, respectively, slope of temperature of 15 °C/min from 100 to 200 °C resulting in a analysis time around 7 min. The injected volume in both cases is of 1 μL and the pressure is at 13.1 psi. The response factor (ratio of areas versus ratio of moles) is linear and crosses the origin of coordinates.

Referring to the reaction, initial exploratory tests were performed by introducing 1.5 mL of sample inside glass vials sealed

hermetically in a thermostatic bath for a temperature of 35 °C. For higher temperatures, a thermal insulated heating plate with a temperature controller of Pt100 was used. No agitation was applied.

The final kinetic determinations were performed in a stirred pressurized reactor PPI Industries Series LC of 300 mL of capacity pressurized at 155 psi and with a stirring speed of 290 rpm.

3. Results

3.1. Preliminary test

No appreciable advance of the reaction is observed when mixtures of reactants are kept 4 h in an isothermal bath at 35 °C, although the acetic acid is in excess. On the contrary, the reaction takes place almost instantaneously when a quantity of sulphuric acid (10% in weight) is added to catalyze the reaction, but a lot of components are detected there. Two mixtures of glycerine and acetic acid were kept at ambient temperature in a sealed vial during three months. 22 components generated by the acetic acid and isomerised acetic acid combinatory substitutions in the three alcohol group positions of the glycerine are detected when the reaction mixture is equimolar, but only seven species are detected when a stoichiometric mixture is used.

3.2. Influence of the acetic acid excess

The preliminary tests have shown the feasibility of the reaction without catalyst, but the rate is very slow at smooth temperature. Also, references indicate reaction temperatures over 100 °C. The influence of the excess of acetic acid was evaluated at 120 °C, without catalyst and 4 h on the heating plate. At stoichiometric mixture, a great number of secondary components are obtained, but when the acetic acid composition increases then the number of secondary components decreases. Four times and six times, the stoichiometry (1:12; 1:18) are studied, and the results are quite similar. As over four times the stoichiometry there is not improvement noticed in the reacting mixture; then, to further study the kinetics, four times the stoichiometric feed was used to collect only in the analysis the components of the main reaction.

3.3. Influence of the temperature on the kinetics

Just as it was expected, in the experiments on the heating plate was observed a great influence of the temperature on the kinetics of the reaction and on the conversion. With four times the stoichiometric ratio on acetic acid, the reaction kinetics at several temperatures (100, 120 and 150 °C) was determined (Fig. 1) and the

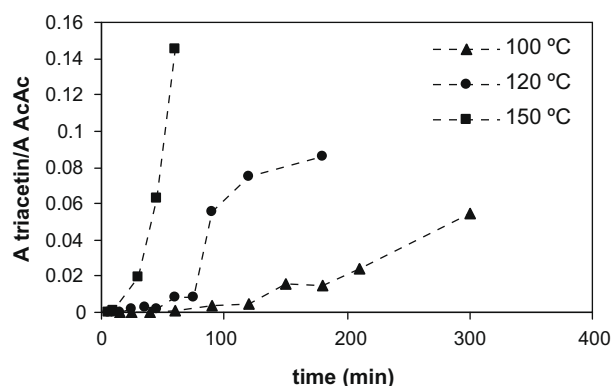


Fig. 1. Reaction kinetics at several temperatures without catalyst and four times the stoichiometric feed of acetic acid.

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