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Revalorization of glycerol: Comestible oil from biodiesel synthesis

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ABSTRACT

High dependence on fossil fuel has caused increase of carbon dioxide concentration in the atmosphere. The actual political trends are towards an increased use of renewable fuels from agricultural origin. One of the main products of the European biorefineries is biodiesel. The main reaction involved in biodiesel synthesis produces a large amount of glycerol as by-product. Two aspects are arising in this respect: the glycerol obtained as residue and the food conversion to fuel. This paper deals with the revalorization of the residual glycerol stream to obtain triacetin (glyceryl triacetate), the lightest comestible oil. The application of glycerol as raw material to produce triacetin is not new. The goal of this paper is to check the feasibility of this transformation in an efficient integrated continuous process which is suitable for processing high quantities of glycerol. A kinetic model was determined experimentally for the production of triacetin from glycerol and acetic acid in the absence of catalyst. The results showed that by process integration of the reaction and distillation in the same unit (reactive distillation), a more sustainable process can be developed. The proposed configuration output is checked by rigorous simulation.

Keywords: Glycerine; Triacetin; Reactive distillation; Process simulation; Biodiesel

1. Introduction

The EU is supporting biofuels with the aim of reducing greenhouse gas emissions, boosting the decarbonization 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 fossil fuel represents 88% of the primary energy consumed in the world. However, fossil fuel resources are becoming more and more difficult to extract and process. Nowadays, the energy supply strongly depends on the events occurring in the main countries which provide great fossil fuel resources. Moreover, the Asian industrialization and growth requires more energy, leading to higher prices for the oil (Fig. 1). In the current context of high oil prices, the development of sustainable energetic sources for the transport becomes a priority. In EU, the main focus is on diesel, whose price is higher than the gasoline for the first time (Fig. 2). At the beginning the diesel was used mainly for slow engines such as for agriculture, fishing ships and transport, for this reason recording lower taxes. Nowadays, the improvement of diesel engines leads to performances similar to gasoline engines and lower fuel consumption. This caused a 75% use of diesel production in regular cars, while only 18% is used for the agriculture. The diesel–gasoline consumption ratio in the 1990s was around 1:10 and today it is around 7:3. The higher demand of diesel in EU generates excess of gasoline, large amounts of diesel are imported and consequently this leads to its price increase. This situation has a direct impact on food prices by the increase of production and transport costs. EU established

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Abbreviations: EU, European Union; RD, reactive distillation; FID, flame ionization detector; GC, gas chromatography; USD, US dollars; Mt, million tons.

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Nomenclature

k_j	kinetic constant
A_j	pre-exponential factor—Arrhenius expression
E_{aj}	activation energy (kJ/kmol)
T	temperature (K)
n	number of moles
x	molar fraction—liquid phase
y	molar fraction—vapour phase

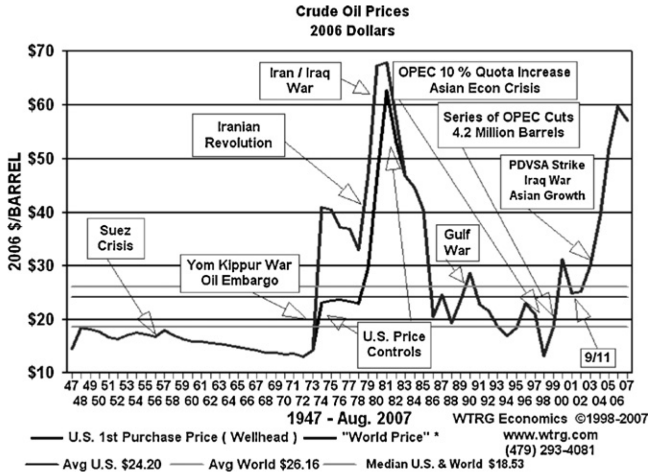

Fig. 1 – Crude oil prices (http://www.wtrg.com/prices.htm).

the aim to mix 5.75% of biofuels in gasoline and diesel until 2010 (O'Driscoll, 2007), USA, Canada, Australia or Japan have taken similar measures. Biodiesel production in the EU was estimated to be about 6 Mt in 2006 and is forecasted to increase to about 12 Mt in 2010 (Behr et al., 2008). A great expansion of the biodiesel production in the next decades in EU is expected.

On the other hand, a continuous increase of population (doubled in last 40 years (Fig. 3)), leads to a leakage of resources. In 2005, the total production of fats and oils was in the range of 144 Mt. Nowadays, only 14% of this material is processed within the chemical industry (Behr et al., 2008). The use of comestible oil to produce biodiesel can lead to a decrease of the oil available as food for people and farm animals. Another issue related to biodiesel production is the large surplus of glycerol generated. Although glycerol has been a well-known renewable chemical for centuries, its commercial relevance has increased considerably in the last few years due to its rising unavoidable formation as a by-product of biodiesel production. A 25% molar of the output stream is the by-product glycerol (10% in weight). The glycerol market is already saturated and more than half of the industries producing glycerol have already closed (Fig. 4). The main strategy used has been to find new applications for the glycerol, apart of the ones that already exist (Leffingwell and Lesser, 1945). Fig. 5 shows some of the main applications (Pagliaro et al., 2007). Nowadays, a large number of biodiesel producers are incinerating the glycerol (O'Driscoll, 2007). An efficient way to convert glycerol to food grade triacetin would be a plausible way to revalorize glycerol because it could be used at least in animal nutrition. Triacetin is one of the main chemical products obtained from glycerol. There are several industrial synthesis alternatives, one of them being the reaction of glycerol and acetic acid. The triacetin is a transparent oil, combustible and of bitter taste. It occurs naturally as cod-liver oil, in butter, and other fats (Grant, 1972). Also known as glyceryl triacetate, it is reported to function as a cosmetic biocide, plasticizer, solvent in cosmetic formulations and also as biodiesel fuel component (García et al., 2008). It is a commonly used carrier for flavours and fragrances. Triacetin was generally recognized as safe human food ingredient by the Food and Drug Administration. More information on its properties and toxicity is presented in the Final Report on the Safety Assessment of Triacetin (2003).

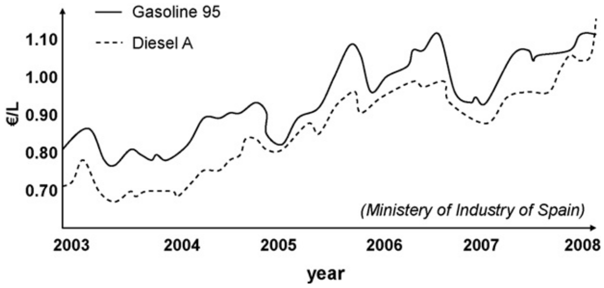

Fig. 2 – Gasoline and diesel prices.

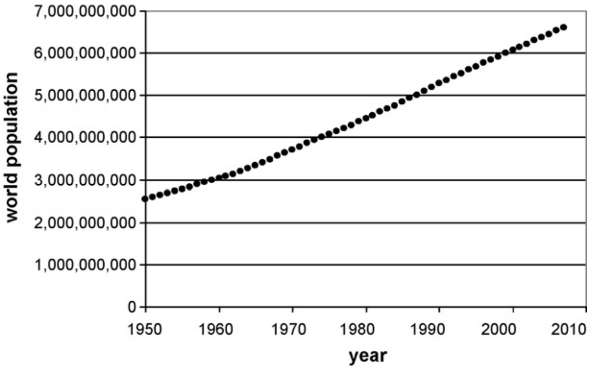

Fig. 3 – World population. (http://www.census.gov/ipc/www/idb/worldpop.html).

The conversion of glycerol to triacetin is an existing procedure which should increase its performance to process high quantities of glycerol in the most environmental friendly way. Nakamori (1952) found that the quantity of triacetin generated was very low compared to the diacetin (glyceryl diacetate) and monoacetin (glyceryl monoacetate) synthesis intermediates. There are several studies in literature searching for catalysts for the reaction of glycerol and acetic acid. For instance Lu and Ma (1991) obtain 87% triacetin in the product stream using acidic ion exchange resin and $MgSO_4$ at room temperature for 72 h. Yang and Lu (1996) and Wu et al. (2007) use $SO_4{}^{2-}/ZrO^{2-}TiO_2$, Hou et al. (1998) use aminosulfonic acid, Zhang (1999) use $SnCl_4{\cdot}5H_2O/C$, Zhang and Yuan (2001) use phosphotungstic acid, Ding et al. (2003) use $H_3PW_{12}O_{40}$, Dong and Guo (2003) use solid sulfated Fe_2O_3/TiO_2, Melero et al. (2007) obtain the best performances using sulfonic acids, Liu et al. (2007) use p-toluenesulfonic acid/C, Li et al. (2007) use ionic liquids ([HSO_3-pmim] [PTSA]). Several patents propose various approaches for triacetine synthesis in the presence of catalysts, such as Bremus et al. (1981), Gawrikow et al. (1982), Pechenev et al. (1995), Mitsuya and Ogawa (1996), Mhaskar and Kulkarni (2002). The general strategies followed to increase the conversion to triacetine involve the use of acetic acid in large excess, the use of acetic anhydride to eliminate water generated, or the simple distillation for water removal.

The innovation proposed in this paper is not related to the catalyst, but to the process. The kinetic parameters are