

High temperature solid-catalized transesterification for biodiesel production

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Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. Biodiesel is a mixture of monoalkyl esters of long chain fatty acids derived from renewable feed stock like vegetable oils and animal fats, mainly made of fatty acid glycerides. It is produced by transesterification processes in which oil or fat are reacted with a monohydric alcohol in the presence of a catalyst. The transesterification process is affected by reaction conditions, alcohol to oil molar ratio, type of alcohol, type and amount of catalysts, temperature and purity of reactants.

Heterogeneous acid catalysts are quite efficient in promoting the transesterification reaction also in the presence of free fatty acids, which get esterified under the same reaction conditions. They also allow a prompt separation of pure glycerol and a simplification of subsequent purification steps of this by-product.

In the present paper, the performance of a titanium doped zirconia solid catalyst is presented, with attention to the effect of water in the reactant feed. Results show that the presence of water is well tolerated and even beneficial for the transesterification process.

Introduction and aim of the work

Monoesters produced by the transesterification of vegetable oils with alcohols are known as biodiesel fuels. Most biodiesel fuels are currently produced by transesterification of refined/edible oils with methanol in the presence of homogeneous basic catalyst, such as sodium or potassium hydroxides, carbonates or metal alkoxides (Ramadhas et al., 2002). The alkaline catalysts show high performance, providing biodiesel fuel of high quality, but the oils often contain significant amounts of free fatty acids, which are turned into soap by reaction with the alkali catalyst. In addition, the outflow of the alkaline catalysts with the biodiesel fuel product is a serious problem that requires the addition of further washing and separation steps to the process (Meher, et al., 2006). An alternative way to process these vegetable oils is to use an acid catalyst. However, homogeneous acids such as hydrochloric acid and sulfuric acid require a long reaction time, one or more order of magnitudes larger than that required by the alkali catalysts, and this becomes a serious problem. The use of liquid acids and bases as catalysts presents not only environmental threats, but also causes difficulties in their

separation from the products (Meher, et al., 2006). An interesting alternative can be found by adopting solid catalysts, both acid and basic (Santacesaria et al., 2007). In fact, heterogeneous catalysts are either easily separated or retained in the reactor and may result into higher quality of both product (esters) and byproduct (glycerol). In fact pure high grade glycerol can be obtained, in this case, without expensive refining operations (Bourney et al., 2005). For these reasons, many heterogeneous catalysts, based on both basic and acid solids, have recently been proposed in the literature (Santacesaria et al., 2006; Furuta *et al.*, 2004; Furuta *et al.*, 2006). In particular solid super acids appear to be well suited for promoting the transesterification of vegetable oils as well as the esterification of free fatty acids (Furuta *et al.*, 2004; Lopez et al. (2007), Lopez et al. 2008).

In this work the performance of the same titanium doped zirconia employed as the solid catalyst by Furuta et al (2004) was tested for the transesterification of rapeseed oil with methanol. Experiments were conducted both in the presence and in the absence of water, with the aim of ascertaining its effects on reaction course.

Materials and methods

The transesterification reaction was carried out using a refined rapeseed oil (Oleificio Zucchi S.p.A) and 99.9 % pure methanol (Carlo Erba). The catalyst was prepared using a titanium-doped amorphous zirconia, $\text{TiO}_2/\text{ZrO}_2$ (11wt% Ti), supplied by Daiich Kigenso Kagaku Kogyo Co., Ltd (Tokyo, Japan). The powder was calcined in air at 400 °C for 2 h, then press-molded and crushed to get irregular particles. These last were sieved and 11.0 g of the fraction between 0.5 and 2.0 mm were employed to fill the reactor. This last was a stainless steel ($\frac{1}{2}$ " OD) fixed-bed continuous-flow reactor. The two reactants streams were mixed by a T- junction and pre-heated before the reactor. At the reactor outlet products passed through a cooling section after which they were collected to be analysed. The methanol vaporizes in the reactor and contacts the catalyst in the gaseous phase, and then liquefies in the cooling zone.

The reactants were fed to the pre-heating system by two 60 ml volumetric syringe pumps Ne-500 Multi-PhaserTM.

The products collected were analyzed by GC analysis following the present European standards as reported in Table 1. A FID GC (Agilent 7890A) was used for the determination of fatty acid methyl ester yields.

Chromatographic analysis	
Oven conditions	140 °C (5 min.), 4 °C/min. to 240 °C (5 min.) ²
Injector temperature	250 °C
Detector	FID, 260 °C
Carrier gas	nitrogen, 20 cm/sec at 175 °C
Sample Injection	1 μL , 100:1 split

Table 1: GC conditions

Results

The influence of reactants flow rate, temperature and water concentration on methyl ester yields was investigated..

1.1 Weight hourly space velocity effect

In Fig. 1 the fatty acid methyl esters yield is reported as a function of the *weight hourly space velocity* (WHSV), defined by:

$$\text{WHSV}[\text{h}^{-1}] = \frac{\text{Reactants Flowrate}[\text{gh}^{-1}]}{\text{CatalystMass}[\text{g}]}$$

while

$$\% \text{Yield} = \frac{\text{FAME weighth}}{\text{TG weighth}} \approx \frac{\text{FAME weighth}}{\text{Total sample weighth}}$$

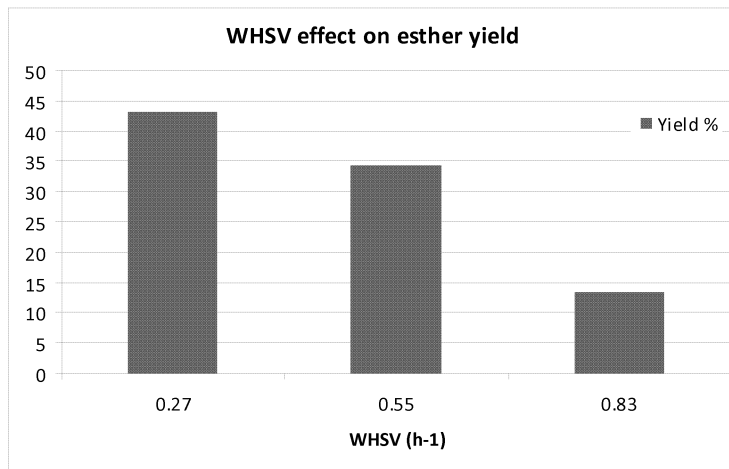


Figure 1: Effect of space velocity on ester yield

As it is possible to note, ester yield decreases while increasing WHSV, as expected.

1.2 Methanol to oil ratio effect

In Fig. 2 the effect of methanol to oil ratio is reported for a WHSV of 0.83 h⁻¹ and system temperature 200°C. As it is possible to see there is no significant modification in ester yield for methanol to oil ratios up to 20:1, while a significant yield increase (about 77%) is observed when the methanol to oil ratio is brought to 40:1. The reasons behind the observed dependence are not clear yet. There likely is a relation to the four-phase fluid dynamics inside the reactor (two liquid phases, one solid phase and a gas phase mainly made of methanol), which is complex and not sufficiently known. It may be speculated that when the methanol to oil ratio is of the order of 40:1 the gas phase velocity increases to the point of promoting and improving methanol mass transfer through the liquid phase film.

1.3 Reaction temperature effect

As regards the influence of reaction temperature on the transesterification reaction, three different temperatures, 200° C, 235 ° C e 245° C, were experimentally tested, the highest temperature being limited by oil smoke point. As it can be seen in Fig. 3, methyl ester yields increase when increasing temperature. Notably the temperature dependence observed is consistent with an Arrhenius activation energy of 57,4 kJ/mol, a figure consistent with Lopez et al. (2008) findings. This clearly indicates that the reaction rate is under kinetic control.

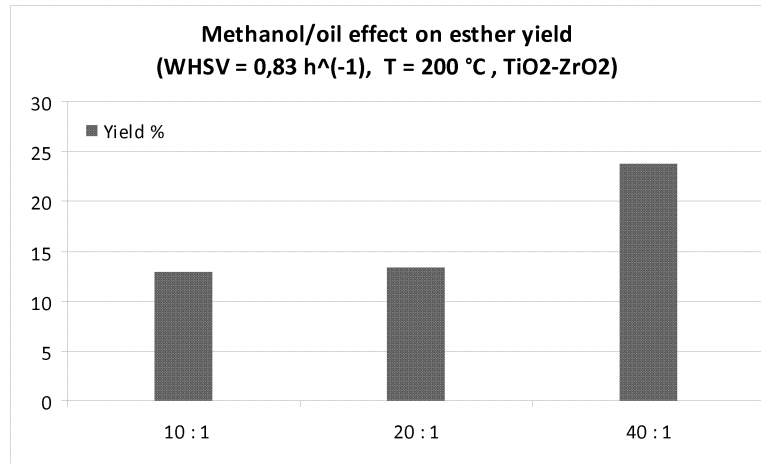


Figure 2: Effect of methanol to oil ratio on ester yield

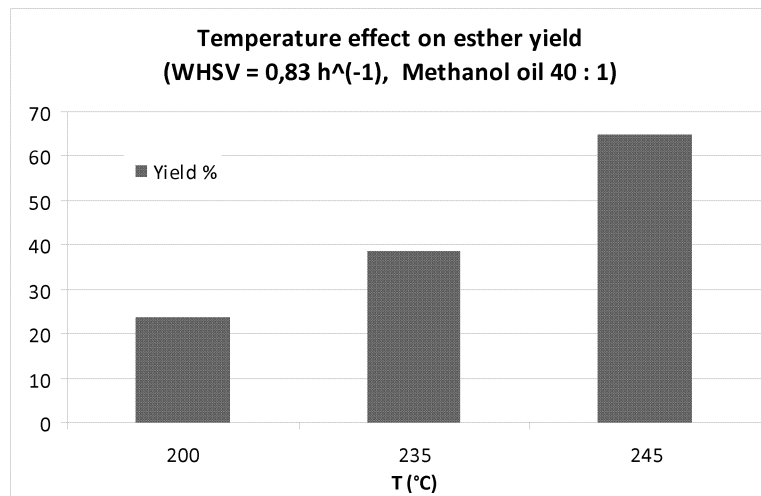


Figure 3: Effect of reaction temperature on ester yield

1.4 Water effect

Typical biodiesel production relies on methanol derived from fossil fuels, leading to some impact in terms of life-cycle CO₂ emissions. The use of bio-ethanol would sort out the problem, but is considered to be inhibited by both cost and residual water content. It is known, in fact, that water reacts with homogeneous basic catalysts so causing an undesirable catalyst consumption as well as a selectivity decrease because of triglycerides saponification. In practice it would be most useful to directly feed sub-azeotropic bio-ethanol, that contains significant quantities of water (typically 5% by weight), so saving the bio-ethanol dehydration step and improving in this way process economics as well as CO₂ emissions. Notably, solid acid catalysts are good candidates for dealing with water contaminated feedstocks as they can promote the *hydrolysis-esterification* of triglycerides (Lopez et al., 2008) which allows the conversion to methyl-esters of the fatty acids obtained from triglycerides hydrolysis (indirect transesterification or hydrolysis-transesterification) and should therefore tolerate well the presence of water in the system. It is for this reason that the behaviour of the present solid catalyzed system was investigated with water contaminated feeds.

In particular 5 % of water was added to the methanol feed stream. The preliminary results obtained are shown in Fig. 4 where methyl esters yields, in the absence and in the presence of water, are reported. As it can be seen an yield increase from 13.4% to 16.0% was observed when feeding the water contaminated stream. Hence not only it is fully confirmed that hydrolysis-esterification conditions may tolerate well a significant presence of water, but this last is found to be even beneficial to reaction yields.

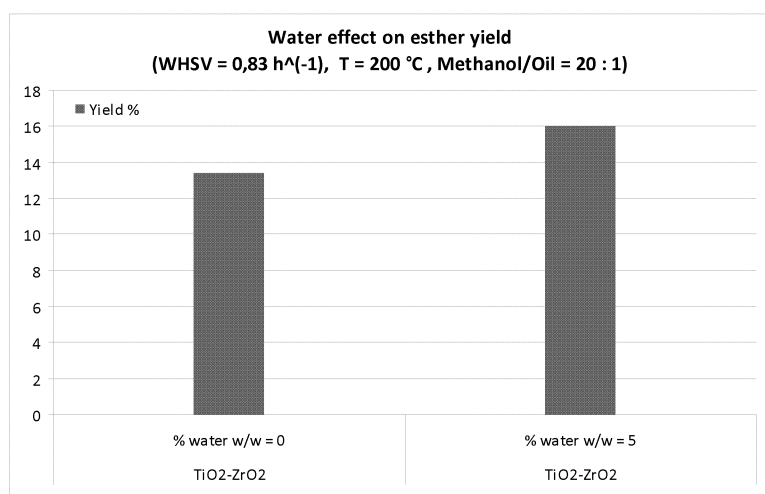


Figure 4: Effect of water on esther yield

Conclusions

A titanium doped zirconia solid catalyst was tested for the transesterification reaction of rapeseed oil with methanol with the aim to explore alternative routes to biodiesel

production. It was found that ester yield decreases when increasing space velocity, temperature and methanol to oil ratio. When 5% water was added to the methanol feed ester final yield improved by about 20%. This is a particularly interesting finding in view of the possibility of using sub-azeotropic bio-ethanol (a fully renewable resource) instead of fossil carbon derived methanol.

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