Elio Santacesaria, Martino Di Serio, Riccardo Tesser
Dipartimento di Chimica
Università di Napoli "Federico II"
elio.santacesaria@unina.it

NEW TECHNOLOGIES IN BIODIESEL PRODUCTION

The cost of biodiesel is nowadays affected by the cost of the raw materials, because the currently used method of preparation requires highly refined vegetable oils containing very low amounts of free fatty acids and moisture. Alternatively, less expensive technologies are possible using heterogeneous catalysts. In the present paper examples of these new technologies, based on the use of heterogeneous catalysts, in the production of biodiesel are described and discussed.

Biodiesel production is currently performed in industry by transesterification of vegetable oils with methanol. The reaction occurs in homogeneous phase, by using alkaline catalysts for promoting the reaction. 10% b.w. of glycerol is formed as by-product. Different drawbacks can be recognised in this process: (i) vegetable oils must be highly refined to remove FFA (Free Fatty Acids) forming soaps with the catalyst. In this way the catalyst is consumed and soaps formed determine long settling time for separating the polar phase containing methanol and glycerol from the emulsionated biodiesel; (ii) also the presence of water is detrimental, forming FFA by hydrolysis of triglycerides; (iii) moreover, at the end of the reaction, the catalyst must be neutralised with mineral acids and formed salts remain dissolved in glycerol increasing the cost of purification.

With this process, the cost of biodiesel remains not competitive and the cost of biodiesel is determined for more than 80% by the cost of the raw materials. The possible main interventions for improving traditional processes can be, therefore:

1) employing new cheaper feedstock like unrefined and waste oils, animal fats etc. All these contain FFA;
2) intervention on the esterification reaction promoted by Brönsted acid catalysts that lowers the free fatty acids content by converting them into methylesters (biodiesel). Residual triglycerides are successively transesterificated;
3) use of new catalysts, in particular heterogeneous catalysts. The ideal catalyst is not affected by the presence of FFA and moisture and would be active in promoting both esterification and transesterification);
4) thermal uncatalysed treatments;
5) to find new uses for the by-product glycerol.

We will consider here only the first three points and we propose a process like the one reported in the following simplified scheme (Fig. 1). It is easy to recognize in the scheme the part relative to the traditional process. As shown the esterification reaction can alternatively be performed on the oil containing FFA or after a preliminary separation of fatty

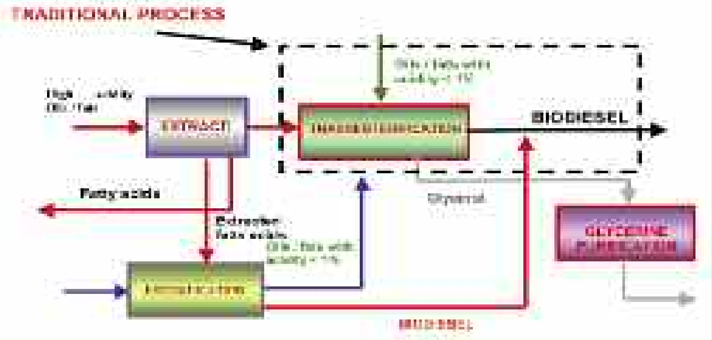
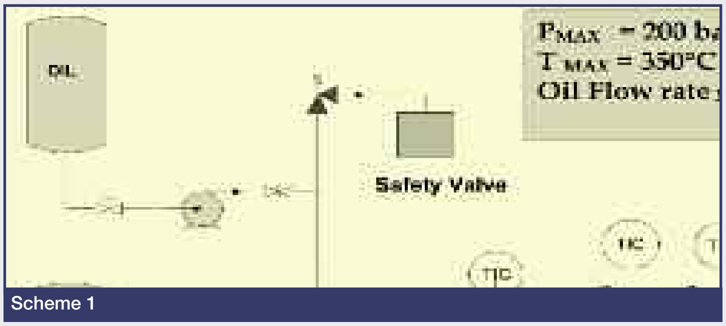


Fig. 1 - The proposal of a new process for biodiesel production starting from cheaper feedstock containing free fatty acids

Paper presented at the workshop "Verso la bioraffineria, carburanti e materie prime da fonti rinnovabili", devoted to Prof. Ferruccio Trifirò in honour of his 70th birthday and of his great contribution in the development of heterogeneous catalysis and industrial chemistry - Milano, November 19th, 2008.



Scheme 1

acids by a selective solvent extraction.

The transesterification reaction can opportunely be promoted by an heterogeneous catalyst in a continuous tubular reactor. In this case glycerol separates promptly from biodiesel and requires less expensive purification. At this purpose, very recently, a big industrial plant for producing biodiesel (160,000 t/y) using an heterogeneous catalyst ($ZnAl_2O_4$) developed by the French Institute of Petroleum has been realised (Esterfip-H) [1, 2].This significant realisation encouraged in the world many researches in this field, as it results from some recent reviews [3-5].

Esterification of FFA promoted by sulphonic exchange resins

Sulphonic acid exchange resins give place to a significant swelling in the presence of methanol or water according to the amount of cross-linking bridges in the particles. This is a well known phenomenon and other esterifications of carboxylic acids of low molecular weigth are made, for example, in a distillation with reaction column using metal basket for blocking the resins particles allowing the swelling without problems. This system is not efficient for the esterification of FFA. In a recent patent [6], the use of stainless steel springs of opportune size and shape, as catalyst diluent, has been proposed by us. By dosing the correct amount of springs, the expansion of the resin particles is compensated by the compression of the springs obtaining, in this way, dimensionally stable tubular reactors. The kinetic behaviour of the exchange resins in the esterification reaction has been studied, first of all, in batch conditions. The obtained results have then been used for simulating the behaviour of tubular reactors of different sizes and shapes containing the same resin opportunely mixed with small springs. Initially, in agreement with other authors [6], a simple pseudo-homogeneous second order equilibrium model has been adopted, with the kinetic law here reported:

$$r = k_c x_A x_M [1 - (x_E x_W / k_e x_A x_M)] C_{cat} \qquad (1)$$

However, this kinetic law was not able to describe the behaviour of some kinetic runs performed at high conversions with different catalysts concentration in the range (1-10 g). This occurs, because, according to relation (1) the final conversion would correspond with the chemical equilibrium that is the same independently of the catalyst concentration. This does not correspond with the experimental observations. It is clear that the primarily proposed kinetic model, commonly used in the literature, is inadequate to describe all the observed experimental aspects. Therefore, a new model has been elaborated based on the following assumptions [7, 8]: (i) exchange resin catalyst particles are swelled by contacting methanol reaching a relatively stable void volume mainly filled of methanol; (ii) in the void volume of the resin all the components, products and reagents, enter but are differently partitioned between the internal part of the void particles volume and the external bulk solution. The two compositions are different, because, water and methanol are retained more selectively than fatty acids and esters as a consequence of the different osmotic pressures determined by the high ionic concentration inside the particles. This aspect has been experimentally quantified by performing different binary absorption runs. A partition model has then been developed by assuming that each component is adsorbed according to the equilibrium here reported:

$$i^b + V_V^R \rightleftharpoons i^R \qquad (2)$$

being V_V^R the void volume inside the resin particles. The net rate of the physical adsorption of each component inside the particle could be represented by the relation:

$$r = k_i C_i^b \varnothing_V^R V^R - k_{-i} \varnothing_i^R V^R \qquad (3)$$

where C_i^b is the concentration of the component i in the bulk, $\varnothing_V^R$ is the void fraction in the particles and V^R is the total volume available for the absorption and $\varnothing_i^R$ is the volumetric fraction occupied by the i component in the resin. By considering the system in equilibrium we can easily derive the concentrations for a multicomponent mixture.

This model is very similar to the Langmuir adsorption isotherm being ρ_i/PM_i the maximum of concentration that can be achieved inside the particles by the *i* component. The model has the advantage of the Langmuir model to well describe the competition in adsorption.

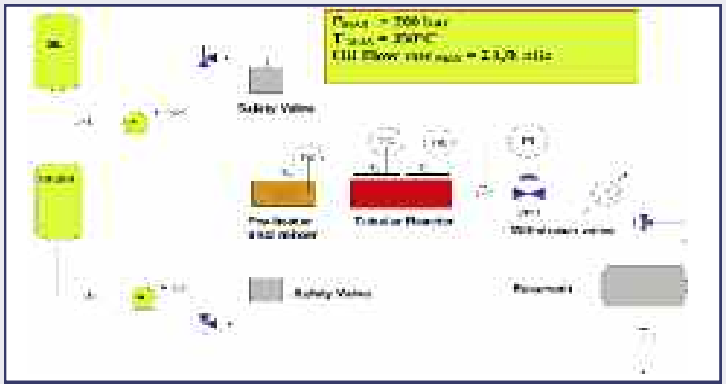


Fig. 2 - Scheme of a high pressure plant for testing heterogeneous catalysts for biodiesel production

Tab. 1 - Performances of a titania/silica catalyst prepared by grafting in the presence of both a neutral and an acid soybean oil containing about 10% of oleic acid in both transesterification and esterification reactions. (oil=2.0 g, methanol=0.88 g, catalyst=0.1 g, T=180 °C)

	Refined Oil	**Acid Oil (10% w/w FFA)**	
Catalyst	FAME Yields (%)	FAME Yields (%)	FFA Conversions (%)
Titania/Silica (TS)	62	40	77
used TS	58	39	70
No catalyst	8-11	25	35

Tab. 2 - List of proven basic heterogeneous catalysts

Type of catalyst	Preparation method
MgO (c)	Commercial product from Merck, calcination at 500 °C
MgO (I)	Precipitation from $Mg(NO_3)_2$ Calcination at 500 °C
MgO (II)	Calcination at 400 °C of $Mg(OH)_2$ for 18 h
MgO (III)	Calcination at 400 °C of $(MgCO_3)_4 \cdot Mg(OH)_2$ for 18 h
γ-Al_2O_3	Commercial from DUTRAL
Hydrotalcite (HT4)	Coprecipitation from $Mg(NO_3)$+$Al(NO_3)_3$ and calcination at 500 °C

The esterification reaction occurs on the acidic catalytic sites with a mechanism of the type represented in Scheme 1.

By assuming (b) as rate determining step, a reliable kinetic law can be derived containing as parameters also the ionic exchange equilibrium constants of each component with methanol on the acidic site. This model has been tested on all the runs mentioned before in both batch and tubular reactors of different sizes with very satisfactory results.

New heterogeneous catalysts for promoting transesterification reaction in biodiesel production

The use of heterogeneous catalysts shows many advantages and few drawbacks. Advantages are: (i) possibility to realize more easily continuous plants; (ii) simple recover and reuse of the catalyst; (iii) high purity of the products; (iv) prompt separation of glycerol, while as drawback we have until now the necessity of more drastic conditions of temperature and pressure. Heterogeneous catalysts have been subjected to evaluation by using three different types of reactors. Catalytic screening has been performed in small vials (about 10 ml) of stainless steel containing a stainless steel ball for the agitation. The vials anchored to a rotating bar were put in an oven and taken at the reaction temperature (normally 180-200 °C) for one hour, then rapidly quenched for stopping the reaction. The catalyst is used in powdered form. The most promising catalysts are then tested also in a 1 L stainless steel autoclave, operating in batch conditions. At last, a continuous liquid-solid tubular reactor, operating at high pressures, has recently been realised for studying the performances of pelletised catalysts that are worth to be industrially developed (see Fig. 2).

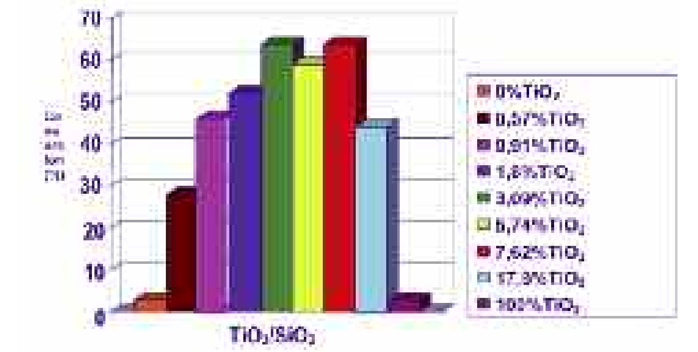


Fig. 3 - Effect of titanium loading on the catalytic activity. Refined soybean oil: 0,1% w/w of free acidity (2 g of oil + 0.9 g CH_3OH + 0.1 g Cat.); temperature program: 50 °C (14 min.); 20 °C/min.-180 °C (60 min.)

Let us consider the performances of some new heterogeneous catalysts for biodiesel production developed by our group that can be classified as:

- *Lewis acids:*

1) mixed oxides of TiO_2/SiO_2 prepared by grafting, by anchoring a titanium alcoxide on the surface hydroxyls of silica [9, 10];

2) systems based on vanadyl phosphate dihidrate ($VOPO_4 \cdot 2H_2O$) or vanadyl phosphate containing trivalent metals M^{3+} (Ga, Cr, Mn, Fe, Al) $[M(H_2O)]xVO_{(1-x)}PO_4 \cdot 2H_2O$ [11, 12].

- *Lewis bases:*

1) magnesium oxides [13, 14];

2) Al-Mg hydrotalcites (HT) [13, 14].

Silica coated with titania catalyst

TiO_2/SiO_2 catalysts where prepared by grafting different amounts of titanium isopropoxide $[Ti(O_iPr)_4]$ onto the silica surface in a nitrogen atmosphere until reaching a monolayer, followed by steam hydrolysis and calcinations. The operation can repeated two or three times coating silica with a greater amount of titania. Depending on titanium loading different types of titanium species could be present, ranging from dispersed surface TiO_x species, both in tetrahedral and octahedral coordination, to small TiO_2 crystallites. The obtained results in transesterification reaction for different amounts of titanium oxide loading, are reported in Fig. 3. As it can be seen, a maximum of the activity has been obtained for 3-11% b.w. of TiO_2 in correspondence of the maximum concentration of Lewis acid sites of medium strength, that is neither too weak nor too strong. The TiO_2/SiO_2 catalysts are stable in the reaction environment don't giving leaching effect but the catalyst is sensitive to the presence of water that very probably poisons the Lewis acid sites responsible of the reaction. The presence of FFA has a negative effect on the catalyst performances, because, the formation of water, being the catalyst active also in promoting the esterification (see Tab. 1).

This catalyst has also been prepared starting from cylindrical silica pellets (diam.=3 mm; length=6 mm) on which surface titanium has been anchored by grafting and has been tested in autoclave by putting the catalyst in a basket anchored to the stirrer and rotating with it. The activity tests has been repeated 28 times on the same catalyst with a negligible loss of activity. A kinetic approach has been developed for this catalyst in batch conditions and preliminary runs performed in the continuous liquid-solid tubular reactor confirmed both the activities and the kinetic approach obtained in batch reactor.

Systems based on vanadyl phosphate

Vanadium phosphate catalysts like:

$VOPO_4 \cdot 2H_2O$, $Me(H_2O)]_{0.2}VO_{0.80}PO_4 \cdot 2H_2O$

(Me=Al, Ga, Fe or Cr) [11, 12] resulted all very active in the transesterification reaction, even if deactivation phenomenon of the catalyst was

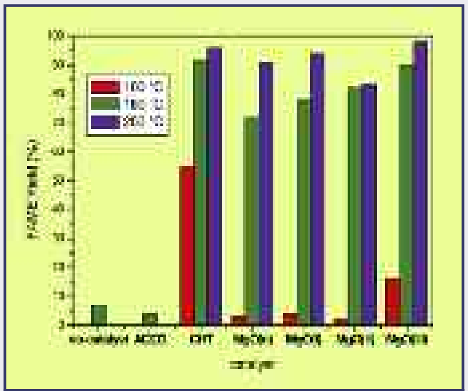


Fig. 4 - Yields of obtained biodiesel in transesterification of soybean oil with methanol for a reaction time of 1 hour. Reaction conditions: oil = 2.0 g; methanol = 0.88 g; catalyst = 0.1 g; reaction time = 60 min.

Tab. 3 - Performances of different basic catalysts like MgO and calcined hydrotalcite in the presence of a neutral and an acid soybean oil containing about 10% of oleic acid in both transesterification and esterification reactions. (oil=2.0 g, methanol=0.88 g (0.44 at 100 °C), catalyst=0.1 g (0.2 g at 100 °C))

	Temperature °C	**Refined Oil**	**Acid Oil (10% w/w FFA)**	
Catalyst		FAME Yields (%)	FAME Yields (%)	FFA Conversions (%)
Hydrotalcite	100	55	-	-
Hydrotalcite	180	92	80	76
MgO	180	75	76	62
used MgO	180	74	62	40
No catalyst	180	8-11	25	35

experimentally detected under the reaction conditions. Both fresh and used catalysts were characterized by using several techniques, such as: BET, XRD, DRUV and Laser-Raman. The characterization results obtained showed that the deactivation is probably due to the slow reduction of vanadium species ($V^{5+} \rightarrow V^{3+}$) by methanol. However, the catalysts can easily be regenerated by calcination at high temperature.

Magnesium oxides and hydrotalcites basic catalysts

A list of the proven catalysts is reported in Tab. 2. Magnesium oxide has been prepared in different ways, reported in the table. The different samples have shown different properties and have given different results. The obtained performances in vial reactors are compared in Fig. 4. As shown hydrotalcite and MgO type III are active also at 100 °C. This is probably due to the presence of superbasic sites that are present on the surface that have been observed by TPD of ammonia performed for the different catalysts. Both hydrotalcite and MgO of type III show this type of site that release ammonia at temperatures greater than 500 °C.

This behaviour has been confirmed for hydrotalcite on a larger scale by performing the reaction in 1 L autoclave increasing linearly the temperature from 25 °C to 220 °C in about 1 hour and reaching a plateau of the yield of 96% in less than one hour. The adopted conditions were: soybean oil=250 g; methanol=114 g, catalyst=2.5 g. Both MgO and hydrotalcite seems to be few sensitive to the presence of moisture and FFA (see data of Tab. 3).

Conclusions

In this work, some new technologies that could be useful to reduce the costs of biodiesel production have been proposed and discussed. It has been shown that the transformation of FFA in biodiesel by esterification is feasible in continuous tubular reactors with the use of acid exchange sulphonic resins catalysts. The transesterification can be promoted in the range of 180-200 °C by using different heterogeneous catalysts and some of them not only are resistant to the presence of FFA and moisture but are also moderately active in esterification.

Acknowledgements: The authors are grateful to ASER srl Co., to Italian Ministry of Foreign Affairs (MAE, code 269/P/0127728) Direzione Generale per la Promozione e la Cooperazione Culturale and of CN/ASIA PRO ECO/11 (109087) for the financial support in developing the present work.

References

[1] G. Hillon *et al.,* Institut Francais du Petrole, EP0924185A1; Pat. US 5,908,946, 1999.
[2] L. Bournay *et al., Catal. Today,* 2005, **106,** 190.
[3] M. Di Serio *et al., Energy & Fuels*, 2008, **22,** 207.
[4] E. Lotero *et al., Ind. Eng. Chem. Res.,* 2005, **44,** 5353.
[5] G.W. Huber *et al., Chem. Rev.,* 2006, **106,** 4044.
[6] R. Tesser *et al., Ind. Eng. Chem. Res.,* 2005, **44,** 7978.
[7] D. Siano *et al.,* Pat. WO 2006/046138 A1.
[8] R. Tesser *et al.,* Kinetics of FFAs Esterification: Batch and Loop Reactor Modeling, Submitted to *Chem. Eng. Journal.*
[9] E. Santacesaria *et al., Applied Catalysis A: General,* 2004, **270,** 177.
[10] D. Siano *et al.,* Patent ITMI2005A02303, Method for producing esters from vegetable oils and animal fats by using heterogeneous catalysts. WO 2006094986 A1 20060914.
[11] D. Siano *et al.,* Patent ITMI 2005/02303.
[12] M. Di Serio *et al., Applied Catalysis A: General,* 2007, **320,** 1.
[13] M. Di Serio *et al., IE&C Research,* 2006, 45, 3009.[14] D. Siano *et al.,* Int. Appl. WO 2006/050925 A1.

RIASSUNTO

Nuove tecnologie nella produzione di biodiesel

Il costo del biodiesel è oggi fortemente influenzato dal costo della materia prima poiché la tecnologia impiegata per la sua produzione, basata sull'impiego di catalizzatori alcalini in fase omogenea, richiede l'impiego di olii vegetali altamente raffinati che contengano quantità esigue di acidi grassi liberi e umidità. Tecnologie alternative vengono oggi studiate a livello mondiale con la speranza di poter utilizzare catalizzatori eterogenei in grado di promuovere in due stadi prima l'esterificazione degli acidi grassi e poi la transesterificazione dei trigliceridi o addirittura di promuovere entrambe le reazioni in un unico stadio. Questo consentirebbe l'impiego di materie prime di più basso costo. Nel presente lavoro vengono descritti, a titolo di esempio, alcuni catalizzatori eterogenei e le loro prestazioni.