# CHIMICA & ENERGIA



Carlo Perego, Daniele Bianchi, Letizia Bua Eni SpA, Research Center for Non Coventional Energies Istituto Eni Donegani - Novara carlo.perego@eni.com

## CATALYTIC **CONVERSION TO FUEL** AND ENERGY

The development of economic processes for the production of liquid fuels from biomass requires large investments. Therefore, the search of new catalysts for the enhancement of both the yields and the quality of biofuels is the key to improve the efficiency and reduce costs. The following paper presents some examples of well established processes and emerging technologies, mainly focused on the production of diesel fuels from renewable feedstocks.

limate change mitigation, energy security, rising oil prices and economic objectives are stimulating strong interest in the development of efficient processes for the production of energy vectors and biofuels. Road transport alone now accounts for about 20% of global anthropogenic carbon dioxide emissions. Therefore a great contribution to the sustainability will come from transport biofuels more clean, economic and renewable [1].

Biomass is an abundant and carbon-neutral renewable energy resource for the production of biofuels, moving the market dependence away from fossil-based energy sources.

Accordingly the production of renewable fuels is continuing to expand worldwide as a result of increasing petroleum prices, government regulations, and commitments to greenhouse gas reduction.

First generation biofuels (i.e. bioethanol and biodiesel) are currently produced from conventional food crops derivatives such as the starch, sugar and oil feedstocks from crops that include wheat, maize, sugar cane, palm oil and oilseed rape. Any major switch to biofuels from such crops would create a direct competition with their use for food and animal feed, and in some parts of the world we are



already seeing the economic consequences of such competition. Many of these problems could be addressed by the production of the second generation biofuels, manufactured from agricultural and forest residues and from ligno-cellulosic non-food energy crops.

Second generation biofuels are expected to be superior to many of the first generation biofuels in terms of energy balances, greenhouse gas emission reduction, land requirement and competition for land, food, fiber and water. The main reason they have not yet been taken up commercialization, despite their potential advantages, is that the involved production technologies are not technically proven at a commercial scale and their costs are at the moment estimated to be significantly higher than that of most first generation biofuels.

Therefore, there is still much work to be done for the improvement of the existing processes and for the development of new efficient technologies. In this concern a paramount contribution is given by catalysis and catalytic processes.

This paper will present some examples of process for the production of biofuels, focusing the attention on the diesel fuel which is presently the most appealing on the European fuel market. In fact, the EU-27 road fuel demand is characterized by a steadily shifting from gasoline to diesel and by a steadily grow of heavy duty diesel demand [2].

### **Biodiesel processes**

Biodiesel is a mixture of fatty acid methyl esters (FAME) produced by transesterification of triglycerides with methanol in presence of a basic catalyst. Glycerol is the main by-product, whose amount is equivalent to approximately 10% of the total FAME production (Fig. 1).



Today the commercial biodiesel production plants are utilizing homogeneous, alkaline catalysts, such as sodium methylate, sodium hydroxide and potassium hydroxide.

The reaction is usually carried out with an excess of methanol at 60 °C. The resulting reaction mixture is a biphasic system consisting in a polar phase, containing most of the glycerol, the catalyst and the co-produced soaps, and an apolar phase containing the FAMEs, a fraction of methanol, traces of the catalyst and most of the soaps.

The current technology for biodiesel production has two main shortcomings. Firstly, the presence of free fatty acids and water in the feedstock causes the lost of the catalyst and the production of soaps, with consequent separation problems because of emulsions formation. Secondly, the alkaline catalyst must be neutralised, and the resulting salts are difficult to remove from the glycerol to get a high purity grade product.

In order to avoid these problems, conventional homogeneous catalysts are expected to be replaced in the near future by environmentally friendly heterogeneous catalysts.

Different heterogeneous basic catalysts have been developed to catalyze the transesterification of vegetable oils, such as Na/NaOH/Al<sub>2</sub>O<sub>3</sub> [4] KNO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> [5] and basic metal oxides (MgO, CaO, SrO, and BaO) [6].

Corma *et al.* [7] evaluated glycerolysis of triglycerides using basic solid catalysts such as Cs-MCM-41, Cs-sepiolite and hydrotalcites. A series of zeolite catalysts was tested by Suppes *et al.* [8], including NaX, faujasite and ETS-10 zeolites exchanged with potassium and cesium.

Recently, the Institute Français de Petrole (IFP) has developed a new technology (Esterfip-H process) [9, 10] based on a basic heterogeneous catalyst (a mixed oxide of Zn and Al with a spinel structure). The Esterfip-H technology operates at 200-250 °C





Fig. 2 - Process scheme for the traditional Biodiesel technology



affording a FAME yield close to 100% with lower catalyst requirements per ton of produced biodiesel.

The process does not require catalyst recovery and aqueous washing treatment of biodiesel, thus avoiding the waste production of low-value fatty acids, the consumption of chemicals and the water saline streams disposal.

The use of heterogeneous catalysts resulted in simpler and cheaper separation processes with reduced capital and energy costs. In addition, the glycerol co-produced from Esterfip-H has a purity higher than 98%, compared to about 80% achieved with homogeneous-catalyst routes, and is free from any salt contaminants.

The advantages of the Esterfip-H process over the traditional biodiesel technology are showed in Fig. 2 and 3, reporting the simplified process diagrams [11].

Currently, refined vegetable oils (containing less than 0.5% of free fatty acids, FFA) are the major feedstocks for biodiesel production. However, waste greases, such as yellow grease from used cooking oils and animal fats, can also be employed because of their availability and low cost.

The high concentration of FFAs (up to 15%) present in these inexpensive feedstocks, make them inappropriate for the conventional base-catalyzed transesterification route to biodiesel due to soap formation.

Although the acid catalysts require a longer reaction time and a higher temperature than the alkali-catalysts, they are more efficient when the amount of free fatty acids in the oil exceeds 0.5%. In this case, a single-step, acid catalysed esterification/transesterification process is more economical than the alkali-catalyzed process, which requires an extra step to convert free fatty acids to methyl esters, thus avoiding soap formation.





Homogeneous catalysts ( $H_2SO_4$ , HCl,  $BF_3$ ,  $H_3PO_4$ , and organic sulfonic acids) [12] although effective, lead to serious contamination problems, due to the formation of decomposition products that make essential the implementation of good separation and product purification protocols, which translate into higher production costs. Solid sulfated oxides, such as  $ZrO_2/SO_4$  and  $SnO_2/SO_4$ , proved to be active catalysts due to their high acid strength, but deactivation phenomena and sulphate leaching were detected under the transesterification conditions [13].

Esterification has been carried out using ion-exchange resins (Amberlyst-15) [14] and Nafion [15] as heterogeneous catalysts. However, most ion-exchange resins are not stable at temperatures above 140 °C, which prohibits their application to reactions that require higher temperatures. For this kind of application, inorganic acid catalysts, such as zeolites, are generally more suitable. Using microporous zeolites catalysts the mass-transfer resistance becomes a critical issue if large molecules, are used as substrates. In this case the reaction takes place mainly on the external surface of zeolite crystals. For this reason, only large-pore zeolites (faujasite, mordenite) have been successfully used in fatty acid esterifications [16].

An additional improvement of the biodiesel process deals with the utilisation of the co-produced glycerol for the synthesis of oxy-

> genated molecules suitable as fuel components. Glycerol is the main by-product of the process, whose amount is equivalent to approximately 10% by weight of the total FAME production. Therefore, the predicted increase of biodiesel production will result in the accumulation of glycerol and could create a glut in the market.

> At present, glycerol has already a great number of utilizations leading to a large number of products for non-fuel application, such as: propane diols, oligoglycerols, glycerol carbonate, glyceric acid, epichlorohydrine, and glycidol.

> In the future, the availability of glycerol could exceed the demand for traditional use and its price will decrease, making it a cost effective raw material for the preparation of fuel components and additives. This approach not only makes a valuable use of the by-product but could also increase the fuel yield in the overall biodiesel processes.

Tab. 1 - Composition (in wt%) of C4 fractions from steam cracking		
Component	Raffinate 1	Raffinate 2( <sup>a)</sup>
Isobutane	3	6
Isobutane	45	<0,1
1-Butene	25	45
1,3-Butadiene	<0.5	<0.8
n-Butane	11	19
Trans-2-Butene	9	17
Cis-2-Butene	7	13

<sup>(a)</sup> After conversion of isobutene

Glycerol cannot be added directly to fuels because of its low solubility and poor thermal stability that raise to engine problems at high temperatures. Therefore, glycerol must be transformed into derivatives that are compatible with diesel and biodiesel, prior to being added to the fuel.

Among these products, glycerol ethers have been extensively studied for their promising physical, chemical and blending properties.

The reaction of glycerol with isobutene yields a mixture of the corresponding mono-, di- and tri-tertiary butyl ethers, as shown in Fig. 4. The mono-ethers are soluble in polar solvents [17], whereas the mixture of di- and tri-ethers are miscible with apolar media and can be used in the formulation of diesel fuels (as particulate matter emission reducers) or gasoline (as octane-booster in substitution of methyl-tertiarybutyl ether MTBE).

The etherification reaction is efficiently promoted by both homogeneous and heterogeneous catalysts such as *para*-toluene sulfonic acid, acid ion exchangers resins like Amberlyst 15, and acid zeolites such as H-Y or H-beta [18, 19].

Typically, the reaction is carried out in liquid phase at 70-90 °C with a 3/1 isobutene/glycerol molar ratio. The final product is a mixture of tri-butyl glycerol, TBG, (3%) and di-butyl glycerol, DBG, (97%) [17].

In the case of an industrial application a mixture of C4 olefins (coproduced in steam cracking or fluid catalytic cracking processes) should be used instead of pure isobutene. The typical composition of this stream from steam cracking (after butadiene extraction) is reported in Tab. 1 as "Raffinate 1".

If a strong acids catalyst, such as a sulfonic acid, is used, only the isobutene fraction of Raffinate 1 reacts with glycerol to give the corresponding tertarybutyl ethers, while the linear C4 olefins are substantially uncreative under the etherification conditions [20].



The composition of the resulting residual C4 mixture is reported in Tab. 1 as "Raffinate 2".

Eni has developed a new process, based on a super-acid catalyst (trfluoromethane sulfonic acid), that makes possible the etherification of glycerol with linear 1- and 2-butenes (unreactive with the traditional catalysts), yielding the corresponding 2-butylethers of glycerol (Fig. 5), with much better properties in diesel blending with respect to the more branched tertiarybutyl ethers [21]. Similar results were obtained using a solid super-acid catalyst, such as Nafion [20].

Due to their high oxygen content, glycerol derivatives can be used as ignition accelerators, antiknock additives, viscosity and melting point enhancers and particle emission reducers.

### **Greendiesel procesees**

Existing technology for producing diesel fuel from vegetable oil are largely centred on production of FAME biodiesel. While FAME has many desirable qualities, such as high cetane, there are other issues associated with its use such as poor stability and high solvency leading to filter plugging problems.

A more radical innovation in bio-based diesel fuels considers the complete hydrogenation of the triglyceride feedstocks to hydrocarbon mixture, avoiding the side-production of glycerol and allowing a better integration of the process and the product in the exiting refinery infrastructure and fuel distribution system.

Several companies have been developing such a kind of triglycerides hydroprocessing (e.g., Neste Oil, Conoco-Phillips, Petrobras, Dynamic Fuels, UOP-Eni, Haldor-Topsoe) [22, 23].

The UOP/Eni EcofiningTM process is based on catalytic hydrodeoxygenation, decarboxylation and isomerization reactions (Fig. 6) to produce a diesel fuel rich in isoparaffins [23]. This alternative product is called green diesel. As this kind of process is very flexible to the feedstocks, it can be considered also for inedible (e.g. jatropha and camelina) and unconventional (e.g. used and cooking oils, animal fats) triglycerides. In this concern green diesel can be considered as a bridge between first and second generation biodiesel [24].

The main improvement of the Ecofining technology compared to the conventional FAME biodiesel, is that it allows refiners to obtain a synthetic fuel that has a similar chemical composition and similar chemical-physical properties compared to petroleum diesel. For this reason the product can be easily blended with conven-



Fig. 6 - Vegetable oil transformation in Ecofining process

### CHIMICA & ENERGIA



tional refinery streams. In addition, all of the Ecofining by-products are already present during normal refinery operation and do not require any special handling.

The green diesel advantages, in comparison to mineral diesel fuels and FAME, are summarized as follows:

- high cetane number (CN>80) that means to have higher engine efficiency;
- green diesel is a hydrocarbon mixture, not an oxygenated organic compound that means to have the same energy content as mineral diesel fuel and higher than FAME;
- better stability and blending properties, due to the absence of double bonds and oxygenated molecules;
- low density. Green diesel can be used to upgrade high density refinery streams, expanding the diesel pool;
- boiling range similar to mineral diesel. This prevent vaporization problem in the combustion chamber;
- the quality of vegetable oil, in particular the fatty acid distribution and the degree of un-saturation can affect the properties of FAME biodiesel, but they do not affect the properties of green diesel;
- green diesel is produced by a "refinery" process that permits quality control of bio-fuel and the use of existing infrastructure and fuel distribution systems;
- green diesel meets the highest requirements of car manufacturers and can be utilized with all diesel automotives without modification;
- the co-production of glycerol is avoided, since it is deoxygenated to propane.

A simplified flow diagram of Ecofining process is shown in Fig. 7. In the first stage, vegetable oil is combined with hydrogen and brought to reaction temperature, then it is sent to a reactor section where it is converted to green diesel. The reactor section can consist of either a deoxygenation reactor or a combination of a hydroprocessing and an isomerization reactors, to achieve better cold flow properties in the green diesel product. The resulting mixture is separated from the recycle gas in the separator and the liquid stream sent to a fractionation section, producing propane, naphtha, and diesel products. In the hydroprocessing stage oxygen is removed from the triglyceride molecules via three competing reactions: hydrodeoxygenation, decarbonylation and decarboxylation (Fig. 6). The three carbon "backbone" yields propane that can be recovered easily when the process is integrated into a refinery. The oxygen contained in the feed is removed from the fatty acid chain either as  $CO/CO_2$  or water. In addition, all olefinic bonds are saturated, resulting in a product consisting of only *n*-paraffins.

The hydroprocessing is carried out at moderate temperature (310 °C) using a bimetallic hydrotreating catalyst (e.g. Ni-Mo or Co-Mo catalyst), specifically tailored for the selected feedstock.

Despite to the high cetane number, the high cloud point of the liquid stream coming out from the hydrotreating reactor has a great impact in limiting the volume that can be blended with mineral diesel. In order to overcome this restriction, this linear paraffinic stream is isomerized in a second stage. For such a purpose a proper hydroisomerization catalyst, based on a precious metal loaded on a mild acidic carrier has been developed.

The scope of this second stage is to control the cold flow properties of the final green diesel. As well explained in open literature [25, 26], the diesel yield from the process will depend on the severity required in the isomerization reactor to meet cold flow specifications.

Typical acidic supports for bifunctional catalysts used in the hydroisomerization reaction are: amorphous oxides or mixture of oxides (i.e. HF-treated  $Al_2O_3$ ,  $SiO_2-Al_2O_3$ ,  $ZrO_2/SO_4$ ), zeolites (Y, Beta, Mordenite, ZSM-5, ZSM-22), silicoaluminophosphates (SAPO-11, SAPO-31, SAPO-41) or mesoporous materials (MCM-41, AIMCM-41) [27].

Unfortunately, beside hydroisomerization, these catalysts also promote undesired cracking reactions [28]. In order to reduce the cracking extent, a proper combination of porosity and mild acidity is necessary. Porosity can be tailored using proper synthetic parameters; e.g. MSA, an amorphous silica alumina with controlled porosity in the region of mesoposous and a mild acidity, is suitable for this purpose after loading with metals selected among Pd, Pt and Ni [29].

A range of vegetable oils have been processed in a pilot plants scale, including soybean, rapeseed, palm and jatropha oil. Other potential feedstocks including tallow and greases derived from animals have been evaluated.

As far as catalyst stability is concerned, a long pilot plant test was carried out and the results show a very good stability and product selectivity after 2000 hours of stream [30].

### **Biomass to Liquid (BTL) processes**

Another catalytic process to transform biomass to liquid fuels, in particular to middle distillates including diesel cuts, is the so called BTL [31]. The main steps of this technology include thermal gasification of biomass, followed by syngas clean up and Fisher-

Tropsch synthesis of synthetic fuels [32]. Similar processes are currently widely used to produce synthetic fuels from coal or gas (i.e. CTL and GTL).

Gasification is a process in which the biomass reacts with air, oxygen, and/or steam to produce a gas mixture (syngas) that contains CO,  $H_2$ , CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> in various proportions:

Biomass +  $O_2 \rightarrow CO + H_2 + CO_2 + H_2O + CH_4$ 

The gasification process is a complex combination of reactions occurring in the solid, liquid, and gas phases including pyrolysis, partial oxidation, combustion, water gas shift (WGS), char gasification, methane reforming and steam gasification:

$C + 0.5O_2 \rightarrow CO$	Partial Oxidation
$C + O_2 \rightarrow CO_2$	Combustion
$C + H_2 O \rightarrow CO + H_2$	Water Gasification
$CO + H_2O \rightarrow CO_2 + H_2$	Water Gas Shift
$CH_4 + H_2O \rightarrow CO + 3H_2$	Methane Reforming

The process is typically carried out at high temperature (800-1000 °C) and low pressure (1-20 bar).

The  $H_2$ /CO ratio in the outlet gas can range between 0,5 and 1,8, depending on the biomass composition, the gasifying agent and the gasification technology.

Different gasification reactors, have been developed, including updraft gasifier, downdraft gasifier and fluidized-bed gasifier [1]. A very critical step in the whole process is the gas cleaning stage.

In fact biomass contain a significant amount of nitrogen, sulphur and chlorine, therefore undesired contaminants, such as  $H_2S$ , COS, NH<sub>3</sub>, HCN, HCI, are produced.

Higher molecular weight hydrocarbons (tars) are also formed and must be removed in order to avoid the blockages of pipes and filter equipments. Tar removal or conversion has been reported to be one of the main technical challenges for the successful development of commercial gasification technologies [33].

Syngas can be used as a feedstock in the production of chemicals (e.g. Fischer-Tropsch diesel, methanol, dimethylether).

Fischer-Tropsch technology was first developed in the early 1900s and used by Germany during the 1930s and 1940s to produce liquid fuels from syngas derived from coal.

Fischer-Tropsch reaction produces hydrocarbons starting from  $H_2$  and CO, according to the general equation:

 $n (CO+2H_2) \rightarrow -(CH_2)_n - + n H_2O$  ( $\Delta H=-167 \text{ KJ/mol}$ )

As a matter of fact, not only paraffins are actually produced; indeed many different reactions occur simultaneously:

$$\begin{split} &nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \qquad & \text{Synthesis} \\ &nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \qquad & \text{Synthesis} \end{split}$$

Synthesis of paraffins Synthesis of olefins  $\begin{array}{ll} nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O & \text{Synthesis of oxygenates} \\ CO + 3H_2 \rightarrow CH_4 + H_2O & \text{Methanation reaction} (\Delta H=-206 \text{ KJ/mol}) \\ CO + H_2O \rightarrow CO_2 + H_2 & \text{Water gas shift reaction} (\Delta H=-41 \text{ KJ/mol}) \\ 2CO \rightarrow C + CO_2 & \text{Boudouard reaction} (\Delta H=-172 \text{ KJ/mol}) \\ H_2 + CO \rightarrow C + H_2O & \text{Coke formation} (\Delta H=-133 \text{ KJ/mole}) \end{array}$ 

The chain growth is promoted at low temperature (200-240 °C) and mid pressure (20-30 bar). In these condition, the methane formation, which is the main side reaction that reduces the overall selectivity to oligomers, is minimized.

Catalysis and the reactor technology play a key role in the Fischer-Tropsch process.

Few metals show activity on Fischer-Tropsch synthesis: the required characteristics are good dissociative CO adsorption,  $H_2$  adsorption, and, at the same time, easy reducibility of the metal oxide. From the point of view of the mechanism, the Fischer-Tropsch reaction can be conceived as a sort of polymerisation, with an adsorption step, a chain initiation, a propagation and a chain growth termination. The first hypothesis, reported in Fig. 8, was proposed by Fischer and Tropsch in 1926 [34]. They supposed the dissociative adsorption of the carbon monoxide on the metal atom, with formation of a carbide species. The insertion of the adsorbed dissociated hydrogen on this carbide generates the active  $CH_2$ -intermediate that gives rise to the propagation step. The growing alkyl chain can desorb from the metal by hydrogenation, forming paraffins, or by  $\beta$ -scission, forming olefins.

On the basis of these considerations, the transition metals belonging to the third, fourth, fifth and sixth group are not good catalysts for Fischer-Tropsch synthesis, because, despite of their favourable dissociative CO adsorption, they form very stable oxide that are not reducible under FT conditions. On the other



### CHIMICA & ENERGIA

#### Tab. 2 - Properties of cobalt and iron based Fischer-Tropsch reaction catalysts

Iron based catalyst	
Econimic	
_ow selectivity to long chain paraffins	
High selectivity to olefins and oxygenates	
Fast deactivation (coke)	
Efficient WGS catalyst	
Flexible H <sub>2</sub> /CO molar ratio	

hand, iridium, platinum, palladium and the metals belonging to the first and second group, are characterized by a non-dissociative adsorption of carbon monoxide, and for this reason they are not active in FT synthesis. The best catalysts are iron, cobalt, nickel, ruthenium, osmium, while rhenium and rhodium behave in the middle [35-37].

Ruthenium is actually the most active catalyst [38], but it is too expensive and poorly available to be used to develop an industrial process. Nickel has a very high hydrogenation activity, so its selectivity to methane is too high for FT purposes. As a matter of fact, cobalt and iron are the only two metals of choice for industrial applications. Iron is economic, but has low selectivity to long chain paraffins, produces a high amount of oxygenates and olefins and is more subject to deactivation than cobalt. Cobalt is more expensive than iron, but it has a very good selectivity to long chain paraffins, low selectivity to oxygenates and olefins, and it is resistant to deactivation. So, if the target is to produce long chain paraffins, cobalt is the best choice; otherwise, to produce chemicals or olefins, iron is to be considered.

To select between cobalt and iron, an important parameter is also the carbon feedstock. Iron has a high water gas shift activity, and for this reason is particularly suitable for hydrogen-poor feedstocks, as those obtained from coal or biomass. Cobalt performs better with an almost stoichiometric ratio of hydrogen and carbon monoxide, so it is preferred when the carbon feedstock is natural gas [39].

The different properties of iron and cobalt based catalysts are summarized in Tab. 2.

Depending on the gasification technology, Fe or Co could be pre-



ferred. However the  $H_2$ /CO molar ratio can be adapted by a WGS unit between gasification and FT reactor.

In any case, it is impossible to selectively produce a well defined range of products (i.e. middle distillates). As a result, the best strategy is working in conditions to obtain the maximum amount of long chain linear paraffins, that can be efficiently transformed into valuable products

by means of a further hydroprocessing stage.

A simplified scheme of a typical BTL overall process is reported in Fig. 9.

An example of a running BTL plant is the Choren-Shell process [40], in Germany. The Alpha plant produce 200 t/y of sundiesel. The yields are around 20%, compared to the biomass. The following generation of this concept will be the Beta plant, with a thousand times capacity.

Other companies who have been developing commercial FT technologies, mainly devoted to GTL applications (e.g. Sasol, Shell, BP, COP, Eni-IFP/Axens, ExxonMobil, Statoil, Rentech, Syntroleum), seem to be in a favourable position for BTL projects [41].

### Conclusions

The production routes of biofuels, both of 1<sup>st</sup> and 2<sup>nd</sup> generations, are characterized by a wide application of catalytic processes, including acid and base catalysis.

The current 1st generation biofuels production is characterize by low conversion and low energy efficiency. For instance, the production of biodiesel uses large amounts of free base catalyst, that are wasted as salts, by neutralization at the end of catalytic cycle. Improvements have been recently introduced with the application of heterogeneous catalysts.

Another drawback of biodiesel is the large side production of glycerol, that could be considered as new biofuel raw material.

Hydroprecessing of vegetable oils to green diesel seems a promising alternative to FAME biodiesel. Eni and UOP have developed a new process (EcofiningTM) which produces an high quality green diesel, with high flexibility to the feedstocks (Soybean,



Canola, Palm, Jatropha, Camelina, Tallow and Used Cooking Oils). This process can be considered a bridge between 1<sup>st</sup> and 2<sup>nd</sup> generation biodiesel.

The 2<sup>nd</sup> generation of biofuels should be produced by more sustainable routes, avoiding competition for land and water and for food and fiber production. However significant technology breakthroughs are required to overcome the technical barriers still existing, not only with respect to the biomass cultivation but also concerning the sustainability of the processes.

BTL seems a promising route for the production of syndiesel from lignocellulosic stuff. However some questions are still opened, i.e.: plant capacity vs. biomass availability and logistics; FT catalyst and reactor technology.

Catalysis is playing a paramount role in these technology challenges, contributing to the development of new processes, more efficient, safe and environmentally friendly.

#### References

- [1] G.W. Huber et al., Chem. Rev. 2006, 106, 4044.
- [2] A. Heilbrunn, World Refining & Fuels Conference, Brussels, May 8-10, 2007.
- [3] A. Srivastava, R. Prasad, *Renewable Sustainable Energy Rev.*, 2000, **4**, 111.
- [4] H.J. Kim et al., Catal. Today, 2004, 93-95, 315.
- [5] W. Xie et al., Appl. Catal. A General, 2006, **300**, 67.
- [6] X. Liu et al., Catal. Commun., 2007, 8, 1107.
- [7] A. Corma et al., J. Catal., 1998, **173**, 315.
- [8] G.J. Suppes et al., Appl. Catal. A: General, 2004, 257, 213.
- [9] G. Ondrey, Chem. Eng., 2004, 10, 13.
- [10] L. Bournay et al., Catal. Today, 2005, 106, 190.
- [11] Adapted from: C. Baudouin, 6<sup>th</sup> European Fuel Conference, Paris, March 14-16, 2005, www.ifp.fr/content/download /57521/1261755/file/ESTERFIP-H\_WRA\_2005.pdf.
- [12] E. Lotero et al., Ind. Eng. Chem. Res., 2005, 44(14), 5353.
- [13] A. Corma, H. Garcia, Catal. Today, 1997, 38, 257.
- [14] S. Steinigeweg, J. Ghmeling, *Ind. Eng. Chem. Res.*, 2003, 42, 3612.
- [15] D.E. López et al., Journal of Catalysis, 2007, 245, 381.
- [16] A. Corma *et al.*, Process for the selective production of monoesters of diols and triols using zeolitic catalysts, 1994, WO9413617.
- [17] V.P. Gupta, Glycerine ditertiary butyl ether preparation, 1995, United States patent US 5,476,971.
- [18] K. Klepacova et al., Applied Catalysis A General, 2005, 294, 141.
- [19] R.S. Karinen, A.O.I. Kause, Applied Catalysis A General, 2006, 306, 128.
- [20] E. Battistel *et al.*, Nuovi componenti ossigenati per carburanti e loro preparazione, 2008, Italian Patent Application MI2008A 000458.

- [21] D. Bianchi, E. Battistel, in DGMK Tagungsbericht, S. Ernst (Ed.), 2008, pp 125-132.
- [22] E. Koivusalmi, J. Jakkula, Process for the manufacture of hydro carbons, 2007, European Patent Application EP 1,795,576
- [23] J. Holmgren, *et al., Hydrocarbon Processing*, 2007, September issue, 67.
- [24] J. Holmgren, 2008 UOP Refining Seminar, Vienna, November 17, 2008.
- [25] F. Alvarez et al., J. Catal., 1996, 162, 179.
- [26] M.J. Girgis, Y.P. Tsao, Ind. Eng. Chem. Res., 1996, 35, 386.
- [27] H. Deldari, Applied Catalysis A: General, 2005, 293, 1.
- [28] V. Calemma et al., Appl. Catal. A: General, 2000, **190**, 207.
- [29] C. Perego *et al.*, Process for producing hydrocarbon fractions from mixtures of a biological origin, 2008, WO 2008/058664 A1.
- [30] F. Baldiraghi *et al.*, in Sustainable Industrial Process,
  G. Centi *et al.* (Eds.), 2009, Wiley-VCH, Weinheim, pp. 427-438.
- [31] P. McKendry, *Bioresource Technology*, 2002, **83**, 47.
- [32] M.J.A. Tijmensen, et al., Biomass and Bioenergy, 2002, 23, 129.
- [33] D. Dayton, Report No. NREL/TP-510-32815; National Renew-
- able Energy Laboratory: Golden, CO, 2002; www.osti.gov/bridge.
- [34] F. Fischer, H. Tropsch, Chem. Ber., 1926, 59, 830.
- [35] I. Wender, Fuel Proc. Technol., 1996, 48, 186.
- [36] C. Elschenbroich, A. Salzer, Organometallics, 2<sup>nd</sup> Rev. Ed., pp. 220-237.
- [37] V. Ponec, Catal Today, 1992, 12, 227.
- [38] M.A. Vannice, J. Catal., 1975, 37, 449.
- [39] C. Perego et al., Catalysis Today, 2009, **142**, 9.
- [40] M. Deutmeyer, 6<sup>th</sup> Annual World GTL Summit, London, May 17, 2006, www.choren.com
- [41] J-L. Duplan, Biofuel2G International Congress, Pamplona, January 23-24, 2008.

### Conversione catalitica di biomassa in combustibile ed energia

Lo sviluppo di processi economici per la produzione di combustibili liquidi da biomassa richiede grandi investimenti. Risulta indispensabile la ricerca di nuovi catalizzatori per migliorare le rese e la qualità dei biocarburanti al fine di migliorare l'efficienza e ridurre i costi. Il presente lavoro, oggetto di una conferenza a Sorrento al congresso della SCI, descrive lo stato dell'arte e le tecnologie emergenti dando particolare enfasi alla produzione di biodiesel da fonti rinnovabili.