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Biomass upgrading through acid–base catalysis

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ABSTRACT

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.

In this scenario, acid and base catalysis plays a crucial role in most of the processes used for the production of biofuels, such as the transesterification of vegetable oils with methanol in the biodiesel process and the hydrolysis of cellulose to fermentable sugars for bioethanol production.

An overview of some of the technologies currently used commercially or tested at pilot and laboratory scale, based on acid and base catalysts, is presented in this paper.

1. Introduction

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 [1].

First generation biofuels, produced primarily from agricultural crops, traditionally grown for food and animal feed purposes, are the initial step in this direction.

The main first generation biofuels are bioethanol, used as a gasoline substitute, produced from sugar containing plants or cereals crops, and biodiesel, produced from vegetable oils after conversion into the corresponding fatty acid methyl esters.

However, most of first generation biofuels have several drawbacks, including the competition with food crops, the competition for water, the potentially negative impact on biodiversity, the limited greenhouse gas emission reduction (with the exception of sugarcane ethanol) and the high production cost.

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 for 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 scenario, acid and base catalysis plays a crucial role in most of the processes currently used for the production of biofuels, such as the transesterification of vegetable oils with methanol in the biodiesel process (catalysed by alkali, i.e. NaOH, MeONa, KOH) and the hydrolysis of cellulose to fermentable sugars for bioethanol production (catalysed by H_2SO_4). The homogeneous catalysts, used in both these processes, have some drawback, mainly due to the neutralization step needed at the end of the reaction.

In order to avoid these problems, many efforts have been devoted to the search of solid acid and base catalysts, more selective, safe and environmentally friendly, or if it is not possible, to develop new technologies for the recovery end recycle of homogeneous catalysts.

The aim of this contribution is to summarize some examples of new industrial processes based on the aforementioned heterogeneous catalysts.

2. Biodiesel processes

Biodiesel is a mixture of fatty acid methyl esters (FAMEs) produced by transesterification of triglycerides with methanol in the presence of a basic catalyst, including sodium methylate, sodium hydroxide and potassium hydroxide. Glycerol is the main byproduct, whose amount is equivalent to approximately 10% of the total FAME production (Fig. 1).

In principle, both acid and base catalysts could be used in the transesterification process, however, base catalysts are generally

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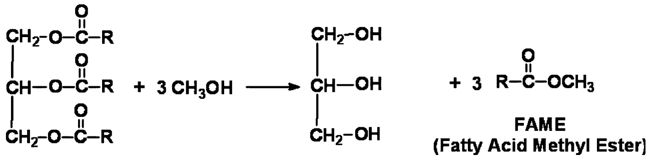

Fig. 1. Vegetable oils transesterification to biodiesel.

preferred for their superior activity (approximately 4000 times higher than that of acid catalysts) [2].

Today the commercial biodiesel production plants are utilizing homogeneous, alkaline catalysts.

The reaction is usually carried out with an excess of methanol (6/1, w/w) 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 neutralized, 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 catalyse the transesterification of vegetable oils, such as Na/NaOH/Al_2O_3 [3], KNO_3/Al_2O_3 [4] and basic metal oxides (MgO, CaO, SrO, and BaO) [5].

Corma et al. [6] evaluated glycerolysis of triglycerides using basic solid catalysts such as Cs-MCM-41, Cs-sepiolite and hydrotalcites. The reaction was carried out at 240 °C and the best conversion was obtained with hydrotalcite (92%) without any significant loss of activity.

A series of zeolite catalysts was tested by Suppes et al. [7], including NaX, faujasite and ETS-10 zeolites exchanged with potassium and cesium. At 100 °C, the ETS-10 provided a conversion of 92% in 3 h.

Recently, the Institute Francais de Petrole (IFP) has developed a new technology (Esterfip-H process) [8,9] 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 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 from homogeneous-catalyst routes, and is free from any salt contaminants.

The advantages of the Esterfip-H process over the traditional biodiesel technology are shown in Figs. 2 and 3, reporting the simplified process diagrams [10].

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.

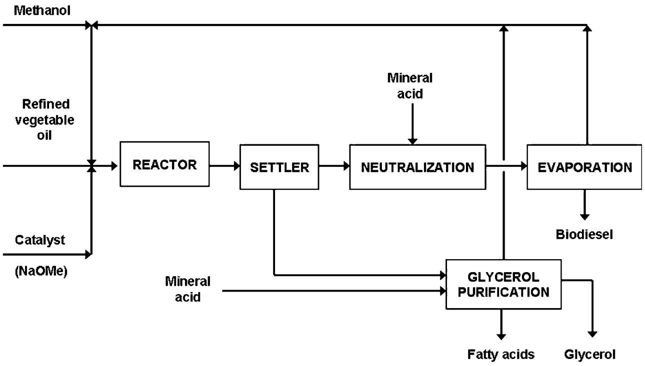

Fig. 2. Process scheme for the traditional biodiesel technology.

The high concentration of FFAs (up to 15%) present in these inexpensive feedstocks, make them inappropriate for the conventional base-catalysed 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-catalysed 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) [11] 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 SO_4/ZrO_2 and SO_4/SnO_2 proved to be active catalysts due to their high acid strength, but deactivation phenomena and sulfate leaching were detected under the transesterification conditions [12].

Esterification has been carried out using ion-exchange resins (Amberlyst-15) [13] and Nafion [14] 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

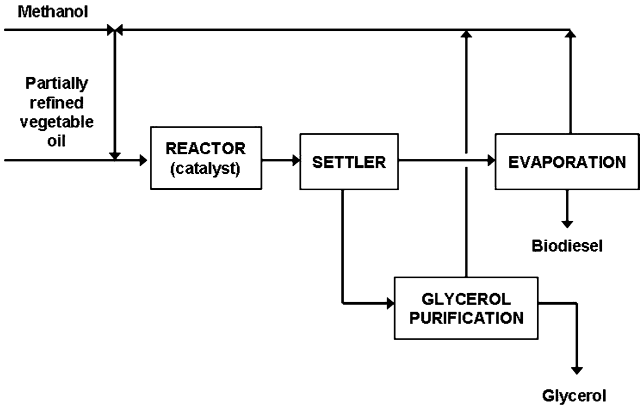

Fig. 3. Process scheme of Esterfip-H technology.

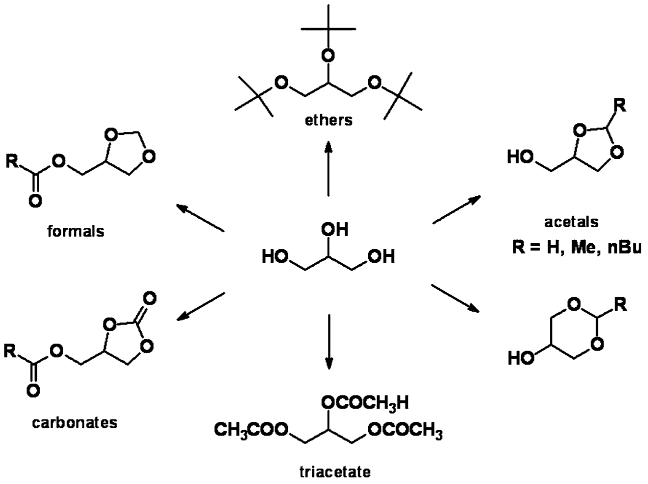

Fig. 4. Fuel components from glycerol.

zeolites (faujasite, mordenite) have been successfully used in fatty acid esterifications [15].

Recently, Rohm and Haas have developed a new catalyst (AMBERLYST^{TM} BD20) for the conversion of high free fatty acid (FFA) feedstock materials into biodiesel. It has been tested with crude vegetable oils, animal fats, greases, fatty acids, and recycled materials with a FFA range from 0.5 to 100%.

The advantages of the new catalyst are the high thermal stability and the low water sensitivity [16]. The process does not require a neutralization stage.

A final alternative route is the enzyme-catalysed transesterification of vegetable oils that can be carried out at neutral pH and moderate temperatures with high yields. Up to now, this method has not been developed to industrial scale due to high cost and low stability of enzymes [17,18].

An additional improvement of the biodiesel process deals with the utilization of the co-produced glycerol for the synthesis of oxygenated 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 (monomers for polyester or polyurethane materials), oligoglycerols (cosmetics, food additives and biodegradable lubricants), glycerol carbonate (solvent), glyceric acid (pharmaceuticals), epichlorohydrine, and glycidol (polymers and pharmaceuticals).

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.

Glycerol cannot be added directly to the 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. Fig. 4 shows some examples of glycerol derivatives proposed for fuel application [19–22].

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.

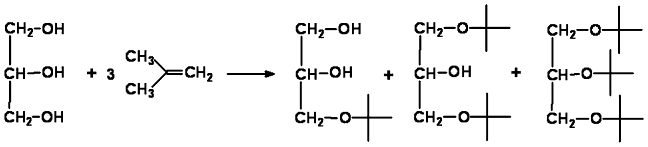

Fig. 5. Etherification of glycerol with isobutene.

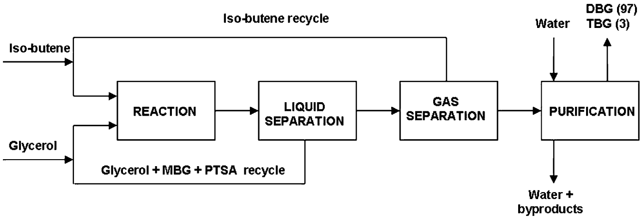

Fig. 6. ARCO (Lyondell) process for glycerol etherification.

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. 5.

The mono-ethers are soluble in polar solvents [23], whereas the mixture of di- and tri-ethers is 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 [24,25].

Typically, the reaction is carried out in liquid phase at 70–90 °C with a 3/1 isobutene/glycerol molar ratio.

Fig. 6 shows the process design developed by ARCO (Lyondell) for the etherification of glycerol using *para*-toluene sulfonic acid as a catalyst [23].

The polar mono-butyl glycerol, MBG, is separated from the apolar phase and recycled to the etherification stage along with unreacted glycerol and the catalyst. The final product is a mixture of tri-butyl glycerol (TBG) (3%) and di-butyl glycerol (DBG) (97%).

In the case of an industrial application a mixture of C4 olefins (co-produced 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 Table 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 tertiarybutyl ethers, while the linear C4 olefins are substantially uncreative under the etherification conditions [26].

The composition of the resulting residual C4 mixture is reported in Table 1 as “Raffinate 2”.

Table 1
Composition (in wt%) of C4 fractions from steam cracking.

Component	Raffinate 1	Raffinate 2[a]
Isobutane	3	6
Isobutene	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

[a] After conversion of isobutene.

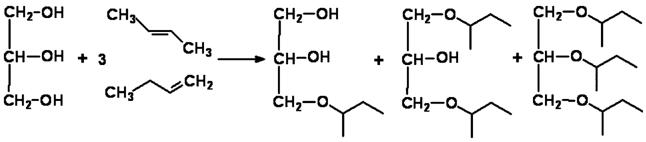

Fig. 7. Etherification of glycerol with linear butenes.

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. 7), with much better properties in diesel blending with respect to the more branched tertiarybutyl ethers [27]. Similar results were obtained using a solid super-acid catalyst, such as Nafion [26].

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) [28,29].

The UOP/Eni Ecofining^{TM} process is based on catalytic hydrodeoxygenation, decarboxylation and isomerization reactions (Fig. 8) to produce a diesel fuel rich in isoparaffins [29]. This alternative product is called green diesel. As this kind of process is very flexible to the feedstocks, if 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 [30].

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 conventional 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 biofuel 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.

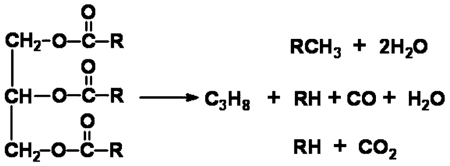

Fig. 8. Vegetable oil transformation in Ecofining process.

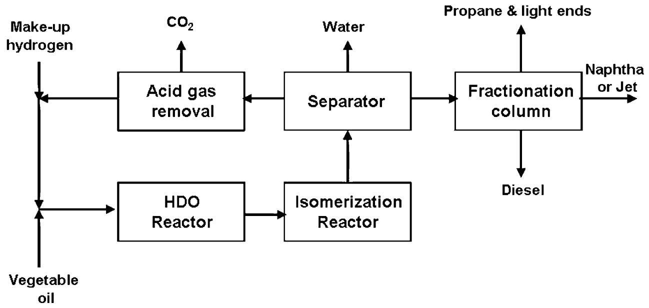

Fig. 9. Simplified Ecofining process flowscheme.

A simplified flow diagram of Ecofining process is shown in Fig. 9. 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 reactor, 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. 8). 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 [31–33], 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^{2-}), zeolites (Y, Beta, Mordenite, ZSM-5, ZSM-22), silicoaluminophosphates (SAPO-11, SAPO-31, SAPO-41) or mesoporous materials (MCM-41, Al-MCM-41) [33].

Unfortunately besides hydroisomerization, these catalysts also promote undesired cracking reactions [34]. 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 mesoporous and a mild acidity is suitable for this purpose after loading with metals selected among Pd, Pt and Ni [35].

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 h of stream [36].

3. Wood biomass hydrolysis

The main sources of ligno-cellulosic biomass, usable as feedstock for second generation biofuels, are wood from conventional and short-rotation forestry, dedicated energy crops, such as switchgrass or miscanthus, residues from forestry and agricultural production and by-products and wastes from industrial and municipal processes.

Wood is essentially composed of cellulose (38–50%), hemicelluloses (23–32%) and lignin (15–25%).

Ligno-cellulosic biomasses saccharification is the key tool for cellulose and hemicellulose conversion into monomeric sugars that can be used as a feedstock in fermentation processes for the production of renewable fuels, such as ethanol, butanol or lipids [37–39].

There are various processes available for converting biomass to fermentable sugars, such as dilute acid hydrolysis, concentrated acid hydrolysis, and enzymatic hydrolysis [40,41].

The critical point of all these technologies is to preserve the produced sugars from decomposition reactions leading to the formation of undesirable by-products, mainly furfural, hydroxymethylfurfural, levulinic acid, acetic acid and formic acid, that not only lower the yields but also act as inhibitors of the fermentation process [42].

The diluted acid methods can be used either as a pre-treatment prior to enzymatic hydrolysis or as the actual method to hydrolyse ligno-cellulose to sugars. The hydrolysis of hemicellulose takes place under relatively mild conditions, while the cellulose fraction is more resistant and requires a more severe treatment.

Using 0.5% sulfuric acid, more than 80% of hemicellulose could be hydrolysed at temperature lower than 200 °C while the maximum glucose yield from the more recalcitrant cellulose is achieved above 200 °C [43,44].

National Renewable Energy Laboratory (NREL) has developed a diluted acid hydrolysis process carried out in two stages, in order to maximize the sugar yields from hemicellulose and cellulose fractions and minimize the by-products formation (Fig. 10) [45].

In the first stage the hydrolysis of hemicellulose is carried out under milder conditions using 0.7% sulfuric acid at 190 °C and a 3-min residence time. The second stage is optimized for hydrolysis of the more resistant cellulose fraction using 2.5% sulfuric acid at 210 °C, and a 3-min residence time. The liquid hydrolysates are recovered from each stage and fermented to ethanol after a neutralization section. Residual lignin is used as boiler fuel for electricity and steam production.

The biggest advantage of dilute acid processes is the fast rate of reaction, which facilitates continuous processing; the biggest disadvantages are the low glucose yield (lower than 60%) and the co-production of salts from the neutralization stage.

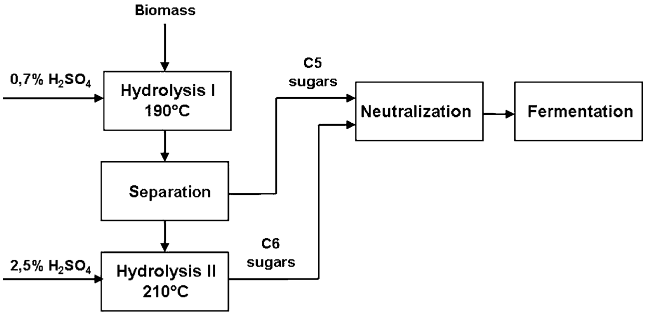

Fig. 10. Two stage dilute acid-catalysed biomass saccharification process (NREL).

Concentrated acid processes are generally reported to give higher sugar yields (up to 90%) and lower by-products formation compared to dilute acid processes. The processes operate at low temperature (80 °C) with a very high acid concentration (70–77%) and longer residence times (1–8 h). Therefore the process requires expensive alloys, specialised ceramics or carbon based non-metallic materials.

In addition, the concentrated acid must be recovered, by continuous exchange or exclusion chromatography [46], to make the process economically feasible (Fig. 11) [47].

The acid recovery is an energy demanding process and, if sulfuric acid is used, the required neutralization process of the residual acid in the sugar solution produces large amounts of gypsum.

Despite these disadvantages, the technology has claimed to have a low overall cost and is currently under development for industrial applications by Arkenol Inc. [48] and Masada Resource Group [49].

The most studied method for the saccharification of lingo-cellulosic biomasses is the enzymatic hydrolysis catalysed by cellulases [50,51].

Cellulases are usually a mixture of several enzymes including endoglucanases, which attack regions of low crystallinity in the cellulose fiber, creating free chain-ends; exoglucanases, which degrade the molecule further by removing cellobiose units from the free chain-end and β-glucosidase, which hydrolyse cellobiose to produce glucose.

Enzymatic processes have several advantages including the mild process conditions (40 °C and neutral pH), the absence of by-products and the low energy requirements. The disadvantages are mainly the low efficiency (the hydrolysis is completed in 70 h) and the cost of the enzyme.

The enzymatic digestibility of cellulose in native biomass is low (<20% yield) because of its structural characteristics. For enzymatic processes to be effective, some kind of pre-treatment process is required to break the crystalline structure of the ligno-cellulosic and remove the lignin to expose the cellulose and hemicellulose molecules [52].

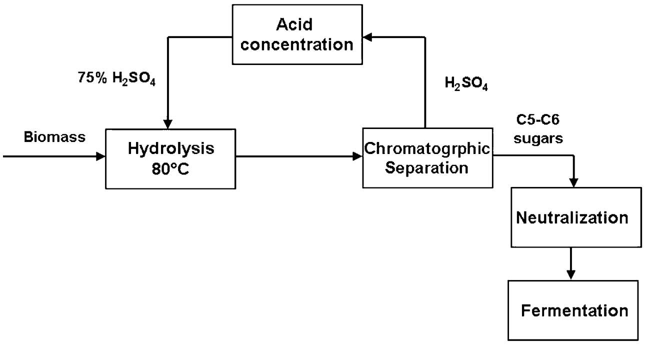

Fig. 11. Concentrated acid biomass saccharification process.

Pre-treatment has been viewed as one of the most expensive steps in cellulosic biomass processing and has great potential for improvement of efficiency and lowering of cost [53]. Pre-treatment methods can be either physical or chemical.

Steam explosion is the most commonly used method for physical pre-treatment of ligno-cellulosic materials. In this process the biomass is treated with high-pressure saturated steam, then the pressure is swiftly reduced and the materials undergo an explosive decompression. Steam explosion is typically carried out in the temperature range between 160 and 260 °C (corresponding to a pressure range between 0.69 and 4.83 MPa) for few minutes before the material is decompressed. The process causes hemicellulose degradation and lignin transformation due to high temperature, thus increasing the digestibility of cellulose.

Addition of H_2SO_4 (or SO_2) or CO_2 in steam explosion effectively improves enzymatic hydrolysis, decreases the production of inhibitory compounds, and leads to more complete removal of hemicellulose [54].

A process based on steam explosion pre-treatment is under development by IOGEN Corporation (Canada) [55].

Acid or base catalysed pre-treatments were also extensively studied to promote the enzymatic cellulose hydrolysis. They act through two different reaction mechanisms: acid treatments selectively remove hemicellulose while basic treatments solubilise lignin.

Alkali pre-treatment processes are usually carried out at lower temperature (ambient to 100 °C) and pressure if compared to other pre-treatment technologies, but they take much longer times (hours to days instead of minutes). Sodium, potassium and calcium hydroxides are the most suitable catalysts [56].

Calcium hydroxide has the advantage that it can be recovered from the waste water by precipitation with CO_2; the resulting calcium carbonate can be reconverted to calcium hydroxide by thermal treatment and recycled to the process [57].

The effect of the alkaline pre-treatment is the removal of lignin from the biomass, thus increasing the reactivity of the remaining polysaccharides. In these conditions hemicellulose is not solubilised but only modified by removal of sugar substituents, such as acetic and uronic acid esters that have a detrimental effect on the enzymatic hydrolysis and can act as fermentation inhibitors.

Up to now, alkaline pre-treatment technology has not found any practical application for the development of commercial processes.

Dilute acid pre-treatments are carried out under more severe conditions (200–215 °C) with shorter reaction times ranging from 1 to 5 min. The acid catalyst, typically sulfuric acid, is used with a concentration ranging from 0.5 to 3% [58].

NREL has developed a chemo-enzymatic process for the saccharification of corn stover based on a diluted acid pre-treatment, carried out at 190 °C for 2 min, using 1.1% sulfuric acid. Under these conditions the xylan yield is higher than 90%. The following enzymatic hydrolysis of the residual cellulose is carried at 40 °C in 36 h, achieving a glucose yield also higher than 90%.

In spite of the high efficiency, dilute sulfuric acid pre-treatment has many drawbacks, similar to these above outlined for the direct dilute acid saccharification process, including corrosion, expensive materials of construction, formation of fermentation inhibitors by-products, chemicals consumption, required neutralization before the sugars proceed to fermentation, disposal of neutralization salts.

In particular, the neutralization stage is one of the critical points of the whole process because of the chemical consumption (lime) and the co-production of large amount of gypsum as by-product (NREL reported the production of 173 g of $CaSO_4$ per kilogram of ethanol) [59].

In order to avoid these limitations, several processes have been evaluated, aiming the recovery of the hydrolysis catalyst.

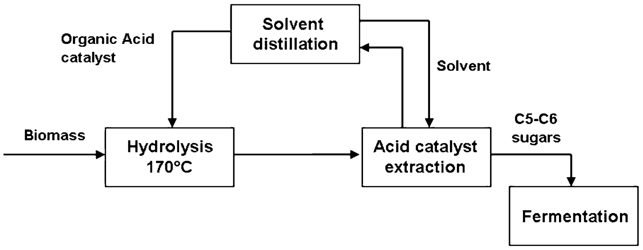

Fig. 12. Biomass saccharification process with organic acids recycle (Eni Spa).

Conventional solid Brønsted acid catalysts, such as niobic acid, H-mordenite, Nafion and Amberlyst-15, proved to be uneffective in the hydrolysis of cellulose. Recently, amorphous carbon bearing SO_3H, COOH, and OH function has been reported as a highly active heterogeneous acid catalyst for the direct saccharification of crystalline cellulose. The catalytic performance of the carbon catalyst is attributed to the ability of the material to adsorb β-1,4 glucan, which does not adsorb to other solid acids [60].

Following a different approach, ENI has developed a new technology based on a water soluble organic acid catalyst (2-naphthalenesulfonic acid), that can be recovered at the end of the reaction by extraction with an organic solvent. The process is carried out at 160–170 °C and both hemicellulose and cellulose are hydrolysed with high yield, with no catalyst consumption and neutralization step is not required. However, an evaporation stage for the recovery of the catalyst from the extraction solvent is necessary in this case (Fig. 12) [61].

A pre-treatment method based on the use of liquid ammonia (Ammonia Fiber Explosion—AFEX) has been proposed as an alternative to the acid-catalysed processes [62,63].

AFEX is a physicochemical pre-treatment in which ligno-cellulosic materials are exposed to liquid ammonia at high temperature and pressure, then the pressure is swiftly reduced as in the steam explosion treatment. In a typical AFEX process, the dosage of liquid ammonia is 1–2 kg ammonia/kg dry biomass, with 30 min of residence time at 90 °C.

AFEX pre-treatment has been successfully applied to improve the saccharification rates of various herbaceous crops and grasses, affording over 90% hydrolysis yields of cellulose and hemicellulose, after the enzymatic hydrolysis stage [64].

To reduce the cost, ammonia must be recycled after the pre-treatment (Fig. 13). In the recovery process, developed by Afex Corporation, the residual ammonia in the treated biomass is striped using a superheated ammonia vapor with a temperature up to 200 °C, and the evaporated ammonia is then recovered and recycled after condensation [62].

The advantages of AFEX process [65] include:

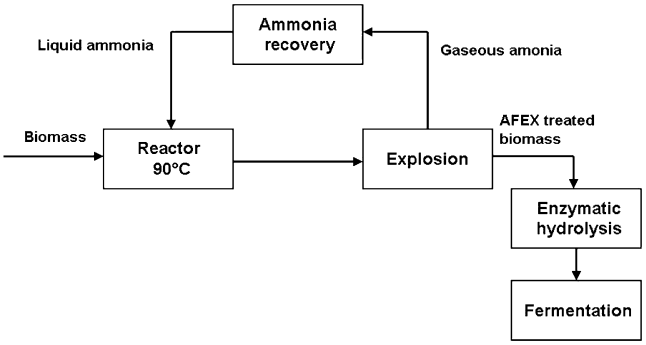

Fig. 13. Ammonia Fiber Explosion (AFEX) biomass pre-treatment.

- nearly all of the ammonia can be recovered and reused while the remaining serves as nitrogen source for microbes;
- essentially dry matter is recovered after the treatment;
- no need for wash stream in the process;
- treated biomass can be fed at very high solid loadings in enzymatic hydrolysis;
- negligible by-products formation;
- no need for neutralization prior to the enzymatic hydrolysis;
- improved enzymatic hydrolysis yields.

4. Other processes

Acid and base catalysts have also been applied to the processing of different biomass and biomass-derived products. Some examples are, the catalytic pyrolysis, the upgrading of pyrolysis oil and lignin and the liquid-phase processing of sugars to fuels.

4.1. Pyrolysis processes

Fast pyrolysis is a thermal process that rapidly heats biomass to a carefully controlled temperature (∼500 °C) in the absence of air, then very quickly cools the volatile products (<2 s) formed in the reactor [66]. The resulting liquid products, called bio-oils, have a very complex chemical composition, high oxygen content (30–40%), high water content (15–30%) and a low pH [67]. Typically, fast pyrolysis oils show a lower heating value (16–19 MJ/kg) compared to heavy fuel oils (40 MJ/kg).

The use of catalysts to accelerate pyrolysis and increase the yield and the quality of desired liquid products is relatively unexplored and represents an interesting area of opportunity [68–70].

The pyrolysis of wood based biomass has been carried out in the presence of microporous acid zeolite catalysts (H-ZSM-5) obtaining an increase of the aromatic fraction (up to 30%) in the resulting bio-oil [71,72].

The acid sites of the catalyst promote a series of dehydration, decarbonylation, decarboxylation, isomerization and dehydrogenation reactions, converting the oxygenated products generated in the pyrolysis process into more stable aromatic compounds, mainly naphthalene, ethylbenzene and xylenes. The shape-selectivity and the acid properties of the catalysts are crucial parameters in the choice of the fast pyrolysis catalysts. Indeed the use of beta-zeolite, Y-zeolite and silica–alumina catalysts lead to the production of large amounts of coke as the main product.

Operating under different reaction conditions, the use of H-ZSM5 catalyst can increase the aromatic fraction in the bio-oil from 7 (obtained in the absence of any catalyst) to 74% [73].

Mesoporous catalysts such as Al-MCM-41, significantly changed the composition of bio-oil, increasing the yields of phenols, hydrocarbons and polycyclic aromatic hydrocarbons (PAH), while decreasing the yields of oxygenated carbonyl and acid compounds [74].

The catalysts modified by introduction of transition metals (Fe–Al-MCM-41 and Cu–Al-MCM-41) provided the best results in terms of phenols production [75].

4.2. Bio-oil upgrading

Bio-oils produced by fast pyrolysis are acidic viscous combustible liquids containing more than 300 compounds that degrade with time, therefore they cannot be directly used for diesel or gasoline fuel blending [76].

Just like for crude oil, further reprocessing is necessary to arrange pyrolysis oil as fuel for combustion engines. The main routes for bio-oil upgrading, by reducing the oxygen content, are the hydrotreating and the catalytic cracking.

Acid zeolites can be used for this purpose, taking advantage of the shape-selectivity of these materials.

Although zeolite upgrading is a cheap route that does not require hydrogen, the process needs a fine tuning in order to avoid the formation of coke [77].

Different catalysts have been tested, including H-ZSM5, H-Y-zeolite, H-mordenite, silicalite, silica/alumina, SAPO 5 and SAPO 11 [78–81]. Among these catalysts, H-ZSM-5 yielded the highest amount of liquid products (up to 34 wt% of feed).

The product composition comprised mostly aromatics for ZSM-5 and aliphatics for silica/alumina catalysts. Gaseous products include CO_2, CO, light alkanes, and light olefins. Large amounts of coke (6–29 wt% of feed), char (12–37 wt% of feed), and tar (12–37 wt% of feed) are formed during the upgrading over zeolites.

Hydrotreating process is typically performed at 300–600 °C in the presence of heterogeneous Co–Mo, Ni–Mo based catalysts under high pressure of hydrogen. In these conditions oxygen is removed as H_2O and CO_2. The hydrogenation of aromatics is not desired, since it would increase the hydrogen consumption [82].

Honeywell/UOP has developed a two-step process for the upgrading of bio-oils produced by fast pyrolysis to give high yield of naphtha, aviation and diesel fuels [83].

The first partial deoxygenation step is carried out at low temperature (315–340 °C) in order to remove the thermal unstable bio-oil components, such as the short chain carboxylic acids and the olefins that would decompose to coke if heated under more severe conditions.

The second hydrotreating stage, carried out at higher temperature (405 °C), involves the full hydrodeoxygenation of the stabilized bio-oil to produce a hydrocarbon oil with less than 2% oxygen.

Both these reactions are promoted by sulfided Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 catalysts.

The second stage can be carried out in the presence of a combined zeolite and amorphous silica–alumina catalyst with metal loading (e.g., Ni, Mo, W).

Zeolites, including beta-zeolite, Y-zeolite, MFI type, mordenite and faujasite, promote the cracking of heavy compounds that are outside the range of gasoline and diesel fuel.

In a different approach the cracking stage can be carried out in a separate reactor, after separation of the stable oil into light and heavy fractions. The heavy fraction (which boils above 350 °C) is sent to the hydrocracker to completely convert the oil to gasoline and diesel blending components [84].

4.3. Lignin to fuel processes

Lignin is a complex polymer of phenylpropane-based monomers joined by ether and carbon-to-carbon linkages. It is obtained as coproduct in the saccharification processes of ligno-cellulosic biomass and is usually utilized as boiler fuel.

Yet, the chemical structure of lignin suggests that it will make an excellent high value fuel component, if it can be broken down into smaller compounds and deoxygenated.

The University of Utah has developed different multi-stage processes for the production of high octane blending components from lignin, using both base and acid catalysts.

In the first step, termed base-catalysed depolymerization (BCD), ether linkages are broken by heating the lignin, suspended in water or methanol, to moderate temperatures (ca. 300 °C) in the presence of a base catalyst. The products are small, low molecular weight phenols [85].

Both homogeneous (e.g., NaOH and KOH) and heterogeneous catalysts (Cs-exchanged X-type zeolites) can be used.

The second stage involves the hydroprocessing of the depolymerized lignin intermediate, carried out in presence of sulfided Co–Mo or Ni–Mo catalysts. Depending on the catalyst, the products can be C7–C10 alkylbenzenes or a mixture of multi-branched paraffins and polyalkylated cyclohexanes [86].

In a different approach, the depolymerised lignin is subjected to a selective hydrocracking treatment which utilizes a Pt modified super-acid catalysts ($Pt/SO_4{}^{2-}/ZrO_2$), producing a mixture of monomeric alkylated phenols and alkoxyphenols. The resulting mixture is subjected to an exhaustive etherification stage with methanol or ethanol in presence of a solid super-acid catalysts, such as sulfated or tungstated metal oxides (Zr, W or Mn), to give a partially oxygenated gasoline product [87].

4.4. Liquid-phase processing of sugars to fuels

Sugars obtained from the hydrolysis of ligno-cellulosic biomass can be converted into hydrocarbons or fuel oxygenated components by low temperature liquid-phase catalytic processing.

The advantages of these processes, with respect to the thermochemical treatments, are the high selectivities and yields of targeted products. A disadvantage is that the biomass feedstock must be pretreated to prepare a feed solution that is appropriate for subsequent liquid-phase processing.

Dumesic and co-workers developed different synthetic routes involving the dehydration of sugars (e.g., fructose) over acid catalysts (hydrochloric acid or an acidic ion-exchange resin) to form hydroxymethylfurfural (HMF), that can subsequently undergo aldol condensation with ketones (e.g., acetone), followed by hydrodeoxygenation to form C9 to C15 alkanes for use in diesel and jet fuels [88,89].

In a different route, hexose sugars (e.g., fructose) can be converted to 2,5-dimethylfuran (DMF) by selective removal of five oxygen atoms [90]. The produced DMF has a high octane number and excellent fuel properties.

The removal of oxygen atoms can be accomplished in two steps: first, removing three oxygen atoms by dehydration to produce hydroxymethylfurfural; and second, removing two oxygen atoms by hydrogenolysis to produce DMF. The first step involves the acid-catalysed (aqueous HCl) dehydration of fructose to produce HMF in a biphasic reactor (water/1-butanol). The HMF extracted by the organic phase is then converted into DMF by hydrogenolysis of C–O bonds over a copper–ruthenium (CuRu) catalyst.

An alternative strategy involves the conversion of sugars and polyols (e.g., sorbitol) to hydrophobic alcohols, ketones, carboxylic acids, and heterocyclic compounds over a Pt–Re catalyst [91].

The liquid organic mixture obtained from sorbitol can be converted to aromatic compounds by first hydrogenating the ketones to alcohols (over a Ru/C catalyst), and then heating to 400 °C at atmospheric pressure over an acid zeolite catalyst (H-ZSM-5).

The main products are paraffins, olefins and aromatics hydrocarbons, obtained with 25%, 29% and 38% yields, respectively, based on the carbon in the sorbitol-derived organic phase.

All these processes are certainly at early stage development and are still far from commercial application, but are promising biomass upgrading possibilities.

5. Conclusions

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

The current 1st generation biofuels production is characterized 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.

The 2nd generation of biofuels should be produced by more sustainable routes, avoiding competition for land and water used for food 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. For instance, the use of large amount of mineral acids (i.e. large mineral salt waste) for the pretreatment of cellulosic biomasses should be avoided. Catalysis will play a paramount role in this technology challenge, leading to the development of new processes, more efficient, safe and environmentally friendly.

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