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Review

Catalysis for the Valorization of Low-Value C-Streams

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A necessidade de uma melhor gestão de carbono e redução das emissões de CO_2 leva na direção de uma melhor gestão de carbono que inclui reciclagem (CR) em detrimento a economia de carbono linear(LCE). Isso implica na utilização de fluxos de processos gasosos e líquidos sub-utilizados até o momento, e frequentemente enviados a combustão ou descartados. Neste trabalho, quatro casos são discutidos, nomeadamente: corrente de alcanos de baixo peso molecular, CO_2 industrial, resíduo ligno-celulósico e glicerol contendo água e sais. O papel da catálise na valorização de tais fontes de C é discutido e exemplos de processos inovadores são apresentados.

The need for a better carbon management and the reduction of CO_2 emissions push away from the linear-carbon economy (LCE) towards a better carbon management including carbon recycling (CR). This implies the utilization of gaseous and liquid process streams so far under-utilized, and often either sent to combustion or disposed of. In this paper, four cases are discussed, namely: low-alkane streams, industrial CO_2, ligno-cellulosic waste and salty-watery-glycerol. The role of catalysis in the valorization of such C-sources is discussed and examples of innovative processes are presented.

Keywords: low-alkanes, CO_2, lignocellulosic materials, salty-watery-glycerol, carbon recycling

1. Introduction

The anthropogenic emission of CO_2 (ca. 33 Gt y^{-1}), despite representing only a few percentage points (4.6%) of the natural carbon cycle (NCC) (ca. 721 Gt y^{-1}), is not buffered by the latter and is causing CO_2 accumulation in the atmosphere. Such increase (from 275 ppm in the preindustrial era to the current 390 ppm) is directly or indirectly considered the origin of climate change (CC) that causes increase (or decrease) of temperature with other side effects. Strategies for the reduction of the CO_2 immission in the atmosphere are under investigation and include: (*i*) efficiency in the production and utilization of electric energy; (*ii*) fuel shift in the production of electric energy and in industry; (*iii*) use of perennial energy sources, such as solar, wind, hydro, geothermal; (*iv*) industrial reduction of waste production; (*v*) CO_2 capture and storage (CCS); and (*vi*) CO_2 capture and utilization (CCU). Technologies (*i*)-(*iv*) avoid the production of CO_2 and improve the use of natural reserves of carbon; CCS disposes of in natural sites (spent natural gas wells, the most secure sites, coal beds, aquifers, deep waters, others) the captured CO_2 from anthropogenic fixed sources; CCU recycles the captured carbon, mimicking nature. Efficiency technologies and carbon recycling[1] are of great value for the future as they reduce the extraction of fossil carbon (FC) and are examples of responsible care towards future generations. Recycling carbon would represent a step away from the linear-carbon economy (LCE) today exploited towards the cyclic carbon economy (CCE).[2]

2. Discussion

The industrial production is today characterized by four negative aspects, namely: (*i*) low carbon utilization fraction (CUF). The ratio $C_{\text{stored in products}}$ / $C_{\text{in raw materials}}$ is, in

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fact, much less than 1. CUF index can be applied also to energy production. The ratio energy produced/extracted fossil carbon rarely exceeds 20%, considering all the steps of the production chain (extraction/shipping of raw materials/refining/conversion/distribution of end-energy form) from source to utilization, with 80% of the original energy lost in many forms, more often as heat transferred to the atmosphere, with perturbation of its thermal structure; (*ii*) high carbon footprint (CF). This index is another way of demonstrating the efficiency of processes: the lower the carbon footprint the higher the efficiency of the process; (*iii*) high waste production presented as E_{factor}, that is the ratio mass of waste produced / mass of usable products.[3] Such factor varies in the range 0.01 → 100. The former is typical of refineries, while the latter is characteristic of the pharmaceutical industry. The intermediates (E_{factor} = 1-5) and the specialty chemicals (E_{factor} = 5-15) are placed between such limits; (*iv*) high energy consumption factor (ECR), representing the ratio of the energy furnished to a process to the energy stored in a product generated in that process: $E_{in}\,E_{out}^{-1}$. This ratio is often much higher than 1.

Such factors should be much improved in order to exploit better production conditions.

In several cases, catalysis can play a key role for a better carbon management, and new catalysts need to be developed for the conversion of the new raw materials that have structural differences with respect to those used today (hydrocarbons), due to the particular inertness or chemical composition (high O-content) of substrates.

In this paper, some selected cases exemplifying potential improvement of carbon utilization will be discussed, that require catalyst development and new synthetic strategies.

2.1. Tail gas streams from the petrochemical and gas industry (C1-C4)

Tail gas streams are produced in the petrol refining[4] and gas processing industry.[5] For a long time, such gas streams were flared, but recently a new approach became necessary, due to the constraints about CO_2 emission and carbon tax implementation in some countries.[6] The new approach foresees the recovery-purification of the gas stream and the separation of components and their utilization. The purification is finalized to the elimination of sulfur residues (SO_2 or H_2S present in the range 1-3%) that produce negative environmental effects. Purity of 99.9% is today reached in China using catalysts such as C234 based on Co-Mo that operate at 515 K.[7] The newest catalyst C-734 operates at a temperature below 500 K with higher energy efficiency. The purified gas stream can undergo fractionation[8] for ethane extraction by turbo-expansion without mechanical refrigeration. Cracking of the gas mixture is often applied that increases the complexity as new species are produced. The final mixture coming from cracking is in general formed by methane, ethane, ethene, propane, propene, butane, butene, and higher hydrocarbons (HCs).

The separation of the components of tail gas is made complex by its physical properties that recall those of natural gas (NG). Table 1 shows the molecular mass, the melting and boiling points and water solubility of some tail gas components compared to NG.

In general, fractions such as C1–C2–C2=, C3–C3=, C4–C4=, >C4 are separated. The low-alkane fraction can be catalytically converted into useful products and such conversion can make the separation of the components easier, as their physical properties would differ more than those of the parent compounds.

Possible conversion would be the photocatalytic carboxylation of alkanes or their selective oxidation to alcohols. Table 2 shows the properties of some derivatives of C1-C4 alkanes. If compared with the same properties of the parent compounds, it is evident that the products can be separated in a easier way as the melting and boiling points differ much more than those of the parent compounds. Obviously, the formation of azeotropes would make the situation less straightforward.

The question is how to realize such conversions. The selective oxidation of alkanes into their alcohol derivatives is not an easy process. It is not yet developed at the industrial level, despite its great importance and economic

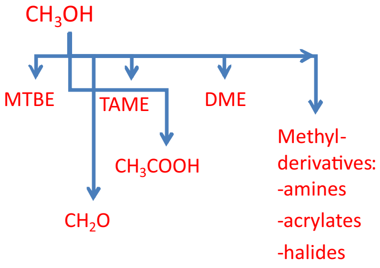
Table 1. Some properties of C1-C4 tail gas (values for natural gas and tail gas represent ranges)

Property	Methane	Ethane	Propane	Propene	Butane	Natural Gas	Tail gas
Molecular mass	16.04	30.07	44.10	42.08	58.12	Mixture	Mixture
Melting point / °C	–182.4	–182.8	–187.6	–185	–138.2	–187.6/ –182.4	–187.6/ –182.4
Boiling point / °C	–161.5	–88.6	–42.1	–48	–0.5	–161.5/ –6.2	–161.5/ –6.2
H_2O sol, 25 °C / (mg L^{-1})	22	60.2	62.4	200	61.2	22/221	22/221

Table 2. Comparison of the physical properties of some derivatives of C1-C3 alkanes

Property	CH_3COOH	CH_3CH_2COOH	$CH_3CH(COOH)CH_3$	$CH_3(CH_2)_2COOH$	C5 acid
Melting point / °C	17	–21	–47	–7.9	–34.5
Boiling point / °C	118	141	155	163.5	186
	CH_3OH	CH_3CH_2OH	$CH_3CH_2CH_2OH$	$CH_3CH(OH)CH_3$	$CH_3(CH_2)_2CH_2OH$
Boiling point / °C	64.7	78.4	96	82	118

value. For example, the single-step direct conversion of methane into methanol would have a great industrial relevance as methanol can be used as fuel, or combustible in fuel cells, or intermediate for the synthesis of several chemicals. Scheme 1 shows the variety of compounds derived from methanol.



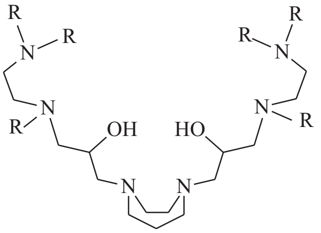
Scheme 1. Chemicals derived from methanol (MTBE: methyl *tert*-butyl ether, DME: dimethyl ether, TAME: tertiary amyl methyl ether).

The selective oxidation of methane into methanol in nature is achieved using Fe(IV) and Cu(II) moieties bearing the Fe(O) and Cu–O–Cu functionalities.[9] Two methane monooxygenase (MMO) enzymes are known to mediate the oxidation process in methanotrophic bacteria: a membrane-bound MMO called particulate-MMO (pMMO) and a water-soluble form referred to as a soluble-MMO (sMMO). pMMO is a multicopper protein, while sMMO is a nonheme-diiron protein. Both systems exploit metal-clusters to catalyze this difficult reaction.

Biomimetic systems try to repeat the catalytic site in a simplified organization. Several attempts have been done so far in order to identify the most active catalysts. So far, tricopper systems, Pt(II)[10] complexes and $FePO_4$ species have been identified as being among the most active ones. The so-called trilobate-Cu-complexes[11] are an interesting example of biomimetic catalysts. The ligands are schematized in Figure 1, while the reaction mechanism is shown in Figure 2.

The conversion yield is still very low for exploitation (1-2%), but the route is selective (100%).

An alternative route is represented by the selective catalytic (modified La_2O_3 oxides) chlorination of CH_4 to CH_3Cl (Scheme 2) followed by the hydrolysis of the latter to CH_3OH.[12]



R= Me, Et

Figure 1. Ligands used in the partial oxidation of CH_4 to CH_3OH using O_2.

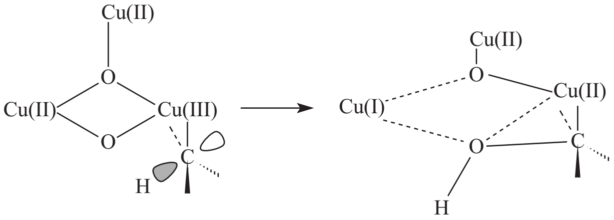


Figure 2. Reaction mechanism in the partial selective oxidation $CH_4 \rightarrow CH_3OH$.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$CH_3Cl + H_2O \rightarrow CH_3OH + HCl$$

$$2HCl + \tfrac{1}{2} O_2 \rightarrow H_2O + Cl_2$$

$$\text{Net reaction: } CH_4 + \tfrac{1}{2}O_2 \rightarrow CH_3OH$$

Scheme 2. Catalytic chlorination of CH_4 to CH_3Cl used as precursor of CH_3OH.

This route gives better yields (a few percentage points), but raises the issue of use of chlorine and the generation of chlorinated waste.

Another interesting approach is the photochemical conversion of alkanes to afford several useful products. Table 3 shows various steps that may convert a low-alkane either into a longer chain or into derivative as carboxylates. The direct carboxylation of low alkanes would be a process of great industrial relevance as the production of carboxylic moieties is today achieved via tortuous routes implying either the oxidation of organic moieties, such as $–CH_3$ groups or aromatic rings or the hydrolysis of cyanides. Such processes are neither selective nor very efficient for carbon utilization.

Table 3. Photocatalytic conversion of methane in the presence of CO_2

$Cat_{Photo} + h\nu \rightarrow h^+ + e^-$
$CH_4 + h^+ \rightarrow \bullet CH_3 + H^+$
$CO_2 + e^- \rightarrow \bullet CO_2$
$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3\text{–}CH_3$
$CH_4 + \bullet CO_2^- \rightarrow CH_3COO^- + \bullet H$
$CH_3COO^- + H^+ \rightarrow CH_3\text{–}COOH$
$\bullet CO_2^- + \bullet H \rightarrow HCOO^-$
$HCOO^- + H^+ \rightarrow HCOOH$

Examples of carboxylation reactions have been recently reported in the literature[13] based on the use of engineered photocatalysts based on TiO_2 as principal photomaterial. TiO_2 has a band gap that does not allow the use of visible light. When modified on the surface with various additives the new photocatalysts can work under solar light and promote C–H activation. Functionalization of activated and non-activated C–H bonds has been reported.[13]

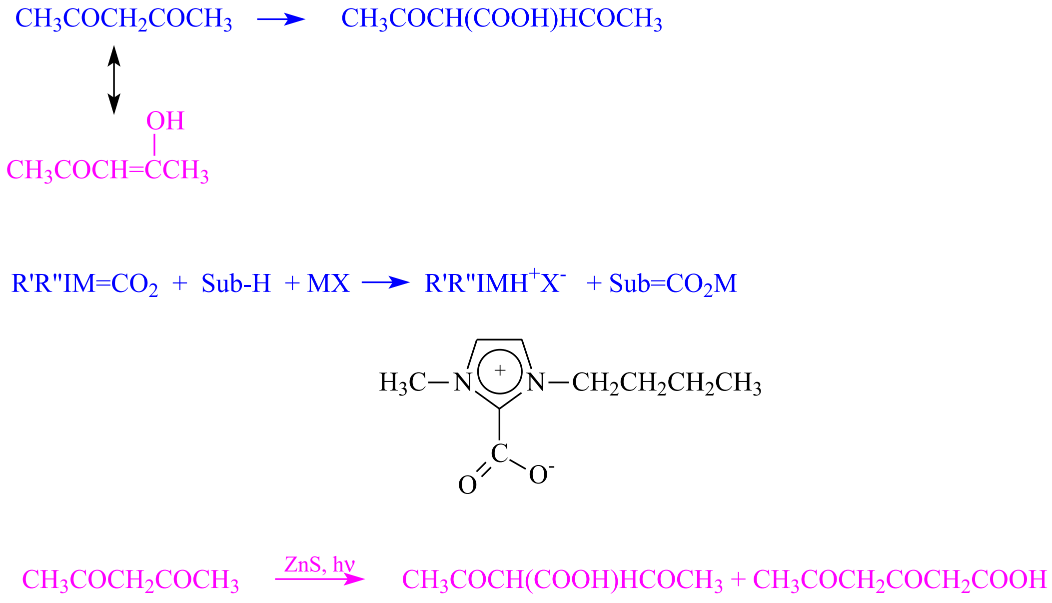
So, acetylacetone (Scheme 3) can be photochemically carboxylated both at the $–CH_2–$ (activated) group and the $–CH_3$ (non activated) group. Interestingly, the photochemical carboxylation with respect to the chemical carboxylation shows a different reactivity. The chemical carboxylation with organic bases[14] or ionic liquids as catalysts[15] brings only to the carboxylation at the $–CH_2–$ moiety. Conversely, photocatalytic carboxylations brings to the production of two compounds: the species carboxylated at the $–CH_2–$ and the new one carboxylated at the $–CH_3$ moiety. The two products have been isolated and fully characterized and were shown to be formed in a $2CH_2$ / $1CH_3$ molar ratio for what concerns the site of carboxylation.

2.2. Utilization of CO_2 in synthetic chemistry and for the synthesis of fuels

Photocarboxylation introduces the topic of CO_2 utilization as a way to recycle carbon. CO_2 is a valuable source of carbon[1,16] for the synthesis of chemicals or fuels. A key point is the source of CO_2. The most abundant is for sure the flue gas from power stations, that suffers from low concentration and presence of pollutants (SOx and NOy, noxious for catalysts and biosystems) which need to be separated with high cost (energetic and economic). Scheme 4 presents some media for CO_2 separation.

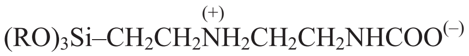
The use of solid phases reduces the loss of sorbents and the environmental impact, but demands higher energy consumption in the release of CO_2. Recently, several large investments have been done by public agencies and industries for the development of high efficiency separation media that are under assessment at the demo-plant size. It is worth emphasizing that whatever one wishes to do with CO_2 (CCS or CCU) it must be first separated from the source stream. This requires that the lowest possible cost (energetic and economic) technology must be applied.

RWE AG (Germany) has implemented the recovery of 90% of emitted CO_2 (300 kg h^{-1}) by a lignite-fired plant with a total efficiency of 43% in Niederaussem: 20% energy reduction in CO_2 separation has been targeted with the use of the new solvent OASE@blue. The plant was developed with BASF-Linde.[17] The Department of Energy (DOE, USA) has developed a pilot plant in Wilsonville designed to limit the increase of levelized cost of electricity to no more than 35% compared to about 80% added cost for existing technologies. The new plant is like the Linde one described



Scheme 3. Photochemical carboxylation of acetylacetone compared with the chemical carboxylation.

Solid phases: $CaO, MgO \leftrightarrow Ca(Mg)CO_3$
Liquid phases: MEA, $HOCH_2–CH_2NH_2$
$HOCH_2CH_2NHCOO^- \ {}^+H_3NCH_2CH_2OH$
Silylamines: $(RO)_3Si–CH_2CH_2NHCH_2CH_2NH_2$



$(RO)_3Si–CH_2CH_2\overset{(+)}{N}H_2CH_2CH_2NHCOO^{(-)}$

Membranes
Ionic liquids
Combined systems
Cryogenic (high cost, emissions connected to the use of electricity produces from fossil C)

Scheme 4. Separation media for CO_2 from process gas streams.

above.[18] KEPRI (Korea)[19] has built (in collaboration with UBC (Canada), AIST (Japan) and NETL (USA)) a pilot plant operated with proprietary "solid sorbents" that has been upgraded to a demo scale (2000 $Nm^3\ h^{-1}$ in 2012) and will be brought to a commercial scale (1.5 MN $m^3\ h^{-1}$) by 2030. This process is said to reduce energy requirements and costs by 30% or more.

Separation technologies are listed in Table 4 and compared for their pros and cons.

Table 4: Separation technologies and their pros and cons

Technology	Pros	Cons
Solid phases	Low loss	Energy consumption
Liquid phases (LP) MEA	Mature	Loss, volume
Membranes (M)	Reduced volume-space	Cost, life-time
Combined (LP/M)	Efficiency	Volume, cost
Cryogenic	Low emission	Cost, use of electricity
Issues: CAPEX, OPEX, energetic costs (energy penalty: 20-40+%)		

CAPEX: capital expenditure; OPEX: operational expenditure.

Cryogenic technology is quite interesting, but the electricity used must come from non-fossil sources. Alternative sources to flue gases from power stations are the industrial sources (Table 5).

Table 5. Industrial sources of CO_2 (average of several sources)

Industrial sector	$Mt_{CO_2}\ y^{-1}$ produced
Oil refineries	850-900
Ethene and other petrochemical processes	155-300
LNG sweetening	25-30
Ethene oxide	10-15
Ammonia	160
Fermentation	> 200
Iron and steel	ca. 900
Cement	> 1000

LNG: liquified natural gas.

All of them do not contain SOx and NOy as pollutants; therefore, the purification cost may be much lower than that of power station flue gases. For example, CO_2 from fermentation is quite pure and, in some applications, can be used without any treatment. CO_2 produced in the NH_3 industry is already recovered and used in the production of urea.

The separated CO_2 can be either disposed of (technology not discussed in this paper) or used. The utilization of CO_2 includes the technological, chemical and enhanced biological exploitation. The latter option is relevant to the conversion of CO_2 into biomass (mainly aquatic) under non-natural conditions (concentration of CO_2 up to 150 times the natural one). Such practice is under serious assessment these days as it is considered to have good potential for large scale CO_2 conversion into useful products (chemicals and fuels) in the medium term.

The actual use of CO_2 sizes at ca. 200 Mt y^{-1}; 172 Mt y^{-1} used for the synthesis of chemicals and 28 Mt y^{-1} in technological applications (Table 6).

The perspective use in terms of production of chemicals, based on the market growth of products with a market > 1 Mt y^{-1},[20] foresees use of some 350 Mt y^{-1} of CO_2 by 2030 with an avoided amount of ca. 1 Gt y^{-1}. It is worth to emphasize that the used CO_2 is the amount fixed in a chemical, while the avoided CO_2 is the non-emitted CO_2, with respect to processes on stream, a benefit derived from the introduction of innovative, more direct, synthetic technologies.[21] A great expectation is the growth of aquatic biomass for the production of chemicals and fuels. The moment being, while the growth of microalgae for the production of chemicals is economically viable, it is not for the production of fuels. Several parameters, such as energy input, source of micronutrients, harvesting, and drying, still need improvement for an economically viable production of fuels. The overall 20-20-20 target in general for biomass is still uncertain, what will be the contribution of aquatic biomass is more difficult to say; the other targets set for 2030 and 2050 are also uncertain.

Table 6. Utilization of CO_2 in the chemical industry and in technological applications

Compound	Actual production	CO_2 used
Urea	155	114
Methanol	50	8
DME	11.4	3
MTBE	30	1.5
CH_2O	21	3.5
Carbonates	0.2	0.005
Polycarbonates	4	0.01
Carbamates	5.3	0
Polyurethanes	> 8	0
Acrylates	2.5	0
Polyacrylates		
Formic acid	0.6	0
Inorganic carbonates	200	ca. 50
($CaCO_3$,	113.9	
soda Solvay, pigments)	50	
Total		172
Non-chemical uses	Amount used	28
EOR	50	10
Others	22	18

DME: dimethyl ether; EOR: enhanced oil recovery.

If we wish that larger volumes of CO_2 be converted into useful products it is necessary to move to the area of fuels,[22] that have a volume market some 12-14 times higher than that of chemicals. But such shift requires the use of hydrogen and energy for CO_2 hydrogenation and reduction. In the short term, such hydrogen (which cannot have a fossil-carbon origin) can be produced by electrolysis of water using excess electric energy; in the medium term the use of photovoltaics (PV) for water electrolysis will play a key role, while in the long term it will be possible to exploit photochemical technologies mimicking natural photosynthesis.[23] Today, the cost of H_2 generated by PV is too high (2.8-4 € kg^{-1} H_2) compared to the cost of H_2 produced by gas reforming (1.10-1.15 € kg^{-1}) for a large scale application.

The foreseen increase of PV efficiency (from current 20 to 40%), lowering of the cost of PV settings, and the longer life of new devices will favor the decrease of the PV technology and a large scale implementation of such technology for CO_2 reduction to fuels. Noteworthy, CO_2 can be directly electroreduced in water avoiding H_2 production/storage/transport.

As a transition technology, that will favor the recycle of carbon and the reduction of the CO_2 immission into the atmosphere, producing fuels to be used in the existing assets of personal and mass transport means, the use of PV for H_2 production for CO_2 conversion into fuels, can be considered as a optimal technology despite the fact that the conversion of electricity into fuels will cause the loss of some 30 percentage points in efficiency and the primary sources (sun and wind) are not continuous. Such loss will most likely be compensated by the gain in efficacy derived from the higher energy density of liquid fuels generated from CO_2 with respect to batteries used today as electric energy storage or as a portable electric energy source. Liquid fuels have a volume energy intensity up to 15 to 100 times higher than batteries, depending on the fuel and the battery considered.[23] Intermittency of the sources is not a major issue as this option must be considered in an integrated system.

2.3. Exploitation of non-edible biomass

Recycling of carbon mimicking nature brings to the exploitation of biomass. Table 7 gives a perspective on future feedstock for the chemical industry and energy based on existing programs of development of use of perennial and renewable sources of materials and energy. The real implementation of such programs is a question impossible to answer today and attach uncertainty to the scenarios in Table 7.

The use of biomass (residual or non-edible) requires the implementation of the biorefinery concept.[24] The approach to the use of biomass is changing from "one

Table 7. Perspective feedstock for the chemical industry and energy production sector

	Short term (2030)	Medium term (2050)	Long term (> 2050)
Chemistry	Oil and gas dominate	Oil and gas	Oil and gas
	Biomass will grow	Coal will re-enter with clean technologies	Coal will be used with clean technologies
		Biomass will reach its maximum	CO_2 will be recovered and used on a large scale
		CO_2 will be used	
Energy	Mix of fossils	Switch to perennial	Substantial grow of perennial
	Wind will grow	Solar will continue to grow and spread	Electricity will play a key role also in the transportation sector
	Solar will grow		Fuels produced from water and CO_2 will share an important part of the market

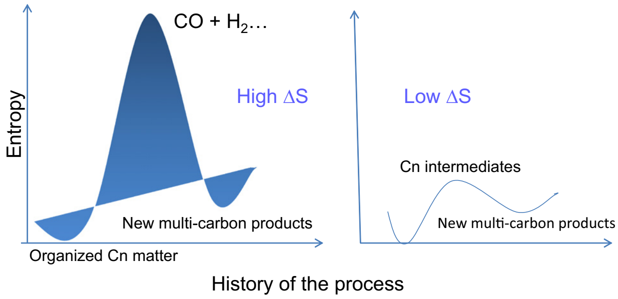


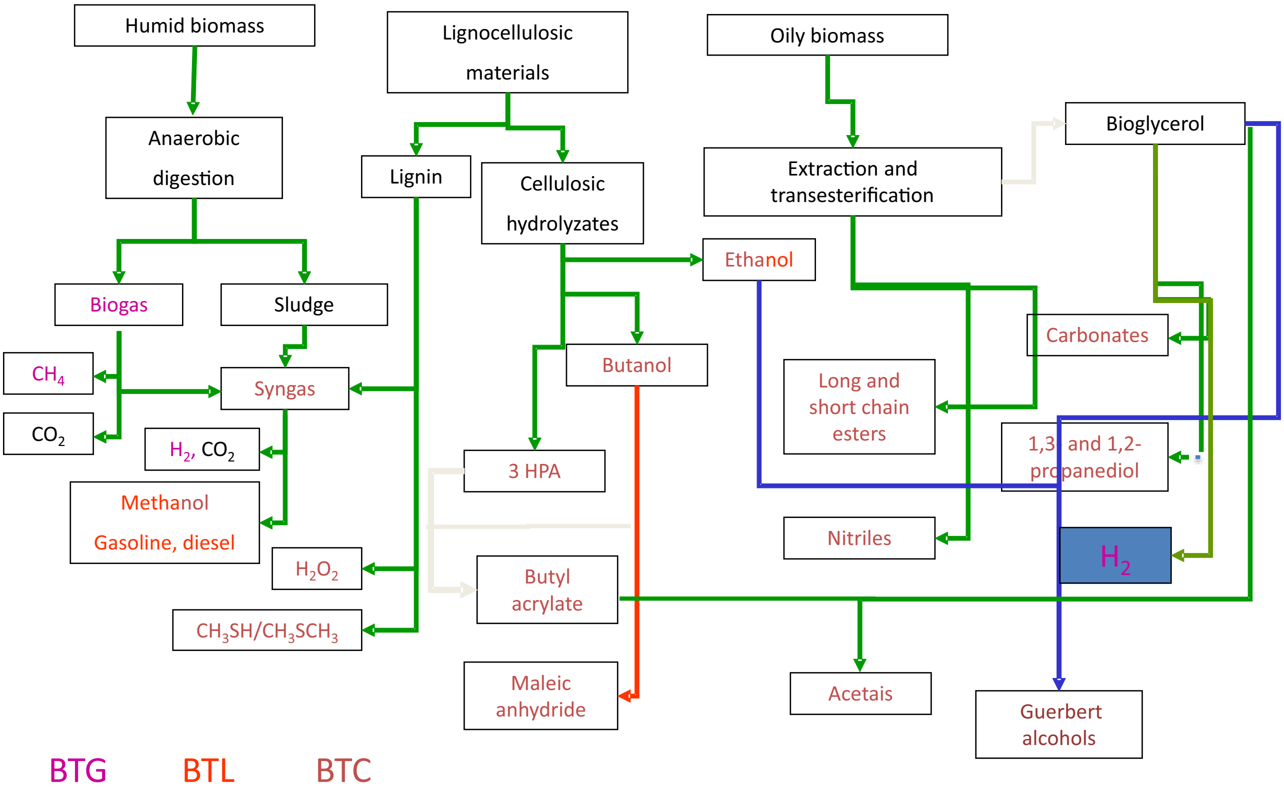
Figure 3. Profile of the entropy change in the gasification process (left) compared to the approach based on biorefinery (right) in which complex structured molecules are extracted from the raw material.

technology (gasification) for any biomass" to "several technologies for a single biomass" with the utilization of a cascade of technologies for a better utilization of the organized structures existing in the biomass. Figure 3 gives a representation of the entropy change in the utilization of biomass as we move from the actual approach (based on syngas production, a strongly endoergonic process that requires high temperature) to the one based on biorefinery. The entropy factor plays a key role in a number of synthetic innovative applications. Several processes that have a negative enthalpy, result to have a positive free Gibbs energy, due to the change in entropy, resulting in a scarce applicability. The extraction of platform molecules (5-hydroxymethylfurfural (5-HMF)) from the cellulosic fraction of solid biomass that may give new monomers for polymers or new-concept fuels, avoids the conversion of biomass into syngas and the subsequent re-production of assembled C-units (see Scheme 5).

Table 7 gives a perspective of the use of feedstock for the chemical industry and the energy sector. The use of biomass will be maximized by 2030. Afterwards, the use of CO_2 will play a key role in C-recycling.

The gasification of biomass to CO and H_2 implies a high entropy increase and requires high temperature. Energy is again spent for building new complex molecules from syngas. The implementation of the concept of biorefinery skips the destruction of organized structures present in the biomass and allows the selective extraction of complex molecules, with a much lower overall entropy change. The energy saving is quite important in such shift and the high temperatures necessary for the production of syngas are avoided. Catalysis is necessary for the modification of raw molecules extracted from biomass. New processes are required that may convert the extracted molecules (polyols or aromatic entities) that have a high oxygen content compared to hydrocarbons now used as feedstock in the chemical industry.

Catalysis, mainly heterogeneous and enzymatic catalysis, plays, thus, a key role in the utilization of biomass. Homogeneous catalysis has its role in the



Scheme 5. Roadmap to the valorization of non-edible biomass.

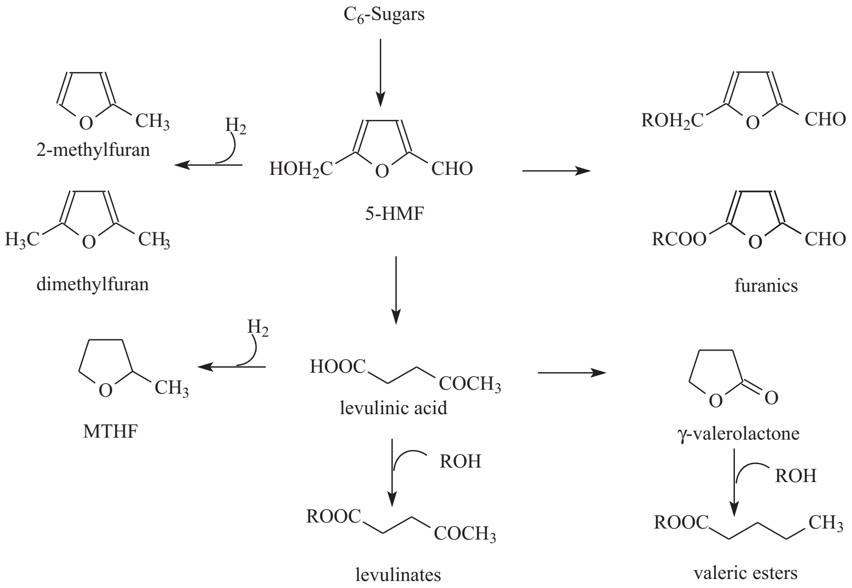
conversion of platform molecules.[25] Scheme 5 shows a possible “roadmap” to the valorization of “non-edible” biomass along three routes: from biomass to gas (BTG), liquids (BTL) and chemicals (BTC).

Cellulose is expected to be one of the main sources of chemicals and fuels. Biotechnology and chemistry combined together can achieve much better results than when the technologies are singly applied. In fact, biotechnology can effectively convert cellulose either into fuels (ethanol, butanol, other molecules) or platform molecules (glucose, fructose, others) and catalysis can further convert the intermediates into fine chemicals or more complex fuels or new biomaterials.

The direct catalytic conversion of cellulose is still an open issue and requires research before exploitation. Scheme 6 shows how C6-sugars, derived from cellulose via biotechnology, can be converted into useful molecules via catalysis.

Table 8 lists a number of processes based on cellulose or cellulose-derived monomers and the catalysts employed, with the indication of the conversion yield and selectivity towards the target product.

It is important to emphasize that when starting from cellulose, it has to be depolymerized first affording glucose and fructose (C6 sugars). A two-step process converts then the C6-sugars into 5-HMF: the glucose isomerization to fructose (base catalyzed) and the dehydration of the latter to 5-HMF (acid catalyzed). Therefore, the overall process itself is quite complex, and also the simpler conversion of C6-sugars obtained upon cellulose depolymerization is not so straightforward as it requires bi-functional catalysts for the best exploitation.



Scheme 6. Use of cellulose-derived C6 for making several platform molecules (in bulk).

Table 8. Chemicals derived from cellulose derived monomers (a selection of opportunities)[26]

Starting material	Product	Catalyst	Solvent	T / K	Yield / %	Selectivity / %
Cellulose	5-HMF	ZrO_2/TiO_2	MIK	–	87	35
Cellulose	Levulinic acid	H_2SO_4 (1.5-3%)	H_2O	–	–	70-80
Glucose	5-HMF	H^+	Water	> 373	30-60	20-50
Glucose	5-HMF	Acid resins	Water	373-473	30-60	20-40
Glucose	5-HMF	Al/Mg hydrotalcite Amberlist-15	Water	–	60	76
Fructose	5-HMF	H-form zeolites	Water	–	60	53
Fructose	–	–	DMSO/MIK/BuOH	–	90	89
Fructose	γ-Valerolactone	Ru/C	H_2O	450	80	62
5-HMF	Furanics (HMF ethers, esters)	Various	Alcohol/organic acids	> 373	Variable	Variable

HMF: 5-hydroxymethylfurfural; MIK: methylisobutylketone.

As shown in Table 8, several raw materials, catalytic systems and reaction conditions have been investigated. Cellulose can be used as raw material, or sucrose, glucose or fructose; the latter affords the best conversion yields and selectivity into its dehydrated form 5-HMF, a platform molecule according to the DOE classification.[27] Inorganic acids and organic bases (amines) have been used in water, with low selectivity due to the condensation of 5-HMF and formation of soluble and insoluble humins. Organic solvents have been used to improve the 5-HMF yield, as they prevent dimerization-oligomerization of the monomer, but require more complex post-process separation technologies. 5-HMF can be converted into a number of products, such as levulinic acid, γ-valerolactone, furanics (ethers or esters of 5-HMF). The latter have an interest as fuels considered that they have a heating value (8.7 kWh L^{-1}) quite close to diesel (8.8 kWh L^{-1}). Research for finding the most active and selective catalysts and the most effective catalytic conditions is still necessary as an effective conversion of cellulose into the species shown in Scheme 6 would be of great economic value. A target is to produce levulinic acid, a potential fuel, at a cost lower than 1 € kg^{-1}.

Lignine has an interesting structure made of aromatic units linked by C3-bridges (glycerol units or its derivatives) (Figure 4).

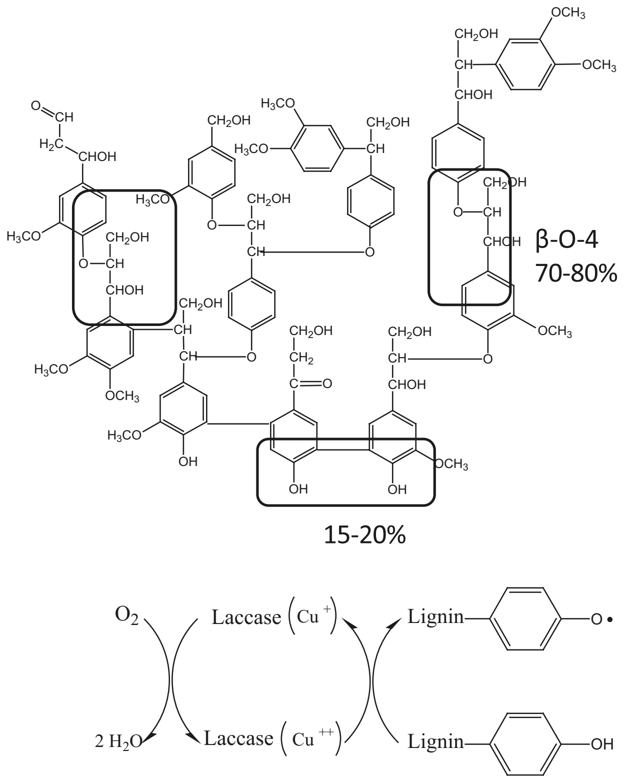


Figure 4. Structure of lignine with the glycerol units in squares.

Nano-sized lignine is a quite useful material used in the production of composites. It can also be the source of a variety of useful monomers to be used as such or after chemical transformation.

Examples of added value chemicals obtained from lignin are: vanillin (fragrance), substituted phenols (antiaging), glycerol, lipids, aromatic di-acids (monomers for polymers; such conversion would be of great industrial value as lignin-derived di-acids would substitute those today produced from fossil sources), and other specialty molecules. The efficient catalytic cleavage of lignin still remains an open issue due to the fact that the cleavage of ethereal bonds is not an easy task. Several strategies have been attempted with alternate success: de-polymerization under basic conditions, radical chemistry, transition metal mediated cleavage of ethereal bonds, and oxidative depolymerization. One of the issues is that often the monomers produced polymerize again affording products not useful or not easily convertible into useful molecules. Table 9 lists some catalysts and products obtained from lignin upon oxidative de-polymerization, an interesting strategy.

Table 9. Catalytic oxidative cleavage of lignin: catalysts and products[28]

Catalyst	Media, supports or co-catalysts	Oxidant	Products
Laccase (multi-Cu enzyme)	Associated HRP (iron protoporphyrin)	O_2 (Laccase) H_2O_2 (HRP)	Oxidized lignine
Co-immobilized laccases and HPR	Clay	O_2, H_2O_2	Oxidized depolymerized lignine
Mn(TMePyP)/clay/HBT (clay-PMS). The Fe analogue can also be used	Hydroxybenzotriazole or veratrilic alcohol	H_2O_2	Oxidized oligomers, and monomers
Co, Cu, Mn(Salen) complexes	Inorganic acids, PPh_3, ethylendiamine	O_2 or H_2O_2	Oxidized monomers from dimers
Polyoxometalates Mo(VI), W(VI), V(V), Nb(V): $XM'_aM''_{12-a}O^{bm-}$ Keggin anions	SiO_2	O_2 or H_2O_2	Oxidized monomers and parent oligomers
O_3ReCH_3	Polymeric ligands: poly-4-vinylpyridine and its N-oxide	H_2O_2	Oxidized monomers and parent oligomers

HPR: horseradish peroxidase; HBT: 1-hydroxybenzotriazole; HRP: horseradish peroxidase.

Figure 5 shows the potential of the oxidative depolymerization.

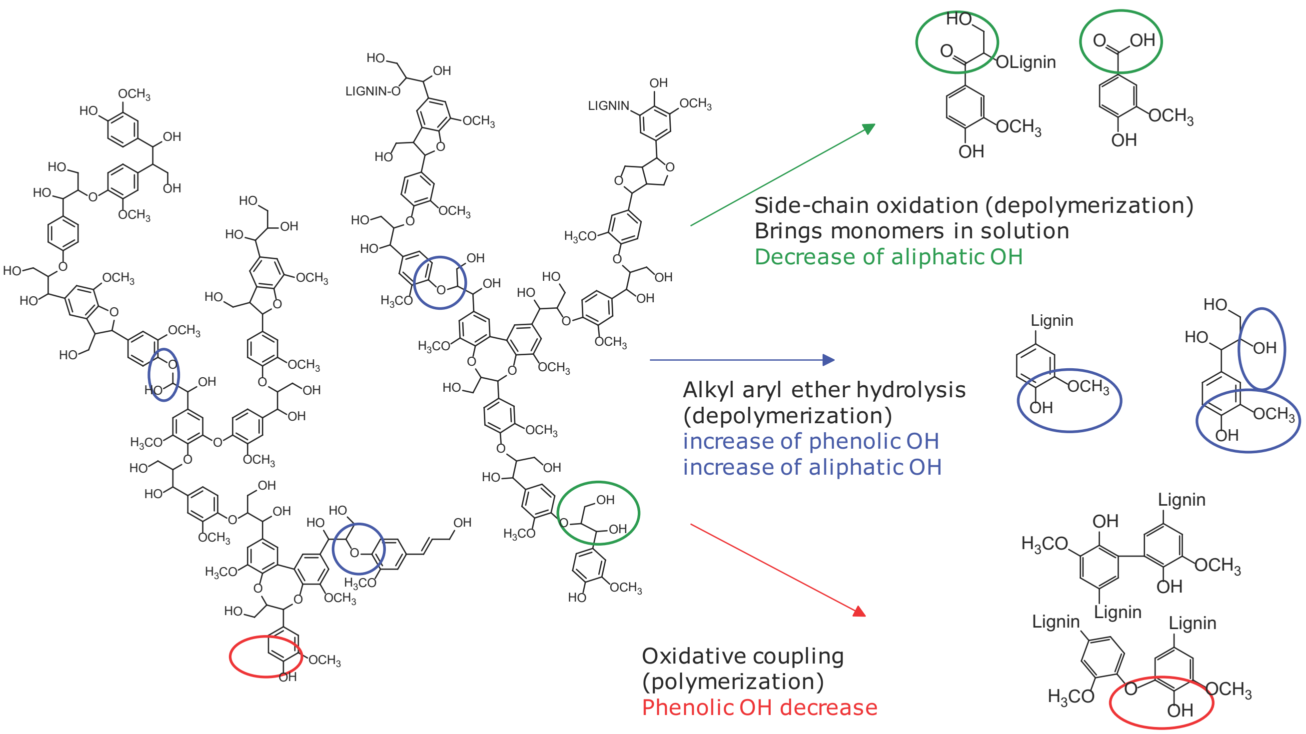
Research in this field is still open and the potential of the catalysis must still be defined.

2.4. Use of process bio-glycerol

The last case we wish to discuss in this paper is bio-glycerol. It is formed in the hydrolysis or transesterification of lipids (Figure 6).

The most extensively used technology for lipid transesterification to fatty acid methyl esters (FAMEs) (used as biodiesel, if they contain maximum one unsaturation) is the base-catalyzed methanolysis in aqueous homogeneous conditions. Such process produces low-value salty aqueous glycerol that requires much energy for purification. Also, such catalysis cannot be conveniently applied to lipids rich in free fatty acids (FFAs), as lipids extracted from aquatic biomass may be, as the base converts the acids into soaps producing a loss of FAMEs and an increase of the complexity of the separation technology due to emulsion formation. As a matter of fact, the base-catalyzed production of FAMEs is applied to lipids containing less than 1% FFAs. It is not usable with lipids derived from aquatic biomass, which may contain up to 20% of FFAs nor with waste oils. An alternative to such process is the hydrolysis of lipids followed by esterification of the FFAs.[29] Most recently, bifunctional catalysts have been developed that catalyze at the same time the transesterification of lipids (that require basic catalysts) and the esterification of FFAs (that requires acid catalysts) and do not require water.[29,30] The result is that non aqueous, salt-free glycerol is produced that could be immediately used in chemical transformation or as fuel.

The bifunctional catalysts are made of mixed oxides that have tunable acid and basic properties. An oxide such

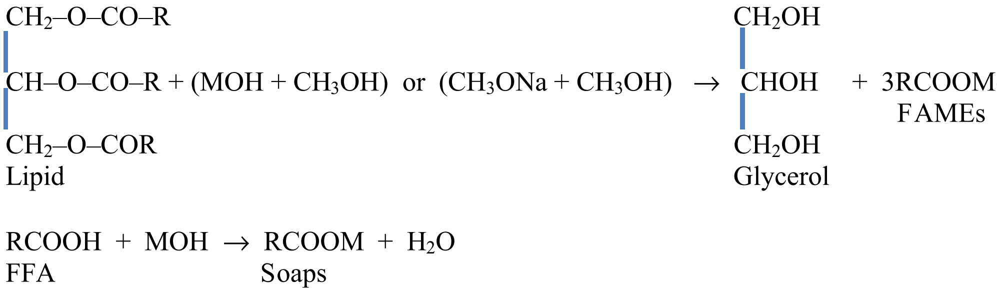


Side-chain oxidation (depolymerization)
Brings monomers in solution
Decrease of aliphatic OH

Alkyl aryl ether hydrolysis
(depolymerization)
increase of phenolic OH
increase of aliphatic OH

Oxidative coupling
(polymerization)
Phenolic OH decrease

Figure 5. Some of the products of the oxidative depolymerization of lignine.



$$\begin{array}{l} CH_2\text{–}O\text{–}CO\text{–}R \\ CH\text{–}O\text{–}CO\text{–}R \\ CH_2\text{–}O\text{–}COR \\ \text{Lipid} \end{array} + (MOH + CH_3OH) \text{ or } (CH_3ONa + CH_3OH) \rightarrow \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \\ \text{Glycerol} \end{array} + \underset{\text{FAMEs}}{3RCOOMe}$$

$$\underset{\text{FFA}}{RCOOH} + MOH \rightarrow \underset{\text{Soaps}}{RCOOM} + H_2O$$

Figure 6. Transeserification of lipids in aqueous solution catalyzed by bases: free fatty acids (FFAs) are converted into soaps.

as CeO_2[29] or WO_2[30] is combined with one or more basic oxides so that the acid-basic properties can be tuned for a more efficient catalysis, as required by the amount of FFAs in lipids, that completely converts lipids and FFAs into FAMEs.[29,30] As mentioned above, the glycerol obtained using bifunctional catalysts is water- and salt-free and more directly usable for conversion into chemicals. This new catalysis improves the quality of glycerol and reduces the cost of its purification for further industrial utilization as raw material to afford many useful products (Figure 7).

Figure 8 shows an example of derivatives that find large application in the chemical industry.

In particular propanediol, acrolein, acrylic acid, and propylene glycol are products that may have markets in the order of several Mt and find, or may find, application, among others, in the polymer industry. Such application is of great interest, as it would produce materials of biological origin in place of fossil carbon-derived chemicals. Glycerol carbonate is an interesting building block for several new chemicals or polymers.[31]

Aqueous-salty-glycerol, which is not easily usable in chemical processes as salts and water may destroy the catalysts, can conversely find use in biotechnological applications, as microorganisms are not so sensitive to salts and live in water. The conversion into 1,3-propanediol has been known for a long time.[32] Recently, new bacterial strains have been developed able to afford both 1,3-propanediol and *n*-butanol.[33] The former is used for the production of 1,3-trimethylene carbonate, a monomer for bio-polymers,[34] the latter for the production of maleic anhydride,[35] that can substitute the fossil carbon-derived phtalic anhydride in polymers.

Another interesting application of aqueous-salty-glycerol is the biotechnological production of hydrogen. Recently, new bacterial strains have been identified that can convert glycerol into H_2 and can work under 0.6 MPa of H_2.[36] This finding is of great interest as one of the issues with bio-hydrogen is the low pressure at which it is generated that requires pressurization for utilization. Collecting bio-H_2 at 0.6 MPa would allow its direct distribution, for

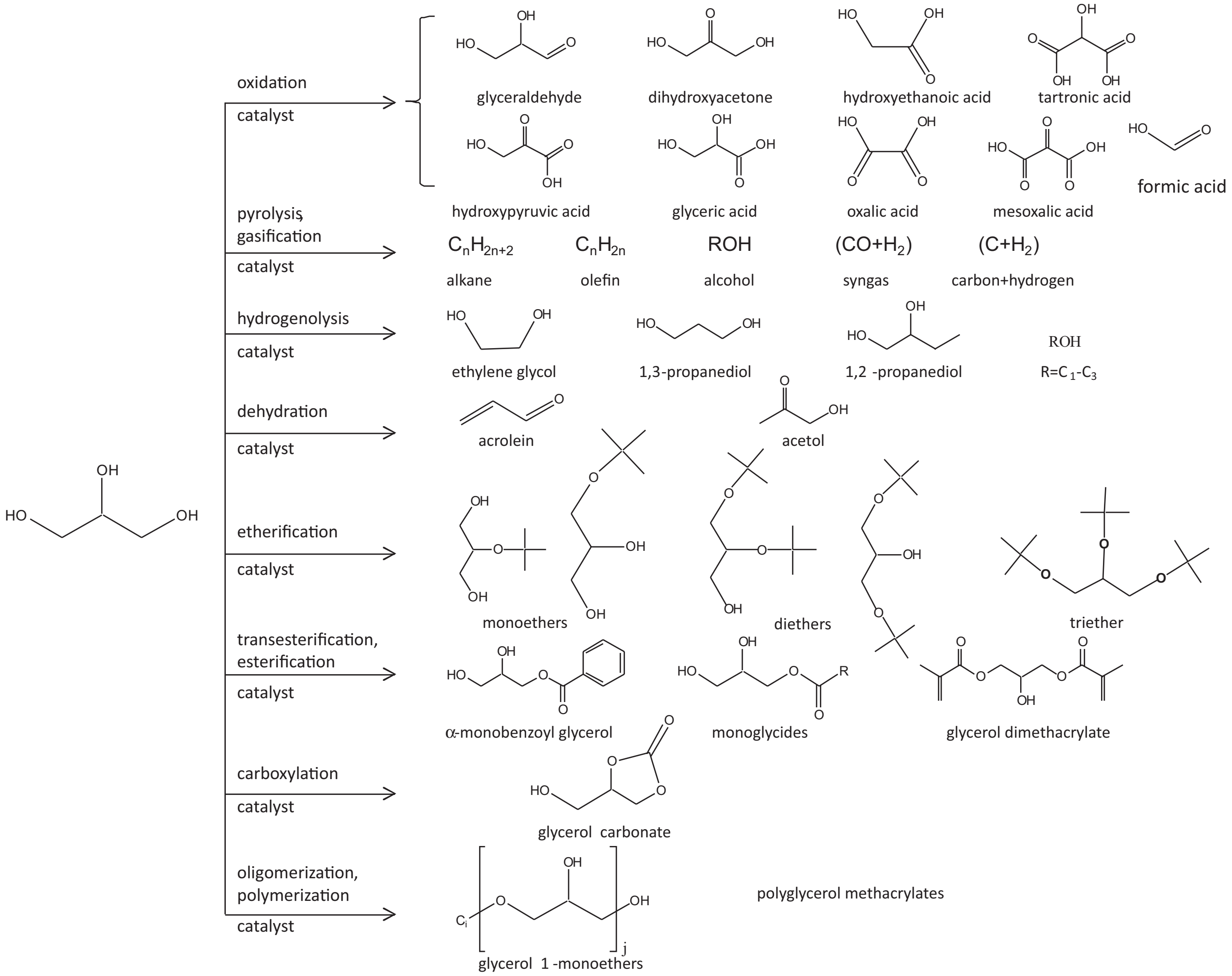


Figure 7. Products derived from glycerol: pure glycerol is needed.

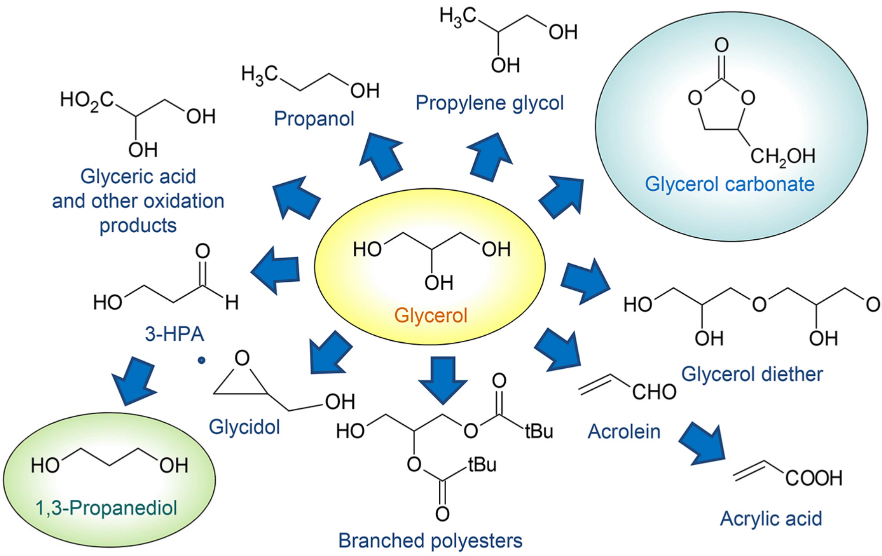


Figure 8. Glycerol conversion.

example, in fuel cells. Table 10 compares the properties of bio-H_2 derived from glycerol and H_2 produced via vapor phase reforming (VPR) of the polyol, a process that has serious issues in the short time-life of the catalysts and the purity of produced H_2.

Table 10. Comparison of the properties of H_2 produced from glycerol via bio-technology (column 2) or VPR (column 3)

Concentration of glycerol	2-6%	1-20%
Conversion of glycerol	100% at 2% feed	100% at 1% feed
Purity of H_2	> 99%	90%
Presence of CO	Absent	Present
Presence of CO_2	Traces	Present
Temperature	Ambient	500-600 K
Pressure	0.6 MPa	2.0-3.0 MPa
Lifetime of the catalyst	More than seven days	Less than one week
Co-products	Organic acids, ethanol	Organic acids and others

It must be emphasized that the biotechnological production is less intensive than VPR, with a lower production *per* unit time and volume, but affords H_2 of much better quality. In particular, bio-H_2 is CO-free, and this is a quite interesting value as such H_2 would be used, for example, in fuel cells without further treatment. VPR-generated H_2, which contains CO, would require partial oxidation (PO) processing for the oxidation of CO into CO_2 that can easily be eliminated. Therefore, bio-H_2 produced at 0.6 MPa from actual aqueous-salty raw glycerol has a great value.

3. Conclusions

Low-value or low-concentration C-streams or residual biomass can conveniently be used as source of carbon for the synthesis of chemicals and fuels. New catalytic processes (chemical or biotechnological or combined) need to be discovered and applied. In general, the molecules to be converted are either inert HCs or are rich in oxygen. Such substrates are quite different from raw materials used until now, mainly represented by HCs and syngas. A new catalysis must be discovered and applied.

Two reactions dominate the new chemistry: (*i*) C–H activation and (*ii*) conversion of high oxygen content substrates. In both cases new catalysts are needed with respect to those actually in use in the chemical industry and this will open new opportunities to chemistry and catalysis. Additionally, new synthetic technologies will be necessary. Photocatalysis can play a key role in driving a number of new reactions, using solar energy as a primary energy source more than fossil carbon. This will require the development of new photocatalysts active in the visible light range.

Heterogeneous catalysis will play a central role in the new transformations of polyols, with metal oxides on the frontline.

CO_2 and water will play a key role in the future: stepping towards a CO_2-H_2O-based economy facilitated by the use of perennial energy sources such as solar/wind/geothermal is a need, not only a dream.

The integration of chemistry and biotechnology is another important strategy that may allow the conversion of unreactive molecules into useful products. In general, biotechnology can be used for the conversion of biomass into platform molecules that can be further converted into fine chemicals using catalysis. In such latter operation, also homogeneous catalysis may play an important role.

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