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CO₂ UTILIZATION: FROM WASTE TO RESOURCE

This paper is devoted to a particular aspect of the CO₂ utilization, related to its transformation, by which CO₂ is chemically altered to produce useful products. Considering that, to positively contribute to the climate goals, the CO₂ utilization technologies must use low-carbon energy and displace products with higher life-cycle emissions, like plastics and building materials, with practically permanent carbon retention.

Hence CO₂ will be regarded as building block for many different chemicals including energy vectors, polymers and chemicals, and inorganic carbonates. Among them, several groups have recently paid attention to the catalytic telomerization of CO₂ with butadiene. This reaction was the subject of pioneering research since 1977 [1], under the supervision of Prof. Paolo Chini, to whom this paper is dedicated.

Introduction

Human activities have led to a massive increase in CO₂ emissions as a primary greenhouse gas that is contributing to climate change with higher than 1 °C global warming than that of the pre-industrial level. Last update (5 November 2021) by Global Monitoring Laboratory indicates that CO₂ concentration is still increasing (413.93 ppm in October 2021 vs. 411.51 ppm of October 2020).

At COP-26, concluded in Glasgow on November 11, 2021, nearly 200 countries agreed the Glasgow Climate Pact to keep the rise of the temperature below 1.5 °C compared to the pre-industrial era and to finalize the outstanding elements of the Paris Agreement (*i.e.* COP-21).

To do that it is compulsory to reduce the amount of CO₂ emitted by humans' activities: 33.9 GtonCO₂ in 2020 [2].

This emission is mainly due to the energy supply. According to the International Energy Agency (IEA) the world primary energy supply in 2020 was 587 EJ [2], corresponding to 12.02 Btoe (billions tons of oil equivalent), so divided:

- Oil 29.5%
- Coal 26.2%
- Natural Gas 23.3%

- Biomass & Waste 10.6%
- Nuclear Power 4.9%
- Hydroelectric 2.7%
- Other Renewables 2.7%.

Hence more than 87% of the CO₂ emitted is due to fossil fuels (oil, coal and natural gas), the remaining due to biomass and waste combustion and other emissions of cement and steel production.

IEA has recently published the “Net Zero by 2050” report, which define a roadmap to reach the net-zero CO₂ emissions (NZE) within 2050 [2].

This very ambitious target can only be pursued through the adoption of a series of actions aimed of reducing energy dependence on fossil sources, but also to valorize CO₂ with a circular economy approach. It means to transform waste CO₂ into products or services with a potential market value. The range of potential CO₂ applications is very broad and it is part of the vast subject known as Carbon Capture Utilization and Storage (CCUS).

CCS and CCU

CCUS includes all the technologies aimed to contribute to the solution of climate change emergency, by capturing and storing (CCS) or utilizing (CCU) CO₂ to produce valuable products. CCS

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technologies capture CO₂ from industrial flue gas and transport it to a geological site for long-term storage. CCU instead converts captured CO₂ into commercial products and applications. CCU technologies are likely to be attractive to large CO₂ industrial emitters, especially in areas where it might not be possible to geologically store CO₂ via CCS. Therefore, CCU technologies can be considered circular economy approaches, regarding CO₂ no more as a waste but as an opportunity.

According to IEA [3], in 2015 around 230 million tons (Mt) of CO₂ were already used. The largest consumer was the fertilizer industry, where 130 MtCO₂ per year was used in urea manufacturing, followed by the oil sector, with a consumption of 70 to 80 MtCO₂ for enhanced oil recovery (EOR). EOR techniques are applied to oil fields to improve the crude oil extraction. To do that CO₂ and water are injected into the reservoir. In these applications, between 1/2 and 2/3 of the injected CO₂ returns with the produced oil and is usually re-injected into the reservoir. The remainder is trapped in the oil reservoir by various means.

A lower percentage of CO₂ is used in food conservation and beverage production, the fabrication of metal, cooling industry, fire suppression and in greenhouses to stimulate plant growth.

However this amount, even considering the increases forecasted by IEA in 2019 [3] (272 MtCO₂) has

been completely overpassed by the recent road map to Net Zero Emission by 2050 [2]. Very ambitious targets have been proposed by IEA with 4 BtCO₂ per year in 2035 to reach 7.6 BtCO₂ in 2050, several times higher than the today utilization.

Therefore, CCUS technologies are the key to unlock the full decarbonization potential.

CO₂ use

Once captured, CO₂ could have three main fates: storage, direct use and transformation into products. Storage is not a CO₂ utilization and therefore is outside the scope of this paper.

Direct use (non-conversion) means when CO₂ is used as such (not chemically altered): food&beverage industry, cooling, dry cleaning, water treatment, fire suppression, crop cultivation in greenhouses, enhanced oil recovery (EOR); while transformation (conversion) when CO₂ is chemically altered to produce useful products.

Three main transformation types can be considered [4]:

- 1) CO₂ to mineral carbonation and construction materials;
- 2) CO₂ to chemicals, fuels, and durable materials;
- 3) CO₂ to biological algae cultivation and enzymatic conversion.

The benefits for the climate associated with CO₂ use will depend on several factors, including the source

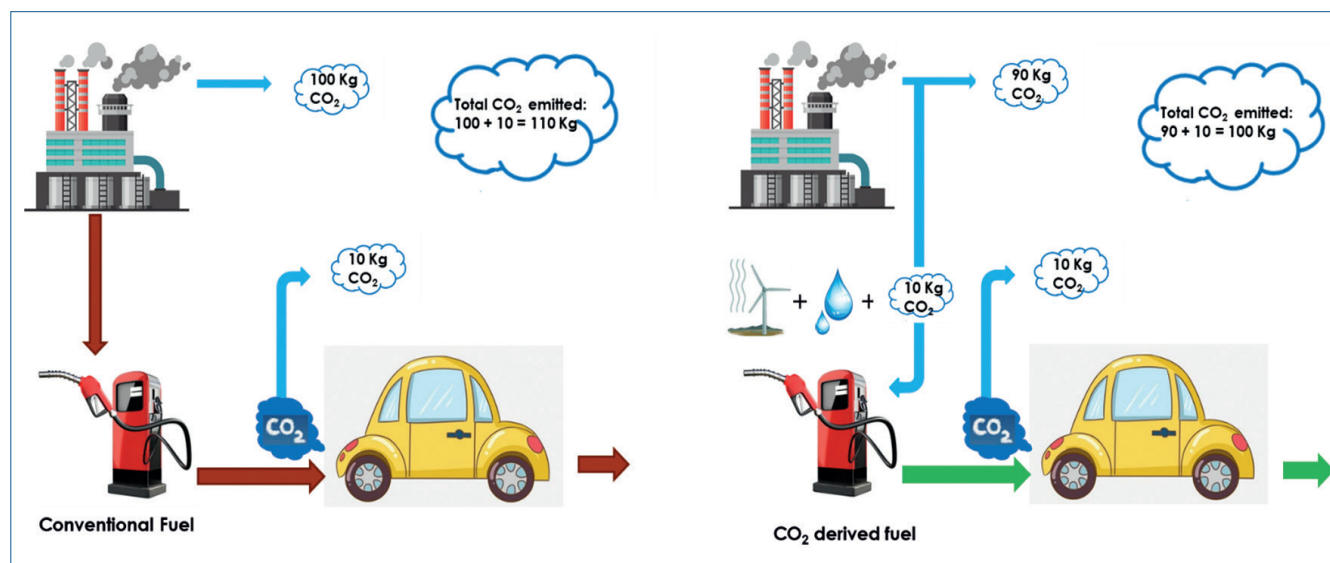


Fig. 1 - The CO₂ avoided concept according to [5]

of CO₂, the energy used for the CO₂ transformation, the product being displaced, and the retention of CO₂ in the final product. Quantifying these benefits is complex and challenging, requiring an accurate LCA (life cycle analysis) approach [5]. While doing it two key points may be thoroughly considered: the CO₂ avoided and the delayed emission.

CO₂ avoided concept

When the product obtained from CO₂ does not replace another one already available on the market, the avoided CO₂ is the balance between CO₂ fixed and CO₂ emitted for its production, also considering the energy utilized.

If the CO₂ products replaces one already available on the market, the comparison must also consider the amount of CO₂ emitted for the product already available.

Let's take as example the production of a fuel by reduction of CO₂. Even if CO₂ is than emitted by fuel combustion, the overall balance is positive, as the new fuel avoided the utilization of an equivalent amount of fossil fuel. This simple concept is summarized in Fig. 1, where part of the CO₂ emitted is captured and transformed in a fuel. Obviously, the energy used for the transformation of CO₂ must be of renewable origin, here exemplified by a wind turbine generator.

CO₂ delayed emission

In practice the utilization of CO₂ corresponds to a delayed emission of it, as sooner or later it will be released again. The carbon retention time for CO₂ use applications can vary per utilization or prod-

Chemical Product or Application	Annual Market (Mt/yr)	Mt CO ₂ used	Average Lifetime
Urea	100	70	6 months
Methanol	40	14	6 months
Inorganic carbonates	80	30	decades to centuries
Organic carbonates	2.6	0.2	decades to centuries
Polyurethanes	10	<10	decades to centuries
Technological	10	10	days to years
Food	8	8	months to years

Tab. 1 - CO₂ used for preparation of chemical products or other applications according to [6]

uct, ranging from weeks for some technological uses, months for beverages and foods, months for fertilizers and fuels (e.g. methanol), up to decades for most chemical intermediates, to decades till centuries for polymers and building materials. The latter being practically considered permanent CO₂ sequestration, as in principle a building material could last for millions of years. Tab. 1 [6], reports some examples.

Accordingly, the preferred utilization should be mineral carbonation to building materials and CO₂ polymerization.

The next part of the paper will be devoted to CO₂ as building block for organic chemistry, in particular, to a route to produce polymers derived from CO₂.

CO₂ as building block in organic synthesis

As CO₂ is the end-product of combustion, it is characterized by a low-energy content from a thermodynamic point of view and hence it is very stable. Different concepts can be applied to enhance its reactivity, such as (1) direct energy usage (e.g., heat, light or electricity), (2) usage of high-energy starting materials (e.g., epoxides, aziridines, alkenes, alkynes, hydrogen) and (3) selection of target compounds with lower energy content (e.g. inorganic and organic carbonates) [7]. As building block in organic synthesis, CO₂ is potentially attractive for [8]:

- CO₂ insertion into C-X bonds;
- CO₂ incorporation into polymers;
- carboxylation with CO₂;
- CO₂ reactions with organometallics.

However, efficient utilization of CO₂ for creating C-C bonds is still problematic, requiring the use of strong carbon nucleophiles, such as organolithiums, Grignard reagents, and phenolates, which also generate (over)stoichiometric amounts of by-products [9].

In contrast to all the above mentioned reactions, the catalytic telomerization of 1,3-butadiene with CO₂ leads straightforward to the unsaturated δ -lactone (2-ethylidene-6-heptene-5-olide), under mild conditions with 100% atom-efficiency [10]. Besides, according to Behr and Henze [11] the δ -lactone is highly functionalized which leads to various reactivities: it has a carboxyl group, an in-



Reaction	Addition of	Products
Hydrogenation	H ₂	Carboxylic acids, saturated lactones, diols
Hydroformilation	H ₂ /CO	Aldehydo-carboxylic acids
Hydroaminomethylation	H ₂ /CO/HNR ₂	Amino-lactones, amino-carboxylic acids
Hydroamination	HNR ₂	Amino-carboxylic acids
Alcoholysis	ROH	Hydroxy-carboxylic acids, alkoxycarboxylic acids
Hydration	H ₂ O	Hydroxy-carboxylic acids
Hydrosilylation	HSi(OEt) ₃	Silano-carboxylic acids
Oxidation	H ₂ O ₂	Lactone epoxides
Polymerization	Dithiols etc.	Polymers

Tab. 2 - Catalyzed reactions of δ -lactone, reviewed by Behr and Henze [11]

terminal and a terminal C=C double bond. Through further conversion with different bulk chemicals several secondary products of potential industrial relevance may be synthesized mainly catalytically. Behr and Henze [11] reviewed these reactions

(Tab. 2) demonstrating that CO₂ can be efficiently integrated as building block for many organic substances within only few reaction steps.

δ -Lactone

The telomerization of CO₂ and butadiene using Pd catalyst has been studied in 1970s by Inoue *et al.* [12, 13] and Musco *et al.* [14-16]. The reaction of two butadiene molecules with one of CO₂ resulted in the formation of different products: lactones, aliphatic acids and esters. While Inoue *et al.*, using a chelating phosphine as Pd ligands produced a γ -lactone in small yields, Musco *et al.* with proper Pd phosphine complexes yielded the δ -lactone together with aliphatic esters.

Following the above pioneering researches several investigations were conducted for the explanation of the reaction pathway. The reaction mechanism is reported in Fig. 2 according to [15]. First a Pd(0) phosphine complex is prepared *in situ* from a Pd(II) compound and a tertiary phosphine.

Through addition of two butadiene molecules species (1) and (2) are formed, in agreement with the accepted mechanism for linear butadiene dimerization.

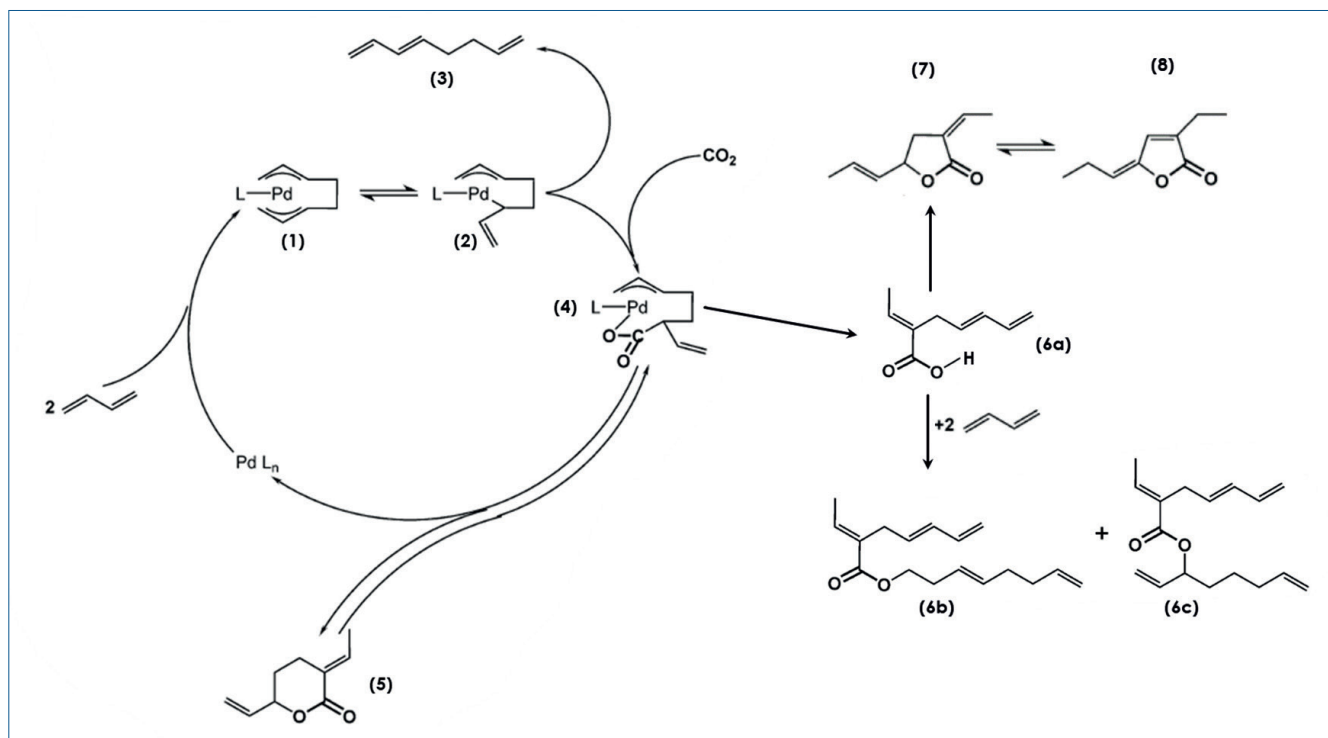


Fig. 2 - Reaction mechanism of telomerization of butadiene with CO₂ catalyzed by Pd(0) phosphine complex [15]

Subsequently, (2) either transforms to 1,3,7-octatriene (3) or reacts with CO₂ forming the carboxylate intermediate (4), from which (E)-2-ethylidene-6-heptene-5-olide (δ -lactone, (5)) or (E)-2-ethylidene-hepta-4,6-dienoic acid (6a). From the latter the corresponding octadienyl esters (6b,6c) are formed. The acid (6a) can also rearrange to (E)-2-ethylidene-5-heptene-4-olide (γ -lactone, (7)) and its conjugated isomer 2-ethylhepta-2,4-dien-4-olide (8). The ethylidene side-chains have the E stereochemistry [15].

This reaction was deeply investigated to optimize the formation of δ -lactone (5) by improving the catalytic system and the reaction conditions.

Behr *et al.* [17] succeeded to develop the reaction in a continuous mini-plant, increasing the selectivity of the δ -lactone above 95%, by recycling of by-products. The reaction was performed feeding butadiene and CO₂ in a continuous stirred tank reactor (CSTR), together with acetonitrile as solvent and the catalyst [Pd(II) acetylacetonate/triphenylphosphine]. The product mixture was continuously fed into a separation unit where unreacted CO₂, butadiene and the solvent are removed in gas phase and recycled to the CSTR. Simultaneously, the δ -lactone/catalyst mixture was fed into a distillation unit. δ -lactone was distilled off in-vacuo, while the catalyst was recycled into the CSTR together with the by-products.

After the outstanding work of Arno Behr and his group, who devoted to this subject quite a number of papers since 1983 [18], recently other groups devoted efforts to improve the reaction system still finalized to the δ -lactone yields.

Using a Pd/TOMPP-catalyst (TOMPP=tris-(*o*-methoxyphenyl)-phosphine), a significant increase of yields of the lactone was obtained with an improved TON=1500 [10, 19]. A more efficient and selective telomerization was reported by using Pd acetate and tris(*p*-methoxyphenyl)phosphine as a catalyst in the presence of *p*-hydroquinone, *N,N*-diisopropylethylamine, and acetonitrile. A TON=4500 was

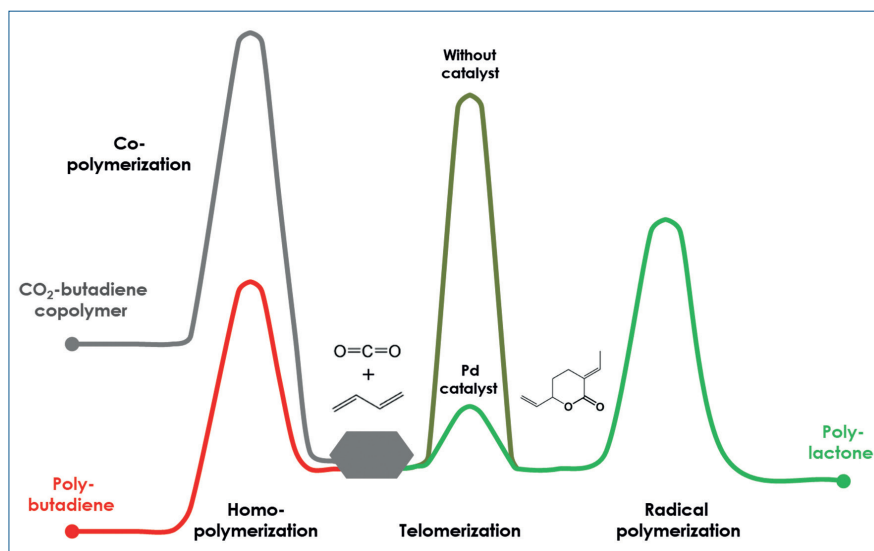


Fig. 3 - Qualitative energy barriers of CO₂/butadiene reactions, adapted by permission from [22]. Copyright 2014 Springer Nature

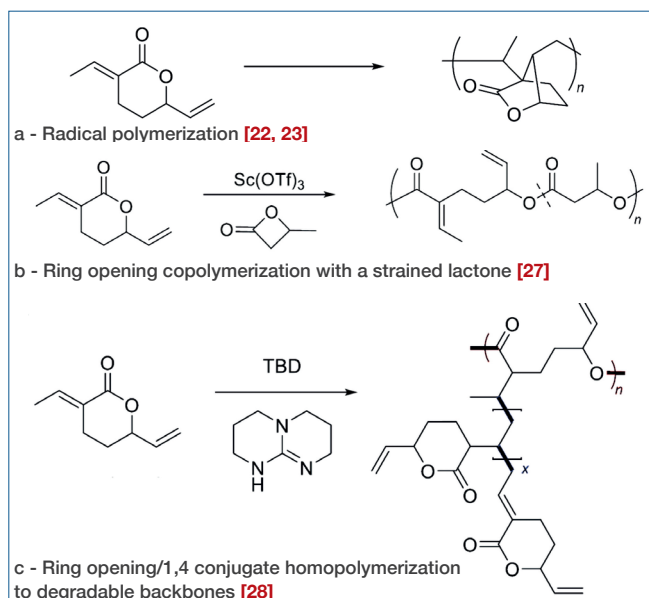
obtained with 96% selectivity to δ -lactone [20]. A new catalyst based on ultras-small Pd nanoparticles has been evaluated for this reaction with quite good results: yield= 86% with 96% selectivity, and TON=1271 [21].

CO₂ to polymers via δ -lactone

According to K. Nozaki *et al.* [22] the major obstacle for CO₂ copolymerization with olefins is that the propagation step involving CO₂ is endothermic; typically, attempted reactions between CO₂ and an olefin preferentially yield olefin homo-polymerization. This is true also for butadiene. Nozaki *et al.* suggested a strategy to circumvent these thermodynamic and kinetic barriers by using a metastable lactone intermediate, as simplified in Fig. 3.

δ -lactone undergoes radical polymerization with [1,1'-azo-bis(cyclohexane-1-carbonitrile), V-40] as initiator. Conversion was 17% with M_n of 5.7 kDa and a narrow M_w/M_n~1.3. A Lewis acid additive, ZnCl₂, and an additional solvent, ethylene carbonate, accelerated the reaction rate, improved the overall yield (48%) and M_n values (62-85 kDa) [22]. The polylactone so obtained contains 29%wt of CO₂ (Scheme 1a).

More recently M. Liu *et al.* [23] reported that radical polymerization can be vitalized simply heating in the presence of O₂. This catalyst-free polymerization did not need additives or solvents. Besides,



Scheme 1 - Polymerization of δ -lactone. Reproduced with kind permission from [28]. Copyright 2021 American Chemical Society

it was characterized by abundant preserved olefins and up to full monomer conversion, providing a convenient and scalable way to obtain CO_2 -derived polymers, potentially tailorable via the modifiable olefins. Conversion of the lactone up to 100% were reported yielding a polylactone with a $M_n=78.6$ -239 kDa. Fig. 4 reports the polylactone formula, with the potentially modifiable double bonds. Also the ester groups in the polylactone are reactive for further derivatization. Nozaki *et al.* [25, 26] reported its post polymerization functionalization by hydrolysis, yielding a polymer possessing *trans*-cyclopentan-1,2-diyl moiety in the chain (see Scheme 2). The reaction is reversible and the dehydrative lactonization took place upon simple heating.

Other δ -Lactone polymerizations

The first successful ring opening polymerization (ROP) of δ -lactone has been reported by S. Yue *et*

al. [27]. The δ -lactone is copolymerized with β -butyrolactone using scandium triflate [$\text{Sc}(\text{OTf})_3$] as catalyst. The so obtained polyester has an average $M_w = 4.1$ kg/mol, in which the δ -lactone content is 38 mol%. This polyester has abundant unsaturated groups on the side chain for modification and it is of great potential to be a precursor for adhesive or surface-coating materials (Scheme 1b). A ring opening homopolymerization of δ -lactone was obtained by the bifunctional organocatalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). A hydrolytically degradable polymer is obtained. According to L.D. Garcia Espinosa *et al.* [28] the polymer arises from a combined vinylogous 1,4-conjugate addition/ring-opening polymerization reaction (Scheme 1c).

CO_2 avoided in CO_2 polymers

As previously discussed, it is of fundamental importance to assess how much CO_2 is fixed into the polymers and how much is the CO_2 avoided, considering the CO_2 mass balance of the overall production process.

The polylactones reported in the above discussed research papers, contain up to 29%wt of CO_2 .

As the polylactone is in practice a copolymer of butadiene and CO_2 , in order to assess the mass

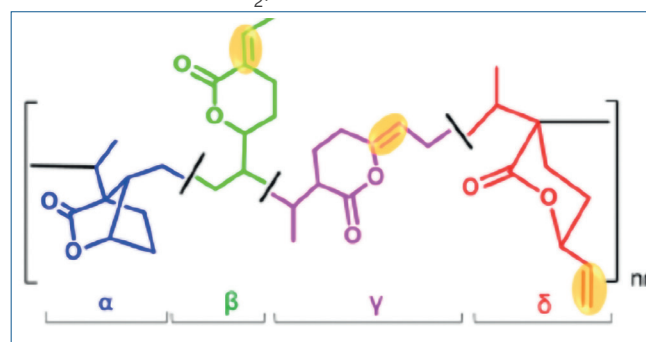
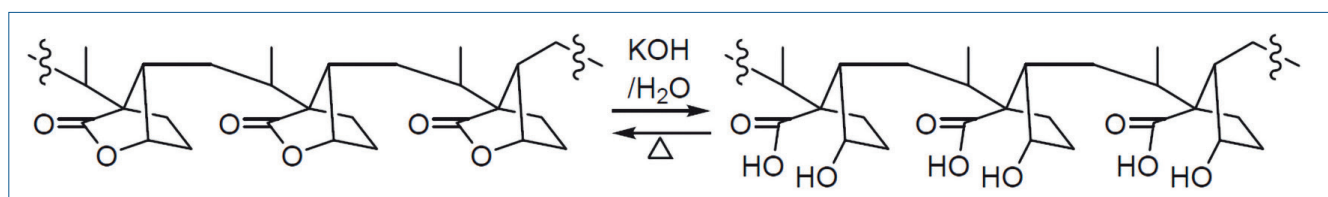


Fig. 4 - The polylactone with four different repeating units (α , β , γ , and δ). Reproduced with kind permission from [23]. Copyright 2017 American Chemical Society [24]



Scheme 2 - Post polymerization-functionalization of the polylactone, by hydrolysis. Reproduced with kind permission from [26]. Copyright 2021 Japan Chemical Society

Butadiene production route	Ethanol from	kg CO ₂ per 0.71 kg butadiene	CO ₂ balance*
Petroleum naphtha cracking		+0.92	+0.63
Ethanol	Corn grain	+1.38	+1.09
Ethanol	Sugarcane	-0.46	-0.75
Ethanol	Corn stover	-0.37	-0.66

*CO₂ related to energy and chemicals consumed during polymerization is not considered

Tab. 3 - CO₂ balance for the production of 1 kg of polylactone (29%wt CO₂)

balance of the process it is necessary to consider the CO₂ involved in the butadiene production.

Today, practically all the butadiene produced in the world comes from petrochemical streams (e.g. C4-cracking fractions or butane dehydrogenation). Butadiene can also be produced from ethanol dimerization. Ethanol in turn can be derived by fermentation of sugars coming from waste biomass saccharification.

Alexis T. Bell *et al.* have reported a new catalyst based on metal promoted Mg-silicate for the production of butadiene from ethanol [29]. The paper also compares the CO₂ emissions to produce 1 kg of petroleum-derived butadiene (1.3 kg CO₂) with that of 1 kg of butadiene produced from ethanol, which in turn is derived from corn grain (1.95 kg CO₂), sugarcane (-0.65 kg CO₂) and corn stover (-0.52 kg CO₂). Tab. 3 reports the CO₂ balance for the production of 1 kg of polylactone (29% wt CO₂) starting from butadiene produced either from petroleum naphtha or ethanol.

Ethanol from sugarcane or from lignocellulosic waste (e.g. corn stover) presents negative CO₂ balance and therefore the polylactone produced from it is potentially beneficial.

Starting from petroleum naphtha or corn does not present any advantage unless the polylactone will be used instead of conventional polymers with large emission factors.

As already evidenced previously, a carefully Life Cycle Analysis must be performed also considering which kind of polymers or products the new polylactone will replace.

Conclusion

CO₂ utilization routes may give an important contribution for reducing GHG emissions, if they fulfill some important criteria prove to be “carbon negative” (on LCA basis).

The use of CO₂ as a co-monomer in the production of polymers has the purpose of permanently fixing carbon dioxide in products of interest, limiting the use of fossil sources and toxic/dangerous reagents.

As already stated by other authors [30, 31], the possibility of obtaining CO₂/diene copolymers with a high CO₂ content (up to 29 wt%) via δ -lactone intermediate, is a significant step forward towards the preparation of more sustainable plastics and could potentially lead to a bulk utilization of CO₂ as a chemical feedstock.

This amount may be significant if bio-butadiene (*i.e.* butadiene from renewables feedstocks) is utilized. In fact, by petroleum derived butadiene the amount of CO₂ fixed is negligible respect to that emitted to produce the monomers.

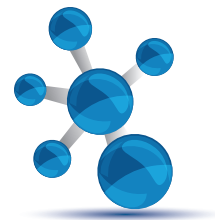
Additional research is needed to optimize the polymer production and to tailor its characteristics to new applications.

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Utilizzo della CO₂: da rifiuto a risorsa

Questo articolo tratta un particolare aspetto dell'utilizzo della CO₂, relativo alla sua trasformazione chimica, per generare prodotti utili. Per contribuire positivamente agli obiettivi climatici, le tecnologie che usano CO₂ devono impiegare energia rinnovabile o comunque a bassa emissione carbonica e fornire prodotti durevoli, come per esempio plastica e materiali da costruzione, in modo da fissare il carbonio il più a lungo possibile. La CO₂ può essere un elemento costitutivo di molti prodotti di consumo, inclusi vettori energetici, fertilizzanti, polimeri, intermedi chimici e carbonati inorganici. Tra le diverse possibili valorizzazioni della CO₂, numerosi gruppi di ricerca hanno recentemente focalizzato l'attenzione sulla sua reazione con il butadiene, attraverso la telomerizzazione catalitica. In questo articolo si fa una revisione dei recenti avanzamenti su questa reazione e sugli sviluppi collegati, in considerazione del fatto che la stessa è stata oggetto di ricerche pionieristiche sin dal 1977 [1], sotto la supervisione del Prof. Paolo Chini, a cui è l'articolo è dedicato.