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GLYCEROL VALORIZATION TOWARDS A BIOREFINERY

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Acknowledgments

To the guys and girls of the aCe group:
to Giacomo, protecting angel, always patient and available to remedy my attempted murders;
to Matthias, with his infinite knowledge of useless but interesting aspects of the reality;
to Cecilia, “mamy” of the group;
to JPR, who taught me the importance of precision and humbleness.
To my family, which had to stand my mood changes.
To Vivian, Martina and Cristina, without whom my experience would have been poorer.

And to Lia:

*“To vidi già nel cominciar del giorno
la parte oriental tutta rosata,
e l'altro ciel di bel sereno addorno;
e la faccia del sol nascere ombrata,
sì che per temperanza di vapori
l'occhio la sostenea lunga fiata:
così dentro una nuvola di fiori
che da le mani angeliche saliva
e ricadeva in giù dentro e di fori,
souvra candido vel cinta d'uliva
donna m'apparve sotto verde manto
vestito di color di fiamma viva.”*

Abstract

The interest in the valorization of biomass and its more reactive nature compared to fossil-based feedstock has propelled extensive research to design solid catalysts able to effectively convert bio-derived compounds into chemicals and fuels. This endeavor does not only comprise the identification of a highly active and selective materials. Various other criteria have to be fulfilled to ensure the viability, economic attractiveness and environmental friendliness of the overall process, including abundancy, toxicity and cost of the active phase, and performance stability in continuous-flow mode, which is industrially more relevant than batch operation owing to the greater scalability, safety and ease of control of the reaction conditions.

The burgeoning amounts of glycerol obtained as a by-product in the biodiesel production over the last 15 years have motivated extensive research targeting its valorization into bulk and specialty chemicals, intermediates and fuel additives. The interest in heterogeneous catalysis as a mean to mediate the proposed chemical routes has generated an ample literature output on the conversion of the triol into organic acids, allylic compounds, carbonates, propanediols, epichlorohydrin, ether and esters.

The present work aims at providing the reader with an analysis of the available technologies for the main glycerol upgrading routes; particular attention is given to epichlorohydrin, 1,2-propanediol, glycerol carbonate and allyl alcohol, on the basis on their environmental and economic assessments. The state-of-the-art catalysts recently introduced for each path are outlined and considered for the modelling of the corresponding processes and their evaluation by life-cycle analysis.

For the case of the glycerol-to-epichlorohydrin process, an experimental activity has been addressed towards the study and the development of a novel catalytic conversion route of the intermediate 1,3-dichloro-2-propanol. A mixed Mg/Al oxide base heterogeneous catalyst is here presented, for the first time, as a viable alternative with respect to the existing process based on the epoxidation-dehydrochlorination reaction by NaOH aqueous solution. The research conducting *leitmotiv* is to find a more economically and environmentally sustainable process able to reduce the undesired aspects related to the actual process.

Estratto

L'interesse rivolto alla valorizzazione di biomasse, e alle loro intrinseche caratteristiche di maggiore reattività rispetto alle materie prime di origine fossile, ha determinato un significativo sforzo nella ricerca e sviluppo di catalizzatori solidi capaci di convertire efficacemente tale materia in prodotti chimici e combustibili. Questo impegno non comprende unicamente l'identificazione di materiali altamente attivi e selettivi. Altri criteri devono essere infatti soddisfatti in modo da assicurare la competitività economica e ambientale dell'intero processo di produzione, inclusi l'abbondanza, tossicità e costo della fase attiva, nonché la stabilità in modalità operativa continua, sicuramente più rilevante rispetto ad un processo discontinuo ai fini di un'implementazione industriale di larga scala grazie a una maggiore facilità in fase di scale-up, sicurezza e controllo delle condizioni di reazione.

La crescente quantità di glicerolo, ottenuto come co-prodotto nella produzione di biodiesel negli ultimi 15 anni, ha costituito un propellente per un'ampia ricerca avente come obiettivo la sua valorizzazione in "commodities", intermedi di sintesi e additivi per applicazioni mobili. L'interesse nella catalisi eterogenea come strumento per l'efficace realizzazione di nuove interessanti vie di sintesi chimica ha di conseguenza generato un'ampia letteratura riguardante la conversione del triolo in acidi organici, composti allilici, carbonati, glicoli propilenici, epicloridrina, eteri ed esteri.

Il presente lavoro ha lo scopo di presentare un'analisi di rilevanti tecnologie di valorizzazione del glicerolo, con particolare attenzione rivolta a epicloridrina, 1,2-propandiolo, carbonato di glicerolo e allil alcol, basata su una valutazione economica e ambientale quantitativa. Le più recenti tecnologie catalitiche sono evidenziate e utilizzate per la modellazione di ipotetici processi di sintesi, e l'utilizzo di specifiche metriche basate sull'analisi del ciclo di vita di prodotti e materie prime permette la loro valutazione oggettiva secondo una logica di impatto ambientale e competitività economica.

Nel caso particolare del processo da glicerolo a epicloridrina, un'attività sperimentale è stata rivolta verso lo studio e lo sviluppo di una nuova via di conversione catalitica dell'intermedio 1,3-dicloro-2-propanolo. Ossidi misti di magnesio e alluminio sono qui presentati, per la prima volta, come possibile alternativa rispetto all'esistente processo basato sull'eossidazione-deidrociorinazione mediata da soluzioni di una base stechiometrica. L'obiettivo è rappresentato dalla volontà di aprire le porte ad un processo più economicamente e

ambientalmente sostenibile capace di ridurre gli aspetti indesiderabili del processo tradizionale legati al consumo di una base omogenea forte e alla produzione stechiometrica di sali clorinati negli effluenti acquosi al processo.

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CHAPTER 1

INTRODUCTION

1.1 Chemical Opportunities from Biomass: a Chemist's View of the Biorefinery

Cheap and largely available fossil oil resources are becoming depleted. In this context, alternatives to fossil fuel-derived carbon sources are increasingly addressed in order to assure the availability of basic raw products through the development of novel technologies for the production of chemicals, fuels, and materials from renewable feedstocks, such as biomass.

The general concept unifying the conversion processes for raw biomass is that of the biorefinery, which integrates biofuels production with the synthesis of a selection of few “platform chemicals”, from which a large number of other added-value chemical products can be obtained. While the biorefinery concept is not new, the motivation in investigating its true potential for the production of carbon-based products is more than ever actual. Indeed, a variety of renewable chemicals have been proposed by many research groups, many of them being categorized as “drop-ins”, i.e. structurally identical to oil-derived chemicals, while others classifiable as novel chemicals, with the potential to displace petrochemicals across several markets.

Nowadays, biomass-derived products competitiveness with respect to petrochemicals has been proved for many highly functionalized chemicals. For each of them, the starting point for a successful synthesis process has always been twofold: exploitation/preservation of the functionality of biomass-derived raw reagents, alongside the development of highly efficient catalytic materials.

1.1.1 General introduction to Biomass Conversion

Nature provides us with complex molecules like cellulose, hemicellulose and oils. A key point of view, which is at the foundations of the exploitation of biomass-derived chemicals, is thus to transform them into chemical products while maintaining aspects of their original structure, rather than converting them to completely different molecules, until eventually to CO₂. In other words, rather than merely pursuing energy content as in the case of biofuels, the concepts of atom efficiency, functionality, versatility, and reactivity are key criteria for the successful valorization of biomass into chemicals [1].

The possibility to develop novel industrially relevant processes to renewable energy and chemicals, from raw biomass components, can be defined by no mean “scientific” and is emblematic of the chemical engineer’s look at the reality. Generally, this has been approached in different ways (Table 1).

Table 1. Comparison of the main processing technologies for the production of platform molecules from biomass [2].

| | Thermal | Biological | Chemical-catalytic | Extraction |
|----------------------|--|--|--|---|
| Advantages | Widely applicable to various biomass types. Can be decentralized (liquefaction at production site) Very fast | Mild conditions Good selectivity Natural products | Widely applicable to various biomass types. Selectivity Fast | Higher-value products Natural products |
| Disadvantages | Complex mixtures produced Harsh conditions Unstable product | Slow Expensive pretreatment, recovery and purification Specific feedstock required | Toxic/corrosive reagents may be needed Heterogeneous catalyst development Heterogeneous transport phenomena as possible limiting factors | Low quantity of products Scalability Limited to a small range of products |

The first and most knowledge-base grounded is biological, mainly by anaerobic digestion and fermentation. Apart from the relatively slowness of these processes and the need of expensive pre- and post-treatment methodologies, the efficiency of this way is often deteriorated by low carbon economy associated to gaseous fermentation products, i.e. CO₂ and CH₄ [3]. Even though this may constitute a useful contribution to the greening up of energy, biomass may be considered to have a more vital role to play in the production of liquid transportation fuels, chemicals and materials.

The second mode of biomass processing, fast pyrolysis, is a thermochemical way, consisting in a direct gasification to bio-gas and liquefaction to bio-oil of solid lignocellulosic biomasses.

This method is still of interest, with several comprehensive reviews having been written in the last 15 years, essentially because of the possibility to directly obtain a liquid product, to tune the gas to liquid yield and to produce valuable products for energy or chemical purposes.

In gasification, biomass is converted into a gas mixture, principally CO and H₂, by partial oxidation at temperatures of ~800÷1,000°C. Being different from pure gasification and liquefaction processes, fast pyrolysis requires a carefully controlled temperature of around 500°C in a fluidized bed reactor, followed by rapid cooling of the pyrolysis vapors to give the bio-oil product, with yields up to ~80% wt on dry feed [4]. This lower temperature process can be conducted in the presence of heterogeneous catalysts to give bio-oil as desired product [5]. Nevertheless, this approach also presents limitations. Indeed, significant quantities of carbon are converted into CO₂ and the gaseous product is mainly relevant to direct power generation, even though when purified to clean synthesis gas, it can be used as starting feedstock for chemicals production, such as GTM, GTO and ammonia processes, or for transportation fuels production, i.e. Fischer-Tropsch process. In addition, the original complexity and functionality proper of biomasses is almost completely lost in favor of the energetic content of the products. Finally, the desired bio-oil product is a highly complex mixture of water, lignin fragments, furans, carboxylic acids, hydroxyaldehydes and ketones, esters, alcohols, sugars, tar, and other products [1]; direct use is not possible and extensive catalytic upgrading is required. Furthermore, due to its heterogeneous and reactive nature, the liquid gradually degrades due to increase in viscosity and phase separation, and thus storage for prolonged periods in its crude state is problematic, even though storage conditions, i.e. temperature, pre-filtration, may have positive effects [6].

The third approach to biomass conversion consists in a pure chemical valorization, i.e. it exploits the chemical versatility of biomass-derived feedstocks to obtain specific single products, or a narrow range of products, by mean of selective reaction routes. Extraction processes can also be included in this category since they represent a mean to directly isolate chemical precursors, i.e. oils and fats, and/or high-value natural components, i.e. waxes, sterols, pigments, flavours and fragrances.

The focus of this introduction, and of the entire work, will be addressed towards the latter biomass conversion approach, as the only strategy able to amplify and diversify the chemical portfolio of a biorefinery. A catalysis engineering approach is in this sense crucial in order to address the proper reaction pathway to the desired products from renewable feedstocks.

1.1.2 Chemical conversion and the interest in glycerol

Chemical-catalytic methods in biomass valorization vary widely in their reaction conditions depending on the type of treated feedstock, the reaction route, and the desired final products, but are generally fast and have the potential to yield a complete carbon economy.

The increasing commercial attention given to these routes is the result of a scientific and social consciousness in considering the possibility to efficiently convert biomass waste into valuable, non-oil-based chemicals. In front of significant initial research and economic efforts to develop selective conversion processes, pure chemical technologies offers a way to process biomass into few versatile “platform molecules”, in the most efficient way as possible and under mild conditions. Homogeneous or heterogeneous catalysis represents a key process issue and a formidable toolbox for the success of this conversion strategies.

In the most general way, a bio-based platform molecule is a chemical compound whose constituent elements originate wholly from biomass, and that can be utilized as a building block for the production of other chemicals [2].

Therefore, in direct comparison with fossil-derived base chemicals (Figure 1), i.e. Ethylene, Propylene, Butadiene, BTX, Methanol etc., the definition of platform molecule encompasses the following two features: *versatility* and *availability*.

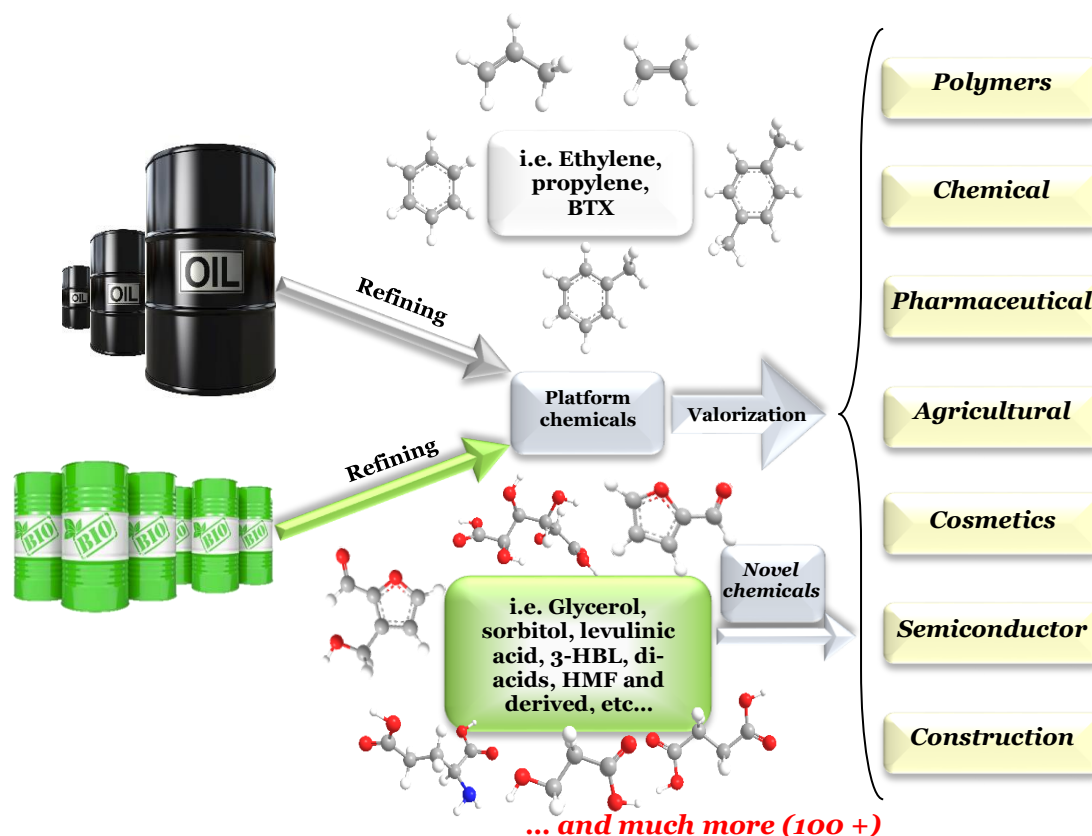


Figure 1. Analogy between the traditional petrochemical industry and the emerging bio-based chemical industry.

In other words, together with the possibility to be used as feedstock for the production of a potentially large number of bio-derived chemicals, a platform molecule must be available in sufficiently high amounts, and at low cost, to be able to partially supply chemical market demands in a competitive way respect to oil-based products. Thus, as the bio-economy

becomes more mature, the importance of bio-based building-block chemicals, with respect to fossil-derived base chemicals, can be measured by the volume they are produced and used in. It is therefore not surprising that a molecule as glycerol has attracted several interests and efforts in the development of valorization routes to high added-value chemicals because of a sharp increase of worldwide biodiesel production capacity. In other words, as world biodiesel capacity increased as a result of the search of alternative fuels to those petroleum-derived, the biorefinery integrated scheme has led to burgeoning amounts of bio-glycerol to be valorized instead of representing a simple waste to disposal. According to this preliminary consideration, bio-glycerol has soon arose as one of the most promising biomass-derived platform molecules [7]. However, glycerol is just one promising product in a very large number of other potential biomass-derived platform molecules.

Table 2 shows only some of the most important examples related to this variety. Since the collection of biomass is limited by its volume and density and since biorefineries have in general a smaller capacity with respect to an equivalent oil refinery, in order to produce meaningful volumes of products, a biorefinery should focus on a specific set of platform chemicals rather than attempting to provide an extended portfolio of products [1].

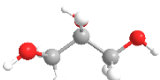
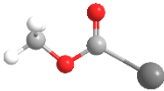
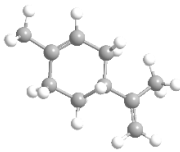
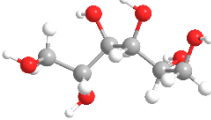
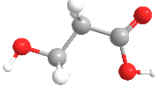
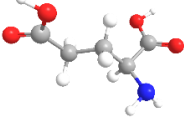
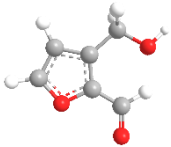
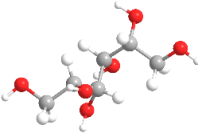

The choice of the most cost-effective approach to produce chemicals from biomasses is challenging, as it depends on the biorefinery objectives and on many other factors:

- **Chemical:** preservation of functionality and achievement of high atom economy are key parameters for the selection of reaction routes to desired platform chemicals. A practical methodology to evaluate this aspect is provided by the modified Van Krevelen plot, presented in [1].
- **Technical:** existence of broad conversion technologies able to efficiently deal with a large spectrum of potential targets. It is mainly a scientific research-related factor.
- **Economic factors:** according to the biorefinery integrated scheme, processes for the production of energy and fuels should be associated in the commercialization of some platform molecules to assure an optimum balance, according to market demands.
- **Feedstock variability:** biomass feedstock supply cannot be assured over time both in term of quantity and composition, since it is also related to geographical and seasonal factors.
- **Market uncertainty:** the production of drop-in and novel chemicals from biomasses are always subjected to a certain grade of uncertainty. In the first case, this is related to the competitiveness of bio-products with respect to petroleum-derived products, while for the latter the uncertainty mainly relies in the presence and in the stability of their “new market”.
- **Political:** since now, policies and subsidies for sustainable development have represented in many cases a fundamental factor for the success of this kind of new

technologies.

It is evident that in such a complex set of possible reaction routes, even further complicated by external non-technical factors, the sustainable and competitive processing of biomasses into a spectrum of marketable bioproducts, and bioenergy, has first to be rationalized in a proper conceptual entity in order to find an optimal development strategy towards the future bio-based economy. This rationalization transposes in the reality through the concept of integrated biorefinery.

Table 2. Example of biomass-derived platform molecules [2].

| Origin | Classification | Examples |
|--------|--|---|
| | Triglycerides derived |   Glycerol FAMES |
| | Terpenes |  Limonene |
| | Reduced sugars |  Sorbitol |
| | Hydroxyacids |  3-Hydroxypropionic |
| | Fermentation products |  Glutamic |
| | Dehydration products |  Hydroxymethylfurfural |
| | Reduced sugars |  Mannitol |
| | Pyrolysis, hydrogenolysis, and hydrolysis products | Hydroxy-, Carboxy-, Carbonyl- substituted phenyl compounds |
| | Gasification products | H ₂ , CO, CO ₂ , H ₂ O, CH ₄ |
| | Hydrolysis products | Aminoacids |
| | Thermal products |  Acrylamide |

1.2 The Biorefinery concept

As presented in the Bioenergy Task 42 Report, by the International Energy Agency (IEA), a “Biorefinery is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat)”. According to this definition, a biorefinery may be viewed as a concept, a process, a plant or even a cluster of facilities; in other words, the broad definition of biorefinery is strictly related to the development of a bio-based economic system.

Even though that of biorefinery is not a new concept, the rapid expansion in biofuel production in the last 15 years, and the need to valorize all the co-products, has driven the development of modern processing technologies. In this sense, the production of bio-based energy, materials and, most of all, chemicals alongside biofuels is seen as a strategy to improve the overall economics of the biorefinery, minimizing at the same time the amount of wastes.

In addition, the possibility to transform this kind of integrated systems into pure chemical refining processes, i.e. in which biomass valorization to chemicals represents the primary source of revenues, is even more attractive as a mean to assure a supply of bio-based products in front of market uncertainties affecting the biofuels economy.

1.2.1 A fundamental integrated approach

Even though biochemicals can be produced in dedicated single-product processes, manufacturing in integrated biorefinery processes producing both bio-based products and energy carriers (fuels, power, heat) is probably a more efficient approach for the sustainable valorization of biomass resources [8].

As said above, in analogy with the modern petrochemical industry, research over the last 15 years has demonstrated that an equivalent biomass industry could be able to deliver a huge variety of drop-in and novel chemicals via a limited set of simple platform molecules. However, the main driver for the development and implementation of biorefinery processes is today the transportation sector: significant amounts of renewable fuels are necessary in the short and mid term to meet policy regulations, both in- and outside Europe. Biofuels have to fill in a large fraction this demand, specifically for heavy duty road transport and in the aviation sector where biofuels are the only reasonable alternative. Both conventional (ethanol, biodiesel) and advanced biofuels (lignocellulosic Methanol, Ethanol, Butanol, Fischer-Tropsch diesel/kerosene, etc...) cannot be in general produced in a profitable way at current crude oil prices. This implicates that they only can enter the market if they are forced to (governmental regulation) or if significant financial support is provided (tax reduction). This artificial market will not be a long lasting one.

A significant reduction in biofuel production costs is required to create a sustainable market [9]. In this context, parallel to the increasing demand of biofuels, the valorization of co-products has become a necessity driven by waste minimization and revenue optimization. In other words, fuels can be produced at competitive prices by exploiting the potential added value associated to co-products, and their derivatives, in biofuels production. According to a 2010 study from the Wageningen university (WUR, The Netherlands), in which twelve full biofuel value chains were technically, economically and ecologically assessed [10], the main overall conclusion was that the production costs of the biofuels could be reduced by about 30% using the biorefinery approach, with a relevant list of additional benefits presented in Table 3.

Table 3. SWOT analysis for the integrated biorefinery system.

| Strengths | Weaknesses |
|--|--|
| <ul style="list-style-type: none"> • Adding value to the use of biomass • Maximizing biomass conversion efficiency minimizing raw materials requirements • Production of a spectrum of bio-based products and energy feeding the entire bioeconomy • Strong knowledge infrastructure available to tackle technical and non-technical issues • Biorefinery is not new, since it is built on agriculture, food and forestry industries • Stronger focus on drop-in chemicals facilitating market penetration | <ul style="list-style-type: none"> • Broad undefined and unclassified area • Involvement of stakeholders for different market sectors over full biomass value chain necessary • Most promising biorefinery processes / concepts not clear • Most promising biomass value chains, including current/future market trends, not clear • Studying and concept development instead of real market implementation • Variability of quality and energy density of biomass |
| Opportunities | Threats |
| <ul style="list-style-type: none"> • Significant contribution to sustainable development • Challenging nation and global policy goals, international focus on sustainable use of biomass for the production of bioenergy • Strengthening of the economic position various market sector, i.e. agriculture, forestry, chemical and energy • Strong demand from brand owners for bio-based chemicals | <ul style="list-style-type: none"> • Economic change and volatility in fossil fuel prices • Biobased products and bioenergy are assessed to a higher standard than traditional products • Availability of raw materials • Possible utilization of undepreciated existing industrial infrastructures • Changing governmental policies • Goals of end users often focused on single products |

1.3 Biodiesel production in the biorefinery context

In the frame of an increasing consciousness of cleaner production technology, the need for an alternative to fossil fuels has engendered extensive research in the last 15 years and biodiesel has been identified as one of the notable options for at least complementing conventional fuels [11].

Indeed, its advantages over petroleum diesel have been widely emphasized: it is safe (higher

flash point), renewable, non-toxic, and biodegradable; it contains no sulphur; and it is a better lubricant. In addition, its use has been associated to numerous societal side benefits, i.e. rural revitalization, creation of new jobs, and reduced GWP [12]. On the other side, the calorific value of biodiesel is lower than that of the regular petroleum diesel and its energy density is dependent on the quality of the feedstock [13].

Its production from renewable sources, i.e. vegetable oils and fats, has been widely reviewed with several reports on biodiesel production from edible oils [11], such as sesame seed oil, hazelnut kernel oil, almond kernel oil, olive kernel oil [14], palm oil, sunflower oil, soybean oil [15], and many others. Feedstock competition with food consumption has therefore been gradually arose as a global concern.

Consequently, the focus has been directed on waste and nonedible oils in biodiesel production, such as jatropha curcas oil [15], neem oil [16], caper spurge oil [17], rice bran seed oil [18], linseed oil, castor oil [14], to reduce or eliminate the competition with food consumption, and to reach compliance with ecological and ethical requirements for biofuels. Algae are currently considered to be one of the most promising alternative sources of non-edible oils for biodiesel, although full-scale commercialization of biodiesel from algae oil has not been launched [11].

Current concerns in biodiesel manufacturing involve [11]:

- Reproducibility, and process assessment, for varying feedstock quality.
- Search for optimal feedstock composition and suitable non-edible alternative raw material, i.e. algae.
- Use of heterogeneous catalysts or biocatalysts, as alternative to conventional homogeneous catalysts, for an improved process economics and environmental impact.
- Disposal / valorization of co-product glycerol.

1.3.1 Techniques for biodiesel production

In [19], the three well-established methods for biodiesel production are presented, i.e. microemulsion, thermal/catalytic cracking and transesterification, with transesterification as the most popular and preferred. Transesterification is the reaction of a fat or oil with an alcohol to form esters and glycerol (Figure 2)

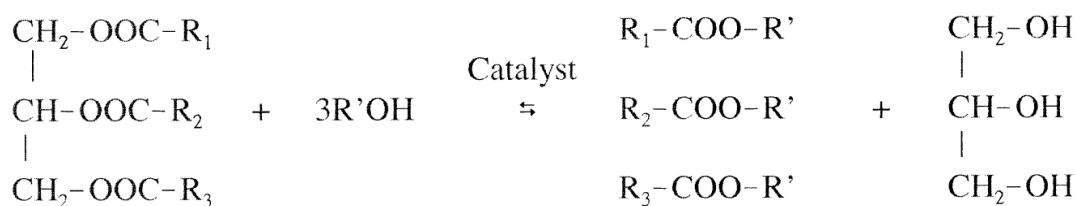


Figure 2. Transesterification of triglycerides with alcohol.

Alcohols are primary and secondary monohydric aliphatic alcohols having 1÷8 carbon atoms, including methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical properties (reactivity and NaOH solubilization) [20]; ethanol is receiving increasing attention as it can be derived from agricultural products, and is renewable and environmentally less objectionable [11]. The stoichiometric 3:1 molar ratio of alcohol to triglycerides is, in practice, increased to drive the equilibrium to a maximum ester yield. The reaction can be catalyzed by alkalis and acids, homogeneous or heterogeneous; enzyme catalysis has also been reported [11, 21].

Transesterification reactions can be carried out in batch or continuous processes. Despite the fact continuous mode of production can reduce drawbacks associated to batch operations, such as higher capital investment due to required large reactors volumes and lower capacity (~7.5 kt/y vs. 8÷125 kt/y [22]), batch processes are mainly reported.

Transesterification of vegetable oil using homogeneous catalysts

This method involves the use of acid and alkali catalysts in liquid form at 30÷60 °C, respectively to promote the protonation of the triglycerides carbonyl group and to create nucleophilic alkoxide from the alcohol. The use of homogeneous catalysts was the first conventional method applied in the biodiesel production industry, therefore its main advantage is related to the presence of well-assessed existing technologies.

An exhaustive review of process reaction conditions and effect of process variables is presented in [19], and is only briefly summarized in Table 4.

Table 4. Acid- vs. base-catalyzed homogeneous transesterification of oils to biodiesel.

| | Homogeneous acid-catalyzed | Homogeneous base-catalyzed |
|----------------------|--|---|
| Advantages | Well-assessed technology Suitable for high FFAs oils Cheaper lower grade feedstock Biodiesel properties can be customized based on the fatty acids present | Well-assessed technology Much faster reaction Lower alcohol to oil ratio required (2÷6) Lower catalyst concentration (< 1 % w/w) |
| Disadvantages | Sensitive to the presence of water Slow reaction Very high alcohol to oil ratio required (~30) Higher catalyst concentration (> 1% w/w) Intensive downstream separation and purification | Very sensitive to the presence of water and FFAs (saponification) Catalyst has to be removed from the product Alkaline waste water requires treatment Intensive downstream separation and purification |

A two-step process has also been proposed for feedstocks containing high free fatty acids (FFAs > 0.5÷3 wt. %), for which alkaline catalysts cannot directly catalyze the reaction [23]. The transesterification of high FFA oils is therefore achieved by employing a two-step process, in which an acid catalyzed process involving esterification of the FFAs to FAMES is followed by an alkali catalyzed transesterification. Ten percent yield increase was recorded using a two-step alkaline catalysis for a feedstock containing 4 % FFAs [24].

Transesterification of vegetable oil using heterogeneous catalysts

The application of solid heterogeneous catalysts in biodiesel production reduces the problems associated with homogeneous catalysis (Table 5): heterogeneous catalysts can be recycled several times, being easily separated from of the product and minimizing material and processing cost. In addition, employed solid materials are environmentally benign and can be used in either batch or continuous mode without the need for further purification steps [11].

Table 5. Heterogeneous catalyzed transesterification of oils to biodiesel, with respect to homogeneous processes.

| Heterogeneous catalyzed transesterification | |
|--|---|
| Advantages | <ul style="list-style-type: none"> Absence of costly and time-consuming water washing for catalyst recovery Absence of neutralization steps for residual catalyst removal Great reduction of contaminated waste water effluent High FAMES purity (> 99%) Almost complete yield achieved Co-product glycerol purity greater than 98% (vs. 80% from homogeneous processes) Heterogeneous catalysts tuned to include desired catalyst properties Much lower sensitivity of the reaction towards FFAs and water content Prolonged catalyst lifetime No corrosion/toxicity issues related to homogeneous catalyst |
| Disadvantages | <ul style="list-style-type: none"> Not mature catalytic technology for biodiesel manufacturing Catalyst formulation, tuning, and optimization requires extensive research efforts Catalyst preparation and regeneration may require expensive and/or complicated procedures Possible leaching phenomena to take into account Minimum activation temperature required (~55 °C for low T catalysts, ~175 °C for high T catalysts) |

The acidic and basic characteristics of heterogeneous catalysts are still important properties suited for use in transesterification of triglycerides.

Solid acid catalysts, such as sulphated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$), tungstated zirconia (WO_3/ZrO_2),

heteropoly acids (HPAs: $Cs_xH_{3-x}PW_{12}O_{40}$) [25], were chosen to catalyze oil transesterification due to the presence of sufficient acid site strength. These catalysts showed very good yield (65-99 %) at temperature slightly above room conditions. Between the high temperature catalysts, alumina-based acid materials, i.e. Al_2O_3/PO_4^{3-} , $Al_2O_3/TiO_2/ZnO$, $Al_2O_3/WO_3/ZrO_2$, $K/\gamma-Al_2O_3$ [25], and Anhydrous iron (III) sulfate [26].

The interest in heterogeneous alkali transesterification lies in the possibility to simplify the production and purification processes, to decrease the amount of basic waste water, to downsize process equipment, and to reduce environmental impact and process costs [27].

Apart from ease of catalyst recovery, it has been shown that activity of a heterogeneous NaOH-treated ($Na/NaOH/Al_2O_3$) catalyst resembles the homogeneous counterpart in the same operating condition [28]; however, low tolerance to FFA and water, and alkali component leaching has prevented the use for direct processing of low grade oils. These problems were reduced or eliminated proposing alkaline earth metal oxide catalysts [25, 29, 30], La-based catalysts [29], and Mg-Al hydrotalcites [31].

Heterogeneous catalysts from natural sources

Some biomass materials have been shown to possess catalytic properties that make them suitable for biodiesel production. For example, catalytic activity has been reported for eggshell, limestone calcite, cuttlebone, dolomite and hydroxyapatite [32] (due to formation of CaO after calcination), and for materials derived from incomplete carbonization of carbohydrates followed by sulphonation (formation of high density of active SO_3H sites)

Solid catalysts derived from renewable and/or natural resources are effective for transesterification reactions; they are recyclable, ecofriendly and are highly suited for the production of biodiesel from oils containing high FFAs. The development of a suitable process that makes use of these catalysts would serve as a good alternative for the conventional heterogeneous chemo-catalysts.

Therefore, the application of these renewable feedstocks and heterogeneous catalysts from natural sources for biodiesel production will certainly lead to the development of a cost-effective process that is environmentally friendly. However, these catalysts require a precise synthesis process, possibly complicated in some cases, requiring great expertise [33].

Other transesterification technologies

While the catalyzed production of biodiesel is the most common route used industrially, the major drawbacks associated to the presence of a homogeneous catalyst, i.e. FFAs/water sensitivity, catalyst stability and removal, wastes produced, low glycerol purity, has propelled the research towards the adoption of supercritical conditions. Under such conditions, the mixture becomes homogeneous and both the esterification of FFAs and the transesterification

to FAMEs occur without the need for a catalyst, rendering this method suitable for any type of raw material, especially those that are otherwise difficult to treat using conventional methods, such as animal fats and oils high in free fatty acids [11]. Though attractive for many reasons, the challenges regarding this method include the high methanol-to-oil molar ratios necessary (42:1), and high operating temperatures (280÷400 °C) and pressures (10÷45 MPa) [11].

Lipase-mediated biocatalysis has been addressed as another suitable alternative to conventional homogeneous alkali processes, especially considering the possibility to improve enzyme stability and reusability by immobilization on several materials [34]. Biocatalysis is characterized by high selectivity and efficiency, and is applicable with a wide range of triglyceride sources, with FFA ranging from 0.5 % to 80 % [11] (Table 6).

Alternative catalytic biodiesel manufacturing processes finally consists in the application of ultrasonication (to induce local bubble cavitation with localized intense mixing and temperature increase) [35], membrane reactor technologies (to promote the reversible equilibrium in transesterification reactions by product continuous removal), reactive distillation technologies (for process intensification and to promote the reversible equilibrium, with simultaneous byproducts distillation).

Table 6. Supercritical synthesis and biocatalysis features in biodiesel manufacturing.

| | Supercritical synthesis | Biocatalysis |
|----------------------|---|--|
| Advantages | Non-catalytic homogeneous conditions Esterification of FFAs and transesterification to FAMEs take place Suitable for any type of raw oleos material No issues related to the presence of homogeneous catalyst High product purity Large reduction of waste streams No necessity for waste water treatment | High selectivity Suitable for high-FFAs oils (0.5÷80 %) Suitable for high H ₂ O content up to 30 % Lower temperature required (30÷40 °C) Lower alcohol to oil ratio required (1.5÷5) |
| Disadvantages | Very high alcohol to oil ratio required (~42) High temperature Very high pressure | High production cost of Lipase Limited regeneration and re-use of biocatalysts Long reaction time (8÷90 h) Biocatalyst destruction/deactivation over temperature and alcohol-to-oil ratio thresholds Additional explosion hazard if an organic solvent is used |

1.3.2 The role of glycerol

The major cost factor in the production of biodiesel is the cost of the raw material. Conversion costs account for about 10% in large facilities, and between 25% and 40% in small

plants [36]. In recent years, the search for a cheaper product has therefore largely been a search for the cheapest raw material, together with a quest for the most economic processing method, and increasing attention has been given to the less traditional sources of triglycerides, such as algae. The research on processing methods has likewise broadened to include the use of heterogeneous catalysis, the use of supercritical methods, and the integration of the biodiesel production with other co-processes, such as power co-generation and biogas production from the digestion of micro-algal waste. The last few years have seen a promise of steady improvement of the economics of biodiesel production based on these research fronts [11]. Other strategies for cost reduction employ waste or nonedible oils with high FFAs content, integration of processes, and optimization of feed combinations [37].

On the other side, downstream strategies mainly involve biodiesel and co-product market valorization. Glycerol, as the principal co-product in biodiesel manufacturing produced in 10:1 w/w ratio, offers the greatest improvements in the overall biodiesel process economics.

Besides application of crude glycerol as energy supplement for ruminants and its purification to the pharmaceutical grade (> 99.5 wt. %) [37], glycerol chemical valorization is nowadays seen as the main opportunity towards a competitive integrated biorefinery scheme in biodiesel manufacturing (Figure 3).

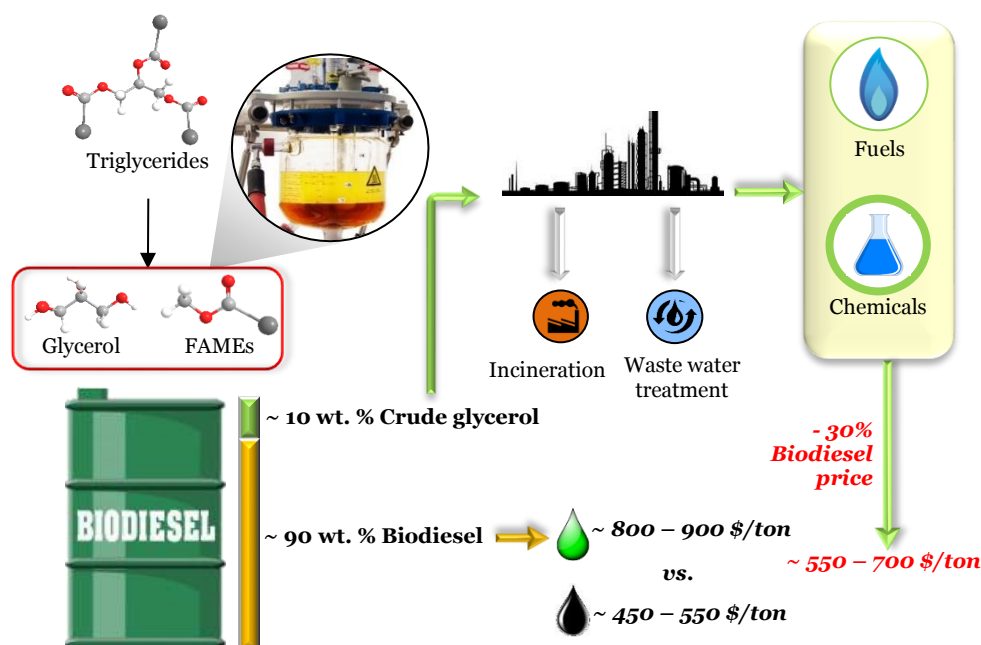


Figure 3. Biodiesel manufacturing and glycerol valorization in the integrated biorefinery approach.

Present market quotations for soybean oil, palm oil and rapeseed oil, i.e. some of the most important oleos feedstock for biodiesel production, are respectively of 705 \$/ton, 621 \$/ton, 830 \$/ton [38], which corresponds to a biodiesel market quotation of ~830 \$/ton (FAMES) and ~880 \$/ton (SMEs, Soybean Methyl Esters) [39]. Oil-derived diesel quotation is ~450

\$/ton [38].

As previously said, according to preliminary studies presented in [10], glycerol valorization to chemicals is expected to increase in a relevant way the competitiveness of biodiesel, towards a gradual reduction of subsidies for its introduction into the energy market.

Therefore, glycerol downstream valorization, associated to the improvement of upstream technologies in biodiesel manufacturing, is seen as the most viable strategy towards the actual implementation of the concept of integrated biorefinery.

1.4 Thesis objectives

The scope of this brief introduction is that of introduce the reader to the complex world of sustainable chemistry with its strict dependency towards technical evaluation and feasibility studies, i.e. the chemist's and the engineer's point of view of a biorefinery. The role covered by glycerol in this complex world is particularly interesting and important, due to its oversupply as co-product in biodiesel production processes.

The starting point of this work is thus the acknowledgement of this situation and the will to transform large, scarcely valorized amounts of glycerol into valuable commodities, specialties or new chemicals. In particular, an analysis of the available state-of-the-art catalytic technologies for the main glycerol upgrading routes is here presented and based on environmental and economic process assessments.

On the experimental point of view, emphasis will be given to the increasingly important synthesis route from glycerol to epichlorohydrin, an important epoxy-compound in the polymer industry; catalytic studies and methodologies are presented for the development of a novel continuous and heterogeneous catalyst as a viable alternative respect to the existing process based on the epoxidation-dehydrochlorination of 1,3-dichloro-2-propanol using stoichiometric aqueous NaOH.

The research conducting *leitmotiv* is always the same: find a more economically and environmentally sustainable process able to reduce, or to eliminate, the undesired aspects related to the actual process.

1.5 Thesis structure

This thesis presents the results of different studies that have been already published or are under review for their publication. The activity included an experimental activity, process modelling and process economic and environmental assessment. In particular, innovative studies were personally conducted for the development of a new route from glycerol to epichlorohydrin and for the economic and environmental assessment of 1,2-propanediol,

glycerol carbonate, allyl alcohol and epichlorohydrin synthesis processes.

The structure proposed is therefore the result of the rationalization of these studies under the concept of biorefinery and sustainable development.

- Chapter 1: Introduction.
General introduction to the wide context related to biomass conversion strategies in the framework of a developing bio-based economy for the future sustainable development. The biorefinery concept is presented and biodiesel manufacturing is addressed as source of waste glycerol.
- Chapter 2: The Glycerol world.
The importance of this platform molecule is presented towards green fuels and green chemicals production.
- Chapter 3: Glycerol valorization to chemicals.
The results of state of the art studies for glycerol valorization to chemicals are here presented for some relevant processes. The analysis of catalytic systems is combined with a LCA-based process assessment to obtain relevant data for the “measurement” of process sustainability.
- Chapter 4: Glycerol to Epichlorohydrin: a novel attempt.
Dedicated chapter to the main activity involved in the present thesis. Catalyst synthesis, screening, characterization, testing and evaluation were the focus of the experimental activity. Experimental setup, conditions and analytical methods are also briefly described. Finally, the LCA-based approach for process assessment is adopted to assess a hypothetic industrial process based on the new reaction pathway.
- Chapter 5: Conclusions.

1.6 References Chapter 1

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CHAPTER 2

THE GLYCEROL WORLD

2.1 Glycerol as platform molecules for green fuels

Biomass has the potential to serve as a sustainable source of energy and organic carbon for our industrialized society [1]. In the frame of developing catalytic transformations of biomass-derived oxygenated feedstocks to chemicals and fuels, one of the major achievements of the new glycerol chemistry is the aqueous phase reforming process (APR), in which glycerol is converted to syngas under relatively mild temperature conditions (225÷300 °C), at pressures above the bubble point of the aqueous mixture (16÷40 bar), using a Pt-Re catalyst in a single aqueous phase reactor. The bio-derived synthesis gas can then be used in the integrated biorefinery context as a source of fuels and chemicals, offering an efficient alternative to transportation fuels derived from petroleum (Figure 4).

In addition, the APR process using a Pt catalyst offers the rapid production of high yields of hydrogen fuel from glycerol at very low CO concentrations, due to more favorable WGS thermodynamics, and with considerably lower energy consumption than traditional methane reforming [2].

Petroleum provides a significant fraction (37 %) of the world's energy, of which almost 70 % is consumed by the transportation sector. Biomass is the main candidate as an alternative source of transportation fuel, since it is renewable, CO₂ neutral, and largely available [3]. Lignocellulosic biomass valorization to fuels encompasses a combination of hydrolysis, fermentation, and distillation operations to liquid alcohols such as ethanol and butanol. However, the overall energy balance for the production of bioethanol from grain-derived starches is not particularly favorable, since it has been estimated that the energy return on investment is in the order of 1-1.2 [4].

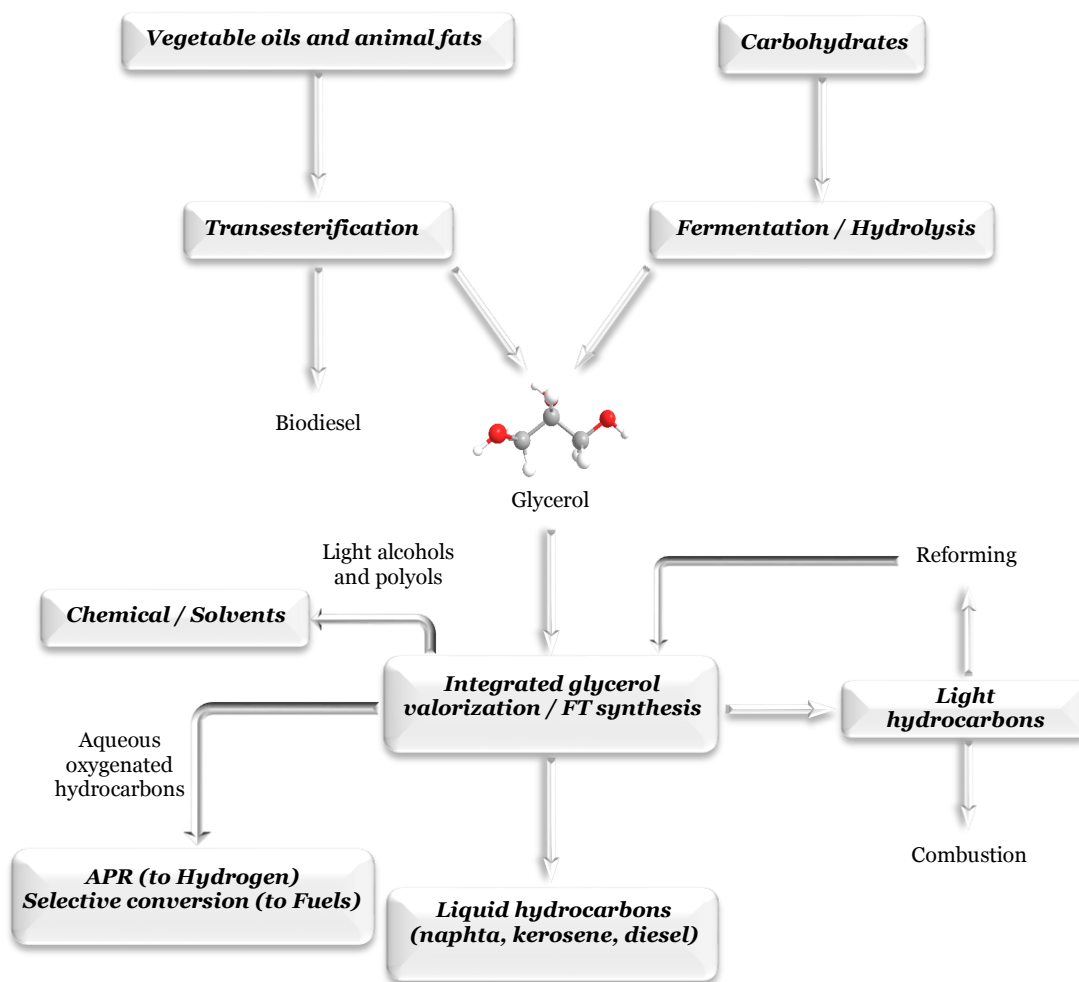


Figure 4. Process pathway for production of liquid fuels from biomass by integrated glycerol conversion to synthesis gas and Fischer-Tropsch synthesis [1].

On the other hand, the energy balance for the coupled APR and Fischer-Tropsch reactions is favorable: the formation of synthesis gas from glycerol is endothermic (80 kcal/mol) but the conversion of synthesis gas to alkanes is highly exothermic (−110 kcal/mol). This means that the conversion of glycerol to alkanes by a combination of reforming and Fischer-Tropsch synthesis is mildly exothermic, and provides the opportunity for improving the economic viability of biomass-based Fischer-Tropsch synthesis by reducing the cost of synthesis gas production and by improving its thermal efficiency [3].

A further advantage in using glycerol is that it can be obtained by the fermentation of glucose, therefore offering an energy efficient alternative to ethanol-based production and assuring a certain grade of process flexibility in terms of feedstock.

Such improvements in synthesis gas generation and in the overall economics of the Fischer-Tropsch synthesis are seen as crucial, in order to develop a glycerol-based process for the production of fuels in a competitive way with respect to the oil-based Fischer-Tropsch

synthesis (competitive only for oil price above 40 \$/barrel) [3].

2.1.1 Production of hydrogen via APR

The gas stream leaving the APR can be utilized directly as a high energy fuel for internal combustion engines, gas-fired turbines, and solid oxide fuel cells. In addition to its use as an energy carrier, hydrogen is a key building block for many chemical processes in ammonia fertilizers production and in oil refineries upgrading processes. It is additionally important in the manufacture of glass, vitamins, personal care products, lubricants, refined metals and food products.

The APR process for the production of hydrogen from glycerol is cost effective since [3] (Table 7):

- it generates hydrogen without the need to volatilize water, representing a major energy saving;
- it takes place at temperatures and pressures where the WGS equilibrium is favorable, making it possible to generate hydrogen with low quantities of CO in a single chemical reactor;
- it occurs at pressures at which the hydrogen-rich effluent can be purified effectively from CO₂ using pressure-swing adsorption (PSA) technology;
- it takes place at low temperatures, minimizing decomposition reactions of the organic feedstock.

Table 7. Comparison of glycerol APR and NG steam reforming in hydrogen production [3].

| NG steam reforming | Glycerol APR |
|--|--|
| $CH_4 + H_2O \longrightarrow CO + 3H_2$ $CO + H_2O \longrightarrow CO_2 + H_2$ | $C_3H_8O_3 + 3H_2O \longrightarrow 3CO_2 + 7H_2$ |
| <ul style="list-style-type: none"> • T = 700 ÷ 900 °C • Energy intensive process • CO separation steps required • Suitable only for large scale H₂ production | <ul style="list-style-type: none"> • T = 220 ÷ 300 °C • Single step reactor • Lower energy consumption • Near zero CO • Renewable feedstock • Suitable also for small scale H₂ production |

The raw water-soluble glycerol waste from biodiesel manufacture is an ideal feedstock for the APR process, even more than other bio-derived polyols, i.e. sorbitol, glucose. Indeed, at typical investigated reaction conditions, CO concentrations are below 300 ppm, operating temperatures are much lower with respect to conventional reforming processes, and H₂ specific productivity per unit mass of catalyst is much higher. In addition, while originally γ -Al₂O₃ -

supported precious metal catalysts were investigated [5], the reaction can be conducted over a range of catalyst compositions, and in particular on inexpensive nickel-based materials [6].

2.1.2 Production of hydrocarbon fuels via APR

Liquid alkanes can be produced directly from glycerol in a two-bed reactor system using an integrated process consisting of APR followed by Fischer-Tropsch conversion [7].

Operation at low temperatures provides the opportunity to couple the endothermic glycerol conversion to syngas with the exothermic Fischer-Tropsch synthesis to produce liquid transportation fuels from aqueous glycerol via an integrated process. In particular, either glycerol conversion or Fischer-Tropsch synthesis can be carried out effectively under the same conditions in a two-bed reactor system. This integrated glycerol-based process improves the economics of Fischer-Tropsch synthesis by reducing costs, by eliminating the need for a biomass gasifier, by reducing the size of the synthesis reactor, by producing an undiluted synthesis gas stream and by eliminating subsequent cleaning steps. In addition, the process can produce synthesis gas of varying $H_2:CO$ ratio suitable for Fischer-Tropsch synthesis, i.e. between $1 \div 1.6$ [3].

Glycerol conversion to synthesis gas and Fischer-Tropsch synthesis leads to synergies in the operations of these processes, such as:

- avoiding the highly endothermic and exothermic steps that would result from the separate operation of these processes;
- eliminating the need to condense water and oxygenated hydrocarbon byproducts between the catalyst beds;
- allowing operation at higher pressures (i.e., 17 bar), with an increase in selectivity to C_5+ hydrocarbons.

Figure 5 shows the product molecular weight distributions for experiments that combined glycerol conversion with Fischer-Tropsch synthesis [7]. These distributions exhibit deviations from the kinetics of the Anderson-Schulz-Flory model [8], indicating α -olefin re-adsorption effects. Indeed, the primary oxygenated hydrocarbon intermediates formed during conversion of glycerol to synthesis gas are ethanol, acetone, and acetol, which all have positive effects on the Fischer-Tropsch synthesis step by re-entering the chain growth mechanism. Consequently, selectivity to oxygenated byproducts is also higher, i.e. pentanones, hexanones, heptanones.

2.1.3 Industrial applications

The advantages and the potential versatility of the glycerol APR process has pushed in the last decade extensive research for industrial implementations.

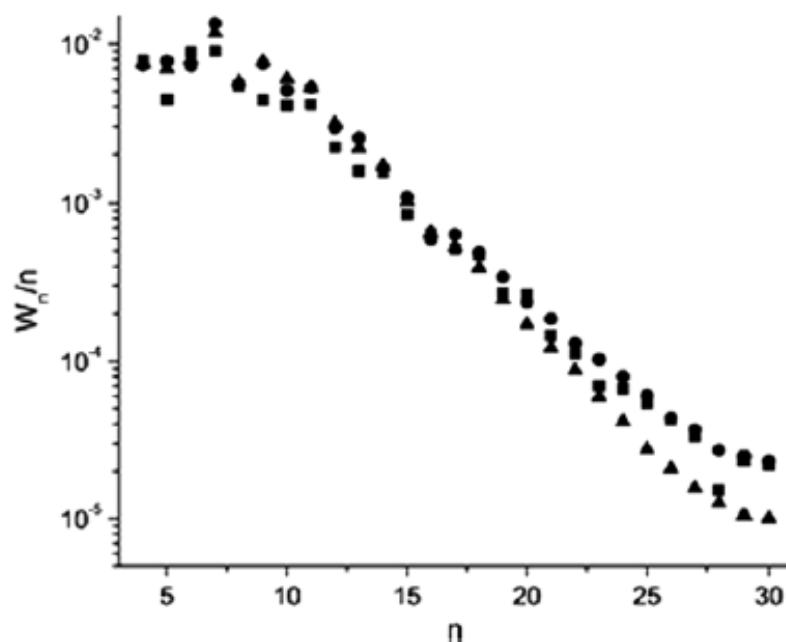


Figure 5. Molecular weight distribution for combined glycerol conversion with Fischer-Tropsch synthesis at 548 K, and 5 bar (■), 11 bar (●), 17 bar (▲) [7].

Initial efforts were directed towards the methanol process, i.e. methanol production from bio-derived syngas, to find alternative manufacturing methods other than that from natural gas, which takes into account for > 90% of produced methanol. In the Netherlands, BioMethanol Chemie Nederland (BioMCN) uses crude glycerol to produce synthesis gas (and CO₂), which is then reformed at high pressure and temperature to make bio-methanol [7, 9]. After the discovery in 2008 of a new supported metal catalyst by the Oxford university [10], the UK company DT Chemicals aimed to have the commercial process completed by early 2010 [11]. The large commercial potential of the APR technology has been reinforced by coupling with Fisher-Tropsch fuel production. The different product streams of the integrated APR-FT process each have potential end uses (Figure 4). With the BioForming process, which enables the production of renewable fuels and chemicals from glycerol and carbohydrates, Virent in 2005 first demonstrated the advantages related to this process, especially on the energetic point of view [12]. The success of the system encouraged large companies such as Cargill, Shell and Honda to invest in the company.

The production of fuels via APR and APR-FT integrated processes, has confirmed that the technology was a viable pathway to the production of liquid fuels and chemicals currently derived from fossil sources. In particular, biodiesel-derived glycerol is a cost-effective feedstock, allowing competitiveness of the APR process with conventional fuels: the primary economic driver for the APR process is indeed the feedstock (Figure 6). The APR technology has been proven to be competitive with respect to a comparable steam reformer utilizing non-renewable natural gas (H₂ cost of 3-4.50 \$/kg).

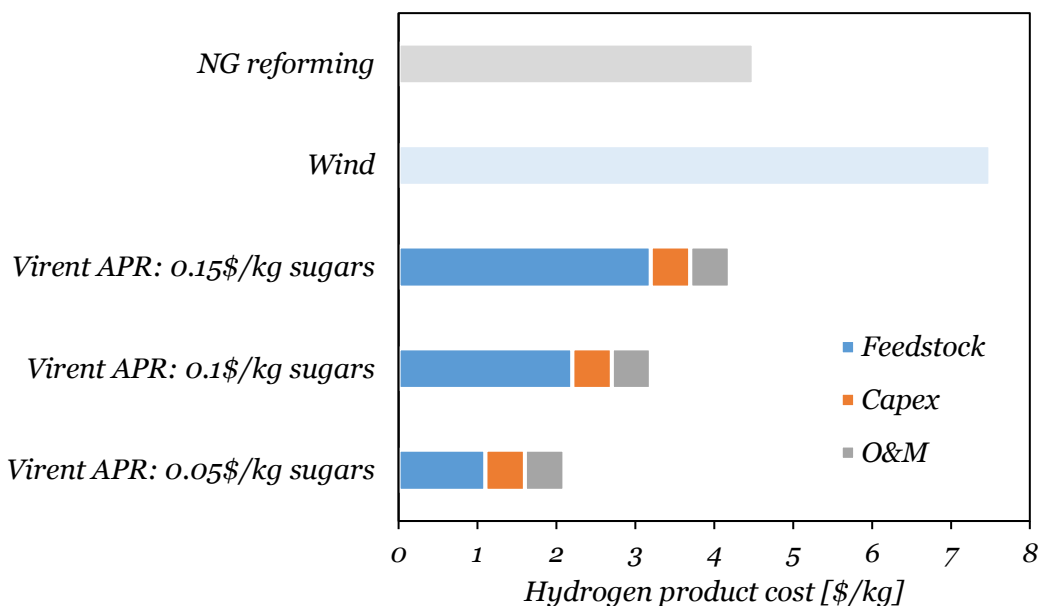


Figure 6. Hydrogen cost for different feedstock; since the cost of the feedstock is the primary driver, increasing biodiesel production will make hydrogen production from glycerol a commercial reality [7].

2.2 Glycerol as platform molecules for chemicals

Biodiesel 2016 annual production of 82 Mton of oil equivalent, with almost 90% accounted for North America, South & Central America, and Europe and with increases of 2.8%, 3.2%, and 12.2% with respect to 2015, 2014, and 2013 [13], gives a clear indication of the potential status of glycerol as a key renewable feedstock for future biorefineries, in which a number of commodity and specialty chemicals (Figure 7) will be produced from it.

Extensive chemical research technologically disclosed routes for glycerol conversion to chemicals finding application in existing and novel markets. This, together with an increasing maturity of more efficient upstream processing technologies for biodiesel manufacturing, i.e. heterogeneously catalyzed and integrated processes, is expected to represent the real push towards the recognition of glycerol as one of the base platform chemical for the future bioeconomy.

The number of opportunities from glycerol, some of them presented in Figure 7, is the result of the high degree of its molecular functionalization, which allows multiple and interconnected conversion paths for a large variety of chemical products. Catalytic conversion is mainly performed through oxidation, dehydration, acetalization, esterification, etherification, carboxylation, and chlorination, which have been summarized in many review papers [3, 14-16].

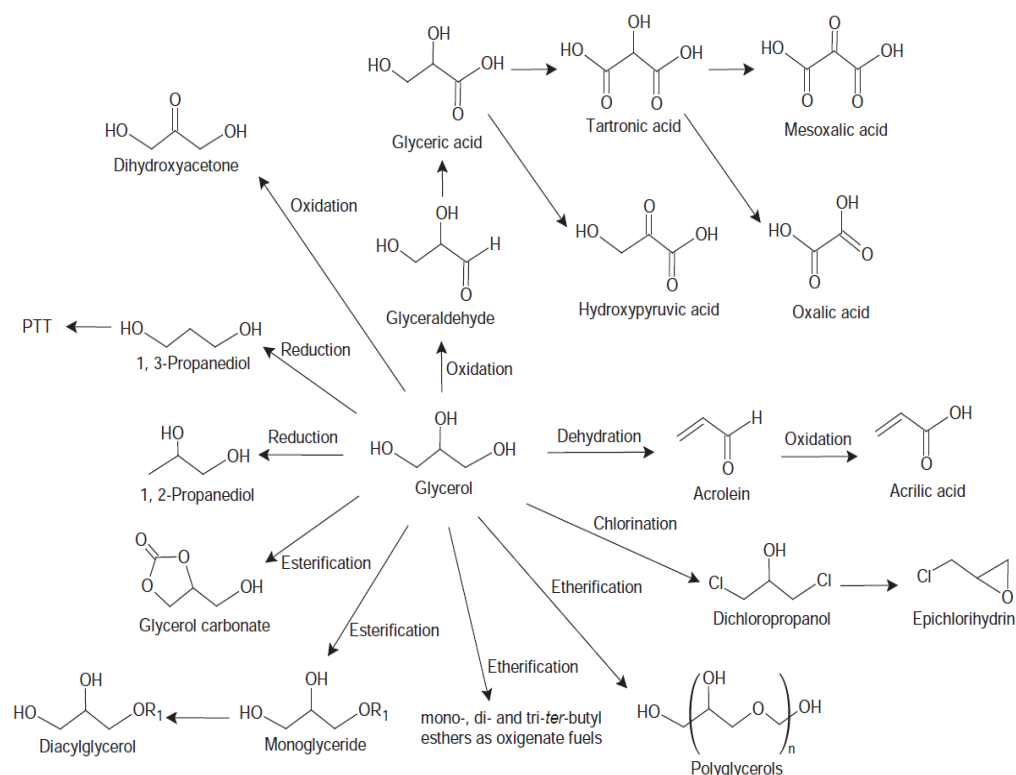


Figure 7. The most important commodity, specialty and novel chemicals from glycerol.

2.2.1 Dehydration and hydrogenolysis products

Glycerol dehydration into acrolein and 3-hydroxypropanal, and hydrogenolysis to 1,2- and 1,3-propanediols, allyl alcohol, monopropansols, and propylene allow the production of well-established commodity chemicals traditionally manufactured from fossil sources (Figure 8). Starting from acrolein a number of end-products can be targeted, including plastics monomers, mono-alcohols and energy gases, such as propane. It is also used as intermediate in the production of the important acrylic acid, even though direct glycerol oxydehydration processes are being developed over bifunctional catalysts [17], disclosing renewable routes to acrylic monomers for the production of polyacrylic compounds. Allyl alcohol is also produced by further hydrogenation, enabling glycerol to allyl derivatives, i.e. glycidol and glycidyl ethers, amines and esters monomers such as diallyl phthalate [18]. Finally, biocatalytic oxidation represents an alternative route to important specialty and fine chemicals, such as glyceraldehyde, glyceric acid and derivatives, and aminoacids.

The importance of 3-HPA arises as it is an intermediate in glycerol dehydration to acrolein and hydrogenolysis to 1,3-propanediol. It also finds direct applications as antimicrobial, in polymer production via 3-HPA hydrate and ether oligomer derivatives, 3-hydroxypropionic acid, acrylic acid, malonic acid and acrylamide [3].

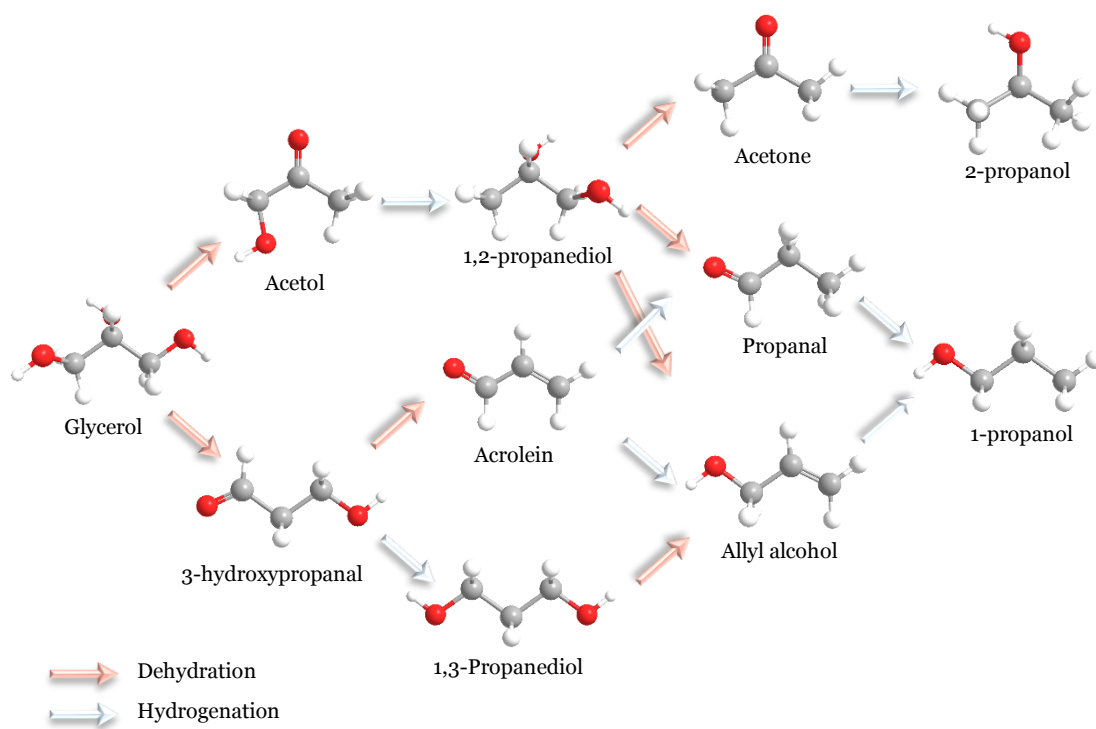


Figure 8. Glycerol hydrogenolysis routes.

Finally, the complex set of interconnected reactions in the frame of glycerol hydrogenolysis enables a large variety of alternative routes to other commodity and specialty chemicals, mainly for application in the polymer industry. The feature of this reaction pathways is typical of the glycerol chemistry and allows to obtain final products from renewable sources assuring at the same time a large grade of flexibility in intermediate production, i.e. the same final product can be obtained from different reaction routes.

2.2.2 Oxygenation products

Together with the reductive hydrogenolysis chemistry, glycerol oxidation scheme to highly functionalized molecules presents a high degree of complexity. As glycerol itself is already a highly functionalized molecule compared to hydrocarbons, the interest in these routes relies in the possibility to more easily obtain valuable oxygenated derivatives. Many important fine chemicals are in this way obtained, i.e dihydroxyacetone (DHA), glyceric acid, hydroxypyruvic acid, oxalic and mesoxalic acid, tartronic acid (Figure 9).

Innovative and potential application of these chemicals, for direct use or as intermediates in further organic synthesis, are numerous and widely celebrated [19-22]. Fine and specialty fields of application involve especially innovative degradable polymer industry, cosmetic and personal care industry, food industry, and pharmaceutical and therapeutic sectors [14, 23]. Traditionally, these products always had a limited market mainly because they were produced

using costly and polluting stoichiometric oxidation processes, e.g. with KMnO_4 , HNO_3 , H_2CrO_4 , or low-productivity fermentation processes [18].

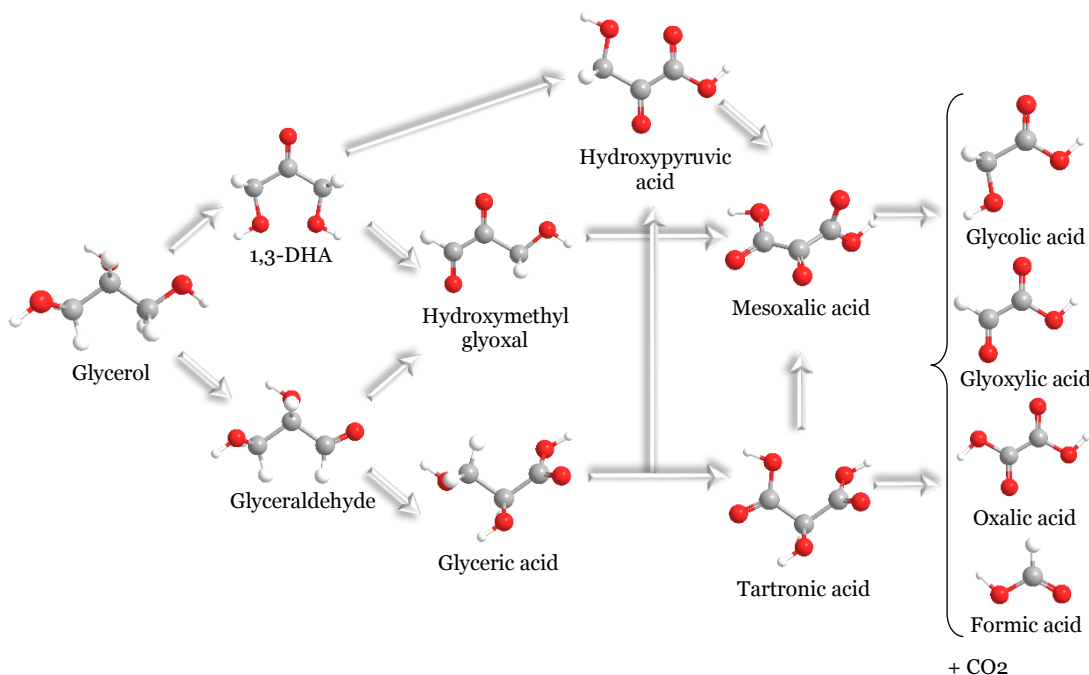


Figure 9. Glycerol oxygenation routes [14].

Glycerol's unique structure makes it possible to conduct the synthesis employing innovative, clean and highly efficient catalytic methods, using inexpensive oxidizing agents, such as air, oxygen and hydrogen peroxide. A new market for oxygenated glycerol derivatives is therefore disclosed by implementation of new cheaper and environmentally friendly processes.

Selective oxidation is the main challenge associated to the development of oxidation catalysts in order to control the chemoselective orientation of the oxidation reactions towards either the oxidation of the primary alcohol functions, to give glyceric acid, or the oxidation of the secondary alcohol function, to produce dihydroxyacetone and hydroxypyruvic acid; overoxidation leads to mesoxalic and tartronic acid. In recent years, increasing number of studies dealing with the chemoselective catalytic oxidation of glycerol have been reported; supported noble metal nanoparticles, such as Pd, Pt, Au, Ag, are suitable heterogeneous catalysts [14]. A Fe-zeolites heterogeneous catalyst was recently presented in glycerol oxidation to DHA, together with an analysis of the scalability of the technically-shaped catalyst at the liter scale, and the environmental and economic assessment of the resulting process [24].

Lactic acid is another attractive chemical which can be derived via oxidation. This compound can not only generate multiple commodity and intermediate chemicals, i.e. acrylic acid, 1,2-propanediol, pyruvic acid, acetaldehyde, 2,3-pentanedione, that already belong to the traditional chemistry portfolio, but it can also be polymerized into the novel biodegradable

plastic polylactide (PLA). Nowadays, lactic acid is prepared via the anaerobic batch fermentation of glucose or sucrose, under strict temperature and pH conditions ($T < 313\text{ K}$, $\text{pH} = 5\text{-}7$), followed by transesterification of the resulting alkyl lactate. The two step process is affected by coproduction of large amounts of gypsum ($1\text{ kg/kg}_{\text{LA}}$) and low productivity of the biocatalyzed process [25, 26]. Alternative pathways based on chemocatalysis have been explored, such as the aqueous-phase isomerisation of 1,3-dihydroxyacetone (DHA) over Lewis acids, La and Pb salts. Solid catalysts have however attracted more pronounced interest due to easiness of separation and the implementation of clean technologies: Sn-containing BEA, MWW and MFI zeolites stand as the best performers [25] (Figure 10).

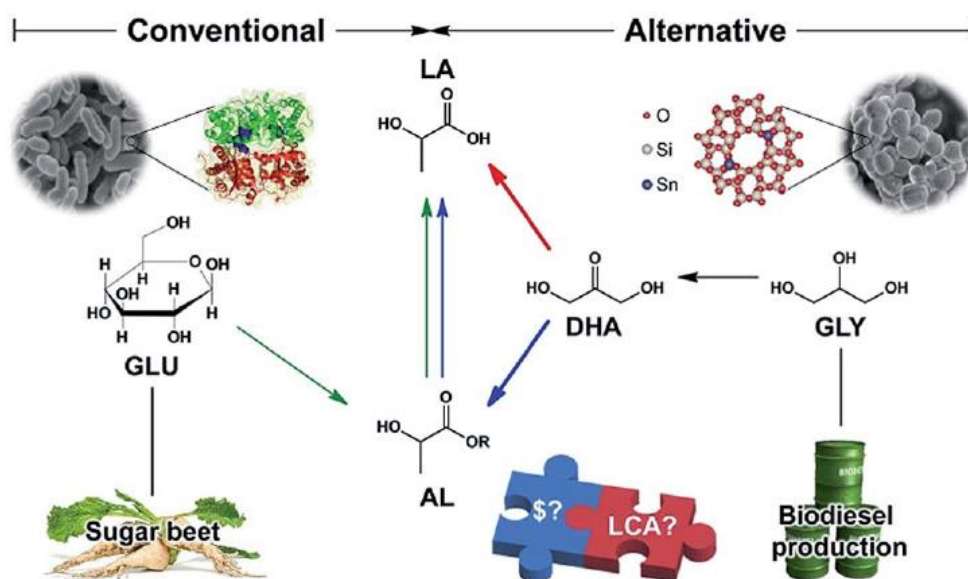


Figure 10. Manufacturing from biomasses: conventional fermentation process and alternative bio-/chemocatalytic route from glycerol via 1,3-DHA. Feedstock availability, and process economic and environmental assessment decide the most viable route [25].

2.2.3 Chlorination products

Studies of glycerol halogenation have focused on production of 1,3-dichloropropanol, an intermediate in epichlorohydrin synthesis. Epichlorohydrin is an important raw material largely used in the plastics industry as monomers precursor for epoxy resins and polymers production. Epichlorohydrin has also minor applications as versatile precursor of other organic compounds in the propellant and the paints industry, as solvent and as insect fumigant. Alongside with traditional application, its polymers, are also used in paper reinforcement, in the food industry (manufacture of tea bags, coffee filters, and sausage / salami casings), in water purification, and in eyeglass lenses and ion-exchange resins manufacturing.

A chapter dedicated to epichlorohydrin production from glycerol will be later presented.

2.2.4 Etherification and esterification products

Selective etherification into valuable fuel additives or solvents with suitable properties represent another opportunity offered by glycerol (Figure 11). Indeed, oxygen-containing components produced by catalytic etherification with alcohols or alkene have potential to be used as diesel fuel additives in gasoline and offer an alternative to oxygenates, such as oil-derived MTBE and ETBE. Homogeneous (p-toluene sulfonic acid, methane sulfonic acid) and heterogeneous (zeolites) acid catalysts, and strong acid ion exchange resins were proposed [14].

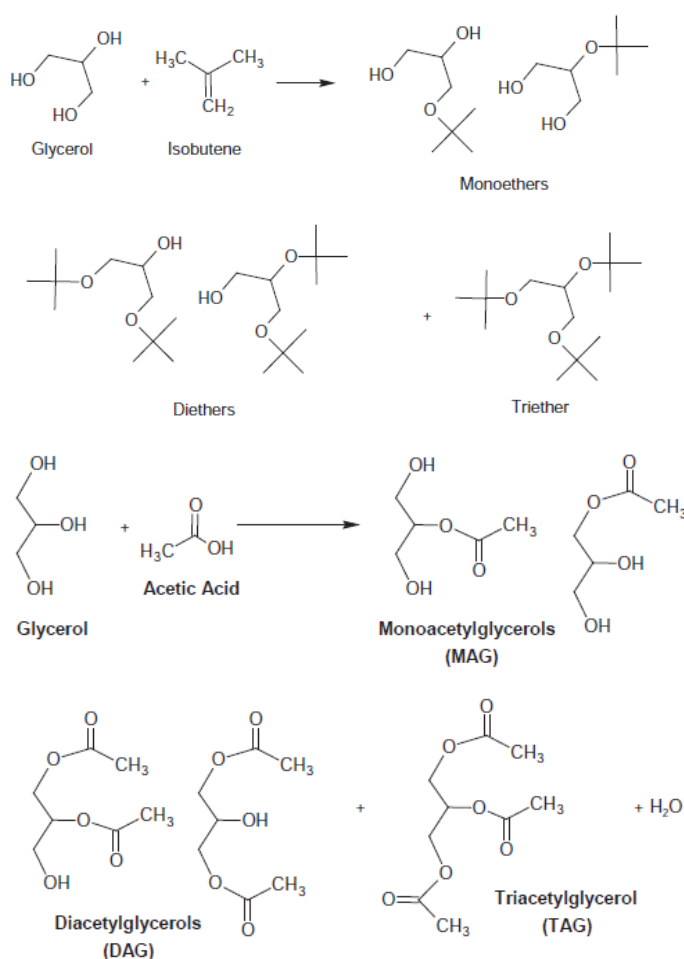


Figure 11. Glycerol etherification with isobutene and esterification with acetic acid [3].

Polyglycerol (PG) and polyglycerol esters have been suggested to be used as biodegradable and biocompatible polymers for biomedical, food and cosmetic applications [27]. Their derivatives offers also additional beneficial properties in competition with the more widely used polyethylene glycols [14]. PG and its esters are obtained from glycerol oligomerization and the esterification of the oligomers with fatty acids or methyl esters in the presence of basic homogeneous catalysts, even though solid base and acid materials have been proposed.

2.2.5 Carboxylation and nitration products

Glycerol carbonate and glycidyl nitrate are the two novel products of interest obtained from this class of reactions [3]. The former is obtained by reaction of glycerol with a carbonating agent, i.e. alkyl carbonates and urea: a dedicated chapter is later presented for the analysis of application, method of production, and process environmental and economic assessment. The latter is obtained by treatment of glycerol with nitrating agents to form a solution containing dinitroglycerol, which then undergoes alkali treatment for epoxide ring closure (Figure 12).

Poly(glycidyl nitrate) is the major product of interest derived from glycidyl nitrate: it is potentially suitable for use in propellants, explosives, gas generators and pyrotechnics.

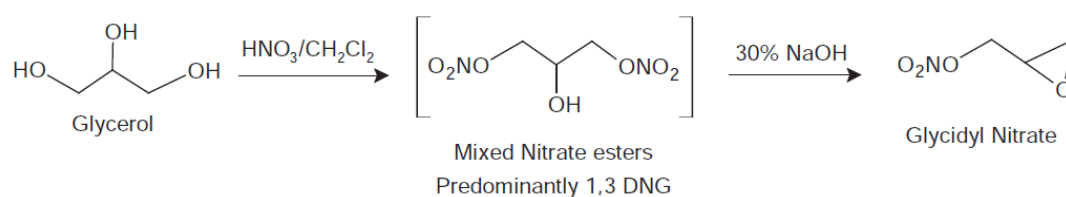


Figure 12. Glycerol nitration, followed by alkali treatment, to glycidyl nitrate [3].

2.3 So, why Glycerol?

The large amounts of glycerol produced as co-product in biodiesel manufacturing and its central role as valuable waste, for direct specialty applications, and in the production of marketable chemicals via sustainable catalytic transformations, have determined an interest in this molecule more than ever actual. In addition, low crude glycerol market price (90÷200 \$/kg [28]), associated to a high degree of molecular functionalization, makes the use of glycerol extremely important to the sustainability of the biodiesel industry, with an estimated number of 1500+ potential uses [29] (Table 8).

In this context, chemical valorization is increasingly addressed as the most important possibility offered by the overproduction of glycerol. Traditionally, the high price of glycerol limited the economic viability of such transformations, except for high value niche products; but nowadays, state-of-the-art research has disclosed chemical catalytic valorization routes from glycerol to drop-in (ex., propanediols, epichlorohydrin, glycidol, carboxylic acids, acrolein, allyl alcohol) and novel (ex., glycerol carbonate, glycidyl nitrate, novel ether/esters for fuel additives and polymer production) products.

In addition, the production of important chemical intermediates has also been revisited with respect to traditional oil-based processes. For example, processes using glycerol-derived allyl alcohol, epichlorohydrin or glycerol carbonate could substitute glycidol production from oil-

based allyl alcohol. This large grade of flexibility would have enormous market implications for glycidol and its family of products.

Table 8. Available and potential uses for crude glycerol [29].

| Field | Application |
|-------------------------------------|---|
| Chemical industry | Textile, plastic, explosive, polymer industries |
| Commodity chemicals | Natural organic building blocks |
| Pharmaceutical and oral care | Additive in drugs, heart disease drugs, health supplements, cosmetics, tanning agent |
| Food | Safe sweeteners, preservation, thickening agent |
| Livestock feed | Animal feed and feed supplements |
| Energy | Liquid fuel, conversion into energy carriers (H ₂ , syngas) for fuel production, conversion into ethanol, fuel for boilers and incinerators. |
| Biotechnology | Organic acids, Omega-3 succinic acid from fermentation, EPA (Eicosapentaenoic Acid) from fungi |
| Miscellaneous | Basic material in product formulation (foams, composites, adhesives, laminates, powders, UV-cured coatings, mouldings, fire resistant novel polyesters, solvents, anti-freeze and other end uses) |

Other processes have been completely reversed, as in the case of epichlorohydrin; while it was used in the past to produce synthetic glycerol, epichlorohydrin is now produced from biodiesel-derived glycerol.

Some other processes to highly functionalized oxidized molecules have been simplified and converted towards a higher environmental friendliness. For example, glyceric, mesoxalic and pyruvic acids involved a complex set of oxidation reactions with stoichiometric oxidative agents from hydrocarbon feedstock; the application of catalytic routes, preferentially heterogeneous, from glycerol could allow easier production of this fine chemicals in greener processes characterized by waste reduction and easier purification.

Good selectivity to the desired products at high glycerol conversion is of course the target in catalyst development, which is nowadays still difficult to obtain in some cases because of the extensive functionalization of glycerol itself and the presence of a complex set of reaction in series and in parallel (ex., hydrogenolysis, oxidation). Extensive research in careful catalyst design is therefore required, i.e. high initial R&D costs. In addition, an important challenge is represented by the usage of glycerol with high levels of contaminants; in this case, biological transformations could help circumvent the disadvantages of chemocatalysis. Therefore, both a novel catalytic process for production of biodiesel that can improve the purity of co-product crude glycerol and a cost effective method for refining and converting glycerol need to be developed. Nevertheless, the potential added value offered by glycerol chemical valorization is nowadays widely recognized and seen as an important factor in future implementation of market strategies, in order to face uncertainties linked to shortage of oil supply, to oil price volatility, and to vegetable oil price volatility.

2.4 References Chapter 2

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CHAPTER 3

GLYCEROL VALORIZATION TO CHEMICALS

3.1 Process modeling methodology

The field of study of conceptual design is the process design, i.e. the branch of chemical engineering dealing with the development of chemical process flowsheets. In particular, the main aim of conceptual design is to find the best flowsheet alternative of a particular process, or, in other words, find the set of process alternatives (selection of process units and the interconnections between them) and process variables in order to develop an “optimal” solution. The optimality has to be regarded as relative with respect to a particular process configuration which is supposed to be the best choice according to some KPIs (Key Performance Indicators). Therefore, the problem of the sustainability of a process can be approached on the basis of economic, environmental and social concerns.

In the present work, the conceptual design of glycerol valorization routes to chemicals is applied in order to develop process layouts to be implemented on an industrial scale. The fundamental aim is thus to quantitatively assess these processes on an economic and environmental perspective in order to produce significant results for the evaluation of the sustainability of glycerol-derived chemicals with respect to the oil-derived ones. The reference KPIs will be the specific operative economic potential [$\$/\text{kg}_{\text{product}}$] and LCA specific indicators (CED [$\text{MJ}_{\text{eq}}/\text{kg}_{\text{product}}$], EI99 [$\text{points}/\text{kg}_{\text{product}}$], GWP [$\text{kgCO}_{2,\text{eq}}/\text{kg}_{\text{product}}$]).

The process design procedure proceeds through a series of successively more detailed synthesis and evaluation stages, in which unit operations are progressively added to the process in order to accomplish the objective of the overall process itself. Therefore, the analysis

can be carried out by mean of a systematic approach; the problem is first approached by developing very simple solutions, then, according to partial quantitative results and/or heuristics, successive layer of detail are added by choosing among all the considered process alternatives. The rationalization of this hierarchical procedure is shown in Table 9 and Figure 13.

Since conceptual design is a useful tool to underline which is the potential best process layout, a precise and optimized quantitative evaluation of process KPIs is not the scope of the present work.

Process development has been performed with calculations in Aspen Plus® V8.6 and using basic reaction data and input information (T, P, x_i , WHSV, GHSV, χ , σ_i) from selected articles and publications.

Table 9. Design decisions for continuous processes [1].

| | |
|----------------|--|
| Level 1 | <i>Batch vs. Continuous</i> |
| Level 2 | <i>I/O structure of flowsheet</i> <ol style="list-style-type: none"> 1. Should we purify the raw material streams before they are fed to the reactor? 2. Should a reversible by-product be recovered or recycled to extinction? 3. Do we need gas recycle and a purge stream? 4. Are there any not valuable reagents we are allowed not to recycle? 5. How many product streams will there be? |
| Level 3 | <i>Recycle structure</i> <ol style="list-style-type: none"> 6. How many reactor systems are required? 7. How many recycle streams are there? 8. Should we use excess of one reactant? 9. Is a gas-recycle compressor required? 10. Should the reactor be operated adiabatically? |
| Level 4 | <i>Separation system</i> <ol style="list-style-type: none"> 11. What is the structure of the vapor and liquid separation systems? 12. Vapor recovery system 13. Is a vapor recovery system needed? 14. What is the best location of the vapor recovery system? 15. What is the best type of vapor recovery system to use? 16. Liquid separation system 17. What separations can be made by distillation? 18. What is the structure of the distillation train? 19. How should the light ends be removed? 20. Should the light ends be vented, sent to fuel or recycled to a vapor recovery system? 21. How should we accomplish the other separations? |
| Level 5 | <i>Heat integration network</i> |

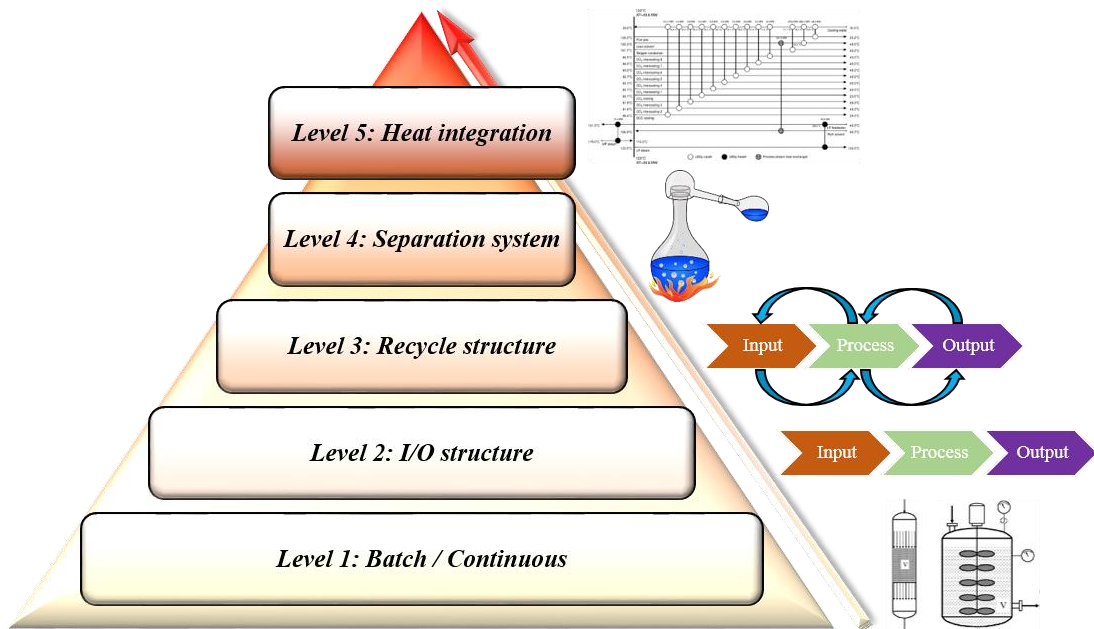


Figure 13. Conceptual design hierarchy of decisions.

The biorefinery concept lead to consider the process as a black box, in which from the bio-glycerol source we obtain a large variety of products (Figure 14). For this reason, a generic glycerol valorization process can be considered composed by three sections:

1. Glycerol pre-purification section.
2. Reaction and recycle section.
3. Purification section.

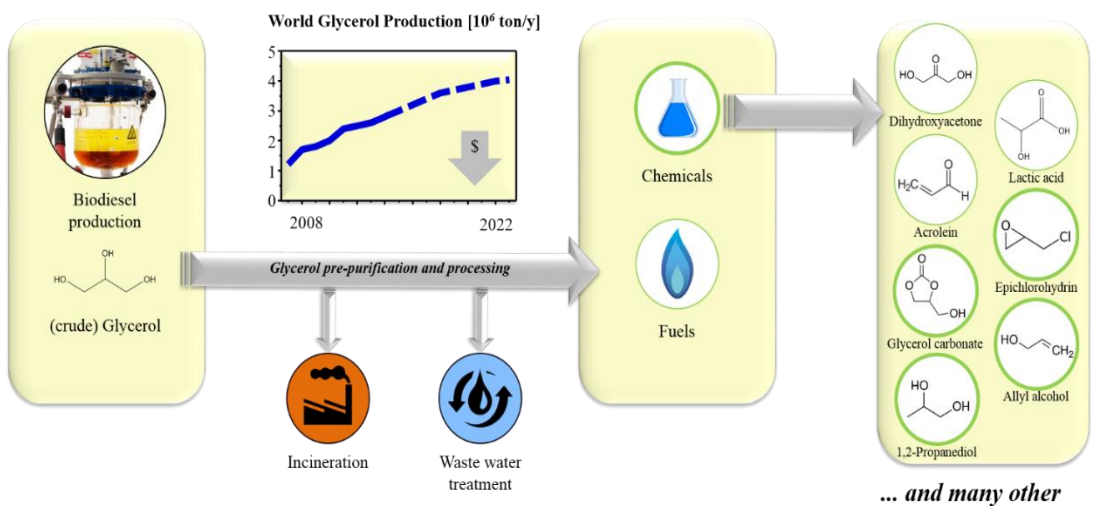


Figure 14. The biorefinery downstream scheme using glycerol as platform molecule.

In the biorefinery framework, glycerol supply is assumed to be constant from a central distribution and purification system, which is in common for all downstream processes. The composition of standard crude glycerol (Table 10) and the upstream processing correspond to

those reported in [2]. The same modelling assumptions are used.

The ash in the crude GLY is almost completely separated (99%) by conventional filtration (SSPLIT filter in Aspen Plus® V8.6) and used for landfill according to the Ecoinvent model [3]. Since in 70% of the US biodiesel production, sodium methylate represents the main constituent of the ash fraction, it is assumed that the ash solely comprises this chemical species [2]. The crude GLY stream is then treated through flash evaporation (FLASH2 separator in Aspen Plus® V8.6) at ambient pressure and 463 K to remove most of the methanol (92%) and the water (85%).

Table 10. Crude glycerol composition considered in the present work.

| Component | Concentration (% wt.) |
|------------------------|-----------------------|
| Glycerol | 76.5 |
| Water | 6 |
| Methanol | 3.3 |
| MONG (methyl stearate) | 9.6 |
| Ash (sodium methylate) | 4.6 |

MONG (Matter Organic Non Glycerol) refers to the residual organic fraction containing free fatty acids (FFAs), fatty acids methyl esters (FAMES) and glycerides deriving from the biodiesel transesterification manufacturing process. These impurities significantly affect glycerol properties and, thus, its conversion to value-added products [4]. Since stearic acid, in its ester and triglyceride form, is one of the most common saturated fatty acid found in nature, following palmitic acid [5], methyl stearate is considered as the representative compound for the non-glycerol organic matter in crude glycerol composition. Although the technology for MONG separation from crude GLY is industrialized by PALL® [6], it is not rigorously modelled: a separator in Aspen Plus® V8.6 is simply applied assuming 100% separation of MONG and of the remaining ash due to the lack of data on the process and as done in [2]. The methanol and MONG waste streams are both treated in a waste-to-energy incineration facility, modelled according to [7]. The upstream processing of crude GLY produces a stream consisting of Glycerol with minor amounts of H₂O (1.2%wt.) and Methanol (0.3%wt.).

A final important modeling assumption is related to the reactor process conditions. Since reference data for catalyst activity are taken from the literature, a strict constraint is put on the respect of the indicated process conditions; in other words, to directly transpose laboratory scale data for process modelling purposes, it is fundamental not to violate the process conditions given in the literature, especially in terms of composition.

Even though this approach does not take into account real conditions at the process scale, such as reactor feed impurities and reactor scale-up, it is believed that, for the objective of the present work, it still represent an important screening methodology to quantitatively analyze the proposed processes.

3.2 Process assessment methodology

A twofold criteria, economic and environmental, is used in order to quantify the sustainability of a process. The economic evaluation of a process focuses on the evaluation of operative costs only. In other words, the attention is given to a process supervision problem in which the economic load of the glycerol valorization route is evaluated in an already existing plant. Even though a proper techno-economic evaluation would encompass a detailed cost and asset accounting, capital costs estimation, and interests, taxes and depreciation evaluation in capital investment [8], this approach allows to better focus the analysis on significant process variables with respect to the sustainability of the proposed bio-based routes. In particular, two main points are considered relevant in the present economic analysis:

1. Process parameters affecting production costs.
2. Estimation of the specific product cost.

The outcome will then be a set of meaningful quantitative results and a process analysis in order to extract general guidelines for the evaluation of biomass valorization processes using glycerol as platform molecule. In particular, comparison with specific product costs for oil-based routes will be presented. Investment costs are outside of the scope of the present study, since the production plants were not optimized for a specific capacity.

The environmental assessment of a process, on the other side, consists in the evaluation of proper relevant environmental indicators, for the production of 1 kg of desired product, according to a life cycle analysis (LCA) approach. The process models were used for estimating the relevant LCI data, i.e. consumption of resources and process emissions, in a cradle-to-gate approach.

The guideline principles are simple: to assess environmental impacts associated with all the stages of a product's life (from raw material extraction through materials processing, manufacture, distribution, use, repair and maintenance, and disposal or recycling), by compiling an inventory of all relevant energy and material inputs and environmental releases (Figure 15). This approach allows:

- Evaluating the potential impacts associated with identified inputs and releases;
- Interpreting the results to help make a more informed decision [9].

Life-cycle analysis (LCA) is not new, but today as never before it is seen by scientists, manufacturers, and policymakers by a useful tool to expose opportunities for reducing environmental impacts across the entire life cycle of products, from production to disposal [10].

Once defined the functional unit and the system boundaries, the outcome of a LCA analysis consists in quantitative indexes, according to the impact categories chosen for the analysis

itself [11]. Three well-known LCA metrics were followed, i.e. the cumulative energy demand (CED), the global warming potential (GWP) and the eco-indicator 99 (EI-99) [12, 13]. CED measures the energy intensity of a product manufacturing process, i.e. the necessary amount of energy per unit of mass of product produced. EI-99 is a number indicating the environmental impact of a material, based on data from a life cycle assessment. The environmental load is calculated with respect to human health, ecosystem quality, and resources depletion according to a rather complex methodology involving standard LCA procedure, damages calculation (according to specific models, with respect to each of the three damage categories), and weighting of the three damage categories to obtain a final index. GWP correlates an energy/material stream with the equivalent amount of CO₂ released for the use, or treatment, of the stream itself. The GWP index is calculated by comparing the amount of heat trapped by a certain mass of the gaseous emission derived from the use/treatment of the stream to that trapped by an equivalent mass of CO₂.

Each input and output stream, energy or material, is associated to a particular LCA index value, according to selected databases [3]. In the case of CED, the non-renewable CED is calculated to focus on the depletion aspect for resource protection, which is the main motivation for a bio-based production.

According to the objective of the present analysis, the LCA procedure is applied only to the product manufacturing process (Figure 15), in order to assess the specific impact of the process itself; the extraction and production of raw materials is automatically taken into account in the definition of the LCA indexes, while an analysis of the complete supply chain to the final user is outside of the actual scope. Once again, the preparation and construction phase of the process site and the materials for the plant construction were not considered.

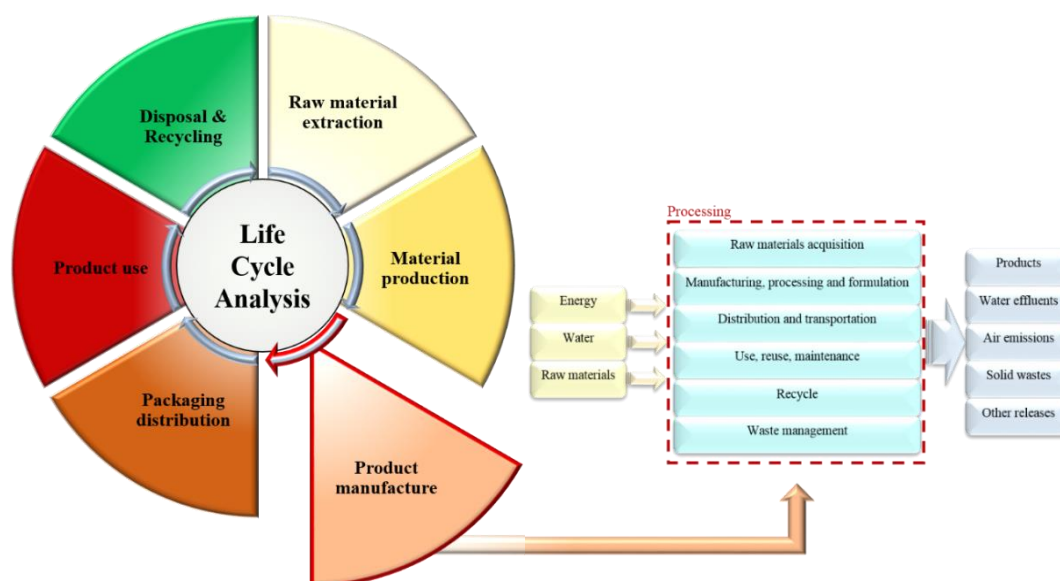


Figure 15. Full range of environmental impacts in a manufacturing process considered in the LCA [10].

3.3 1,2-propanediol

Propanediols (PDOs) are important commodity chemicals. 1,2-PDO has a valuable use as a less toxic alternative to other chemicals in paint, liquid detergent, cosmetics, food and tobacco and can be used as an antifreeze and de-icing agent. It is also extensively used as feedstock in the preparation of polyester resins for film, in fiber manufacture and in the pharmaceutical industry [14].

Even though various approaches, such as fermentation, hydroformylation-hydrogenation and hydration methods, are applied to manufacture propanediols by some companies, propanediols are most commonly produced from propylene via a process that involves selective propylene oxidation to propylene oxide and subsequent hydrolysis [14].

Glycerol can be converted into propanediols via catalytic hydrogenolysis, which provides a new promising synthesis route with respect to the propylene-based one from fossil sources.

3.3.1 Brief literature review

The overall stoichiometry of glycerol hydrogenolysis reaction to propanediols consists in the removal of H_2O and the addition of one H_2 ; depending on which hydroxyl group is removed, 1,2-PDO or 1,3-PDO is the favorite product. Competing reactions include the C-C breaking to ethylene glycol (EG) and over-hydrogenolysis of C-C and C-O bonds to monoalcohols and alkanes [15] (Figure 16).

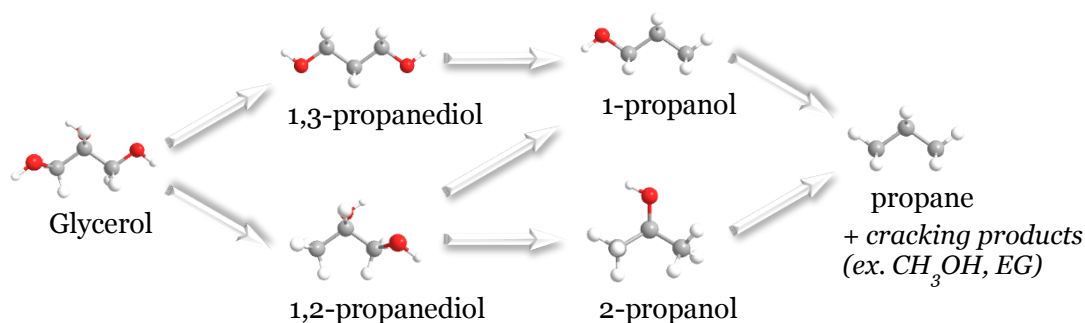


Figure 16. Pathways and products in glycerol hydrogenolysis [15].

The operating mechanism depends on the properties of the reaction systems, i.e. acidic, basic, metallic catalytic properties, and three typical reaction mechanisms (Figure 17) have been generally accepted, namely: dehydration-hydrogenation (acid catalysis), dehydrogenation-dehydration-hydrogenation (basic catalysis), direct-hydrogenolysis (noble metal catalysis).

Considering the accepted mechanisms, catalysts for the hydrogenolysis of glycerol have two catalytic functions, i.e. acidic/basic functionality dehydration and oxidation-reduction functionality for hydrogenation/dehydrogenation activity. Traditionally, the metal components of the catalysts play roles in activating hydrogen and the metal oxides or acidic or

basic supports are used to provide the acid-base function [14]. This has been demonstrated in several works using transition metals, typically Pt, Ru, Cu [16-19] in liquid phase, proposing both Lewis-acid catalyzed [20] or Brønsted-acid catalyzed [16] dehydration mechanism.

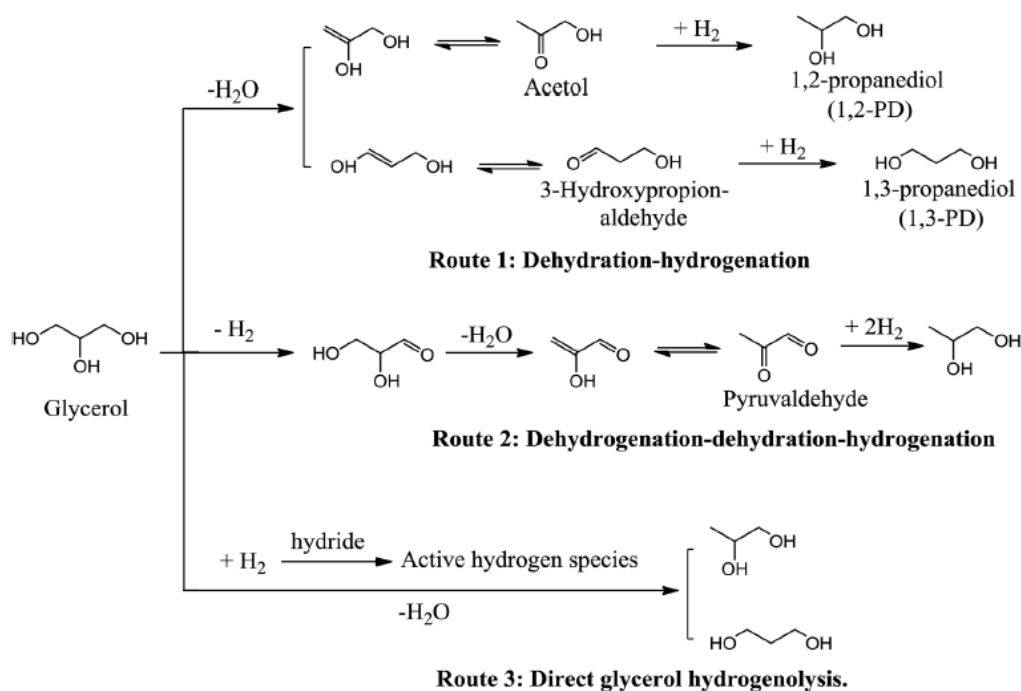


Figure 17. Proposed mechanisms of glycerol hydrogenolysis to propanediols [14].

However, from the abundant reports performed in liquid phase, it seems that the species of the loaded metals significantly affect the selectivity to 1,2-PDO rather than the acid-base properties of the supports.

Vapor phase hydrogenolysis has been widely addressed in [21-24] showing high activity and selectivity to 1,2-PDO for Cu-based, and Ag-doped Cu-based catalysts supported on Al_2O_3 or Cr_2O_3 . It has also been shown [25-27] that Cu catalyzes glycerol dehydration to acetol and its following hydrogenation to 1,2-PDO as well, therefore excluding any relevant catalytic function of the Al_2O_3 support. In addition, Cu is able to catalyze 1,2-PDO dehydrogenation to acetol but not the further dehydration to propanal and allyl alcohol.

It is nowadays commonly accepted that the support metal oxides, both for the liquid- and vapor-phase hydrogenolysis, seem to work only as inert supports for dispersing the metal component but do not seem to catalyze the dehydration step of glycerol into acetol in the formation of 1,2-PDO. Indeed, evidences are given, in the vapor-phase glycerol dehydration, by the difficulty to selectively obtain acetol over metal oxides catalysts, i.e. Al_2O_3 [25], ZrO_2 and TiO_2 [28].

A comprehensive review of relevant available catalytic studies for the liquid-phase glycerol hydrogenolysis is reported in Table 11.

Table 11. Catalysts for liquid-phase batch glycerol hydrogenolysis to 1,2-PDO [29].

| Catalyst | T [°C] | P [bar] | Glycerol / catalyst [g/g] | t [h] | X [%] | $\sigma_{1,2PDO}$ [%] | Ref. |
|---|-----------|------------|------------------------------|----------|----------|--------------------------|------|
| Precious metal catalysts | | | | | | | |
| Pt/SiO ₂ -Al ₂ O ₃ | 220 | 45 | 6.0 | 24 | 19.8 | 31.9 | [30] |
| Rh/SiO ₂ | 120 | 80 | 27.8 | 10 | 19.6 | 34.6 | [31] |
| Rh-Re/SiO ₂ | 120 | 80 | 27.8 | 2 | 38.4 | 46.9 | [32] |
| Ru/CeO ₂ | 180 | 50 | 12.5 | 10 | 85.2 | 62.7 | [33] |
| Ir/C | 180 | 50 | 10.1 | 24 | 85.0 | 76.0 | [34] |
| Ru/bentonite-TiO ₂ | 150 | 20 | 4.8 | 7 | 69.8 | 80.6 | [35] |
| Ru/CaZnMgAlO | 180 | 25 | 34.8 | 18 | 58.5 | 5.5 | [36] |
| Ag/Al ₂ O ₃ | 220 | 15 | 7.6 | 10 | 46.0 | 96.0 | [37] |
| Transition metal catalysts | | | | | | | |
| Copper-chromite | 200 | 21 | Unclear | 24 | 65.3 | 89.6 | [38] |
| Cu/ZrO ₂ | 200 | 40 | 16.7 | 8 | 10.0 | 90.0 | [39] |
| Cu/ZnO | 200 | 20 | 17.4 | 16 | 37 | 92 | [40] |
| Cu/boehmite | 200 | 40 | 20 | 6 | 77.5 | 92.5 | [41] |
| Cu/Al ₂ O ₃ | 220 | 50 | 10 | 6 | 61 | 93.3 | [42] |
| Cu/SiO ₂ | 240 | 80 | 166.7 | 5 | 51.9 | 96.6 | [43] |
| Cu/MgO | 180 | 30 | 7.1 | 20 | 72.0 | 94.6 | [44] |
| Cu/MgAlO | 180 | 30 | 7.1 | 20 | 80 | 98.2 | [45] |
| Co/ZnAlO | 200 | 20 | 13.3 | 12 | 70.6 | 57.8 | [46] |
| Raney Ni | 190 | 10 | 4 | 20 | 63 | 77 | [47] |
| Bimetallic catalysts | | | | | | | |
| Pd-Re/La ₂ O ₃ | 200 | 80 | 29.1 | 18 | 52.9 | 89.3 | [48] |
| Cu-Ru/TiO ₂ | 200 | 25 | 46.2 | 12 | 39 | 90 | [49] |
| Cu-Ru/bentonite | 230 | 100 | 5.5 | 18 | 100 | 86.4 | [50] |
| Cu-Ag/Al ₂ O ₃ | 200 | 15 | Unclear | 10 | 27 | 96.0 | [51] |
| Cu-Pd/MgAlO | 180 | 20 | 7.1 | 10 | 76.9 | 97.2 | [52] |

Almost all the precious metals can be used for glycerol hydrogenation into 1,2-PDO, while the supports play an important role on the catalytic activity of the precious metals by dispersing it. The acid-base property of the support affects the dispersion of the precious metals. Although the liquid-phase reactions are performed at relatively low temperatures, C-C bond cleavage products, such as methanol, ethanol, and ethylene glycol, are significantly produced over precious metal catalysts, except Ag, which shows almost complete selectivity. In all cases, both high conversion and high selectivity are difficult to be achieved at the same time, which indicates that 1,2-PDO is usually unstable in liquid-phase catalytic conditions and that consecutive reactions to monoalcohols and hydrocarbons occur [29].

Among the three base metals, Cu shows the highest activity for 1,2-PDO formation, since 1,2-

PDO cannot be selectively produced over Co- and Ni-based catalysts due to competitive C-C cleavage reactions. Selectivity higher than 90% can be achieved over most of the Cu-supported catalysts, and is favored by high dispersion and Cu small particle size. Comparing with precious metals, the lower C-C cleavage activity of Cu allows maintaining high 1,2-PDO selectivity with time, although hydrogenolysis of 1,2-PDO still proceeds slowly with increasing the reaction time [29].

Bimetallic catalysts have been developed and studied in order to exploit different metal features to obtain high 1,2-PDO yields. Proved synergistic effect, i.e. improved Ru dispersion in the presence of Cu, reduction of Cu species by Ag, improved H-spillover to Cu in the presence of Pd, allowed to reach selective glycerol conversions.

Finally, liquid-phase reaction panorama is closed by glycerol hydrogenolysis using in situ generated H₂ (Table 12).

Table 12. Catalysts glycerol hydrogenolysis to 1,2-PDO using in situ generated H₂ [29].

| Catalyst | T [°C] | P [bar] | Solvent (H donor) | Glycerol/catalyst [g/g] | T [h] | X [%] | $\sigma_{1,2PDO}$ [%] | Ref. |
|--------------------------------------|--------|----------------------|-------------------|-------------------------|-------|-------|-----------------------|------|
| Pt/NaY zeolite | 230 | 1 (air) | Glycerol | 5.3 | 15 | 85.4 | 64 | [53] |
| Pt-Sn/SiO ₂ | 200 | 3 (N ₂) | Glycerol | 4.1 | 2 | 54 | 59 | [54] |
| Pd/Fe ₂ O ₃ | 180 | 5 (inert) | 2-propanol | 5.1 | 24 | 100 | 94 | [55] |
| Cu/MgAlO | 200 | 30 (N ₂) | Ethanol | 8.1 | 10 | 93.9 | 93.1 | [56] |
| Ni-Cu/Al ₂ O ₃ | 220 | 45 (N ₂) | Formic acid | 10.9 | 24 | 89.9 | 81.6 | [57] |
| Pd/Co ₃ O ₄ | 180 | 5 (N ₂) | 2-propanol | 6.1 | 24 | 100 | 64 | [58] |
| Cu/ZnAlO | 220 | 35 (N ₂) | Methanol | 1.7 | 4 | 86.6 | 51.9 | [59] |

Differently from the previous hydrogenolysis processes, where H₂ is used as gaseous H-donor at high partial pressure, a catalytic transfer hydrogenation mechanism is here applied for the H-transfer from a liquid solvent to glycerol. An exhaustive summary of catalytic transfer hydrogenation (CTH) for glycerol hydrogenolysis to propanediols is reported in [60], therefore the mechanism details and the mechanistic insights will not be here reported. The in situ-generated hydrogen is supplied by the solvent donor (CTH), such as monoalcohols and formic acid, producing the corresponding carbonylic compound, or by glycerol itself via aqueous phase reforming (APR), producing CO and CO₂.

Vapor-phase glycerol hydrogenolysis into 1,2-PDO is finally the most desirable operation for industrial applications, even though not so many studies widely addressed it (Table 13).

Vapor phase reaction suffers of equilibrium limitations in the dehydration-hydrogenation steps to 1,2-PDO [21, 62]. Reaction conditions characterized by lower temperatures and higher hydrogen pressures shift the equilibrium from acetol to 1,2-PDO. At the same time, lower reaction temperatures inhibit glycerol dehydration to acetol, together with the formation of cracking products such as ethylene glycol.

Table 13. Catalysts for vapor-phase continuous glycerol hydrogenolysis to 1,2-PDO [29].

| Catalyst | T [°C] | P [bar] | WHSV [h ⁻¹] | TOS [h] | X [%] | $\sigma_{1,2PDO}$ [%] | Ref. |
|---|-----------|------------|----------------------------|------------|----------|--------------------------|------|
| Cu/Al ₂ O ₃ | 200-130 | 1 | 0.06 | 1-5 | 100 | 96.1 | [21] |
| Ag-Cu/Al ₂ O ₃ | 170-105 | 1 | 0.03 | 1-5 | 100 | 98.3 | [24] |
| Raney Cu | 205 | 14 | 0.18 | 6.2 | 100 | 95 | [27] |
| Cu/SiO ₂ | 255 | 15 | 2.2 | Unclear | 100 | 87 | [61] |
| Copper chromite | 200 | 1 | 0.04 | 0.5 | 100 | 55.5 | [62] |
| Cu-B ₂ O ₃ / SiO ₂ | 200 | 50 | 0.08 | 56 | 100 | 98 | [63] |
| Cu/SiO ₂ | 200 | 50 | 0.08 | 300 | 100 | 98.3 | [64] |
| Cu/CeO ₂ | 180 | 50 | 0.15 | 300 | 100 | 96.9 | [65] |
| Cu-ZnO/Al ₂ O ₃ | 190 | 6.4 | 0.08 | Unclear | 96.2 | 92.2 | [66] |
| Cu-ZnO/Al ₂ O ₃ | 250 | 32 | 2.8 | 12 | 100 | >90 | [67] |
| Cu-ZnO/Al ₂ O ₃ | 250 | 1 | 0.05 | 48.5 | 85.5 | 83.7 | [68] |
| Cu/SBA-15 | 220 | 1 | 1.03 | 10 | 90 | 84 | [69] |
| Ag/OMS-2 | 200 | 50 | Unclear | 92 | 30 | 65 | [70] |
| Ru/MCM-41 | 230 | 1 | 2.09 | 10 | 62 | 38 | [71] |

Since the dehydration and hydrogenation steps are respectively favored by high and low temperatures, a continuous direct process, over Cu/Al₂O₃ catalyst at atmospheric hydrogen pressure, was proposed in [21] by applying gradient temperatures across the catalytic bed: 96.1% 1,2-PDO yield is achieved at complete conversion. This study also showed how catalytic performances are not sensitive towards glycerol dilution, in the range of composition 30-94 wt. % aqueous glycerol. Further selectivity improvement, with reduction of ethylene glycol yield, has been presented in [24] by adding Ag to Cu/Al₂O₃, in order to inhibit the cracking activity of Cu. Due to the relatively low hydrogenation activity of Ag, an optimal solution at 98.3% 1,2-PDO yield was proposed with double-layered catalyst bed: Ag-Cu/Al₂O₃ is loaded on the high temperature zone (upper layer) while Cu/ Al₂O₃ is loaded in the low temperature zone (lower layer). The study was performed only for a 20 wt. % glycerol aqueous solution.

Other Cu-based catalysts has been investigated in isothermal conditions but performance comparable to those reported for layered catalyst beds could be reached only in the presence of high hydrogen pressure.

Finally, Ag- and Ru-based catalysts are also studied for the vapor-phase glycerol hydrogenolysis, whereas these catalysts do not show better catalytic performance than Cu-based catalysts.

3.3.2 Process design

Reference article selection

An industrially relevant process is chosen to develop a realistic and competitive process layout. Within this regard, considering activity data reported for the discontinuous liquid-phase process and the CTH/APR process, vapor-phase continuous glycerol hydrogenolysis has been directly addressed as the preferred reaction process.

A liquid-phase batch process has been discarded mainly due to the impossibility to reach high conversion and selectivity value at the same time, besides the reduced capacity of a batch plant. As a more interesting solution, CTH process has been properly analyzed with respect to the vapor-phase process (Table 14). Indeed, CTH has been recently addressed as a potential alternative process, which does not require handling of high pressure H_2 . In particular, some very interesting features arose in the presence of formic acid as most promising H-donor. On the process point of view, CO_2 as gaseous co-product does not lead to additional separation issues; on the sustainability point of view, valorization of formic acid from the Biofine¹ process [72] would lead to a complete sustainable process having waste raw materials as reagents. However, the premature state-of-the-art of CTH technologies, together with still high prices of formic acid, does not allow a process competitiveness with respect to the vapor-phase process [73]. Among the heterogeneous catalysts listed in Table 13, [21] is chosen as reference paper for activity data. Indeed, besides the high yield data, ambient pressure operation is reported, with relevant advantages in the process economics. In addition, activity data have been evaluated with respect to the initial mass composition of aqueous glycerol, in the range 30-94%; this would allow the generation of different process scenarios in order to evaluate the effect of different amounts of water in the system.

¹ Commercially viable technology for the fractionation of lignocellulosic biomasses to their monomeric constituents, to be further converted into valuable platform chemicals. Cellulose is hydrolyzed in pure water by attack by the electrophilic hydrogen atoms of the H_2O molecule on the glycosidic oxygen: acid catalysis is usually involved. The Biofine process uses dilute H_2SO_4 for the hydrolysis to monosaccharides, which then undergo multiple acid-catalyzed reactions to directly give the platform chemicals levulinic acid and furfural. Formic acid is a co-product in levulinic acid production.

Table 14. SWOT analysis for CTH process to 1,2-PDO.

| Strengths | Weaknesses |
|---|---|
| Do not require molecular H ₂ as reactant | Require a H-donor solvent as reactant |
| Easiness of storage, transport and pressurization of the solvent | Excess of solvent required to achieve 100% HTE |
| Energy benefit from liquid-phase process | Risk of condensation product formation in highly concentrated glycerol environment |
| Lower pressure process | Lower conversion and selectivity values |
| | Additional separating operations for solvent recycling |
| | Additional separating operations for carbonyl co-product (not for formic acid, where CO ₂ is easily separable) |
| Opportunities | Threats |
| Adding value to waste glycerol | Formic acid (most promising H-donor) expected to be an economic raw material as waste from the Biofine process |
| Adding value to potential bio-derived waste product (formic acid) | Availability of raw materials |
| Assure complete sustainability of the process | |
| No oil-based H ₂ dependency | |

Process modeling

The process can be roughly divided into three main blocks:

1. upstream processing of crude glycerol for removing ash, MONG and methanol;
2. catalytic gas-phase dehydration/hydrogenation of glycerol to 1,2-PDO;
3. condensation of the reactor effluent to remove recycle gases and further separation and purification of the liquid effluent into 1,2-propanediol and by-products.

Each step is described in detail below with respect to the process conditions and modelling assumptions except for step-1, which has been already mentioned before. Process layout is presented in Figure 18. For the sake of clarity, only relevant equipment is reported in the scheme.

A base reference capacity of 1000 kg/h of crude glycerol is considered for the calculations.

The glycerol-containing stream from step-1 is heated up to and evaporated at ambient pressure at 551K. A pure H₂ stream and the gaseous recycle stream are heated and mixed with the glycerol-containing stream at the inlet of the reactor; the fresh H₂ flow rate molar ratio is adjusted to obtain at the reactor inlet a H₂/glycerol molar ratio of 141 [21]. Whenever necessary, a dilution water stream is also added to obtain the desired concentration of glycerol at the reactor inlet (30-94 %wt., on H₂-free basis); water is evaporated and fed as vapor at 1 bar.

The reactor is a catalytic fixed bed reactor (RSTOICH reactor in Aspen Plus® V8.6). Hydrogenolysis reaction is performed at gradient temperatures [21]; since only yield data are relevant, isothermal conditions are adopted after verifying that the reactor heat load does not change significantly with temperature.

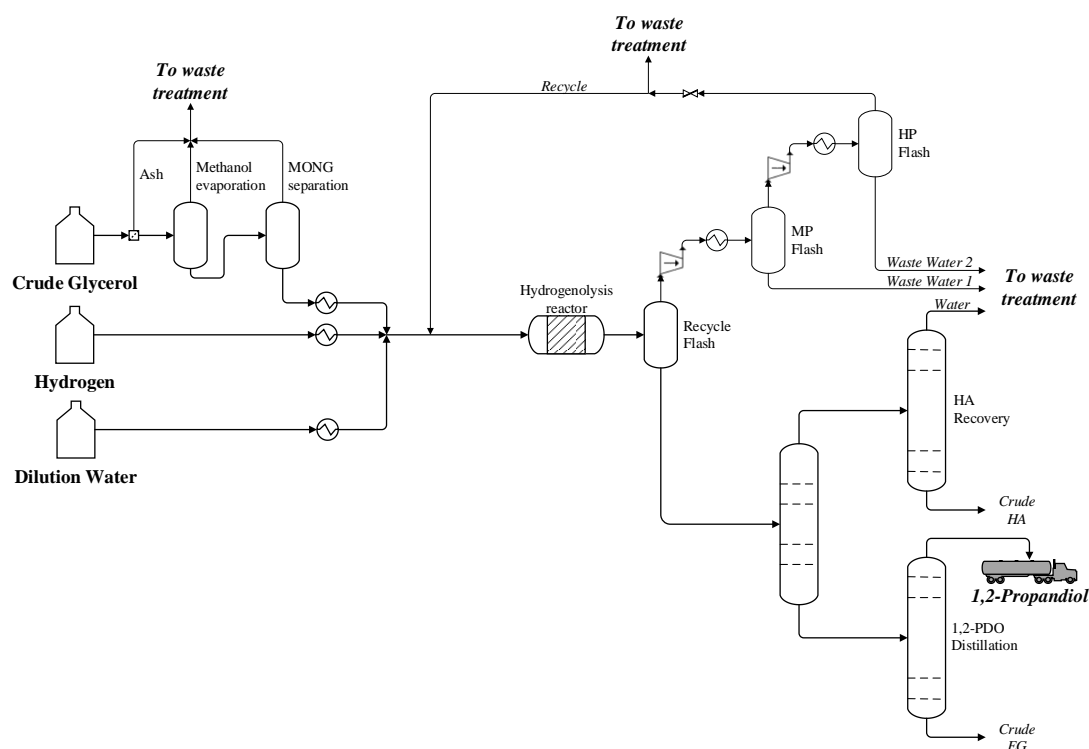


Figure 18. Process flow diagram for 1,2-propanediol manufacturing, with mixed sequence distillation.

Gradient temperature conditions help overcoming yield limitations related to a trade-off problem between the dehydration and the hydrogenation. The dehydration needs relatively high reaction temperatures, whereas the hydrogenation favors low temperatures; accordingly, a reactor inlet temperature of 473K is used, in front of a reactor outlet temperature of 403K. No further information is given by the authors about the features of the actual temperature gradient along the catalytic bed or about temperature control strategies. In any case, an externally cooled reactor is to adopt: outlet reaction temperature of 403K allows the use of cooling water, with generation of low pressure steam (2 bar).

For the process assessment of this unit, the use of conversion and selectivity-related information of the reactions taking place in the gas-phase hydrogenolysis of glycerol to 1,2-propanediol is sufficient [21]. The stoichiometric reactions considered in the present work are reported in Table 15.

Table 15. Stoichiometric reactions considered in the hydrogenolysis reactor.

| Description | Reaction |
|---|---|
| Glycerol hydrogenation to 1,2-PDO | $\text{GLY} + \text{H}_2 \rightarrow 1,2\text{-PDO} + \text{H}_2\text{O}$ |
| Glycerol dehydration to hydroxyacetone | $\text{GLY} \rightarrow \text{HA} + \text{H}_2\text{O}$ |
| Glycerol hydrogenation and cracking to ethylene glycol and methanol | $\text{GLY} + 2\text{H}_2 \rightarrow \text{EG} + \text{CH}_3\text{OH}$ |
| Glycerol hydrogenation to 1-propanol | $\text{GLY} + \text{H}_2 \rightarrow 1\text{-PO} + \text{H}_2\text{O}$ |

In the present analysis, without any additional information given by [21], 1-propanol is considered as the representative compound for other unspecified products obtained in the process.

Detailed information about the reaction kinetics, mass and heat transfer phenomena, pressure drop, *etc.*, would be required for a detailed design of a full-scale, plug-flow reactor, which is outside the scope of the present study.

The reactor effluent contains excess H_2 , H_2O , the main product 1,2-propanediol and by-products. Among all by-products, only ethylene glycol and hydroxyacetone could be exactly quantified from the available selectivity data (Table 16) while the residual by-products can only be quantified from the mass conservation balance and are assumed to consist only of 1-PO. As previously said, only 1-PO is taken as reference compound for residual by-products, as this is the heaviest component between those possibly present [24] (Table 17).

Table 16. Activity data for hydrogenolysis catalyst [21].

| Glycerol aqueous concentration (reactor inlet) [wt. %] | χ [%] | $\sigma_{1,2-PDO}$ [%] | σ_{HA} [%] | σ_{EG} [%] | σ_{other} [%] |
|---|---------------|---------------------------|----------------------|----------------------|-------------------------|
| 30 | 100 | 96.1 | 0.8 | 2.2 | 0.9 |
| 60 | 100 | 95.4 | 0.9 | 2.2 | 1 |
| 80 | 100 | 95.5 | 0.8 | 2.7 | 1 |
| 94 | 100 | 95.2 | 0.9 | 2.4 | 1.5 |

Table 17. List of components considered for 1,2-PDO manufacturing.

| Component | T_{nb} [°C] | MW [kg/kmol] |
|------------------------|------------------|-----------------|
| <i>Glycerol</i> | 288 | 92 |
| <i>Ethylene glycol</i> | 197 | 62 |
| <i>1,2-propanediol</i> | 188 | 76 |
| <i>Hydroxyacetone</i> | 146 | 74 |
| <i>Water</i> | 100 | 18 |
| <i>1-propanol</i> | 97 | 60 |
| <i>2-propanol</i> | 83 | 60 |
| <i>Ethanol</i> | 78 | 46 |
| <i>Methanol</i> | 65 | 32 |
| <i>Hydrogen</i> | -253 | 2 |

The reactor effluent is cooled down to 298K to condense and separate 1,2-propanediol from the gases. This preliminary operation results in a total removal in the gas phase of excess H_2 , as well as ca. 90% of residual 1-PO and methanol and 70% of water.

Due to the large excess of H_2 used in the reaction, a gas-phase recycle with purge was introduced. The purge ratio is adjusted to avoid accumulation of products, by-products and

impurities in the recycle loop, thus obtaining the desired glycerol concentration at the reactor inlet. It should be noted that, in the present work, all the impurities introduced in the reactor with the feed (methanol) or the recycle stream (methanol, 1-propanol) are considered inert in the catalytic reactor; in any case, their concentration was limited by keeping the glycerol/methanol molar ratio over 5.

Whenever a low water concentration is required at the reactor inlet (80 and 94 wt. % glycerol, on H₂-free basis), this is removed from the recycle stream using two additional compression stages, with intermediate cooling at 298 K and removal of the condensate. This way, the purge ratio and, thus, the amount of fresh H₂ required could be reduced. The pressure levels of the medium pressure (2 bar for 80 wt. % glycerol case, 5.5 bar for 94 wt. % glycerol case) and the high pressure (5 bar for 80 wt. % glycerol case, 30 bar for 94 wt. % glycerol case) flash stages are adjusted to obtain the desired water condensation, minimizing the purge ratio.

The condensates removed from the compression stages are sent to a conventional wastewater treatment facility or to an incineration facility depending on their net low heating value (min. LHV = 3 MJ/kg). The H₂-rich purge flow is sent to an incineration facility.

Since no particular separation challenges have been identified for the present system, i.e. non-ideal mixture behaviors, azeotropes, product thermal stability, product reactivity, a simple atmospheric distillation train can be adopted.

Column sequencing has been determined by simple heuristics considerations while column specifications have been set after proper sensitivity analysis in Aspen Plus® V8.6 in order to obtain reasonable sub-optimal values able to minimize the overall energy consumption of the distillation train. The number of trays is selected to obtain a column reflux ratio equal $1.3 \div 1.7$ times the minimum reflux ratio and the feed stage is determined as optimal feeding stage able to minimize the reflux ratio for a given number of stages. In addition, the number of trays is limited to keep the height/diameter ratio desirably lower than 30-40, to avoid possible structural deficiencies of the column. The sub-optimal values for the number of stages and design specifications found in one case (30 wt. % glycerol) have been used also in the other cases. The overall outcome of the separation section is a minimum mass recovery of 90% up to > 99% of hydroxyacetone, ethylene glycol, and 1,2-propanediol, with respect to the initial 1,2-PDO-rich stream.

A mixed column sequence is employed for the cases 60-80-94 wt. % glycerol, in which 1,2-PDO is first separated, from a water-rich stream containing HA, together with ethylene glycol. The product is then purified (min. 99.9 wt. %) with recovery of ethylene glycol (min. wt. 95 %). Hydroxyacetone (98 wt. %) is also recovered from the wastewater. A direct column sequence is employed for the case 30 wt. % glycerol, in which water is first separated, from a 1,2-propanediol-rich stream containing hydroxyacetone and ethylene glycol. Hydroxyacetone is then separated at the desired purity and finally 1,2-propanediol is purified with recovery of ethylene glycol (min. wt. 95%) (Figure 19).

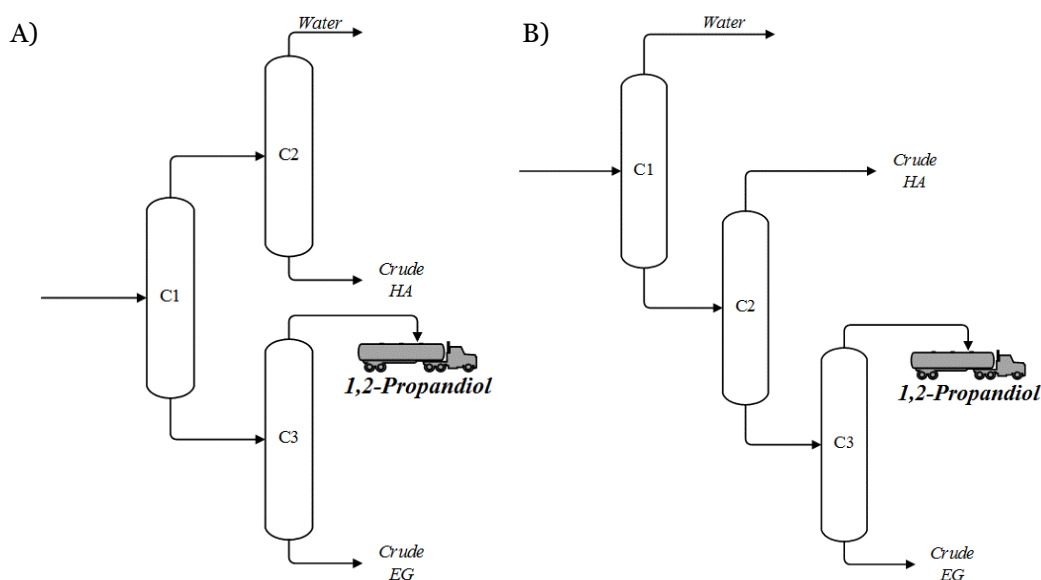


Figure 19. Mixed (A) and direct (B) distillation sequence respectively for 30-60-80 wt. % GLY and 94 wt. % GLY cases.

Modeling in Aspen Plus® V8.6 employed in all cases a RadFrac model for simple distillation columns, except for C₁ in which the RadFrac model with partial condenser has been considered (Condenser Vapor Fraction = 0.0015) to remove traces of hydrogen.

The water removed from the separation section is sent to a conventional wastewater treatment facility.

Due to the required energy intensive separations by distillation, process heat integration has been performed in order to reduce costs associated to thermal utility consumption (cooling water, steam, natural gas). High integration potential is present because of the high reaction and separation temperatures. Indeed, first principle calculations, performed on the case 80 wt. % GLY by pinch analysis methodology, reveal a ~75% hot utility saving with respect to the case without heat integration. The resulting heat exchanger network (Figure 20) has been designed according to heuristic considerations, considering a realistic minimum temperature approach of 10 K: with a very simple network of few heat exchangers, about 96.5% of the maximum integrable heat can be recovered. This can be attributed to the very high energy content associated to the reaction section, i.e. hydrogenolysis reactor, reactor effluent, vaporized reactor feed to be cooled to the reaction temperature.

As a result of this configuration, the total hot utility requirement is reduced by about 72%. According to the previous considerations, and due to the similarities between the different process cases, this result has been used for all cases.

3.3.3 Economic and environmental assessment

The background and inventory data used in this study for the environmental and

economic assessment with respect to the consumption of resources are presented in Table 18 and Table 19.

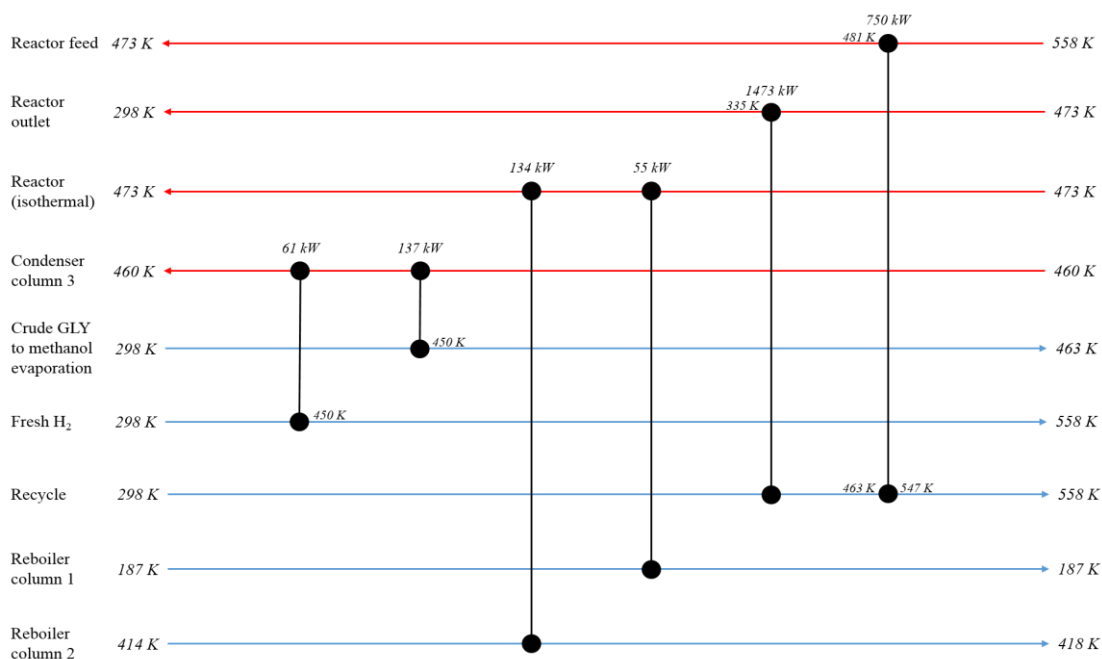


Figure 20. Heat exchanger network, according to heuristic considerations.

Table 18. Background data for the environmental (non- renewable resources) and economic assessment of 1,2-propanediol manufacturing process [3, 74, 75].

| Substance | CED (MJ _{eq} /kg) | EI99 (Points/kg) | GWP (kg _{CO2-eq} /kg) | Price (\$/t) |
|----------------------------------|-------------------------------|------------------------|-----------------------------------|-----------------|
| Process water | 2.8 · 10 ⁻⁴ | 1.8 · 10 ⁻⁶ | 2.4 · 10 ⁻⁵ | 1 |
| CuO | 31.0 | 4.54 | 1.95 | 3188 |
| Al ₂ O ₃ | 19.1 | 0.19 | 1.24 | 355.6 |
| Crude glycerol – to incineration | -19.7 | -0.063 | 0.20 | 111 |
| Crude glycerol – to WWTP | 9.97 | 0.021 | 0.92 | 111 |
| Steam | 1.57 | 0.01 | 0.10 | 20 |
| Electricity* | 9.87 | 0.02 | 0.49 | 0.10 |
| Cooling water from river | 0.00 | 0.00 | 0.00 | 0.15 |
| H ₂ | 69.7 | 0.24 | 1.67 | 3404 |
| Natural gas** | 1.24 | 0.004 | 0.012 | 0.01 |
| Hydroxyacetone*** | 56.4 | 0.16 | 1.91 | 5000 |
| Ethylene Glycol | 51.2 | 0.18 | 1.57 | 815.3 |
| 1,2-propanediol | 99.9 | 0.33 | 4.07 | 1420 |
| Ash disposal | 0.28 | 0.02 | 0.009 | - |

*Electricity is measured per kWh.

**The values for natural gas are measured per MJ and they refer to heat-production purposes.

*** Since no database values are present, LCA background data for HA are calculated with FineChem.

Table 19. Inventory data used for the environmental and economic assessment of 1,2-PDO manufacturing process.

| Materials and energy | Production of EPCH | | | | Units |
|-----------------------|--------------------|----------|----------|----------|-------------------------|
| | 94 wt. % | 80 wt. % | 60 wt. % | 30 wt. % | |
| Crude glycerol | 1.74 | 1.73 | 1.71 | 1.70 | kg/kg _{1,2PDO} |
| Hydrogen | 0.123 | 0.172 | 0.222 | 0.222 | kg/kg _{1,2PDO} |
| Process water | 0 | 0 | 0.101 | 1.92 | kg/kg _{1,2PDO} |
| Hydroxyacetone | 0.006 | 0.006 | 0.009 | 0.022 | kg/kg _{1,2PDO} |
| Ethylene glycol | 0.021 | 0.023 | 0.023 | 0.019 | kg/kg _{1,2PDO} |
| Catalyst | 0.005 | 0.006 | 0.006 | 0.008 | kg/kg _{1,2PDO} |
| Heat | 1.62 | 4.72 | 5.12 | 6.57 | MJ/kg _{1,2PDO} |
| Natural gas | 0.422 | 1.23 | 1.33 | 1.71 | MJ/kg _{1,2PDO} |
| Electricity | 29.9 | 12.4 | 0 | 0 | MJ/kg _{1,2PDO} |
| Cooling water | 410 | 315 | 120 | 153 | kg/kg _{1,2PDO} |
| Ashes | 0.095 | 0.094 | 0.093 | 0.092 | kg/kg _{1,2PDO} |
| Wastewater | 0.165 | 0.278 | 0.345 | 2.13 | kg/kg _{1,2PDO} |
| Waste to incineration | 0.579 | 0.490 | 0.558 | 0.574 | kg/kg _{1,2PDO} |

The different modelled scenarios evidence the glycerol concentration at the reactor inlet as key parameter affecting process specific energy and material consumptions, while at the same time not influencing catalyst activity and stability. The most important cost- and environmental-effective influenced variables are (Figure 21):

1. Distillation train energy consumption.
2. Recycle/purge ratio.
3. Fresh H₂ consumption.
4. Compression work.
5. Process water consumption.
6. Waste streams.

The specific energy consumption of the separation and purification section is directly affected by the amount of water to be separated and, therefore, the grade of dilution of the system. The hot utility consumption is indicative of this, i.e. steam and natural gas, required by the process (Table 19) and of which the distillation train is the main contributor.

Higher amount of water leads to more difficult purification of diluted streams in order to reach the final specification for products to be separated, i.e. 1,2-propanediol, hydroxyacetone, ethylene glycol. In particular, the duty required by columns C₁ and C₂ in the mixed distillation sequence and column C₁ in the direct distillation sequence is largely affected, accounting for up to 60% of the distillation train energy consumption in the most diluted scenario, since they are involved in water separation.

The purge ratio, fresh H₂ consumption and compression work are all affected by the

configuration of the recycle structure and are automatically controlled in order to respect the required inlet reaction conditions. The lower the required dilution, the higher the purge ratio and the compression work are, due to the need to limit the amount of recycled water to the reactor. In addition, as a consequence of the larger purge ratio, higher amount of fresh H_2 is required.

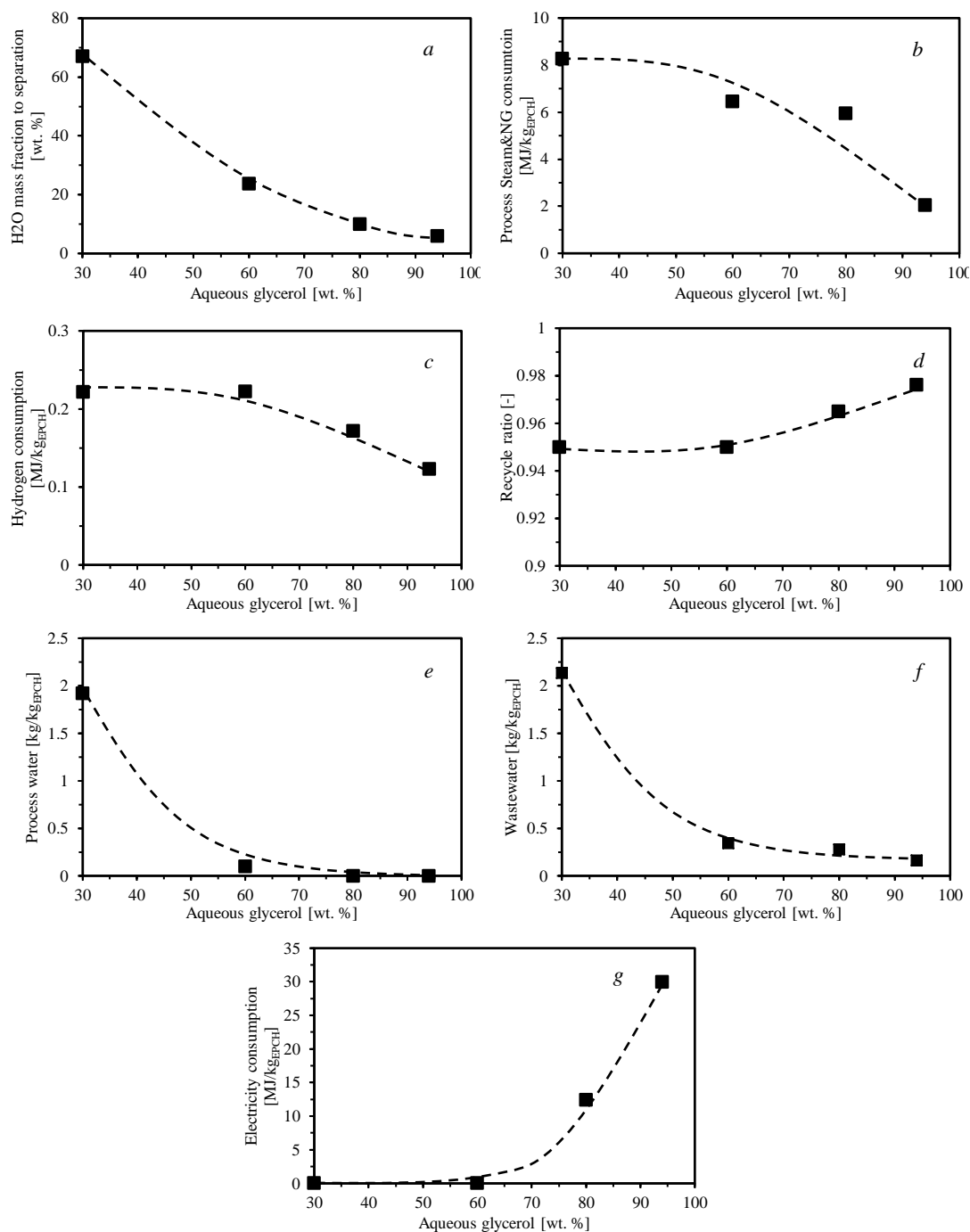


Figure 21 Effect of glycerol dilution on (a) water content of the stream to purification, (b) hot utility consumption, (c) H_2 consumption, (d) recycle ratio, (e) process water consumption, (f) wastewater amount, (g) electricity consumption.

Since both costs related to electricity (energy) and H₂ (material) consumption represent a relevant cost factor, a nearly optimal situation has been calculated balancing the compression pressure level and the purge ratio, for the 80% and 94% scenarios. No compression costs are present in the 30 and 60 % scenarios, since there are no issues related to water accumulation at the reactor inlet, which is controlled by the amount of process water fed to the process: in these cases, the purge ratio has been fixed to a safety value in order to prevent methanol build-up in the recycle.

The amount of process water required by the process is strictly correlated to the required grade of dilution. In the 60% and 30% cases, process water is required to reach dilution specifications which could not be reached by exploiting water build-up in the recycle. This consumption corresponds to higher volumes of wastewater streams to be treated.

Assessment results for the different scenario are reported in Figure 22 and reflect previous considerations.

Since one of the main drivers for a bio-based production of chemicals is to decrease the dependence on non-renewable fossil resources, the non-renewable LCA indexes are reported with respect to the production of 1 kg of products and to the single contributions provided by process material, energy, and waste treatment requirements. In addition, no alternative fate for crude glycerol was considered, i.e. CED, EI-99, GWP equal to zero for crude glycerol; if the assessment is performed with respect to particular alternative fate for crude glycerol, the corresponding metric has to be subtracted in order to take into account for the use of glycerol as raw material for chemical production and not as a waste (Table 20).

In this context, the environmental impact of all scenarios, for both the considered alternative fates for crude glycerol, is in all cases lower compared to those for oil-based 1,2-propanediol. The only exception is in the CED metric for the 94% scenario.

In particular, if the alternative fate of glycerol is the treatment in wastewater treatment plants, the environmental impact for 30%, 60% and 80% scenarios attains values lower than those corresponding to the WWTP plant. This indicates that using glycerol to produce 1,2-propanediol has a smaller impact than treating crude glycerol as a conventional waste. On the other side, if the energy content of the crude glycerol stream is valorized in a waste-to-energy incineration plants, higher LCA index values are found except for the GWP in the 30%, 60% and 80% scenarios.

This behavior was already expected, since glycerol treatment in incineration facilities produces more favorable conditions in terms of energy recovery (negative CED) and since no direct emission of crude glycerol waste into the environment is produced (negative EI-99), even though CO₂ emissions are expected due to thermal valorization (positive GWP). In comparison, chemical valorization encompasses energy utilization and waste production to obtain the desired chemical conversion, which in any case produces less environmental impact than those expected for oil-based 1,2-propanediol.

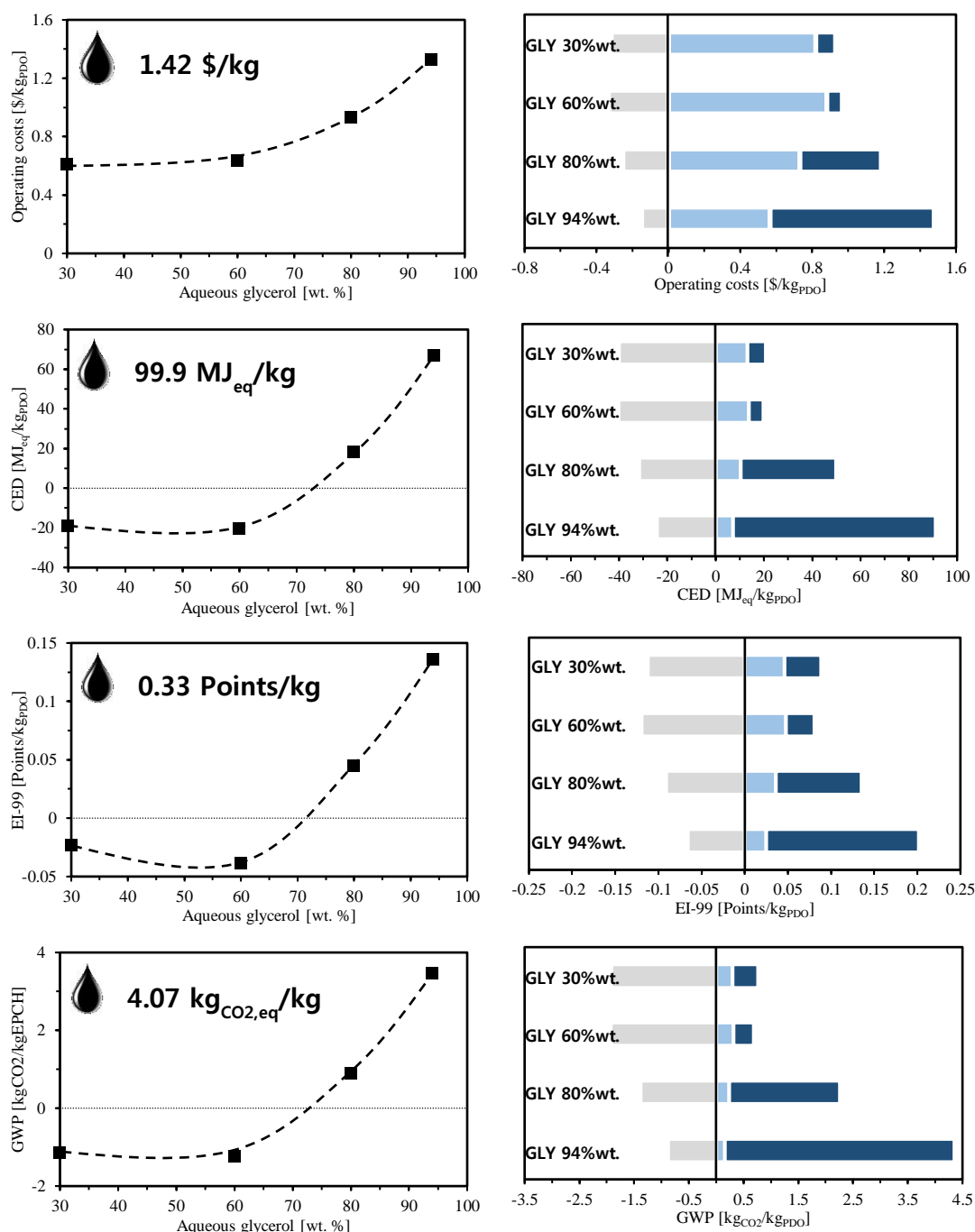


Figure 22. Economic and environmental assessment results for glycerol-to-1,2-PDO manufacturing process (■ material, ■ energy, ■ waste). No crude glycerol alternative fate considered.

Looking at the categories contributing to the environmental impacts, it is clear that the main difference lies in the energy consumption of the processes. A closer look reveals that the use of electricity in compressors dominates the behaviors of the 80% and 94% scenarios, totally overcoming the more favorable hot utility consumption as a result of the lower grade of dilution of the system. Process material requirement is a relevant voice in the overall

environmental impact and mostly accounted by fresh H₂ consumption: its relative weight among the scenarios is not however a decisive factor, since recycle ratios are attained in the narrow 0.95÷0.98 range. As a consequence of this, also the waste relative influence is not of particular relevance: it has however to be noticed how waste treatment is dominated by thermal valorization of the purge stream (> 99 mol. % H₂), leading to very positive contributions related to energy recovery (CED, Price) and to simple H₂O emission with respect to H₂ (EI-99, GWP).

Table 20. Economic and environmental assessment results for glycerol-to-1,2-PDO manufacturing process considering crude glycerol alternative utilization scenarios in incineration facilities or wastewater treatment plants.

| Scenario | LCA metric | Alternative crude glycerol fate | |
|----------|---|---------------------------------|---------|
| | | To incineration | To WWTP |
| | <i>CED (MJ_{eq}/kg_{PDO})</i> | 101.12 | 49.43 |
| | <i>EI-99 (Points/kg_{PDO})</i> | 0.25 | 0.099 |
| | <i>GWP (kg_{eq,CO2}/kg_{PDO})</i> | 3.12 | 1.87 |
| | <i>CED (MJ_{eq}/kg_{PDO})</i> | 52.49 | 1.11 |
| | <i>EI-99 (Points/kg_{PDO})</i> | 0.15 | 0.0086 |
| | <i>GWP (kg_{eq,CO2}/kg_{PDO})</i> | 0.55 | -0.70 |
| | <i>CED (MJ_{eq}/kg_{PDO})</i> | 14.04 | -36.56 |
| | <i>EI-99 (Points/kg_{PDO})</i> | 0.071 | -0.072 |
| | <i>GWP (kg_{eq,CO2}/kg_{PDO})</i> | -1.54 | -2.77 |
| | <i>CED (MJ_{eq}/kg_{PDO})</i> | 15.38 | -35.06 |
| | <i>EI-99 (Points/kg_{PDO})</i> | 0.086 | -0.057 |
| | <i>GWP (kg_{eq,CO2}/kg_{PDO})</i> | -1.44 | -2.66 |
| | <i>CED (MJ_{eq}/kg_{PDO})</i> | | 17.0 |
| | <i>EI-99 (Points/kg_{PDO})</i> | | 0.036 |
| | <i>GWP (kg_{eq,CO2}/kg_{PDO})</i> | | 1.56 |
| | <i>CED (MJ_{eq}/kg_{PDO})</i> | -33.5 | |
| | <i>EI-99 (Points/kg_{PDO})</i> | -0.11 | |
| | <i>GWP (kg_{eq,CO2}/kg_{PDO})</i> | 0.34 | |

* Values corresponding to the reported glycerol indexes, multiplied by 1.7 kg_{GLY}/kg_{PDO}.

Finally, operating costs for the difference scenarios fully reflect previous considerations regarding material and energy consumptions. Same trends are observed as the environmental impacts, underlying once more the decisive influence of electricity consumption also on the process economics. Considering material requirements (0.6÷0.8 \$/kg_{PDO}) and waste contribution dominated by positive H₂ thermal valorization (-0.2÷-0.4 \$/kg_{PDO}), product costs in the range 0.6÷1.4 \$/kg_{PDO} are obtained, with the most diluted 30% and 60% cases providing the most favorable scenarios. For these cases, significant margin of ~0.8 \$/kg_{PDO}, with respect to the oil-based route, provides a promising alternative for 1,2-propanediol production, also in

the case of future increasing glycerol prices. Additionally, one has to consider the different technology readiness levels between the industrial production and the processes presented here, as well as that the investment costs have not been included.

3.4 Glycerol carbonate

Glycerol carbonate is one of the most celebrated products from glycerol reported in the last years, due to its physical properties as well as on its reactivity. GC is a not flammable, water-soluble, biodegradable, nontoxic, and viscous liquid with a very low volatility (bp 110-115°C at 0.1 mmHg). In addition, the renewable content of this molecule ranges from 76%, if obtained from glycerol and another raw material different from CO₂, and 100%, if manufactured directly from glycerol and CO₂. GC has also an almost unique number of reactive sites, which open numerous possibilities for using GC as a raw material for synthesizing chemical intermediates as well as polymers such as polyesters, polycarbonates, hyperbranched polyglycerols, polyurethanes, and non-isocyanate polyurethanes (NIPUs) with a lot of potential applications in the manufacture of useful materials such as coatings, adhesives, foams, and lubricants [76, 77]. All these features make GC a green chemical that can be used in a number of applications (Figure 23). However, due to market price higher than 8 \$/kg and the novel nature of this chemical, it is still not widely used in commercial application, with a reported limited usage of only few ktons per year [78].

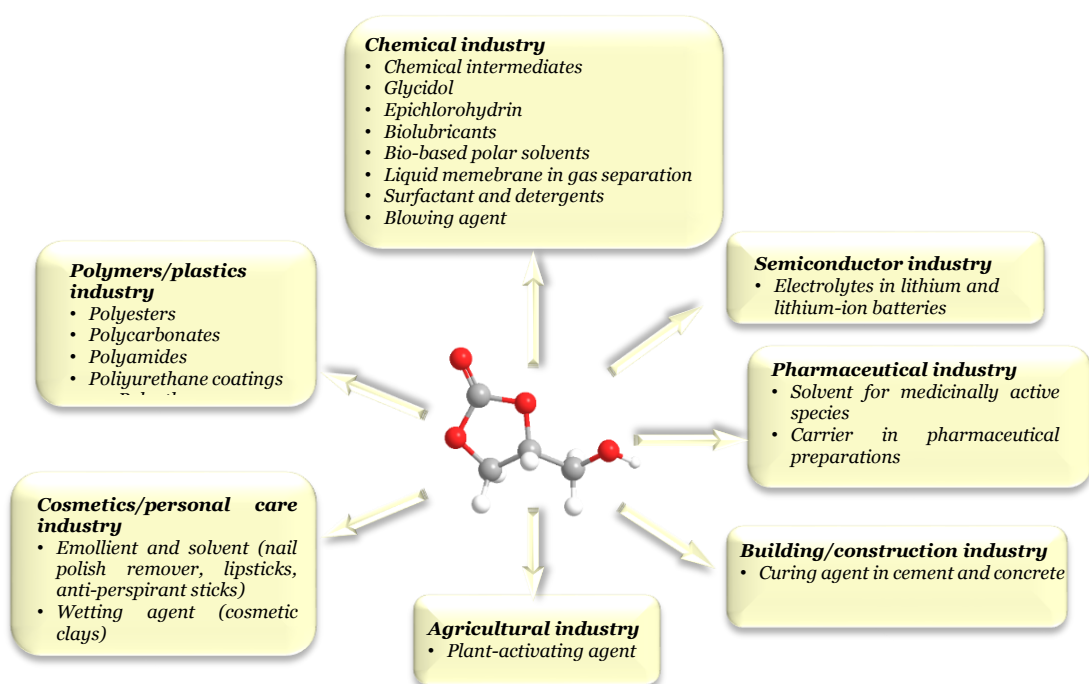


Figure 23. Potential uses of glycerol carbonate in various industries [77].

3.4.1 Brief literature review

Several routes to upgrade the large quantities of waste glycerol into glycerol carbonate were investigated [77]. The most promising routes are focusing on reactions based on inexpensive, bio-based and readily available raw materials in a chemical cycle that overall results in the chemical fixation of CO₂ [79]. The state of the art has always addressed the investigation of these different routes in liquid-phase batch operations and under mild temperature conditions ($T < 423$ K), using homogeneous or heterogeneous catalyst salts (Table 21)

In the direct synthesis of glycerol carbonate from glycerol, carbon monoxide or carbon dioxide are used as carbonating agents. Two types of catalytic systems were reported using CO + O₂: Cu(I)-catalysts and PdCl₂ (1,10-phenanthroline) with KI. This synthetic route had limited uses because of the toxicity of carbon monoxide and the inherent difficulty to handle it safely both at laboratory and industrial scales [79].

Catalytic glycerol carboxylation by CO₂ has also been investigated. Sn-catalysts were the first reported, showing how the addition of alcoholic solvents tends to accelerate the rate and improve the yield. However, due to thermodynamic limitations, reported yields were quite low. An alternative proposed synthetic approach consists of three steps: CO₂ capture through carbonation source formation (K₂CO₃ or KHCO₃), 3-chloro-1,2-propanediol synthesis from glycerol, conversion into glycerol carbonate from the reaction with the previously made carbonation source. Yields up to 80% glycerol carbonate, together with substantial production of glycidol were obtained. The same approach was also proposed using triethylamine as both a solvent and a CO₂ fixation and activation agent, obtaining glycerol carbonate yield of 90%. From an ecological point of view, the direct carbonation of glycerol has the advantage of using glycerol, which is a bio-based reactant, and a waste produced by other industries. However, most synthesis methods require the use of organic solvents, uneasily recoverable and/or homogeneous catalysts, high pressure and long reaction times, which have negative ecological impacts.

Indirect synthesis routes consist of transcarbonation reaction, i.e. carbonate exchange reaction between alcohols and carbonate sources. Conversion from one carbonate to another results from the nucleophile attack of the carbon atom of the carbonate group by the oxygen atom of the hydroxyl group of the alcohol. Therefore, glycerol carbonate can be obtained by the transcarbonation of a carbonate source with a 1,2-diol, such as glycerol [79].

Three types of carbonate sources were reported: phosgene, not of interest anymore due to safety and environmental issues, alkylene carbonate (ethylene carbonate, propylene carbonate) and dialkyl carbonate (dimethyl carbonate, diethyl carbonate).

Ethylene carbonate and propylene carbonate are commercially available chemical produced

from ethylene oxide and propylene oxide [80]. Similar reaction conditions are employed for both carbonating agents, i.e. $T < 80\text{ }^{\circ}\text{C}$ and P down to 35 mmHg to have favorable thermodynamic reaction conditions (higher equilibrium constant and easier removal of the glycol co-product). Several catalytic systems were reported to provide good yields: basic zeolites, Amberlyst ion exchange resins, basic oxides (MgO) or hydrotalcite-derived mixed oxides, ionic ammonium salts immobilized on MCM.

The most studied dialkyl carbonates are dimethyl carbonate (DMC) and diethyl carbonate (DEC). As an environmentally benign chemical, which can be prepared from methanol and urea, dimethyl carbonate has attracted several interests [79] and its synthetic route to glycerol carbonate is one of the most studied. A large selection of catalysts have been proven to work: alkylammonium salts, K_2CO_3 , Sn-catalysts, base catalysts i.e. CaO, MgO, hydrotalcite-derived materials, metal-exchanged hydrotalcite-derived materials, hydroxyapatite. Also enzymatic ways have been studied, not here reported.

From an ecological point of view, transcarbonations from cyclic alkylene carbonate or dialkyl carbonate have the same advantage. Some synthesis methods present additional environmentally-friendly characteristics, since they require no organic solvent, heterogeneous and/or easily recoverable catalysts (ion exchange resins, zeolites, oxides), and work under atmospheric pressure for a moderate reaction time and temperature. However, some other synthesis methods require the use of organic solvents and uneasily recoverable and/or homogeneous catalysts, which have negative ecological impacts.

Finally, the catalytic synthesis of glycerol carbonate from glycerol and urea is attractive considering the environmental friendliness of reactants and the easiness of co-product separation, NH_3 . Lewis catalysts produce satisfying results.

The reaction of glycerol with urea leads to the production of high quantity of ammonia as a co-product, which is limiting its industrial implementation. A possible solution would be to combine on the same plant a chemical unit producing glycerol carbonate from urea with other chemical units consuming its ammonia by-product, ex. regeneration of urea.

A list of operative conditions for the catalytic conversion of glycerol to glycerol carbonate is reported in Table 21. Despite the fact continuous operations are industrially more relevant and attractive than a discontinuous processes, the only promising study for the continuous conversion of glycerol to glycerol carbonate has been presented, since now, in [81]. In this study, solvent screening, catalyst screening, and technical shape formulation of the catalyst were studied. Hydrotalcite-derived Mg-Al mixed metal oxides, formulated in a technical body with bentonite as binder, were identified as superior catalytic heterogeneous materials able to reach 60 % glycerol carbonate yield with complete selectivity. The reaction is carried out in the liquid phase using γ -butyrolactone (GBL) as solvent, at 423 K and 10 mbar; stoichiometric urea/glycerol ratio is used. Stability tests also showed high performance stability, with deactivation down to 45 % yield due to fouling and complete restoration of catalyst activity

after calcination and burning-off of the carbonaceous materials.

Table 21. Experimental conditions for batch glycerol carbonate synthesis from glycerol [77, 79].

| Reactants | Solvent | Catalyst | T [°C] | P [bar] | t [h] | Y [%] | Ref. |
|---|--------------|--|-----------|------------|----------|----------|-------|
| <i>Direct synthesis routes</i> | | | | | | | |
| Excess CO/O ₂ | - | 10 mol. % CuCl ₂ | 110 | 6 | 63 | 47 | [82] |
| Excess CO/O ₂ | Nitrobenzene | 10 mol. % CuCl ₂ | 130 | 8 | 20 | 96 | [82] |
| Excess CO/O ₂ | DMF | 0.25 mol% PdCl ₂ +2.5 mol% KI | 140 | 30 | 2 | 85 | [83] |
| Excess CO ₂ | - | 6 mol. % Bu ₂ Sn(OMe) ₂ | 180 | 50 | 15 | 7 | [84] |
| Excess CO ₂ | MeOH | 1 mol. % Bu ₂ SnO | 80 | 35 | 4 | 35 | [85] |
| Excess CO ₂ | MeOH | RhCl ₃ + PPh ₃ + KI | 140 | 50 | 59 | 0.24 | [86] |
| 1:3:3 (K ₂ CO ₃ -HCl-gly) | - | KOH, HCl | 80 | 1 | 0.5 | 80 | [87] |
| 1.5:1:1 (NEt ₃ -HCl-gly) | - | - | 100 | 25 | 1 | 90 | [88] |
| <i>Indirect synthesis routes</i> | | | | | | | |
| 2:1 (EC-gly) | - | Amberlyst A26 HCO ₃ ⁻ | 80 | 1 | 1 | 88 | [89] |
| 2:1 (EC-gly) | - | Zeolite | 80 | 1 | 2 | 81 | [89] |
| 2:1 (EC-gly) | - | 7 wt. % Al/MgO hydrotalcite | 50 | 1 | 5 | 82 | [90] |
| 2:1 (EC-gly) | - | MgO | 50 | 1 | 5 | 78 | [90] |
| 2:1 (EC-gly.) | - | 7 wt. % Al/Mg hydrotalcite | 50 | 1 | 5 | 68 | [90] |
| 2:1 (EC-gly) | - | RNX-MCM41 | 80 | 1 | 1.5 | 92 | [91] |
| 2:1 (DMC-gly) | - | 3.3 mol. % Bu ₄ NBr | 120 | 1 | 6 | 92 | [92] |
| 3:1 (DMC-gly) | - | K ₂ CO ₃ | 75 | 1 | 3 | 97 | [93] |
| 1:1 (DMC-gly) | - | 6 mol. % Bu ₂ Sn(OMe) ₂ | 180 | 50 | 15 | 65 | [84] |
| 3:1 (DMC-gly) | - | CaO | 75 | 1 | 1.5 | 91 | [94] |
| 2.5:1 (DMC-gly) | Benzene | CaO | 60 | 1 | 2 | 95 | [95] |
| 5:1 (DMC-gly) | DMF | Uncalcined Mg-Al hydrotalcite | 100 | 1 | 1 | 75 | [96] |
| 2:1 (DMC-gly) | - | 3 wt. % KF/hydroxyapatite | 78 | 1 | 1 | 99 | [97] |
| 5:1 (DMC-gly) | - | Mg/Al/Zr | 75 | 1 | 1.5 | 95 | [98] |
| 5:1 (DMC-gly) | DMF | Calcined hydrotalcite-hydromagnesite | 100 | 1 | 0.5 | 79 | [99] |
| 1:1 (Urea-gly) | - | Calcined manganese sulfate | 150 | 0.04 | 2 | 61 | [100] |
| 1:1 (Urea-gly) | - | ZnS | 140 | 0.03 | 2 | 86 | [101] |
| 1:1.5 (Urea-gly) | - | CaO, La ₂ O ₃ , MgO, ZrO ₂ , Al ₂ O ₃ | 150 | 0.11 | 3 | 28-93 | [102] |
| 1:1 (Urea-gly) | - | Zirconium phosphate | 145 | 0.0002 | 3 | 80 | [103] |
| 1:1 (Urea-gly) | - | Calcined Zn-hydrotalcite | 145 | 0.039 | 5 | 72 | [90] |
| 1:1 (Urea-gly) | - | Co ₃ O ₄ /ZnO | 145 | 1 | 4 | 69 | [104] |
| 1.5:1 (Urea-gly) | - | Au, Ga Zn on oxides and ZSM-5 | 150 | 1 | 4 | 55 | [105] |
| 1:2 (Urea-gly) | - | 0.5 wt. % calcined La ₂ O ₃ | 140 | 0.03 | 1 | 91 | [106] |
| 1:1 (Urea-gly) | - | ionic liquid on Merrifield resin | 140 | 0.14 | 6 | 46 | [107] |

3.4.2 Process design

Reference article selection

Reference article selection has been driven by the opportunity to develop an industrially relevant continuous process. Accordingly, activity data presented in [81] are taken for the process design for the continuous manufacturing of glycerol carbonate (Table 22).

Indeed, the proposed technically shaped Mg-Al hydrotalcite-derived catalyst was able to reach yield values, i.e. 60 %, competitive with the state-of-the-art batch studies, was stable and easily regenerable, and did not present any leaching phenomena. In addition, catalyst active phase is composed by abundant, cheap and non-toxic chemical species, which is a relevant point on an environmental point of view. Finally, the establishment of a formulation technology of the catalyst into technically-shaped bodies is of fundamental importance for a future scale-up assessment of the continuous process.

Table 22. SWOT analysis for the continuous catalytic conversion to glycerol carbonate presented in [81].

| Strengths | Weaknesses |
|--|--|
| Total glycerol carbonate selectivity | Urea not soluble in glycerol |
| Competitive glycerol carbonate yield | Continuous operation requires a solvent to solubilize reactants |
| Continuous process | High dilution in GBL solvent (90 mol. %) |
| Stability of catalyst activity | Vacuum reaction conditions |
| Easily regenerable catalyst | Uncomplete conversion requires the separation of urea, which is not possible by distillation |
| Physical stability of the technically-shaped catalyst (no leaching and crushing phenomena) | High amount of NH ₃ effluent as co-product |
| Glycerol carbonate is easily separated by distillation | |
| NH ₃ co-product easily separable | |
| Opportunities | Threats |
| Adding value to waste glycerol | Glycerol carbonate expected to replace oil-based chemicals due to its superior properties |
| Environmental friendliness of reactants (glycerol, urea) | High product added-value |
| Higher plant capacity/productivity | Availability of raw materials |
| Glycerol carbonate as potential chemical in many sectors | |

Process modeling

Neglecting the upstream processing of crude glycerol for removing ash, MONG and methanol, the process is just composed of the reactor section and the recycle and purification section. Process layout is presented in Figure 24.

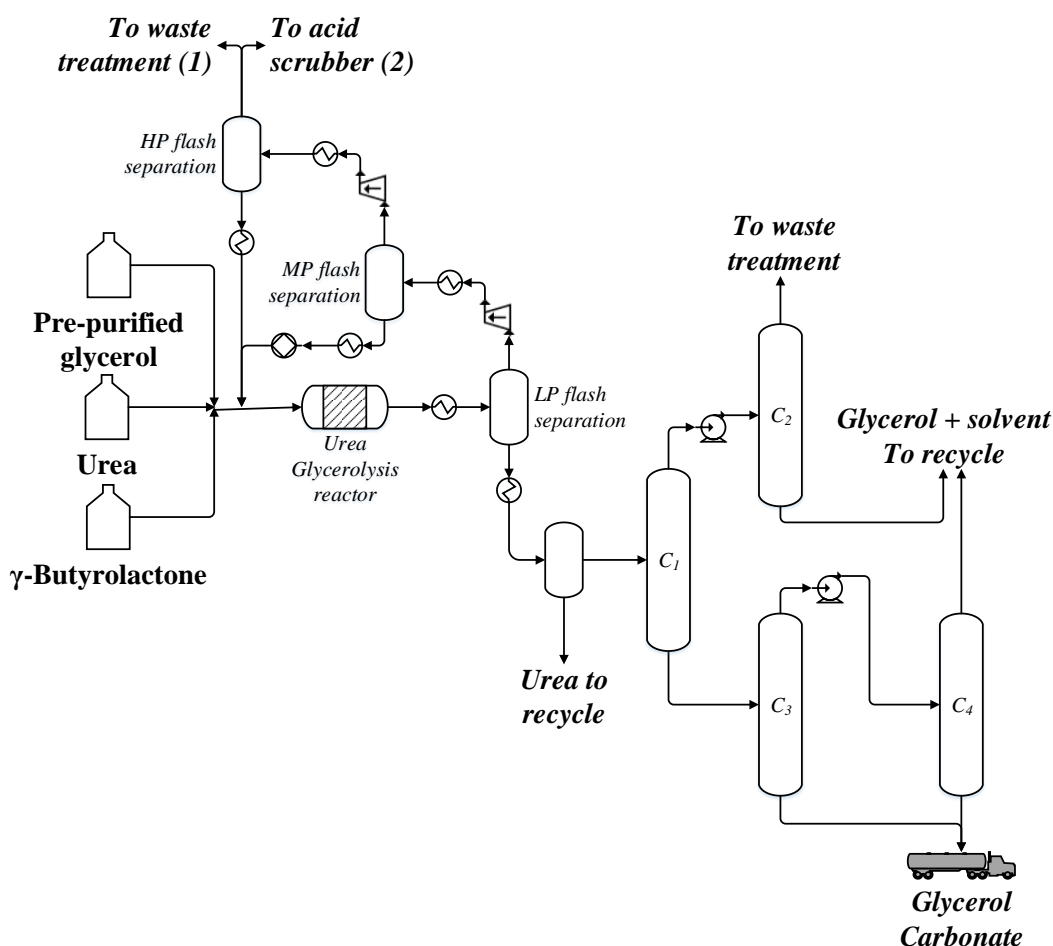
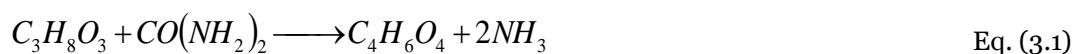


Figure 24. Glycerol carbonate manufacturing process. Scenarios (1) and (2) differ in the fate of NH_3 gaseous emissions.

The glycerol-containing stream from step-1 is mixed with urea and the reaction solvent (GBL) and sent to the reaction section, previous mixing of the recycle streams, i.e. unconverted glycerol and urea, recovered GBL from the liquid and gaseous effluents. Urea and GBL flow rates are adjusted to obtain at the reactor inlet an equimolar glycerol/urea ratio and a 90 mol. % of GBL.

The reactor is a catalytic fixed bed reactor; for the process assessment of this unit, the use of conversion and selectivity-related information of the reactions taking place in the liquid-phase is sufficient. All data related to reaction process conditions and hydrotalcite-based catalyst activity are taken from the reference article [81] (Table 23). Since complete selectivity to glycerol carbonate is claimed, the only reaction considered in the present work is the following:



The reaction is totally selective to glycerol carbonate and is performed isothermally at 423 K and under vacuum (10 mbar). This would help overcome equilibrium limitations in GC synthesis while stabilizing the system in the liquid phase.

Table 23. Activity data for glycerolysis catalyst, 423 K, 10 mbar [21].

| Component reactor inlet concentration [mol. %] | | | X [%] | σ_{gc} [%] |
|--|------|-----|-------|-------------------|
| Glycerol | Urea | GBL | | |
| 5 | 5 | 90 | 60 | ~100 |

Detailed information about the reaction kinetics, mass and heat transfer phenomena, pressure drop, *etc.*, would be required for a detailed design of a full-scale, plug-flow reactor, which is outside the scope of the present study.

Urea is a solid reactant; process high dilution conditions in GBL and process temperature levels allow a complete solubilization of urea in the liquid streams without the risk of possible crystallization or decomposition phenomena. Therefore, for the sake of modeling simplicity, no solid components were considered in the process.

The reactor effluent contains unconverted glycerol and urea, and products glycerol carbonate and ammonia, in a highly GBL-diluted stream. Easy separation of the light components, i.e. NH_3 , is readily done by vacuum flash separation; the flash temperature is adjusted in order to achieve a GC mole recovery of 99.99%. This preliminary operation results in an almost total removal of NH_3 and methanol, introduced in the system as crude glycerol impurity, in the vapor phase. About 10% of the solvent is also lost, together with negligible amounts of glycerol and glycerol carbonate.

Direct venting of the vapor phase is not desirable due to the high amount of lost solvent. Additional, higher pressure (0.1 bar and 1 bar) flash separation stages are used to recover the solvent. Flash temperatures are adjusted to obtain a recovered GBL with ≥ 98 wt. % purity to recycle. The vented phase mainly contains NH_3 , with residual lost GBL; it is sent to incineration.

The liquid removed from the preliminary flash stage is composed by unreacted glycerol and urea, glycerol carbonate and about 90% of the initial solvent. A preliminary urea separation stage by precipitation is adopted, since this compound is not distillable and, in any case, prolonged residence time at temperature near or above 403K would lead to possible crystallization or decomposition phenomena [108]. Conventional methods for urea separation from organic solutions have not been reported, i.e. crystallization or extraction unit operations cannot be rigorously applied due to the lack of available data. Destructive separation methods, i.e. hydrolysis and thermal decomposition, are as well not applicable since no information are available regarding the overall behavior of the mixture; furthermore, they lead to a loss in urea and possible product degradation. The recovered urea is recycled to the reactants.

A sequence of distillation columns is adopted in order to separate purified glycerol carbonate, recycle recovered glycerol and solvent, and remove residual light ends (Table 24). A first vacuum column is employed for solvent separation from a mixture of glycerol and glycerol carbonate at the bottom; a second atmospheric column accomplish the separation of residual

light ends before the recycle of the solvent. The crude glycerol carbonate mixture is separated in a sequence of two columns working at vacuum and atmospheric pressure levels; almost 50 % of product recovery is accomplished in the first vacuum separation, and completed in the atmospheric column. The product streams are then obtained with the desired purity (min. 99 wt. %) while the residual glycerol is recycled.

Table 24. List of components considered for GC manufacturing.

| Component | T _{nb} [°C] | MW [kg/kmol] |
|---------------------------|---|-----------------|
| <i>Glycerol carbonate</i> | 324 (estimated at 1 bar) 110-115 (at 0.1 mmHg) | 118 |
| <i>Glycerol</i> | 288 | 92 |
| <i>Urea</i> | - | 60 |
| <i>γ-butyrolactone</i> | 204 | 86 |
| <i>Water</i> | 100 | 18 |
| <i>Methanol</i> | 65 | 32 |
| <i>Ammonia</i> | -33 | 17 |

The distillation train configuration is the result of considerations regarding easiness of separation, energy requirements, operation flexibility, and product purity, which could not be easily achieved in a single column. Modeling in Aspen Plus® V8.6 employed a RadFrac model for simple distillation columns.

Due to the required energy intensive separations by distillation, process heat integration has been performed in order to reduce costs associated to thermal utility consumption (cooling water, steam, natural gas).

Heat integration potential is present because of the different temperature levels, at which available energy exists, between the reaction and separation section. However, first principle calculations reveal just ~50% hot utility saving with respect to the case without heat integration. This is not surprising if one considers that the separation section, which accounts for almost half of total hot utility, presents higher temperature levels with respect to the reaction section. Therefore, just minor heat recovery can be easily performed for the cold reactor inlet and the feed to the vaporization/precipitation urea stage, using the hot reactor effluent as energy source. Heuristically designed heat exchanger network, considering a realistic minimum temperature approach of 10 K, led to about 91.5% recovery of the maximum integrable heat. As a result of this configuration, the total hot utility requirement is reduced by about 46%.

3.4.3 Economic and environmental assessment

The background and inventory data used in this study for the environmental and economic

assessment are presented in Table 25 and Table 26, while assessment results are reported in Figure 25 with respect to the production of 1 kg of products and to the single contributions provided by process material, energy, and waste treatment requirements. No alternative fate for crude glycerol was considered; the results performed with respect to incineration or WWTP glycerol fates are instead reported in Table 27.

Table 25. Background data for the environmental (not- renewable resources) and economic assessment of glycerol carbonate manufacturing process [3, 74, 75].

| Substance | CED (MJ _{eq} kg ⁻¹) | EI99 (Points kg ⁻¹) | GWP (kg _{CO2-eq} kg ⁻¹) | Price (USD t ⁻¹) |
|----------------------------------|---|------------------------------------|---|---------------------------------|
| MgO | 2.7 | 0.12 | 1.06 | 280 |
| Al ₂ O ₃ | 19.1 | 0.19 | 1.24 | 355.6 |
| Catalyst disposal | 0.32 | 0.002 | 0.01 | - |
| Crude glycerol – to incineration | -19.7 | -0.063 | 0.20 | 111 |
| Crude glycerol – to WWTP | 9.97 | 0.021 | 0.92 | 111 |
| Steam | 1.57 | 0.01 | 0.10 | 20 |
| Electricity* | 9.87 | 0.02 | 0.49 | 0.10 |
| Cooling water from river | 0.00 | 0.00 | 0.00 | 0.15 |
| Natural gas** | 1.24 | 0.004 | 0.012 | 0.01 |
| Urea | 30.2 | 0.14 | 1.53 | 267 |
| GBL | 70.0 | 0.25 | 3.29 | 22900 |
| Glycerol carbonate | 128 | 0.26 | 5.70 | 8141*** |
| Sulfuric acid | 2 | 0.04 | 0.12 | 0.04 |
| Ammonium sulphate | 10.7 | 0.05 | 0.65 | 0.114 |
| Ash disposal | 0.28 | 0.02 | 0.009 | - |

*Electricity is measured per kWh.

**The values for natural gas are measured per MJ and they refer to heat-production purposes.

*** Teng, W.K., Ngoh, G.C., Yusoff, R., Aroua, M.K. (2014). A review on the performance of glycerol carbonate production via catalytic transesterification: effects of influencing parameters. *Energy Conversion and Management*, 88, 484-497.

Heterogeneous-catalyzed urea glycerolysis reaction to glycerol carbonate has been regarded as an attractive opportunity to implement a greener process as it involves environmentally benign or waste chemicals as feedstocks, i.e. waste crude glycerol and harmless urea from NH₃ and CO₂, the easiness of co-product separation, i.e. NH₃, and the use of easily recoverable, environmentally friendly heterogeneous base catalysts, i.e. hydrotalcite-derived. On a green chemistry perspective, concerns regard stoichiometric co-production of NH₃, to be treated as gaseous effluent in incineration facilities with NO_x abatement, and the use organic solvents, i.e. γ -butyrolactone for the proposed process.

Process assessment results fully reflect these considerations (Figure 25, scenario 1). In this context, the material and energy categories dominate the environmental impacts for all the LCA indexes, while the waste contribution is negligible and negative.

Table 26. Inventory data used for the environmental and economic assessment of glycerol carbonate manufacturing process.

| Materials and energy | GC - Scenario 1 | GC - Scenario 2 | Units |
|-----------------------|-----------------|-----------------|---------------------|
| Crude glycerol | 1.05 | 1.05 | kg/kg _{GC} |
| Urea | 0.51 | 0.51 | kg/kg _{GC} |
| GBL | 0.024 | 0.024 | kg/kg _{GC} |
| Process water | - | 0.85 | kg/kg _{GC} |
| Catalyst | 0.019 | 0.019 | kg/kg _{GC} |
| Heat | 32.5 | 32.7 | MJ/kg _{GC} |
| Natural gas | 1.8 | 1.8 | MJ/kg _{GC} |
| Electricity | 0.005 | 0.005 | MJ/kg _{GC} |
| Cooling water | 537 | 553 | kg/kg _{GC} |
| Ashes | 0.057 | 0.057 | kg/kg _{GC} |
| Wastewater | - | 1.09 | kg/kg _{GC} |
| Waste to incineration | 0.52 | 0.21 | kg/kg _{GC} |
| Ammonium sulfate | - | 0.92 | kg/kg _{GC} |
| Sulfuric acid | - | 0.85 | kg/kg _{GC} |

A closer look reveals that urea consumption is the main factor determining > 90% of CED, EI-99, and GWP material category, followed by the solvent contribution. Material contributions are however smaller compared to the impact associated to the energy requirements, which are largely determined by the separation section utility consumption (70%), i.e. distillation train and urea precipitation stage. High solvent dilution conditions greatly affect these requirements, as consequence of the augmented process flow rates to be treated: this, together with overall poor heat integration possibilities, leads to a higher process specific energy consumption. It is interesting to assess how environmental concerns related to the presence of the solvent are linked to energy requirements and not to make-up requirement, which is still very low, or to emissions as liquid or gaseous effluent; specific LCA metrics evidence indeed the environmental friendliness of γ -butyrolactone and the amount of lost solvent in waste effluents is very low. Finally, positive waste contributions are dominated by thermal valorization of the purge stream (> 95 mol. % NH_3), and derives from the energy recovery (CED) and to N_2 emissions after NO_x abatement (EI-99, GWP).

On the other side, operating costs present some different trends (Figure 25, scenario 1). The material and energy categories still dominate together the overall product cost, with material requirements, and specifically GBL consumption, being preponderant as a consequence of the very high solvent price. This calls for a sharp recovery of the solvent in the process, minimizing emissions in waste streams. A relevant 44% of the product cost is however determined by the waste contribution. Almost $0.3 \text{ kg}_{\text{NH}_3}/\text{kg}_{\text{GC}}$ is co-produced in the reactor and vented as gaseous effluent after solvent recovery; thermal valorization in an incineration facility must be followed by NO_x conversion to harmless N_2 [7], determining the high waste treatment cost of 1 \$/kg_{GC}.

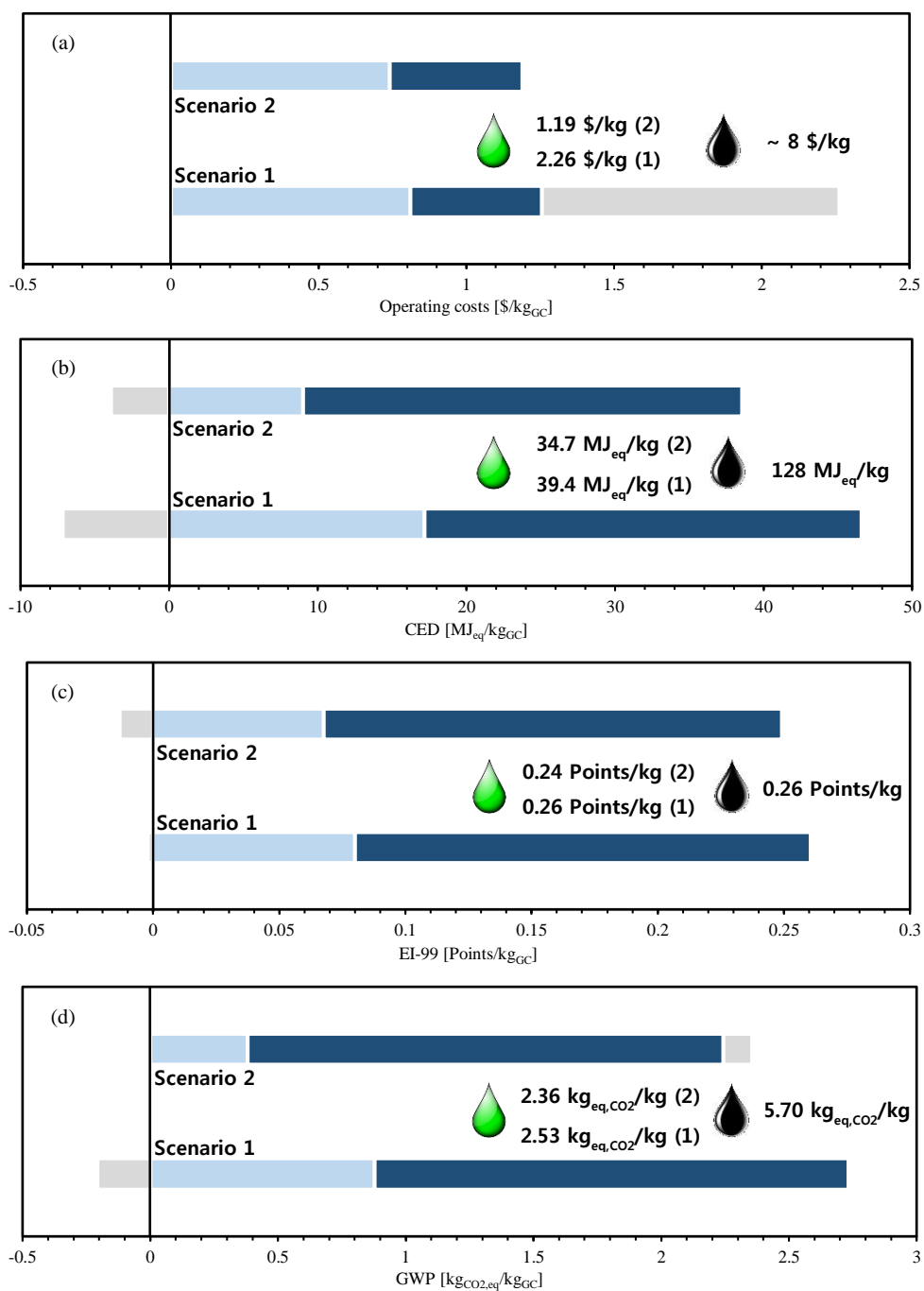


Figure 25. Economic and environmental assessment results for glycerol-to-glycerol carbonate manufacturing process (■ material, ■ energy, ■ waste). No crude glycerol alternative fate considered.

Nevertheless, significantly lower LCA impact values and operating costs than the corresponding oil-derived glycerol carbonate are calculated, evidencing concrete possibilities associated to the production of this novel chemical. Product costs of 2.26 \$/kg_{GC} provide a very high profit margin, also taking into account glycerol price fluctuations and investment costs.

Table 27. Economic and environmental assessment results for glycerol-to-glycerol carbonate manufacturing process considering crude glycerol alternative utilization scenarios in incineration facilities or wastewater treatment plants.

| Scenario | LCA metric | Alternative crude glycerol fate | |
|----------|--|---------------------------------|---------|
| | | To incineration | To WWTP |
| | <i>CED (MJ_{eq}/kg_{GC})</i> | 71.2 | 23.4 |
| | <i>EI-99 (Points/kg_{GC})</i> | 0.36 | 0.22 |
| | <i>GWP (kg_{eq,CO2}/kg_{GC})</i> | 2.2 | 1.04 |
| | <i>CED (MJ_{eq}/kg_{GC})</i> | 66.4 | 18.6 |
| | <i>EI-99 (Points/kg_{GC})</i> | 0.34 | 0.20 |
| | <i>GWP (kg_{eq,CO2}/kg_{GC})</i> | 2.03 | 0.87 |
| | <i>CED (MJ_{eq}/kg_{GC})</i> | | 10.5 |
| | <i>EI-99 (Points/kg_{GC})</i> | | 0.022 |
| | <i>GWP (kg_{eq,CO2}/kg_{GC})</i> | | 0.97 |
| | <i>CED (MJ_{eq}/kg_{GC})</i> | -20.7 | |
| | <i>EI-99 (Points/kg_{GC})</i> | -0.066 | |
| | <i>GWP (kg_{eq,CO2}/kg_{GC})</i> | 0.21 | |

* Values corresponding to the reported glycerol indexes, multiplied by 1.05 kg_{GLY}/kg_{GC}.

LCA metrics also show a positive scenario, especially with respect to the “WWTP” glycerol alternative fate (Table 27), providing quantitative evaluation of the environmental sustainability of the proposed process.

An alternative scenario has been proposed in order to reduce the economic impact associated to the treatment of NH₃ gaseous effluent by adding an acid scrubber on the high pressure flash vent line. A 50 wt. % sulfuric acid aqueous solution in a eleven-stage reactive absorption column is used in order to remove NH₃; conversion to ammonium sulfate, an important compound commonly used as nitrogen-based fertilizer, is expected to generate a positive economic and environmental impact by co-production of a valuable product and by reduction of gaseous ammonia to incineration treatment [109]. For this purpose, a filtration-evaporation stage is employed in order to obtain the solid compound from the aqueous stream. Assessment results (Figure 25, scenario 2) confirm a total reduction of waste treatment costs, with also minor additional revenues coming from co-production of ammonium sulfate in the material category, while maintaining almost unvaried environmental impacts. Therefore, this strategy evidences the importance and feasibility of NH₃ gaseous waste valorization in the glycerol-to-glycerol carbonate manufacturing process.

3.5 Allyl alcohol

Allyl alcohol is a very important organic commodity chemical mainly used as a raw

material in the plastics and polymer industry. It was also used for the production of synthetic glycerol. The raw material in all commercial processes for allyl alcohol production is propene; although allyl alcohol can be made via a variety of intermediates, only the processes proceeding via allyl chloride and propylene oxide are of major commercial importance. Hydrolysis of allyl chloride to allyl alcohol uses 5-10 % sodium hydroxide solution at 150 °C and 13-14 bar, yielding 85-95 % allyl alcohol. Catalytic isomerization of propylene oxide, partially replacing the allyl chloride process, uses lithium phosphate catalyst in a fixed bed reactor (vapor phase, 250-350 °C, 70-75 % allyl alcohol yield) or suspended in high-boiling solvents with bubbling propylene oxide (liquid-phase, 280 °C, Conversion is 55%, allyl alcohol yield) [80].

Sustainability concerns are mostly related to the very high degree of oil dependency of the manufacturing processes, i.e. all raw materials are oil-derived.

3.5.1 Brief literature review

Figure 26 shows the main reactions involved in the complete mechanism of glycerol hydrogenolysis. As the industrial production of allyl alcohol is based on the hydrogenation of propene-derived acrolein [80], and the latter can be attained from glycerol through dehydration, a two-step transformation has been initially proposed.

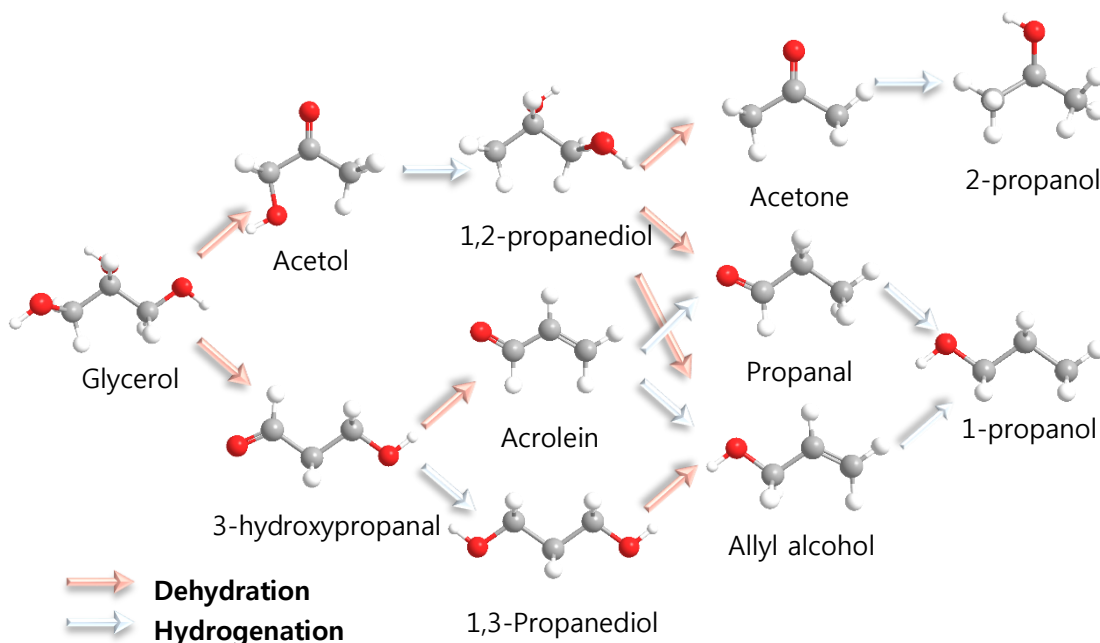


Figure 26. Reaction routes of glycerol hydrogenolysis to allyl alcohol, propanediols and propanols [29].

In the initial dehydration, two water molecules are removed from glycerol, typically in the gas phase [20]. Brønsted acid sites have been identified as selective, whereas Lewis functionalities lead to hydroxyacetone [110]. Thus, strong solid acids, such as heteropolyacids, sulfated

zirconia, and zeolites, belong to the state-of-the-art heterogeneous catalysts [111].

The selective hydrogenation of acrolein to allyl alcohol is particularly challenging owing to the conjugation of the C=O and the C=C bond. Palladium, ruthenium, rhodium, and platinum are fully selective to propanal [112-114], whereas silver and gold catalysts show an allyl alcohol selectivity of 50-60% in gas-phase experiments [115, 116]. Alloying silver with cadmium and zinc increased the yield up to 70% and this technology is industrially exploited [114].

The combination of the two reactions over a single catalyst has been tackled infrequently and was typically performed in the presence of an organic hydrogen donor. Indeed, due to the difficulty to achieve high selectivity to allyl alcohol in 1,2-propanediol dehydration, 1,3-propanediol dehydration and acrolein hydrogenation, all the successful reports are performed through a hydrogen transfer reaction in which either alcohols or acids are used as the H-donor instead of H₂.

Table 28 summarizes the most performing liquid-phase glycerol hydrogenolysis processes to allyl alcohol through a hydrogen transfer reaction. Although high yield values are achievable in, the generation of low-value ketones from the alcohols in equimolar amounts to allyl alcohol represents a strong drawback toward an industrial process. In addition, byproduct formation and the loss of part of the donor as a result of dehydration over the acidic material emerged as additional disadvantages to the formation of the ketones.

Finally, whenever glycerol itself is used as H-donor, maximum yield is limited to 50%. Continuous vapor-phase tests have been performed with glycerol as H-donor and some results are reported in Table 29. FeO_x-based catalyst plays an important role for allyl alcohol formation from glycerol.

Table 28. Batch liquid-phase glycerol hydrogenolysis to allyl alcohol through hydrogen transfer reaction [29].

| Solvent (H-donor) | Catalyst | T [°C] | P [bar] | T [h] | Y _{AA} [%] | Ref. |
|-------------------|--------------------|---------|---------|-------|---------------------|-------|
| Formic acid | - | 230-240 | 1 | 3 | 89 | [117] |
| 3-octanol | MeReO ₃ | 170 | 1 | 2.5 | 90 | [118] |
| Glycerol | NaReO ₄ | 165 | 1 | 1 | 38 (max. Y = 50 %) | [119] |

Table 29. Continuous vapor-phase glycerol hydrogenolysis to allyl alcohol (glycerol H-donor, max. Y_{AA} = 50%).

| Reactants | Catalyst | T [°C] | P [bar] | TOS [h] | WHSV [h] | X [%] | σ _{AA} [%] | Ref. |
|---------------------------|---|--------|---------|---------|----------|-------|---------------------|-------|
| 35 wt. % aqueous glycerol | Fe ₂ O ₃ | 320 | 1 | 6 | 2.5 | 100 | 23 | [120] |
| 50 wt. % aqueous glycerol | ZrO ₂ -FeO _x | 350 | 1 | 6 | 1 | 100 | 20 | [121] |
| 10 wt. % aqueous glycerol | K/ZrO ₂ -FeO _x | 350 | 1 | 6 | 0.2 | 100 | 27 | [122] |
| 35 wt. % aqueous glycerol | Rb/FeO _x -Al ₂ O ₃ | 340 | 1 | 3 | 0.3 | 89.8 | 13 | [123] |

Nevertheless, high reaction temperature is required, which results in many kinds of by-products, such as carboxylic acids (acetic acid and propionic acid), ketones (acetone and 2-

butanone), and aldehydes (acrolein and acetaldehyde) [29]. Therefore, in such a process, it is difficult to selectively produce allyl alcohol.

The improvement of the catalyst system is considerable to be necessary for selective production of allyl alcohol. Considering the state of the art catalysts for the separate dehydrogenation (acid zeolites) and hydrogenation (Au-, Ag-based) steps, and considering the related disadvantages of the catalytic hydrogen transfer reaction, the development of combined catalysts, which contain both the proper acidity for glycerol dehydration to acrolein and the suitable hydrogenation activity for the partial hydrogenation of acrolein to allyl alcohol, is to be attempted in a direct conversion of glycerol to allyl alcohol in an H₂ atmosphere.

To the author knowledge, the first study in this direction has been presented in [111]. Here, Ag nanoparticles supported on a hierarchical zeolite is presented as an efficient bifunctional catalyst for the H₂-mediated transformation of glycerol into allyl alcohol in a continuous gas-phase process. The catalyst design firstly encompassed the tailoring of the porous and acidic properties of MFI-type aluminosilicates through post-synthetic base and acid treatments to increase their selectivity and long-term stability in the dehydration of the substrate to acrolein. Secondly, different metals deposited onto the optimized zeolite were tested to identify the best hydrogenation phase for the reduction of the intermediate to allyl alcohol. Thereafter, the metal loading was tuned along with the operating conditions to boost the productivity and on-stream durability of this novel catalytic technology. Final activity values of $\chi = 80\%$ and $\sigma_{AA} = 20\%$ were obtained, at 673 K and 40 bar in H₂ atmosphere, using 20 wt. % aqueous glycerol. Minor activity loss was also displayed over a 100 h TOS test. The other main by-products observed were hydroxyacetone (35 %), acrolein (25 %), and propanal (20 %), as a result of non-selective dehydrogenation and/or hydrogenation steps.

3.5.2 Process design

Reference article selection

In order to design high capacity plant for the production of the commodity allyl alcohol, attention was given only to continuous processes. Indeed, together with reduced plant capacity and more difficult control strategy, liquid-phase batch processes present the additional disadvantage of using an H-donor solvent, which is the source of stoichiometric amount of the corresponding dehydrogenation product.

At present, glycerol hydrogenolysis continuous conversion has been mainly studied in vapor-phase catalytic transfer hydrogenation reactions, using glycerol itself as H-donor. Maximum achieved allyl alcohol yields were in the order of ~25 %, in front of a maximum theoretical

value of 50%.

Due to this important limitation, the bifunctional catalyst presented in [111] is taken as reference state-of-the-art catalyst for the continuous manufacture of allyl alcohol from glycerol, with comparable allyl alcohol yields, using molecular hydrogen, with respect to those previously reported. In addition, this work first discloses the development of a bifunctional catalyst, highlighting and providing new insights into the key parameters to be taken into account in the development and optimization of the catalyst. For these reasons, a process modelling and assessment activity has been considered by the author as an efficient way to preliminary obtain some results related to the sustainability of this process. This way, process variables could be analyzed in order to provide some useful insights related to the effect of catalyst activity at the process scale.

Two-step processes, i.e. with separate dehydration and hydrogenation reaction sections, are not considered in the present work, since the focus is on the state-of-the-art catalytic technologies.

Table 30. SWOT analysis for the continuous catalytic conversion to allyl alcohol presented in [111].

| Strengths | Weaknesses |
|---|---|
| Single stage process | Poor selectivity to allyl alcohol |
| Vapor-phase continuous process | High selectivity to by-products |
| No H-donor reagent required | High glycerol water dilution |
| Competitive allyl alcohol yield with respect to existing state-of-the-art vapor-phase processes | Very high water dilution of reactor effluent, as a consequence of dehydration reactions |
| No stoichiometric production of H-donor-derived ketones | Expensive and difficult downstream purification due to high water dilution and homogeneous azeotropic behaviors |
| Stable activity | Dependence on oil-derived H ₂ Harsh reaction conditions (400 °C, 40 bar) |
| Opportunities | Threats |
| Adding value to waste glycerol | Allyl alcohol is a well-established commodity |
| Replacement of oil-based allyl alcohol in already existing markets | Marketing strategy might claim superior “bio-properties” of glycerol-derived allyl alcohol |
| | Availability of raw materials |

Process modeling

The process can be divided into three main blocks, comprising the reaction section, the vapor recycle section with vapor-purification system, and a liquid recycle section with liquid recycle and products purification. Process layout is presented in Figure 27. For the sake of clarity, only relevant equipment is reported in the scheme.

A base reference capacity of 1000 kg/h of crude glycerol is considered for the calculations.

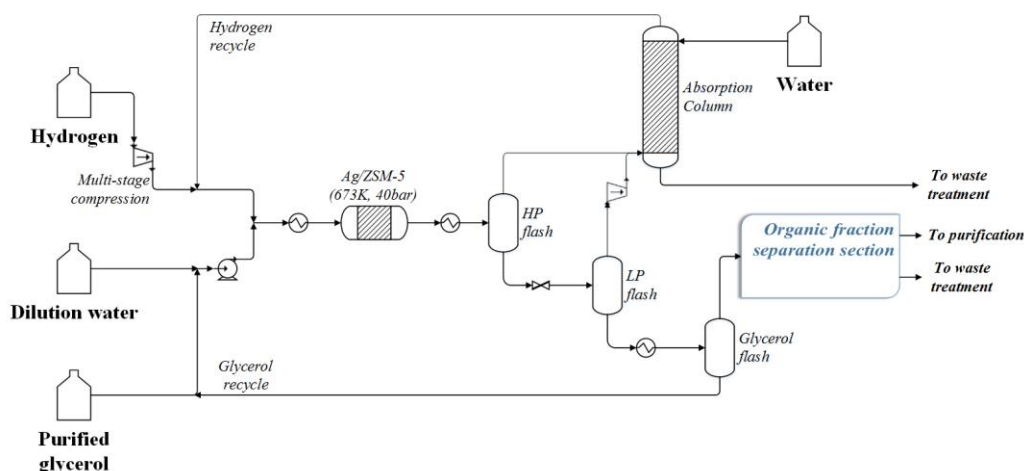


Figure 27. General process flow diagram for allyl alcohol manufacturing.

The purified glycerol stream, together with recycled glycerol and process water for dilution, is compressed to 40 bar and mixed with the hydrogen stream, coming from the multi-stage compression with intermediate refrigeration and from the gaseous recycle. Two stages, with intermediate cooling down to 298 K, are employed, which allow saving ~55 % electric energy consumption. The feed is then heated to 673 K and fed to the reactor. From data presented in [111], inlet composition is 48.9 mol. % hydrogen, 48.7 mol. % water, 2.4 mol. % glycerol: very high dilution conditions are therefore required in hydrogen atmosphere. The composition constraint is respected by manipulating fresh hydrogen and dilution water streams.

The reactor is a catalytic fixed bed reactor (RSTOICH reactor in Aspen Plus® V8.6). Isothermal conditions are assumed, providing an external cooling utility for the removal of reactor exothermic heat load. For the process assessment of this unit, the use of conversion and selectivity-related information of the reactions taking place in the gas-phase hydrogenolysis of glycerol to allyl alcohol is sufficient [111] (Table 31). The stoichiometric reactions considered in the present work are reported in Table 32.

Table 31. Activity data for Ag-based bifunctional catalyst [111].

| Glycerol aqueous concentration (reactor inlet) [wt. %] | χ [%] | σ_{AA} [%] | σ_{HA} [%] | σ_{ACR} [%] | σ_{PA} [%] |
|---|---------------|----------------------|----------------------|-----------------------|----------------------|
| 20 | 82.5 | 18.7 | 32.8 | 29.9 | 18.6 |

Table 32. Stoichiometric reactions considered in the allyl alcohol hydrogenolysis reactor.

| Description | Reaction |
|---|-------------------------------------|
| Glycerol dehydration to acrolein | $GLY \rightarrow ACR + H_2O$ |
| Glycerol dehydration to hydroxyacetone | $GLY \rightarrow HA + H_2O$ |
| Glycerol hydrogenation to allyl alcohol | $GLY + H_2 \rightarrow AA + 2 H_2O$ |
| Glycerol hydrogenation to propionaldehyde | $GLY + H_2 \rightarrow PA + 2 H_2O$ |

Detailed information about the reaction kinetics, mass and heat transfer phenomena, pressure drop, *etc.*, would be required for a detailed design of a full-scale, plug-flow reactor, which is outside the scope of the present study.

The reactor effluent contains large excess H₂, H₂O, the desired product allyl alcohol and by-products. It is cooled down to 298K to condense and separate the organic fraction from the large excess of hydrogen to recycle. This preliminary operation results in almost total removal in the gas phase of H₂, as well as condensation of an aqueous stream with molar recovery > 99.5 % for all components heavier than allyl alcohol (Table 33). Only by-products acrolein and propionaldehyde are partially lost, i.e. respectively ~22 % and ~12 % molar, in the gaseous effluent.

Table 33. List of components considered for AA manufacturing.

| Component | T _{nb} [°C] | MW [kg/kmol] |
|------------------------|-------------------------|-----------------|
| <i>Glycerol</i> | 288 | 92 |
| <i>Hydroxyacetone</i> | 146 | 74 |
| <i>Water</i> | 100 | 18 |
| <i>Allyl alcohol</i> | 97 | 58 |
| <i>Benzene</i> | 80 | 78 |
| <i>Methanol</i> | 65 | 32 |
| <i>Acrolein</i> | 53 | 56 |
| <i>Propionaldehyde</i> | 49 | 58 |
| <i>Dichloromethane</i> | 40 | 84.9 |
| <i>Hydrogen</i> | -253 | 2 |

The hydrogen flow must therefore be purified before being recycle. A simple water absorption system is used to remove at least 99 % of the residual organics by manipulating the washing water flow rate. An absorption column (18 equilibrium stages) has been employed; the number of stages, as well as the minimum L/G ratio, have been calculated according to shortcut methods [1]. The resulting aqueous stream contains the lost organics; however, due to the extremely high degree of dilution, the low amounts of lost acrolein and propionaldehyde, and the presence of water-acrolein-propionaldehyde azeotropes, this stream is simply treated as a waste. In addition, acrolein and propionaldehyde are two low valuable by products (< ~1 \$/kg). The liquid effluent is a very high water-diluted stream of the condensed organic fraction; multiple flash separation stages are used to first remove residual light ends at 1 bar, then to separate heavy glycerol at 383 K. Glycerol, as the heaviest component, is this way easily separable: flash temperature is adjusted for a minimum 99 % glycerol recovery, together with lower amounts of water and hydroxyacetone.

The vapor effluent from the glycerol flash is sent to the organic purification section, which represents the complex sequence of separation and purification operations in order to obtain

purified products from the process. Considering the extremely high amount of water and the presence of several azeotropic behaviors, involving also allyl alcohol, the dehydration of the organic fraction is performed by liquid-liquid extraction. Liquid-liquid extraction is a reasonably mature separation operation but, in the thermodynamics of liquid-liquid extraction, experimental equilibrium data are in many cases preferred over predictions based on activity-coefficient correlations [124]. However, the NRTL semi-theoretical activity-coefficient model has been proven to provide good thermodynamic equilibrium estimations and therefore is used for the description of the system.

The choice of the solvent is a critical point influencing the performances of the extraction. The ideal solvent should possess:

1. High selectivity for the solute relative to the carrier, so as to minimize the need to recover carrier from the solvent.
2. High capacity for dissolving the solute, so as to minimize the solvent-to-feed ratio.
3. A minimal solubility in the carrier.
4. A volatility sufficiently different from the solute that recovery of the solvent can be achieved by distillation.
5. Stability and inertness, to maximize the solvent life and minimize the solvent make-up requirement.
6. A low viscosity to promote phase separation, minimize pressure drop, and provide a high solute mass transfer rate (not relevant if equilibrium operation is assumed).
7. Nontoxic, nonflammable, non-foaming, and non-scumming characteristics to facilitate its use.
8. Availability at a relatively low cost.

In solvent selection, initial consideration is usually given first to selectivity and second to capacity. Also environmental concerns possibly represent an initial weighting factor [124].

Two solvents have been considered:

- Benzene: diffused extractive agent in organic extraction from water [124].
- Dichloromethane: well-known extractive agent in allyl alcohol dehydration operations by extractive distillation or solvent extraction [125].

In the present study, solvent selection also encompasses the analysis of the subsequent downstream purification operations following the extractor, since the extraction target is represented by all the organic phase, which then has to be purified. Therefore, different scenarios have been generated using different solvents; the evaluation of the extraction performances, make-up requirements, easiness of separations, and separation energy requirements, allowed then to choose the best solvent.

Solvent extraction capacity, selectivity and carrier affinity are very similar, for a given solvent

flow rate and number of equilibrium stages (Table 34): slightly higher water content in the extract phase and higher make-up requirements are to be expected for dichloromethane as a result of slightly higher affinity between the solvent and water.

Distillation column sequencing for products recovery has been determined by heuristics considerations. Column design specifications was selected to obtain a column reflux ratio equal 1.3÷1.7 times the minimum reflux ratio and the feed stage is determined as optimal feeding stage able to minimize the reflux ratio for a given number of stages. In addition, the number of trays is limited to keep the height/diameter ratio desirably lower than 30-40, to avoid possible structural deficiencies of the column. The same solvent flow rate basis was chosen for a proper comparison: 2400 kg/h was found to be the minimum flow rate for a 99 % allyl alcohol extract recovery (Figure 28, Figure 29). Column specifications and reboiler duties are reported in Table 35.

Table 34. Solvent extraction performances (Solvent = 2250 kg/h, N = 30 stages).

| Component | Extract recovery [%] | |
|------------------------|----------------------|-----------------|
| | Benzene | Dichloromethane |
| <i>Glycerol</i> | 9.8 | 11 |
| <i>Hydroxyacetone</i> | 15.9 | 17.3 |
| <i>Water</i> | 0.12 | 0.68 |
| <i>Allyl alcohol</i> | 97.5 | 97.4 |
| <i>Benzene</i> | 99.6 | - |
| <i>Methanol</i> | 8.8 | 6.8 |
| <i>Acrolein</i> | 100 | 100 |
| <i>Propionaldehyde</i> | 100 | 100 |
| <i>Dichloromethane</i> | - | 97.7 |

Table 35. Column specifications and reboiler duties for the benzene and dichloromethane layouts.

| Name | C ₁ | C ₂ | C ₃ | C ₄ | C ₅ |
|--------------------------------|---|---|--|--|-----------------------------|
| Benzene | | | | | |
| <i>N</i> | 50 | 27 | 30 | 20 | 7 |
| <i>R</i> | 1.53 | 0.32 | 8.46 | 0.38 | 0.1 |
| <i>Specifications</i> | Rec _{CC6H6} = 99.92% Rec _{CAA} = 99.9% | Pur _{HA} = 99% Rec _{CHA} = 99.9% | Rec _{ACR} = 99% Rec _{CC6H6} = 99.8% | Rec _{CAA} = 99.9% Pur _{AA} = 99.5% | Rec _{CHA} = 99.99% |
| <i>Reboiler duty [Gcal/hr]</i> | 0.71 | 3.06 | 0.26 | 0.02 | 0.03 |
| Dichloromethane | | | | | |
| <i>N</i> | 60 | 25 | 18 | 18 | 10 |
| <i>R</i> | 2.198162 | 0.466755 | 0.510836 | 0.357386 | 0.0168 |
| <i>Specifications</i> | Rec _{CH2Cl2} = 99.99% Rec _{CPA} = 90% | Pur _{HA} = 99.1% Rec _{CHA} = 99.9% | Rec _{ACR} = 99.9% Rec _{CAA} = 99.9% | Rec _{CAA} = 99.9% Pur _{AA} = 99.5%* | Rec _{CHA} = 99.99% |
| <i>Reboiler duty [Gcal/hr]</i> | 0.67 | 3.11 | 0.03 | 0.02 | 0.03 |

*Allyl alcohol minimum purity of 99.5 wt. % [126]

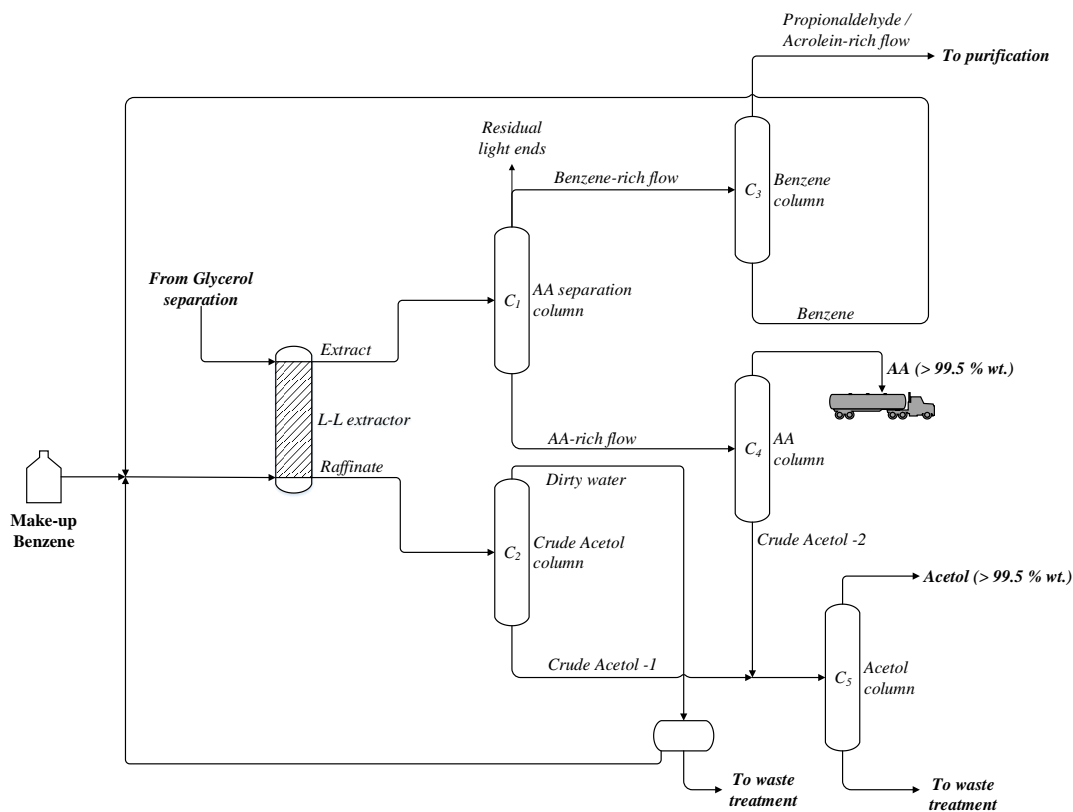


Figure 28. Distillation sequence flowsheet using benzene in the L-L extractor.

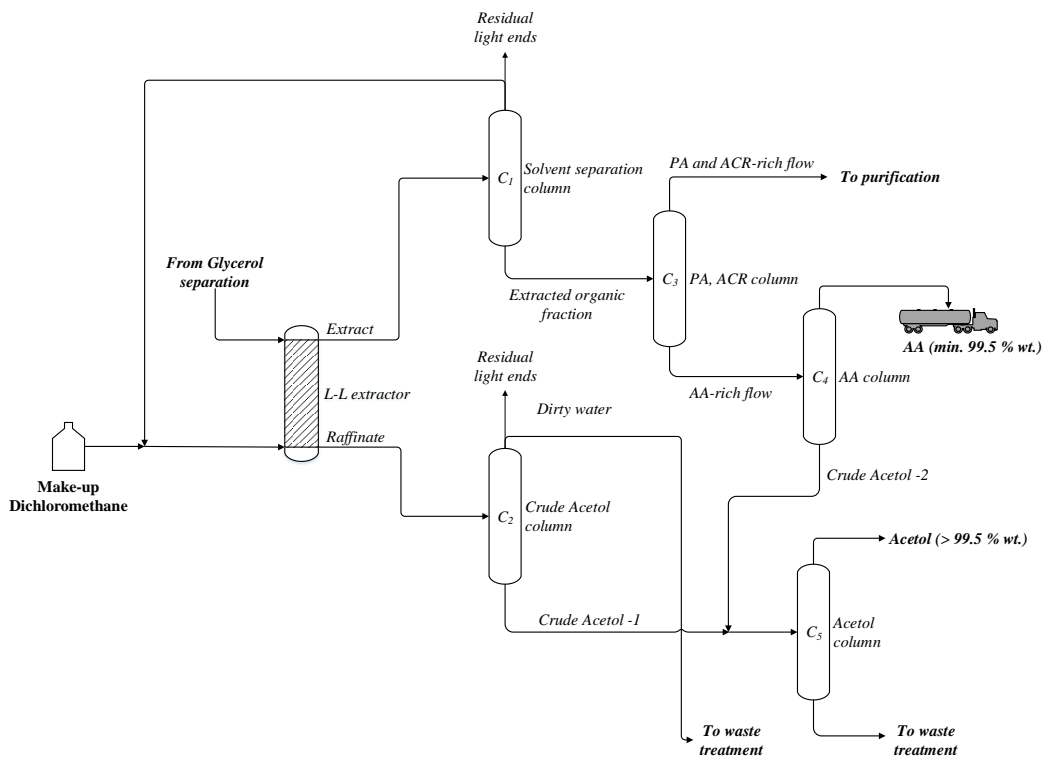


Figure 29. Distillation sequence flowsheet using dichloromethane in the L-L extractor.

The differences in process layouts are the results of the different solvent boiling point, i.e. $T_{C_6H_6} = 80\text{ }^\circ\text{C}$ and $T_{CH_2Cl_2} = 40\text{ }^\circ\text{C}$. A proper comparison of the two developed sub-optimal configurations reveals that the most cost effective factor, which is the hot utility consumption in the reboilers, is $\sim 5.5\%$ lower for the CH_2Cl_2 layout as consequence of easier separations, in which the solvent could be removed and recycled immediately. This was not of course possible with benzene, since it was an intermediate boiling compound in the organic mixture.

The overall separation efficiency of the two processes, i.e. the overall products recovery, are very similar using the same amount of solvent in the extractor. The only difference is represented by the required solvent make-up, which is $\sim 40\text{ kg/h}$ higher for dichloromethane: indeed, solvent losses in the raffinate dirty water are higher due to the slightly higher solubility limit in water, with respect to benzene.

Another important factor is represented by the residual amount of water in the organic products, and in particular in the acrolein/propanal-rich flow. Despite the fact dichloromethane is slightly more affine to water, the higher amount of water can be totally removed easier with the solvent in C_1 by exploiting the presence of water- CH_2Cl_2 azeotrope (99 wt. % CH_2Cl_2). This could not be done as easy with benzene, since the residual lower amount of water tends always to be separated as propanal-acrolein-water homogeneous ternary azeotrope. As a consequence, much higher amount of residual water will be present in the acrolein/propanal flow, possibly preventing final desired purity.

For these reasons, dichloromethane is chosen as preferred solvent. Modeling in Aspen Plus® V8.6 employed in all cases a RadFrac model for distillation columns with total or partial condenser (vapor fraction = 0.001), to remove H_2 traces. The water removed from the separation section is sent to a conventional wastewater treatment facility, while the light ends streams were sent to incineration or to a conventional wastewater system after condensation, according to their lower heating value.

The acrolein-propionaldehyde separation strategy has been reproduced from [127] by exploiting the reactivity of propionaldehyde with an extractive agent, i.e. ethylene glycol, to produce 2-ethyl-1,3-dioxolane and enabling the recovery of acrolein in a first column (Figure 30). Up to 68.5% acrolein is recovered by this method, with simultaneous conversion of all the propionaldehyde and $\sim 12.5\%$ of the fed solvent (540 kg/h ethylene glycol) to 2-ethyl-1,3-dioxolane. After solvent recovery, a final optional column is used to recover 2-ethyl-1,3-dioxolane; some acrolein is necessarily lost.

Finally, heat integration procedure has been applied as usual. Preliminary calculations reveal a maximum hot utility saving of $\sim 65\%$ with respect to the case without heat integration and the designed heat exchanger network, considering a realistic minimum temperature approach of 10 K, led to $\sim 95\%$ recovery of the maximum integrable heat; as a result, the total hot utility requirement is reduced by $\sim 62\%$.

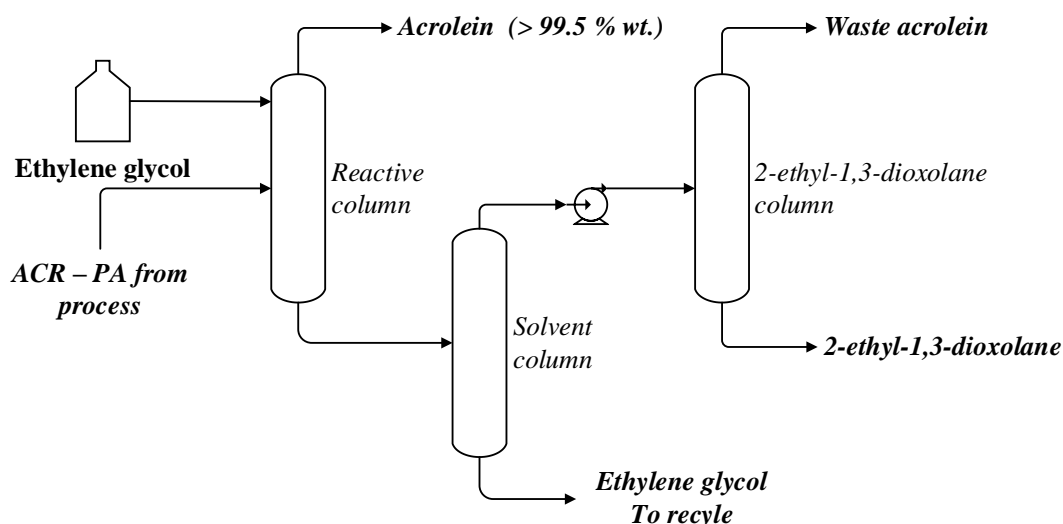


Figure 30. Acrolein separation flowsheet.

Heat integration potential is mainly present as available sensible heat of the reactor effluent to be used for feed pre-heating, which alone accounts for almost 50% of the recovered heat; this is a direct consequence of the very high reaction temperature level, i.e. 673K, which calls for a necessary heat integration between the feed and the effluent. Other integration opportunities are present due to very different temperature levels between the reaction and the downstream section, and within the reaction section itself due to the complex set of distillation unit operations.

3.5.3 Economic and environmental assessment

The background and inventory data used in this study for the environmental and economic assessment with respect to the consumption of resources are presented in Table 36 and Table 37, with the corresponding assessment results with respect to no crude glycerol alternative fate (Figure 31) and to alternative WWTP or Incineration treatment (Table 38). Being the state-of-the-art catalyst for the continuous, vapor phase, H₂-based manufacture of allyl alcohol from glycerol, zeolite-supported silver nanoparticles activity has been taken as reference. Very low product selectivity characterizes reactor performances, leading to significant glycerol conversion to byproducts hydroxyacetone, acrolein and propanal, i.e. ~80%. Assessment results are directly affected by this behavior and, in particular, by a positive contribution coming from the sale of all reaction product; all environmental indexes show very negative material contribution. On the other side, low product selectivity directly determine the presence of a complex downstream purification section and, therefore, a very high process energy specific consumption by distillation, as evidenced by the dominant contribution of the energy category in the LCA indexes.

Table 36. Background data for the environmental (not- renewable resources) and economic assessment of allyl alcohol manufacturing process [3, 74, 75]

| Substance | CED (MJ _{eq} kg ⁻¹) | EI99 (Points kg ⁻¹) | GWP (kg _{CO2-eq} kg ⁻¹) | Price (USD t ⁻¹) |
|----------------------------------|---|------------------------------------|---|---------------------------------|
| Process water | 2.8·10 ⁻⁴ | 1.8·10 ⁻⁶ | 2.4·10 ⁻⁵ | 1 |
| Ag | 1360 | 83.1 | 100 | 226000 |
| Zeolite (ZSM-5) | 73.7 | 0.39 | 4.20 | 400 |
| Catalyst disposal | 0.32 | 0.002 | 0.01 | - |
| Crude glycerol – to incineration | -19.7 | -0.063 | 0.20 | 111 |
| Crude glycerol – to WWTP | 9.97 | 0.021 | 0.92 | 111 |
| Heat | 1.57 | 0.01 | 0.10 | 20 |
| Electricity* | 9.87 | 0.02 | 0.49 | 0.10 |
| Cooling water from river | 0.00 | 0.00 | 0.00 | 0.15 |
| Natural gas** | 1.24 | 0.004 | 0.012 | 0.01 |
| Hydrogen | 69.7 | 0.24 | 1.67 | 3404 |
| Hydroxyacetone | 56.4 | 0.16 | 1.91 | 5000 |
| Acrolein | 69.6 | 0.29 | 2.49 | 1220 |
| Propionaldehyde | 92.9 | 0.33 | 3.31 | 1460 |
| Dichloromethane | 40.2 | 0.20 | 3.39 | 1245 |
| Benzene | 67.5 | 0.24 | 1.79 | 780 |
| Ethylene Glycol | 51.2 | 0.18 | 1.57 | 815.3 |
| 2-ethyl-1,3-dioxolane*** | 152 | 0.43 | 7.63 | - |
| Ash disposal | 0.28 | 0.02 | 0.009 | - |

*Electricity is measured per kWh.

**The values for natural gas are measured per MJ and they refer to heat-production purposes.

*** Price not available: no product marketability for industrial quantities.

Waste contribution is finally relevant only in the GWP final value, where evident is the effect coming from the treatment of the very large amount of process dirty water effluents, i.e. from the washing of recycle H₂ and due to very diluted conditions; negative contributions in the CED and EI-99 indexes come from ash thermal valorization and do not affect significantly the overall behavior.

A similar trend is present in operating costs evaluation, where material contributions are totally dominant and lead to even allyl alcohol negative price, i.e. the desired could be given away for free. Given total selectivity losses of ~80%, of which almost 63% to highly valuable hydroxyacetone, this result totally reflects the actual state of allyl alcohol as “by-product” and is valid only under the assumption of a totally available market, i.e. side products can be totally absorbed by an existing market. While this assumption might be valid for acrolein and propionaldehyde commodities, respectively having market capacities of ~6000 kt/y (from acrylic acid data, [128]) and >200 kt/y (1998, [80]), it would not be necessarily true for

hydroxyacetone and 2-ethyl-1,3-dioxolane, specialties chemical mainly used as flavoring agent the first and as intermediate in complex pharmaceutical industry synthesis the latter.

In the worst case scenario, no product other than allyl alcohol could be sold, therefore being treated as wastes.

Table 37. Inventory data used for the environmental and economic assessment of allyl alcohol manufacturing process.

| Materials and energy | Production of allyl alcohol | Units |
|-----------------------|-----------------------------|---------------------|
| Crude glycerol | 11.5 | kg/kg _{AA} |
| Hydrogen | 0.079 | kg/kg _{AA} |
| Process water | 65.5 | kg/kg _{AA} |
| Hydroxyacetone | 2.25 | kg/kg _{AA} |
| Acrolein | 0.91 | kg/kg _{AA} |
| Propionaldehyde | 0 | kg/kg _{AA} |
| Dichloromethane | 0.63 | kg/kg _{AA} |
| Ethylene Glycol | 0.77 | kg/kg _{AA} |
| 2-ethyl-1,3-dioxolane | 1.08 | kg/kg _{AA} |
| Catalyst | 0.047 | kg/kg _{AA} |
| Heat | 190 | MJ/kg _{AA} |
| Natural gas | 4.7 | MJ/kg _{AA} |
| Electricity | 0.75 | MJ/kg _{AA} |
| Cooling water | 3271 | kg/kg _{AA} |
| Ashes | 0.63 | kg/kg _{AA} |
| Wastewater | 70.2 | kg/kg _{AA} |
| Waste to incineration | 2.39 | kg/kg _{AA} |

Table 38. Economic and environmental assessment results for glycerol-to-allyl alcohol manufacturing process considering crude glycerol alternative utilization scenarios in incineration facilities or wastewater treatment plants.

| Scenario | LCA metric | Alternative crude glycerol fate | |
|----------|--|---------------------------------|---------|
| | | To incineration | To WWTP |
| | <i>CED (MJ_{eq}/kg_{GC})</i> | 250.5 | 90.9 |
| | <i>EI-99 (Points/kg_{GC})</i> | 1.53 | 0.57 |
| | <i>GWP (kg_{eq,CO2}/kg_{GC})</i> | 8 | -0.27 |
| | <i>CED (MJ_{eq}/kg_{GC})</i> | | 114.7 |
| | <i>EI-99 (Points/kg_{GC})</i> | | 0.24 |
| | <i>GWP (kg_{eq,CO2}/kg_{GC})</i> | | 10.6 |
| | <i>CED (MJ_{eq}/kg_{GC})</i> | -226.6 | |
| | <i>EI-99 (Points/kg_{GC})</i> | -0.72 | |
| | <i>GWP (kg_{eq,CO2}/kg_{GC})</i> | 2.3 | |

* Values corresponding to the reported glycerol indexes, multiplied by 11.5 kg_{GLY}/kg_{GC}.

Quantitative analysis reveals that, together with ~40% energy consumption reduction and ~3% increase of the total wastewater effluent, no beneficial material contribution is in this case present, i.e. only raw material costs are present, leading to total product cost in the order of 4-4.5 \$/kg. Therefore, a very high sensitivity of operating cost towards by-product marketability especially that of hydroxyacetone, is evidenced.

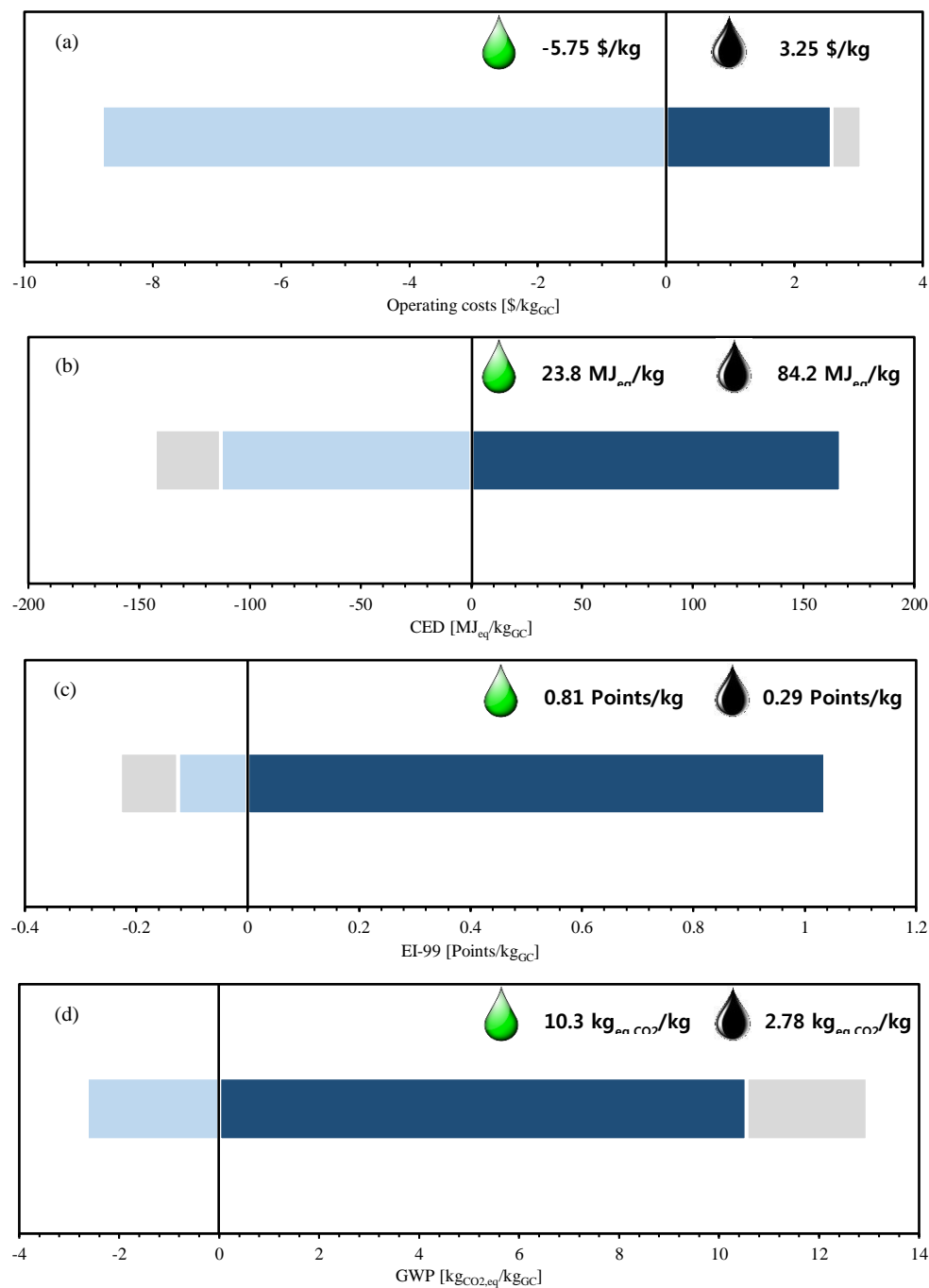


Figure 31. Economic and environmental assessment results for glycerol-to-allyl alcohol manufacturing process (■ material, ■ energy, ■ waste). No crude glycerol alternative fate considered.

Furthermore, additional concerns regard allyl alcohol limited throughput capacity, lack of flexibility in production, byproducts overproduction, and consequent augmented waste generation; in addition, economic and environmental sustainability performances driven by byproducts generation lead to substantial dependency of allyl alcohol towards multiple external market factors. For these reasons, reported assessment results must be read in term of preliminary quantitative data able to underline the present features of the proposed process. A key aspect research should focus on is represented by catalyst activity and selectivity towards allyl alcohol. In particular, Brønsted-acid functionality for dehydration and precious metal hydrogenation activity must be optimized in order to selectively address the initial dehydration of glycerol to acrolein, followed by selective hydrogenation of the carbonylic bond to allyl alcohol. This would encompass an overall catalyst optimization, i.e. addressing simultaneously the dehydration and hydrogenation phases' activity, in order to exploit possible synergistic effects affecting catalyst's coking and dehydration activity. Indeed, while the strength and concentration of Brønsted acid sites is beneficial towards the dehydration step to acrolein, it is known that a simultaneous relevant increment of condensation reactions activity lead to deleterious coking with deactivation [111]. However, the presence of a hydrogenation phase would finally help preventing coke deposition: as a result, higher dehydration selectivity to acrolein is reached. Lower operating temperature, i.e. < 673 K, would also help in limiting coke phenomena, enabling a stronger Brønsted acid character of the zeolite support. On the other side, precious metal hydrogenation activity is strongly affected by the nature of metal, its loading, its dispersion on the support, and support surface area. Addressing these factors would help in higher catalyst selectivity to allyl alcohol, with respect to propionaldehyde, while maintaining at the same time the suitable hydrogenation activity for coking prevention.

3.6 References Chapter 3

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CHAPTER 4

REGENERABLE BASES FOR EPICHLOROHYDRIN PRODUCTION

Epichlorohydrin is a high volume commodity chemical, with a 2012 worldwide production near to $2 \cdot 10^6$ t [1], largely used in the plastics industry as monomers precursor for epoxy resins and polymers production. The most important application is indeed its conversion to Bisphenol A diglycidyl ether, a building block in the manufacture of epoxy resins, by O-alkylation with Bisphenol A [2].

Traditional applications have also been employed for the manufacture of synthetic glycerol by dehydrochlorinating hydrolysis. This process is nowadays not any longer competitive on the commodity market due to the rapid increase in glycerol availability as co-product in biodiesel manufacturing; small amounts of synthetic glycerol are nowadays used only in fine and specialty applications (sensitive pharmaceutical and personal care applications) where quality standards are very high [3].

Epichlorohydrin has also minor applications as versatile precursor of other organic compounds in the propellant and the paints industry, as solvent and as insect fumigant. Alongside with traditional application, its polymers, are also used in paper reinforcement, in the food industry (manufacture of tea bags, coffee filters, and sausage/salami casings), in water purification, and in eyeglass lenses and ion-exchange resins manufacturing [4].

Figure 32 show the evolution of the global production capacity of bioplastics in recent years. Together with few others bio-based precursors, i.e. lactic acid, the importance of Epichlorohydrin in the near future is thus predicted to grow. The interest in this important chemical is thus also justified by an increasing industrial interest in bio-based plastics from an economical and environmental point of view.

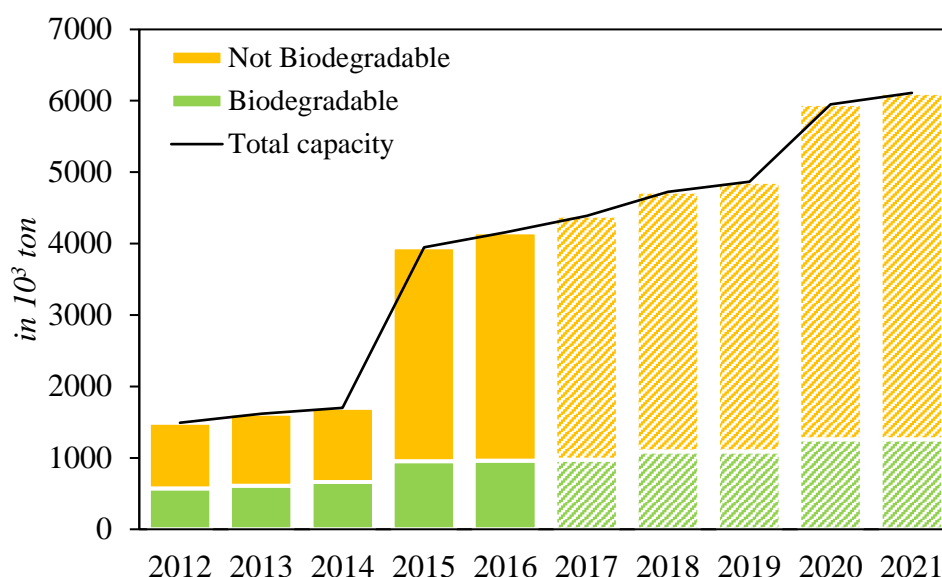


Figure 32. Global production capacity of biodegradable and not biodegradable bioplastics [5].

4.1 Actual processes and motivation for innovation

4.1.1 Oil-based process

In the framework of the oil-based chemical industry, epichlorohydrin has always been produced from propylene. Figure 33 shows the most important chemical pathways to the final product.

On the process point of view, the preferred route to epichlorohydrin is the two-step synthesis from allyl chloride (Figure 33). The overall process consists in the allylic chlorination of propylene to allyl chloride followed by hypochlorination, resulting in a 3:1 mixture of 1,3-dichloro-2-propanol (1,3-DCH) and 2,3-dichloro-1-propanol (2,3-DCH). The product mixture is then treated with an alkali to obtain epichlorohydrin [6].

Although this process is widely used at large scale, it suffers from some undesirable features, particularly the low yield in terms of chlorine usage. Only one out of the four chlorine atoms employed in the manufacture of epichlorohydrin using this route is retained in the product molecule, while the rest emerges as byproduct hydrogen chloride and waste chloride anion. Additionally, inefficiencies in the propene chlorination, DCHs hypochlorination and HOCl synthesis lead to the formation of unwanted chlorinated compounds, such as mono- and dichloropropane, mono- and di-chloropropene, and HOCl-derived inorganics, that together with the large amount of wastewater produced are expensive to dispose [7].

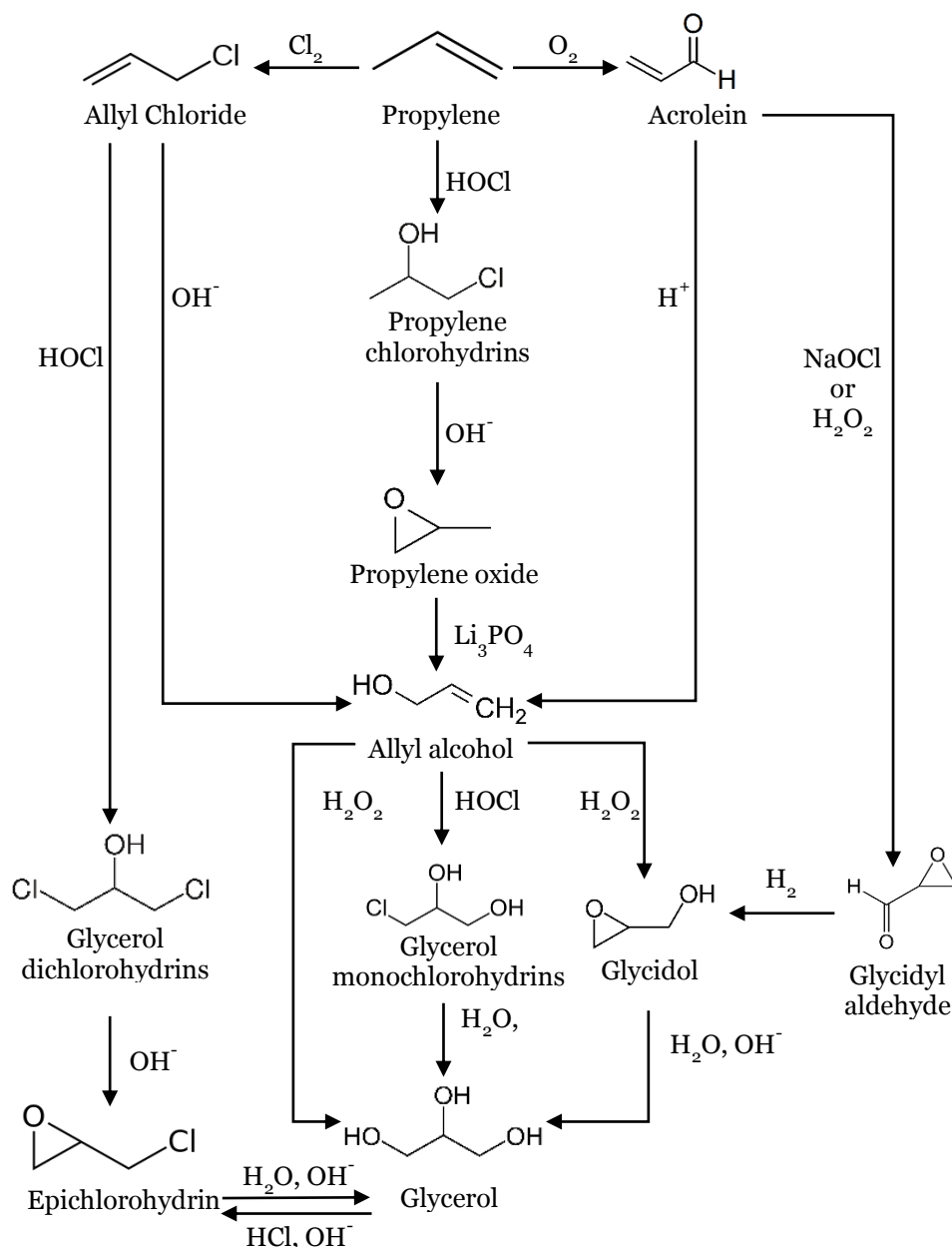


Figure 33. Routes for the manufacture of epichlorohydrin and glycerol in the petrochemical industry [8].

For the conventional production process for epichlorohydrin (Figure 34), produced by-products represent $30\% \text{ kg/kg}_{EPCH}$; they are considered as waste and sent to incineration or waste water treatment. The voluminous water flow of $\sim 40 \text{ m}^3/\text{t}_{EPCH}$ mainly originates from the DCH synthesis (80%) and the final alkaline treatment with NaOH, or $\text{Ca}(\text{OH})_2$, and contains NaCl, or CaCl_2 , and chlorinated compounds in concentrations of $25\text{-}75 \text{ mg/l}$ [7].

Even though some alternative oil-based routes exist to reduce these environmental issues, a complete sustainability of the process cannot be in any case assured due to the oil-based source of carbon, i.e. propylene.

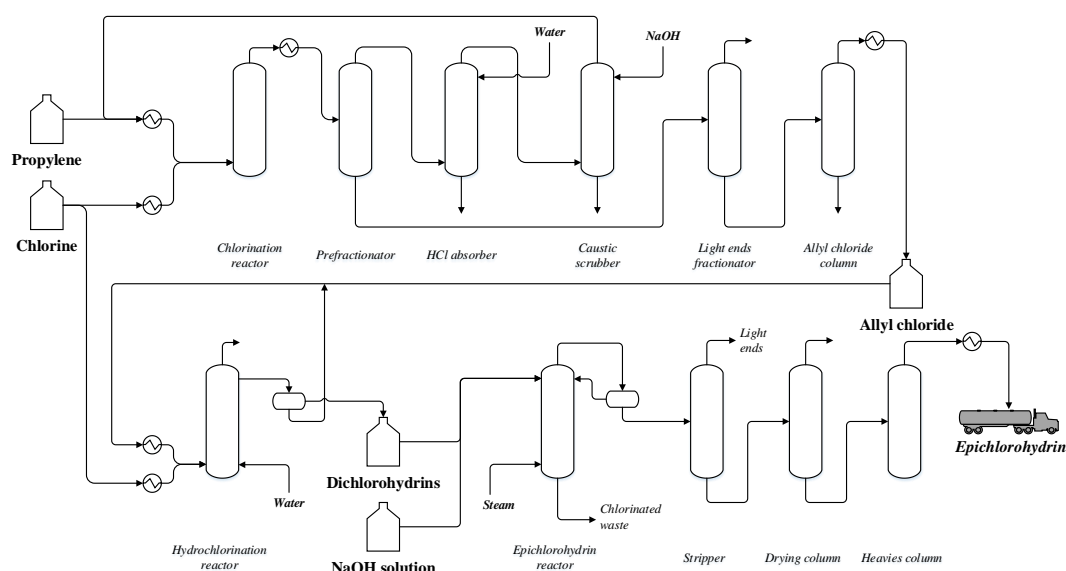


Figure 34. Epichlorohydrin complete oil-based manufacturing process [9].

4.1.2 Glycerol-based process

In the frame of a developing bio-based economy and a non-stable international context for oil, glycerol has been seen as an opportunity to develop more atom-efficient and environmentally friendly alternative routes to epichlorohydrin. Epichlorohydrin can be produced from glycerol in a two-step process involving dichlorohydrins synthesis followed by alkali treatment.

Glycerol hydrochlorination

Glycerol hydrochlorination is a parallel-consecutive reaction (Figure 35, usually carried out in the presence of homogeneous organic acid catalysts (< ~10 wt. %), i.e. acetic, propionic and malonic acids, in the temperature range of 70-120°C. Batch and semi-batch reactor technologies are applied, while a continuous reactor for glycerol hydrochlorination has not been fully investigated, even though this class of apparatus would be highly interesting for industrial applications due to its higher throughput capacity [10]. HCl can be introduced in the system either in gaseous form or as an aqueous solution of hydrochloric acid.

In addition, it has been proposed to directly use crude glycerol in the reaction, with evident economic advantage: only very few studies have however been proposed [11]. Indeed, the necessity of a purge during the recycle of the homogeneous catalyst to eliminate the impurities contained in crude glycerol coming from biodiesel production is seen as an important technical aspect.

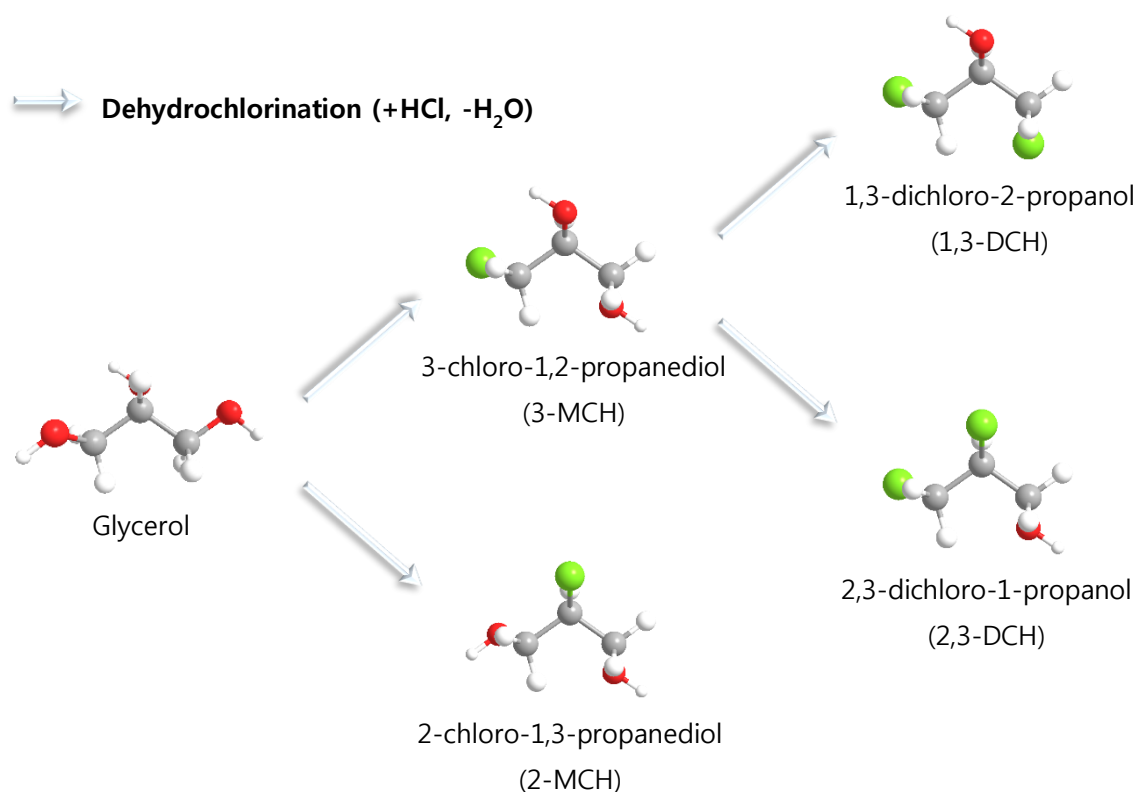


Figure 35. Overview of glycerol dehydrochlorination process.

It is experimentally observed that, the first chlorination can take place in either of the OH positions, however, the second chlorination can only proceed via the 3-chloro-1,2-propanediol (α -MCP) compound [12]. The yield to 1,3-DCH is very selective, in contrast with respect to the allyl chloride route; the final dichlorohydrins mixture's typical composition is in the range 30-50:1 of 1,3-DCH over 2,3-DCH [13]. This is an important advantage, because 1,3-DCH is much more reactive than 1,2-DCH and, consequently, epichlorohydrin can be obtained easier in more favorable-sized plants. The commonly accepted mechanism of the carboxylic acid catalyzed hydrochlorination of polyols is presented in Figure 36.

Several studies [14-16] presented an extensive homogeneous catalyst screening in terms of yields and selectivities. Twenty-seven organic acids for the glycerol hydrochlorination using gaseous HCl were tested and no correlation was observed between the catalyst pKa values and its selectivity and activity; some results are reported in Table 39. Heterogeneous catalysts for glycerol hydrochlorination with aqueous HCl have been addressed in [17] by analyzing yields and selectivities using heteropolyacids. Considerably lower reaction rate, yields and selectivities were reported than those obtained by the use of organic acids. In addition, no heterogeneous reaction mechanism was proposed.

The reaction happens in a glycerol rich solution and it is common agreement that the presence of water has a negative effect on the hydrochlorination reaction rate. This effect was first

reported in [18] adducing the reversibility of the reaction, later refuted in [14] after explaining the irreversibility of Cl addition reactions. In [19], solvation phenomena were invoked to explain such inhibition, confirmed also in [20], where they show how, for reactions that depend upon the interaction of ions of different charges, an increase in solvent polarity causes a decrease in the reaction rate.

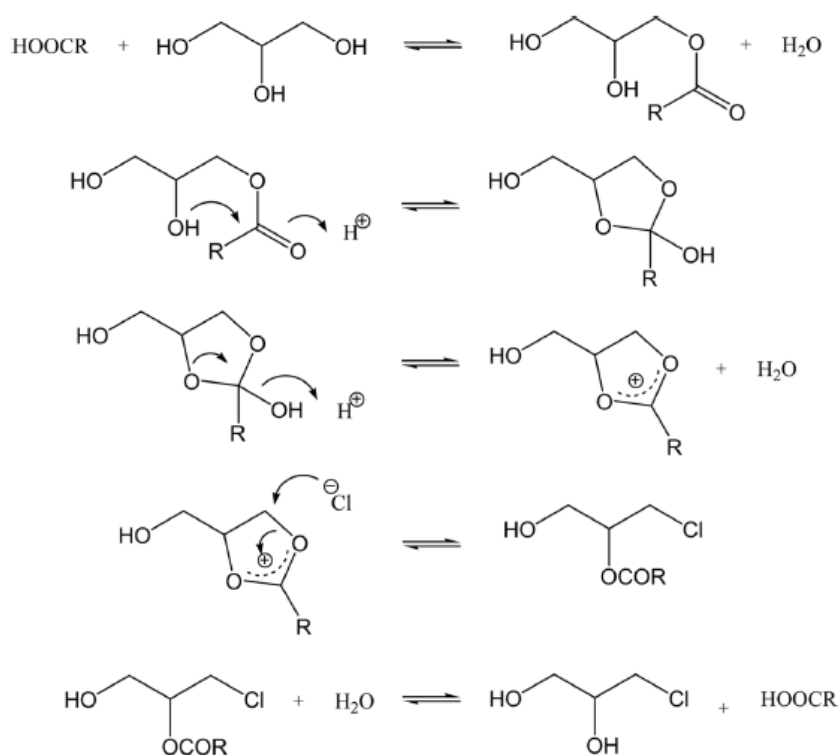


Figure 36. Mechanism of carboxylic acid-catalyzed hydrochlorination of glycerol to mono- and dichlorohydrins [13]; this mechanism precludes the formation of 1,2,3-trichloropropane since two adjacent hydroxyl groups are required to form the acetoxonium cation. It also explains the low selectivity to 1,2-DCH.

Therefore, the solvent polarity is also a plausible explanation for the lower hydrochlorination kinetics in the presence of aqueous solutions. Quantitative confirmation of this aspect has been presented in [12] with a comparative study of the kinetic constants estimated using gaseous and aqueous HCl, in the presence of acetic acid as the catalyst; higher activation energies were reported for HCl solutions.

As previously said, a variety of carboxylic acids are known as effective catalysts for the hydrochlorination reaction, although the vast majority of studies have employed acetic acid. While acetic acid performs well in laboratory-scale batch reactions, and can be used in appropriately configured commercial processes, its volatility is too high for some recycle process configurations. Among the major products from the hydrochlorination of glycerin, the desired dichlorohydrins, 1,3-DCH and 2,3-DCH are the most volatile. This makes a recycle process, in which DCHs are stripped from the product stream after reaction, and recycle of any

unreacted glycerin or MCHs and catalyst back to reaction, particularly attractive. For this option to be viable, it is preferred that the catalyst, and its esters with the products or intermediates, should be less volatile than the DCHs, so that they remain in the stripper bottoms for easy recycle. Carboxylic acid catalysts containing six or more carbon atoms meet this requirement [13].

Table 39. Acid catalyst screening results reported by Santacesaria and coworkers at 100°C.

| Acid catalyst | pK _a | P [bar] | Glycerol / catalyst [g/g] | t [h] | χ [%] | σ ₂ -MCH [%] | σ ₃ -MCH [%] | σ _{2,3} -DCH [%] | σ _{1,3} -DCH [%] | Ref. |
|-------------------|-----------------|---------|---------------------------|-------|-------|-------------------------|-------------------------|---------------------------|---------------------------|------|
| Acetic | 4.75 | 8 | 19.23 | 4 | 100 | 1 | 8 | 3 | 89 | [21] |
| Malonic | 2.84 | 5.5 | 11 | 3 | 99 | 56 | 7 | 0 | 36 | |
| Propionic | 4.87 | 5.5 | 15 | 3 | 100 | 50 | 9 | 0 | 41 | |
| Adipic | 4.43 | 5.5 | 8 | 3 | 100 | 22 | 5 | 1 | 72 | |
| Succinic | 4.20 | 5.5 | 10 | 3 | 98 | 62 | 7 | 0 | 31 | |
| Citric | 3.13 | 5.5 | 6 | 3 | 95 | 74 | 7 | 0 | 19 | |
| Levulinic | 4.59 | 5.5 | 10 | 3 | 100 | 60 | 7 | 0 | 32 | |
| Pivalic | 5.10 | 5.5 | 11 | 3 | 12 | 77 | 14 | 0 | 9 | |
| Benzoic | 4.19 | 5.5 | 14 | 3 | 14 | 91 | 9 | 0 | 0 | |
| Trichloroacetic | 0.70 | 5.5 | 15 | 3 | 17 | 88 | 12 | 0 | 0 | |
| Tartaric | 3.03 | 5.5 | 8 | 3 | 86 | 91 | 9 | 0 | 0 | |
| Fumaric | 3.05 | 5.5 | 10 | 3 | 94 | 90 | 8 | 0 | 1 | |
| Oxalic | 1.25 | 5.5 | 13 | 3 | 66 | 91 | 8 | 0 | 0 | |
| Maleic | 1.88 | 5.5 | 10 | 3 | 95 | 80 | 10 | 0 | 9 | |
| Formic | 3.74 | 5.5 | 29 | 3 | 76 | 88 | 10 | 0 | 2 | |
| Chloro-succinic | 2.67 | 5.5 | 8 | 3 | 94 | 87 | 8 | 0 | 4 | |
| EDTA | 2.00 | 6 | 19 | 3 | 54 | 83 | 9 | 0 | 7 | |
| Aspartic | 3.9 | 4.5 | 8.67 | 4 | 90 | 77 | 7 | 0 | 15 | |
| Glutamic | 4.07 | 4.5 | 7.84 | 4 | 100 | 22 | 4 | 1 | 72 | |
| Cystein | 8.37 | 4.5 | 9.52 | 4 | 59 | 85 | 9 | 0 | 6 | |
| Glycolic acid | 3.83 | 4.5 | 15.17 | 4 | 100 | 48 | 5 | 1 | 45 | |
| Diglycolic acid | 2.90 | 4.5 | 8.61 | 4 | 100 | 57 | 1 | 1 | 41 | |
| Thioglycolic acid | 3.73 | 4.5 | 12.52 | 4 | 100 | 32 | 6 | 1 | 61 | |

In addition, as further final conclusion presented in [13], the steric bulk of the catalyst largely determines the rate of glycerol hydrochlorination in a negative way. Hexanoic acid was shown to be as a possible feasible catalyst meeting volatility and steric bulk requirements.

The same study conducted with gaseous HCl revealed that the reaction is equilibrium limited at low pressure by the HCl vapor-liquid equilibrium, and that this limitation can be largely overcome by increasing the applied hydrogen chloride pressure. Typical reaction conditions

adopt an operating pressure up to 5-7.5 bar [13, 22].

Despite singular aspects have been properly addressed, glycerol hydrochlorination lacks a unified investigation of the effects of temperature, catalyst concentration and partial pressure on the reaction kinetics.

Dichlorohydrins dehydrochlorination

Epichlorohydrin synthesis process from glycerol dichlorohydrins is a rather old process used in both oil-based and glycerol-based routes. The main reaction involved are shown in Figure 37.

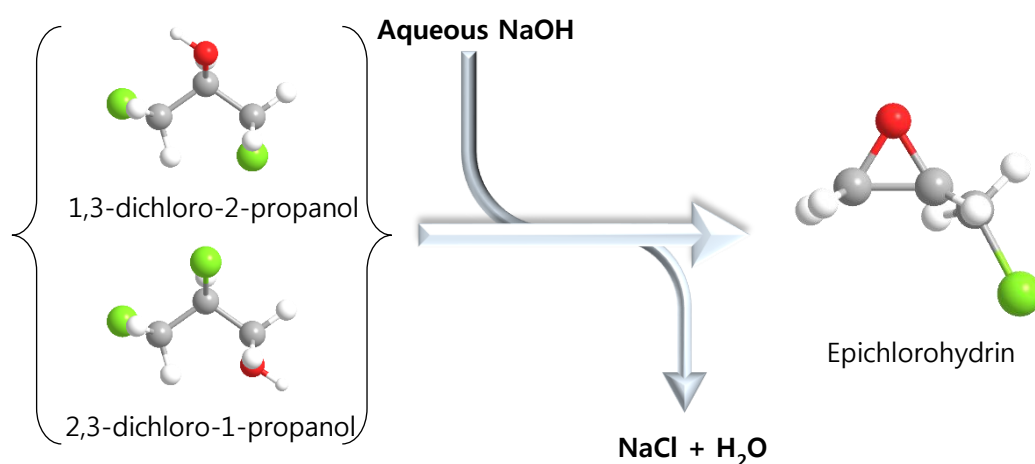


Figure 37. Overview of glycerol dichlorohydrins dechlorination to epichlorohydrin.

The composition of the reacting mixture coming from the hydrochlorination stage is rich in dichlorohydrins (min. ~90% [23]). For the glycerol process, 1,3-DCH is the major component. The industrial process usually involves the continuous manufacturing of epichlorohydrin by mean of a reactive distillation column, properly sized to obtain a satisfactory conversion also of the less reactive 2,3-DCH while limiting the formation of undesired byproducts as a consequence of long residence times. Product stability is indeed a primary concern and the main reason according to which reactive distillation methods are employed: the presence of a stripping agent, usually steam, helps removing epichlorohydrin as soon as possible from the liquid reaction environment. This way, further hydrolysis of the product to chlorohydrins, glycidol or glycerol is minimized.

The alkali treatment involves the introduction in the system of a stoichiometric base, i.e. NaOH, or an aqueous suspension of Ca(OH)₂, with co-production of equivalent amounts of the chlorinated salt. The reactor modeling requires a deep knowledge of the kinetic law of the occurring reactions and related parameters to reduce the amount of by-products (glycidol, glycerol, mono-chlorohydrin), as described in [24, 25].

The organic phase, comprising mostly dichlorohydrins and a small amount of water dissolved,

is heated up to the reaction temperature ($\sim 90^{\circ}\text{C}$) and sent to the column. The fresh alkali solution, and the one prepared with the separated water from the hydrochlorination stage, is prepared in a stirred tank. The base is sometimes fed to the process in excess (~ 5 mol. %) of the dichlorohydrins. In addition, part of the base is used for neutralization of residual aqueous HCl coming from the first reaction stage (Figure 38).

The reactant streams are only mixed in the reactor at the top stage of the tower, to prevent early formation of epichlorohydrin and its decomposition: recent configurations usually prefer structured packing than trays. Isothermal conditions are preferable to minimize the yield of hydrolysis products; the use of steam as bottom stripping agent also helps in this. Vacuum conditions, in the order of 30 kPa, are also employed to make easier the azeotropic distillation [26]. The amount of water introduced with the alkali solution and the steam used for Epichlorohydrin stripping are such that the top stream approaches the epichlorohydrin- H_2O azeotrope (Table 40).

Table 40. Water-epichlorohydrin heterogeneous azeotrope, at 1 bar [27].

| Components | T_b [$^{\circ}\text{C}$] | $T_{b,az}$ [$^{\circ}\text{C}$] | Composition [%wt.] | H_2O rich phase [%wt.] | EPCH rich phase [%wt.] |
|------------------|---------------------------------|--------------------------------------|-----------------------|---|---------------------------|
| H ₂ O | 100 | | 26 | 94.1 | 1.2 |
| Epichlorohydrin | 117 | | 74 | 5.9 | 98.8 |

A simple decanter is used to break the heterogeneous azeotrope in order to obtain an Epichlorohydrin-rich stream, while the aqueous phase is treated as waste. Waste water treatment of this stream is needed to remove the ~ 6 wt. % Epichlorohydrin [6].

The Epichlorohydrin-rich stream is finally purified according to specifications; a dehydration column was used in previous process versions [25]. PSA/TSA systems for water adsorption on molecular sieves are employed in recent configurations [6]: 3A or 4A zeolite beds, with adsorption capacity for water vapor of 0.15 kg/kg at 11kPa and 100°C [28], are used in parallel to assure the continuity of the process [6]. This method is preferred due to the low amount of residual water and since an additional thermal separation is avoided.

The bottoms of the reactive column is a waste water stream, with dissolved substances such as epichlorohydrin, NaCl/ CaCl_2 , unreacted dichlorohydrins, excess NaOH, and byproducts. This stream is simply cooled and disposed as a waste product.

4.1.3 Objective

The conventional glycerol process to epichlorohydrin has been immediately addressed as an efficient way to produce competitive bio-based epichlorohydrin at reduced environmental impact (Figure 39).

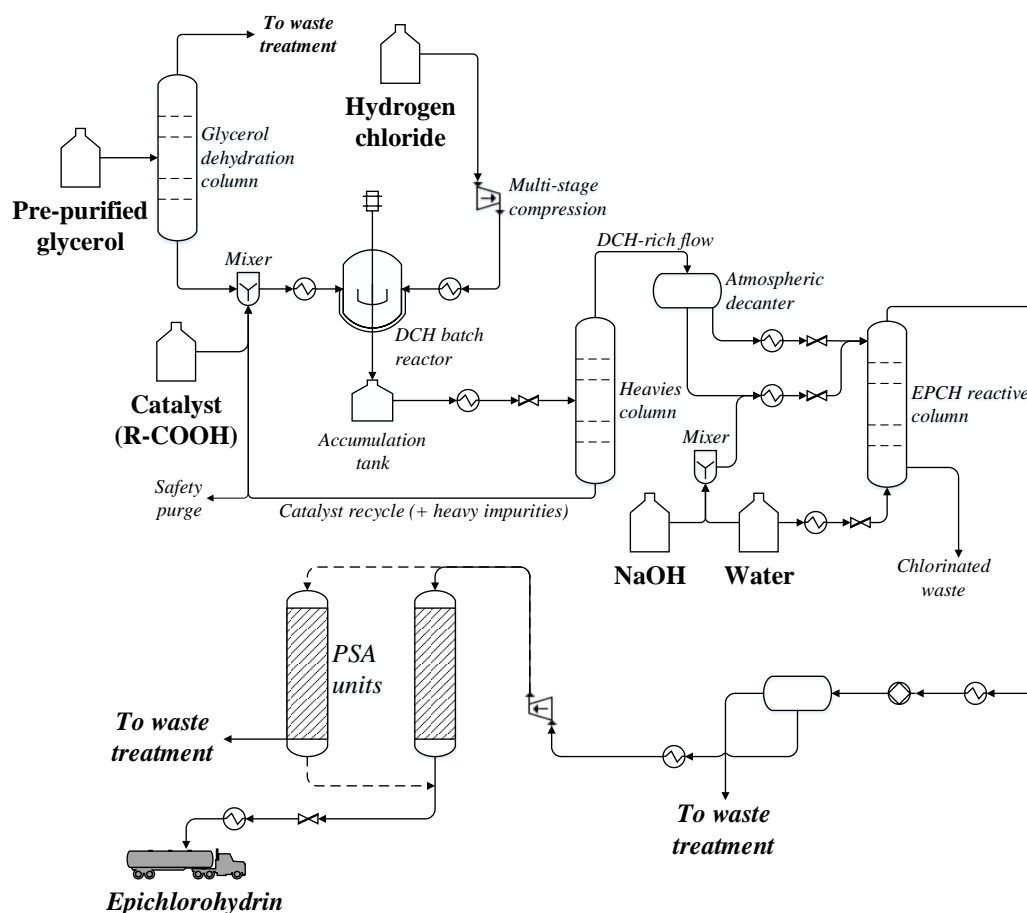


Figure 38. Conventional glycerol-based process flow diagram for epichlorohydrin manufacturing [6].

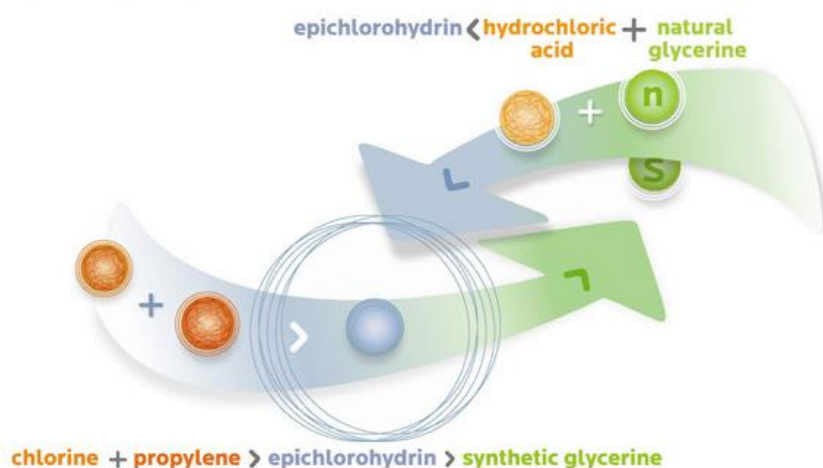


Figure 39. Change in trend in epichlorohydrin manufacturing and in glycerol utilization [29].

Solvay announced in December 2011 the building of an epichlorohydrin plant in China with initial capacity of 100 kt/y using glycerol as feedstock. According to Solvay, Epicerol® technology reduces the energy consumption by 57 %, the equivalent greenhouse gas emissions

by 61 % (GWP indicator), divides water consumption by 10, and volume of chlorinated byproducts by 8 compared to the traditional propylene-based process [29, 30]. Due to the very low price of glycerol, also other companies adopted the new bio-based routes, i.e. Dow Shanghai's epichlorohydrin plant expected to start-up in 2012.

Despite this, the process suffers from some undesirable features (Table 41). Hence, the introduction of heterogeneous catalytic technologies for the dehydrochlorination of dichloropropanols to epichlorohydrin is of primary importance to increase the sustainability of its glycerol-based production.

Table 41. Undesirable features associated to the conventional alkali treatment.

| Process issues | Environmental / economic issues |
|---|---|
| <i>Introduction of aqueous NaOH in the system as reagent.</i> | <i>Required stoichiometric amount of base (NaOH)</i> |
| <i>High sensitivity towards process conditions</i> | <i>High amount of chlorinated co-products / by-products in waste water streams</i> |
| <i>Epichlorohydrin stability in the aqueous basic reaction environment</i> | <i>Stoichiometric co-production of NaCl, contained in the waste stream and to be disposed</i> |
| <i>Reactive stripping/distillation column required to minimize EPCH residence time in the liquid reaction phase</i> | <i>Lower overall process atom economy due to salt production and chlorinated by-products</i> |
| <i>Corrosion issues due to the presence of Cl⁻ salts in basic environment (passivation)</i> | |

The identification of a suitable catalyst appears as a challenging endeavor. Indeed, hydrochloric acid is generated, which is expected to interact with the active basic sites in a strong manner [31], possibly leading to activity loss by poisoning and calling for the development of efficient regeneration strategies. This issue has been encountered upon the dehydrohalogenation of alkyl halides over basic metal oxides (CaO, MgO), which were converted into metal halides upon reaction and could be regenerated by simple calcination at 823 K [32, 33]. Aiming at minimizing deactivation, one appealing strategy is the use of a sufficiently high reaction temperature to operate the process in the gas phase and in continuous mode.

In this work, mixed oxides of magnesium and aluminum obtained by calcination of hydrotalcite-like materials are introduced as efficient solids for the gas-phase conversion of dichloropropanols to epichlorohydrin. The superiority of these basic materials is identified by screening different type of acid and basic solids and that of the gas-phase operation conditions. The selectivity to epichlorohydrin is maximised by tuning the concentration and strength of the basic sites through variation of the Mg/Al ratio and the activation conditions of the hydrotalcite-like solids, which offers insights into structure-activity relations. Testing of the best performer over prolonged reaction times evidences deactivation; after unraveling the origins of the activity decay, strategies to restore the original level are demonstrated.

Lastly, qualitative and quantitative conclusions, based on process modelling, are drawn on the ecologic and economic advantages of using a heterogeneous rather than a homogeneous base.

4.2 Experimental

4.2.1 Material preparation

γ -Al₂O₃ (Alfa Aesar, 99.997% metals basis), MgO (Strem Chemicals, 99.5%), a USY zeolite in protonic form with a bulk Si/Al ratio of 405 (Zeolyst, USY) and a Y zeolite in sodium form with a bulk Si/Al ratio of 2.6 (Zeolyst, CBV100) were used as received.

Two Mg- and Al-based hydrotalcite-like materials with a nominal Mg/Al ratio of $x = 2$ and 4 (HTx) were prepared by co-precipitation at pH 10. A volume of 500 cm³ of a 0.25· x and 0.25 M aqueous solution of Mg(NO₃)₂·6H₂O (Riedel-de Haen, >99%) and Al(NO₃)₃·9H₂O (Sigma-Aldrich, >98%), respectively, was added to 600 cm³ of 2 M aqueous Na₂CO₃ (Sigma-Aldrich, >99.5%) at a rate of 3.5 cm³ min⁻¹ while magnetically stirring (500 rpm) at ambient temperature. A 40 wt. % NaOH (Sigma-Aldrich, 97%) solution was simultaneously added dropwise to keep the pH constant at 10. The obtained slurry was aged at 333 K for 6 h under stirring. After filtering and washing (3 times, 200 cm³ of deionized water each time), the precipitate was dried at 333 K for 18 h. Mixed metal oxides were obtained by calcination of the hydrotalcite-like materials at 673-973 K (5 K min⁻¹) for 5 h. These samples were labelled as HTx- cy , where y is the calcination temperature expressed in K.

An alkaline-activated USY zeolite with basic character (USY-AT) was synthesized by adding 3.3 g of a high-silica USY zeolite (Si/Al = 405, Zeolyst) to 100 cm³ of a 0.1 M methanolic (Sigma-Aldrich, 99.8%) solution of NaOH. After stirring for 10 min at room temperature, the solid was filtered and washed with methanol (3 times, 100 cm³ each time) [34].

An alkali-activated Y zeolite (Y-AT) was prepared in two steps. Firstly, a zeolite Y (Zeolyst, CBV100) was dealuminated at 373 K in a 0.15 M solution of H₄EDTA (Fluka, >99%, 15 cm³ per gram of zeolite) for 24 h, recovered by filtration, washed with deionized water (3 times, *ca.* 30 cm³ per gram of zeolite) and dried at 338 K for 16 h. Thereafter the solid obtained was treated in 0.05-0.2 M aqueous NaOH (30 cm³ per gram of zeolite) at 338 K for 30 min, using an Easymax 102 setup (Mettler Toledo). After quenching in an ice bath and filtering, the zeolite was washed with deionized water (3 times, *ca.* 30 cm³ per gram of zeolite) and dried at 338 K for 16 h [35]. MgO/USY was prepared by dry impregnation. A volume of 4 cm³ of a 0.25 M aqueous solution of Mg(NO₃)₂·6H₂O (Fluka, 99%,) were added dropwise to 4 g of the USY zeolite at room temperature. The sample was dried at 338 K overnight and calcined at 823 K (5 K min⁻¹) for 5 h [31].

4.2.2 Material characterization

The elemental composition of the materials was determined by X-ray fluorescence

spectroscopy (XRF) using an Orbis Micro XRF instrument equipped with a Rh source operated at 35 kV and 500 mA.

N₂ sorption at 77 K was conducted using a Micromeritics TriStar analyser. Prior to the measurements, the solids were degassed at 573 K under vacuum for 3 h.

Powder X-ray diffraction (XRD) was performed using a PANalytical X'Pert PRO-MPD diffractometer with Ni-filtered Cu K α radiation ($\lambda = 0.1541$ nm), acquiring data in the 10-60° 2 θ range with an angular step size of 0.05° and a counting time of 2 s per step.

Al magic angle spinning nuclear magnetic resonance (²⁷Al MAS NMR) spectroscopy was conducted in a Bruker Avance 700 spectrometer operated at 182.4 MHz using 4-mm ZrO₂ rotors spun at 10 kHz. Spectra were acquired accumulating 512 scans using a pulse length of 1 ms, a recycle delay of 1 s and solid (NH₄)Al(SO₄)₂ as a reference ($d = 0.00$ ppm).

Temperature-programmed desorption of carbon dioxide (CO₂-TPD) and temperature programmed oxidation (TPO) was carried out using a Micromeritics Autochem II chemisorption analyser coupled with a MKS Cirrus 2 quadrupole mass spectrometer. For the first, the samples (0.05 g) were treated in a He flow (20 cm³ min⁻¹) at 373 K for 2 h. Afterwards, CO₂ (50 pulses, 1 cm³ each pulse) carried by He (10 cm³ min⁻¹) was adsorbed at 323 K, followed by He purging at the same temperature for 1 h. CO₂ desorption was performed using a He flow of 10 cm³ min⁻¹ and monitored in the 323-973 K range (10 K min⁻¹). The concentration of basic sites (CB), expressed as mmol_{CO₂} g⁻¹, was obtained by multiplying the area of the desorption curve by a calibration factor obtained from the decomposition of known amounts of Na₂CO₃ (Sigma-Aldrich, >99.5%) and dividing it by the mass of the sample. In the latter, the samples (0.05 g) were treated in a He flow (20 cm³ min⁻¹) at 373 K for 2 h. Thereafter, the temperature was lowered to 323 K, the flow composition and rate modified to 10% O₂ in He and 10 cm³ min⁻¹, respectively, and the composition of the gas evolved was monitored in the 323-973 K range (10 K min⁻¹).

The chlorine and the carbon contents of the used solids were determined by elemental analysis using a LECO CHN-9000 instrument.

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy of the spent catalyst was conducted using a Bruker Vertex 70 spectrometer equipped with a liquid-N₂ cooled MCT detector and a diffuse reflectance cell (Harrick). The sample was degassed in Ar (10 cm³ min⁻¹) at 373 K for 1 h. Thereafter, the temperature was increased to 773 K (10 K min⁻¹) and spectra were recorded every 50 K in the 4000–600 cm⁻¹ range with a resolution of 4 cm⁻¹.

Scanning transmission electron micrographs (STEM) and elemental maps were acquired using a FEI Talos F200A instrument equipped with a high brightness field emission gun and high-angle annular dark-field (HAADF) and large collection angle energy-dispersive X-ray spectroscopy (EDX) detectors and operated at 200 kV. Beam transparent sections (80-nm thick) were obtained from resin-embedded granules by ultramicrotomy and were supported on copper grids coated with a continuous carbon film.

4.2.3 Material testing

The gas-phase dehydrochlorination of 1,3-dichloro-2-propanol (Aldrich-Fine Chemicals, 98%) was studied at ambient pressure using a continuous-flow fixed-bed reactor setup (Microactivity Reference, PID Eng&Tech) comprising: (i) a syringe pump for the admission of the 10 wt.% aqueous solution of the reactant, (ii) a mass flow controller for feeding N₂ (PanGas, 99.99%), (iii) a tubular quartz reactor (12 mm internal diameter) equipped with a thermocouple to monitor the catalyst bed temperature and heated in an oven and (iv) a condenser operated at 273 K. A mass of 0.1-0.5 g of material (0.2-0.5 mm sieve fraction) were loaded into the reactor and the system was heated to the desired temperature (373-673 K) under a N₂ flow of 100 cm³ min⁻¹. Thereafter, the liquid feed was admitted and samples were collected every 15 min from the condenser, which were analysed by gas chromatography using an HP 6890 chromatograph equipped with an HP-5 capillary column and a flame ionisation detector. Quantification was achieved based on the absolute peak areas. Calibration curves were measured in the 0.5-10 wt.%, 0.5-7 wt.%, 0.5-3 wt.% ranges for 1,3-dichloro-2-propanol, epichlorohydrin and chloroacetone, respectively. The calibration response factor of unknown compounds was assumed to be the same as that of epichlorohydrin.

The conversion of the substrate was calculated as the number of moles of substrate reacted divided by number of moles of substrate fed and the selectivity to the product *i* as the number of moles of product formed divided by the total number of moles of products, according to the following formulae, where the subscripts 0/1 refer to the reactor inlet/outlet mixture:

$$\chi_{dichloropropanol} = \frac{n_{dichloropropanol0} - n_{dichloropropanol1}}{n_{dichloropropanol0}} \quad \text{Eq. (4.1)}$$

$$\sigma_i = \frac{n_{i,1}}{n_{dichloropropanol0} - n_{dichloropropanol1}} \quad \text{Eq. (4.2)}$$

The weight hourly space velocity (WHSV) was calculated with respect to the actual flow of dichloropropanol.

The carbon balance was calculated as the ratio between the number of moles of products and the number of moles of glycerol fed and was always higher than 90%. The experimental error, determined by three repetitions of selected runs, was within 5%.

A low amount of conversion was observed in the blank tests, i.e., tests conducted with empty reactor: these results were collected and used for the identification of relevant thermal peaks in GC chromatograms.

4.3 Experimental results and discussion

4.3.1 Evaluation of solids acids and bases

Since the identification of suitable solids for the dehydrochlorination of dichloropropanol to epichlorohydrin is here tackled for the first time, a diverse set of materials was selected for screening. In analogy with the stoichiometric homogeneous reactants commonly used in the established liquid-phase processes, such as NaOH or KOH, part of the compounds comprised solid bases of different nature and strength. Specifically, they included earth-alkali oxides (MgO), alkali-activated zeolites (USY-AT), and hydrotalcite-like materials in as-synthesized form, i.e. layered double hydroxides with formula $[Mg^{2+}_nAl^{3+}_m(OH)_{2(n+m)}]^{m+}[CO_3^{2+}]_{m/2} \cdot H_2O$ (here with $n=4$ and $m=2$, HT2), or in calcined state, i.e., Mg-Al mixed oxides (here calcined at 823 K, HT2-c823). These materials have a strong Lewis-, strong Brønsted-, weak Brønsted- and strong Lewis-basic character, respectively. γ -Al₂O₃ and a zeolite Y in its sodium form (bulk nominal Si/Al ratio of 2.6) were chosen as representative of strong and weak Lewis acids, in this order. Strong Brønsted acidity was featured in an ultra-stable Y zeolite in protonic form (bulk nominal Si/Al ratio of 405), i.e. H-USY. Finally, to assess the relevance of the co-presence of acidity and basicity, 1.1 wt.% of MgO was supported on the H-USY zeolite (MgO/USY) and the zeolite Y was modified by an alkaline treatment in 0.15 M NaOH (Y-AT). The porous and acid/base properties of these solids are reported in Table 42 and Table 43.

All of the systems were tested in a continuous-flow fixed-bed reactor kept at 473 K by feeding an aqueous dichloropropanol solution (5 wt.%) along with an inert carrier for 0.5 h. Solids possessing Brønsted and Lewis acidity generally displayed very low activity (< 1% dichloropropanol conversion, Figure 40) and selectivity to epichlorohydrin (<15%).

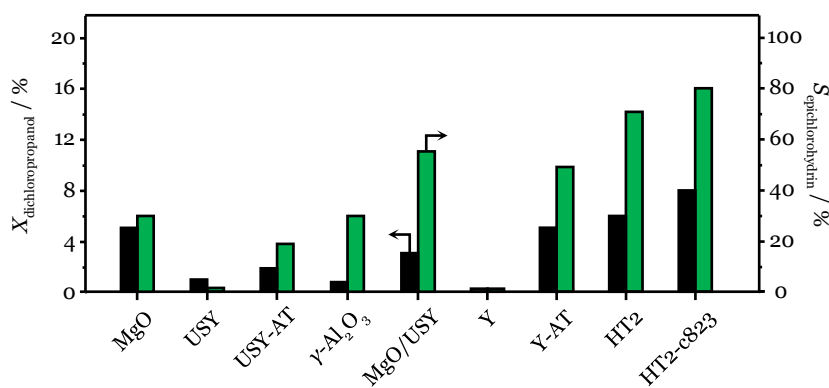


Figure 40. Dichloropropanol conversion and epichlorohydrin selectivity over different materials. $T = 473$ K, $P = 1$ bar, and $WHSV = 6$ h⁻¹.

This behavior was rationalized by the capability of acid sites to catalyze dehydration and

oligomerization reactions, leading to fouling [36], which was evidenced by the black color assumed by the white powders upon the test and confirmed by CHN analysis (up to 8% wt. % C, Table 42). In addition to the generation of carbonaceous species, chloroacetone was formed as a by-product with a selectivity up to 25%. The poor performance of solid acids improved through the incorporation of basic sites. In fact, the dichloropropanol conversion increased from 0.5 and 1.0% to 2.2 and 3.8% over Y-AT and MgO/USY, respectively, and the epichlorohydrin selectivity raised up to *ca.* 50% over both solids. However, coke was still produced in a significant amount in both cases (4-5 wt. % C), due to the marked acidity retained by the zeolites upon their modification. Superior epichlorohydrin yields were attained over purely basic solids, except for USY-AT. Indeed, MgO, the Mg- and Al-based hydrotalcite-like material and the mixed Mg-Al oxide displayed a conversion of 5, 6 and 8% and an epichlorohydrin selectivity of *ca.* 30, 70 and 80%, respectively. Notably, coke formation was very limited over these materials (< 3 wt. % C).

Table 42. Characterization data and coke content of the screened catalysts.

| | $S_{\text{BET}}^{\text{a}}$ [m ² g ⁻¹] | $V_{\text{pore}}^{\text{b}}$ [cm ³ g ⁻¹] | C_{B}^{c} [μmol g ⁻¹] | C_{A}^{d} [μmol g ⁻¹] | C^{e} [wt. %] |
|----------------------------------|--|--|--|--|---------------------------|
| USY | 648 | 0.53 | 0 | 58 | 8.4 |
| Y | 680 | 0.48 | 19 | 221 | 5.2 |
| γ-Al ₂ O ₃ | 85 | 0.50 | 5 | 85 | 5.6 |
| Y-AT | 406 | 0.27 | 389 | 161 | 4.1 |
| MgO/USY | 612 | 0.51 | 181 | 68 | 5.0 |
| USY-AT | 600 | 0.49 | 184 | 12 | 2.1 |
| MgO | 482 | 0.45 | 364 | 6 | 3.0 |

^a BET method; ^b volume adsorbed at $p/p_0 = 0.98$; ^c CO₂-TPD; ^d infrared of adsorbed pyridine; ^e elemental analysis

Table 43. Characterization data and coke content of the hydrotalcites and the mixed metal oxides derived upon thermal activation.

| | Mg/Al ^a | Phase ^b | $S_{\text{BET}}^{\text{a}}$ [m ² g ⁻¹] | $V_{\text{pore}}^{\text{b}}$ [cm ³ g ⁻¹] | C_{B}^{c} [μmol g ⁻¹] | $T_{\text{des}}^{\text{f}}$ [K] | $T_{\text{dec}}^{\text{f}}$ [K] | C^{e} [wt. %] |
|----------|--------------------|--------------------|--|--|--|------------------------------------|------------------------------------|---------------------------|
| HT2 | 1.97 | HT | 81 | 0.47 | 85 | 404 | 623 | 0.9 |
| HT4 | 3.52 | HT | 65 | 0.42 | 89 | 395 | 595 | 0.4 |
| HT2-c823 | 1.82 | MMO | 197 | 0.58 | 600 | 532 | - | 1.0 |
| HT4-c673 | 3.31 | HT+MMO | 148 | 0.45 | 412 | | 650 | 0.3 |
| HT4-c823 | 3.50 | MMO | 223 | 0.60 | 482 | 573 | - | 1.0 |
| HT4-c973 | 3.52 | MMO | 203 | 0.58 | 355 | 536 | - | 1.1 |

^a XRF; ^b XRD. HT = hydrotalcite, MMO = mixed metal oxide; ^c BET method; ^d volume adsorbed at $p/p_0 = 0.98$;

^e CO₂-TPD; ^f Temperature corresponding to the maximum of desorption (des) and decomposition (dec) peaks in the CO₂-TPD analyses. ^g elemental analysis.

4.3.2 Design of Mg-Al mixed oxides

Based on its outstanding performance, the Mg-Al oxide was selected for further development. Since such compound was obtained from a hydrotalcite-like precursor, it was conceived to vary its properties by altering the composition of the starting double layered hydroxide. Thus, an additional sample was prepared with an Mg/Al ratios of 4 (HT4). A ratio lower than 2 was excluded, since for this value it is not feasible to attain a solid with pure hydrotalcite structure, while a ratio higher than 4 was irrelevant, since it leads to materials with limited ion-exchange properties. The actual metal ratio in the as-synthesised materials was close to the nominal value and, in all cases, the surface area was comprised between 70-80 m² g⁻¹ (Table 43). The XRD patterns of the solids (Figure 41a) show the typical reflections of a rhombohedral (3R) layered double hydroxide structure, which are shifted to lower 2 θ values for the higher Mg contents due to the expansion of the unit cell size [37]. Transmission electron microscopy (TEM) confirmed the plate-like structure of the crystals (Figure 42a), which exhibit extensive intergrowth and are oriented in a random fashion. All of the Al magic-angle spinning nuclear magnetic resonance (²⁷Al MAS NMR) spectra display a signal centered at 10 ppm, indicating the octahedral (Oh) symmetry of the Al centres (Figure 41b).

The basicity of the hydrotalcite-like solids was probed by CO₂-TPD (Figure 41c). For all samples, the curves evidence a low-intensity peak centered at *ca.* 400 K, indicating the presence of few weak basic sites, which is accompanied by a second, very pronounced signal peaking at 600-700 K, which was produced by the decomposition of interlayer carbonates (Figure 41c). The area of this second contribution is larger for HT2 than for HT4, in line with the larger Al substitution and thus capacity of accommodating interlayer anions. After calcination at 823 K, the samples possessed the same Mg/Al ratios as the corresponding starting hydrotalcite-like materials (Table 43) and 2.5- or 3.5-fold higher surface area (200-220 m² g⁻¹). Their diffractograms (Figure 41d) almost exclusively comprise two relatively broad reflections at 43° and 62° 2 θ , which indicate the transformation of the double layered hydroxide into a mixed oxide. Platelet-like crystals were visualized by TEM (Figure 42b), which also highlighted an increased disorder, *i.e.*, an augment of intercrystalline mesoporosity. The latter is in line with the higher surface area (Table 43). ²⁷Al MAS NMR spectroscopy (Figure 41e) revealed that about a third of the Al atoms changed their environment upon calcination attaining a tetrahedral geometry (*T_d*), which is generally quite distorted considering the broad shape of the resonance at 80 ppm, and, based on the appearance of a peak at 18 ppm, about half of the remaining octahedral sites became highly distorted (*C_{3v}*). The density of basic centers of the calcined samples underwent a *ca.* 8-fold increase (Figure 41f and Table 43) and was maximal for HT2-c823. Still, although preserving sites of mild and moderate strength, HT4-c823 possessed the strongest centers (*T_{des}* > 773 K).

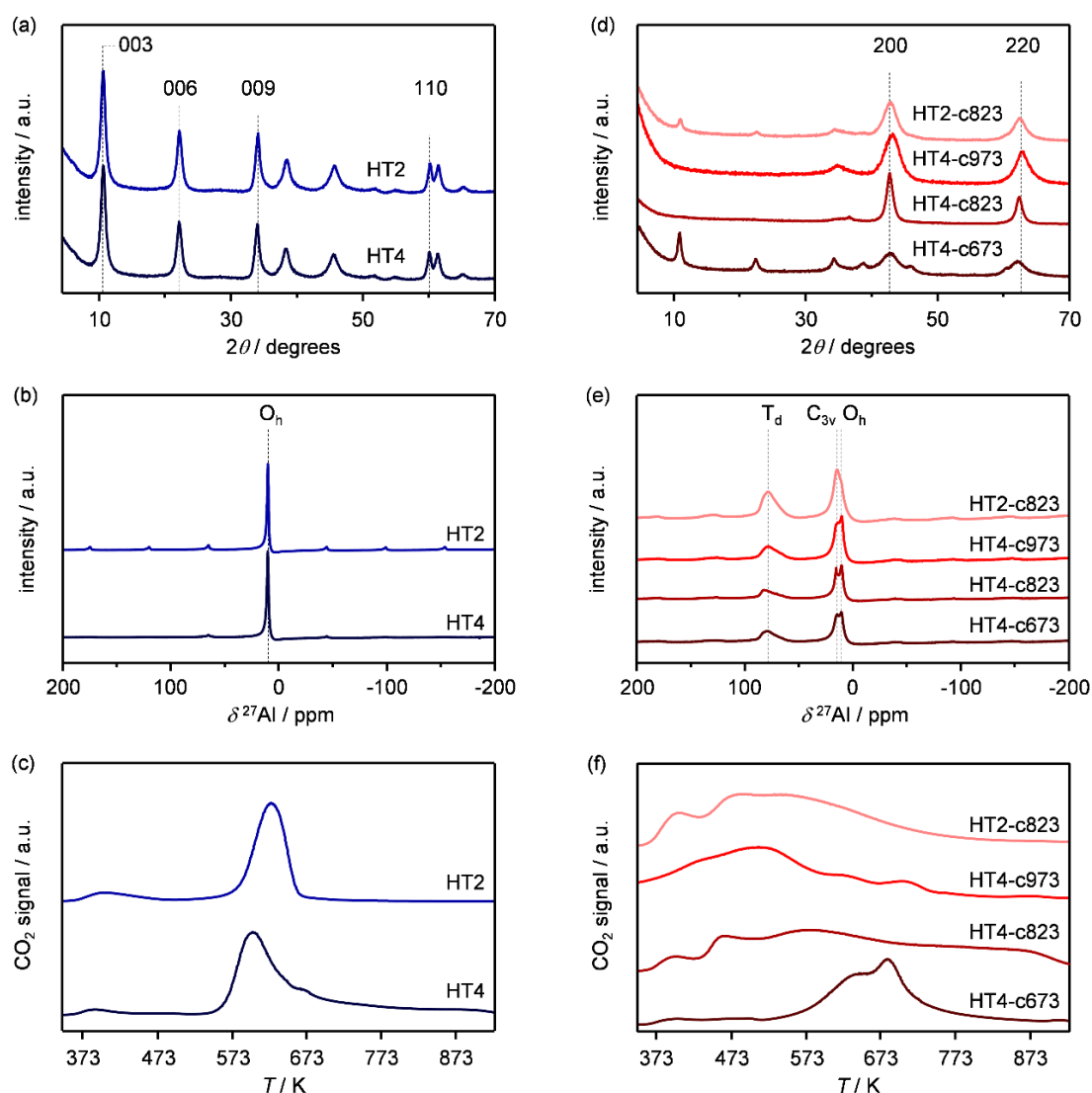


Figure 41. (a,d) XRD, (b,e) ^{27}Al MAS NMR and (c,f) CO_2 -TPD profiles of the (a,b,c) as-synthesised HTx and (d,e,f) calcined HTx-cy materials.

To modify the characteristics of the mixed oxide, we also considered the thermal treatment of the starting hydrotalcite-like material, tuning its temperature. Thus, HT4 was additionally calcined at 673 and 973 K. The milder treatment led to an only partial decomposition of the hydrotalcite to the mixed oxide, as demonstrated by the surface area, which was intermediate between that of the precursor and that of the mixed oxide obtained upon calcination at 823 K, by detection of unconverted precursor in the XRD pattern (Figure 41d) and by the coexistence of both octahedral and distorted octa- and tetrahedral species in the ^{27}Al MAS NMR spectrum. After calcination at 973 K, only a mixed oxide phase was present, which featured sharper peaks than the other two samples, suggesting a moderate increase of the crystallite size due to sintering at high temperatures.

The two new sets of samples were tested in the dehydrochlorination of dichloropropanol under

the same conditions applied in the initial evaluation of materials. With respect to the hydrotalcite-like solids, HT4 showed an only slightly lower conversion and epichlorohydrin selectivity than HT2 (5 *versus* 6% and 70 *versus* 75% respectively, Figure 43a). A noticeable boost in activity and selectivity was observed over all calcined solids, which were maximized over HT4-c823 (18% dichloropropanol conversion, 95% epichlorohydrin selectivity). It should be noted that these two parameters are linked, *i.e.*, a higher selectivity is achieved at a higher conversion level. This is explained by the fact that the concentration of chloroacetone, the main by-product, was equal in all tests, suggesting that their rate of formation is not influenced by the material and that they are likely formed through thermally-driven pathways (Figure 44).

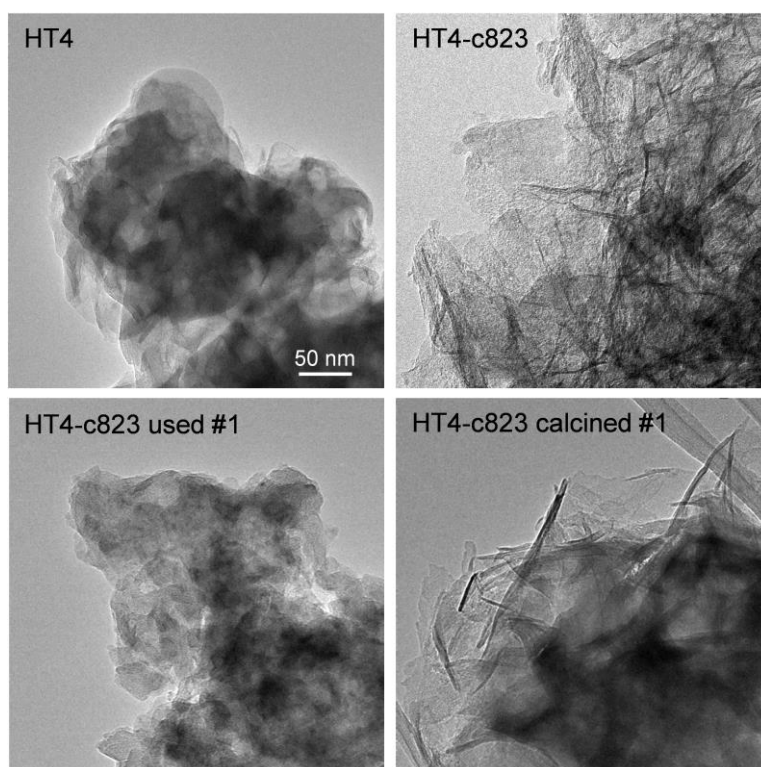


Figure 42. TEM images of the HT4 precursor and of the calcined HT4-c823 material in its fresh, used and regenerated forms.

By analogy with the decomposition of other epoxides [38], it was hypothesized that this by-product arises from the thermal isomerization of the epichlorohydrin. Indeed, experiments conducted feeding the latter over a HT4-c823 catalyst bed at 673 K yielded the ketonic product with a yield of 70%, with simultaneous very low carbon balance 72% due to coke formation and deposition. Dichloropropanol pure thermal decomposition was determined upon blank runs and was found to be limited to 5% and 20% in the 373÷473 K and 473÷673 K ranges, respectively (Figure 44). Since no dependence of these amounts on acid/base or textural properties was observed, thermal mechanisms might be held responsible for its formation. Comparison of the dichloropropanol conversion over the various mixed oxides with the type of their basic sites did not unveil any correlation, while their surface area appeared as a better

descriptor for activity (Figure 43b), hinting at the active-site accessibility, rather than its nature, as the most relevant parameter.

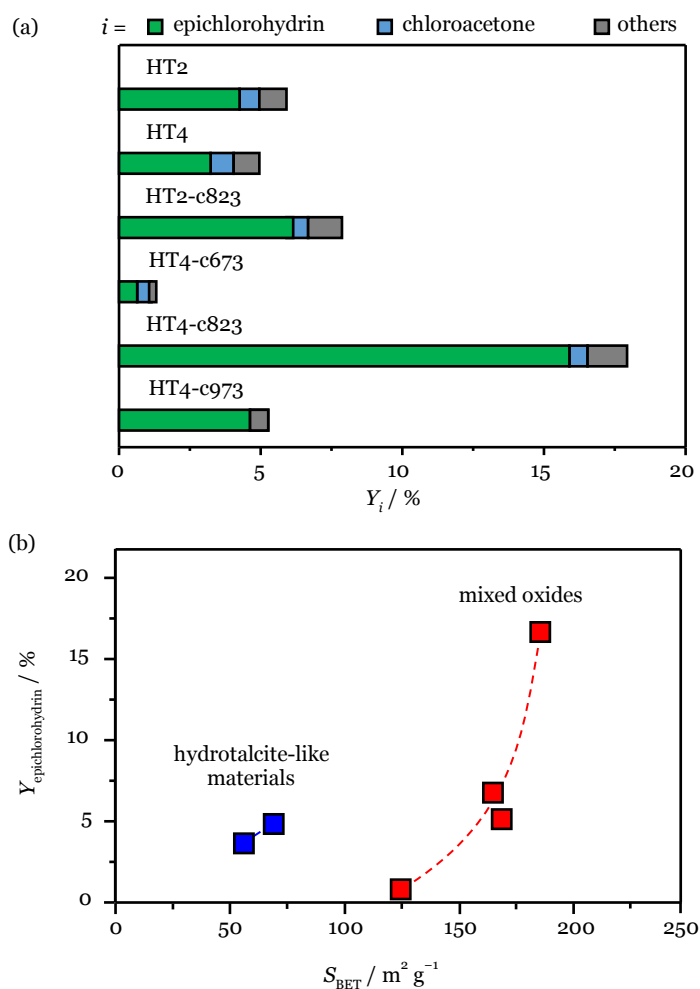


Figure 43. (a) Epichlorohydrin, chloroacetone and other by-products yield using HTx and HTx-cy materials. (b) Epichlorohydrin yield as a function of their specific surface area. $T = 423$ K, $P = 1$ bar, $t = 0.5$ h and $WHSV = 6$ h⁻¹.

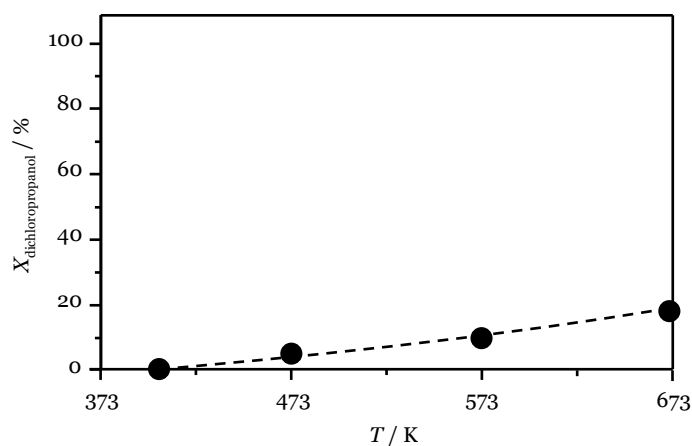


Figure 44. Dichloropropanol conversion versus temperature in experiments conducted in the absence of any additional reagent at $P = 1$ bar and $WHSV = 1.2$ h⁻¹.

4.3.3 Optimization of the reaction conditions

In view of the superior epichlorohydrin yield obtained in the presence of HT4-c823, the influence of the reaction parameters on the performance was investigated using this sample. In the 423-673 K range, the dichloropropanol conversion increased monotonously with temperature (Figure 45a). In contrast, the selectivity to the desired product, epichlorohydrin, was close to 100% below 423 K and rapidly decreased in the range 473÷573 K, approaching 0% at the highest temperature.

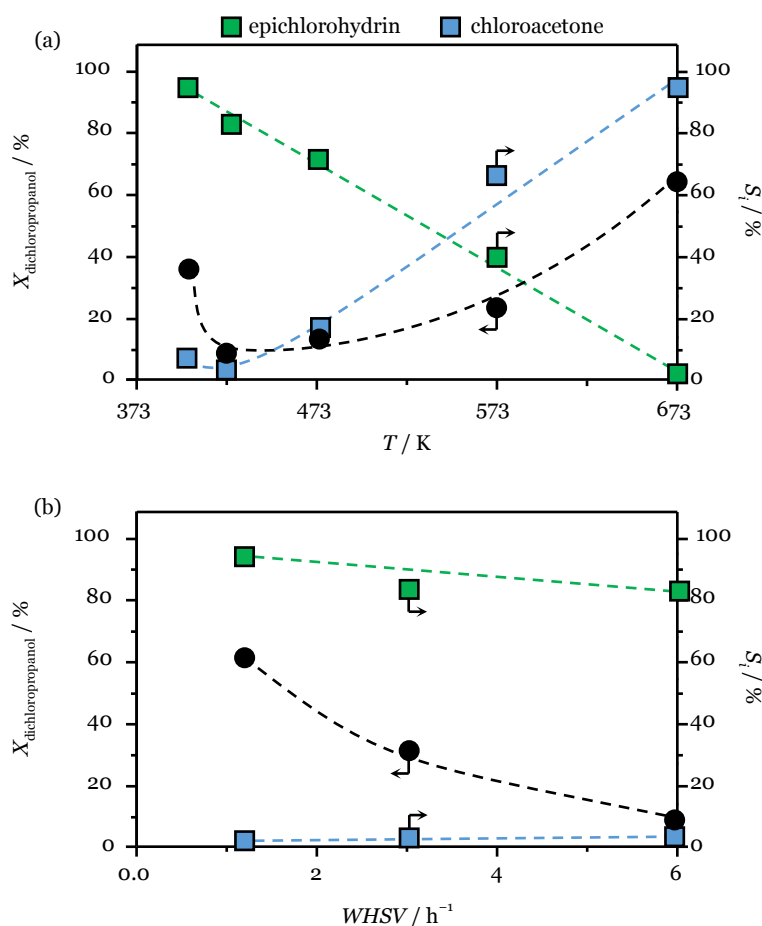


Figure 45. Dichloropropanol conversion and selectivity towards epichlorohydrin and chloroacetone in the presence of HT4-c823 as a function of (a) temperature and (b) weight hourly space velocity. $T = 423$ K, $P = 1$ bar, $t = 0.5$ h and $WHSV = 6$ h⁻¹.

The selectivity trend for chloroacetone, the main by-product, was exactly opposite to the one of epichlorohydrin, i.e., the formation of the ketonic compound was negligible at low temperatures and almost exclusive at high temperatures, in line with blank experiments results. An increase of the WHSV produced a decrease in the conversion, while it did not alter significantly the selectivity towards epichlorohydrin and chloroacetone (Figure 45), in agreement with the observations previously made about the thermally-driven generation of

the by-product.

The best performing material, HT4-c823, was tested over a prolonged reaction time under the optimized conditions of temperature and flow. The initially high (*ca.* 60%) dichloropropanol conversion was found to rapidly decrease to 15% during the first hour (Figure 46a). Similarly, the high selectivity observed in the first stage diminished, in line with the fact that chloroacetone and coke were generated at a constant yield.

4.3.4 Characterization of the used solid

In order to gain insights into the fate of the solid in the reaction, the used HT4-c823 was characterized thoroughly. Elemental analysis indicated a high chlorine content (10.7 wt. %, Table 44), which was comparable to the amount effectively released upon formation of the epichlorohydrin and chloroacetone products, which confirms the exclusive participation of the mixed oxide as a solid reactant in the conversion of dichloropropanol. From a structural viewpoint, a portion of the material re-assumed the hydrotalcite structure that characterized the precursor (Figure 47a).

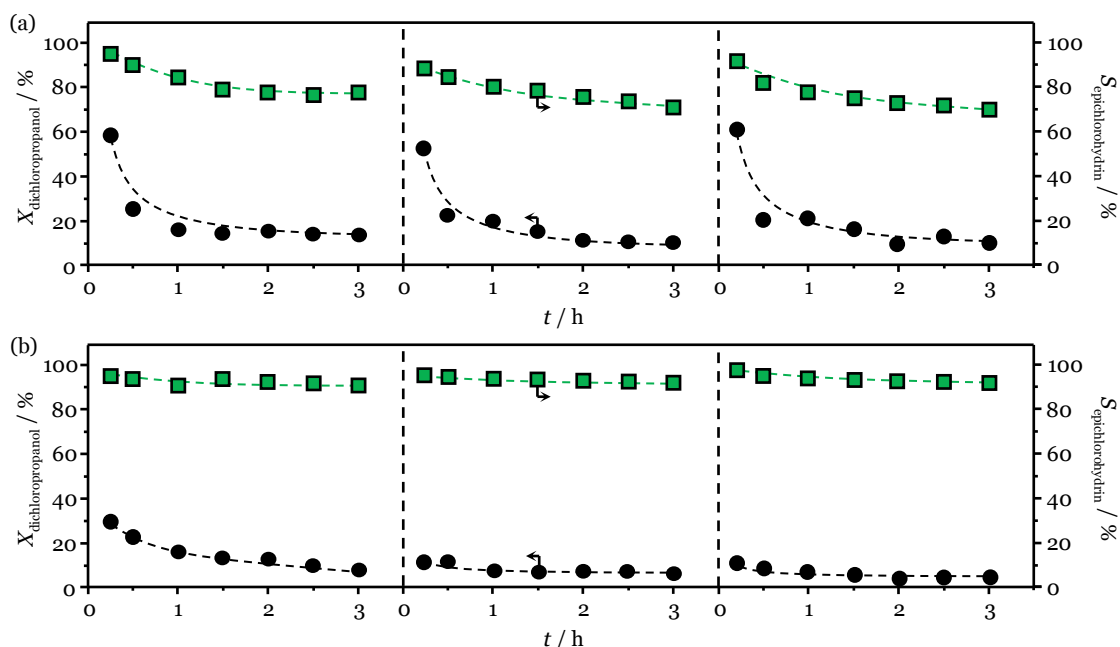


Figure 46. Dichloropropanol conversion and selectivity towards epichlorohydrin in three consecutive reaction cycles with intermediate regeneration of HT4-c823 at (a) $T = 423$ K, $P = 1$ bar and $WHSV = 1.2$ h⁻¹ and (b) $T = 403$ K, $P = 1$ bar and $WHSV = 6$ h⁻¹.

It is well known that upon contacting layered double hydroxide-derived oxides with liquid water or with its vapour at 303–423 K the material converts back into a layered structure featuring hydroxide instead of carbonate anions. [39] Due to the smaller size of OH⁻, the interlayer spacing is lower than for the original material and the reflections in the XRD pattern

appear at slightly higher angles. The presence of water in the reaction, the comparable conditions and the shift in peak position (*ca.* 1.0°) in the diffractogram are consistent with the hydration of the mixed oxide. Still, in view of the fact that HT2-c823 acquires chlorine upon use, no metal chlorides are formed and the chlorine anion has a comparable size to OH^- , Cl^- species shall occupy interlayer positions. Actually, it is supposed that the mixed oxide is firstly converted into a rehydrated hydrotalcite, in which the OH^- species serve as basic sites for the reaction with dichloropropanol and are progressively substituted by Cl^- ions (Figure 48).

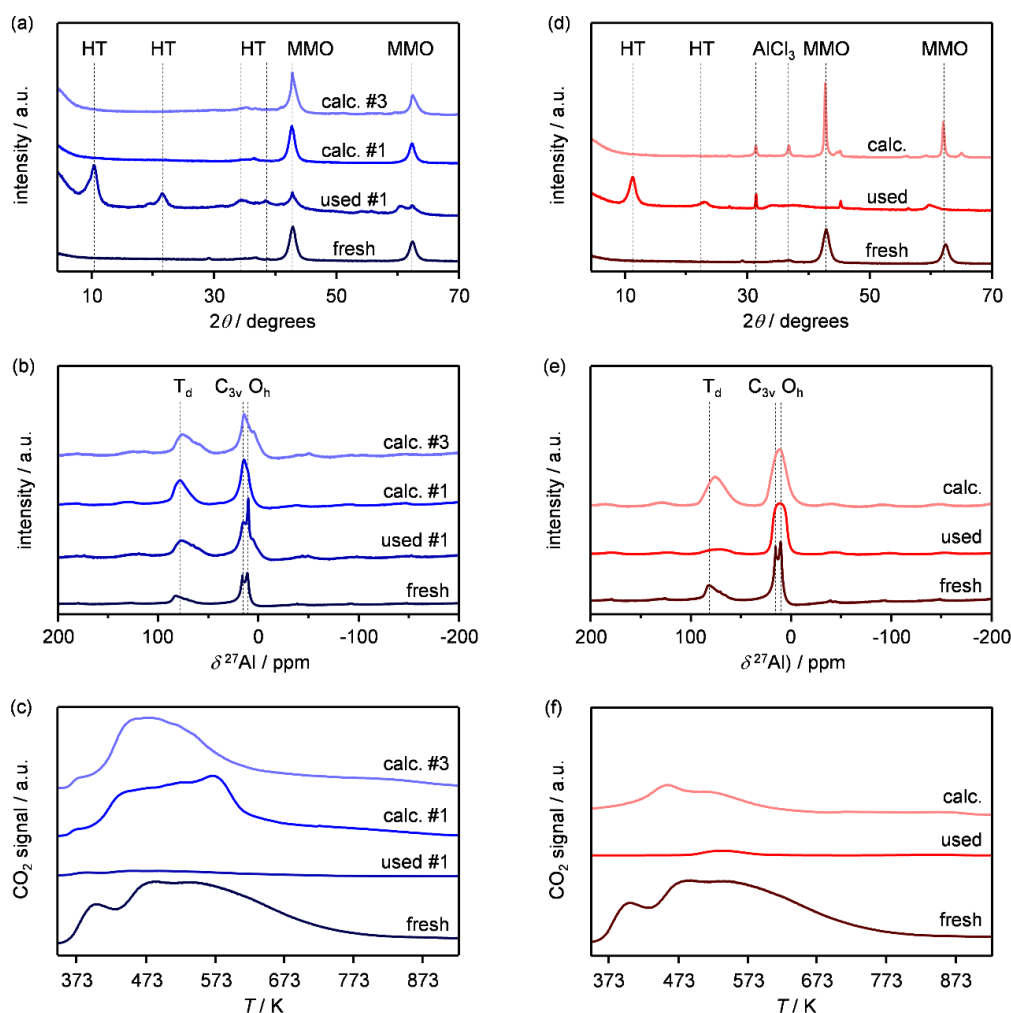


Figure 47. (a-d) XRD, (b-e) ^{27}Al MAS NMR and (c-f) CO_2 -TPD profiles of the HT4-c823 material used respectively at 423 K and at 403 K.

In analogy to these considerations, it is speculated that carbonate species might have been at least partly replaced by hydroxide species in HT2 and HT4 upon use and that their inferior conversion level compared to mixed oxides is likely due to the milder basicity of residual carbonates and their lower surface area. In line with the structural changes, the surface area of HT4-c823 after reaction diminished to an intermediate value between those determined for

HT4 and HT4-c823 in fresh forms (Table 43 and Table 44). TEM analysis evidenced that the layered organization of the solid was retained, although the morphology of the platelets became less defined (Figure 42). In agreement with the conversion of part of the aluminium sites from a tetrahedral or distorted octahedral into an octahedral geometry, the signal at 18 ppm in the ^{27}Al MAS NMR spectrum exhibited a comparatively higher intensity (Figure 47b).

The CO_2 -TPD profile indicated that the sample did not have any basic property anymore (Figure 47c). This corroborates the exclusive presence of the neutral Cl^- anion rather than the basic OH^- species in the interlayer spaces probed by CO_2 and hints that the residual mixed oxide phase is located in the interior of the particles, which cannot come into contact with the external gaseous environment either upon reaction or analysis.

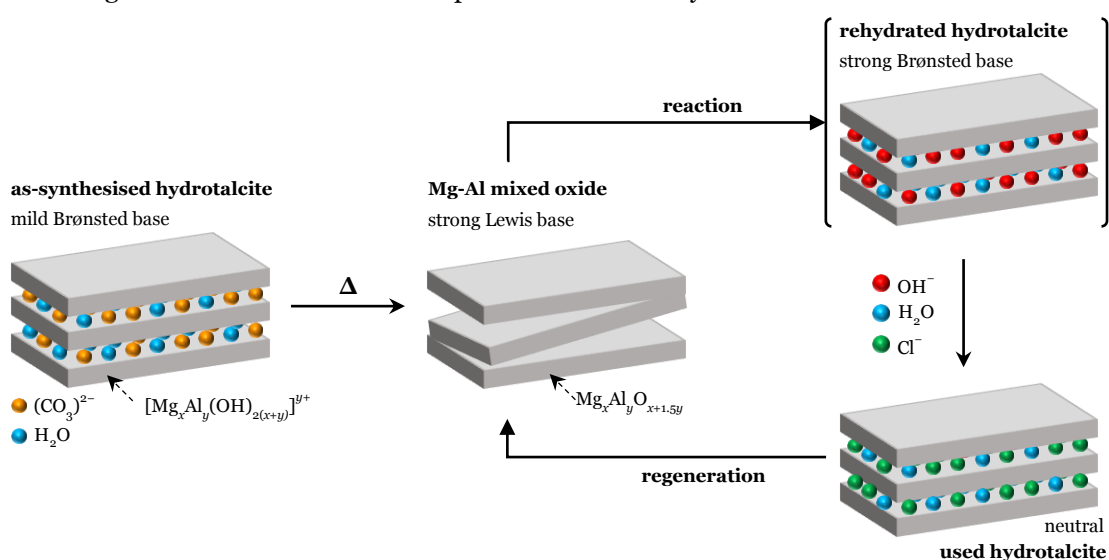


Figure 48. Generation of the Mg-Al mixed oxide by calcination of a HTlc, its modification upon use in the dichloropropanol-to-epichlorohydrin reaction and its subsequent regeneration by calcination.

4.3.5 Regeneration studies

In order to recover the original mixed oxide structure, the used sample was subjected to calcination at 823 K, which was effective in reducing the chlorine content to less than 1 wt.%. Based on the chemical behavior of metal chlorides [32], it is put forward that the elimination of chlorine from the HTlc generated in the reaction could follow two main mechanisms involving molecular oxygen provided in the treatment or water released by the solid upon heating





In the first case, the chloride ion is oxidized to elemental chlorine, while along the second path HCl is produced through an acid-base reaction. Since only HCl was detected by MS analysis upon TPO of the used material (Figure 49), the second route was predominant. XRD confirmed the disappearance of the hydrotalcite-like phase and the restoration of the mixed oxide (Figure 47a). Accordingly, the surface area increased back to an only slightly lower value than for the fresh HT4-c823 sample (Table 44) and ^{27}Al MAS NMR indicated that the proportion between aluminium sites with tetrahedral and octahedral geometry was similar to that of the original material (Figure 47b). Moreover, CO_2 -TPD evidenced that the solid regained basicity (Figure 47c).

Notably, the concentration of basic sites of the regenerated oxide is almost equal to that of the starting material when relating the values to their surface areas (Table 44). In addition, the mass and Mg/Al ratio of the calcined sample were equivalent to the data measured for the fresh solid, considering the amount of chlorine that remained in the material, indicating no metals leaching was present. Testing of the calcined sample produced analogous results to those obtained in the first run (Figure 46a), except for the slightly inferior initial activity, which is in line with the moderately lower surface area and basicity and the small amount of residual chlorine contained.

Table 44. Characterization data and coke content for HT4-c823 upon subsequent use-regeneration cycles.

| | Mg/Al ^a | Phase ^b | S _{BET} ^c [m ² g ⁻¹] | V _{pore} ^d [cm ³ g ⁻¹] | C _B ^e [mol g ⁻¹] | T _{des} ^f [K] | Cl ^g [wt.%] | C ^g [wt.%] |
|--------------------|--------------------|--------------------|--|--|---|--------------------------------------|---------------------------|--------------------------|
| <i>Used</i> * | 3.25 | HT+MMO | 125 | 0.47 | 6 | - | 10.7 | 0.9 |
| <i>Calcined</i> | 3.41 | MMO | 205 | 0.51 | 425 | 540 | 0.9 | 0.0 |
| <i>Used #2</i> * | 3.38 | HT+MMO | 110 | 0.42 | 8 | - | 10.0 | 1.1 |
| <i>Calcined #2</i> | 3.45 | MMO | 199 | 0.52 | 409 | 545 | 1.1 | 0.0 |
| <i>Used #3</i> * | 3.32 | HT+MMO | 112 | 0.44 | 5 | - | 11.3 | 0.9 |
| <i>Calcined #3</i> | 3.38 | MMO | 195 | 0.50 | 397 | 500 | 0.8 | 0.0 |
| <i>Used</i> * | 1.81 | HT+MMO+others | 89 | 0.41 | 2 | - | 12.1 | 0.6 |
| <i>Calcined</i> | 1.75 | MMO+others | 145 | 0.47 | 227 | 473 | 6.2 | 0.0 |

^a XRF; ^b XRD. HT = hydrotalcite, MMO = mixed metal oxide; ^c BET method; ^d volume adsorbed at $p/p_0 = 0.98$; ^e CO_2 -TPD; ^f Temperature corresponding to the maximum of desorption (des) and decomposition (dec) peaks in the CO_2 -TPD; ^g Elemental analysis. * $T = 423$ K, $P = 1$ bar, $\text{WHSV} = 6$ h⁻¹; + $T = 398$ K, $P = 1$ bar, $\text{WHSV} = 6$ h⁻¹.

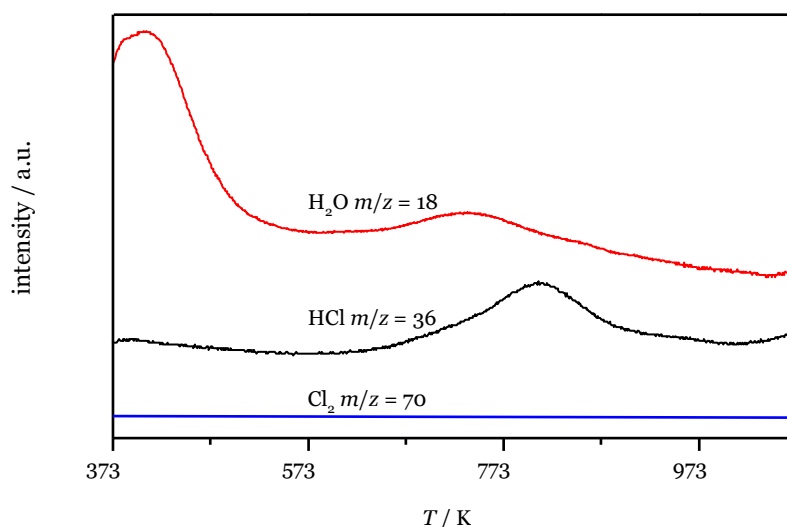


Figure 49. Mass spectrometry analysis of the outlet gas upon the temperature-programmed oxidation (O_2 concentration in He = 10 vol. %, ramp rate = 10 K min^{-1}) of spent HT4-c823.

Remarkably, calcination of the re-used material was equally effective in regenerating the mixed oxide as the treatment conducted after the first reaction (Table 44) and, accordingly, the reaction data collected in the third test were comparable to those of the second run (Figure 46a).

Finally, since the epichlorohydrin selectivity was higher at 403 K, HT4-c823 was assessed also at this 20-K lower temperature. Under these conditions, the dichloropropanol conversion progressively decreased reaching a similar level to that attained at the end of the run at 423 K (Figure 46b). In contrast, the selectivity towards epichlorohydrin remained almost unperturbed at *ca.* 95%. This is rationalized by the minor occurrence of the thermal decomposition of the product to chloroacetone at 403 K. Analysis of the used material uncovered substantial differences with respect to the sample retrieved after the reaction at 423 K. In this case, the mixed oxide phase was fully converted into a hydrotalcite-like phase as well as AlCl_3 (Figure 47d). Thus, Cl^- ions formed upon reaction not only exchanged OH^- species at interlayer positions but also generated a metal salt. ^{27}Al MAS NMR spectroscopy only detected hexacoordinated Al sites (Figure 47e), in line with the octahedral geometry of this metal in the hydrotalcite and in AlCl_3 , and CO_2 -TPD indicated a full depletion on the basicity (Figure 47f), as expected from the neutral nature of OH-free hydrotalcite and the metal chloride. The distinct alterations underwent by the sample at 403 K are likely due to the pronounced condensation observed on the solid reactant at this temperature, suggesting that the transformation took place in a liquid phase. Although the equilibrium diagram indicates that a pure vapour phase should be present, capillary condensation might have been induced by the surface rugosity and/or the liquid mixture might not have fully vaporized due to insufficient heat transfer rates during the short residence time in the heated zone of the reactor. The presence of water greatly facilitates ion migration within the solid, which helped

the formation of more thermodynamically-stable phases, *i.e.* aluminium chloride [40]. Calcination of this material converted the hydrotalcite phase into the mixed oxide, but the latter produced very sharp reflections, which is indicative of a severe increase of the particle size. XRD also evidenced that AlCl_3 remained in the material, in line with its decomposition temperature in excess of 900 K [40]. These findings are in agreement with the only partial restoration of the surface area and the still high Cl content in the sample (Table 44). The basicity of the calcined solid was strongly inferior to that of the fresh mixed oxide in view of the enrichment in Mg of the system. In line with the characterization data, the initial activity of the calcined solid was remarkably lower than that of the freshly prepared mixed oxide. A subsequent regeneration-reaction cycle showed a further deterioration of the performance. Accordingly, operation of the mixed oxide in the gas phase is a prerequisite to attain stable reaction-regeneration cycles. For this purpose, the well-known memory effect of layered double hydroxides is another crucial factor, since it enables the interconversion between hydrotalcite and mixed oxide forms with minimal modification of their basic and textural properties. From a practical viewpoint, a continuous production of epichlorohydrin can be realized operating multiple reactors simultaneously, alternatively dedicated to the desired transformation and to the regeneration of the solid base.

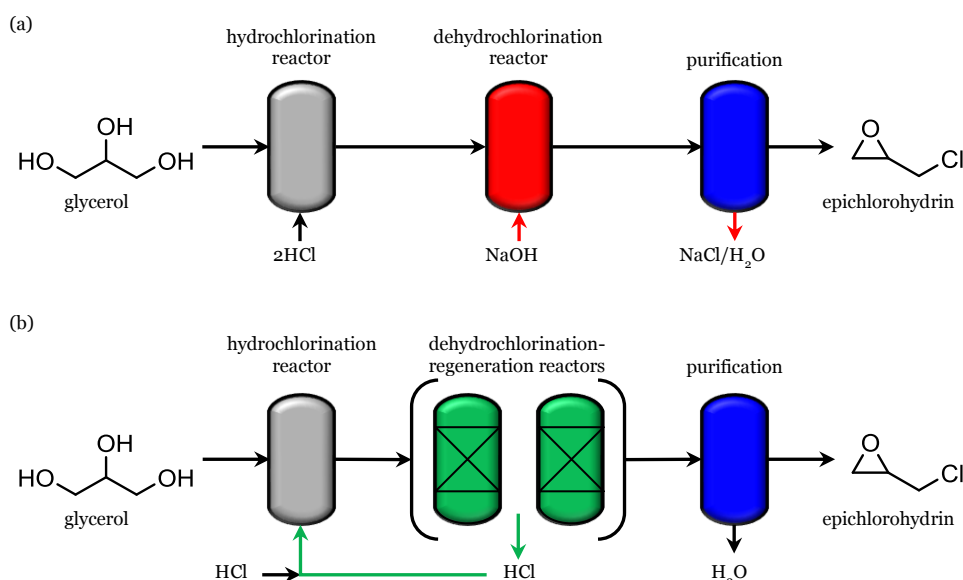


Figure 50. Simplified flow sheet for (a) the conventional glycerol-to-epichlorohydrin process and (b) the HT-derived oxides process herein introduced.

Overall, the use of a solid base in the gas phase in place of homogeneous alkaline solutions allows the compliance of the glycerol-to-epichlorohydrin process with three main green chemistry principles. Firstly, the generation of a salt byproduct is avoided, simplifying downstream purification and reducing waste treatment efforts. Secondly, the solid reactant is regenerable, reducing the material needs. Thirdly, the HCl evolved upon its regeneration could be easily recycled in the hydrochlorination of glycerol to dichloropropanols (Figure 50),

maximising the atom economy and the cost-related performance of the overall glycerol-to-epichlorohydrin route. Additionally, it is worth noting that the solid base shares an equivalent non-toxic nature to the homogeneous counterpart.

4.4 Process design

The epichlorohydrin process model was considered with respect to the model proposed by [6], which is made up of:

- Glycerol pre-purification.
- Hydrochlorination section, to dichloropropanols (DCHs).
- Purification of 1,3-DCH and recycle of catalyst and unreacted heavy components.
- Dehydrochlorination-epoxidation section, to epichlorohydrin (EPCH).
- Purification of EPCH, by PSA system.

According to the present study, only the dehydrochlorination-epoxidation step is analyzed in order to have a proper comparison between the conventional process [6] and the new proposed process. For this purpose, only the significant sections of the process, i.e. representative of the differences between the two processes, and the same 1,3-DCH basis (5800 kg/h [6]).

The considered subsection of the new process comprises (Figure 51):

- (i) reaction-regeneration section;
- (ii) HCl purification section;
- (iii) EPCH separation;
- (iv) DCH separation, with recycle.

4.4.1 Reaction-regeneration section

Experimental activity data for the hydrotalcite-based material have been used in order to model a fixed bed material reactor; experimental process conditions are respected ($T = 423$ K, $WHSV = 12.3$ h⁻¹, DCH = 10 wt. %). Due to the rapid catalyst deactivation, a continuous regenerative configuration has been proposed, with N in-parallel reactors working alternatively in reaction and regeneration mode; a total catalyst lifetime of 100 reaction-regeneration cycles is arbitrarily considered.

The number of reactors depends on the assumed reaction and regeneration times: for the present analysis $t_{reaction}$ and $t_{regeneration}$ are taken respectively equal to 0.5 h and 6 h, for a $t_{cycle} = 6.5$ h, therefore $N = 13$. Average values of catalyst activity are calculated by integration of the deactivation curve over time, while the regeneration time has been increased by 1 h, with respect to the experimental conditions, to take into account dead times.

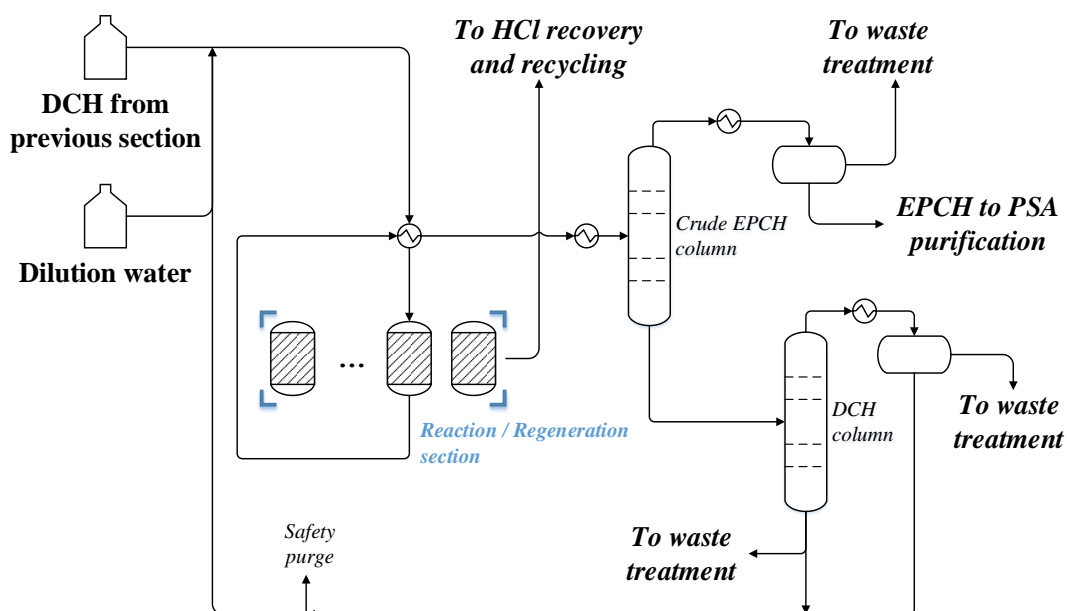


Figure 51. Process layout for dichloropropanol dehydrochlorination to epichlorohydrin using the new hydrotalcite-derived material.

For the process assessment of the reactor unit, the use of conversion and selectivity-related information from the experimental section is sufficient (RSTOICH reactor in Aspen Plus® V8.6). Detailed information about the reaction kinetics, mass and heat transfer phenomena, pressure drop, *etc.*, would be required for a detailed design of a full-scale, plug-flow reactor, which is outside the scope of the present study.

4.4.2 HCl purification section

The change in Water-HCl azeotrope composition with pressure (20.5 wt. % at 1 bar, 17.5 wt. % at 4 bar) is exploited to break the distillation boundary present at 1 bar (Figure 52, Figure 53). Therefore, a low- and a high-pressure column are used to separate water from an HCl-rich flow. The maximum boiling azeotrope is always recovered at the bottom. Two flash condensation stages in series, working at 389 K and 348 K, are finally used to recover gaseous HCl with a minimum 99 wt. % purity.

Column design specifications, i.e. N_{stages} and R , have been chosen according to proper sensitivity analysis, which took into account costs trade-off between capital and operative expenses, and heuristics, such that $R = 1.1 \div 1.7 \cdot R_{\text{min}}$. The cost- and environmental-determining factors for this process section are reported in Table 45.

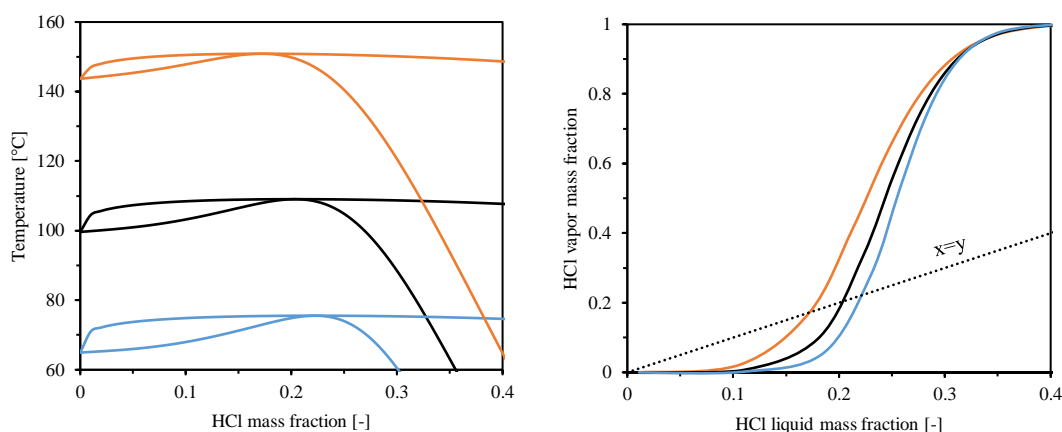


Figure 52. HCl T-x L-V equilibrium diagram (-Figure 53. HCl y-x L-V equilibrium diagram (- 0.25 bar, - 1 bar, - 4 bar).

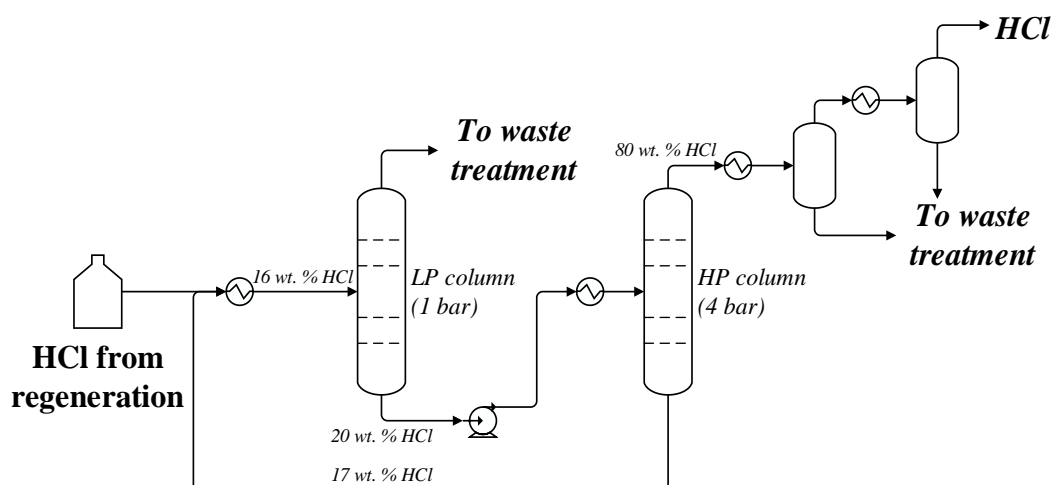


Figure 54. HCl pressure-swing (1-4 bar) azeotropic distillation

Table 45. Cost-and environmental-determining factors for HCl purification section.

| Type | Classification | Assumptions |
|----------------------|----------------|--|
| Distillation columns | CAPEX&OPEX | <ul style="list-style-type: none"> Column depreciation time (straight line) = 20y. Trays depreciation time (straight line) = 5y. |
| Heat exchangers | OPEX | <ul style="list-style-type: none"> CAPEX assessed to be negligible. |

4.4.3 EPCH and DCH separation section

The reactor effluent contains H₂O, the main product EPCH, unreacted DCH and by-products. Among the by-products, only chloroacetone has been experimentally identified; other heavier by products are indeed also present. Since the overall yield in by-products is very

low (< 1%), and considering that all the by-products are heavier than the EPCH-water and DCH-water minimum boiling azeotropes, the presence of these components in the process is neglected. It is indeed assumed that they are always removed as heavies together with the waste water streams.

The ternary system EPCH-DCH-water is therefore analyzed. Thermodynamic liquid-liquid equilibrium data and residual distillation curves, calculated according to the UNIFAC model, are reported in the ternary diagram shown in Figure 55. The ternary system is characterized by the presence of a large non-miscibility zone, in which two heterogeneous binary azeotropes are present (Table 46). Azeotropic distillation is therefore exploited to take into advantage the presence of minimum boiling heterogeneous azeotropes, in order to break the distillation boundary present at 1 bar.

Table 46. Node point analysis for the system Water-DCH-EPCH, at 1 bar (UNIFAC model).

| Component | Composition [mol. %] | | | T _{nb} [K] | Classification |
|---------------------------|----------------------|-----|------|------------------------|----------------|
| | Water | DCH | EPCH | | |
| Water | 100 | 0 | 0 | 373 | Stable node |
| DCH | 0 | 100 | 0 | 447 | Stable node |
| EPCH | 0 | 0 | 100 | 391 | Saddle |
| Heterogeneous azeotrope 1 | 95.2 | 4.8 | 0 | 371.9 | Saddle |
| Heterogeneous azeotrope 2 | 65.8 | 0 | 34.2 | 362 | Unstable node |

Due to the high degree of dilution of the reactor effluent (Table 47), the starting point lies in the smaller distillation region, outside the non-miscibility zone. Therefore, the EPCH column performs a separation to obtain the EPCH-water heterogeneous azeotrope as distillate stream and, according to the mass balance, a diluted DCH-stream as bottom (0.9 mol. %). A decanting stage allows then to recover the EPCH-rich layer (96.4 wt. % EPCH), which is sent to further dehydration by PSA system on zeolites [6].

The aqueous layer is sent to a conventional wastewater treatment system, modelled according to [41, 42].

Column design specifications, i.e. N_{stages} and R, have been chosen according to proper off-line sensitivity analysis, which took into account costs trade-off between capital and operative expenses. Geometric constraint on the maximum H/D ratio has also been set to 30.

The bottom diluted DCH solution is sent to the following azeotropic distillation section to obtain the DCH-water heterogeneous azeotrope as distillate, further separated by simple decanting. The procedure for the determination of column design specification is the same as previously described. The DCH stream is recycled back to the reaction section; part of the bottom water stream (~100 % water) is used to adjust the recycle DCH concentration to the reaction value (10 wt. % DCH), while the remaining stream is sent to a conventional waste water treatment facility. A safety purge, arbitrarily fixed at 5 % of the recycle, is put in order to

take into account for the presence of by-products impurities which could not be quantified.

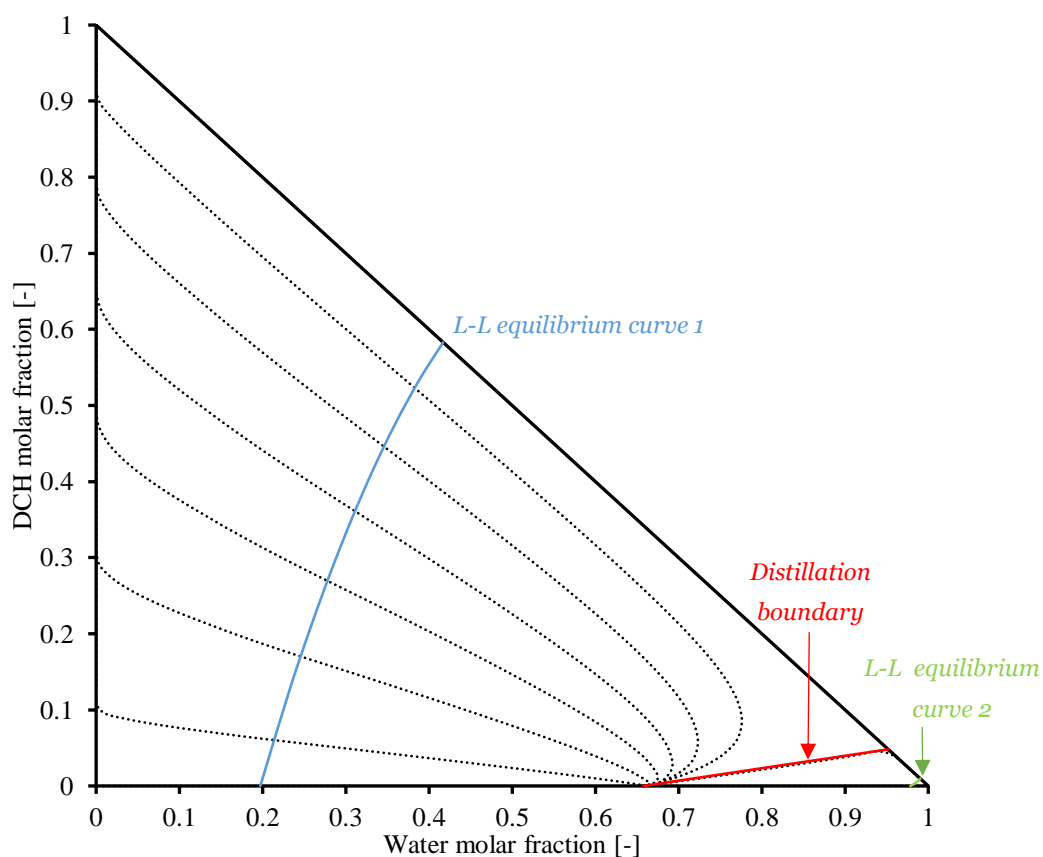


Figure 55. Ternary diagram for the system water-EPCH-DCH, at 1 bar (UNIFAC model).

Table 47. Molar composition for the relevant streams in the purification section.

| Component | Composition [mol. %] | | |
|------------------|----------------------|-------|-------|
| | Water | DCH | EPCH |
| Reactor effluent | 98.5 | 0.9 | 0.6 |
| EPCH-rich layer | 16 | trace | 84 |
| EPCH-poor layer | 98.5 | trace | 1.5 |
| DCH-rich layer | 38.7 | 61.3 | Trace |
| DCH-poor layer | 99.4 | 0.6 | Trace |

Table 48. Cost-and environmental-determining factors for EPCH-DCH separation and recycle section.

| Type | Classification | Assumptions |
|----------------------|----------------|--|
| Distillation columns | CAPEX&OPEX | <ul style="list-style-type: none"> Column depreciation time (straight line) = 20y. Trays depreciation time (straight line) = 5y. |
| Heat exchangers | OPEX | <ul style="list-style-type: none"> CAPEX assessed to be negligible. |

Modeling in Aspen Plus® V8.6 employed in all cases a RadFrac model for simple distillation columns and the cost-and environmental-determining factors for this process section are reported in Table 48.

Due to the required energy intensive separations by distillation, process heat integration has been performed in order to reduce costs associated to the thermal utility consumption (cooling water, steam, natural gas). However, temperature levels do not favor an efficient process heat integration; the presence of minimum boiling azeotropes lowers the level of available heat. The only way to reduce hot utility consumption to heat the feed to the reaction temperature is to recover as much available energy as possible in the reactor effluent; a maximum reduction of ~78% of hot utility requirement can be achieved, if minor integration is also done with the reactor and the hot streams in the HCl section. This integration threshold is set by the physical limit, in the reactor effluent heat exchanger, of non-crossing of temperature profiles.

The benefits coming from this reduction are extremely important, considering that process energy consumption is very high due to the presence of a recycle stream, and therefore of much higher process flow rates. No further integration is possible in the purification section due to the temperature level constantly below 373 K.

4.5 Economic and environmental assessment

The background and inventory data used in this study for the environmental and economic assessment with respect to the consumption of resources are presented in Table 49 and Table 50. No LCA data were considered for the environmental assessment of the impact associated to building materials. The same approach has been used to evaluate also the sub-section of the process presented in [6].

From preliminary qualitative considerations and quantitative inventory data, some strengths and weaknesses of the innovative “HT process” could be pointed out (Table 51). The main advantages are related to reduced material needs of the process (excluding inexpensive process water), i.e. no NaOH required, to recyclable HCl co-production, i.e. higher process Cl atom economy achievable, and to the lower amount of organics in waste water streams which is reduced by a factor of 3, i.e. 0.36 vs 1.12 kg/kg_{EPCH}.

Nevertheless, the much higher process energy requirements, due to feed vaporization and downstream purifications, strongly affect the economic and environmental sustainability, resulting in significantly increased values of the LCA indicators which surpass the benefits associated to the process material requirements (Figure 56). This is a direct consequence of the lower per pass conversion of the fixed bed reactor, which determines the necessity of an energy-consuming dichloropropanol-recovery column and of a process recycle, and of the

much higher dilution of the reactor feed, which directly affects the water content of the streams and the energy requirements of the thermal unit operations involved in the process, ex. heat exchangers and distillation columns. In addition, process heat integration potential is low, as previously pointed out.

Further issues arise from the presence of a complex reaction-regeneration system, required to assured the continuity of the process in the presence of a very low stability of the MMO material.

Table 49. Background data for the environmental (not- renewable resources) and economic assessment of EPCH manufacturing process (sources: [43, 44]).

| Substance | CED (MJ _{eq} kg ⁻¹) | EI99 (Points kg ⁻¹) | GWP (kg _{CO2-eq} kg ⁻¹) | Price (USD t ⁻¹) |
|--------------------------------|---|------------------------------------|---|---------------------------------|
| Process water | 2.8 10 ⁻⁴ | 1.8 10 ⁻⁶ | 2.4 10 ⁻⁵ | 1 |
| MgO | 2.7 | 0.12 | 1.06 | 280 |
| Al ₂ O ₃ | 19.1 | 0.19 | 1.24 | 355.6 |
| Catalyst disposal | 0.32 | 0.002 | 0.01 | - |
| NaOH | 21.4 | 0.06 | 1.10 | 243 |
| HCl | 60.3 | 0.22 | 2.06 | 160 |
| EPCH | 71.8 | 0.25 | 3.37 | 1320 |
| Heat* | 1.57 | 0.01 | 0.10 | 20 |
| Electricity* | 9.87 | 0.02 | 0.49 | 0.10 |
| Cooling water from river | 0.00 | 0.00 | 0.00 | 0.15 |
| Natural gas** | 1.24 | 0.004 | 0.012 | 0.01 |

*Heat is measured in MJ (except from the price of steam which is per tonne) and electricity in kWh.

**The values for natural gas are per MJ and they refer to natural gas used for producing heat.

Table 50. Inventory data used for the environmental and economic assessment of EPCH manufacturing process.

| Materials and energy | “HT process” | “NaOH process” [6] | Units |
|-------------------------|--------------|--------------------|-------------------------------------|
| DCH | 1.8 | 1.8 | kg kg _{EPCH} ⁻¹ |
| Process water | 16 | 2 | kg kg _{EPCH} ⁻¹ |
| Catalyst | 0.06 | - | kg kg _{EPCH} ⁻¹ |
| NaOH | - | 0.57 | kg kg _{EPCH} ⁻¹ |
| HCl | 0.37 | - | kg kg _{EPCH} ⁻¹ |
| Heat | 55 | 0.83 | MJ kg _{EPCH} ⁻¹ |
| Cooling water | 763 | 1130 | kg kg _{EPCH} ⁻¹ |
| Natural gas | 0.19 | - | MJ kg _{EPCH} ⁻¹ |
| Electricity | - | 0.32 | MJ kg _{EPCH} ⁻¹ |
| Total aqueous waste | 16 | 3.8 | kg kg _{EPCH} ⁻¹ |
| Total organics in waste | 0.36 | 1.12 | kg kg _{EPCH} ⁻¹ |

Table 51. SWOT analysis for the new proposed EPCH process.

| | |
|--|--|
| <p>Strengths</p> <ul style="list-style-type: none"> • Lower material requirements • EPCH hydrolysis issues not relevant in aqueous neutral environment • No stoichiometric production of salt • Higher Cl atom economy after recovery and purification of the co-product HCl • Simpler design of a single reactor (fixed bed reactor) • Lower amount of organics in waste water streams | <p>Weaknesses</p> <ul style="list-style-type: none"> • High water dilution • Recycle needed to achieve high overall process conversion • Not stable activity of hydrotalcite-derived material, resulting in a complex reaction-regeneration system • Very high process energy requirements • Low process heat integration potential • High total aqueous waste water effluent |
| <p>Opportunities</p> <ul style="list-style-type: none"> • Adding value to waste crude glycerol • Innovative solution for epichlorohydrin manufacture, to be improved • No longer dependency on electrolytic NaOH reactant • Process feasibility assured simply by the availability of crude glycerol only. | <p>Threats</p> <ul style="list-style-type: none"> • Availability of raw materials (crude glycerol) • Economic competitiveness in future more favorable energetic scenarios (lower cost/impact of energy) • Economic/environmental competitiveness for implementation in a biorefinery plant (energy integration) • Development of active and stable catalysts, with simplification of downstream purification section |

Finally, the total volume of the wastewater effluent is much higher, as further consequence of the high amount of water present in the system. This offsets the benefits deriving from the lower amount of organics actually present in the wastewater streams.

Nevertheless, comparison of the operating costs of the two processes revealed a difference in

just 0.3 $\$/\text{kg}_{\text{EPCH}}$. In this case, the higher cost of utilities in the novel process is partially compensated by the reduced cost of materials, suggesting that this process could even be competitive in a different energy scenario, i.e. where heat in the form of electricity or combustible is available at lower price.

Assessment results reported in Figure 56 fully reflect the strengths and weaknesses associated to the novel process, especially in terms of lower material requirements. Indeed, for the same 1,3-dichloro-2-propanol processing capacity, the possibility offered by HCl recycling and by the absence of a stoichiometric base enables much lower economic and environmental material contributions. As previously said, process energy requirements offset this positive contribution and dominate the performances of the novel process.

Since one of the main drivers was to decrease undesirable aspects related to chlorinated waste streams disposal, it is useful to have a closer look on the waste streams output results. Figure 56 and Table 52 shows very similar results for the two processes, also highlighting a low environmental impact associated to the waste streams with respect to the energy and material consumption contributions respectively for the novel and the conventional processes. It is however of fundamental importance to underline the much lower specific LCA index values and costs per unit of treated waste water streams for the novel process, i.e. one order of magnitude lower (Table 52).

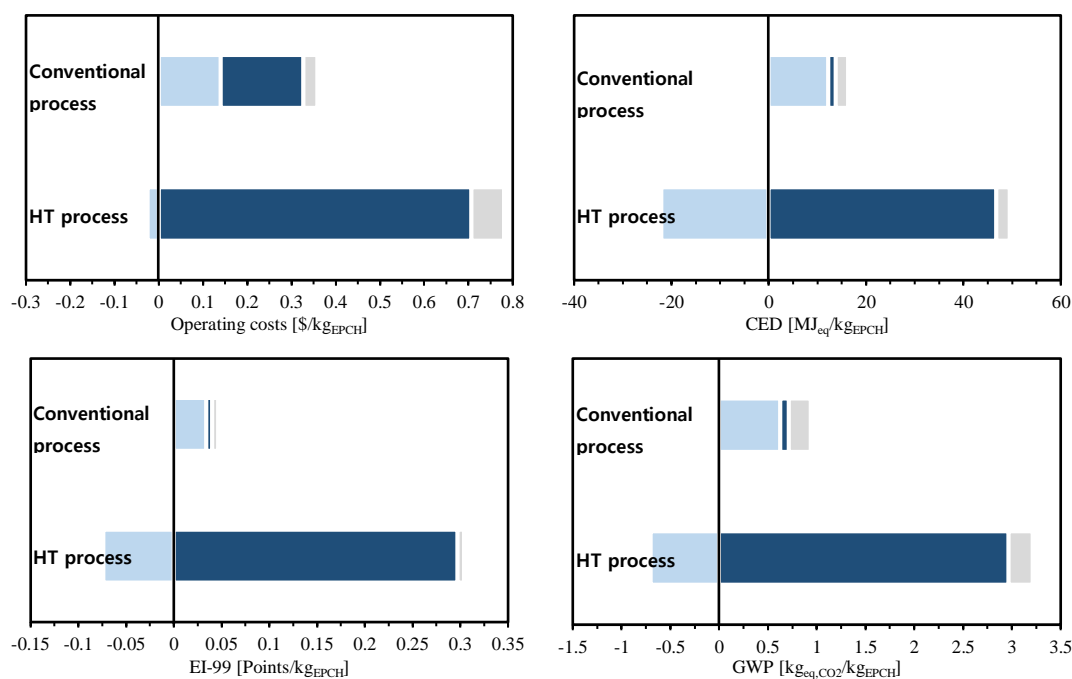


Figure 56. Economic and environmental assessment results for glycerol-to-epichlorohydrin manufacturing process (■ material, ■ energy, ■ waste). Comparison results for the dehydrochlorination subsection.

Table 52. Waste stream assessment results per unit of epichlorohydrin and of total waste water produced for the novel and the conventional process.

| Process | CED [MJ _{eq} /kg] | | EI-99 [Points/kg] | | GWP [kg _{eq,CO2} /kg] | | Cost [\$/kg] | |
|---------------------|-------------------------------|---------------------|----------------------|---------------------|-----------------------------------|---------------------|--------------------|---------------------|
| | kg _{EPCH} | kg _{WASTE} | kg _{EPCH} | kg _{WASTE} | kg _{EPCH} | kg _{WASTE} | kg _{EPCH} | kg _{WASTE} |
| Novel | 2.78 | 0.17 | 0.007 | 0.0004 | 0.25 | 0.016 | 0.07 | 0.0046 |
| Conventional | 2.48 | 0.66 | 0.006 | 0.0015 | 0.23 | 0.06 | 0.03 | 0.0081 |

Even though assessment results per unit of produced epichlorohydrin reveal no apparent benefits, the same results referred to the unit of produced wastewater highlight a strong advantage offered by the novel process. This is not surprising if one considers the lower amount of chlorinated species actually contained in the waste streams (Table 50) as a result of the higher chlorine atom efficiency of the process, in front of a much higher total volume of waste water. Therefore, relevant improvements are expected from the development of a process in which less diluted conditions are applied.

The “NaOH process” is conducted at 80 K lower temperature, no phase transitions is required except for the reactive column, and the high temperatures required for the regeneration (823 K) are avoided. In addition, much lower dichloropropanol dilution is employed (~ 35 wt. %), reactive distillation column per pass conversion of 95% with 99% selectivity are achieved, and epichlorohydrin is directly obtained by using steam as stripping agent. Stripping of the only epichlorohydrin in the reactive column is an important simplification, introduced by [6], not taking into account rigorous liquid-liquid-vapor equilibrium calculations; diluted epichlorohydrin might contain a certain low amount of impurities, mainly stripped dichloropropanol, to be further separated by distillation. Therefore, the actual energy requirement of the “NaOH process” is expected to be higher than that calculated according to the presented process [6], as well as the LCA indicators: an order of magnitude analysis, based on the energy consumption of the crude EPCH column of the “HT process” (Figure 51), reveals values higher of 5 MJ_{eq}/kg_{EPCH}, 0.03 Points/kg_{EPCH}, 0.3 kg_{eq,CO2}/kg_{EPCH} respectively for CED, EI-99, GWP.

Nevertheless, the novel process performances are still eligible of relevant improvement. In particular, research should focus on the identification of a suitable stable catalyst, or of an easily regenerable solid reactant, able to convert concentrated feed with total selectivity, i.e. minimum yield of ~90-94%, feed concentration > 10 wt. %. Only this way, the performance of the hydroxide mediated route could be matched by necessitating the same simplified purification, by reducing the total amount of water present in the system, and by eliminating the necessity of a dichloropropanol recycle.

4.6 References Chapter 4

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Conclusions

In this work, a solid and regenerable base is introduced as alternative to alkali hydroxides for the dehydrochlorination of glycerol-derived dichloropropanol to epichlorohydrin. Upon testing of compounds with variable acid/base properties, Lewis-basic mixed oxides obtained from hydrotalcite-like materials emerged as the best-performing solids. Their selectivity pattern was found to be strongly influenced by temperature, since total selectivity towards epichlorohydrin was achieved below 423 K, while the product thermally decomposed to chloroacetone under harsher conditions. Optimization of the space velocity and temperature conditions enabled epichlorohydrin yields as high as 60% while characterization tests enabled the elucidation of the reaction mechanism. It is hypothesized that the latter involves the initial formation of the actual active phase from the lamellar mixed oxide, a rehydrated hydrotalcite, and the subsequent progressive replacement of the hydroxide ions at the interlayer positions by chlorine ions. Simple calcination appeared effective in restoring the mixed oxide phase with equivalent porous, structural and basic properties and, thus, reactivity to the starting solid after a first and second reuse. Since this treatment releases HCl, a closed chlorine loop within the whole glycerol-to-epichlorohydrin process was proposed for the reutilization of hydrochloric acid for the halogenation of the triol.

Secondarily, process design and assessment allowed to quantify the sustainability of the new proposed process with respect to the conventional glycerol-to-epichlorohydrin route by evaluating CED, EI-99, GWP, and operating costs as indicators. Reduced material requirements and lower amount of organics in wastewater streams were identified as the main advantages, as results of the absence of a stoichiometric alkali base and the higher overall chlorine atom economy after implementation of the hydrochloric acid recycle loop. Nevertheless, much higher process energy requirements totally offset the benefits associated to the reduced material requirements, as consequence of the much higher dilution conditions and the presence of a dichloropropanol recycle loop. On the other side, waste stream results underline much lower specific LCA index values and costs per unit of treated waste for the novel process. This, together with operating costs higher of just 0.3 \$/kg_{EPCH}, suggests that relevant sustainability improvements are expected from the development of a process in which less diluted conditions are applied. In addition, economic competitiveness could also be assured in a different energy scenario, where energy would be available at lower price, or in a

context of extended heat integration possibilities offered by a biorefinery scheme. In any case, the identification of a suitable stable catalyst or regenerable solid providing minimum yield of ~90-94%, at feed concentration > 10 wt. %, is regarded as the most important research-related factor for a more efficient and sustainable implementation of the novel glycerol-to-epichlorohydrin process.

The same LCA-based methodology has been applied for the assessment of 1,2-propanediol, glycerol carbonate, and allyl alcohol novel manufacturing processes, which were analyzed with respect to the most influencing parameters.

The proposed glycerol-to-1,2-propanediol process produces the desired product with lower LCA metric values and operating costs compared to the conventional, propylene-derived, counterpart. Furthermore, environmental indexes results indicate that chemical valorization to 1,2-propanediol has a smaller impact than treating crude glycerol in a conventional waste water treatment plant. Analysis of the individual contributions to the environmental and economic indicators revealed that H₂ and electricity consumption play a major role respectively within the material and energy contributions and are directly influenced by the required grade of dilution of the system, while waste treatment is dominated by positive effects related to heat valorization of the purged H₂. Overall results underline a trade-off among the environmental- and economic-influencing process parameters for a required glycerol aqueous concentration ≤60 wt. %, therefore evidencing a beneficial effect towards a reasonable grade of dilution of the system.

The environmental attractive heterogeneous-catalyzed urea glycerolysis reaction to glycerol carbonate has been as well assessed, evidencing significantly lower CED, EI-99, GWP, and operating costs than the corresponding oil-derived glycerol carbonate and providing quantitative evaluation of the environmental sustainability of the proposed process. Concerns regarding the presence of an organic solvent concretize in a relevant environmental impact in the energy category, with less influence of the material contribution due to the benign characteristics of both urea and γ -butyrolactone; negligible and positive contribution from waste streams derive from the thermal valorization of NH₃, followed by NO_x abatement. Conversely, relevant waste stream contribution to operating costs is evidenced together with material requirements, respectively due to complex gaseous NH₃ treatment and very high solvent price. This calls for a sharp recovery of the solvent in the process and minimization of gaseous emissions. Indeed, the alternative scenario involving NH₃ acid scrubbing with aqueous H₂SO₄, with co-production of ammonium sulfate fertilizer, generates a positive economic value, evidencing a suitable strategy for gaseous waste valorization while not affecting significantly the environmental impact and leading to product costs down to 1.2 \$/kg_{GC}.

Lastly, state-of-the-art catalyst activity for glycerol hydrogenolysis to allyl alcohol using molecular hydrogen has been used for the modelling and assessment of a novel glycerol-based

process. Very low product selectivity poses serious limitations towards a realistic industrial implementation, as a result of significant glycerol conversion to byproducts hydroxyacetone, acrolein and propanal characterized by different market sectors and sizes. Concerns regard allyl alcohol limited throughput capacity, lack of flexibility in production, byproducts overproduction, and consequent augmented waste generation; in addition, economic and environmental sustainability performances driven by byproducts generation lead to substantial dependency of allyl alcohol towards multiple external market factors. Assessment results fully reflect these considerations and, despite the lack of maturity of this state-of-the-art catalytic technology, they should be considered in term of preliminary quantitative data able to underline the features of the proposed process. Catalyst activity and selectivity improvement is regarded as the key aspect research should focus on; simultaneous optimization of Brønsted-acid functionality for dehydration and precious metal hydrogenation activity, with possible lower process temperature conditions, would help in selectively address the reaction pathway to allyl alcohol while minimizing coking phenomena.

Overall, this study emphasized the importance and potential of combining experimental results, rigorous process modelling and multi-criteria analysis to assess the sustainability performance of proposed chemical production processes and to attain indications about the most crucial variables for a specific technology. The glycerol biorefinery concept is regarded as the most important opportunity for the concrete industrial implementation of the proposed processes, in a context of extended possibilities offered by comprehensive energy integration, expanded market opportunities, and waste-minimization-driven valorization.