CHAPTER 2

Introduction to High Pressure CO$_2$ and H$_2$O Technologies in Sustainable Biomass Processing

YDNA M. QUESTELL-SANTIAGO AND
JEREMY S. LUTERBACHER*

Laboratory of Sustainable and Catalytic Processing, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Station 6, CH.H2.545, Lausanne 1015, Switzerland
*Email: jeremy.luterbacher@epfl.ch

2.1 Introduction

Petroleum is a major raw material for the production of fuels, chemicals and materials used in our daily lives. The continuous growth in the consumption of these products requires the increased exploitation of fossil resources. In turn, this exploitation has led to environmental and economic issues linked to climate change, resource depletion and political instabilities due to the unequal distribution of fossil deposits.[1] The global primary energy consumption increased by a constant rate of 2.4% per year $\pm$0.08% since 1850 and shows no sign of slowing down.[2] The global community, increasingly aware of the dangers linked to diminishing fossil reserves and climate change, is encouraging the development of renewable carbon sources.

In 2013 the world total energy supply was 13.5 Gtoe and only 10.2% of this energy was supplied by biofuels and wastes.[3] According to the International Energy Agency (IEA) this fraction is projected to increase to 27% of the energy demand in the transportation sector by 2050.[4]

Using biomass and organic wastes as a feedstock for renewable carbon represents a promising and sustainable alternative to fossil carbon.[5] However, exploiting biomass fully is associated with many challenges including the development of suitable conversion technologies both from an environmental and economic standpoint coupled with political support issues. The production of fuels from biomass has been criticized due to the so-called fuel *vs.* food competition. The potential for large-scale biomass exploitation to drive up the price of competing food crops has led to increased attention to the substitution of non-fuel petroleum-based materials and jet fuel by biomass-derived molecules. Both jet fuels and these carbon-based chemicals are difficult or impossible to substitute with renewable electricity and are potentially more valuable than other transportation fuels. Furthermore, the demand for non-fuel carbon-based molecules and jet fuel is significantly lower than for total fuel and therefore leads to less competition issues for land used in food production. For these reasons, the production of jet fuel and carbon-based chemicals from biomass has attracted less controversy and has helped promote the concept of an integrated biorefinery.[6] This concept is defined as the production of at least one energy product (besides heat and electricity) and the production of at least one high value chemical or material, along with low-grade and high-volume products in a single biomass conversion plant.[7]

Biorefineries include multiple conversion technologies used in a sustainable manner to comply with the production of the diverse biomass feeds mentioned. Current conversion technologies are usually designed for a specific type of biomass and can suffer from low yields, high energy requirements and elevated operation costs that makes the integration of bioproducts difficult in a competitive market. Several approaches have attempted to improve the efficiency of biomass processing while applying sustainable development principles. Here, we provide an overview of the use of CO_2 and CO_2–H_2O mixtures for biomass processing and how such approaches have contributed to the development of more efficient and sustainable processes. We will begin by discussing the characteristics and categories of biomass feedstocks and will briefly describe the typical processes employed in biorefineries with their main bioproducts. We will then introduce the principle applications of CO_2 and CO_2–H_2O mixtures in biomass processing by reviewing the main features of this system. We also provide an overview of the principle applications where CO_2 and CO_2–H_2O mixtures are used and discuss the advantage that their use has provided. Finally, we briefly examine the challenges for implementing processes using high pressure CO_2.

2.2 Biomass as Feedstock

Biomass refers to a renewable organic material created biologically and is defined as "a substance wholly comprised of living or recently living (non-fossil) material".[8] This concept includes an extensive range of materials, *e.g.* whole or parts of, plants, trees, animals, microorganisms and aquatic organisms, which are classified as edible and non-edible crops. When considered as a source of fuel, biomass is sub-classified into three categories referred to as first, second or third generation biofuels.[8,9] First generation biofuels or bioproducts refer to fuels and chemicals made from edible crops that are used for the production of products containing starch (*e.g.* corn, flower, *etc.*), sugar, vegetable oil, lipids and/or proteins. Second generation biofuels or bioproducts refer to molecules made from lignocellulosic materials, which are non-edible crops, mainly composed by polysaccharides. Lignocellulosic material tends to be more difficult to convert to fuels but usually provides more material per plant growth area and requires less fertilizer to grow.[10,11] Both of these attributes lead most experts to agree that second generation biofuels and bioproducts are more sustainable than their first generation equivalents. The composition of lignocellulosic material is usually about 40–50% cellulose, 25–35% hemicellulose and most of the remainders is lignin.[1,12] Products produced from microalgae have sometimes been referred to as third generation biofuels and bioproducts. Algae has mainly been considered for the production of oil and lipids.[9,13] Figure 2.1 shows the chemical structure of the main components of the feedstocks used for the three generations of bio-based molecules.

As discussed, biomass has the potential to replace fossil-based feedstock for the production of chemical intermediates and fuels. However, the chemical structure and composition of biomass is considerably different from that of crude oil, which is the major conventional fossil feedstock.[14] Hence, all biomass processing employ reforming steps to produce direct or indirect petrochemical replacements. We briefly discuss the principal reforming efforts for each generation of bio-derived products below.

2.2.1 First Generation Biofuels and Bioproducts – Edible Crops

First generation biofuels and bioproducts are produced from biomass with significant edible fractions, such as corn, sugar cane, wheat, palm oil and rapeseed. These feedstocks are the primary sources of starch, sugars and vegetable oil, mainly used to produce energy products that include biogas, bioethanol and biodiesel.[7] Biogas is produced by the anaerobic digestion of mixtures of starch, manure and other organic wastes, and is used to produce electricity and in some countries as transportation fuel, after purification and pressurization of the resulting methane. In such cases, starch, free sugars, oils and proteins can generally be converted to gas by microorganisms
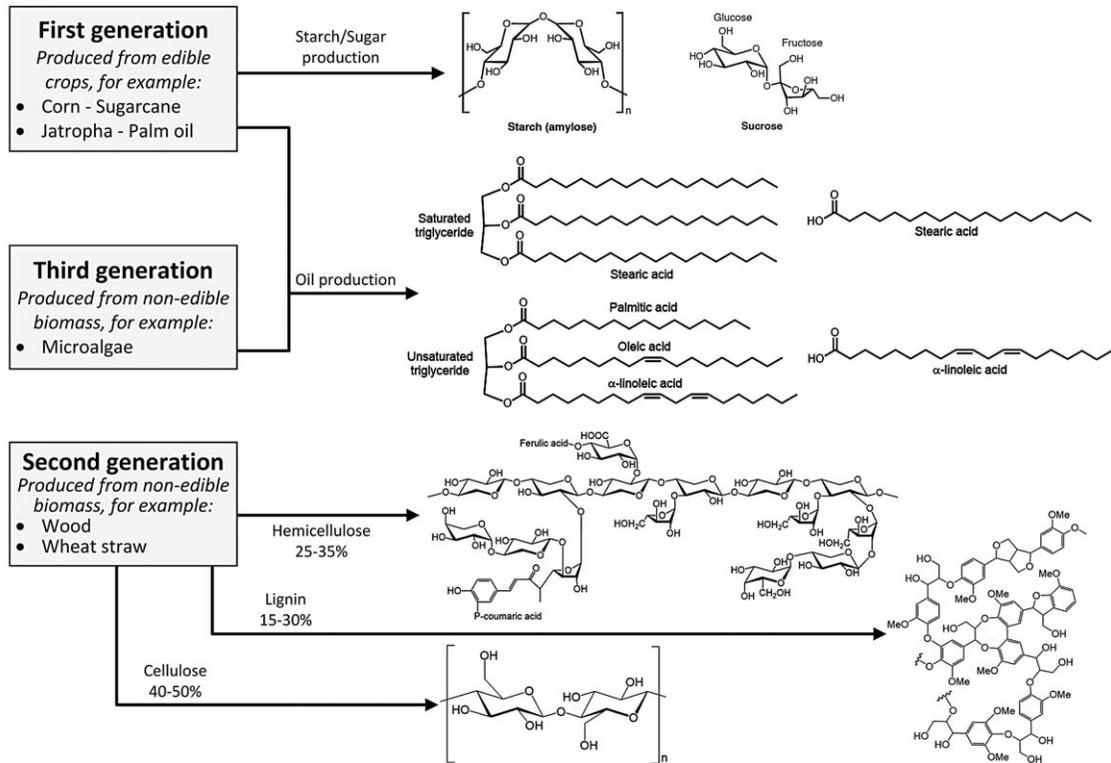
Types of biofuels and bioproducts:

Figure 2.1   The main components of all three major biomass categories.

but other inedible biomass fractions generally remain untouched. Bioethanol is recovered from the fermentation of simple sugars derived directly from plants such as sugarcane, sugar beets or indirectly from starch-containing crops. Simple sugars are fermented directly, while amylase enzymes are generally added to the starch-based biomass before fermentation to break down the starch to simple sugars. Currently, bioethanol is the largest biofuel produced worldwide with a total world production of 94 billion litres of bioethanol in 2014.[15] The largest producer of bioethanol in 2014 was the USA with a production of 54.5 billion litres, Brazil was second with 26.3 billion litres and Europe third with 5.6 billion litres. Another transportation fuel with a large worldwide production capacity is biodiesel, which is produced from oil-based crops including palm oil, rapeseed and soybean. The two world leaders in biodiesel production in 2014 were Europe (11.7 billion litres) and the USA (4.8 billion litres).[15]

Feedstocks used to produce first generation biofuels and bioproducts are very easy to convert to biofuels due to their availability within the plant structure (which is why these fractions are considered edible). However, first generation products have several issues including their competition with food, their limited availability, their high fertilizer use and, therefore, their minimal savings in terms of CO_2 emissions compared to their fossil equivalent. For these reasons, the global biofuel demand in 2050 is not expected to be met by edible crops and is rather expected to be supplied almost entirely from second and third generation biofuels and bioproducts, which represents a future requirement of *ca.* 30 ExaJoules (EJ).[16]

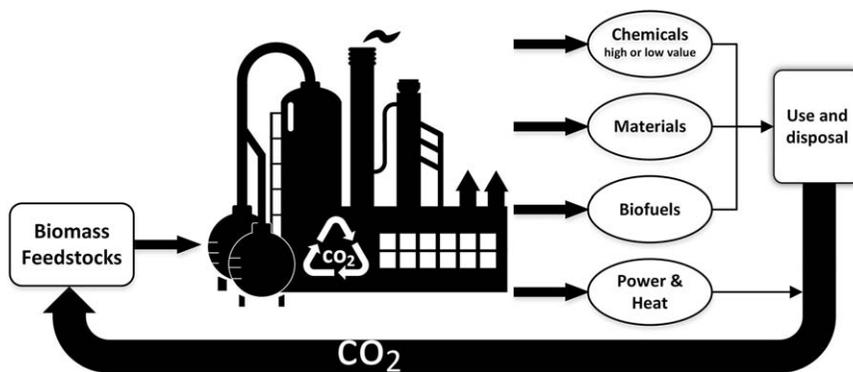### 2.2.2 Second and Third Generation of Biomass – Non-edible Crops

Lignocellulosic biomass, microalgae and organic wastes are described as non-edible crops. The bulk of terrestrial biomass is represented by lignocellulosic materials, composed mainly by three natural polymers: cellulose, hemicellulose and lignin. Agriculture and forestry residues are examples of lignocellulosic biomass that are being considered for the production of a wide variety of biofuels and fine chemicals. Common upgrading routes often involve the fractionation and depolymerization of hemicellulose, cellulose and lignin to produce 5-carbon sugars, 6-carbon sugars and aromatic chemicals, respectively. However, other direct processes target platform molecules such as dehydration products or sugar hydrogenation to alcohols.[1] Organic wastes mainly refer to sewage sludge, pulp and paper mill sludge, food waste, manure and other agricultural residues, which are composed of carbohydrates, proteins, lipids and lactose.[17,18] These feedstocks can be directly processed or pre-treated prior to conversion for the production of biogas, hydrogen and C_2 to C_4 hydrocarbons.[18] Microalgae (sometimes referred to as the feedstock for third generation biofuels and bioproducts) are being considered mainly for the production of biodiesel

from extracted lipids by catalytic or enzymatic transesterification.[19] Due to their higher photosynthetic efficiency, they have an impressive potential for the production of biofuels in comparison to lignocellulosic biomass, although this potential has never been achieved at an industrial scale.[20] Sugarcane production can reach values around 4900 kg of bioethanol per hectare,[21] while microalgae's potential has been said to reach 52 000–121 100 kg of biodiesel per hectare.[20] Microalgae can also be used as a source of natural dyes, antioxidants, carbohydrates and other fine chemicals.[20] After extraction, the remaining algae can be processed into ethanol, methane, livestock feed or fertilizer.

2.3   The Biorefinery Concept

A biorefinery is a facility where a sustainable process integrates the production of fine chemicals, materials, biofuels and heat/power from biomass with the least amount of leftovers after treatment. The representation of an integrated biorefinery incorporating the re-utilization of CO_2 within its processes is shown in Figure 2.2. The concept of a biorefinery is analogues to today's petroleum refineries, where multiple carbon-based products and fuels are produced from crude oil.[7] Proposed biorefinery processes employ a wide range of technologies to fractionate biomass into valuable compounds (polysaccharides, sugars, oils, lipids, proteins) and for subsequent upgrading these compounds in subsequent steps. Feedstock fractionation is a crucial step due to the heterogeneity of the biomass and the multiple functional groups that are present.

Currently, most bio-products produced from edible crops are manufactured in single production chains and not within a biorefinery. Because these plants have already been built, so far, the main focus of processing plants based on edible crops has been to further optimize their processes and reduce costs rather than implement new technologies.[12] However,

Figure 2.2   A schematic representation of the biorefinery concept with integrated CO_2 use and recycling.

biorefineries based on second and third generation biofuels and bioproducts have the opportunity to exploit many more routes and achieve larger scales due to a larger biomass potential yield per cultivation area, which limit biomass transportation restrictions.[7] Such scales could also allow the implementation of new conversion technologies that only become economical at very large scales, which include the high-pressure systems required for high-pressure CO$_2$ use.

2.3.1 Biorefinery Products

Presently, the chemical industry refines crude oil into fractions that include naphtha (from which all the major bulk chemicals are derived), gasoline, kerosene, gas oil and residues.[22] The processes employed in the refinery industry include numerous cracking and refining catalysts as well as distillation as the dominant separation strategy. An important characteristic and advantage of the naphtha fraction compared to biomass, is its low oxygen content. Most bulk chemicals produced in refineries are derived from molecules containing no oxygen such as ethylene, propylene, C$_4$-olefins and the aromatics benzene, toluene and xylene (BTX).[22]

In principle, most petrochemical refinery platform molecules could be derived from renewable carbon sources. Unfortunately, this is currently only possible at relatively low yields and high costs.[22] For this reason, it has been proposed that the biorefinery industry produce a number of petrochemical substitutes through a selection of simple platform molecules that are different from those currently used in the petrochemical industry.[7] Given the chemical complexity of biomass, there is a range of platform chemicals that could be produced from one type of feedstock depending on the chosen processing strategy. Nevertheless, several of these building block chemicals are expected to be derived from the carbohydrate fraction of biomass, which, due to it being a major component of all types of biomass, is likely to play a crucial role in future biorefineries. In 2004, the US Energy Department identified twelve building block chemicals of major importance that could be produced from sugar by biological or chemical conversions.[23] These twelve sugar-based building block chemicals are shown in Figure 2.3 along with the main chemicals and products (in bold) that can be easily derived from these intermediates and that are likely to be found in an integrated biorefinery.

2.3.2 Main Biorefinery Processes

The main processes in proposed biorefineries will likely be used to fractionate, depolymerize and deoxygenate biomass components. Since biomass is already highly oxidized, several hydrogenation and/or dehydration transformations are usually required. These transformations are key steps for the conversion of biomass into building blocks molecules and value-added compounds. These processes can be classified into two main categories

Figure 2.3 The principal conversion routes and products found in an integrated biorefinery.

depending on the nature of biomass transformation: physical or chemical treatments.

Physical or mechanical processes are usually involved as the first step in biorefineries as a preconditioning step, although they are not always required.[7] These processes do not change the composition of the biomass, but only lead to particle size reduction or separation of the feedstock components. Biomass size reduction refers to changes in particle size, shape or bulk density within specific ranges depending on further conversion processes requirements. Separation procedures can consist of increasing the concentration of valuable compounds without the transformation of their components by extractions methods, mainly using organic solvents or supercritical fluids.

Chemical processes involve changes in the chemical structure of one or more of the molecules by introducing high temperatures or catalytic species into the reaction media. For the purpose of this chapter, we classified these processes as thermochemical and catalytic. We define thermochemical pathways as pathways that are rapid and largely driven by high temperatures rather than just by the presence of catalysts. These thermochemical processes have been used for the production of syngas, bio-oil, bio-char/bio-coal and power from biomass[24] and include gasification, pyrolysis and dry/wet torrefaction. Gasification consists of keeping biomass at high temperatures (>700 °C) with limited oxygen concentration to produce hydrogen, methane, syngas, and/or power. Hydrogen and methane can also be in liquid conditions at high pressure if hydrothermal gasification (HTG) conditions are used. HTG operates within the subcritical or supercritical region of water (374 °C and 22.1 MPa) usually with a catalyst and generally uses biomass feedstocks with a high-water content, *e.g.* manure, that benefit most from avoiding a pre-drying step in the process.[18,25] Syngas is an important intermediate in several biorefinery processes that could lead to multiple fuels or chemicals.[23] The Fisher–Tropsch (FT) process is a well-known route for the upgrading of syngas into long chain liquid hydrocarbon and alkanes and short alcohols (C$_1$ to C$_3$) by multiple catalytic syntheses using mostly cobalt and iron-based catalysts.[26] Other catalysts such as nickel and ruthenium, have shown high catalytic activity in FT processes, but under operational conditions nickel promotes methanation, which is undesirable for this route, and ruthenium is expensive, which increases process costs. Higher alcohols (C$_4$ to C$_{10}$), used as additives in the reformulation of gasoline[27] and for the production of C$_2$ to C$_4$ olefins,[28] are also produced from syngas using a several catalytic routes.

Pyrolysis is defined as the processing of biomass at temperatures between 300 °C and 600 °C in the absence of oxygen, to produce bio-oil, charcoal and light gases similar to syngas. Bio-oil is usually the most desirable product and its production can be maximized by applying what is known as fast pyrolysis conditions (which involves rapid heating up to 500 °C and short residence times at high temperatures, *e.g.* seconds).[24] Bio-oil can be upgraded to mixtures of molecules that can be used as transportation fuels or

chemicals. However, the high production of char and coke, and the important hydrogen consumption still remain problematic.[7] Dry torrefaction, sometimes referred to as a mild pyrolysis, is performed under an inert environment at atmospheric pressure with a retention time around one hour at low temperatures (200 °C to 300 °C or 180 °C to 260 °C in case of wet torrefaction (WT)).[29,30] In both conditions the main product is bio-char or bio-coal, which is used as a feedstock for combustion or gasification. The advantage of this char over raw biomass is that its characteristics are more stable and that it has a higher energy density, which makes its transportation less environmentally and economically intensive.

Catalyzed chemical reactions play a vital role in the upgrading of building platform molecules to petrochemical equivalents and they can be found at various stages of biomass conversion. The most common catalyzed reactions that occur in biorefineries are hydrolysis, dehydration, hydrogenation and transesterification reactions. Hydrolysis uses acids, alkalis or enzyme catalysts to depolymerize polysaccharides and proteins to their corresponding sugars or amino acids. Acid catalyzed dehydration reactions and metal-catalyzed hydrogenation reactions are important deoxygenation reactions notably for sugars. Transesterification is used to produce biodiesel from lipids or oils by an acid or base-catalyzed reaction with a short alcohol such as methanol. Other important chemical reactions are FT synthesis, methanation and steam reforming, which involve syngas conversion in the gas phase and are used to produce hydrocarbons, methane or hydrogen, respectively.[7] Of all the biochemical reactions currently implemented in various industries, there are mainly three types found in biorefineries: fermentation, anaerobic digestion and enzymatic reactions. Fermentation and anaerobic digestion involve live cells whereas enzymatic-based reactions usually involve cell free mixtures of proteins. Fermentation generally refers to the production of specific non-volatile chemicals such as alcohols, organic acids or even alkanes from carbohydrates. CO_2 is almost always a co-product of fermentative processes. Anaerobic digestion refers to a subset of fermentation reaction that produce gaseous products (mainly methane and CO_2) from carbohydrate and proteins found in biomass and organic wastes. Enzymes are usually used to facilitate the deconstruction of various polymers including polysaccharides and proteins.

Each of these processes presents significant conversion challenges, which continues to encourage innovation within biorefinery research. Multi-disciplinary efforts have been carried out in the design of novel catalysts, high-pressure systems, solvent engineering and multi-scale modelling in order to surpass current process limitations.[14] Research in high-pressure CO_2 and CO_2–H_2O systems is an example of these efforts. In the past 20 years, research publications related to the application of CO_2 in green processes and biomass conversion has increased significantly.[31] Below, we outline the features of CO_2 and CO_2–H_2O systems that have contributed to this increased interest and the potential advantages of their use in biomass conversion.

2.4 High-pressure CO_2 and CO_2–H_2O Systems Within the Biorefinery Concept

2.4.1 Essential Features of High-pressure CO_2 and CO_2–H_2O Systems

Carbon dioxide is an attractive replacement for organic solvents because it is abundant, inexpensive, non-flammable, environmentally benign and can be easily recycled and disposed of.[32] Its physical properties such as small molecular size and absence of surface tension (at high pressure) grant CO_2 high penetrating capabilities and lead to high mass and heat transfer co-efficients.[31] Despite its inertness, CO_2 can also participate as a catalyst or inhibitor, and interact with other catalysts and substrates, which can affect reaction performance. Presently, high-pressure CO_2 is often considered for high-pressure sustainable process development due in part to its low critical pressure and temperature,[9] which are easily reachable in industrial re-actors.[31] The special combination of gas-like viscosity and diffusivity, and liquid-like density of high-pressure CO_2 makes it a highly tunable solvent and leads to many opportunities for process development. Moreover, when CO_2 is used in confined processes it can be considered as sequestered given that it was generally obtained from natural deposits or man-made pro-duction, *e.g.* ammonia plants.[31,33] Though opportunities offered by CO_2 use exist across many fields they extend to several processes that are being considered within biorefineries.

High-pressure CO_2 has a dielectric constant that depends on its density but always remains relatively low, which can be disadvantageous for dis-solving the polar compounds found in biomass. However, CO_2 is very well suited for dissolving apolar and lipophilic molecules such as fats, oils and lipids considered as high valuable compounds in biomass processing. Although CO_2 has a limited miscibility with water, their combination leads to the *in situ* formation of carbonic acid inducting pH values around 3 at saturation, which is achieved by the double dissociation of water with CO_2 to form carbonic acid per the following equations:

$$CO_2 + 2H_2O \leftrightarrow HCO_3{}^- + H_3O^+, \ HCO_3{}^- + H_2O \leftrightarrow CO_3{}^{2-} + H_3O^+$$
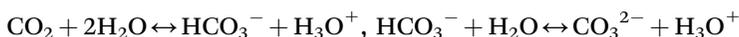
A very interesting feature of this system is that pH values can be tuned by temperature and pressure allowing acid-catalyzed reaction rate enhancements and neutralization by depressurization. The pH values of CO_2–H_2O binary system can be estimated using the equation $pH = (8.00 \times 10^{-6})T^2 + 0.00209T - 0.216 \ \ln(p_{CO_2}) + 3.92$, developed by van Walsum *et al.*, in the range of 100–250 °C and up to 150 atm in CO_2 partial pressure (T and P values should be in Celsius and atmospheres, respectively), which is calculated using Henry's Law.[34]

In addition, using a parameter known as reaction severity can facilitate the comparison of process conditions for different acid catalysts and

temperatures by calculating the combined severity parameter (CS)[35] shown in equation $CS = \log(R_0) - \text{pH}$. These parameters can be particularly useful for comparing the addition/use of CO_2 during biomass processing to that of other acids and reaction mixtures. The combined severity parameter takes into consideration the acid concentration (pH values given above when CO_2 is used), the reaction time and the reaction temperature, which are used to calculate the severity factor, R_0. The severity factor is defined in equation $R_0 = t \exp\left(\dfrac{T - 100}{14.75}\right)$ and was proposed by Overend *et al.*[36] for biomass hydrolysis in batch and plug-flow reactors (t and T values should be given in minutes and Celsius).

Given the attractive properties of this mixture, the use of high-pressure CO_2 and CO_2–H_2O systems has led to several improvements and developments in biomass processing.[5,37] In particular, CO_2 and CO_2–H_2O systems have led to promising results in areas involving high value compound extraction/purification, hydrolysis and dehydration of carbohydrates and biomass-derived hydrogenation. Table 2.1 lists several processes in which CO_2 has been used within biorefinery processes. Below, we highlight the principal applications and benefits of CO_2 and CO_2–H_2O mixtures in different types of biomass conversion technologies including physical and chemical processes.

2.4.2 Physical Processes Employing High-pressure CO_2 or CO_2–H_2O Systems

The utilization of CO_2 in physical processes has been extensively explored with a tremendous number of associated publications being available on the subject. Because of CO_2's ability to dissolve lipophilic substances,[38] the extraction of bioactive or high-value compounds using supercritical CO_2 ($scCO_2$) is one of the most common approaches used for the valorization and fractionation of biomass.[9,39–45] This approach is notably used extensively in industry especially for the production of food additives or medicinal products due to CO_2's non-toxic nature.[46] Within bioenergy applications, the targeted compounds during extractions have mainly been lipids, waxes, proteins, lignin and phenolic compounds for the production of biodiesel, fatty acids, amino acids, power/heat, aromatic compounds and other fine chemicals. The advantages of using CO_2 as an extraction or purification mediator over conventional processes such as organic solvent extraction and distillation include: reduction of operational steps, elimination of solvent waste, moderate operational temperatures, high quality of the extracts and cost saving while reducing negative impacts on the environment and human health risks.[38,47–49] $ScCO_2$ extraction has notably been extensively explored for the extraction of lipids from algae.[49–51] Several pilot scale studies and energy evaluation have been conducted to assess the performance of CO_2-based extractions.[50,51] Compared to organic solvent extractions, $scCO_2$ has shown higher efficiency and selectivity towards triglycerides avoiding the

solubility of undesired components such as pigments or polar lipids.[49] The purification of biodiesel is an excellent example of the simplicity of CO$_2$-based processes; where, in a single injection step, biodiesel as pure as what is obtained by conventional purification was obtained but with much lower waste generation.[52] A similar use of CO$_2$ was described by Bourne *et al.* for the simultaneous production and purification of γ-valerolactone (GVL) from levulinic acid and water, where GVL was delivered almost pure with lower energy requirements than using a conventional reactor.[53] GVL is a biomass-derived precursor to several high-value chemicals and has excellent properties when used as a solvent for lignocellulosic biomass deconstruction and further upgrading reactions.[54–58] CO$_2$ can play a significant role in the recovery of GVL after reaction. Notably, liquid CO$_2$ was used to extract over 99% of GVL from the reaction media of several biomass conversion processes.[59,60] After its addition, a CO$_2$-expanded phase was created with GVL, which was no longer miscible with water. This lead to the production of a GVL phase and a concentrated aqueous phase containing over 90% of the carbohydrates produced from biomass which allowed for an easy recovery of GVL.[59–62]

Another important approach developed for biorefinery processes has been the use of CO$_2$ explosion to disrupt raw cellulosic substrates.[63–67] The instantaneous release of CO$_2$ at high pressure promotes the disruption of the cellulosic structure and leads to increases in the accessible surface area of the substrate used for further hydrolysis.[68] Processes that serve to increase accessible surface area in biomass play an especially key role for enzymatic hydrolysis. CO$_2$ has a similar ability to penetrate to accessible pores in biomass to water and ammonia ,which have comparable molecular sizes and are used in two well-known explosion treatments for biomass pre-treatment prior to enzymatic hydrolysis.[69,70] Some studies have reported that CO$_2$ explosion can be more cost-effective than ammonia explosion,[63] and can reduce the formation of inhibitor compounds produced during steam explosion through the degradation of sugars due to its lower operational temperatures.[68]

2.4.3 Chemical Processes Employing High-pressure CO$_2$ or CO$_2$–H$_2$O Systems

2.4.3.1 *Thermochemical Processes*

The addition of CO$_2$ in thermochemical processes has led to several beneficial effects on conversion, reaction rates, energy consumption and even selectivity. Butterman and Castaldi[71] reported that CO$_2$ enabled a more complete biomass gasification to volatiles. Notably, they reached an H$_2$/CO ratio suitable for FT fuel synthesis at a lower temperature than when using an N$_2$ environment. Also, a more efficient separation of lignin from holocellulose was possible. In the case of WT, the integration of CO$_2$ not only improved the conversion of biomass to volatiles but the resulting solids also showed an increase in heating value of up to 0.54 MJ kg^{-1} and a reduction of

Table 2.1 Examples of the principal CO_2-assisted processes proposed for use in biorefineries.

Main reactant	Process	Reaction media	Effect of CO_2 or CO_2–H_2O use	Source
Biomass [raw material]	Gasification	CO_2, $CO_2 + H_2O$	Higher yields to volatiles with a H_2/CO ratio more suitable for Fisher–Tropsch fuel synthesis, more efficient separation of lignin from holocellulose and the production of a very reactive and porous char at less severe conditions than in a N_2 environment.	71
	Wet torrefaction	$CO_2 + H_2O$	Higher ash removal, higher heating value, less specific gridding energy, reaction rate enhancement and less solid production due to the acidic catalysis effect compared to N_2-WT.	72
		$CO_2 + H_2O$	Higher ash removal, same hydrochar yield with a reduced heating value and less specific grinding energy compared to hydrothermal conditions.	73
	Pyrolysis	CO_2	Increase in CO production and six-fold increase in char surface area with a different chemical composition than chars produced under a N_2 environment. Inhibition of the secondary char formation and tar polymerization.	74
	Extraction	CO_2, $CO_2 + H_2O$; $CO_2 + EtOH$; $CO_2 +$ organic alcohol or ether	Complete separation of cellulose and hemicellulose from lignin; fractionation of alkanes and fatty alcohols (waxes), extraction of phenolic compounds and α-mangostin; extraction of β-glucan from barley grains, precipitation of proteins from soy meal extracts or milk; extraction of a mixture of fatty acids, phenolic compounds, and fucoxanthin from *S. muticum*; extraction of lipids from living cells (microalgae); over 90% lignin removal from rice husk.	9, 39–45

	CO_2 explosion	CO_2, $CO_2 + H_2O$	Changes in chemical composition and crystallinity of the material with higher surface area and enhancement of enzymatic digestibility compared to the pure water treatment. Prevention of inhibitor produced in steam explosion and less sugar degradation due to lower temperature.	63–67
	Extraction and enzymatic transesterification	CO_2 + methanol–*tert*-butanol	Integrated extraction of fat from microalgae with no need for a solvent separation unit and the production of a high quality glycerol-free biodiesel.	48
	Acid hydrolysis	$CO_2 + H_2O$, high solid loading	Production of oligosaccharides and furfural from the hemicellulose fraction of biomass with a reduction in the crystallinity of the cellulose-rich fraction and higher susceptibility to enzymatic hydrolysis compared to hydrothermal conditions. Production of a highly concentrated monosaccharide solution after enzymatic hydrolysis. 33% less amount of enzyme required in later saccharification when CO_2 was used compared to diluted sulfuric acid pre-treatment.	76–81, 86
Cellulose	CO_2 explosion	CO_2 + buffer solution	Increase in accessible surface area of the cellulosic substrate and changes in the crystallinity of the material. Reduced production of inhibitors produced in steam explosion and less sugar degradation due to the lower temperature that is used with CO_2.	63, 66, 67
	Acid hydrolysis	$CO_2 + H_2O$	Enhancement in the hydrolysis rate constant compared to subcritical water treatment.	75
	Enzymatic hydrolysis	$CO_2 + H_2O$	Kinetic hydrolysis constant enhancement and retention of cellulase activity.	106–108

Table 2.1 (*Continued*)

Main reactant	Process	Reaction media	Effect of CO_2 or CO_2–H_2O use	Source
Starch	Acid hydrolysis	$CO_2 + H_2O$	Quasi-proportional increase in glucose yield from starch with the addition of CO_2. Hydrolysis rate constant increase.	75, 82
	Acid hydrolysis and dehydration	$CO_2 + H_2O$	Enhancement in dehydration and hydrolysis rates during the production of 5-HMF from inulin due to the formation of carbonic acid.	89
Hemicellulose or pentose	Acid hydrolysis, dehydration and extraction	$CO_2 + H_2O$	Production of furfural and its simultaneous extraction without the addition of acid.	90
Lignin	Depolymerization	$CO_2 + H_2O + acetone + HCOOH$	Production of phenolic oil composed of oligomers fragments and aromatic monomers from lignin with slightly higher yields compared to catalytic steam processing.	99
	Purification	$CO_2 + H_2O$	Selective purification of lignin oxidation products from aqueous solution with lower energy requirements.	103
Protein	Acid hydrolysis	$CO_2 + H_2O$	Production of amino acids from bovine serum albumin with increased rates for peptide bond hydrolysis.	88
Polyalcohol	Dehydration	$CO_2 + H_2O$	Increase in THF yield from the dehydration of 1,4-butanediol. Enhancement in the dehydration rate of triol compounds compared to high-temperature liquid water. Increase in acetol yields due to dehydration rate enhancement and acetol stability compared to high-temperature liquid water.	83, 109, 110

| Fatty acids | Hydrogenation | CO_2 | Increase in the concentration of hydrocarbon compounds with diesel-like properties from cattle fat during hydrogenation. | 91 |
Triglycerides/ Lipids	Transesterification/ Enzymatic transesterification	CO_2 + methanol, CO_2 + enzymes	Reduction in mass transfer limitations and increased catalytic active site exposure led to improvements in reaction. Reduction in the reaction temperature and time at 92% conversion.	96, 97
Levunic acid	Hydrogenation/ Purification	CO_2 + H_2O	Production and simultaneous purification of GVL from levulinic acid with lower energy requirements.	53
5-HMF or furfural	Hydrogenation	CO_2 + H_2O	Full conversion of 5-HMF and furfural to 2,5-DMF and 2-MF, respectively, with 100% selectivity. Tunable products profile by tuning the water : CO_2 ratios.	95
Biodiesel	Purification	CO_2	Purification of biodiesel in a single step without any loss in quality compared to conventional processes.	52

6.5 kWh t^{-1} in specific gridding energy.[72] However, the same research group also reported that the CO_2-enriched WT produced similar hydrochar yields with less heating value compared to N_2-WT, but with a significant increase in ash removal.[73] Similar to the impacts of CO_2 in biomass gasification, CO_2-assisted pyrolysis showed an enhancement in the production of CO as a result of reactions between CO_2 and other gases, tar and char.[74] The resulting char presented a six-fold increase in surface area with a different chemical composition than chars produced with a N_2 environment. It also appeared that CO_2 inhibited secondary char formation and tar polymerization.

2.4.3.2   Catalytic Processes

Some of the most versatile routes to produce bio-fuels and bio-products involve the upgrading of the carbohydrate fractions found in biomass. Given the large variations in biomass composition and chemical structure, the conversion technology that is employed generally has to be tailored to the biomass characteristics and to the subsequent upgrading routes to avoid low yields, high energy expenditures and excessive waste production.[5] For this reason, the initial biomass processing, including biomass pre-treatment, is one the most challenging and expensive steps in the biorefinery and has a significant influence on downstream processing. The utilization of CO_2–H_2O mixtures in the pre-treatment and hydrolysis media have several advantages compared to conventional processes such as the dilute acid or organosolv processes.[75–82] Notably, the formation of carbonic acid can enhance the rate of acid-catalyzed reactions, which include hydrolysis and dehydration, without the drawback of neutralization and/or solvent recovery.[75,76,82–86] The use of CO_2–H_2O mixtures during biomass pre-treatment has also been shown to reduce the crystallinity of the cellulose-rich fraction allowing a reduction in enzyme loading of 33% during subsequent saccharification.[86] Relvas *et al.* modelled the kinetics of the hemicellulose, xylan and arabinan hydrolysis in the presence of CO_2 added during hydrothermal processes and demonstrated that the formation of carbonic acid led to an increase in the kinetic reaction constants for both intermediates and final products.[87] The kinetics of cellulose and starch hydrolysis in CO_2–H_2O mixture have been the subject of similar studies and have demonstrated that CO_2 addition led to significant increases in reaction rates compared to pure water (see Figure 2.4 and Figure 2.5).[75] Other examples in which the *in situ* formation of carbonic acid have accelerated reaction rates include the hydrolysis of proteins for the production of amino acids,[88] and the dehydration of poly-alcohols and monosaccharides from starch and hemicellulose for the production of tetrahydrofuran (THF),[83] 5-hydroxymethylfuran (5-HMF)[89] and furfural,[90] respectively. Further reaction examples accompanied with a discussion of the effects and advantages of CO_2 use are given in Table 2.1.

The hydrogenation or hydrodeoxygenation of low value feedstocks, such as cattle fat (rich in free fatty acids), is another pathway being considered for
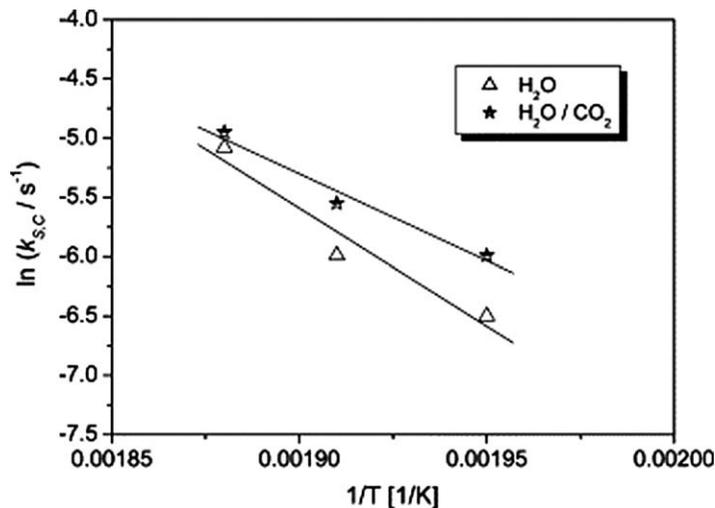
Figure 2.4   Arrhenius plots of cellulose hydrolysis in water and water–CO_2.
Reprinted from T. Rogalinski, K. Liu, T. Albrecht and G. Brunner, *Hydrolysis Kinetics of Biopolymers in Subcritical Water*, vol. 46,[75] Copyright (2007) with permission from Elsevier.
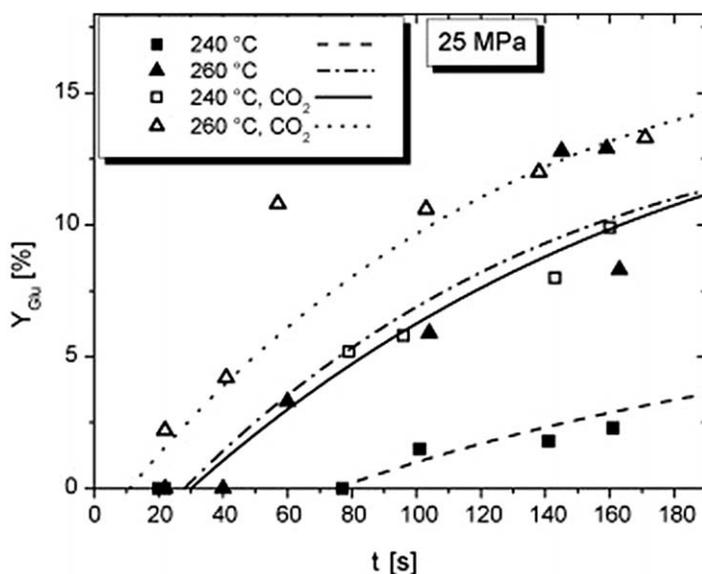

Figure 2.5   Glucose yields during subcritical water hydrolysis of cellulose at different residence times and temperatures in the presence and absence of dissolved CO_2.
Reprinted from T. Rogalinski, K. Liu, T. Albrecht and G. Brunner, *Hydrolysis Kinetics of Biopolymers in Subcritical Water*, vol. 46,[75] Copyright (2007) with permission from Elsevier.

biomass valorization.[91,92] However, several of these reactions can suffer from low reaction rates due to mass transfer limitations especially when they involve liquid-phase reactions. Notably, mass transfer limitations arise due to H_2 low solubility in common solvents. This leads to hydrogenation rates being controlled by the transfer of H_2 between the gas and liquid phase as opposed to the reaction itself. In contrast, CO_2 is highly miscible with most gases, which can greatly enhance gas solubility and any associated homogeneous or heterogeneous catalyzed reactions that suffer from gas-to-liquid mass transfer limitations.[93] In fact, the ability of CO_2 to enhance the solubility of several gases has been demonstrated in multiple reactions,[94] including several in biomass processing.[53,91,95] The rate of hydrodeoxygenation of cattle fat was enhanced by the addition of CO_2 which doubled the content of hydrocarbons in the final products, giving it diesellike properties.[91] Interestingly, the presence of CO_2 induced a change in the catalyst's morphology leading to a reorganization of the kaolinite-based catalyst's internal structure in a similar way to what has been reported in literature when other processing effects such as flow, shear, electric polarization or colloids modified the catalyst properties.

Hydrogenation reactions also play important roles in several downstream upgrading routes proposed for biomass conversion including the production of several molecules proposed as fuel substitutes including 2,5-dimethyfuran (2,5-DMF) and 2-methylfuran (2-MF). 2,5-DMF and 2-MF are produced by the hydrogenation of 5-hydroxymethylfurfural (HMF) and furfural, which are derived from the dehydration of glucose and xylose, respectively. Recently, Chatterjee *et al.* reported that the addition of CO_2 into the reaction media led to full conversion of both substrates with 100% selectivity to the targeted products.[95] Figure 2.6 demonstrates how modifying the water/CO_2 ratio allows to tune the product distribution.

Also of importance for liquid biofuel production, the transesterification of triglycerides and methanol to fatty acid methyl esters (FAMEs) suffers from similar obstacles related to kinetics, selectivity and yields.[96] CO_2 was also used to enhance mass transfer between the substrates and catalyst leading to higher yields and modified product profiles. The reaction rates were also increased by the addition of CO_2 due to higher mass transfer but also because of CO_2's ability to swell the catalyst (the acid exchange resin, Nafion[®]) allowing greater exposure of the reactant to the active sites.[96] Transesterification reactions can also use enzymes as catalysts including lipases. The use of enzymes avoids side reactions and reduces the energy requirements involved in chemical methods due to the enzyme's near 100% selectivity and its ability to function at ambient or near ambient temperatures.[97] Lipases have been used in the presence of high-pressure CO_2 without denaturation for transesterification, hydrolysis and other reactions.[98] Hu *et al.* optimized the transesterification of phytosterol and soybean oil in scCO_2 using enzymes and achieved a conversion of 92% with significantly lower reaction temperatures and time than without CO_2.[97] The ability to use enzyme in CO_2–water mixtures has led to the integrated and continuous processing of
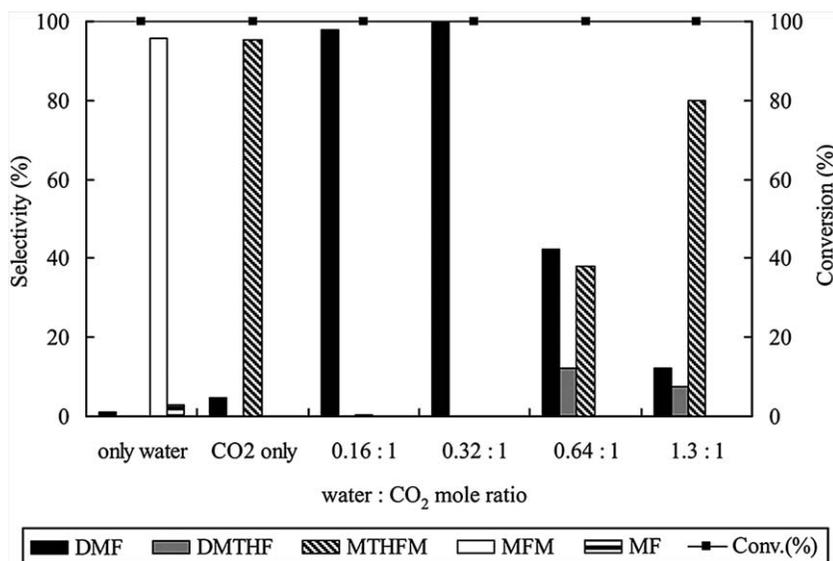
Figure 2.6   Effect of the variation of the water–CO₂ mole ratio on product
distributions of furan hydrogenation. DMF = 2,5-dimethylfuran,
DMTHF = 2,5-dimethyl-tetrahydro-furan; MTHFM = tetrahydro-5-methyl-
2-furanmethanol, MF = 2,5-bis(hydroxymethyl)furan (MF), MFM =
5-methylfuranyl methanol.
Reproduced from ref. 95 with permission from The Royal Society of
Chemistry.

microalgae lipids, including the extraction and biodiesel production steps
via the enzymatic transesterification, in scCO₂.[48] The resulting biodiesel,
dissolved in scCO₂, was easy to recover and its properties complied with the
international standards and regulation without the need for further purifi-
cation or glycerol separation.

The depolymerization and upgrading of lignin is also described as a
key step in the production of liquid transportation fuel or aromatic mole-
cules, and for furthering the economic development of lignocellulosic
biorefineries.[99,100] However, the conversion of lignin to high-value chemicals
and fuels presents many challenges due to its complex aromatic structure
and poor chemical stability during depolymerization. Currently, 98% of
lignin is burned for the production of heat and power in the pulp and paper
industry.[101] Gosselink *et al.* studied the depolymerization of lignin to a
phenolic oil (up to 45% based on lignin) in a supercritical fluid consisting of
CO₂/acetone/water/formic acid.[99] The resulting phenolic oil was composed
of oligomers fragments and contained several aromatic monomers corres-
ponding to a 10–12% yield based on the original lignin. These monomers
yields were slightly higher than those previously observed using catalytic
steam processing.[102] Moreover, Assmann *et al.* showed that the selective
extraction of lignin oxidative products is possible by changing the CO₂
pressure.[103] Through calculations, they suggested that the purification of

lignin oxidative products using multi-stage CO_2 extractions could be used to produce single monomers at high purities while using a much more eco-friendly and cheap process compared to vacuum distillation and crystallization. In general, supercritical fluid extractions (SFE) require considerably less energy than conventional purification methods, but the operation costs of SFE is expensive.[104] Economic considerations in the case of vanillin purification have shown that, in order to be commercially competitive, the feed solution must contain at least 50% vanillin. This example illustrates the typical challenges of implementing SFE.

2.4.4   Challenges for Implementing Processes Using CO_2

In summary, high-pressure CO_2 and CO_2–H_2O systems provide the opportunity to engineer reaction conditions, reduce energy requirements and tune reaction rates, product selectivity and catalyst activity by manipulating only pressure, temperature or CO_2 content.[93] However, CO_2's low solvation of polar compounds requires the utilization of large quantities of CO_2[31] that can seriously compromises its industrial implementation. In fact, no integrated high-pressure CO_2 or CO_2–H_2O technologies currently exist in industrial biorefineries. Implementation concerns are related to high capital costs, the lack of specialized process engineers, low familiarity in CO_2-based processes advantages and safety issues in large scale operations.[52] These processes operate under high pressure and designing, building and controlling a high-pressure process needs specialized equipment and personnel.[31] However, though capital costs are often higher, the overall costs of these high-pressure processes are not always greater than their low-pressure alternatives. Daza Serna *et al.* compared the cost efficiency of the conventional acid pre-treatment with a $scCO_2$ pre-treatment for the conversion of rice husk and found that the $scCO_2$-based pre-treatment can be more cost effective leading to a reduction in the sugar production cost to 0.20 USD per kg from 1.88 USD per kg with a lower environmental impact.[9] A major fraction of the cost in high-pressure CO_2 processes is due to the high energy requirements for CO_2 conditioning (cooler and pump systems). However, the easy recovery of CO_2 and resulting high product concentrations represent opportunities for reducing the cost of raw material and energy savings during purification. Recently, Sharifzadeh *et al.* explored the economic feasibility and environmental performance of an integrated process utilizing CO_2 from biomass pyrolysis for the production biodiesel *via* microalgae.[105] The results showed a significant reduction of 45% to 6% of total carbon inputs in the flue gas and a potential increase of biomass to fuel yields from 55% to 73%, which compensated for the cost of CO_2 conditioning.

2.5   Conclusion

In this introduction, we discussed the general goals and possible routes for biomass conversion and biorefineries with attention to the possibilities of

using high-pressure CO$_2$ and CO$_2$–H$_2$O. These high-pressure systems have shown to be beneficial in multiple steps during the biomass conversion chain and offer the added benefit of being non-toxic, green and renewable solvents. Furthermore, their use has been shown to benefit the production of first, second and third generation biofuels and bioproducts. Finally, when CO$_2$ is used and recycled in confined processes it can be considered as ''sequestered'' if its source is natural deposits or man-made production. Some of the principal benefits associated with CO$_2$ use include:

  i. Acid-catalyzed reaction rate enhancements
  ii. Tunability of the product distribution
  iii. High products concentration after CO$_2$
  iv. Increase in catalysts activity through solvent effects or catalyst swelling
  v. Reduction of mass transfer limitations
  vi. Milder process conditions
  vii. Simplified efficient purification/extraction steps
  viii. Lower environmental impact through reduced waste production.

Although the cost-effectiveness of high-pressure technologies over conventional processes is not systematic and must be evaluated for each individual process, the advantages associated with the use of CO$_2$ can help compensate for the energy and capital requirements of high pressure processing and CO$_2$ use. Nevertheless, industrial implementation is still hindered by the lack of specialized process engineers and safety concerns over large-scale high pressure operations. Therefore, additional fundamental understanding of high-pressure CO$_2$ and CO$_2$–water systems combined with detailed techno-economic modelling is needed to ensure an optimal process design for each application and facilitate the beneficial use of CO$_2$ in future biorefineries.

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