

FEASIBILITY OF INDUSTRIALIZING THE CONVERSION OF CO₂ AND EPOXIDES INTO POLYMER PRODUCTS



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ABBREVIATIONS

CAGR = compound annual growth rate

CB = conjugated backbone

CDCF = cumulative discounted cash flow

CHO = cyclohexene oxide

Mn = number-average molecule weight

n.m. = not measured

NCB = non-conjugated backbone

NPV = net present value

OP = oxygen permeability

OTR = oxygen transfer rate

PBP = payback period

PC = propylene carbonate

PCHC = poly(cyclohexene carbonate)

PDI = polydispersity index

PFD = process flow diagram

PO = propylene oxide

PPC = poly(propylene carbonate)

ROR = rate of return

Td = decomposition temperature

Tg = glass transition temperature

TOF PO = turnover over frequency propylene oxide

TS = tensile strength

WU = Water uptake

WVTR = Water vapor transfer rate

INTRODUCTION

The majority of the polymers produced in the current plastic industry are produced from petroleum. Since petroleum is a non-renewable feedstock, there is an increasing demand in the development of an alternate method for the production of polymers with renewable feedstock. Carbon dioxide (CO₂) is an inexpensive, bio-renewable resource that has the ability to fulfill this request (Coates, Moore, 2004).

The use of CO₂ is beneficial as it is one of the leading causes of global warming. The sustained rise of CO₂ emissions in the atmosphere has proven to be one of the most important causes of the 'greenhouse' effect (Solomon et al., 2009). Utilization of this alternate method can help to decrease the amount of CO₂. Although this impact will deliver a minor contribution in the preliminary phases after implementation, it is a promising start to find a solution for this problem.

In 1969 Inoue and his colleagues first discovered the possibility of copolymerization of CO₂ and epoxides. As they found out, CO₂ has the ability to link the epoxides together, resulting in an alternating copolymerization of CO₂ and epoxide (Inoue, Koinuma & Tsuruta, 1969) . For an extensive historical background reading these articles is recommended (Darensbourg, Donald J., Holtcamp, 1996, Coates, Moore, 2004, Darensbourg, Donald J., 2007, Sugimoto, Inoue, 2004, Darensbourg, Donald J. et al., 2004, Klaus et al., 2011).

From that point, many advances have been achieved, with selected studies layed out below. Recent studies have discovered different pathways in this copolymerization. Various metals, epoxides and numerous conditions have been used, for the production of a variety of polymers (Darensbourg, Holtcamp, 1996, Coates, Moore, 2004, Darensbourg, 2007, Sugimoto, Inoue, 2004, Darensbourg et al., 2004, Kamphuis, Picchioni & Pescarmona, 2019, Pescarmona, Taherimehr, 2012, Taherimehr, Pescarmona, 2014).

In this report the feasibility of the industrialization of the conversion of CO₂ and epoxides will be discussed utilizing literature studies of various aspects in this venture. The technology itself will be discussed with analysis of the product, the feedstock and the waste. Furthermore, the application, and the market will be analyzed. Finally, a simulation will be used to analyze the economic, and the sustainability aspect of the process.

STAKEHOLDER ANALYSIS

The main stakeholders in this analysis will be the companies considering CO₂ as feedstock for the synthesis of their polymers. Because they consider the use of the application of this technology, they are the only ones with a major financial interest in this review. These companies can also be important as the rise of this technology can give major sustainable benefits for the whole world. The current production and market is small, but several companies are already industrializing this technology and have patented several methods for production, a.o. Novomer, Covestro, and Empower Materials (Sant'Angelo, Chen & McGinnis, 2019, Allen et al., 2011, Müller et al., 2015, Novomer, 2013).

Because there are numerous companies patenting the technology and only a few who are producing this technology, the current timing of entering this market would likely be the early adopters phase (see figure 1).

Early adopters and innovators may find a few advantages by stepping into the market at an early stage. First, because of the perceived technological leadership of the company by its customers, the company creates brand-equity and brand-loyalty. This 'buyer lock-in' is advantageous as customers are likely to stay with a company due to this loyalty, perceived equity and because of switching costs. Other advantages entail early access to limited information, the possibility of patenting the most promising conversion methods and having a head start on the experience curve.

By investing ahead of the majority, however, companies may find challenges such as: less knowledge over the technology when comparing it to the later categories and uncertainty of the success of industrializing the technology (Patterson, 1993, Lieberman, Montgomery, 1988, Kerin, Varadarajan & Peterson, 1992, Frynas, Mellahi & Pigman, 2006).

Other stakeholders include the University of Groningen, and other Universities and companies working on different pathways for the production of the conversion of CO₂ with epoxides. If their technology is patented, they can acquire a financial compensation for their research.

In figure 2 the visualization is seen of the stakeholders of the system. As can be seen, the start-up companies have the same interest as the researchers, but have more power, since they have the financial resources to industrialize the technology, whereas the researchers have not.



Figure 1: Innovation Adoption curve: depicting the categories of timing to enter a new market (Rogers, 2010)



Figure 2: Power/Interest diagram

SYSTEM DESCRIPTION

This report will not consider the entirety of the venture of the industrialization of the technology. Therefore, it is critical to set a clear scope of the report. First, it is important to understand that the reaction of epoxides with CO₂ can deliver cyclic carbonates and polycarbonates. In this report, only the process of the production of polycarbonates will be investigated. Next, because the report will focus on the feasibility of industrializing the chemical process of the conversion of CO₂ with epoxides, the report will mainly consider the final product. This can, however, not be done without including the kind of epoxide and catalyst use, as this will affect the final product. This will also affect the amount of polycarbonate produced, which is important for the economic evaluation of the process. In figure 3 a schematic overview of the system is given with the scope. The Circles in red represent the scope of the research. More in-depth information of the process itself will be given in the system mechanism, but a schematic representation is given in figure 4. Furthermore, the properties of the polycarbonate produced will be an important factor as this product will have to compete with the industrial ‘state-of-the-art’ polycarbonate. At last, the waste stream will be analyzed to determine the sustainability of the process.

In the end, this feasibility report will touch on all the aspects of which knowledge is required to provide a good overview of the industrialization of this technology.

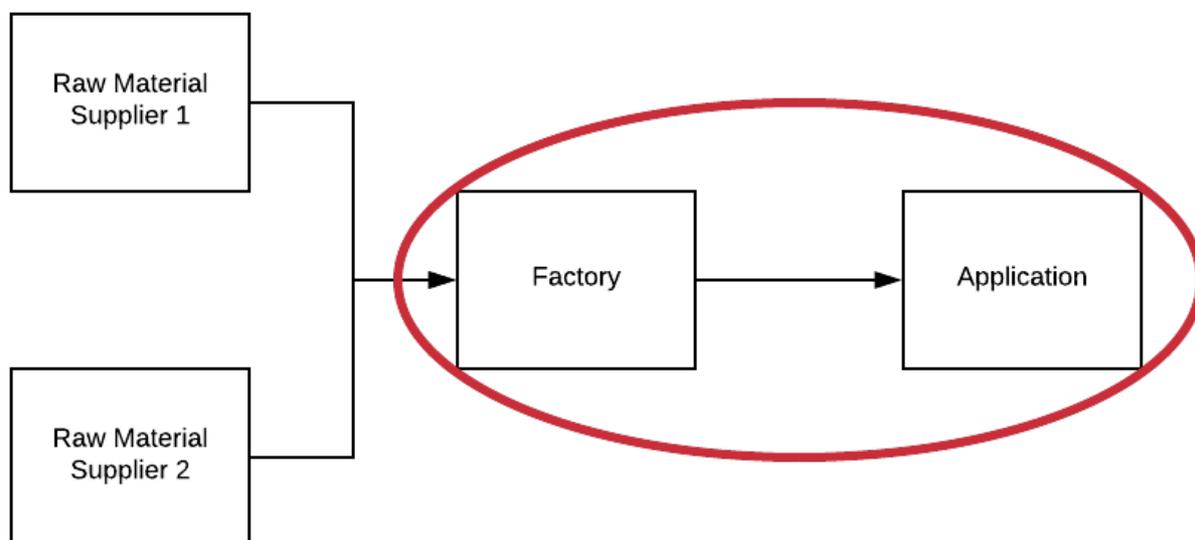


Figure 3: Schematic overview of the System. Red circle represent the scope of the research

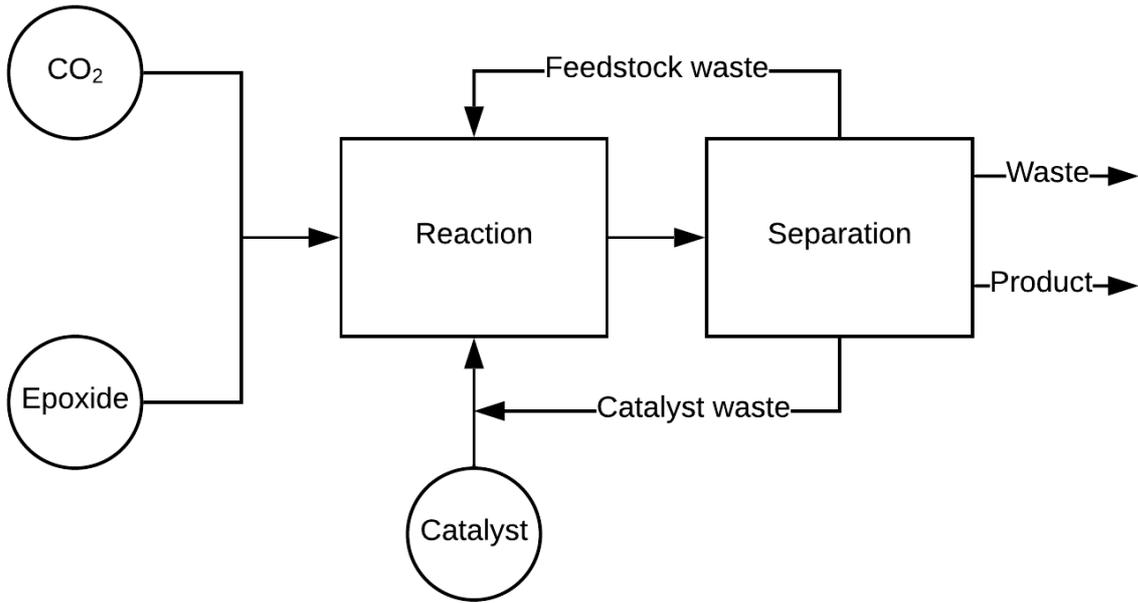


Figure 4: Schematic overview of the process in the factory.

RESEARCH QUESTIONS

The copolymerization of CO₂ with epoxides is a promising technology, but many questions still need to be answered. In this research the main research question is: “Taking into account the technical and financial aspects of copolymerization of CO₂ and epoxides, is it advantageous industrializing this technology, and if so with which feedstock and products will it achieve the most promising results?” This research question will be answered with the help of other sub-questions, which will offer more insight into the matter.

- What is the underlying mechanism? This research question will help with the observation of the various techniques and mechanisms applied in this technology. Through this analysis different pathways can be reviewed for their potential in industrialization.
- Which methods offer the most promising polymer yield considering different catalysts? Through answering this research question various catalysts will be reviewed.
- What is the sustainability gain by using CO₂ as feedstock? This offers an insight in the potential sustainable impact it can deliver by using a ‘greenhouse gas’ as feedstock. If this technology has the potential of considerably reducing the greenhouse effect, this might be a technology worth subsidizing.
- What are the product specifications? Using different feedstock and pathways will result in different product specifications. If this technology wants to be industrialized, the product must compete with the industrial state-of-the-art polymers. This means the specifications of the end-products must have similar properties to polymers produced via the ‘normal’ pathway.
- What are the expected profits and costs when industrializing this production process? Companies will merely have interest in investing in a technology if the production is profitable. Giving an estimation of the costs and profits will help in the assessment of the financial part of the main research question.
- What are applications for the products produced via the copolymerization of CO₂ with epoxides? This research question will give insight in the various markets the end-product will compete in. This is important because applications make the product useful and therefore give reason to produce the end-product.

PROCESS DESCRIPTION

The reaction between the epoxides and the CO₂ can produce two products: cyclic carbonates or polycarbonates as seen in figure 6. In the copolymerization CO₂ has a coupling role, coupling the monomeric epoxide units, thereby producing a polymeric product. This production, however, requires a catalyst to obtain the selective production of polycarbonates with a high yield. The catalyst also allows for polymerization under relatively milder conditions (Taherimehr, Pescarmona, 2014).

The main mechanism for the conversion of CO₂ to polymers is given in figure 6. In the first step the Lewis acid activates the epoxide ring. This leads to the addition of a nucleotide by the Lewis base. Through this attack the ring opens. At this point the CO₂ reacts with the alkoxide intermediate to produce a carbonate intermediate. From point 3 it can go through two pathways: the production of a cycling carbonate or a polycarbonate. If the ring is closed, the product will lead to a cyclic carbonate, but if the molecule undergoes polymerization, alternating between more epoxides and CO₂, it becomes a polycarbonate (Kamphuis, Picchioni & Pescarmona, 2019).

Researches in this field also have focused on the use of homogeneous and heterogeneous catalysts to increase the selectivity to the polycarbonate or the cyclic carbonates. This research will not cover these topics, but for further reading into this topic and more in-depth review of the process, these papers are recommended (Kamphuis, Picchioni & Pescarmona, 2019, Taherimehr, Pescarmona, 2014). In addition, two popular polymeric products are displayed in figure 5, from which PPC is the most researched one.

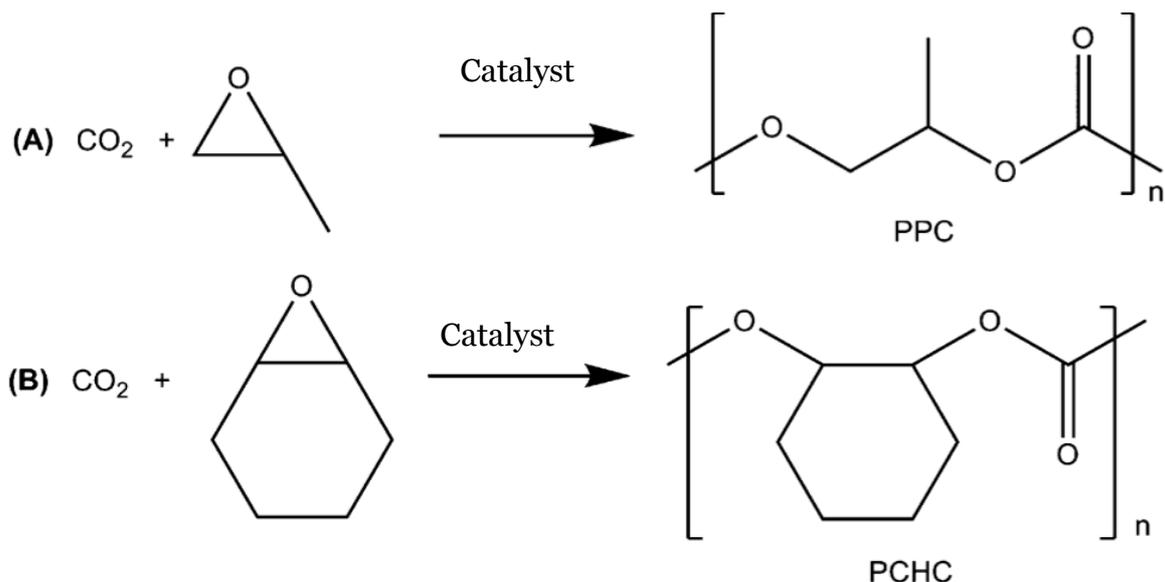


Figure 5: Copolymerization of propylene oxide (PO) and cyclohexene oxide (CHO) to industrially potentially polymers polypropylenecarbonate (PPC) and poly(cyclohexene carbonate) (PCHC) (Klaus et al., 2011)

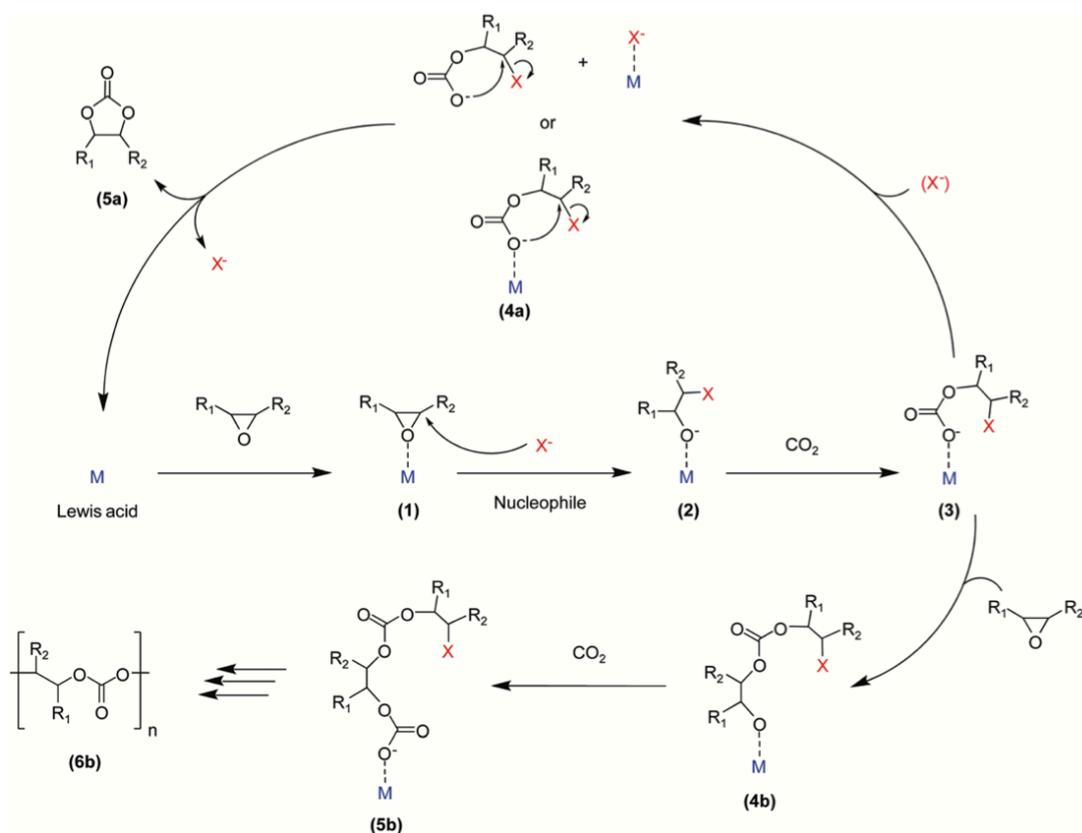


Figure 6: Proposed mechanism for the production of cyclic carbonates and polycarbonates using Lewis acid and a Nucleophile (Kamphuis, Picchioni & Pescarmona, 2019)

CATALYST SELECTION

The selection of a catalyst can be very important as the catalyst determines the selectivity, operating conditions, stability and costs of the process. The variety of catalysts that can be used for this process is enormous. Because this feasibility review will focus on the production of polycarbonates, the analysis of catalysts will only be done on the catalysts which have a selectivity towards polycarbonates instead of cyclic carbonates.

The first distinction of a catalyst can be made on the basis of the phase it is in. This can be defined in two categories: homogenous catalysts and heterogenous catalysts. The distinction of the two is very simple. 'Homo' means same, which is why these catalysts are in the same phase as where the process takes place. In this case the reaction takes place in the liquid phase, so the homogenous catalysts are in liquid or dissolved form. This form of catalysts is studied mostly in respect to this topic. The catalysts which are mostly used are metallic-homogenous catalysts where the metal center acts as the Lewis acid site as can be seen in the proposed mechanism in figure 6. This can be with one metal, but a bimetallic pathway is also proposed in various studies. Non-metallic pathways have been studied as well, but are more likely to have a selectivity towards cyclic carbonates (Kamphuis, Picchioni & Pescarmona, 2019).

Besides homogenous catalysts, there has been an increasing focus on heterogenous catalysts. This means that the catalysts is in a different phase as the reacting phase, usually a solid phase. This can give both economically and sustainable benefits as recycling this type of catalyst is much easier (Farnetti, Di Monte & Kašpar, 2009).

Because of the extensive selection of catalysts, it is out of the scope of the project to compare them all. For a more detailed overview of different catalysts, it is recommended to read these articles (Trott, Saini & Williams, 2016a, Kember, Buchard & Williams, 2011a, Pescarmona, Taherimehr, 2012). The scope in this project, however, will be limited to salen complexes containing Chromium (III) and zinc glutarate. These catalysts are chosen because of their outstanding performance in their category (Darensbourg, 2007, Kember, Buchard & Williams, 2011b) and because a comparison can be made between homogenous and heterogenous catalysts. In addition the process analysis will also be based on a salen complex with Chromium (III) (Demirel, 2015). Therefore it is in the interest of this research to limit the scope to these two catalysts.

In table 1 the properties of the selected catalysts are displayed. The catalysts were measured on their reaction time, operating conditions (pressure and temperature), selectivity, production, number-average molecule weight (M_n), and their Polydispersity index (PDI). Additionally, a visualization of the homogenous catalyst is given in figure 7.

Catalyst	time (h)	temperature (°C)	pressure (MPa)	Selectivity PPC: PC	Conversion (%)	TOF PO (h ⁻¹)	Mn (g/mol)	PDI (Mw/Mn)
Zn-glutarate	40	50	5,23	96:4*	90*	3,4	26580* ^a	9,1* ^a
Salen	4	75	1,3	62:38	68	256	13400	1,69
Cr(iii) CB	4	75	1,3	82:18	50	188	15800	1,89
Salen	4	75	3,5	71:29	60	226	16700	1,38
Cr(iii) CB	4	75	1,3	18:82	64,5	243	10100	1,36
Salen	4	75	1,3	18:82	64,5	243	10100	1,36
Cr(iii) NCB								

Table 1: Properties of selected catalysts. CB: Conjugated backbone. NCB: Non-conjugated backbone. TOF: Turnover frequency. *This data was found under 60 °C and 5MPa. ^aMeasured after 2,5 hours. (Chisholm, Navarro-Llobet & Zhou, 2002, Eberhardt, Allmendinger & Rieger, 2003, Allen et al., 2002).

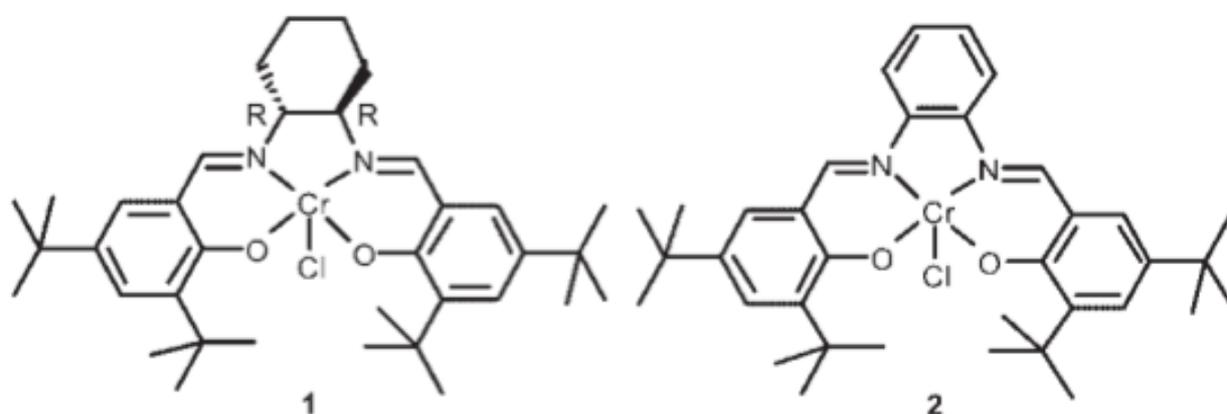


Figure 7: Chromium (III) Salen Complex with non-conjugated backbone (1) and conjugated backbone (2)(Eberhardt, Allmendinger & Rieger, 2003)

PRODUCT SPECIFICATION

To be competitive in the polymer market, the end-product must compete with the state of the-art industrial polymers. Therefore it is important to define the competition of the CO₂-produced polymers. The seemingly obvious choice is that the renewable based polycarbonates could replace the non-renewable based polycarbonates. Therefore, the first focus will be on the state of the art polycarbonates. As for this moment the majority of industrially produced polycarbonates are produced with bisphenol-A. This product is produced with the non-renewable feedstock petroleum. The bisphenol-A polycarbonate is seen as a high-quality polycarbonate because of its mechanical and thermal properties. To compare a polycarbonate to bisphenol-A, it is thus important to define the parameters which make bisphenol-A a high-end polycarbonate. In table 1 an overview is given of selected polycarbonates with their mechanical and thermal properties.

The parameters which are used for the analysis are the glass transition temperature (T_g), the decomposition temperature (T_d), Tensile modulus, Tensile strength, elongation at break, impact strength, and transparency.

The glass transition temperature is a transition temperature at which amorphous materials change from a relative hard and glassy state towards a rubbery state (Angell et al., 2000). This thermal property is important as it determines the range of applications the material is capable of. For example, a glove needs to have a low glass transition temperature to function, otherwise it would hinder the movement of the hand.

The decomposition temperature is the temperature at which a material starts to decompose. In most cases this entails that eliminations and rearrangements in the molecule take place, changing its behavior and/or structure (Anonymous, 2005). This means that the operating conditions of the polymer must be far below this characteristic temperature to be able to perform.

The value of the tensile modulus (also known as Young's modulus) describes its behavior with respect to its resistance towards elastic deformation. Elastic deformation occurs when a force is applied to an object, which causes its shape to change, but changes back in place when the force is removed. A higher tensile modulus means a higher resistance towards elastic deformation. This is an important characteristic as different applications, require different elastic behaviors. For example, the automotive industry requires high resistance towards elastic deformation, because a car needs to be stiff to be able to perform (Askeland, Fulay, 2005).

Tensile strength is the value representing the amount of stress that can be applied to the material before it breaks (Askeland, Fulay, 2005). In many applications this value

is important. For example if a rope swing was made out of plastic which had a low tensile strength the rope would break if it was used.

Impact strength is the ability of a material to absorb a sudden applied load of force, before breaking (Askeland, Fulay, 2005). In the automotive industry this is very important, because of car safety in case of accidents.

The elongation at break is the percentage the material is stretched before it breaks. Elongation at break and the tensile modulus are linked with each other, as the less a material can be stretched, the fewer it can be elongated.

<i>Polycarbonates</i>	<i>Mn</i> (kg/mol)	<i>Tg</i> (°C)	<i>T_{d, initial}</i> (°C)	<i>T_{d50%}</i> (°C)	<i>Tensile modulus</i> (Mpa)	<i>Tensile strength</i> (Mpa)	<i>Elongation at break</i> (%)	<i>Impact strength</i> (J/cm)	<i>Transparency</i> (%)	<i>Reference</i>
<i>Poly(ethylene carbonate)</i>		10	217		3--8		>600			(Thorat et al., 2003)
<i>Poly(propylene carbonate)</i>	7,5	28	235		212	9	8			(Thorat et al., 2003)
		38			1353	14,7	203,1	7,27		(Hsu, Tan, 2002a)
	69,5	42		252						(Ren et al., 2010)
		25--45	240		700--1400	7--30				(Luinstra, 2008)
<i>Poly(butene carbonate)</i>	180	9		241						(Seong et al., 2009)
<i>Poly(pentene carbonate)</i>	7,5	-4	246							(Thorat et al., 2003)
<i>Poly(hexene carbonate)</i>	9,5	-10	250							(Thorat et al., 2003)
		-15		253						(Seong et al., 2009)
<i>Poly(cyclohexene carbonate)</i>	8	105	282		2460	11,8	0,5			(Thorat et al., 2003)
	63	118		310						(Ren et al., 2010)
		125			2707	29,4	1,3	1,31		(Hsu, Tan, 2002)
<i>Poly(cinyl-cyclohexene carbonate)</i>		107			2110	36,7	1,3	1,02		(Hsu, Tan, 2002)
<i>Poly(limonene carbonate)</i>	53,4	130	250*	265***	950	55	15		94	(Hauenstein et al., 2016)
	3,69	72	226**							(Martín, Kleij, 2016)
	10,6	112								(Pena Carrodeguas et al., 2015)
<i>Poly(limonene oxide carbonate)</i>	11,4	135								(Li, C., Sablong & Koning, 2016)
<i>Poly(indene carbonate)</i>	9,7	138	239	257						(Darensbourg, Donald J., Wilson, 2013)
<i>Bisphenol-A-polycarbonate</i>		149		458	2000--2800	43--51	15--75	9	89	(Stretz, Cassidy & Paul, 1999, Hauenstein, Agarwal & Greiner, 2016, Kember, Buchard & Williams, 2011)

Table 2: Mechanical and thermal properties of selected polycarbonates (Kamphuis, Picchioni & Pescarmona, 2019)

FACTORY PROCESS ANALYSIS

In this section of the report the article of (Demirel, 2015) is discussed. Through personal contact with Demirel additional data was acquired to evaluate the process, this data is shown in the appendix.

Demirel has simulated the process of the conversion of CO₂ with propylene oxide (PO) to propylene carbonate (PC) and poly(propylene carbonate) (PPC). The process uses (salen) CrIII Cl complex as catalyst. Additionally, kinetics from (Darensbourg, Donald J. et al., 2003) were used for kinetics data. This is shown in the equation below:

$$k = k_0 \exp(-E / RT) = 17452614 \exp(-67600.00 / RT)$$

In this equation k_0 represents the pre-exponential factor, E the activation energy, R is the gas constant, and T is the temperature.

In figure 8, the process can be seen, simulated through Aspen®. CO₂ and PO are used as feedstock and enter the process with a mass flow of 6587.6 kg/hr and 8693.7 kg/hr respectively. CO₂ enters with a temperature of 25 °C and a pressure of 1.0135 MPa, which then enters the compressor, indicated by C101, and the temperature exchanger, indicated by E101, where its temperature is increased to 30 °C and its pressure to 5.861 MPa. The PO also enters the stream at 25 °C and is heated towards 30 °C and a pressure of 4.826 MPa, before being dispersed with the catalyst (salen) CrIII Cl in mixer M101 in which the pressure is increased towards 5.861 MPa. The streams then, both, end up in the reactor R101. After the reaction has taken place, the stream first goes to separator, indicated by SEP103, where it is assumed that 90% of the catalyst will be recovered. The other 10% first has to be treated, before re-entering the system with the stream MKUPCT as can be seen in figure 8 below. The stream containing the end-products is indicated by S7 and goes F101 where the stream is flashed at 0.0345 MPa and the majority of the CO₂ and PO is recycled and enters the compressor, indicated by C102, after which it enters the heat exchanger, where the temperature and pressure is adjusted towards the reacting conditions, which are 30 °C and 5.861 MPa, after which it re-enters the reactor R101. The stream containing the products, with minor part CO₂ and PO, is cooled down to 20 °C and its pressure adjusted to 0.101 MPa. After this process, the poly(propylene carbonate) is separated with a stream of 13718.58 kg/hr. The stream containing propylene carbonate and the remaining CO₂ and PO is then separated, where propylene carbonate leaves the system at 789 kg/hr, and the CO₂ and PO is fed back to the compressor C102.

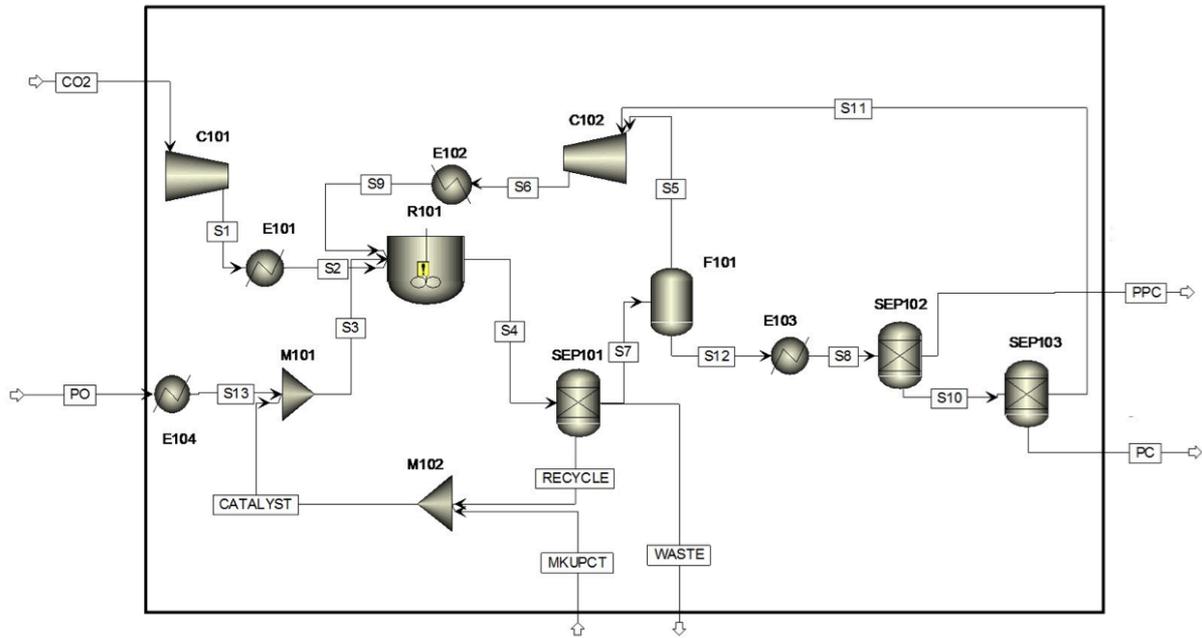


Figure 8: Process Flow Diagram (PFD), whereby PO represents propylene oxide, PPC represents poly(propylene carbonate), and PC represents propylene carbonate (Demirel, 2015).

	CO_2	PO	PC	PPC
Temperature, °C	25	30	25	25
Pressure, MPa	0,101	4,83	0,101	0,101
Vapor Frac	1	0	0	0
Mass Flow, kg/hr	6587,61	8.693,74	789	13709,5
Volume Flow, m^3/hr	3642,7	10.661	669,27	32,596
Enthalpy, GJ/hr	-55,9	-58,9	-4,96	-85,5
Density, kg/m^3	1,81	815,3	1179	420,5
Mass Flow, kg/hr				
CO_2	6587,61		0,0113	
PO		8693,73	0,645	
PPC			6,858	13709,5
PC			781,512	
Mass Fractions				
CO_2	1		15 PPM	
PO		1	817 PPM	
PPC			0.01	1
PC			0.99	

Table 3: Major Streams for the Poly(propylene) Carbonate (PPC) and Propylene carbonate (PC) Productions from Propylene Oxide (PO) and CO_2 (Demirel, 2015)

ECONOMIC ANALYSIS

In this analysis the process of the production plant will be economically evaluated. Demirel, (2015) has provided the data for the economic evaluation of the process which was done through a program called CAPCOST®. In this program an estimate was made of all economic aspects of the process. These aspects include among others fixed capital investment, land, feedstock costs, labor costs, and waste treatment cost. The analysis is done over a period of 10 years, whereby the discounted cash flow diagrams are following the depreciation method of 'Maximum Accelerated Cost Recovery System'. This been done with a 7-year recovery term. Additionally, the selling price of PPC was set to \$2,16/kg, the interest rate was set to 4,5%, and the tax was set to 30%. When these variables are filled in the CAPCOST® program, it gives a table of the cumulative discounted cash flow. The raw data which resulted out of the CAPCOST® program is depicted in Appendix 1.

Using the data of Appendix 1, a cumulative discounted cash flow diagram can be made for each year of production (figure 9). From this diagram it can be seen that the process must run for a minimal of 7 years for the discounted cash flow to become positive.

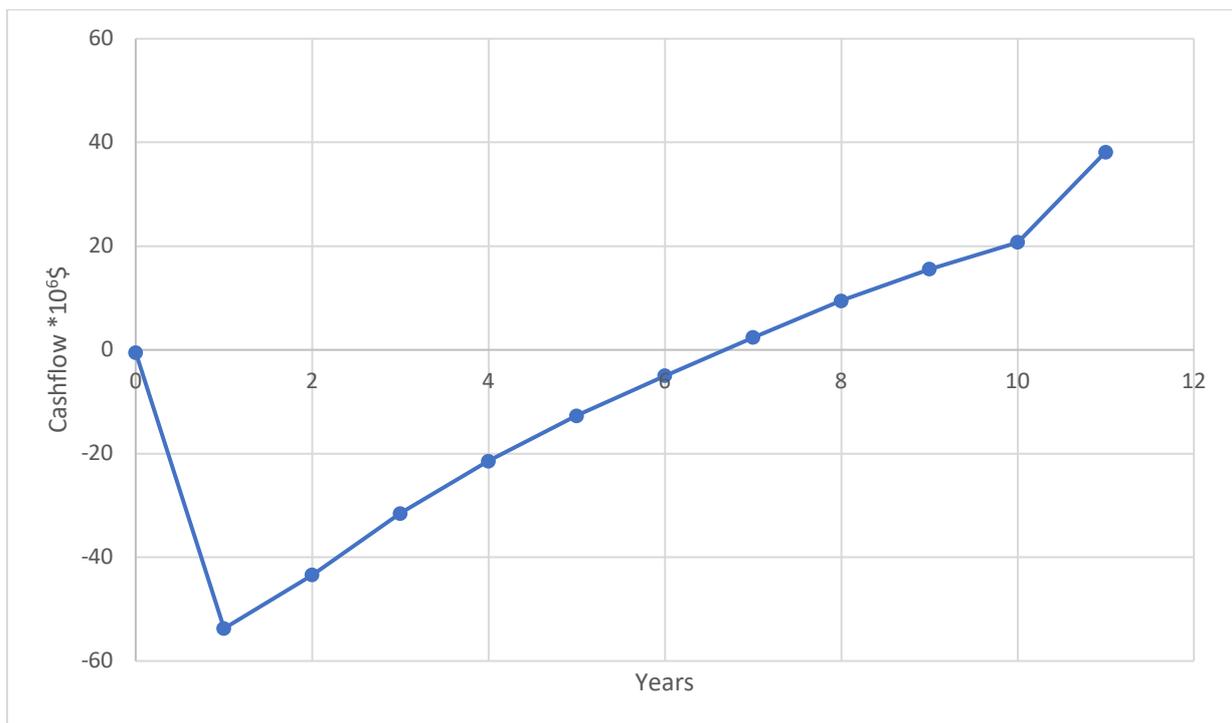


Figure 9: Cumulative Discounted Cash Flow (CDCF) Diagram obtained from the data of Appendix 1.

Additionally, figure 10 was made depicting the rate of return (ROR), the net present value (NPV), and the payback period (PBP) graphed to give a clear depiction of these rates versus the selling price of PPC. The ROR is calculated by subtracting the current value from the initial value, which is then divided by the initial value. This comes down to a net profit or loss over an investment during a period of time (Kenton, 2019b). In addition, the NPV is a value which depicts difference between the present value of cash inflows and the present value of cash outflows over a period of time (Kenton, 2019a). PBP, defined as the time the investment reaches a break-even point, the shorter this value is the better (Kagan, 2019). The values of the graph are taken from the paper of Demirel, (2015). Demirel, (2015) mentions that at least two of these values should be favorable for a process to be economically feasible. For ROR this means a percentage higher than the interest rate of 4,5%, for the NPV this means a positive value, and for PBP this means a value higher than the useful life of operation. This last value is determined by the investor whether he thinks the payback period is short enough.

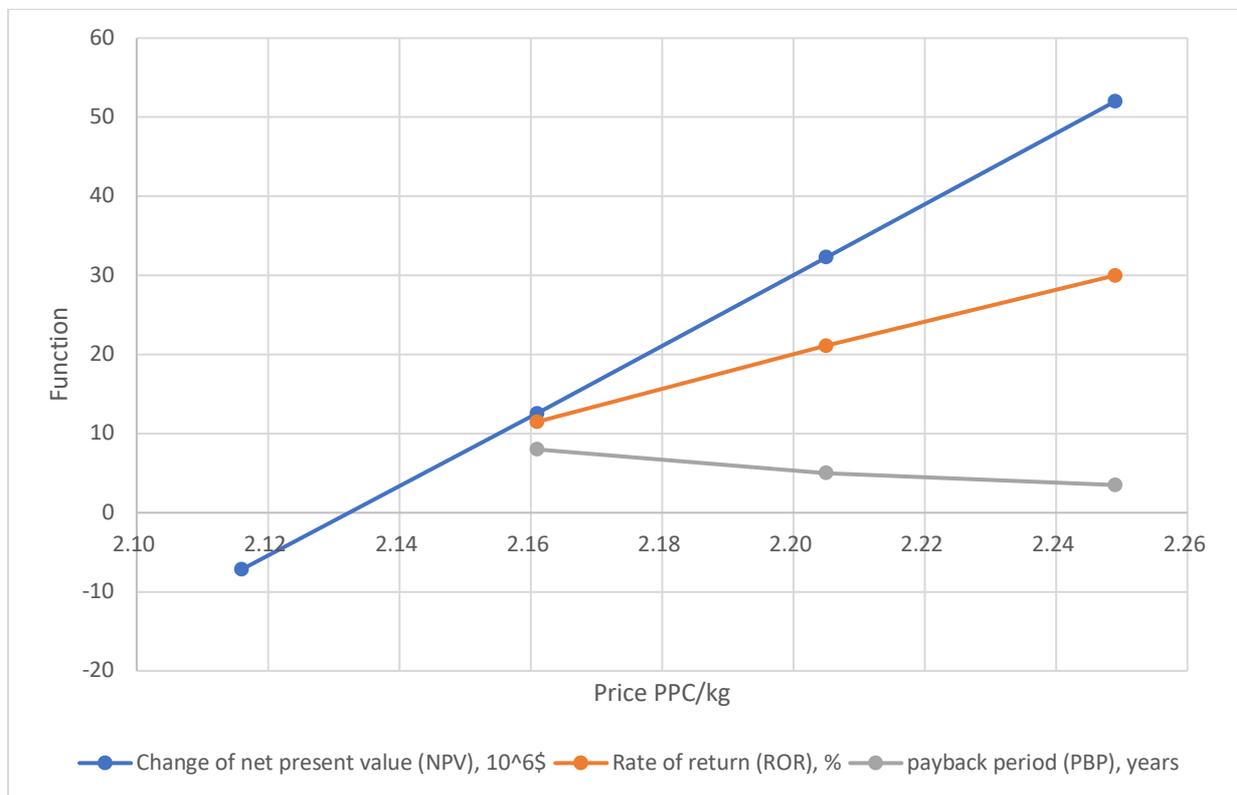


Figure 10: Change of NPV, PBP, and ROR with the price of PPC.

SUSTAINABILITY ANALYSIS OF PROCESS

Sustainability is becoming an important aspect of businesses. Not only for the consumer perceived excellence, but government policies are making it crucial that a company reduces its emissions. In the UK, for example, the policies strive to achieve a 60% decrease in its CO₂ emissions (Clift, 2007). Sustainability is acknowledged as the balance of the economic system, the ecological system, and the societal system. In this research the typology of indicators follows the proposal of Sidkar in considering these dimensions of sustainability. He proposes that sustainability has 3 dimensions (also depicted in figure 11):

- One-dimensional (1D) indicators: These indicators represent the data of only one of the dimensions; these are the economic, ecological, and sociological indicators.
- Two-dimensional (2D) indicators: These indicators represent data which simultaneously comes from 2 of the 3 systems. These are socio-economic, eco-efficiency, and socio-ecological indicators.
- Three-dimensional (3D) indicators: These indicators or sustainability indicators cover all 3 dimensions and is therefore considered the sustainability metric (Sikdar, 2003)

In the paper of Martins et al., (2007) he defines the 3D metrics for any system and proposes a hierarchical framework for these metrics, this is illustrated in figure 12. In his data he has researched the metrics and has defined the 4 3D metrics which can be calculated: material intensity, energy intensity, potential environmental impact, and potential chemical risk. In the research of Demirel, (2015) the assumption was made that there are no toxic material emissions in the process described in the factory. Therefore, this last metric was not taken in the calculation. The results of the calculation of these metrics is shown in table 3. The hierarchical framework of Martins et al., (2007) starts with the definition of the system and the surroundings of the system. All the inputs and outputs that come in and out the system are quantified, this includes the materials that enter the system, but also the gas emissions that leave the system. In step 2 the 3D metrics are calculated. Hereafter, the cost estimation is performed. In the paper of Demirel, (2015) this cost estimation was made with CAPCOST®. In the last step the decisions are made based on the information of the cost analysis and the calculation of the 3D metrics.

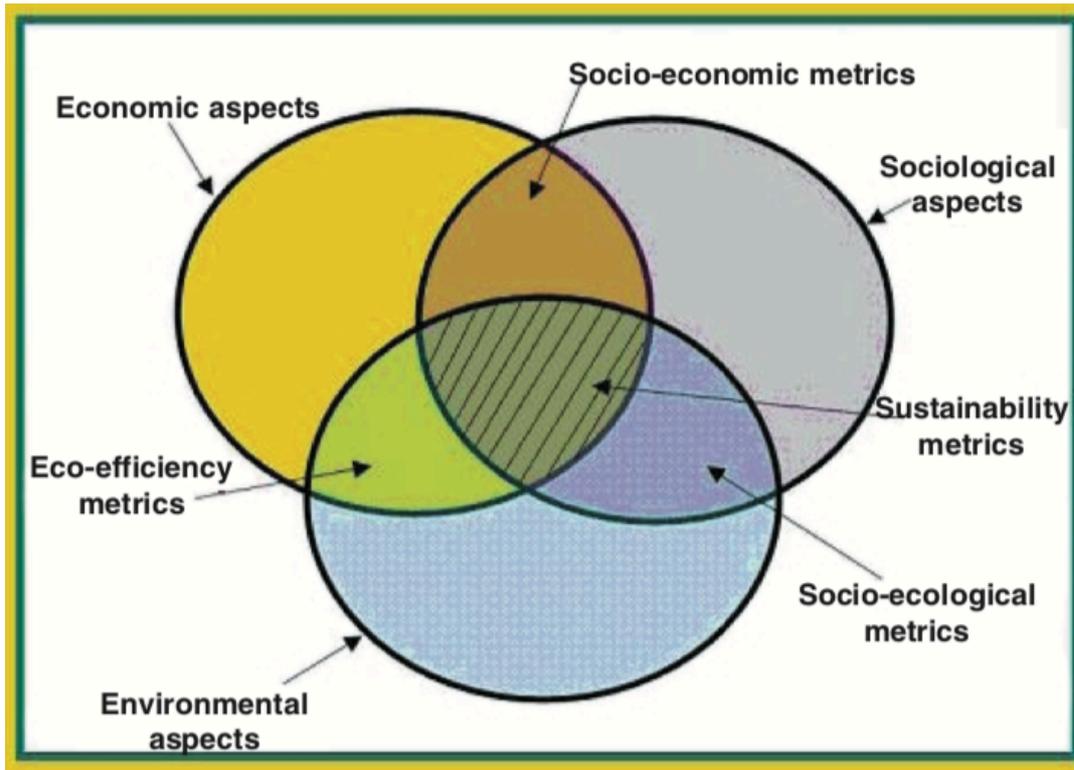


Figure 11: Circles illustrating the 3 dimensions of sustainability (Sikdar, 2003)

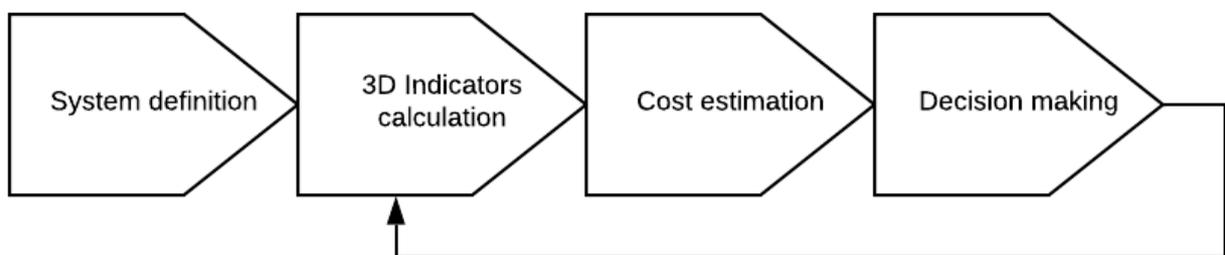


Figure 12: Schematic hierarchical framework for sustainability metrics.

	PPC
Material intensity	
<i>Net stream of PO, kg/hr</i>	8693,73
<i>Mass of product, kg/hr</i>	13709,4665
<i>Net PO/Unit mass of product</i>	0,634
<i>Net PO/Unit mass of (PPC+PC)</i>	0,599
Energy intensity	
<i>Total heating duty, gJ/hr</i>	30,881486
<i>Total cooling duty, gJ/hr</i>	44,3334
<i>Net duty (heating and cooling), gJ/hr</i>	-13,262
<i>Net duty/Unit mass of product, kJ/kg</i>	-953,66
<i>Net duty/Unit mass of (PPC+PC), kJ/kg</i>	-907,14
<i>Total heating cost, \$/hr</i>	231,7
<i>Total cooling cost, \$/hr</i>	9,4
<i>Net cost (heating + cooling), \$/hr</i>	241,1
<i>Net cost/Unit mass of product, \$/kg</i>	0,01759
<i>Net cost/Unit mass of (PPC+PC), \$/kg</i>	0,01663
Environmental impact	
<i>Feed stream CO₂, kg/hr</i>	-6587,6127
<i>Utility CO₂, kg/hr</i>	1892,6595
<i>Net stream CO₂, kg/hr</i>	-4694,953
<i>Net stream CO₂/Unit mass of product</i>	-0,342
<i>Net stream CO₂/Unit mass of PPC+PC</i>	-0,323

Table 4: Sustainability metrics of the production process of PPC (Demirel, 2015)

APPLICATION & MARKET ANALYSIS

With the recent development of new processing technologies and new catalysts the market of CO₂-produced polycarbonates increasing. For example, PPC is a polymer with many industrial advantages for the market. The excellent mechanical properties of the carbonate, along with its biodegradability properties have various potentials. In forecasts the worldwide market is even expected to grow with a compound annual growth rate (CAGR) of 8,8% till 2024. This will come down to a market revenue of 395100 million US\$ in 2024 (360 Market Updates, 2013).

CO₂-produced polycarbonates have the property of being very compatible with a large variety of fibers and fillers. The fiber reinforced polycarbonates, on the other hand, have the great potential of enhancing the thermal and mechanical properties of the material. Furthermore, biodegradable composites are being used in among others the packaging and the medical world (Muthuraj, Mekonnen, 2018). In this part of the report selected applications for the CO₂-produced polymers are investigated.

PACKAGING

In the last few decades most packaging materials have made the transition from glass and metals to plastics. Plastics are more light-weight, are cheaper and have more flexibility when it comes to design. This, however, has given rise to the problem of plastic waste. In 2015 448 million tons of plastic has been produced and 275 million metric tons of waste was produced. From this waste 12,7 million metric tons ended up in the ocean. If no action is undertaken, researchers predict this amount of waste can increase by the magnitude in 2025 (Jambeck et al., 2015). The amount of plastic that is recycled globally is 18%, from the 0% in 1980 (Parker, 2018). So it can be concluded that the awareness and importance of biodegradability of plastic is increasing. To fulfill the requirements of a packaging material, however, a material must fulfill a couple of requirements. These are acceptable mechanical properties, optical transparency, high barrier to water and oxygen, and biodegradability (Reddy et al., 2013). PPC has excellent biodegradability when comparing it to other plastics like polystyrene (see figure 13). Furthermore, the permeability of water and oxygen are a bit lower with polymers which are not biodegradable, such as nylon or polyethylene, but are much higher than the biodegradable PBS or PLA. (Bahramian, Fathi & Dehghani, 2016, Qin, Wang, 2010).

Ease of recycling by type*

- ▲ Easy
- ▲ Manageable
- ▲ Difficult
- ▲ Very difficult

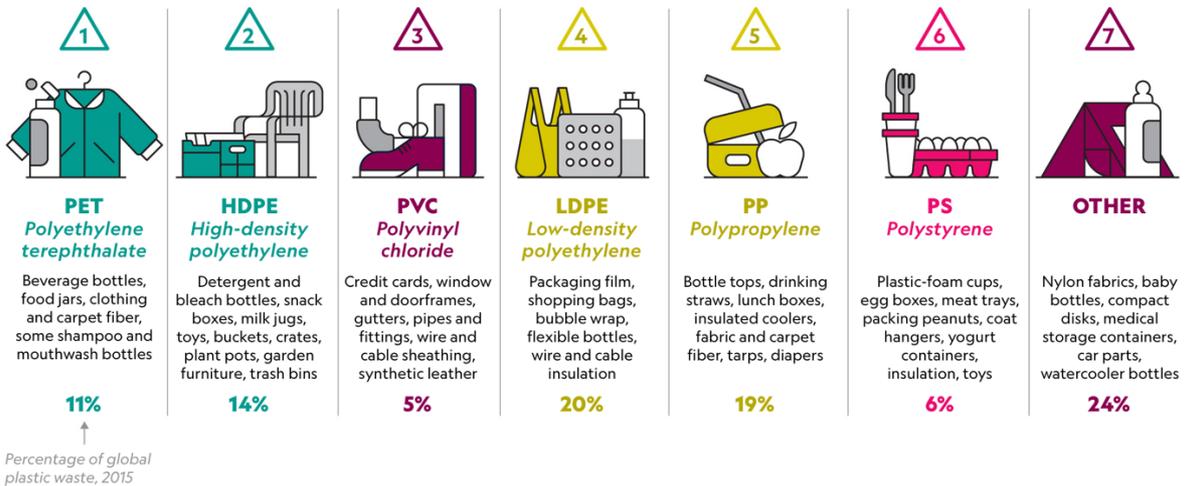
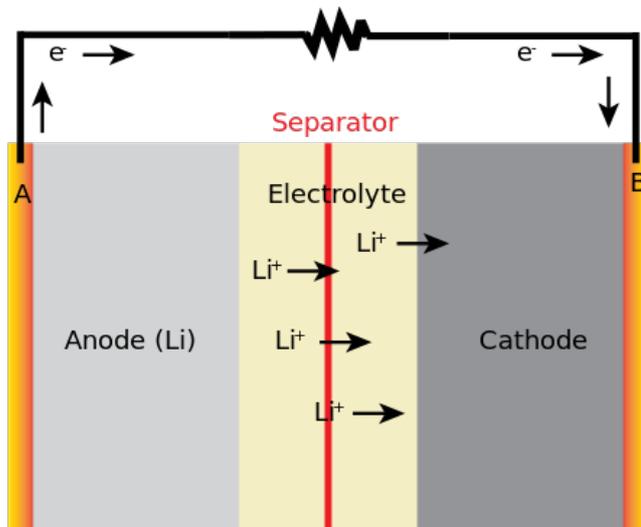


Figure 13: Percentages of global plastic waste per sort plastic, along with its recyclability. (Parker, 2018)

ELECTROLYTE

The fuel cell market is growing. With electric cars now becoming the standard in the industry, the market has never been so big. The fuel cell market is expected to reach a market revenue of \$8,643 million and a CAGR of 17,36% (Prasad, 2016). An electrolyte is a component in a battery or a fuel cell which is used as a barrier between the terminals, to allow positively charged ions to travel from a positive to a negative terminal which frees negatively charged electrons which then power the device in question (Larminie, Dicks & McDonald, 2003). In figure 14 a schematic representation of a battery cell is presented, where it can be seen that the electrolyte is the barrier between the anode and the cathode. There have been various researches on the application of CO₂-based polycarbonates as electrolytes, which will be outlayed more in depth in the discussion. In the beginning only liquid electrolytes were used, which are bulky, non-design friendly and can present risk for fire and explosions if they get punctured (University of pennsylvania, 2018). Polymeric Solid electrolytes show great potential as they show high mechanical strength and dimensional strength when comparing it to liquid electrolytes (Xu, K., 2004). This means that they can be manufactured in a far more shapes and forms. Secondly, by using non-flammable polymers, the chance of explosion is also lowered (Xu, 2004).



A/B: Current collectors; negative (A), positive (B)

Figure 14: Schematic representation of a battery cell.

OTHER APPLICATIONS

CO₂-based polycarbonates have also seen applications in polyurethane, biomedical applications, electromagnetic shielding, coatings, or adhesives. These applications can be read in depth further in these articles, but are not within the scope of this research (Muthuraj, Mekonnen, 2018, Kamphuis, Picchioni & Pescarmona, 2019).

DISCUSSION

In this part of the report the data acquired from the literature will be discussed. The parts that will be discussed are: the catalyst selection, product specification, factory process analysis, economic analysis, sustainability analysis, and the market analysis.

CATALYST SELECTION

In the catalyst selection, the heterogenous catalyst zinc glutarate and the homogenous catalyst (salen) CrIII Cl complex are compared with respect to their reaction time, operating conditions (:pressure and temperature), selectivity, conversion percentage, production, number-average molecule weight (M_n), and their Polydispersity index.

The conversion rate of PO is higher with zinc glutarate than with the (salen) CrIII Cl complex (90 vs 61 avg.). This conversion percentage was measured of zinc glutarate after 40 hours and of (salen) CrIII Cl complex after 4 hours. This means that they cannot be compared as the conversion percentage is a function of time. It is mentioned in the article of Chrisholm (2002) that a conversion rate of 70 percent was already shown in the first 5 – 10 hours. This is relatively similar to that of CrIII Cl. To make these values comparable, the experiment should be done in the same conditions, comparing it after the same amount of time.

The results in the experiments, shown in table 1, show that zinc glutarate, the heterogenous catalyst, achieved a TOF of 3,4 in 40 hours. When comparing these values against the (salen) CrIII Cl complex values, which has an average TOF of 228, it can immediately be noticed that the specific activity of the (salen) CrIII Cl complex centre is much higher in only 1/10 of the time it took for the zinc glutarate complex to come to 3,4. This shows that the homogeneous catalyst does achieve a considerably higher functionality when compared to the heterogenous catalyst.

Next, the M_n of zinc glutarate shows a relatively a higher value than that of the (salen) CrIII Cl complex (26580 vs 14000 avg.). This means that the average weight of a PPC molecule with zinc glutarate is about 2 times as large as a molecule produced with a (salen) CrIII Cl complex. A greater weight indicates a higher level of polymerization. This value has a direct relation to the brittleness of the polymer. Often, low molecular weight additives are added to decrease the brittleness of the polymer for products like inflatable beach toys. Here, the M_n gives a relatively good insight in the quality of the product (Cazes, 1989). This means that the brittleness of PPC created with zinc glutarate will be higher than with (salen) CrIII Cl complex. Because high polymerization is often preferred, because this means higher melting temperatures and mechanical properties, the values of the zinc glutarate are preferred (Kim, S., Jang, 2013, Flory, Vrij, 1963).

Although the separation of the catalysts is harder and more expensive than heterogeneous catalysts (Farnetti, Di Monte & Kašpar, 2009), it has been shown that salen complexes have achieved high recovery rates in other systems. In the system of

the conversion of epoxides and CO₂, the recovery rate is not mentioned in detail, therefore the analysis will evaluate the recovery rate of the salen complex in other systems. In the factory analysis Demirel (2015) assumed that the recovery rate of the salen complex was 90% for immediate re-use. The other 10% was also extracted, but was washed before re-entering the system. This comes down to a recovery rate of 100% with additional washing steps. To analyze these assumptions, salen complex recovery rates and cycle rates were examined from other systems. For example, with conventional continuous liquid-liquid extraction catalyst recovery rates from up to 86% (Baleizao, Garcia, 2006). With polyelectrolyte a recovery rate of 93% of a homogeneous catalyst was even found, however this article of 2003 also mentions that the techniques used in that particular research are not ready for commercialization e.g. due to their loss of functionality (Cole-Hamilton, 2003). In the paper of Mercer, he, however, shows a new method of homogeneous catalyst recovery with a significant loss of functionality only after the fourth cycle. On the fourth cycle a conversion 97% was still found, resulting in a decrease of 2% when comparing it to the first cycle (Mercer et al., 2012). These values raise doubts over the validity of the assumption of Demirel (2015). Although the systems where the salen complex operates in is not the same as the system of Demirel (2015), the numbers do show such divergent values that the assumption seems doubtful. More research of this catalyst in terms of recovery rates must be done to come to real conclusions.

PRODUCT SPECIFICATION

In the product specification the properties of selected polycarbonates are given in table 1 with additional properties from the state-of-the-art industrial polycarbonate: Bisphenol-A.

As can be seen in table 1 there are, for mechanical strength, 3 important parameters: tensile modulus, tensile strength, and impact strength. Bisphenol-A shows the highest value in this category with a modulus of up to 2800 MPa, followed by Poly(cyclohexene carbonate) with a modulus of 2707 MPa, Poly(cinyl-cyclohexene carbonate) with a modulus of 2110 MPa, and Poly(propylene carbonate) with a modulus of up to 1400 Mpa.

It is notable that the highest tensile strength is not from bisphenol-A, which has a tensile strength of 51 MPa, but from Poly(limonene carbonate), which has a tensile strength of 55 MPa. Here bisphenol A shows the highest value, of 9 J/cm. Values for many of the other polycarbonates are not available, so further research must be done to make any evident conclusions of this section.

Another parameter worth mentioning is the transparency of the material. Since this parameter can be very important in applications, where people want to look through things it is noticeable that poly(limonene carbonate) has a higher transparency than bisphenol A (94% versus 89% respectively)

For characteristic temperatures such as glass transition temperature, bisphenol A has the highest Tg of all the polycarbonates with a Tg of 149°C. This makes bisphenol-A highly suited for circumstances in which hard, glass like plastics are needed. The polycarbonates which come the closest to temperature resistance are the poly(limonene carbonate), the poly(limonene oxide carbonate), and the poly(indene carbonate) with Tg's of up to 130°C, 135°C, and 138°C respectively (see table 1). These carbonates have great promise to fulfill the properties of Bisphenol-A polycarbonates, but the mechanical strength of poly(limonene oxide carbonate) and poly(indene carbonate) has not yet been tested, and can therefore not be appointed as the replacement polycarbonate (Kamphuis, Picchioni & Pescarmona, 2019). However, it is a polycarbonate worth looking into, when more research has been done. The other polycarbonates, including poly(propylene carbonate) have much lower glass transition temperatures. This means that they behave more like rubbers at operating temperatures. This is a less desired property in the polycarbonate industries, such as electronics and automotive industries, which require harder plastics, making the majority of the CO₂-produced polycarbonates not suited as engineering plastics in those circumstances (Fukuoka et al., 2003). Because the Tg of the other polycarbonates is at room/body temperature their application narrowed, because to be applied as film, the Tg must have a much lower value, but for the use as containers a higher Tg is more favorable. This makes their application and competition more narrowed (Luinstra, Borhardt, 2011). Muthuraj et al. (2018) addresses this issue and made an analysis of applications for the CO₂-produced polycarbonate: poly(propylene carbonate). There the main solution to the problem is combining the plastic with other

plastics or reinforce it through several techniques to make it ready for application. This means, however, that comparison with other plastics in its industry will not say anything as these parameters will be altered through these modifications for the application of the plastic. Therefore, the comparison will not be made with plastics used in the industries CO₂-polymers are competing in. The application and market of the polycarbonates is explored further in the market and application analysis.

The degradation temperature of bisphenol-A is superior in comparison to the CO₂-engineered plastics. This degradation temperature is important in the industry bisphenol-A is used for, as engineering plastics used in construction are often exposed to high temperatures. In contrast, plastics used in, for example, packaging are not exposed to high temperatures above the 200 °C.

As mentioned in the paragraph above, polycarbonates can be altered by a variety of strategies. Because of some unusual properties, such as its T_g, these strategies are needed to compete in other markets. Kamphuis et al. (2019) mentions 5 strategies to do so. Because of the CO₂ as feedstock and the excellent biodegradability specifications (Luinstra, Borchardt, 2011), the CO₂-produced polycarbonates are very attractive to use in a variety of different ways. Additionally, the CO₂-produced carbonates can help with mechanical stability in a.o. polyurethane foams (Langanke et al., 2014). Firstly, terpolymerization can be used. This entails a strategy where a third monomer can be applied to the process. This can be a caprolactone, an anhydride or another epoxide. More information about this strategy can be found in these researches (Liu et al., 2006, Xu, Y. et al., 2018, Koning et al., 2013, Scharfenberg, Hilf & Frey, 2018a). Secondly, block-copolymerization can be applied. This strategy entails the subsequent growth of a polymer composed of blocks, of which one of those blocks is the copolymerization of CO₂ with epoxides. More information about this strategy can be found in these researches (Li, Y. et al., 2015, Hsu, Tan, 2002b, Kim, J. G. et al., 2011, Aida, Inoue, 1982).

Thirdly, post-polymerization modification can be applied. This is a strategy whereby at the end of the polymerization, the functional groups are modified. This could be helpful if the functional groups were incompatible with the polymer process. This way those groups still can be modified to acquire the desired functionality. Further reading about this strategy can be found in these researches (Gauthier, Gibson & Klok, 2009, Scharfenberg, Hilf & Frey, 2018b, Darensbourg, Donald J., Tsai, 2014).

Fourthly, using functional compounds as chain transfer agents to achieve end-group modification. Further reading about this strategy can be done in these researches (Cyriac et al., 2011a, Willcock, O'Reilly, 2010, Perrier, Takolpuckdee & Mars, 2005, Cyriac et al., 2011b).

Fifthly, blending the polycarbonate with other polymers or inorganic solids. With this strategy there is the possibility to combine polycarbonates from table 1 to acquire the specifications needed. Further reading about this strategy can be done in these articles (Tominaga, Yamazaki, 2014, Zhang et al., 2003).

The application of these blends and adaptations of the CO₂-produced polycarbonates are discussed in the application and market analysis discussion.

Polycarbonates all have different properties. Bisphenol-A still seems to be the polycarbonate with the best specifications for uses with hard-engineering plastics, with a high T_g, tensile modulus, tensile strength, and impact strength. Some recent researchers have found excellent properties for CO₂ produced polycarbonates, such as poly(limonene carbonate), with excellent T_g, tensile strength and tensile modulus. Furthermore, for applications which require amorphous plastics, poly(propylene carbonate) shows excellent mechanical strength. These properties can all be modified by the strategies shown above. In addition, the plastics can also be used in other industries, such as an electrolyte in a battery. Mover these applications in the market and application analysis.

FACTORY PROCESS ANALYSIS

The program in Aspen® uses the kinetic data of (Darensbourg et al., 2003) for the conversion rates of the catalyst and the overall kinetics of the situation. However, this research dates back to 2003. In recent experiments, the salen complex still shows excellent kinetics when compared to other catalysts (Ren et al., 2010, Trott, Saini & Williams, 2016b). Although the chromium salen complex is not an outdated catalyst, using more recent kinetics from Darensbourg would have made it a more up-to-date analysis (Darensbourg, D. J., Yeung, 2015).

Furthermore, the assumption was made in this experiment that the recovery rate was 90%. This 90% flows directly back to the reactor, the 10% is then cleaned and also re-enters the reactor. This comes down to a net loss of 0% of the catalyst. When comparing this to literature studies of similar systems, this seems not achievable (Mercer et al., 2012, Cole-Hamilton, 2003, Baleizao, Garcia, 2006). Furthermore, the 90% continuously re-enters the reactor, whereas shown in recent studies, the functionality of a catalyst does decrease with each cycle of use when a salen catalyst was used in a similar way (Mercer et al., 2012). This means that in reality the analysis should take a loss of catalyst flow in account. Also, the re-use should be taken into account, which is not realistic at this point due to their cleaning operation with only 10% of the catalyst.

Because there are no further detailed process analyses on basis of Aspen®, the process Demirel (2015) cannot be benchmarked with other literature studies. Micro-reactors or more Aspen simulations have to be made to fully benchmark the process of Demirel (2015).

ECONOMIC ANALYSIS

The graphs in the economic analysis are all based on the raw data provided in the Appendix. Discounted cash flow is a valuation method in the economic sector used to estimate the value of an investment based on the future cashflows. Discounted cash flow determines this value of expected cashflow with a discount rate. This interest rate is mainly based on the principle of time value for money. The discount rate takes the interest earned or paid into account. This can be from a loan or from a bank deposit (Kruschwitz, Löffler, 2006). In the graph in figure 7 for cumulative cashflow it can be seen that the company first has to do a big investment. This can be accounted to the fixed capital investment which is an investment of 54,5 million dollar. This is the lowest annual cumulative cash flow of this entire industry. This can be seen because the cumulative cashflow, does not drop lower than this point. After the first year, the cumulative cashflow begins to rise, even though the cost of manufacturing costs 219 million dollars. This is because the revenue is also made from this year, which comes down to an increase of 10,34 million dollars. One thing that also must be noted is that the book value is dropping each year. This can be explained because the book value is the measure of all company's assets. This also means the manufacturing equipment which depreciate each year. From figure 7 it can also be seen that it takes 7 years to end up with a positive cumulative cashflow.

In figure 8 the PBP, ROR, and the NPV are given as a function of the selling price of PPC. For an investment to be attractive, two out of three of these values should give a favorable value (Demirel, 2015). First, the payback period is given, which is displayed as 8 years. This seems strange as the ADCF is positive after 7 years. Because this value is smaller, it seems that Demirel et al. (2015) made a mistake, since these values should match or PBP should be even smaller; this is because PBP usually does not take value over money into account. For the value to be favorable, the investors have to be satisfied with the waiting time of 7 or 8 years. The rate of return is 11,5% which is well over the interest rate of 4,5%. This means that this rate is favorable. In addition, the NPV is 12,55 which may seem strange because the ADCF is lower, but Demire et al. also adds the book value to this value for NPV. Because the NPV is positive this should also be considered as a favorable value, which makes the investment attractive according to Demirel, (2015).

It should be noted in the end that the cost of manufacturing will end up higher as the use of the catalyst is considered very favorable as mentioned in the factory process analysis.

SUSTAINABILITY ANALYSIS

As can be seen in table 4, the material intensity metric presents a net PO usage per unit mass of PPC of 0,634. This ratio is lowered to even 0,599 when PC is also considered. A higher value means a more efficient process, as the amount of feedstock is divided by the amount of product. This means that more product equals a lower ratio. These values are not given for the researches found in this analysis, so the values will be compared to that of the example process given by (Martins et al., 2007) to give an idea about the sustainability of the process. So if these values are compared to the values measured in the process analyzed by (Martins et al., 2007) it shows a much lower value (0,599 vs. 2,15). This is mainly due to the fact that CO₂ is not taken into the calculation, this was done because CO₂ is considered in the environmental impact analysis and will not be considered as a nonrenewable material in this analysis. The net amount of CO₂ divided by the net amount of PPC and PC equals 0,323, which is also a very low ratio. This does show, however, that the material intensity of PO is higher than that of CO₂. CO₂ values are negative, because normally the CO₂ -waste minus consumption value would be in positive. This is now in the negative, showing that the operation utilizes more CO₂ than it produces. This given has great potential to be subsidized. With this negative value, the plant already will be saving \$81216/year which is normally issued for the carbon tax (Demirel, 2015). The energy intensity of the process has a net duty of -13,262 gJ /hr. This value is below zero because Demire et al. (2015) decided that the net duty should be the heating utilization minus the cooling utilization. This value is taken minus each other, because he likely assumes that the heating stream can heat the cool stream and which thereby is heated. However, in the Aspen® simulation Demire used a heater for this, and a cooler for the cooldown of the streams. This along with the assumption that a net duty of energy is created by the heating and cooling system seems strange, because energy is still needed to cool the process down, since this value of duty is much higher. Compared to the lowest value of the paper of Martins et al (2007), this value is still much lower (10,8 MJ vs. -0,907 MJ). This indicates that the energy intensity of the process is very low or that the process given in the paper of Martins et al. (2007) is very energy intensive, but those conclusions were not made in his paper. The economic analysis of the heating and cooling process comes down to a value below the 2 cents per kg product. Because the selling value of the product is \$2,16, 2 cents for the utility is very low. The process seems to be very sustainable considering the metrics discussed above. Because the process also utilizes CO₂ with a net stream of 4694,953 kg per hour, this process shows big promise as a way to utilize CO₂, and therefore helping with the cause of the 'greenhouse' effect on the earth. The process is also partly self-sufficient, as the process can utilize the CO₂- stream which is now considered as waste.

APPLICATION & MARKET ANALYSIS

The CO₂-engineered plastics have for product specifications mainly 2 especially attractive aspects. First the material uses CO₂ as feedstock. Second the material has very good biodegradability specifications (Luinstra, Borchardt, 2011). The mechanical properties of the material are also relatively high as can be seen in table 2. As mentioned in the application and market analysis, for a packaging material the material needs to have the acceptable mechanical properties, optical transparency, high barrier to water and oxygen, and biodegradability (Reddy et al., 2013). However, the glass transition temperature is also very important. As mentioned by Luinstra, Borchardt, (2011) about PPC, this material has a too low glass transition temperature for an engineering plastic, but a too high value to be used as a rubber. In addition, the degradation temperature of the material is too low to be used in the production of packaging materials such as polyester (PBT; PET) or common polyamides (PA6,6, PA6) (Luinstra, Borchardt, 2011). The material does, however, show better barrier properties when comparing it to polyethylene (Paszkievicz et al., 2015). Several papers have shown to increase the barrier properties, mechanical properties and the thermal properties. In table 5, the properties of selected composites have been laid out.

Seo et al., (2011) uses PPC along with nanocomposites consisting of zinc oxide. He investigates the composites as a function of the percentage of ZnO and prepared the composites via the solution-blending method. PPC/ZnO composites with 0, 1, 3, 5, and 10% of ZnO were investigated.

For optical properties, the increase of ZnO, had a relationship with the absorption of 200-370 nm. A higher content of ZnO was equal to a higher absorption of that particular wavelength. It was thus concluded that ZnO improves the weather ability of PPC, with potential marketing applications such as cosmetics or coatings. As for thermal properties, first it was found that the thermal degradation of the composites was different from the pure PPC. Whereas PPC first encounters a random main chain scission, followed by unzipping, the composites degraded in one step. Furthermore, a decrease in the thermal stability was found, which may be the result of morphological imperfections, because the ZnO nanoparticles on themselves have a higher thermal stability than PPC (Seo et al., 2011).

Next, water uptake, oxygen transmission, and the diffusion coefficient were investigated for the different composites. Here it was found that the water uptake, oxygen transmission, and the diffusion coefficient rates dropped until the percentage of 5% ZnO, after which these rates increased.

The antibacterial activity was also tested in this paper and it increased with the increase of ZnO. It was found that PPC on itself had no antibacterial activity against both *E. coli* and *Lactobacillus*, with a decrease of bacterial cell activity of 100% and 87,5% respectively.

In the research of Zhai et al., (2015), composites of PPC with aluminum flakes (ALF) of 3,5 μm are investigated. Composites of PPC/ALF with 0, 1, 3, 5, 7% of ALF were tested and were prepared via the melt-blending method (Zhai et al., 2015). The tensile strength increases as the amount of ALF increases. This is expected as the tensile strength of ALF is much higher than PPC (Zhai et al., 2015). Furthermore, the glass transition temperature of the composite increases with the increase of ALF. This is different from the research of Seo et al., (2011), where was mentioned that there was a decrease in thermal stability. This raises the question if the blending method of melt-blending method give better morphological results than the solution-blending method or that the size of the composite flakes are more important (Zhai et al., 2015).

The barrier properties of the composite become better as the ALF increases until the percentage of 5% is reached. The composites containing 7% ALF see a big decrease in its barrier properties, which are even worse than the 1% ALF. This phenomenon is probably due to the cracks that begin to form at the interface between the matrix with 7% ALF and the aggregation of ALF (Zhai et al., 2015).

In the report of Lee et al., (2013), the composites of PPC with exfoliated graphite (EFG) particles are researched. The particles had an average size of 7.4 μm and a thickness of 30–50 nm. The composites were prepared via the solution blending method. The tensile strength of the composite increases until the EFG reaches 2%, after which it rapidly decreases. Lee et al., (2013) reasons that this is probably due to the dispersion of the graphite particles. The glass transition temperature increased as the EFG percentage increased, as was expected. The barrier properties also improve as the percentage of EFG increases.

In the study of Jiang et al., (2017), 8 grams of PEG was dissolved in deionized water, after which CNC's were added of 0, 1, 3, 5, and 7 wt% CNC. Hereafter the PEG/CNC powder was mixed with the PPC powder with a ratio of 10:90 respectively. Lastly, the mixed powders were compression molded. The tensile strength was increased after pure PEG was added. The tensile strength improved further after an increase of CNC. It was also mentioned that an increase in the storage modulus was found. The Tg was first decreased when pure PEG was added to PPC. This is because PEG has a Tg of -60°C. The increase of CNC resulted in an increase in the Tg, although the changes in Tg were minimal. It must be noted that the measurements seem to be very random. The values go up and down, and an associated relationship for these fluctuations cannot be found. The oxygen permeability was found to drop up to 95%, which shows great promise in that regard.

The kind of packaging they would be competing the most would be PET, because of its most similar thermal properties (Jiang et al., 2017). PET has a glass transition temperature of 80°C, and a Tm of 250°C, which is similar to certain PPC blends. Furthermore, its mechanical properties are superior to the PPC blend, but the barrier properties of certain blends of PPC were found to better than pure PET (see table 5)

(Jiang et al., 2017, Cheremisinoff, 2001). This means that PET has very similar properties, with slightly better mechanical properties, but slightly less oxygen permeability properties. Additionally, the specifications of PLA are given in table 5, since this is the most used biodegradable food packaging, with which PPC directly competes. PLA shows very similar mechanical properties, and shows slightly better barrier properties.

Sample	thickness (μm)	WVTR ($\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$)	WU (wt %)	OP ($\text{ml}\cdot\text{mm}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$)	OTR ($\text{mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$)	TS (Mpa)	Tg ($^{\circ}\text{C}$)
PPC	18	n.m.	2,01	n.m.	554	n.m.	n.m.
PPC/ZnO 1%	18	n.m.	1,34	n.m.	272	n.m.	n.m.
PPC/ZnO 3%	20	n.m.	0,94	n.m.	296	n.m.	n.m.
PPC/ZnO 5%	19	n.m.	0,62	n.m.	145	n.m.	n.m.
PPC/ZnO 10%	22	n.m.	0,65	n.m.	140	n.m.	n.m.
PPC	485	4,6	n.m.	2,25	4,6	12,2	31,8
PPC/ALF 1%	510	2,6	n.m.	1,31	2	14,2	31,9
PPC/ALF 3%	574	1,9	n.m.	1,1	1,9	14,3	32,5
PPC/ALF 5%	563	1,3	n.m.	0,73	1,3	17,4	33,5
PPC/ALF 7%	559	3,2	n.m.	1,82	3,2	20,7	34,4
PPC	30	24,8	10,6	n.m.	93,4	17,4	48,3
PPC/EFG 0,5%	30	21,1	4,9	n.m.	74,8	23,9	49,6
PPC/EFG 1%	30	21,2	3,6	n.m.	74,1	27,6	49,9
PPC/EFG 2%	30	21,1	3,3	n.m.	62,9	34,8	50,7
PPC/EFG 3%	30	20,7	1,7	n.m.	54	23,2	51,2
PPC/EFG 5%	30	20,4	1	n.m.	51,8	17,2	52,1
PPC	1000	n.m.	n.m.	6,102*	n.m.	8,46	33,3
PPC/PEG	1000	n.m.	n.m.	8,134*	n.m.	10,47	31,4
PPC/PEG/0.1CNC	1000	n.m.	n.m.	4,238*	n.m.	10,91	34,1
PPC/PEG/0.3CNC	1000	n.m.	n.m.	1,457*	n.m.	11,06	31,3
PPC/PEG/0.5CNC	1000	n.m.	n.m.	0,624*	n.m.	11,28	34,6
PPC/PEG/0.7CNC	1000	n.m.	n.m.	0,278*	n.m.	12,61	33
PLA	20	15,3	n.m.	n.m.	56,33	50,5**	62,1
PET	18000	3,48	n.m.	n.m.	9,44	46	80

Table 5: Selected PPC composites used in packaging applications. WVTR: Water vapor transfer rate, WU: Water uptake, OP: Oxygen permeability, OTR: Oxygen transfer rate, TS: Tensile strength, Tg: Glass transition temperature, n.m.: not measured.*These values were measured with another non-convertible unit: $\text{cm}^3\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$.Measured at a thickness of $71\mu\text{m}$ (Siracusa et al., 2008, Auras, Singh & Singh, 2005, Seo et al., 2011, Lee et al., 2013, Zhai et al., 2015, Rhim, Hong & Ha, 2009).**

In the electrolyte industry various polycarbonates have been tested for their capacity in ionic conductivity, cycle rate, and mechanical strength. (Yue et al., 2016) gives the

minimum mechanical and electrical requirements for all-solid-state electrolyte polymer. These minimum requirements will be used in this research as benchmark tool. Yue et al., (2016) sets the minimum requirement for the Li ion conductivity for 25 °C at $10^{-5} \text{ S} \cdot \text{cm}^{-1}$. Furthermore, the mechanical stability must handle a minimum force of 30 MPa.

Poly(ethylene carbonate) has seen much research in the past decade. In a recent study by (He, Fan, 2018), poly(ethylene carbonate) was used in combination with lithium bis(trifluoromethanesulfonyl)imide in a 2:8 ratio with a polyamide fiber as backbone. The SPE was prepared using a solution-casting method.

The poly(ethylene carbonate) composite was tested and an ionic conductivity of $4.05 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 55 °C was found. This value is higher than the minimum requirement, but since the ionic conductivity increases with temperature it would be lower on 25 °C. Nevertheless, it is a good ionic conductivity. Furthermore, it is mentioned that the battery has an excellent mechanical strength, but He, Fan (2018) does not mention any specifics, so any conclusions about the mechanical strength could not be made. After implementation it showed a stable cycling performance with a specific capacity of 125,7 mAh \cdot g $^{-1}$ at 1. This can be ascribed because the good wettability of the electrolyte improved ionic conductivity in the electrodes (He, Fan, 2018).

When poly(ethylene carbonate) was combined with poly(ethylene carbonate) and Li bis-(fluorosulfonyl) imide and filled with 1 wt % TiO₂ particles, a conductivity of $10^{-5} \text{ S} \cdot \text{cm}^{-1}$ was reached at 30 °C, which is very similar, but just below the minimum requirement. The mechanical strength and cycle rate were not tested in this research.

Next to poly(ethylene carbonate), PPC has also found its application in the electrolyte industry. In a recent research, PPC was mixed with poly(ethylene oxide) with a mass ratio of 1:1. Additionally 10 wt% LiClO₄ was added. After testing a conductivity of $10^{-5} \text{ S} \cdot \text{cm}^{-1}$ was found at room temperature, which is within the minimum requirement of conductivity. Nothing about the cycle rate and the mechanical strength were mentioned in this research.

Additionally, poly(propylene carbonate) has found to give an enhanced performance to the electrolytes when added in the composite. When polypropylene was mixed with polyethylene in a molar 1:1 ratio and mixed with 10 wt% LiClO₄, a conductivity of $10^{-5} \text{ S} \cdot \text{cm}^{-1}$ was found at room temperature and a conductivity of $10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at 80 °C. (Dukhanin, Gaidadin & Novakov, 2014)

CONCLUSION

This report has given a broad overview of all the aspects of CO₂- produced polycarbonates. The CO₂-produced polycarbonates have multiple options when it comes to catalysts, but as of this moment, the heterogenous catalysts, despite their ability for easy re-use, are dominated by the homogenous catalysts in terms of speed and conversion. As for the thermal and mechanical properties it has shown that the polycarbonates are not able to compete with the state-of-the-art polycarbonate bisphenol-A. These properties can be adapted using composites or blends, but not in such a major way that the competition with bisphenol-A would be feasible. In addition, it can be seen that most research for properties of the material has been done for PPC and blends of PPC. For the factory, an aspen simulation has shown to produce as feasible production of PPC, although the assumption of the re-use of the catalyst is unrealistic as the recycle rate is 100%, the overall process makes use of scientifically proven kinetics. The process also shows a major utilization of CO₂, from which it may benefit from additional sustainable and economic benefits. From a CAPCOST® analysis the process simulated in Aspen displays to have economic feasibility concerning the industrialization over a period of 7 to 8 years. This has been proven through a discounted cash flow data, from which the payback period, net present value and rate of return which all displayed favorable values. Moreover, several companies have already industrialized this technology which further proves the feasibility of the industrialization. Since this technology is only simulated in Aspen®, the recommendation would be to simulate the process in a micro plant to further analyze the process, this gives the stakeholders a more detailed view of the process. The sustainability analysis displayed a very good result. With major utilization of CO₂. Along with its biodegradability the production of CO₂-produced polycarbonates give promise for a new pathway for sustainable plastics. As for application of the material, it has shown that for CO₂- produced polycarbonates to be applied in several sectors, the material is always modified through blends or composites. Especially PPC has seen application researches in many industries.

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APPENDICES

<i>L,\$</i>	<i>0.50</i>	<i>n</i>	<i>FCI</i>	<i>D</i>	<i>BV</i>	<i>R</i>	<i>COM</i>	<i>NP</i>	<i>DCF</i>	<i>CDCF</i>
<i>FCI,\$</i>	54.54	0	-0.50	0.00	65.44	0.00		0.00	-0.50	-0.50
<i>WC,\$</i>	10.91	1	-54.54	0.00	65.44	0.00		0.00	-53.23	-53.73
<i>S,\$</i>	1.09	2	-10.91	9.35	56.09	231.61	219.28	11.29	10.34	-43.39
<i>R,\$</i>	231.61	3	0.00	15.90	40.20	231.61	219.28	13.58	11.90	-31.49
		4	0.00	11.45	28.75	231.61	219.28	12.02	10.08	-21.41
<i>COM,\$</i>	219.28	5	0.00	8.17	20.58	231.61	219.28	10.88	8.73	-12.69
<i>t</i>	0.35	6	0.00	5.84	14.73	231.61	219.28	10.06	7.73	-4.96
<i>i%</i>	0.05	7	0.00	5.84	8.89	231.61	219.28	10.06	7.39	2.43
		8	0.00	5.84	3.06	231.61	219.28	10.06	7.07	9.50
<i>n,year</i>	10.00	9	0.00	2.92	0.00	231.61	219.28	9.04	6.08	15.58
<i>k,year</i>	7.00	10	0.00	0.00	0.00	231.61	219.28	8.01	5.16	20.74
		11	12.49	0.00	0.00	231.61	219.28	8.01	17.43	38.18
			L+WC+S						(P/F,I,n)	NPV

Appendix 1: Cumulative Discounted Cash Flow for Poly(propylene) Carbonate Production (in million US\$). CDCF: Cumulative Discounted Cash Flow; FCI: Fixed capital investment; WC: Working capital; D: Depreciation; BV: Book value; R: Revenue; COM: Cost of manufacturing; NP: Net profit; DCF: Discounted cash flow; L: Cost of land; S: Salvage value; NPV: Net present value; t: tax, and i: interest rate of bank loan. Depreciation method: Maximum Accelerated Cost Recovery System (MACRS).(Demirel, 2015)

REFERENCES

- Chapter 2 Thermal decomposition of polymers* 2005, , Elsevier.
- 360 Market Updates 2013, *Polypropylene Carbonate (PPC) Market Overview 2019, Raw Materials Analysis, Market Drivers and Opportunities*.
- Aida, T. & Inoue, S. 1982, "Synthesis of polyether-polycarbonate block copolymer from carbon dioxide and epoxide using a metalloporphyrin catalyst system", *Macromolecules*, vol. 15, no. 2, pp. 682-684.
- Allen, S.D., Cherian, A.E., Simoneau, C.A. & Farmer, J.J. 2011, *Aliphatic polycarbonates*.
- Allen, S.D., Moore, D.R., Lobkovsky, E.B. & Coates, G.W. 2002, "High-activity, single-site catalysts for the alternating copolymerization of CO₂ and propylene oxide", *Journal of the American Chemical Society*, vol. 124, no. 48, pp. 14284-14285.
- Angell, C.A., Ngai, K.L., McKenna, G.B., McMillan, P.F. & Martin, S.W. 2000, "Relaxation in glassforming liquids and amorphous solids", *Journal of Applied Physics*, vol. 88, no. 6, pp. 3113-3157.
- Askeland, D. & Fulay, P. 2005, "Mechanical properties 1&2" in *The Science & Engineering of Materials* Cengage Learning, , pp. 138-265.
- Auras, R.A., Singh, S.P. & Singh, J.J. 2005, "Evaluation of oriented poly (lactide) polymers vs. existing PET and oriented PS for fresh food service containers", *Packaging Technology and Science: An International Journal*, vol. 18, no. 4, pp. 207-216.
- Bahramian, B., Fathi, A. & Dehghani, F. 2016, *A renewable and compostable polymer for reducing consumption of non-degradable plastics*.
- Baleizao, C. & Garcia, H. 2006, "Chiral salen complexes: an overview to recoverable and reusable homogeneous and heterogeneous catalysts", *Chemical reviews*, vol. 106, no. 9, pp. 3987-4043.
- Cazes, J. 1989, "A Question of Molecular Weight", *International Division, Waters Associates*, .
- Cheremisinoff, N.P. 2001, *P*, Butterworth-Heinemann, Boston.
- Chisholm, M.H., Navarro-Llobet, D. & Zhou, Z. 2002, "Poly (propylene carbonate). 1. More about poly (propylene carbonate) formed from the copolymerization of propylene oxide and carbon dioxide employing a zinc glutarate catalyst", *Macromolecules*, vol. 35, no. 17, pp. 6494-6504.
- Clift, R. 2007, "Climate change and energy policy: the importance of sustainability arguments", *Energy*, vol. 32, no. 4, pp. 262-268.

- Coates, G.W. & Moore, D.R. 2004, "Discrete metal-based catalysts for the copolymerization of CO₂ and epoxides: discovery, reactivity, optimization, and mechanism", *Angewandte Chemie International Edition*, vol. 43, no. 48, pp. 6618-6639.
- Cole-Hamilton, D.J. 2003, "Homogeneous catalysis--new approaches to catalyst separation, recovery, and recycling", *Science*, vol. 299, no. 5613, pp. 1702-1706.
- Cyriac, A., Lee, S.H., Varghese, J.K., Park, J.H., Jeon, J.Y., Kim, S.J. & Lee, B.Y. 2011a, "Preparation of flame-retarding poly (propylene carbonate)", *Green Chemistry*, vol. 13, no. 12, pp. 3469-3475.
- Cyriac, A., Lee, S.H., Varghese, J.K., Park, J.H., Jeon, J.Y., Kim, S.J. & Lee, B.Y. 2011b, "Preparation of flame-retarding poly (propylene carbonate)", *Green Chemistry*, vol. 13, no. 12, pp. 3469-3475.
- Darensbourg, D.J. & Yeung, A.D. 2015, "Kinetics of the (salen) Cr (III)-and (salen) Co (III)-catalyzed copolymerization of epoxides with CO₂, and of the accompanying degradation reactions", *Polymer Chemistry*, vol. 6, no. 7, pp. 1103-1117.
- Darensbourg, D.J. 2007, "Making plastics from carbon dioxide: salen metal complexes as catalysts for the production of polycarbonates from epoxides and CO₂", *Chemical reviews*, vol. 107, no. 6, pp. 2388-2410.
- Darensbourg, D.J. & Holtcamp, M.W. 1996, "Catalysts for the reactions of epoxides and carbon dioxide", *Coordination Chemistry Reviews*, vol. 153, pp. 155-174.
- Darensbourg, D.J., Mackiewicz, R.M., Phelps, A.L. & Billodeaux, D.R. 2004, "Copolymerization of CO₂ and epoxides catalyzed by metal salen complexes", *Accounts of Chemical Research*, vol. 37, no. 11, pp. 836-844.
- Darensbourg, D.J. & Tsai, F. 2014, "Postpolymerization functionalization of copolymers produced from carbon dioxide and 2-vinylloxirane: amphiphilic/water-soluble CO₂-based polycarbonates", *Macromolecules*, vol. 47, no. 12, pp. 3806-3813.
- Darensbourg, D.J. & Wilson, S.J. 2013, "Synthesis of CO₂-derived poly (indene carbonate) from indene oxide utilizing bifunctional cobalt (III) catalysts", *Macromolecules*, vol. 46, no. 15, pp. 5929-5934.
- Darensbourg, D.J., Yarbrough, J.C., Ortiz, C. & Fang, C.C. 2003, "Comparative kinetic studies of the copolymerization of cyclohexene oxide and propylene oxide with carbon dioxide in the presence of chromium salen derivatives. In situ FTIR measurements of copolymer vs cyclic carbonate production", *Journal of the American Chemical Society*, vol. 125, no. 25, pp. 7586-7591.
- Demirel, Y. 2015, "Sustainability and economic analysis of propylene carbonate and polypropylene carbonate production processes using CO₂ and propylene oxide", *J Chem Eng Process Technol*, vol. 6, no. 3.

- Eberhardt, R., Allmendinger, M. & Rieger, B. 2003, "DMAP/Cr (III) catalyst ratio: The decisive factor for poly (propylene carbonate) formation in the coupling of CO₂ and propylene oxide", *Macromolecular rapid communications*, vol. 24, no. 2, pp. 194-196.
- Farnetti, E., Di Monte, R. & Kašpar, J. 2009, "Homogeneous and heterogeneous catalysis", *Inorganic and bioinorganic chemistry*, vol. 2, pp. 50.
- Flory, P.J. & Vrij, A. 1963, "Melting points of linear-chain homologs. The normal paraffin hydrocarbons", *Journal of the American Chemical Society*, vol. 85, no. 22, pp. 3548-3553.
- Frynas, J.G., Mellahi, K. & Pigman, G.A. 2006, "First mover advantages in international business and firm-specific political resources", *Strategic Management Journal*, vol. 27, no. 4, pp. 321-345.
- Fukuoka, S., Kawamura, M., Komiya, K., Tojo, M., Hachiya, H., Hasegawa, K., Aminaka, M., Okamoto, H., Fukawa, I. & Konno, S. 2003, "A novel non-phosgene polycarbonate production process using by-product CO₂ as starting material", *Green Chemistry*, vol. 5, no. 5, pp. 497-507.
- Gauthier, M.A., Gibson, M.I. & Klok, H. 2009, "Synthesis of functional polymers by post-polymerization modification", *Angewandte Chemie International Edition*, vol. 48, no. 1, pp. 48-58.
- Hauenstein, O., Agarwal, S. & Greiner, A. 2016, "Bio-based polycarbonate as synthetic toolbox", *Nature communications*, vol. 7, pp. 11862.
- Hauenstein, O., Reiter, M., Agarwal, S., Rieger, B. & Greiner, A. 2016, "Bio-based polycarbonate from limonene oxide and CO₂ with high molecular weight, excellent thermal resistance, hardness and transparency", *Green Chemistry*, vol. 18, no. 3, pp. 760-770.
- He, Z. & Fan, L. 2018, "Poly(ethylene carbonate)-based electrolytes with high concentration Li salt for all-solid-state lithium batteries", *Rare Metals*, vol. 37, no. 6, pp. 488-496.
- Hsu, T. & Tan, C. 2002a, "Block copolymerization of carbon dioxide with cyclohexene oxide and 4-vinyl-1-cyclohexene-1, 2-epoxide in based poly (propylene carbonate) by yttrium–metal coordination catalyst", *Polymer*, vol. 43, no. 16, pp. 4535-4543.
- Hsu, T. & Tan, C. 2002b, "Block copolymerization of carbon dioxide with cyclohexene oxide and 4-vinyl-1-cyclohexene-1, 2-epoxide in based poly (propylene carbonate) by yttrium–metal coordination catalyst", *Polymer*, vol. 43, no. 16, pp. 4535-4543.
- Inoue, S., Koinuma, H. & Tsuruta, T. 1969, "Copolymerization of carbon dioxide and epoxide", *Journal of Polymer Science Part B: Polymer Letters*, vol. 7, no. 4, pp. 287-292.

- Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R. & Law, K.L. 2015, "Plastic waste inputs from land into the ocean", *Science*, vol. 347, no. 6223, pp. 768-771.
- Jiang, G., Zhang, M., Feng, J., Zhang, S. & Wang, X. 2017, "High oxygen barrier property of poly (propylene carbonate)/polyethylene glycol nanocomposites with low loading of cellulose nanocrystals", *ACS Sustainable Chemistry & Engineering*, vol. 5, no. 12, pp. 11246-11254.
- Kagan, J. 2019, May 20,-last update, *Payback period*. Available: <https://www.investopedia.com/terms/p/paybackperiod.asp>.
- Kamphuis, A.J., Picchioni, F. & Pescarmona, P.P. 2019, "CO₂-fixation into cyclic and polymeric carbonates: principles and applications", *Green Chemistry*, vol. 21, no. 3, pp. 406-448.
- Kember, M.R., Buchard, A. & Williams, C.K. 2011a, "Catalysts for CO₂/epoxide copolymerisation", *Chemical Communications*, vol. 47, no. 1, pp. 141-163.
- Kember, M.R., Buchard, A. & Williams, C.K. 2011b, "Catalysts for CO₂/epoxide copolymerisation", *Chemical Communications*, vol. 47, no. 1, pp. 141-163.
- Kenton, W. 2019a, Apr 24,-last update, *Net Present Value (NPV)*. Available: <https://www.investopedia.com/terms/n/npv.asp>.
- Kenton, W. 2019b, May 24,-last update, *Rate of Return – RoR*. Available: <https://www.investopedia.com/terms/r/rateofreturn.asp>.
- Kerin, R.A., Varadarajan, P.R. & Peterson, R.A. 1992, "First-mover advantage: A synthesis, conceptual framework, and research propositions", *Journal of Marketing*, vol. 56, no. 4, pp. 33-52.
- Kim, J.G., Cowman, C.D., LaPointe, A.M., Wiesner, U. & Coates, G.W. 2011, "Tailored living block copolymerization: multiblock poly (cyclohexene carbonate) s with sequence control", *Macromolecules*, vol. 44, no. 5, pp. 1110-1113.
- Kim, S. & Jang, J. 2013, "Effect of degree of polymerization on the mechanical properties of regenerated cellulose fibers using synthesized 1-allyl-3-methylimidazolium chloride", *Fibers and Polymers*, vol. 14, no. 6, pp. 909-914.
- Klaus, S., Lehenmeier, M.W., Anderson, C.E. & Rieger, B. 2011, "Recent advances in CO₂/epoxide copolymerization—new strategies and cooperative mechanisms", *Coordination Chemistry Reviews*, vol. 255, no. 13-14, pp. 1460-1479.
- Koning, C.E., Sablong, R.J., Nejad, E.H., Duchateau, R. & Buijsen, P. 2013, "Novel coating resins based on polycarbonates and poly (ester-co-carbonate) s made by catalytic chain growth polymerization of epoxides with CO₂ and with anhydride/CO₂", *Progress in Organic Coatings*, vol. 76, no. 12, pp. 1704-1711.

- Kruschwitz, L. & Löffler, A. 2006, *Discounted cash flow: a theory of the valuation of firms*, John Wiley & Sons.
- Langanke, J., Wolf, A., Hofmann, J., Böhm, K., Subhani, M., Müller, T., Leitner, W. & Gürtler, C. 2014, *Carbon dioxide (CO₂) as sustainable feedstock for polyurethane production*, .
- Larminie, J., Dicks, A. & McDonald, M.S. 2003, *Fuel cell systems explained*, J. Wiley Chichester, UK.
- Lee, Y., Kim, D., Seo, J., Han, H. & Khan, S.B. 2013, "Preparation and characterization of poly (propylene carbonate)/exfoliated graphite nanocomposite films with improved thermal stability, mechanical properties and barrier properties", *Polymer International*, vol. 62, no. 9, pp. 1386-1394.
- Li, C., Sablong, R.J. & Koning, C.E. 2016, "Chemoselective Alternating copolymerization of limonene dioxide and carbon dioxide: a new highly functional aliphatic epoxy polycarbonate", *Angewandte Chemie*, vol. 128, no. 38, pp. 11744-11748.
- Li, Y., Hong, J., Wei, R., Zhang, Y., Tong, Z., Zhang, X., Du, B., Xu, J. & Fan, Z. 2015, "Highly efficient one-pot/one-step synthesis of multiblock copolymers from three-component polymerization of carbon dioxide, epoxide and lactone", *Chemical science*, vol. 6, no. 2, pp. 1530-1536.
- Lieberman, M.B. & Montgomery, D.B. 1988, "First-mover advantages", *Strategic Management Journal*, vol. 9, no. S1, pp. 41-58.
- Liu, Y., Huang, K., Peng, D. & Wu, H. 2006, "Synthesis, characterization and hydrolysis of an aliphatic polycarbonate by terpolymerization of carbon dioxide, propylene oxide and maleic anhydride", *Polymer*, vol. 47, no. 26, pp. 8453-8461.
- Luinstra, G.A. 2008, "Poly (propylene carbonate), old copolymers of propylene oxide and carbon dioxide with new interests: catalysis and material properties", *Polymer Reviews*, vol. 48, no. 1, pp. 192-219.
- Luinstra, G.A. & Borchardt, E. 2011, "Material properties of poly (propylene carbonates)" in *Synthetic biodegradable polymers* Springer, , pp. 29-48.
- Martín, C. & Kleij, A.W. 2016, "Terpolymers derived from limonene oxide and carbon dioxide: access to cross-linked polycarbonates with improved thermal properties", *Macromolecules*, vol. 49, no. 17, pp. 6285-6295.
- Martins, A.A., Mata, T.M., Costa, C.A. & Sikdar, S.K. 2007, "Framework for sustainability metrics", *Industrial & Engineering Chemistry Research*, vol. 46, no. 10, pp. 2962-2973.
- Mercer, S.M., Robert, T., Dixon, D.V. & Jessop, P.G. 2012, "Recycling of a homogeneous catalyst using switchable water", *Catalysis Science & Technology*, vol. 2, no. 7, pp. 1315-1318.

- Müller, T.E., Gürtler, C., Subhani, M.A. & Leitner, W. 2015, *Method for producing polyether ester carbonate polyols*.
- Muthuraj, R. & Mekonnen, T. 2018, "Carbon Dioxide–Derived Poly (propylene carbonate) as a Matrix for Composites and Nanocomposites: Performances and Applications", *Macromolecular Materials and Engineering*, vol. 303, no. 11, pp. 1800366.
- Novomer 2013, Sep 24,-last update, *Novomer Catalytic Process Using Waste CO₂ and Shale Gas Targets \$20 Billion Market and Up to 110% Carbon Footprint Reduction Content*. Available: <https://www.novomer.com/novomer-catalytic-process-using-waste-co2-and-shale-gas-targets-20-billion-market-and-110-carbon>.
- Parker, L. 2018, *Plastic: We made it. We depend on it. We're drowning in it*, National Geographic Society.
- Paszkiwicz, S., Szymczyk, A., Pawelec, I., Lisiecki, S., Jotko, M., Spitalsky, Z., Mosnacek, J. & Roslaniec, Z. 2015, *Oxygen Barrier Properties and Melt Crystallization Behavior of Poly(ethylene terephthalate)/Graphene Oxide Nanocomposites*, .
- Patterson, W.C. 1993, "First-mover advantage: the opportunity curve", *Journal of Management Studies*, vol. 30, no. 5, pp. 759-777.
- Pena Carrodeguas, L., González-Fabra, J., Castro-Gómez, F., Bo, C. & Kleij, A.W. 2015, "AlIII-Catalysed Formation of Poly (limonene) carbonate: DFT Analysis of the Origin of Stereoregularity", *Chemistry–A European Journal*, vol. 21, no. 16, pp. 6115-6122.
- Perrier, S., Takolpuckdee, P. & Mars, C.A. 2005, "Reversible addition–fragmentation chain transfer polymerization: end group modification for functionalized polymers and chain transfer agent recovery", *Macromolecules*, vol. 38, no. 6, pp. 2033-2036.
- Pescarmona, P.P. & Taherimehr, M. 2012, "Challenges in the catalytic synthesis of cyclic and polymeric carbonates from epoxides and CO₂", *Catalysis Science & Technology*, vol. 2, no. 11, pp. 2169-2187.
- Prasad, E. 2016, *Fuel Cell Market by Type (Solid Oxide Fuel Cells, Proton Exchange Membrane Fuel Cell, Molten Carbonate Fuel Cell, Phosphoric Acid Fuel Cells, and Others), and by Application (Portable, Stationary, Transport) - Global Opportunity Analysis and Industry Forecast, 2017-2023*, Allied Market Research.
- Qin, Y. & Wang, X. 2010, "Carbon dioxide-based copolymers: Environmental benefits of PPC, an industrially viable catalyst", *Biotechnology journal*, vol. 5, no. 11, pp. 1164-1180.

- Reddy, M.M., Vivekanandhan, S., Misra, M., Bhatia, S.K. & Mohanty, A.K. 2013, "Biobased plastics and bionanocomposites: Current status and future opportunities", *Progress in polymer Science*, vol. 38, no. 10-11, pp. 1653-1689.
- Ren, W., Zhang, X., Liu, Y., Li, J., Wang, H. & Lu, X. 2010, "Highly active, bifunctional Co (III)-salen catalyst for alternating copolymerization of CO₂ with cyclohexene oxide and terpolymerization with aliphatic epoxides", *Macromolecules*, vol. 43, no. 3, pp. 1396-1402.
- Rhim, J., Hong, S. & Ha, C. 2009, *Tensile, water vapor barrier and antimicrobial properties of PLA/nanoclay composite films*.
- Rogers, E.M. 2010, *Diffusion of innovations*, Simon and Schuster.
- Sant'Angelo, J.G., Chen, X. & McGinnis, V.D. 2019, *Functionalized poly(alkylene carbonate), and use thereof* .
- Scharfenberg, M., Hilf, J. & Frey, H. 2018a, "Functional polycarbonates from carbon dioxide and tailored epoxide monomers: Degradable materials and their application potential", *Advanced Functional Materials*, vol. 28, no. 10, pp. 1704302.
- Scharfenberg, M., Hilf, J. & Frey, H. 2018b, "Functional polycarbonates from carbon dioxide and tailored epoxide monomers: Degradable materials and their application potential", *Advanced Functional Materials*, vol. 28, no. 10, pp. 1704302.
- Seo, J., Jeon, G., Jang, E.S., Bahadar Khan, S. & Han, H. 2011, "Preparation and properties of poly (propylene carbonate) and nanosized ZnO composite films for packaging applications", *Journal of Applied Polymer Science*, vol. 122, no. 2, pp. 1101-1108.
- Seong, J.E., Na, S.J., Cyriac, A., Kim, B. & Lee, B.Y. 2009, "Terpolymerizations of CO₂, propylene oxide, and various epoxides using a cobalt (III) complex of salen-type ligand tethered by four quaternary ammonium salts", *Macromolecules*, vol. 43, no. 2, pp. 903-908.
- Sikdar, S.K. 2003, "Sustainable development and sustainability metrics", *AIChE Journal*, vol. 49, no. 8, pp. 1928-1932.
- Siracusa, V., Rocculi, P., Romani, S. & Dalla Rosa, M. 2008, "Biodegradable polymers for food packaging: a review", *Trends in Food Science & Technology*, vol. 19, no. 12, pp. 634-643.
- Solomon, S., Plattner, G., Knutti, R. & Friedlingstein, P. 2009, "Irreversible climate change due to carbon dioxide emissions", *Proceedings of the national academy of sciences*, vol. 106, no. 6, pp. 1704-1709.

- Stretz, H.A., Cassidy, P.E. & Paul, D.R. 1999, "Blends of bisphenol A polycarbonate and rubber-toughened styrene–maleic anhydride copolymers", *Journal of Applied Polymer Science*, vol. 74, no. 6, pp. 1508-1515.
- Sugimoto, H. & Inoue, S. 2004, "Copolymerization of carbon dioxide and epoxide", *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 42, no. 22, pp. 5561-5573.
- Taherimehr, M. & Pescarmona, P.P. 2014, "Green polycarbonates prepared by the copolymerization of CO₂ with epoxides", *Journal of Applied Polymer Science*, vol. 131, no. 21.
- Tominaga, Y. & Yamazaki, K. 2014, "Fast Li-ion conduction in poly (ethylene carbonate)-based electrolytes and composites filled with TiO₂ nanoparticles", *Chemical communications*, vol. 50, no. 34, pp. 4448-4450.
- Trott, G., Saini, P.K. & Williams, C.K. 2016a, "Catalysts for CO₂/epoxide ring-opening copolymerization", *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 374, no. 2061, pp. 20150085.
- Trott, G., Saini, P.K. & Williams, C.K. 2016b, "Catalysts for CO₂/epoxide ring-opening copolymerization", *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 374, no. 2061, pp. 20150085.
- University of pennsylvania 2018, "Engineers design new solid polymer electrolyte, paving way for safer, smaller batteries and fuel cells", .
- Willcock, H. & O'Reilly, R.K. 2010, "End group removal and modification of RAFT polymers", *Polymer Chemistry*, vol. 1, no. 2, pp. 149-157.
- Xu, K. 2004, "Nonaqueous liquid electrolytes for lithium-based rechargeable batteries", *Chemical reviews*, vol. 104, no. 10, pp. 4303-4418.
- Xu, Y., Lin, L., Xiao, M., Wang, S., Smith, A.T., Sun, L. & Meng, Y. 2018, "Synthesis and properties of CO₂-based plastics: Environmentally-friendly, energy-saving and biomedical polymeric materials", *Progress in Polymer Science*, vol. 80, pp. 163-182.
- Yue, L., Ma, J., Zhang, J., Zhao, J., Dong, S., Liu, Z., Cui, G. & Chen, L. 2016, *All solid-state polymer electrolytes for high-performance lithium ion batteries*.
- Zhai, L., Li, G., Xu, Y., Xiao, M., Wang, S. & Meng, Y. 2015, "Poly (propylene carbonate)/aluminum flake composite films with enhanced gas barrier properties", *Journal of Applied Polymer Science*, vol. 132, no. 11.
- Zhang, Z., Mo, Z., Zhang, H., Wang, X. & Zhao, X. 2003, "Crystallization and Melting Behaviors of PPC-BS/PVA Blends", *Macromolecular Chemistry and Physics*, vol. 204, no. 12, pp. 1557-1566.