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Process development for the catalytic conversion of cyclohexene oxide and carbon dioxide into poly(cyclohexene carbonate)

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Abstract

The synthesis of polycarbonates from carbon dioxide is an alternative route to the use of phosgene for the introduction of the carbonate functionality in these polymers. In this work, a preliminary process design has been made for the catalytic conversion of cyclohexene oxide and carbon dioxide into poly(cyclohexene carbonate). For this purpose, the low- and high-pressure phase behaviour, reaction rate and downstream removal of residual cyclohexene oxide from the product stream are described. Based on these findings a design for such a process is suggested and evaluated from a technical and economic perspective. The economic evaluation indicates that the required selling price of PCHC is intermediate to the market price of engineering and specialty polymers.

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Keywords: Poly(cyclohexene carbonate) synthesis; Carbon dioxide; Phase behaviour; Process design; Economic evaluation

1. Introduction

The current interest in the industrial application of CO_2 has developed from two different perspectives. First of all, CO_2 is considered to provide a stable and non-toxic alternative to traditional solvents. Secondly, CO_2 is considered to be an interesting starting material for the synthesis of fine chemicals and intermediates that are currently being produced from fossil fuels. From the point of view of solvent replacement, CO_2 and supercritical CO_2 in particular are considered to offer a combination of opportunities associated with the generally accepted environmentally benign character of CO_2 and the physical properties of supercritical fluids (SCFs) [1–7]. Typical advantages of SCFs are the possibilities to control density, solvent strength and diffusivity by relatively small changes in pressure and temperature. Additionally, supercritical CO_2 provides a chemically stable reaction medium which displays total miscibility with gasses and good solubility towards both fluorous and non-polar organic compounds. From an operational point of view the pressure-temperature tuneability of $scCO_2$ makes it a very versatile reaction and processing medium.

The utilization of CO_2 as a starting material for the synthesis of fine chemicals and intermediates provides a sustainable alternative to the use of traditional fossil fuel based carbon resources [8–11]. Present industrial examples for this type of CO_2 utilization include the production of urea, salicylic acid and various carbonates. This work focuses on the synthesis of polycarbonates from CO_2, which provides an alternative route to the use of phosgene for the introduction of the carbonate functionality in these polymers. This alternative route for the synthesis of polycarbonates has been studied since the discovery of this type of reaction by Inoue et al. in the 1960s [12]. This has resulted in a large amount of catalytic systems, most of which are discrete organometallic complexes based on various transition metals with emphasis on Zn, Cr and Al. In this work the alternate copolymerisation of CO_2 and cyclohexene oxide (CHO) into poly(cyclohexene carbonate) (PCHC) is studied as a model reaction (Fig. 1).

Many organometallic complexes have been reported to be active in the copolymerisation of CO_2 and CHO, of which the most successful are based on zinc [13–15]. Recently, the focus in the development of these complexes has shifted from heterogeneous mixtures to discrete and single-site

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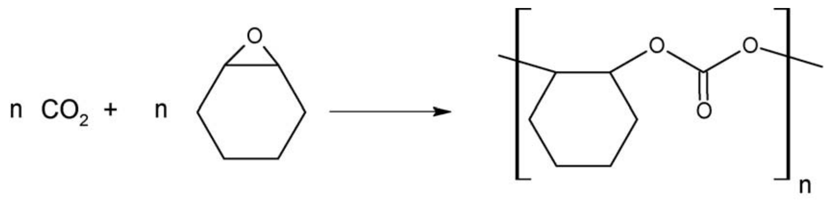

Fig. 1. Reaction scheme for the copolymerisation of CO_2 and cyclohexene oxide (CHO), model reaction for the copolymerisation of CO_2 and oxiranes.

complexes. For the discovery of this type of reaction Inoue et al. used a mixture of $ZnEt_2$ and water [12]. Many other mixtures of $ZnEt_2$ and dihydric sources, such as resorcinol, carboxylic acids and primary amines, have provided complexes with relatively low catalytic activities. In 1978 Inoue reported the first single-site catalyst based on aluminium tetraphenylporphyrin able to copolymerise propylene oxide and CO_2 [13]. Although the activity of these systems is rather low, their living character results in monodisperse polycarbonate. Darensbourg et al. have reported on the synthesis and activity of zinc bis(phenoxide) catalysts which are the first known discrete complexes for this reaction [14,15]. Coates et al. have reported living zinc β-diiminate catalysts that show a high activity under relatively mild conditions [16]. A variation on this system with a non-symmetrical ligand geometry and modifications with electron withdrawing cyano substituents increase the activity of this catalyst to 2290 mol CHO per mol Zn per hour at 50 °C and 7 bar [17]. Although not as active as this one, many other catalysts such as aluminium and chromium salen complexes, aluminium alkoxides and chromium tetraphenylporphyrines have been reported [18–20]. Nevertheless, the development of new, better performing and more stable catalysts for this reaction is very important. In this work, the rate of reaction of a new active zinc complex is studied.

In this contribution the results of a feasibility study for a process design based on this reaction are presented. For this purpose a comprehensive treatment of the low- and high-pressure phase behaviour, reactant conversion and downstream removal of residual cyclohexene oxide from the product stream is given, followed by a preliminary process design and an economic evaluation of this design.

2. Poly(cyclohexene carbonate) solubility in CO_2

In general, phase behaviour plays an important role in the development of polymerisation processes. The miscibility of the reactants and solubility of the produced polymer and catalyst can favour one particular mode of polymerisation, e.g. solution, precipitation or emulsion polymerisation. This section focuses on the solubility of PCHC in CO_2, CHO and mixtures thereof.

CO_2 is known to be a poor solvent for most polymers with the exception of amorphous fluoropolymers and polysiloxanes. Studies discussing the factors contributing to polymer–CO_2 phase behaviour generally agree that relatively small differences in polymer structure can have relatively large effects on phase behaviour [21]. In general, the phase behaviour of systems containing both polymers and compressed CO_2 is complex and it cannot be modelled using predictive methods. E.J. Beckman reported on the solubility of low molecular weight copolymers of cyclohexene oxide in CO_2 with a low carbonate content [22]. Recently, the solubility of poly(cylcohexene carbonate) (PCHC) in CO_2 and the effect of molecular weight and CHO concentration thereon have been reported [23]. These measurements have indicated that pressures up to 350 MPa are required to dissolve 0.5 wt.% of intermediate molecular weight PCHC (12,000 g/mol) in CO_2. Addition of relatively small amounts of CHO has resulted in a significant decrease of the cloud-point pressure (Fig. 2). Moreover, it has been demonstrated that at high temperatures the PC-SAFT equation of state allows for a quantitative description of the phase behaviour, whereas at lower temperatures PC-SAFT tends to overestimate the cloud-point pressures.

From these experimental observations we have concluded that performing this reaction in CO_2 under typical reaction

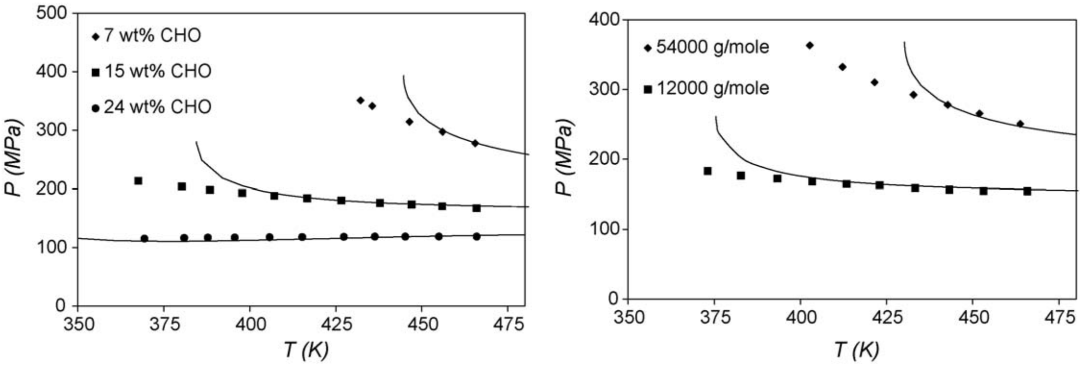

Fig. 2. Cloud-point pressures of 1 wt.% PCHC (25,000 g/mol) in various mixtures of CO_2 and CHO (left) and cloud-point pressures of 1 wt.% PCHC in 87 wt.% CO_2 and 12 wt.% CHO (right). Symbols represent experimental data and lines are calculated using the PC-SAFT equation of state [23].

conditions (320–400 K and up to 15 MPa) will cause precipitation of the polymer when the polymer molecular weight increases and the CHO concentration in the reaction medium decreases. The solubility of the polymer can be significantly increased by maintaining a relatively high CO_2 pressure and CHO concentration (typically above 100 MPa and 24 wt.%, respectively). At lower pressures precipitation is expected to occur at relatively low conversion and low polymer molecular weight. Although polymer precipitation can have certain advantages, if this happens in an uncontrolled way the accessibility of the active sites of the catalyst by CHO and CO_2 can become severely hindered. Consequently, mixing and control over the reaction will become more complicated.

3. Phase behaviour under typical reaction conditions

The behaviour of the system described in the previous section suggests that polymerisation would be more efficient in a medium with better transport characteristics than a precipitated polymer phase. At relatively low pressures this can be accomplished by adding a solvent or using an excess of CHO to the reaction mixture. In the latter case the process can still be considered as a solvent-free process and the reaction medium is a CO_2-expanded liquid phase. It is known from literature that this reaction can be performed homogeneously in an excess of CHO without using additional solvents [18–20]. Therefore, the phase behaviour of systems that are relatively rich in CHO was studied experimentally. Particular interest is on the effect of an increasing PCHC concentration on the phase behaviour of these mixtures. The phase behaviour of the CHO–CO_2 binary system has been studied and reported [24]. The relation between liquid phase composition, pressure and temperature has been experimentally determined for the binary system from 10 to 50 mol% CO_2 and temperatures ranging from 354 to 424 K. Application of the Peng–Robinson equation of state and van der Waals one-fluid mixing rules [25] has resulted in a satisfactory correlation of these data (Fig. 3) with one temperature-dependent binary interaction parameter k_{ij} [24].

Addition of PCHC to mixtures of CHO and CO_2 resulted only in small changes of the bubble point pressure. Phase transitions of samples containing up to 50 wt.% PCHC were studied up to 423 K and 14 MPa similar to the method previously used for the binary system [24]. Although precipitation of polymer is expected to occur at elevated CO_2 pressures and increased polymer concentrations, this is not observed. All phase transitions are identified as vapour–liquid to liquid transitions similar to the transitions observed in the polymer-free binary system. Due to the viscosity increase no measurements can be performed on samples containing a higher polymer concentration. These results indicate that polymerisations performed under these conditions remain homogeneous up to relatively high conversions.

The measured effect of increased polymer concentration on the vapour pressure of the liquid phase is relatively small. This is demonstrated in Fig. 4. In this figure, the effect of a 5 mol% change in CO_2 to CHO composition on vapour pressure is compared to the effect of adding 17 and 21 wt.% of PCHC to the same mixture. This demonstrates that in this range the vapour pressure of the PCHC–CHO–CO_2 mixtures is primarily determined by the CHO to CO_2 ratio. Additionally, these results indicate that high conversions can be obtained in systems where CHO is in excess without precipitation of the polymer. Although these systems remain homogeneous, transport properties are expected to deteriorate as the polymer concentration increases.

4. Determination of conversion during polymerisation

The relation between liquid phase composition and vapour pressure in the PCHC–CHO–CO_2 system as it has been demonstrated in the previous section can be used to determine the composition of the reaction mixture during polymerisation. As the effect of PCHC on vapour pressure is relatively small it can be neglected in a first approximation of the composition of the liquid phase. At the beginning of the reaction, i.e. in the absence of reaction products, the liquid phase composition can be directly calculated from the system pressure and temperature with a high accuracy. During polymerisation a more accurate estimation of liquid phase composition can be used if the effect of PCHC on the vapour pressure on CHO–CO_2 mixtures is

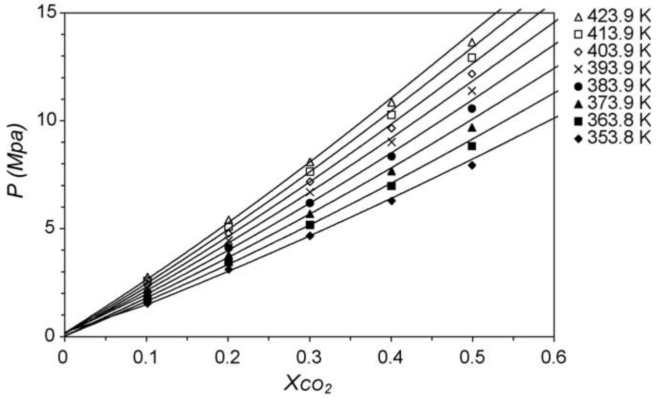

Fig. 3. Bubble point isotherms for the binary system CO_2 + CHO (symbols) correlated with the Peng–Robinson equation of state and van der Waals one-fluid mixing rules [19].

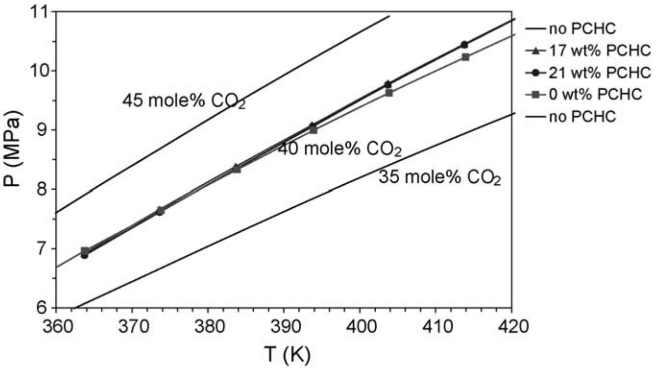

Fig. 4. Comparison of the effect of PCHC concentration and CO_2 to CHO ratio on vapour pressure.

known quantitatively. As this effect has been accurately determined over a wide range of pressures, temperatures and compositions, it can effectively be taken into account. The experimental procedure for these determinations is similar as described previously for the measurements on the binary system [24]. If the effect of PCHC is considered, then vapour–liquid equilibrium in a three-component system implies that the number of degrees of freedom increases from 2 to 3, because of the Gibbs phase rule. However, one degree of freedom can be cancelled if the initial composition and stoichiometry of the reaction are known or are assumed to be known. This reduces the possibilities in terms of system composition. In this case the composition can be expressed in terms of two variables, i.e. the initial composition and conversion. These methods neglect the effect of mass transfer from vapour to the liquid phase and assume thermodynamic equilibrium between the two phases. Therefore, it is imperative to minimize the volume of the vapour phase during the experiments. The assumptions on the stoichiometry of the reaction as used in the second method are verified at the end of each reaction by analysis of the product mixture.

These methods have been applied to study the extent of reaction during polymerisation. Polymerisations were performed in a set-up as depicted in Fig. 5. This set-up consisted of a 100 mL stainless steel autoclave, which was mechanically stirred and heated using a jacket. The liquid feed was separately prepared in a 500 mL stainless steel autoclave that was also thermostated and mechanically stirred. In this autoclave dry CHO was saturated with CO_2 at the desired conditions. Separation of reaction and feed preparation allowed for a precise control of initial composition, pressure and temperature in the polymerisation and faster injection of the catalyst. In this experimental set-up the catalyst can be injected using CO_2 pressure or as a solution in CHO, depending on the solubility in and reactivity towards CHO. All catalysts were kept under argon during storage and transfer to the polymerisation reactor.

The catalyst was provided by the Polymer Chemistry Group of Eindhoven University of Technology. The complex is a dimeric species containing two silsesquioxane cages bound together by four zinc atoms with the following formula; $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Zn_4Me_4$. For more results and details on the synthesis, characterization and performance of these zinc complexes the reader is referred to Ref. [26]. A typical result obtained with this catalytic system is presented in Fig. 6. The decrease of pressure upon reaction is used to estimate the decrease of CO_2 concentration, which is subsequently interpreted in terms of CO_2 conversion. Analysis of the reaction mixture with ^{1}H NMR after 95 h on-stream results in a calculated CO_2 conversion of 60% with more than 99% CO_2 incorporation and a TON of 458 (mol CO_2 per mol Zn). This is in good agreement with the CO_2 conversion estimated from the decrease of the vapour pressure. Similar experiments suggest that typical deviations between ^{1}H NMR analysis and the estimation using vapour pressure data are smaller than 3%.

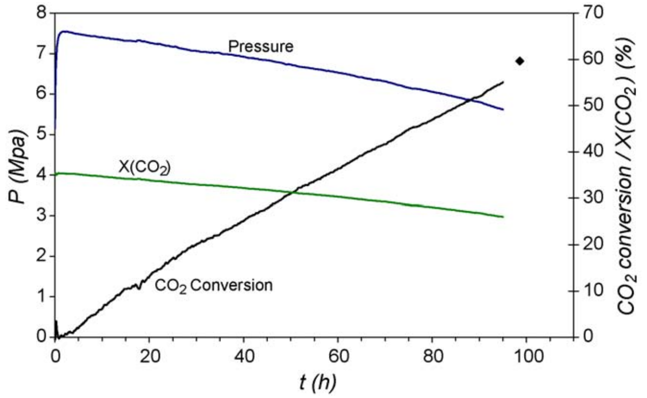

Fig. 6. Determination of composition change and CO_2 conversion from vapour pressure during the copolymerisation of CHO and CO_2. Initial conditions are 389 K and 7.6 MPa.

5. Extraction of residual CHO with supercritical CO_2

In general, monomer conversion in bulk and solution polymerisations becomes more difficult at elevated polymer concentrations as a result of diffusion limitation. If, like in this case, no additional solvent is used, the maximum conversion of both CHO and CO_2 is limited. Although addition of CHO at the

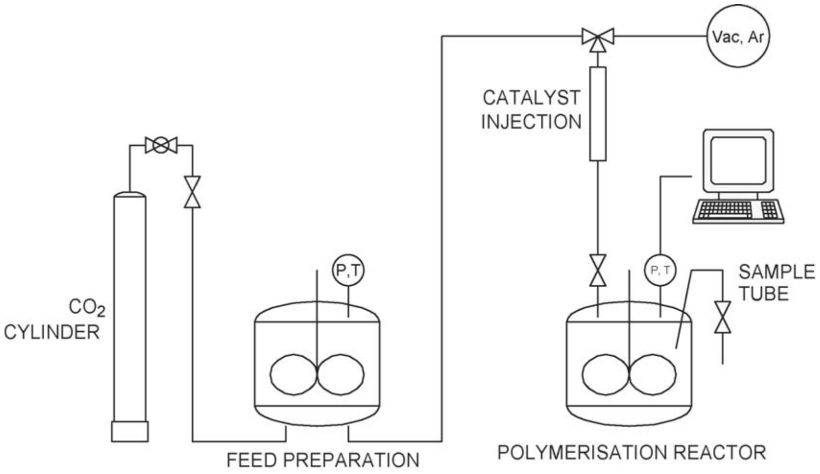

Fig. 5. Schematic outline of the set-up used for the determination of conversion during the copolymerisation of CHO and CO_2.

end of the reaction is expected to further increase the rate of polymerisation, this creates the problem of a significant amount of residual monomer present in the product mixture. In olefin polymerisations increasing the reaction temperature can often increase the reaction rate at high conversions. As most of the catalysts used in this reaction are relatively sensitive to temperature this is not an option. Another method to remove residual monomer from the product stream is by devolatilisation. As CO_2 is gaseous at ambient conditions it can be removed relatively easy by directly venting it to the atmosphere. Probably the major part of CHO can be removed simultaneously with CO_2, especially if this is done at elevated temperatures. In this case polymer foaming and CHO losses to the environment are major concerns for the further development of such a process. Extraction of CHO from the polymer melt is another option. CO_2 would be an ideal extraction medium in this case, because of the difference in solubility of CHO and PCHC. As can be seen in Fig. 2, at pressures below 100 MPa less then 1 wt.% of PCHC dissolves in CO_2 even when CHO concentrations are as high as 24 wt.%. Additionally, CO_2 makes the supercritical region relatively accessible, which results in improved solvent tuneability and transport characteristics. This is especially useful in continuous extraction and the solvent recovery step. Finally, no additional compounds need to be introduced for downstream processing.

In this process counter-current flow in a single screw extruder is used at elevated pressures. Consequently, supercritical CO_2 can be forced to flow over the polymer melt in the opposite direction while extracting CHO from the polymer melt. This is possible because the driving force for transport of the melt is the result of friction forces between the extruder and the polymer melt while the extraction medium flows over the polymer phase as a result of a pressure gradient. This negative pressure gradient requires the formation of two dynamic seals [27]. These can be created by variations in the screw thickness, which locally decrease the void volume and increase the degree of filling in the screw. This is schematically represented in Fig. 7. In this Figure the recycle stream is fed to a flash drum separating the extract in a CHO rich and CHO lean stream. The CHO lean top stream can be subsequently condensed and pumped back to the extraction zone.

Design criteria for such a counter-current extraction zone are developed using a simplified representation of the melt flow in combination with a mass transfer model. As already mentioned, the polymer is transported as a result of frictional forces that induce polymer flow in a direction with a component perpendicular and parallel to the screw. While the parallel component causes transport of the melt through the extruder, the perpendicular component induces circulation of the polymer phase perpendicular to the direction of the polymer flow. As a result, the polymer at the polymer–CO_2 interface is continuously refreshed with polymer from the bulk. The mass transfer model used here assumes that all resistance to mass transport is in the polymer phase, that there is equilibrium at the polymer–CO_2 interface and that there is no diffusion due to concentration gradients in the direction parallel to the screw. The circulation in the polymer phase results in relatively short contact times followed by mixing with the polymer bulk phase. Therefore, penetration theory can be used in combination with an instantaneous transport coefficient that is averaged over the contact time. The dependence of this coefficient on contact time (τ) and the diffusion coefficient of CHO in the polymer melt (D) is expressed by:

$$k = 2\sqrt{\frac{D}{\pi \cdot \tau}} \tag{1}$$

The driving force for transport is the concentration difference between the bulk and surface concentration of CHO. The latter is related to the CHO bulk concentration in CO_2 ($C_{\mathrm{CHO,CO_2}}$) via a volumetric partition coefficient K, quantifying the equilibrium partitioning of CHO over the two phases:

$$N = k\left(C_{\mathrm{CHO,PCHC}} - \frac{C_{\mathrm{CHO,CO_2}}}{K}\right) \tag{2}$$

The values of the parameters required for this extraction model, i.e. K and D, are estimated to have typical values of 0.1 and 10^{-11} m^2/s, respectively. The results of the model calculations suggest that a significant reduction of CHO content in PCHC can be obtained by counter-current extraction in a single screw extruder with technically feasible dimensions. Details on equipment sizing are presented in the following section.

6. Process design for a feasibility study

Within the scope of a feasibility study, the process structure that is suggested here is based on the combined experimental

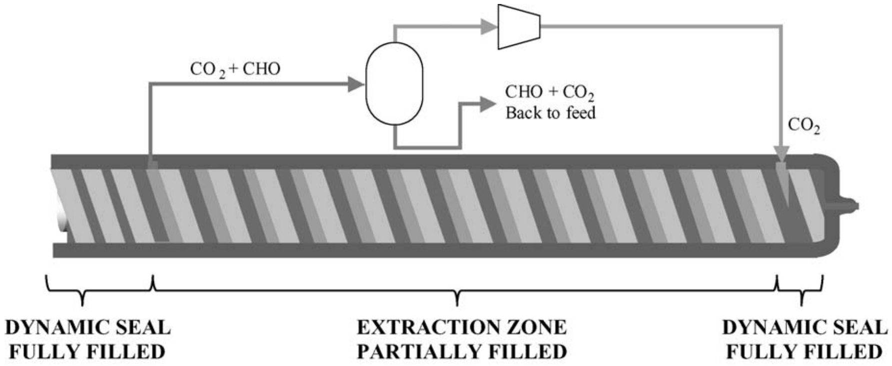

Fig. 7. Schematic representation of a counter-current extraction zone in a single screw extruder.

and theoretical knowledge on the phase behaviour, transport properties, rheology and reaction kinetics of this system. The phase behaviour as it has been addressed above and the lack of experimental evidence regarding the possibility to perform this reaction at high pressures (i.e. above 50 MPa) suggest that this polymerisation should be performed in accordance with typical reaction conditions as found in literature [13–15]. It should also be noted that this is a living polymerisation and consequently the polymer molecular weight distribution strongly depends on the residence time distribution. Therefore, the use of a plug flow reactor is suggested. In practice this could be a tubular reactor containing coils or static mixer elements to improve plug flow characteristics. An advantage of the presence of polymer in the reaction mixture in laminar flow reactors is its shear thinning effect, which significantly narrows the residence time distribution. Moreover, this distribution also becomes narrower due to entrance effects at the beginning of the reactor and after each mixing section. Preliminary calculations suggest that a tubular laminar flow reactor with less than 10 static mixers provides sufficient mixing for the desired control of the residence time. However, at high conversion the polymer concentration increases which causes deterioration of both transport and rheological properties. Diffusion limitation may severely reduce the rate of polymerisation and the increase of viscosity requires increasingly steeper pressure gradients. As in this feasibility study a single screw extruder is applied for the extraction of residual monomer with supercritical CO_2, it is obvious to introduce a mixing zone between the tubular reactor and the extraction zone, also located in the extruder. Because the input of mechanical energy can be very high in extruders, mixing in this zone can be significantly improved. This is expected to decrease the effect of transport limitations and thereby further increase monomer conversion. It should be noted that a similar effect could be obtained by the combination of a gear pump and a series of static mixers.

A schematic outline of the suggested process is presented in Fig. 8 and primarily consists of four stages. After the first stage, in which reactants, catalyst and a recycle stream are mixed, these are introduced into a tubular reactor with plug flow characteristics as described above. In this second stage CHO and CO_2 are converted into PCHC up to intermediate conversions (50%). Further conversion occurs in the first part of an extruder in which mixing is significantly enhanced. In the second part of this extruder unreacted CHO is extracted in counter-current mode with supercritical CO_2. The extractant phase is fed to a flash drum in which it is separated in a CHO rich and CHO lean stream. The CHO lean top stream can be subsequently condensed and pumped back to the extraction zone. The CHO rich stream is fed back to the first stage of the process where it is mixed with catalyst and fresh reactant.

The process as outlined in Fig. 8 is used as a base case scenario for a feasibility study for the design of a new plant with an annual production capacity of 10 kT of PCHC and an operating factor of 8000 h/year. For the evaluation of this process AspenTech software is used. The phase behaviour as presented in Figs. 2 and 3 has been implemented. Reaction rate is assumed to be first order in CHO concentration with an effective rate constant independent of the CO_2 concentration, accounting for a constant catalyst concentration. Rate constants are taken from literature [28], the effect of diffusion limitation is neglected and the catalyst is not recovered. The results of these process simulations in terms of equipment sizing and relevant process flows are summarised in Table 1. The temperature and minimum pressure in both reactor zones are set to 323 K and 0.7 MPa, respectively. Design and sizing of the extraction zone are performed based on the mass transfer model as discussed in the previous section.

7. Process economics

For the construction and start-up of a new plant for the process described in the previous section an economic evaluation is performed using Icarus software from AspenTech. It should be noted that for this economic evaluation the second reaction zone and the extraction zone are combined in one single screw extruder. Taking into account that this is a feasibility study, a new plant with this scale of operation results in a required selling price for PCHC of € 3.6 to € 8.4 per kilo.

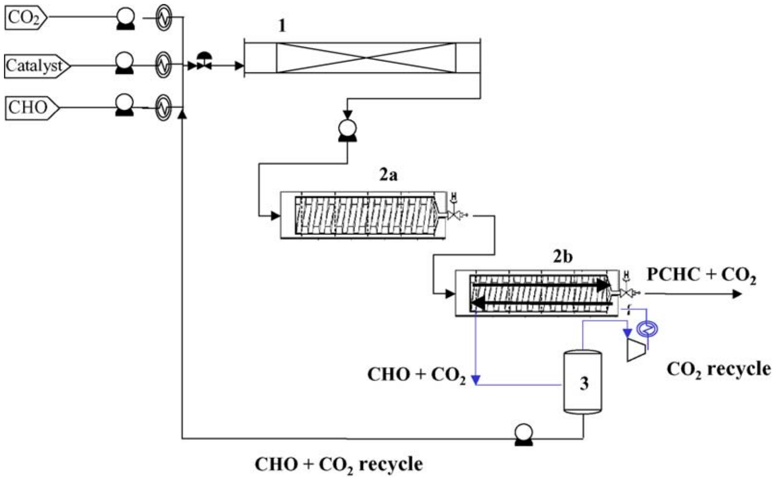

Fig. 8. Schematic process structure including a plug flow reactor (1), extruder reaction zone (2a), extruder extraction zone (2b), flash drum (3) and auxiliary equipment.

Table 1
Summary of results from process simulation, equipment sizing and flow sheet calculations

	Equipment sizing		Process parameters	
Feed to reactor zone			Catalyst	0.24 g/s
			CHO	0.24 kg/s
			CO_2	0.05 kg/s
Recycle to reactor zone			CHO	35 g/s
			CO_2	9.5 g/s
CO_2 recycle to extraction zone				7.0 kg/s
Tubular reactor	Length	90 m	Conversion[a]	50%
	Diameter	0.2 m	Mw	273000 g/mol
	Residence time	2.5 h	PDI	1.1
Reaction zone in single screw extruder	Length	4 m	Conversion[a]	86%
	Diameter	0.2 m	Mw	470000 g/mol
	Residence time	0.7 h	PDI	1.2
Extraction zone in single screw extruder	Length	10 m	$scCO_2$ flow	7.0 kg/s
	Diameter	0.5 m	Polymer flow	0.35 kg/s
	Residence time	7.3 s	CHO content in[b]	10 wt%
	Pressure	15 MPa	CHO content out[b]	0.5 wt%

[a] Conversion based on PCHC yield from CHO.
[b] CHO content expressed relative to PCHC.

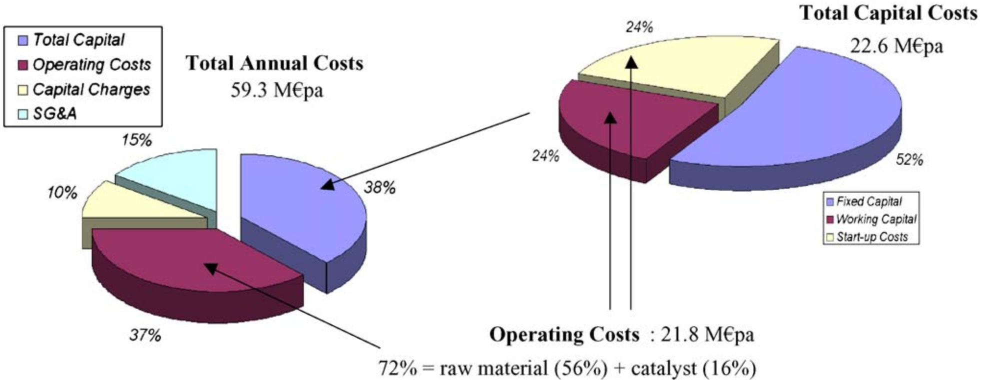

Fig. 9. Relative contribution of total capital and operating costs to the required selling price of PCHC.

This price accounts for a 15% charge for sales and capital charges based on a return on investment (ROI) of 15%. As can be seen in Fig. 9, the operating costs consist for 56% and 16% of raw material and catalyst costs, respectively. The costs for catalyst production include labour, equipment and ingredient costs and amount to € 239, per kilo in total. The operating costs and capital costs contribute about equally to the required selling price of PCHC. It should be noted that working capital and start-up capital are directly related to the operational costs and make up 50% of all the capital costs. In summary, the costs of catalyst and raw materials have a disproportionate effect on the required selling price relative to the costs of fixed capital.

A reduction of the costs of CHO and catalyst synthesis would significantly reduce the required selling price of PCHC. The current estimated price of PCHC places it between engineering and specialty polymers. The lower side of the price range corresponds to current market prices for polyurethanes, while the upper part of this range corresponds to the market price of poly(acrylic acid), polycaprolactone and copolymers of methylmethacrylate.

8. Conclusions

A feasibility study for a preliminary process design for the catalytic conversion of cyclohexene oxide and carbon dioxide into poly(cyclohexene carbonate) is performed. For this purpose a comprehensive treatment of the low- and high-pressure phase behaviour, reaction rate and downstream removal of residual cyclohexene oxide from the product stream is given. A design for such a process is suggested, which has served as a basis for a technical and economical evaluation. In contrast to supercritical CO_2, CHO is a very good solvent for PCHC. Therefore, the process is based on a polymerisation in an excess of CHO. Because of the importance of the residence time distribution on the product characteristics, a tubular laminar flow reactor is used in combination with static mixers for polymerisation up to intermediate CHO conversion. For the removal of unreacted

CHO a counter-current extraction zone in a single screw extruder is suggested. As extractant supercritical CO_2 can be used and a polymerisation zone can be integrated in the extruder to overcome diffusion limitations. An economic evaluation of the construction, start-up and operation of such a process indicates that the required selling price of PCHC is between the market price of engineering and specialty polymers.

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