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CeO_2-catalyzed synthesis of 5-membered cyclic carbonates from CO_2 and diols

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ABSTRACT

All the environmental issues related to greenhouse gases have led to a huge improvement of the research about CO_2 capture and utilization over the last decades. Carbon dioxide, due to the wide availability and the non-toxicity, is a suitable feedstock material for producing chemicals and its non-reductive conversion allows the synthesis of different organic compounds like methane, methanol, urea and carbonates.

The latter class has many applications in chemical industry, such as solvents in liquid-liquid extractions or electrolytes for secondary batteries.
A new eco-friendly process is the synthesis of cyclic carbonates from CO_2 and diols using cerium oxide, or ceria, as catalyst. The equilibrium limitation given by the formation of water as product can be avoided exploiting a dehydrating agent, like 2-cyanopyridine.

In this work, the synthesis of two different 5-membered cyclic carbonates, styrene and 1,2-butylene carbonates, starting from styrene glycol and 1,2-butanediol respectively, was detected.
At first, reactions with different conditions were performed in order to study the influence of time and temperature.
Results for the former substrate did not show yields high enough to justify a pursuing of the research.
As regards the latter, instead, great conversions can be achieved even for low temperatures.
Afterwards, two different parameters were investigated for the butylene carbonate synthesis: the amount of dehydrating agent and the CO_2 pressure.
An excess of dehydrant is required for obtaining good yields, but a ratio of 2:1 compared to diol is a sufficient trade-off.
The study also showed that a decrease of the pressure leads to an improvement of the process.

Overall, while the synthesis of styrene carbonate is not a suitable option at the moment, butylene carbonate has a great potential due to the opportunity of obtaining remarkably high yields also for short reaction times and relatively low temperatures.

SOMMARIO

L’inesorabile aumento della quantità di gas serra presenti nella nostra atmosfera ha portato a un importante sviluppo della ricerca riguardante la cattura e l’utilizzo di CO_2 negli ultimi decenni. L’anidride carbonica, grazie all’abbondante disponibilità e alla non tossicità, risulta essere una risorsa ideale per la produzione di sostanze chimiche e la sua conversione non-riducente permette la sintesi di composti organici quali metano, metanolo, urea e carbonati.

Quest’ultimi sono coinvolti in numerose applicazioni dell’industria chimica, in particolare come solventi nelle estrazioni liquido-liquido o come elettroliti nelle batterie.

Un processo innovativo e sostenibile è la sintesi di carbonati ciclici a partire da dioli e CO_2, sfruttando come catalizzatore l’ossido di cerio, o ceria. Il limite di resa causato dalla formazione di acqua può essere superato mediante l’utilizzo di agenti deidratanti, come la 2-cianopiridina.

In questo studio è stata investigata la sintesi di due diversi carbonati ciclici a 5 membri, stirene e butilene carbonato, utilizzando come substrati 1-fenil-1,2-etandiolo e 1,2-butandiolo, rispettivamente.
Inizialmente è stata studiata l’influenza di temperatura e tempo di reazione effettuando prove a diverse condizioni.
I risultati relativi al primo reagente non sono stati sufficientemente positivi da giustificare un prosieguo della ricerca.
Per quanto riguarda il secondo, invece, sono state raggiunte ottime conversioni anche a basse temperature.

Due ulteriori parametri sono stati investigati per quanto riguarda la sintesi di butilene carbonato: la quantità di agente deidratante e la pressione di CO_2.
Per ciò che riguarda il primo è stata confermata la necessità di un eccesso rispetto al diolo, ma un rapporto di 2:1 risulta essere un buon compromesso tra resa e costi.
L’analisi ha dimostrato, inoltre, che al diminuire della pressione di CO_2 aumenta la quantità di prodotto sintetizzato.

In conclusione, mentre la sintesi di stirene carbonato non risulta, al momento, una strada percorribile, quella di butilene carbonato sembra avere un potenziale notevole, grazie alle elevate rese raggiungibili anche per brevi tempi di reazione e temperature relativamente basse.

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ACRONYMS / ABBREVIATIONS

1,2-BD	1,2-butanediol
2-CP	2-cyanopyridine
BC	Butylene carbonate
BET	Brunauer - Emmett - Teller
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
COP	Conference of parties
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
DMSO	Dimethyl sulfoxide
EDLC	Electric double layer capacitor
EOR	Enhanced oil recovery
FID	Flame ion detector
GC	Gas chromatography
GHG	Greenhouse gases
IEA	International Energy Agency
MEA	Monoethanolamine
MOFs	Metal organic frameworks
NMR	Nuclear magnetic resonance
PA	Picolinamide
PM	Particulate matter
OSC	Oxygen storage capacity
RWGS	Reverse water gas shift
SA	Sigma-Aldrich
SC	Styrene carbonate
SG	Styrene glycol
TBAB	Tetrabutylammonium bromide
TCI	Tokyo Chemical Industry
TMS	Tetrametylsilane
XRD	X-ray diffraction

RIASSUNTO

I – INTRODUZIONE

I.I – CO_2 ed effetto serra

L'anidride carbonica, gas naturalmente presente all'interno dell'atmosfera terrestre a causa di eruzioni vulcaniche, scambio con l'oceano e respirazioni animali e vegetali, rientra in ciò che è definito ciclo del carbonio. Tale fenomeno è rimasto in equilibrio fino all'avvento della rivoluzione industriale, quando il crescente uso di combustibili fossili lo ha destabilizzato. Da allora, l'aumento della quantità di CO_2 nel nostro pianeta non si è mai arrestato e nel 2022 le emissioni antropiche hanno raggiunto valori vicini alle 36 Gt.
Per questo motivo, oggigiorno l'anidride carbonica è universalmente riconosciuta come maggiore rappresentante dei gas serra, i quali devono il nome al catastrofico fenomeno a cui hanno dato vita. L'effetto serra consiste nell'intrappolamento delle radiazioni infrarosse emesse dalla riflessione della luce solare da parte della superficie terrestre a causa dell'eccessiva presenza di tali gas nella nostra atmosfera. Questa mancata fuoriuscita comporta un accumulo di calore e, quindi, un progressivo aumento della temperatura media dell'intero pianeta. Al momento questo incremento è pari a circa 1 °C rispetto al periodo preindustriale ed è destinato ad aumentare.

Per mettere un freno a questo fenomeno, le maggiori potenze mondiali hanno siglato una serie di accordi internazionali volti a limitare le emissioni di gas serra. Il più importante, stipulato a Parigi nel 2015 e attualmente in vigore, si è posto come obiettivo il mantenimento dell'aumento della temperatura media al di sotto dei 2 °C rispetto al periodo preindustriale.
Per raggiungere questo traguardo, tutte le attività antropiche devono subire un processo di decarbonizzazione. In questo panorama l'industria gioca un ruolo fondamentale, contribuendo al 28,9% delle emissioni totali, e in particolare quella chimica risulta essere il primo settore per consumo energetico e il terzo per emissioni totali.

Immaginare un'industria chimica priva di prodotti a base di carbonio, tuttavia, è un qualcosa di irrealizzabile. Per questo motivo, si parla prettamente di una riduzione delle emissioni di gas serra e di un processo di defossilizzazione, il quale consiste nel ricavare il carbonio da fonti diverse da quelle fossili. A questo scopo, le tre strade perseguibili sono tre:

- **Cattura e Stoccaggio del Carbonio (CCS)**: questa tecnologia consiste nell'intrappolamento della CO_2 emessa all'interno di giacimenti sotterranei.
- **Cattura e Utilizzo del Carbonio (CCU)**: tale metodo prevede l'utilizzo del carbonio presente nella CO_2 come fonte alternativa a quello derivante da combustibili fossili.
- **Biomassa**: simile alla CCU, prevede lo sfruttamento del carbonio contenuto in composti biodegradabili.

I primi due approcci sono accomunati da quello che è il sequestro della CO_2. Quello post-combustione può essere realizzato attraverso quattro processi principali.
Il primo è l'assorbimento chimico, il quale sfrutta l'affinità del gas con solventi liquidi, solitamente monoetanolammina o idrossidi, all'interno dei quali viene dissolto.
Un secondo metodo è l'adsorbimento su materiali porosi quali zeoliti, carbone attivo o strutture metallorganiche (MOFs).
Esistono, infine, due tecnologie meno sviluppate, vale a dire la separazione attraverso membrane e quella criogenica, la quale sfrutta cicli di refrigerazione e condensazione.

I.II – Cattura e Utilizzo del Carbonio (CCU)

Tra le strade sopra elencate per la riduzione dei gas serra, sebbene non preveda una rimozione totale della CO_2, la CCU è quella che ha suscitato maggiore interesse nel mondo nella ricerca negli ultimi anni, grazie alla sua stabilità a lungo termine e al fatto che può essere considerata parte di un'economia circolare.

Anche in questo caso, le varie tecnologie esistenti per l'utilizzo dell'anidride carbonica possono essere classificate in quattro categorie: fisico, biologico, per la mineralizzazione e chimico.

All'interno della prima classe rientrano gli utilizzi nel campo petrolifero, per il recupero terziario dai giacimenti o per la loro frattura, e nel campo alimentare, per le bevande gassate o per la conservazione degli alimenti.

L'utilizzo biologico consiste nello sfruttamento dell'anidride carbonica per la simulazione del processo di fotosintesi, come fertilizzante per le piante o come fonte di crescita per microalghe che possono essere convertite, in un secondo momento, in biocombustibili.

La mineralizzazione è una tecnologia che sfrutta la reazione tra la CO_2 e composti minerali per la formazione di precipitati, i quali possono essere poi impiegati come materiali da costruzione.

L'ultima categoria, infine, è probabilmente quella più comune. Essa sfrutta l'anidride carbonica come risorsa per la produzione di altre sostanze, le quali possono essere prodotti chimici, materiali polimerici o biocombustibili. Non costituisce, tuttavia, una strada per la decarbonizzazione, a causa dell'energia richiesta per le trasformazioni e il fatto che la maggior parte dei prodotti ritornerà ad essere, in un tempo più o meno lungo, CO_2.
I composti più importanti che vengono sintetizzati mediante questa tecnologia sono:

- **Metano**: è il componente principale del gas naturale e ha un ruolo fondamentale sia nell'industria sia per la società in generale, essendo la fonte più utilizzata per il riscaldamento.
  Può essere prodotto mediante il processo di metanazione, nel quale l'anidride carbonica reagisce con 4 moli di idrogeno per formare metano e acqua. Si tratta di una reazione fortemente esotermica, catalizzata solitamente da metalli nobili, come rutenio e rodio, o da sistemi a base di nichel.

- **Metanolo**: si tratta di un composto chiave per l'industria chimica per le sue applicazioni come solvente, nelle celle a combustibile o nella sintesi di acido acetico e formaldeide. Si può ricavare dall'idrogenazione della CO_2, ma è necessario utilizzare catalizzatori con un'elevata selettività per evitare la reazione di *water gas shift*, la quale porta alla formazione di monossido di carbonio. I sistemi catalitici più efficaci sono a base di rame supportato su ZrO_2.
  Anche dal monossido, tuttavia, si può arrivare, in seguito a una nuova idrogenazione, alla sintesi di metanolo.

- **Urea**: circa il 75% della produzione annuale utilizza l'anidride carbonica come base di partenza, sfruttando la sua reazione con ammoniaca e la successiva deidratazione del carbammato di ammonio.

- **Syngas**: è una miscela di gas, solitamente monossido di carbonio e idrogeno, largamente utilizzata come combustibile nelle turbine o come prodotto chimico di partenza per i processi Fischer-Tropsch. Si ricava dal cosiddetto *dry reforming* del metano. I catalizzatori più sfruttati sono metalli nobili supportati su allumina o MgO, e il loro ruolo è fondamentale per evitare il fenomeno del *coking*, vale a dire la formazione di filamenti di carbone solido che vanno a inibire l'attività catalitica.

Altri due processi che rientrano nella CCU sono la riduzione elettrochimica e fotochimica della CO_2. Queste tecnologie sfruttano l'energia elettrica e la luce del sole come innesco di reazioni redox per la riduzione del diossido di carbonio e la conseguente produzione di composti quali metano, metanolo, monossido di carbonio e acido formico. Sebbene siano strade molto innovative e aventi un enorme potenziale, non risultano ancora economicamente convenienti e richiedono investigazioni e ottimizzazioni per migliorarne l'efficienza.

In generale, i processi appena descritti possono essere suddivisi in due macrocategorie: riducenti e non-riducenti.
I primi implicano un cambio dello stato di ossidazione del carbonio, come l'idrogenazione o la riduzione elettrolitica.
I secondi, invece, consistono nell'incorporazione della CO_2 all'interno di altre strutture chimiche. L'energia richiesta per questo tipo di trasformazioni è sensibilmente inferiore alle precedenti. Uno dei processi inclusi in questa categoria è la sintesi di carbonati organici a partire da anidride carbonica.

I.III – Carbonati organici

I carbonati organici sono una classe di composti protagonista di numerose applicazioni nell'industria chimica. Ne esistono diverse tipologie, ma la classificazione più importante è quella tra carbonati lineari e ciclici.

I carbonati lineari e in particolare i suoi due maggiori rappresentanti, il dimetil e il dietil carbonato (DMC e DEC), sono largamente utilizzati come additivi per combustibili o come solventi per estrazioni e sintesi.

I carbonati ciclici, invece, oltre all'utilizzo come solventi, sono impiegati nella sintesi di materiali polimerici, come additivi nei cosmetici e, soprattutto, all'interno delle batterie a ioni di litio e nei supercondensatori.

Il metodo più classico per la sintesi di carbonati organici prevede l'utilizzo di fosgene ($COCl_2$) e di suoi derivati come reagenti di partenza. Sebbene questo metodo garantisca la possibilità di produrre quasi tutti i tipi di carbonati, le sostanze coinvolte sono altamente tossiche e il loro utilizzo costituisce un serio rischio dal punto di vista operativo e ambientale. Per questo motivo c'è stato un progressivo abbandono della fosgenazione negli ultimi anni.

Una seconda tecnica è la carbonilazione ossidativa di alcoli e fenoli, principalmente usata per la sintesi di carbonati dialchilici. Essa sfrutta la reazione tra il monossido di carbonio e composti metallici derivanti dall'ossidazione di sali e gruppi alcolici.

I carbonati organici possono essere ricavati anche dall'urea, grazie alla sua reazione catalizzata con alcoli. Tale processo porta alla formazione di ammoniaca, la quale può essere riciclata nella sintesi dell'urea stessa come visto nella sezione precedente, rendendo tale sintesi una trasformazione indiretta dell'anidride carbonica.

Un'ulteriore tecnologia classificabile come CCU, la quale ha suscitato un enorme interesse nel mondo della ricerca negli ultimi anni, è la cicloaddizione di CO_2 a epossidi e ossetani. Essa porta alla formazione di carbonati ciclici a 5 e 6 membri, rispettivamente. Numerosi sistemi catalitici sono stati investigati per tale processo, tra i quali ossidi e sali metallici, liquidi ionici, zeoliti e organocatalizzatori.

Quest'ultimo processo è utilizzato per la sintesi di numerosi carbonati ciclici a 5 membri, tra cui stirene carbonato e butilene carbonato.
Il primo è un carbonato aromatico sfruttato principalmente come elettrolita in batterie alcaline e a ioni di litio, grazie alla sua elevata polarità, e come reagente di base per la produzione di dioli vicinali, poliuretano, policarbonati e polioli.
Il secondo, invece, è un carbonato alifatico avente caratteristiche importanti quali un elevato punto di fiamma e una polarità pronunciata. Per questo motivo viene solitamente utilizzato come solvente per le estrazioni e, soprattutto, all'interno di celle elettrolitiche e supercondensatori.

I.IV – Obiettivo del progetto

Il presente lavoro di tesi è basato su un metodo innovativo per la sintesi di carbonati ciclici a partire da anidride carbonica e dioli, protagonista della ricerca del gruppo guidato dal prof. Tomishige da diverso tempo. Questo processo fa dell'ecosostenibilità la sua principale caratteristica. Essa è dovuta a due fattori: il primo è legato al fatto che l'unico prodotto di reazione, oltre al carbonato, è l'acqua. Il secondo, invece, è la possibilità di ottenere i dioli direttamente a partire dalla biomassa.

Dalla carbossilazione di 1,2- e 1,3-dioli, catalizzata da ossido di cerio (CeO_2), o ceria, è possibile ottenere carbonati ciclici a 5 e 6 membri, rispettivamente.

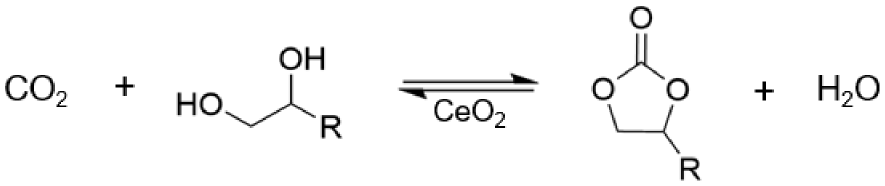


Figura I – Reazione di sintesi di carbonati ciclici a partire da CO_2 e dioli

Il problema principale di tale processo è legato all'equilibrio, quasi totalmente spostato verso i reagenti. Esso comporterebbe delle rese basse in condizioni normali. Per ovviare a tale inconveniente, si sfrutta l'effetto di sostanze azotate, in particolare 2-cianopiridina e 2-furonitrile, le quali, reagendo con l'acqua generata nella reazione principale, vanno a formare ammidi. Questo permette il consumo di un prodotto e il conseguente miglioramento della sintesi di carbonato. L'idratazione della 2-cianopiridina a picolinamide è mostrata in **Figura II**.

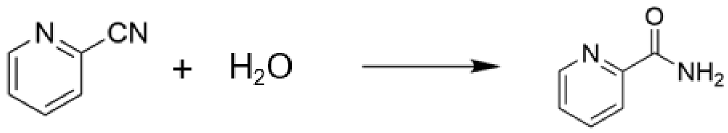


Figura II – Reazione di idratazione della 2-cianopiridina

Come già accennato in precedenza, il sistema catalitico utilizzato è costituito da ossido di cerio. Tale composto risulta essere particolarmente efficace, soprattutto grazie alla sua *oxygen storage capacity*, cioè la capacità di immagazzinare ossigeno e rilasciarlo in un secondo momento. Esso possiede, inoltre, dei siti acido-base utili all'adsorbimento dei gruppi ossidrilici.

Grazie a precedenti studi è stato dimostrato che la parte attiva di questo catalizzatore è quella cristallina e non quella amorfa. Per tale motivo, la forma calcinata risulta essere più efficace per tale processo. In particolare, i migliori risultati in termini di resa e selettività sono stati ottenuti in seguito a calcinazione a 800 K per 3 ore, la quale risulta un buon compromesso tra cristallinità e area superficiale.

L'obiettivo del progetto è lo studio e l'ottimizzazione della sintesi di due diversi carbonati ciclici, lo stirene carbonato e il butilene carbonato, a partire da 1-fenil-1,2-etandiolo e 1,2-butandiolo, rispettivamente. Le reazioni coinvolte sono mostrate di seguito.

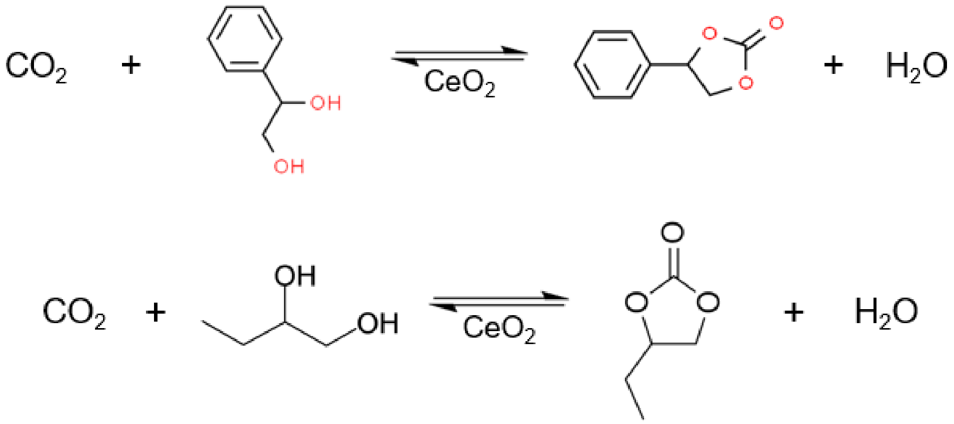


Figura III – Reazioni di sintesi di stirene carbonato **(a)** e butilene carbonato **(b)**

Come agente deidratante è stata utilizzata 2-cianopiridina, mentre come catalizzatore l'ossido di cerio.

In particolare, l'attenzione è stata rivolta all'influenza sulla resa in carbonato di quattro parametri: temperatura e tempo di reazione, quantità di 2-cianopiridina e pressione di CO_2.

I prodotti di reazione sono stati analizzati e quantificati mediante due tecniche analitiche strumentali: la gas cromatografia e la spettroscopia di risonanza magnetica nucleare (NMR).

II – SEZIONE SPERIMENTALE

Tutte le prove sperimentali sono state realizzate utilizzando un reattore sigillato avente un volume di 190 mL, al cui interno sono stati inseriti: 2 mmol di CeO_2 (0,34 g), 12,5 mmol di diolo, 100 mmol di acetonitrile, avente la funzione di solvente, e una quantità variabile di 2-cianopiridina.
Dopodiché, è stato pressurizzato con anidride carbonica e riscaldato fino al raggiungimento della temperatura desiderata, mantenendo attiva l'ancoretta magnetica per la miscelazione a una velocità di 250 rpm. La temperatura è stata monitorata costantemente attraverso una termocoppia inserita in un apposito foro all'interno del reattore.
A reazione conclusa e dopo aver raffreddato a temperatura ambiente, i prodotti sono stati recuperati utilizzando circa 20 g di etanolo.

Per la preparazione dei campioni destinati alla gas cromatografia, è stata aggiunta una quantità nota di 1-esanolo come standard interno (circa 0,4 g) e il tutto è stato filtrato per separare il catalizzatore dal liquido.

Per la spettroscopia NMR, invece, sono stati utilizzati circa 0,15 g di DMSO come standard interno e, dopo aver filtrato, circa 0,3 g di soluzione finale sono stati mescolati con metanolo-d_4, usato come solvente per la determinazione.
L'introduzione di una seconda tecnica analitica si è rivelata necessaria per la valutazione della sintesi di butilene carbonato. Dalle determinazioni gas cromatografiche, infatti, i picchi caratteristici di carbonato e di 2-cianopiridina sono risultati sovrapposti (**APPENDIX A**). Nonostante i diversi tentativi utilizzando colonne diverse o variando la rampa di riscaldamento durante l'analisi, non è stato possibile ottenere una separazione. La spettroscopia NMR, quindi, è risultata il modo più efficace per una valutazione robusta e accurata del processo di sintesi.

Come già accennato, per la valutazione quantitativa dei prodotti di reazione è stato sfruttato il metodo dello standard interno, il quale consiste nell'addizionare al campione una quantità nota di standard, il quale avrà un suo picco all'interno dello spettrogramma. Essendo le aree dei picchi legate alle concentrazioni, effettuando una semplice proporzione è possibile risalire alla quantità dei prodotti incogniti.

Ogni sostanza interagisce a suo modo con lo strumento e per questo sono necessari dei fattori correttivi per ottenere un'analisi accurata.
Per quanto riguarda la spettroscopia NMR, l'area dei picchi è proporzionale al numero dei protoni contenuti nel composto.
Per la gas cromatografia, invece, per ogni sostanza è necessario individuare una costante caratteristica della dipendenza lineare tra concentrazione e area dei picchi. Per fare ciò, sono state realizzate delle rette di taratura preparando campioni contenenti quantità note del composto. Dopodiché, i risultati ottenuti dall'analisi sono stati interpolati ed è stata ricavata la costante, coincidente con la pendenza della retta ottenuta.

III – RISULTATI

III.I – Stirene Carbonato

Una prima analisi della sintesi di stirene carbonato è stata realizzata andando a variare i due parametri principali: tempo e temperatura di reazione. Le reazioni sono state eseguite utilizzando 1-fenil-1,2-etandiolo di due diversi produttori, *Tokyo Chemical Industry* e *Sigma-Aldrich*. Questo cambiamento è risultato necessario a causa dell'impossibilità di reperire, al momento delle prove, il reagente utilizzato per i test iniziali.

Per investigare l'influenza della temperatura, sono stati effettuate prove a 110, 130 e 150 °C mantenendo costanti il tempo di reazione, la quantità di 2-cianopiridina e la pressione di CO_2, pari rispettivamente a 24 ore, 50 mmol e 5 MPa. Per il secondo reagente, quello della compagnia *Sigma-Aldrich*, è stata aggiunta anche una quarta prova a 180 °C.

I grafici (**Figura IV-V**) mostrano tre aspetti importanti di questo processo. Il primo è una dipendenza dalla temperatura, il cui aumento comporta un miglioramento in termini di resa in carbonato. Il secondo, più penalizzante ai fini dello studio, è un'efficienza di reazione molto bassa. Per entrambi i reagenti, infatti, la conversione del diolo è molto limitata e si arriva, nelle prove a 150 °C, a valori di resa pari al 7,7% circa. Il terzo, infine, è legato alla natura dei due substrati. Per le prove a temperature più basse, infatti, i valori di resa sono sostanzialmente diversi, in particolare risultano essere inferiori per i test realizzati con il reagente *Sigma-Aldrich*. Questa differenza si va poi ad appianare all'aumentare della temperatura. Una possibile spiegazione di questo comportamento è che la maggiore purezza del composto targato *TCI*, superiore al 98% contro il 97% dell'altro, abbia facilitato l'innesco della reazione in condizioni di temperatura più basse.

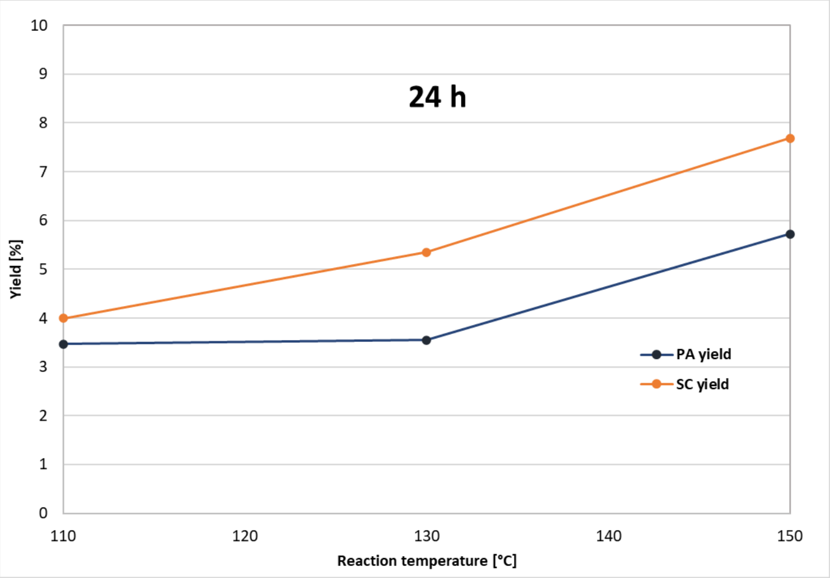


Figura IV - Resa in stirene carbonato (SC) e picolinamide (PA) al variare della temperatura per il reagente *TCI*

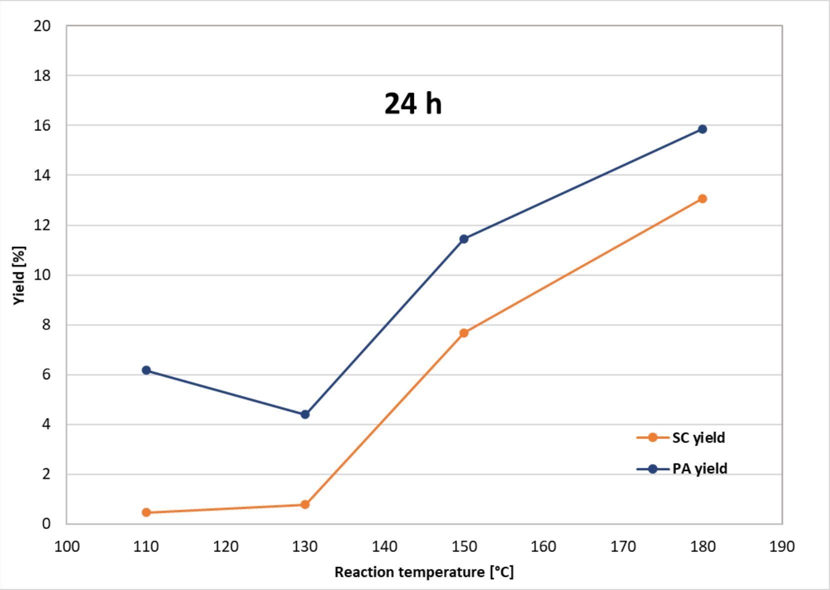


Figura V - Resa in stirene carbonato (SC) e picolinamide (PA) al variare della temperatura per il reagente *Sigma-Aldrich*

Il secondo parametro investigato è stato il tempo di reazione. Fissando la temperatura a 130 °C, sono state effettuate prove della durata di 36 e 48 ore. In questo caso è stato utilizzato soltanto il substrato della *Sigma-Aldrich*. I risultati sono mostrati in **Figura VI**.

Anche in questo frangente, nonostate un miglioramento all'aumentare del tempo di reazione, la resa in carbonato è risultata tutt'altro che positiva, con un valore massimo pari al 4% per il test più lungo, dimostrando l'influenza minima di questo parametro sulle sorti del processo.

I dati ottenuti hanno portato alla scelta di non proseguire ulteriormente le analisi sulla sintesi di stirene carbonato, essendo i risultati non abbastanza promettenti nonostante le condizioni di reazione dispendiose in termini di tempo e, soprattutto, di energia necessaria al raggiungimento e al mantenimento di determinate temperature.

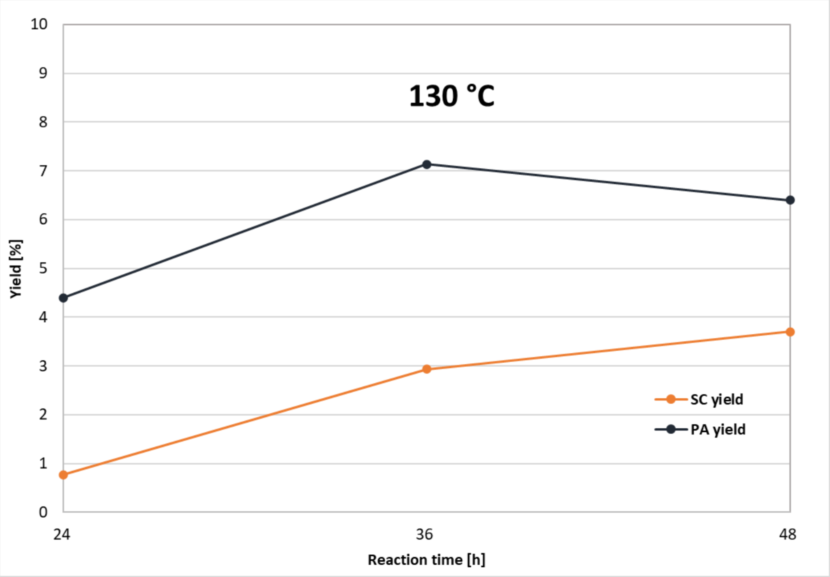


Figura VI - Resa in stirene carbonato (SC) e picolinamide (PA) al variare del tempo di reazione

III.II – Butilene Carbonato

Lo stesso approccio è stato adottato per lo studio della seconda sintesi. Un primo set di esperimenti è stato realizzato mantenendo costante il tempo di reazione (1 ora), la quantità di agente deidratante e la pressione, ma andando a variare progressivamente la temperatura. In particolare, quest'ultima è stata fissata a 70, 90, 110 e 130 °C.

I risultati hanno subito messo in luce la forte influenza che ha questo parametro sulle sorti del processo. Mentre a 70 °C la reazione non sembra avvenire, o almeno non in maniera quantificabile attraverso le misurazioni, a 130 °C risulta estremamente rapida. È stata registrata, infatti, una conversione superiore al 97%, nonostante il ridotto tempo di reazione. Tale risultato è senza dubbio ottimale dal punto di vista del processo in generale, in quanto dimostra una fattibilità reale della sintesi. Tuttavia, per quanto riguarda lo scopo della ricerca, una conversione estremamente alta non avrebbe permesso una comprensione adeguata dell'influenza dei parametri di reazione e per questo motivo è stata presa la decisione di proseguire lo studio con test aventi tempi di reazione maggiori (2, 4, 8 e 24 ore) soltanto alle due temperature intermedie e con un terzo valore, aggiunto in un secondo momento, pari a 100 °C.

Dai grafici (**Figura VII-VIII-IX**) è possibile notare quanto l'efficienza del processo cresca all'aumentare dei due parametri investigati.
Per i test effettuati a 90 °C, la dipendenza, sia della resa in carbonato sia di quella in picolinamide, ha un andamento quasi lineare. L'analogia tra i due trend dimostra la reale efficacia della 2-cianopiridina in termini di consumo dell'acqua generata. Nonostante ciò, andando ad analizzare la produttività di carbonato, 90 °C risulta essere un valore non sufficientemente alto, essendo la conversione massima raggiunta, per la prova più lunga, pari ad appena il 63%.
Passando a una temperatura leggermente superiore, 100 °C, si nota un comportamento differente. In questo caso, i livelli di resa raggiunti hanno subito variazioni molto più significative soprattutto per tempi di reazioni più bassi. Questa esplosione inziale si attenua con il tempo, ma in ogni caso il valore di resa massimo per questo set di esperimenti risulta essere, per la prova più lunga, di poco inferiore al 96%. In termini di prodotto sintetizzato, la stessa quantità di carbonato generata in 24 ore utilizzando una temperatura di 90 °C (di poco inferiore a 8 mmol) è stata superata, in questo caso, in un terzo del tempo. Dal grafico in **Figura VIII** si può notare anche un punto in corrispondenza di un tempo di reazione pari a 0 ore. Questo dato è stato raccolto andando a raffreddare il reattore non appena è stata raggiunta la temperatura prestabilita.
L'ultimo valore di temperatura investigato, 110 °C, ha confermato la forte dipendenza del processo da tale parametro. La resa in carbonato risulta superiore all'80% perfino dopo 1 ora e quasi la stessa quantità sintetizzata in 24 ore a 100 °C è stata prodotta, in questo caso, in un sesto del tempo.

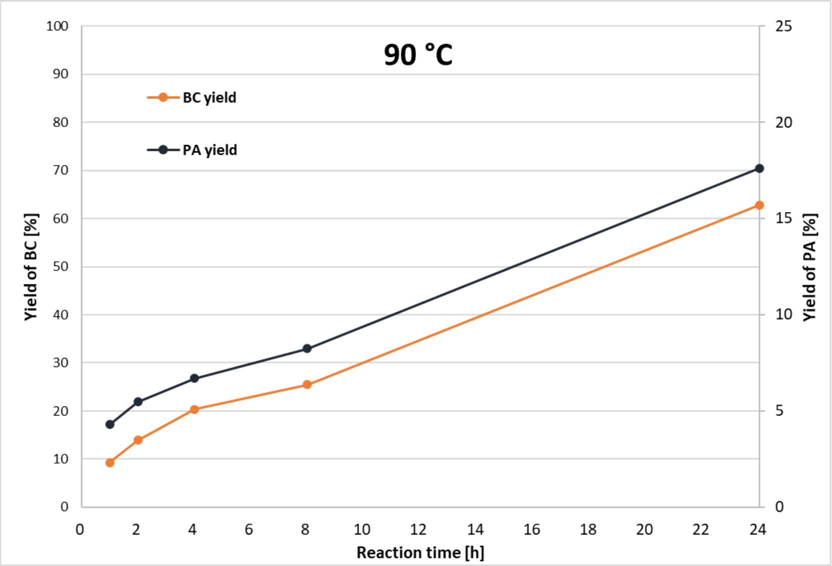


Figura VII - Resa in butilene carbonato (BC) e picolinamide (PA) a 90 °C al variare del tempo di reazione

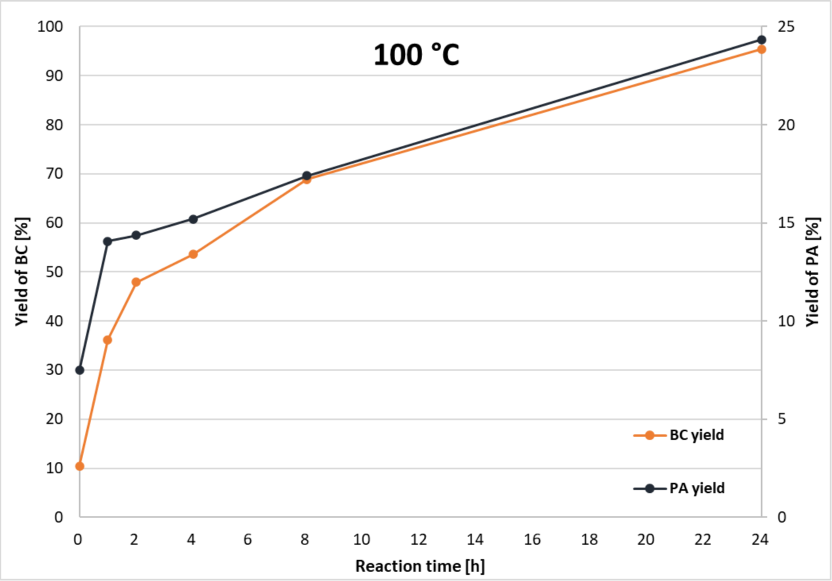


Figura VIII - Resa in butilene carbonato (BC) e picolinamide (PA) a 100 °C al variare del tempo di reazione

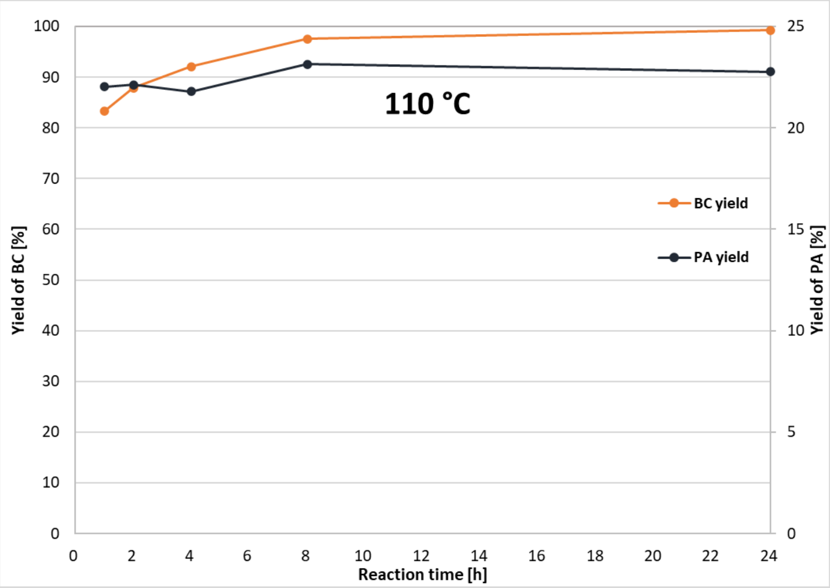


Figura IX - Resa in butilene carbonato (BC) e picolinamide (PA) a 110 °C al variare del tempo di reazione

Questi risultati mettono in mostra quello che è il fattore determinante per un'efficace sintesi di butilene carbonato, vale a dire la temperatura di reazione. Tale importanza si può notare, con maggiore evidenza, nel grafico in **Figura X**.

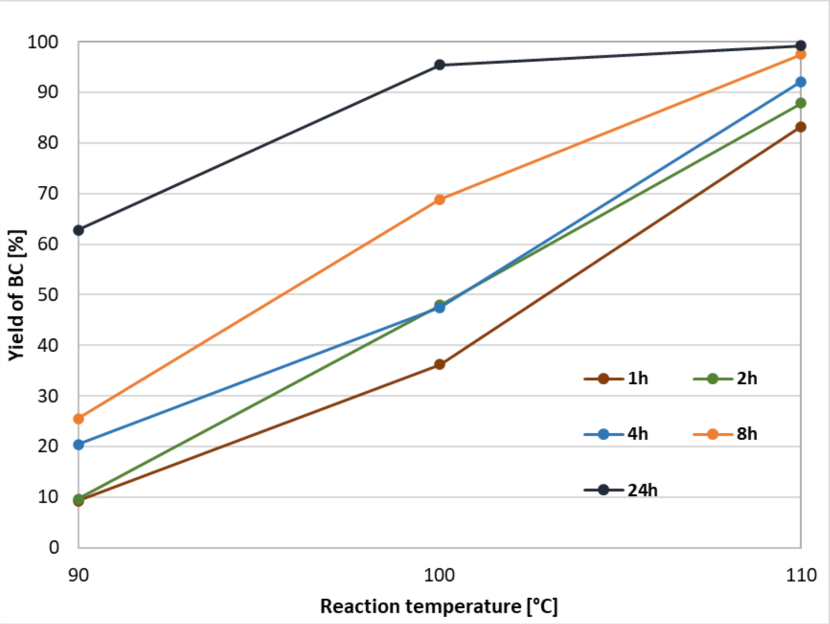


Figura X - Resa in butilene carbonato (BC) per diversi tempi di reazione al variare della temperatura

Mentre per i due valori più bassi di temperatura il tempo di reazione costituisce ancora un parametro importante per l'ottenimento in una resa in carbonato elevata, incrementando la temperatura a 110 °C i valori tendono ad avvicinarsi tra loro in maniera sostanziale, dimostrando la presenza di una reazione molto rapida.

Tuttavia, così come spiegato in precedenza per l'esclusione delle prove a 130 °C, i successivi test per lo studio dell'influenza dei due parametri rimanenti, la quantità di 2-cianopiridina e la pressione di CO_2, sono state realizzati a una temperatura di 100 °C, in modo da non ottenere dei valori di resa troppo elevati che non avrebbero permesso l'individuazione della reale importanza dei fattori sopra citati per il processo di sintesi.

Come illustrato nel capitolo **I.IV**, sebbene la reazione teorica preveda una quantità stechiometrica di diolo e 2-cianopiridina, in questa tipologia di processo si tende a lavorare con un eccesso di composto azotato (4:1). Tuttavia, essendo dispendioso in termini economici, una sua riduzione gioverebbe in modo sostanziale al processo, rendendolo molto più redditizio. Per valutare la fattibilità di questa condizione, sono state realizzate delle prove diminuendo la quantità di 2-cianopiridina, pari inizialmente a 50 mmol, del 50% e del 75%, arrivando, quindi, dapprima a un rapporto di 2:1 rispetto al diolo e, in un secondo momento, a una quantità stechiometrica.

I test sono stati effettuati andando a variare il tempo di reazione, come fatto per gli esperimenti iniziali, e mantenendo invariata la pressione di anidride carbonica. I risultati sono mostrati di seguito.

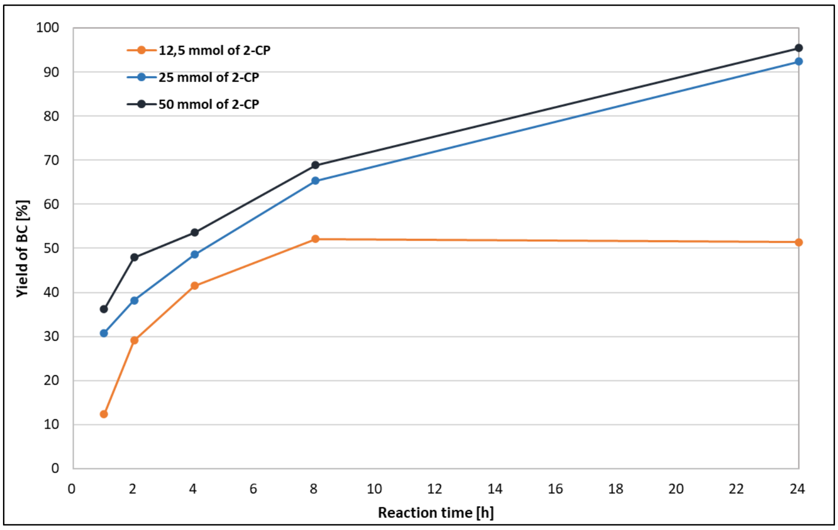


Figura XI - Resa in butilene carbonato (BC) per diverse quantità di 2-cianopiridina al variare del tempo di reazione

È possibile individuare due trend. Per quanto riguarda le reazioni con 25 e 50 mmol di 2-cianopiridina, l'aumento di resa con il tempo è molto simile e la quantità di carbonato sintetizzato differisce di circa 1,2 mmol per ogni test.

Le prove con una quantità stechiometrica di agente deidratante, invece, hanno mostrato un peggioramento significativo in termini di resa rispetto alla condizione iniziale. La reazione, inoltre, sembra arrestarsi dopo le 8 ore, come è chiaramente visibile in **Figura XI**.

Queste analisi hanno dimostrato la necessità di un eccesso di 2-cianopiridina rispetto al diolo per ottenere un efficace consumo di acqua e, di conseguenza, una produzione rilevante di carbonato. Tuttavia, non è necessario lavorare con un rapporto di 4:1 come fatto per i test iniziali, ma una quantità doppia risulta un buon compromesso tra resa e impiego di reagente.

Nella fase finale della ricerca, è stato realizzato uno studio circa l'influenza della pressione di CO_2 sulla sintesi. Il valore usato per tutti gli esperimenti precedenti, 5 MPa, costituisce un sostanziale eccesso di anidride carbonica rispetto al diolo presente nel reattore, oltre ad essere una pressione elevata che comporterebbe un costo significativo in un eventuale processo su larga scala.
Fissando tempo, temperatura e quantità di 2-cianopiridina a 1 ora, 100 °C e 25 mmol rispettivamente, sono state effettuate prove andando a diminuire progressivamente la pressione fino a un valore minimo di 0,1 MPa. I risultati sono mostrati in **Figura XII**.

Le analisi hanno mostrato un comportamento inaspettato. Con un pressione minore all'interno del reattore, era stato ipotizzato un peggioramento rispetto al valore di partenza a causa di tre fattori: condizioni termodinamicamente più sfavorevoli, una minore quantità di anidride carbonica disponibile per la carbossilazione e, infine, una minore solubilità della CO_2 all'interno della fase liquida, dove avviene la reazione.
Come si può vedere dal grafico, invece, al diminuire della pressione si ha un incremento progressivo della resa in carbonato fino a un massimo nella prova a 1 MPa, in cui si arriva a un valore superiore al 52% contro il 30,6% iniziale, seguito da un nuovo decremento per i due valori più bassi.

Tale miglioramento può essere dovuto a due fenomeni. Il primo è una maggiore efficienza del catalizzatore, i cui siti attivi potrebbero essere occupati, in caso di maggiore pressione, dall'elevato eccesso di anidride carbonica. Il secondo, invece, è legato alla concentrazione di 1,2-butandiolo nelle due fasi. A pressione più alta, infatti, c'è una migrazione del diolo verso la fase gassosa, il che comporta una minore quantità di substrato disponibile per conversione all'interno del liquido.
Questo comportamento, apparantemente anomalo, è stato riscontrato anche in altri studi presenti in letteratura, il che rende plausibili le due ipotesi appena menzionate.
In ogni caso, è un risultato estremamente positivo, sia per ciò che riguarda l'efficienza della sintesi, sia per l'eventuale diminuzione di costi operativi in un processo su larga scala.

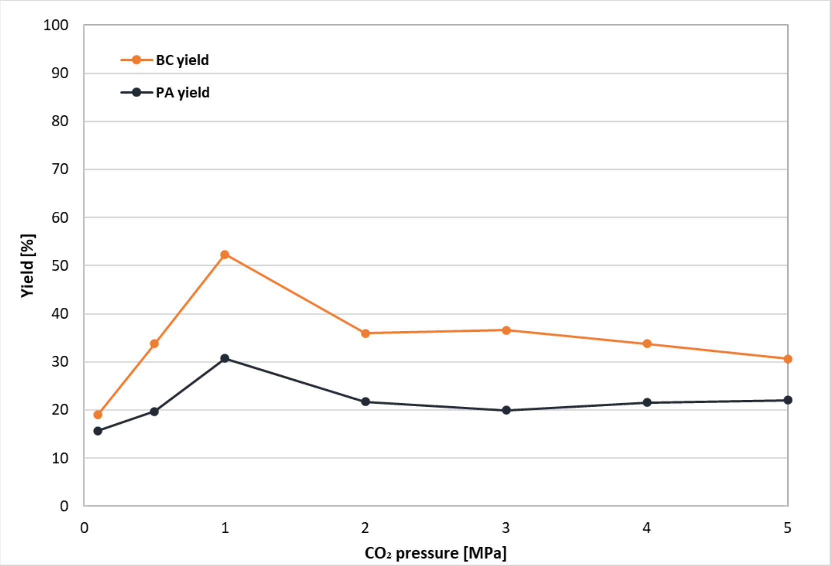


Figura XII - Resa in butilene carbonato (BC) e picolinamide (PA) al variare della pressione di CO_2

CHAPTER 1 - INTRODUCTION

1.1 - CO_2 and greenhouse effect

Carbon dioxide is a colourless gas naturally present in Earth's atmosphere, deriving from different sources: plant and animal respiration, ocean-atmosphere exchange, soil respiration and decomposition and volcanic eruptions. These phenomena constitute what is called the carbon cycle. This whole equilibrium has endured until the advent of the industrial revolution, when the rising use of fossil fuels destabilized it. From that moment, the increase of the amount of carbon dioxide has never stopped, indeed became faster over the years. In the period 1970-2000, anthropogenic emissions grew at an average rate of 1,72% per year, which became 2,6% for the 2000-2014 period.[1] In 2022, global carbon dioxide emissions from fossil fuel combustion and cement production reached 36,1 Gt.[2]

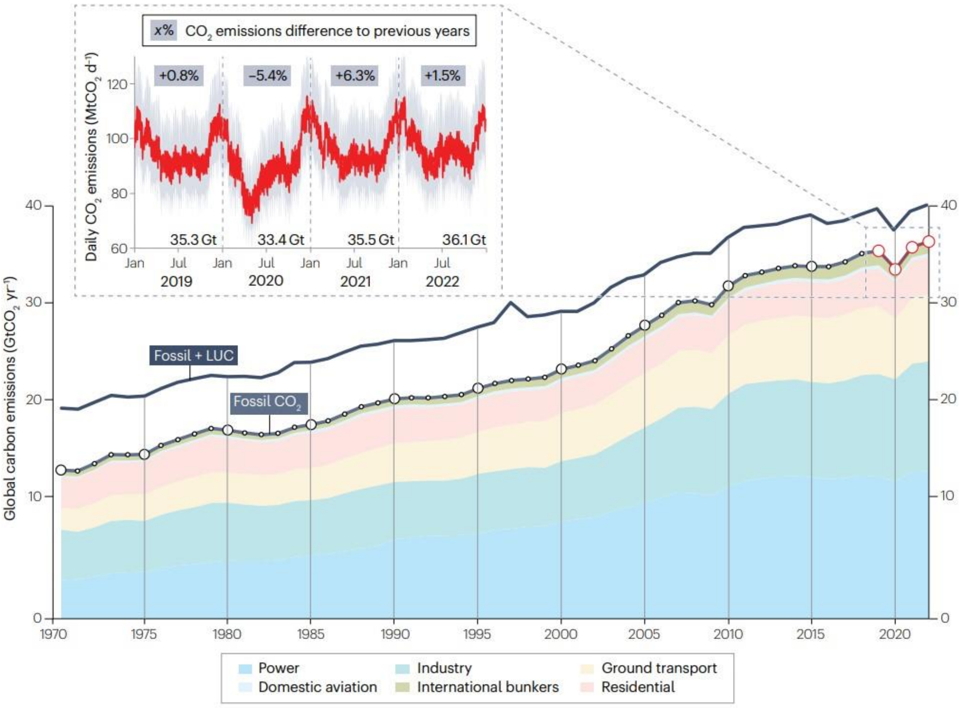


Figure 1 - Global CO2 emissions 1970-2022[2]

This inexorable process led to a dangerous climate crisis which is endangering the survival of our planet, mainly due to the so-called greenhouse effect. The excess of CO_2 in the atmosphere, together with other greenhouse gases (GHG), does not allow the release of the infrared radiation emitted by the Earth's surface after being struck by sunlight. This leads to an increase of the average temperature of the planet, compromising the stability of the whole environment.

Earth's temperature has risen by an average of 0,06 °C per decade since 1850, but the rate from 1982 is significantly higher, about 0,2 °C. Nowadays, the increase is around 1 °C compared to pre-industrial era (1850-1900).[3]

These numbers, which can seem small, correspond to a huge amount of accumulated heat and it has a serious impact on various aspect of our lives. Without a real change in our society, the situation will get worse in the near future. Global temperature is projected to warm by 1,5 °C by 2050 and 2-4 °C by 2100.[4]

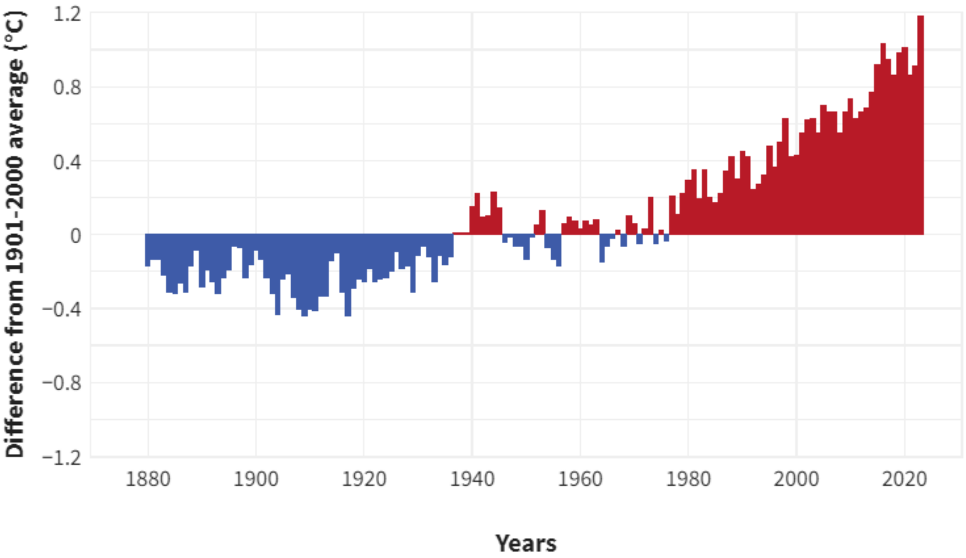


Figure 2 - Global average surface temperature in the period 1880-2023[3]

1.2 - Climate change mitigation policies and technologies

Starting from 1992, when the first international summit on climate, known as COP 1, was organized, a lot of international agreement have been signed to limit greenhouse gases emissions and climate changes in general. The latest of them, stipulated in Paris in 2015 during the COP 21 and became effective from 2016, set a very stringent goal: "holding the increase in the global average temperature to well below 2 °C above pre-industrial levels and pursuing efforts to limit the temperature increase to 1.5 °C above pre-industrial levels".[5] This agreement was an historical event on the fight against climate change since was the first signed by all the biggest countries, including USA and China.

To avoid the average temperature increasing over the maximum limit stipulated by the Paris agreement, all human activities should exploit a decarbonization. The impact of industry on global CO_2 emissions is significant, equal to 28,9%, second only to the power sector, which contributes for a 39,3%.[2] Chemical industry is the largest industrial energy consumer and the third largest industry subsector in terms of direct CO_2 emissions, according to IEA.[6] This is because the majority of chemicals are C-rich substances, hence their primary source are fossil fuels which, at the end of all the transformations, will turn on gaseous species like carbon dioxide or methane. Anyway, the hypothesis of a carbon free chemical industry is unachievable, so there are only two potential solutions: a reduction of the GHG emitted in the atmosphere and a defossilization of processes, with the aim of obtaining the required carbon from other sources.

Nowadays, there are three main routes to achieve these goals:

- **Carbon Capture and Storage (CCS)**: it does not require a modification of the traditional processes but simply consists of trapping and returning the CO_2 generated back to the lithosphere, where it can be safely stored.

- **Carbon Capture and Utilization (CCU)**: this technology consists in the utilization of the low-energy oxidized carbon in CO_2 as a source, instead of the high-energy reduced one from fossil fuels.

- **Biomass-based**: similar to CCU, it implies the utilization of biomass as source for the production of C-rich chemicals.[7]

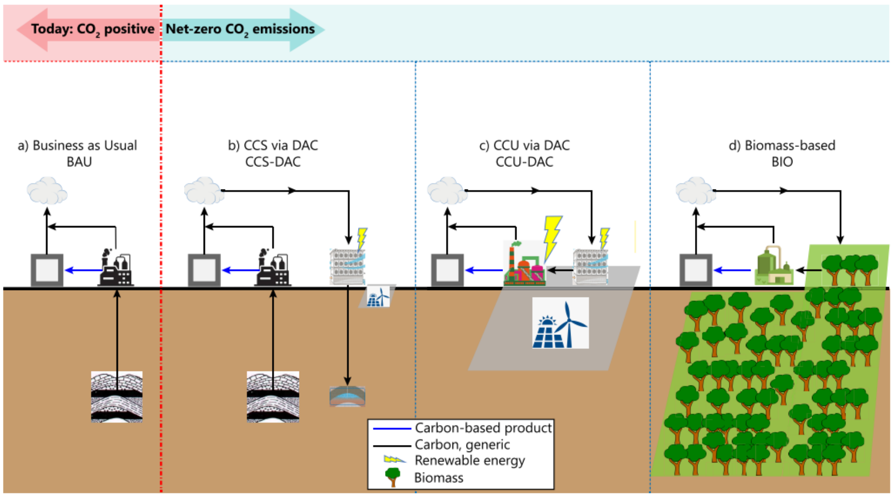


Figure 3 - Routes for the production of a carbon-based product [7]

While the last technology is linked to the biorefinery and does not involve carbon dioxide directly, the other two have a common point, which is the CO_2 capture. This process can be classified into three main types: pre-combustion capture, oxy-fuel combustion technology and post-combustion capture.[8] Since only the last one does not need appropriate materials to meet high-temperature requirements, it is the most studied.[9] There are different ways to pursue this operation but they can be summarized in four categories:

- **Chemical absorption**: carbon dioxide is separated from other gases through the dissolution in affine liquid solvents such as monoethanolamine (MEA) or potassium hydroxide (KOH). It is a process which ensures a high efficiency but has drawbacks like equipment corrosion and elevated costs for solvent regeneration. In particular, MEA, which is more corrosive than secondary and tertiary amines, leads to the formation of corrosive degradation products reacting with oxygen.[10,11,12]

- **Physical adsorption**: this method exploits van der Waals or electrostatic forces between CO_2 and solid sorbent materials. The efficiency of the capture depends both on the properties of the sorbate particles, in particular molecular size and polarity, and on the characteristic of the adsorbent surface, in terms of pore size and spacing.[12] Adsorption is an exothermic process, hence the regeneration of the solid material can be easily performed increasing the temperature.[13] The commonly used sorbent are zeolites, activated carbon and metal-organic frameworks (MOFs).[14,15,16]

- **Membrane separation** is a low-cost technology suitable also for low purity gas streams. Its advantages are the high separation energy efficiency and the elevated packing density. However, the treatment of huge flow rates requires a very large membrane surface and also an expensive compression equipment, which increases significantly the overall cost. Polymeric membrane are widely used due to the high performance and the mechanical stability, but a refrigeration system is required because an elevated temperature of the gas mixture, in case of post-combustion capture, would easily damage the membrane.[12]

- **Cryogenic separation**: is an alternative technique which consists of consecutive refrigeration and condensation of a gas mixture. The low temperatures are obtained through a closed-cycle refrigeration system and multiple cold traps are built to condense air components at different temperatures. The main advantage of this technology, which is the simultaneous separation of water and CO_2, is also a drawback since a too high water content could lead to the formation of ice in the system. Obviously, the main economic issue of this separation method is related to the refrigeration phase.[12,17]

These technologies refer only to the capture of carbon dioxide from a point source, which is easier and cheaper than the one of atmospheric CO_2, which has high energy requirements due to the lower concentrations, approximately equal to 400 ppm.[18]

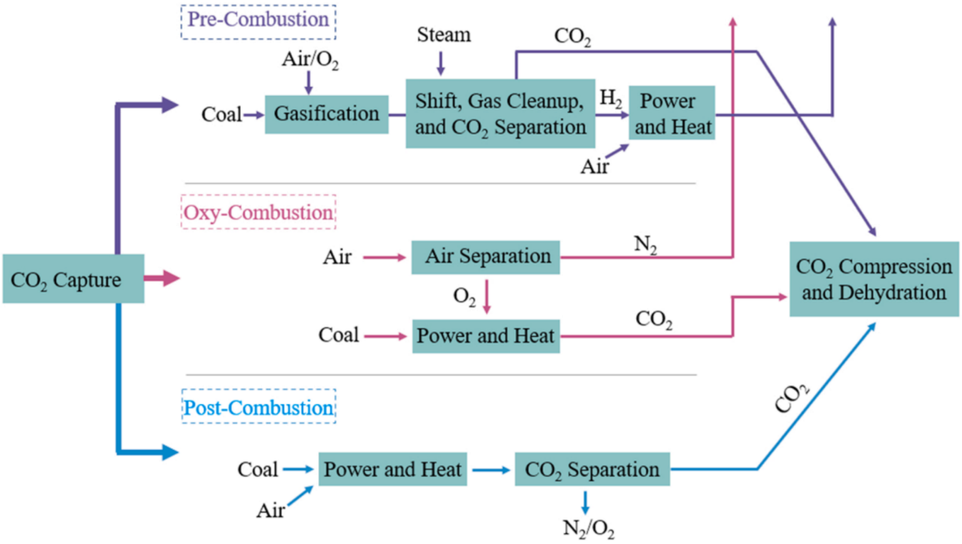


Figure 4 - Roadmap of carbon capture technologies[9]

1.3 - Carbon Capture and Utilization (CCU)

Among the three main technologies for the limitation of greenhouse gases, CCU has been aroused a lot of interest in policymakers and researchers all over the world, even if is unreasonable to achieve net-zero-CO_2 emission through this process due to the electric energy demand of the utilization phase.[7] Therefore, CCU usually cannot be classified as a carbon dioxide removal technique. Nevertheless, it is characterized by a long-term stability and is seen as part of the circular economy and a form of sustainable waste processing, avoiding the high costs and the geological issues of CCS, such as the possibility of small earthquakes.[9,18]

Different routes have been developed for CO_2 utilization and they can be summarized in four categories: physical, chemical, biological and mineralization.

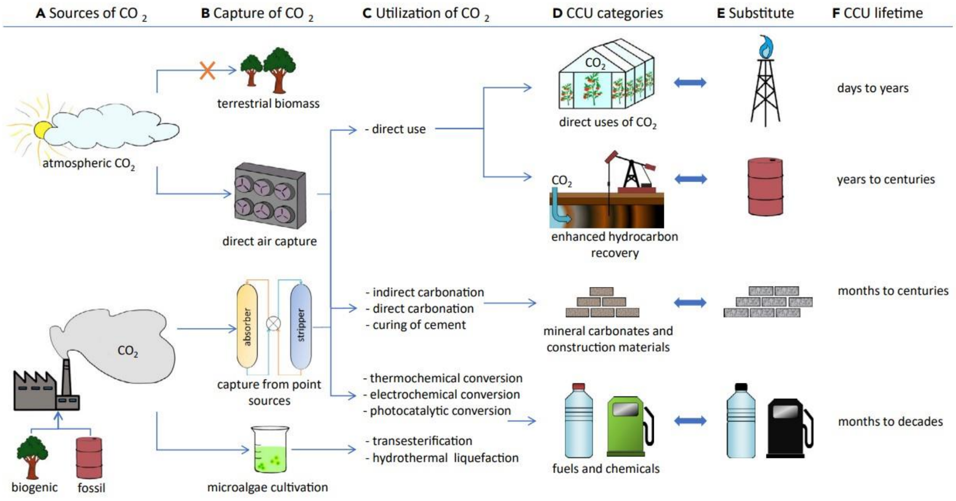


Figure 5 - Scope of CCU[18]

1.3.1 - Physical utilization

Physical utilization is mainly exploited in the following industries:

- **Food and beverage**: the number of carbonated drinks daily consumed all over the world is astonishing and this leads to a huge annual demand of CO_2, evaluated in about 1078 tons in 2021. Besides the effect on taste, carbon dioxide has also a role for its anti-corrosion properties and the capacity of extending the average expiration date. As regards food, CO_2 is used in storage environments for improving the freshness of fruits and vegetables and for limiting the reproduction of bacteria.[9]

- **Petroleum**: the injection of carbon dioxide into reservoirs constitutes the so-called Enhance Oil Recovery (EOR) or tertiary recovery. The easiest extraction of oil exploits only the natural pressure of the formation but the amount of fuel extracted is very limited, less than 20% of the underground reserves.[19] To increase it up to 40%, water can be injected into the reservoir and this technique is called secondary recovery.[20] Finally, to reach an extraction of 60-70%, carbon dioxide flooding can be used. Due to high pressure and temperature and CO_2 dissolution, it ensures a decrease of the viscosity of the oil, making the recovery more efficient.[21]

Another application in the fossil fuel industry is the utilization of supercritical CO_2 as a fracturing medium. In supercritical conditions, reached for values of temperature and pressure higher than 31 °C and 74 bar approximately,[22] carbon dioxide has an excellent solvation ability and the absence of water avoids the expansion of the reservoir clay.[9]

It is important to underline that almost all physical uses, except flooding, are not decarbonization technologies since they only delay the release of CO_2, but they still have economic benefits.[9]

1.3.2 - Biological utilization

Carbon dioxide utilization has the aim of simulate photosynthesis of plants and it mainly consists in two applications:

- **Plant fertilizer**: since CO_2 plays a crucial role on photosynthesis, introducing it inside a closed environment, usually a greenhouse, can accelerate the growth process and improve plant yield. This route requires a high-purity CO_2.[9]

- **Biofuels production**: microalgae can easily sequestrate carbon dioxide from a gas stream and use it for growing. Afterward, they can be easily converted into biofuels. This technology can be seen both as a carbon capture and a utilization method. Depending on the conversion, chemical, biological or thermochemical, it is possible to obtain different biofuels, such as biodiesel, methane, hydrogen and bio-oil.
  This technology has a great potential for CO_2 utilization, but has also some issues, mostly related to the energy required before the conversion process to remove water from microalgae.[9,11,23,24]

1.3.3 - Mineralization utilization

This type of utilization exploits the reaction between carbon dioxide and mineralized raw materials to form different precipitates. Depending on whether the raw material reacts directly with CO_2 or is previously converted into an intermediate product, the mineralization is classified as direct or indirect. The former has a very slow reaction rate, while the latter, even if is more efficient, requires additional costs for energy and additives.[9,25]
Different raw materials contained in industrial residues can undergo the mineralization process, particularly silicate ores or alkaline oxides. The final products find application mainly as building materials.[26,27,28]
Also natural ore are suitable for this process, but there are some issues related to conversion and reaction rate, therefore their utilization is limited.[29]
The mineralization of solid waste has multiple benefits: despite the decarbonization, it is a good option for reducing the amount of industrial waste in an efficient way and there is also the possibility of recover energy, since it is an exothermic reaction. Nevertheless, different drawbacks need still a solution, in particular the ones related to the high costs for the management of raw materials.[9,30]

1.3.4 - Chemical utilization

Among all the four routes, chemical utilization is maybe the more common. The large availability and the non-toxicity of CO_2 make it a suitable feedstock material for the production of chemicals, even if, as the physical one, does not lead to a complete decarbonization due to the energy required for the transformation and the fact that most of the products will return to carbon dioxide soon or later. A lot of different compounds can be synthesized starting from CO_2, but they all belong to three categories: bulk chemicals, organic fuels and polymeric materials.[9]

The more significant products of chemical utilization, for both economic and industrial applications relevance, are the following:

- **Methane**: it is the main component of natural gas and plays a crucial role not only for industries but for the society in general, since it is the main cooking and heating medium and its price variations can have a serious impact on world economy.[10]
  The production of methane starting from CO_2 is known as methanation process. The reaction is the following:

  $$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O \qquad \textbf{R1}$$

  It is also called Sabatier-Sanderens reaction. It is strongly exothermic, hence one issue related to its application inside reactors is the management of heat release in order to ensure the maintenance of thermodynamically favourable conditions and to avoid catalyst sintering.[10] For this reaction, many catalytic systems made by noble metals, such as ruthenium and rhodium, supported on Al_2O_3, TiO_2, SiO_2 or CeO_2, have been studied, but the Ni-based ones have been recognized as the most effective in terms of selectivity and stability.[10,31]

- **Methanol**: it is a key product in chemical industry due to the wide range of applications. It is used as solvent, fuel additive and in fuel cells. In addition, it is a crucial building block for the synthesis of several chemicals, such as acetic acid and formaldehyde.[10] The world demand was almost 100 million tons in 2019.[32]
  Methanol can be synthesized through catalytic hydrogenation of CO_2 (**R2**), but it involves also the so-called water gas shift reaction (RWGS), which leads to the formation of carbon monoxide (**R3**).

  $$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O \qquad \textbf{R2}$$

  $$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \textbf{R3}$$

  Hence, to pursue this process the selection of catalyst is a key step, both for avoiding the side reaction and for maintaining a good efficiency also in presence of water.[33]
  One of the most investigated catalysts is copper, particularly its nanoparticles. The natural tendency to agglomerate, which would lead to an increase of water gas shift reaction rate, can be avoided using a Cu/ZrO_2 catalytic system, which ensures a good dispersion and an inhibition of the side reaction.[34]

  However, also water gas shift can lead to the synthesis of methanol through a different pathway, which consists in **R3** and **R4**.

  $$CO + 2\,H_2 \rightleftharpoons CH_3OH \qquad \textbf{R4}$$

  About 40 million tons of methanol are produced annually through this route,[35] but the high request of hydrogen constitutes an important limitation.

- **Urea**: through the synthesis of ammonium carbamate and its consecutive dehydration, is possible to synthesize urea starting from carbon dioxide and ammonia. The two stages are illustrated in **R5** and **R6**:

$$2\,NH_3 + CO_2 \rightleftharpoons NH_4COONH_2 \qquad \textbf{R5}$$

$$NH_4COONH_2 \rightleftharpoons NH_2CONH_2 + H_2O \qquad \textbf{R6}$$

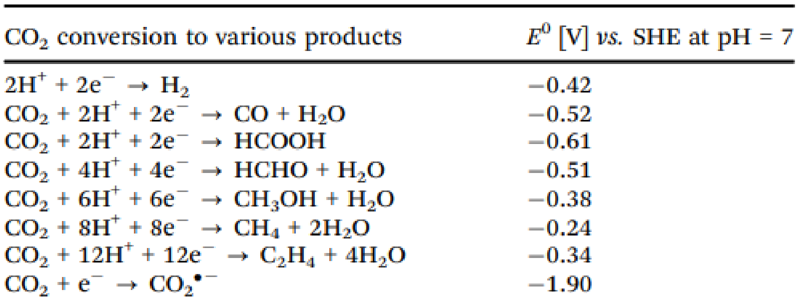
  R5 is a very fast and exothermic reaction, hence the heat released is used for the second step, which is, instead, slower and endothermic.
  This process takes place at around 185-190°C and at a pressure of 180-200 atm.[33]
  About 112 million tons out of a total of 150 million tons of urea produced exploits CO_2 utilization as feedstock.[36]

- **Syngas**: dry reforming of methane, shown in **R7**, exploits carbon dioxide for the production of the so-called syngas, a mixture of gases, mainly hydrogen and carbon monoxide, which is widely used in industry, in particular as fuel for gas turbines and as a chemical feedstock for Fischer-Tropsch processes, crucial for the production of chemicals like methane, paraffins and olefins.[37,38]

$$CO_2 + CH_4 \rightleftharpoons 2\,CO + 2\,H_2 \qquad \textbf{R7}$$

  The main problem of dry reforming reaction is the formation of filamentous-type coke on the catalyst surface due to CH_4 decomposition or CO disproportionation.
  The most studied catalysts for avoiding this drawback are nickel or noble metals (Rh, Ru and Pt) supported on alumina or MgO. In particular Rh and Ru show both high activity and stability.[33]

There also two more technologies which allow the production of different substances starting from carbon dioxide but without the occurrence of a proper chemical reaction: electrochemical and photochemical reduction of CO_2.
The former consists in reducing carbon dioxide through electric energy. Introducing CO_2 inside an electrochemical cell, depending on the type of electro-catalyst on the electrodes, different reactions can take place, with the consequent production of various compounds. A summary of the most important transformations and the relative standard potentials is shown in **Figure 6**. Despite the huge number of research works on this technology, only the production of carbon monoxide and formic acid results economically convenient.[33]



CO_2 conversion to various products	E^0 [V] *vs.* SHE at pH = 7
$2H^+ + 2e^- \rightarrow H_2$	−0.42
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.52
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	−0.61
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.51
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−0.38
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	−0.24
$CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	−0.34
$CO_2 + e^- \rightarrow CO_2^{\bullet -}$	−1.90

Figure 6 – Electrochemical reactions of CO_2 and their standard potentials[10]

The latter, instead, exploits solar energy to convert CO_2 into valuable chemicals. The electrons required for the process come from the excitation of a photo-catalyst. This material, due to the effect of photons, is subjected to a charge generation, electrons and holes, which promotes redox reactions: reduction of carbon dioxide and oxidation of water, in case of an aqueous-phase environment. This is a real innovative technology, but despite remarkable progress have been made in the last years, a better development of catalyst is required to reach a technical feasibility.[10,33,39]

Overall, all the chemical transformations can be classified in two main categories: reductive and non-reductive.
The former one implies a change of the oxidation state of carbon. Since it is very high, the amount of energy required is not negligible. In addition, CO_2 is thermodynamically stable. This category includes hydrogenation and photochemical reduction.
Non-reductive conversion of CO_2, instead, implies that the formal oxidation state of the carbon centre does not change upon its incorporation into organic scaffolds.[40] This involves a lower demand of energy and a consequent potential higher efficiency. Different processes belong to this category and one of the most interesting and studied is the synthesis of organic carbonates starting from carbon dioxide.[33,41]

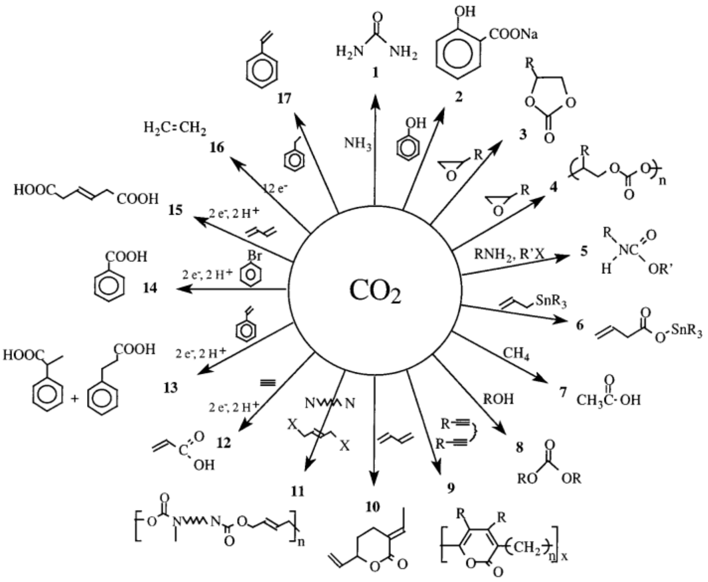


Figure 7 - Chemical transformations of CO_2[42]

1.4 - Organic carbonates

Stable organic carbonates derive from the esterification of hemicarbonic acid, the monoester of carbonic acid, with a molecule of another hydroxy compound.[43]

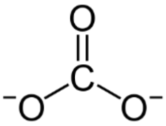


Figure 8 - Functional group of organic carbonates

Physical characteristics of this class of substances strongly depend on their structure. Aliphatic carbonates are liquid and most of them are soluble in water. In addition, the lower ones form azeotropic mixtures with various organic solvents. Aromatic carbonates, instead, are mostly solid and soluble in organic polar solvents like esters, ethers or ketones.[43] Aliphatic-aromatic carbonates have intermediate properties.

Another significant classification is between linear and cyclic carbonates.
Linear and especially dialkyl carbonates are widely used in the chemical industry. Dimethyl carbonate (DMC), probably the most famous and employed carbonate, is a very effective fuel additive for diesel engines. Studies reported that a low level addition of DMC (4 vol%) to diesel fuel can reduce emissions of CO, hydrocarbons and particulate matter (PM) up to 50%.[44] In addition, due to the low vapor pressure, the suitable liquid temperature range and the solubility properties, there is a strong interest towards dialkyl carbonates, like DMC and DEC, as solvents for synthesis, extraction and electrochemical applications, resulting in an excellent alternative to halogenated solvents or ketones.[45] Others applications of liner carbonates, besides the chemical ones, are in cosmetic products, in oil processing industry and as cleaning cosolvents.[46]
Cyclic carbonates are used in chemical industry as a starting material for polymer synthesis, polar solvents, additives, electrolyte in secondary batteries (lithium-ion batteries) and supercapacitors, resins, cleaning, cosmetics and personal care products.[47,43,48] However, their applications are not limited only to chemical industry. They are also used in the pharmaceutical sector, like for the synthesis of oxazolidinones, or in agriculture as additives.[49,50] The annual production of cyclic carbonates was estimated at 0,1 Mt in 2010.[51]

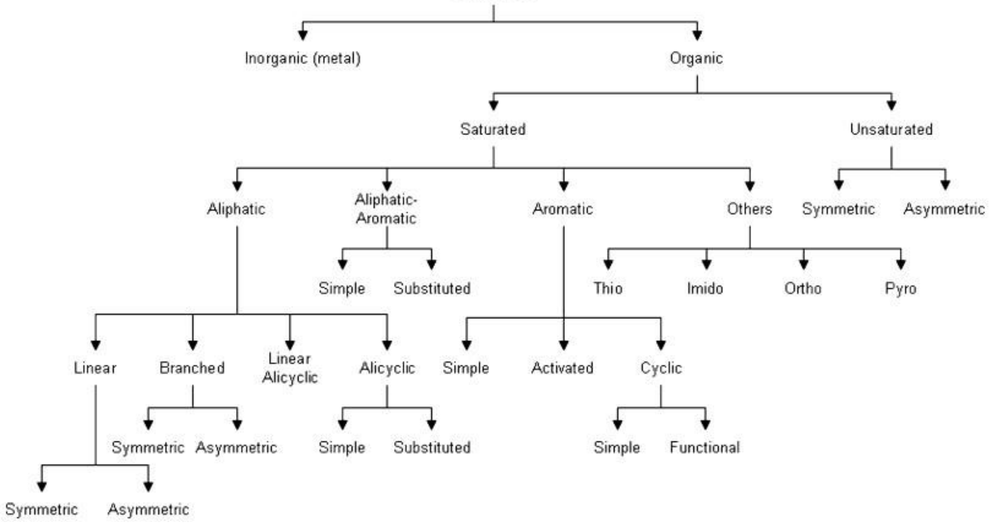


Figure 9 - Classification of carbonates[52]

1.4.1 - Synthesis routes for organic carbonates

The classic method for organic carbonates synthesis is the phosgenation technique. Hydroxy compounds are dissolved in anhydrous solvent, like benzene or toluene, with an excess of an acid acceptor, usually pyridine and phosgenated. They react with phosgene ($COCl_2$) to form an ionic adduct which leads to the formation of the carbonate. Symmetrical carbonates are obtained in one step, while unsymmetrical ones require two steps. The general reaction scheme is shown in **Figure 10**.

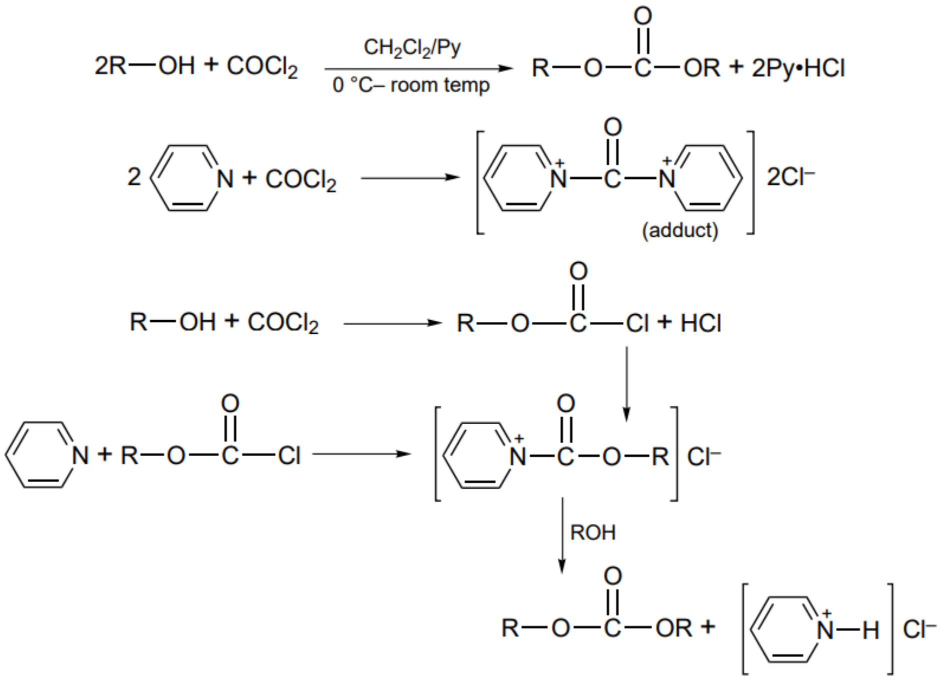


Figure 10 - Phosgenation method[43]

Nearly all the organic carbonates can be synthesized through this technique with good yields in a short period of time. Phosgene can also be substituted by diphosgene and triphosgene. However, there are serious drawbacks which led to the phase-out of this preparation method. Pyridine and phosgene are toxic and hazardous chemicals and their utilization is dangerous both on an operative and an environmental point of view. In addition, purification steps are required to neutralize the excess of pyridine and to remove by-product salts.[43]

A second route is the oxidative carbonylation of alcohols or phenols and is mainly related to the production of dialkyl carbonates. It consists in the reaction between carbon monoxide and metal compounds deriving from the oxidation of a metal catalyst and alcohol. Usually, copper chloride is used. A reaction scheme for the synthesis of dimethyl carbonate is shown below (**R8-R9**).[53]

$$2\,CuCl + 2\,CH_3OH + 1/2\,O_2 \rightleftharpoons 2\,Cu(OCH_3)Cl + H_2O \qquad \textbf{R8}$$

$$2\,Cu(OCH_3)Cl + CO \rightleftharpoons (CH_3O)_2CO + 2\,CuCl \qquad \textbf{R9}$$

Organic carbonates can also be synthesized starting from urea. Its reaction with alcohols, catalyzed by zinc or lead acetate, leads to the formation of carbamates. Prolongations of the reaction or the addition of a cocatalyst, such as triphenylphosphine, allows the formation of carbonate.[43] The general reaction scheme is shown in **Figure 11**.

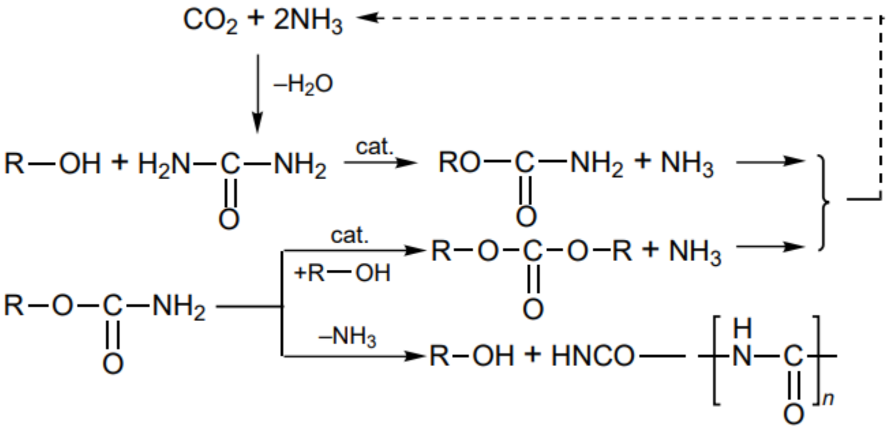


Figure 11 - Synthesis of carbonates starting from urea and alcohols[43]

Since urea has an important role in CCU, as mentioned in **1.3.4**, this method can be considered as an indirect transformation of carbon dioxide. Recycling the liberated ammonia, for the urea production (**R5**), overall only CO_2 and alcohol would be consumed.[8]
The main drawbacks of this method are the high temperatures required and the formation of by-products, such as isocyanic or isocyanuric acid.

A widely investigated route for the synthesis of cyclic carbonates, which is also a CCU technology, is the cycloaddition of CO_2 to epoxides and oxetanes, which leads to the formation of 5-membered and 6-membered cyclic carbonates, respectively.

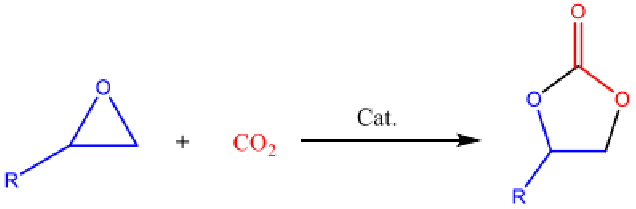


Figure 12 - Cyclic carbonate synthesis from epoxide and CO_2[41]

This easy mechanism has attracted a lot of interest in the research world and an extremely high number of studies have been performed to identify the best catalysts for achieving high yield and selectivity. The main homogeneous and heterogeneous catalytic systems investigated involve the utilization of metal oxides, ionic liquids, metal salts, organocatalysts, complexes, Schiff bases, zeolites and talc. There are also studies on the utilization of innovative systems, such as electrolytic cells and microwave irradiation.[41,47,51,54]

Other suitable routes for the synthesis of organic carbonates, in particular cyclic ones, are oxidation of olefins with CO_2, transesterification of diols with dialkyl carbonate and depolymerization of bisphenol.[55,56]

1.4.2 - Styrene carbonate

4-phenyl-1,2-dioxolan-2-one, commonly known as styrene carbonate, is a 5-membered ring aromatic carbonate. Even if is not one of the most famous of its class of compound, its applications run on a wide range of industrial sectors. It is used as an additive for polymer-coated fertilizer granules in agriculture, or as a component of nonaqueous electrolyte in alkali metal and lithium batteries due to its high polarity property.[50,57,58] In addition, it is widely used for chemical synthesis of various compounds, in particular vicinal diols, non-isocyanate polyurethane, thermoplastic aromatic polycarbonate and aliphatic polyol.[59,60,61]

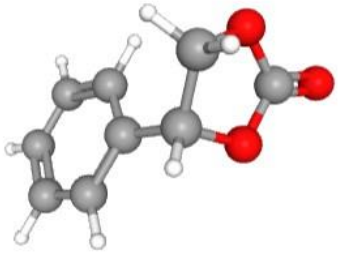


Figure 12 - Styrene Carbonate[62]

Currently, the main route for the synthesis of styrene carbonate starts from the epoxide.
The process is common also for other cyclic carbonates, as mentioned in the previous section. It usually involves a two-step reaction: the epoxidation of styrene followed by the cycloaddition of CO_2 (**Figure 13**). A study demonstrated that the reaction can proceed under different conditions of pressure and solvent.[61] In addition, various catalysts have been tested over the years, like metal oxides, tetrabutylammonium bromide (TBAB), $ZnBr_2$ and nanogold supported on carbon nanotubes.[58,63,64,65,66,61]

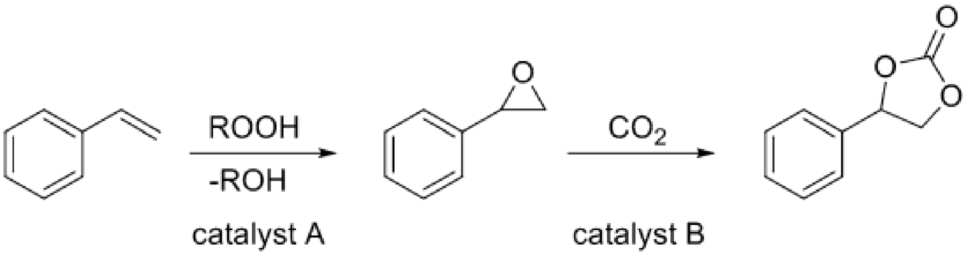


Figure 13 - Synthesis of styrene carbonate from styrene[61]

Nowadays, due to the complexity of the synthesis and the recovery, the price of styrene carbonate is very high. The one sold for chemical use can reach 930 € for 1 g.[67]

1.4.3 - Butylene carbonate

4-ethyl-1,3-dioxolan-2-one or 1,2-butylene carbonate is a 5-membered cyclic aliphatic carbonate. It is involved in several industrial applications, in particular as solvent in extractions and as electrolyte in electric double-layer capacitors (EDLCs) or supercapacitors.

As solvent, it has good characteristics, including high flash point and polarity (dielectric constant of 65,1). Moreover, is assigned in level 0 for health and instability and in level 1 for flammability by National Fire Protection Association.[68] Various studies have demonstrated its ability as extraction solvent of metal chelates or in liquid-liquid extraction, like for methylene blue.[68,69] It is also used for hydrogenation and telomerisation reactions.[70,71]

However, the main application of butylene carbonate is the one linked to electrochemical cells and EDLCs.[72,73,74,57] In this field, its suitability is mostly related to the great oxidation resistance, which prevent the risk of explosions, one of the most serious issue of this type of equipments.[75]

Others applications are in agriculture and pharmaceutical sectors.[50,76]

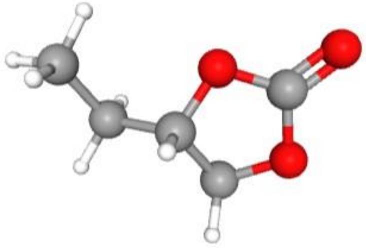


Figure 14 - Butylene carbonate[77]

Also butylene carbonate, as other cyclic carbonates, is usually synthesized through the cycloaddition of CO_2 to 1,2-epoxybutane, like shown in **Figure 15**. This process can be effectively catalyzed by bifunctional phosporous-based organocatalysts or by an heterogeneous graphene-inorganic nanocomposite catalyst.[78,79]

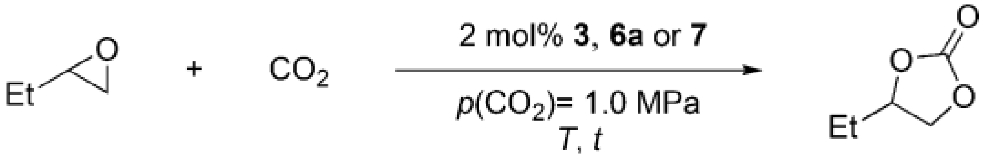


Figure 15 - Synthesis of butylene carbonate from CO_2 and epoxide[78]

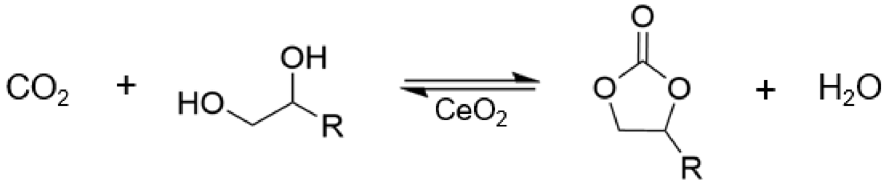
At the moment, the price of butylene carbonate for chemical applications is approximately 200 € for 100 g.[80]

1.5 - Synthesis of cyclic carbonates from CO_2 and diols

As illustrated in **1.4.1**, a lot of different routes for the production of cyclic carbonates have been investigated in the last years.
The direct synthesis of cyclic carbonates from CO_2 and diols is an alternative and eco-friendly route since it has, besides the CO_2 utilization, two more remarkable advantages. Firstly, the only reaction product is water. This avoids all the potential issues related to the purification or the disposal of other chemicals, making the overall process cheaper and more sustainable. In addition, diols can be obtained from biomass, as demonstrated in many studies made also by members of Tomishige Lab where this research work was performed.[81,82,83]

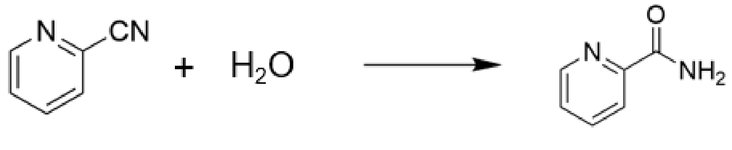
The process is also suitable for the synthesis of dialkyl carbonates, like DMC, starting from alcohols.[84]

From the carboxylation of 1,2-diols and 1,3-diols over CeO_2 catalyst, 5-membered and 6-membered ring carbonates can be synthesized, respectively. **R10** is the general reaction starting from 1,2-diol.



R10

The natural equilibrium of this reaction is almost completely shifted towards reactants, hence the amount of carbonate in normal conditions would be very low, around 2%.[85] In addition, side reactions can lead to the dehydration of diols and the consequent formation of water, which affects negatively the equilibrium.[86]
Therefore, a fundamental aspect for the synthesis of carbonates is the shift of the equilibrium towards the products side. This can be realized exploiting the effect of dehydrating agents, such as nitriles. In particular, 2-cyanopiridine was found to be very effective for this kind of purpose.[87] Its hydration leads to the formation of picolinamide, as follows:



R11

2-cyanopiridine, in addition to its dehydrating effect, is able to enhance the reaction rate between carbon dioxide and the substrate due to the formation of strong base sites via the attachment on the catalyst surface.[88] Anyway, it can also lead to the formation of by-product like carbamate and picolinate.
Also 2-furonitrile has been found as an effective dehydrant for this reaction.[89]

Thinking about the overall process, one disadvantage of using 2-cyanopriridine is its difficult regeneration from picolinamide. Usually, acid catalysts are used for this type of reaction, but they would be easily poisoned by the basicity of both the substances. Anyway, SiO_2-supported alkaline ion catalysts have been developed.[90]

The overall reaction scheme is shown in **Figure 16**.

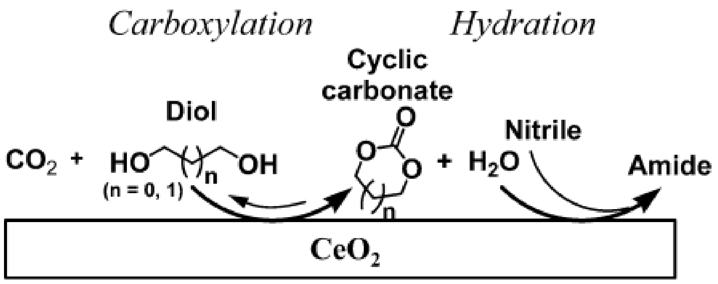


Figure 16 - Carboxylation/hydration cascade for cyclic carbonates synthesis[55]

Although this route is often mentioned as difficult to realize because of the equilibrium limitation, important progress have been made in terms of yield and selectivity over the last years.[45,91]

1.5.1 - Ceria

Recently, a wide range of homogeneous and heterogeneous catalysts have been developed to catalyze the reaction for the generation of cyclic carbonates. Homogenous catalysts show an higher activity but they are undesirable in industry because of the difficult separation which leads to a waste of energy and may cause the decomposition of the catalyst itself.[92,93] On the other hand, despite a lower catalytic activity and the necessity of a solvent, heterogenous catalysts can be easily separated from products and regenerated for multiple reuses.[94]

Over the last years, cerium oxide, also called ceria, has been subject to a lot of studies as a catalyst in CO_2 conversion reactions, due to the low cost and high abundance.[95]
Its application as a catalyst is related to unique properties, particularly the so-called oxygen storage capacity (OSC). Due to its oxygen vacancies, it is able to store oxygen when there is an excess and give it back at a later time.
Ceria has also acid-base sites, which are useful for the adsorption of -OH groups of alcohols or diols and also CO_2. For these kind of processes, two kinds of mechanisms have been proposed: Eley-Rideal and Langmuir-Hinshelwood. The former implies the adsorption of alcohols with the formation of oxides species, which later react with carbon dioxide. The latter, instead, involves the adsorption of both the species with the consequent intermolecular reaction.[96]

Various research works on the activity of ceria for carbonates synthesis have been done over the years. In particular, a study suggested that the active part for this reaction is not the amorphous but the crystalline CeO_2, in particular a stable surface such as (1 1 1). This hypothesis is justified by the increase of the yield of carbonate for catalysts calcinated at higher temperatures, which have a better crystal growth (**Figure 17**) despite a significant decrease of the surface area, like reported in **Figure 18**. The results of this study demonstrate that the better catalyst for this kind of reaction is the CeO_2-HS, characterized by a fluorite structure, calcinated at 873 K for 3 hours, an optimal trade-off between crystallinity and surface area.[84]

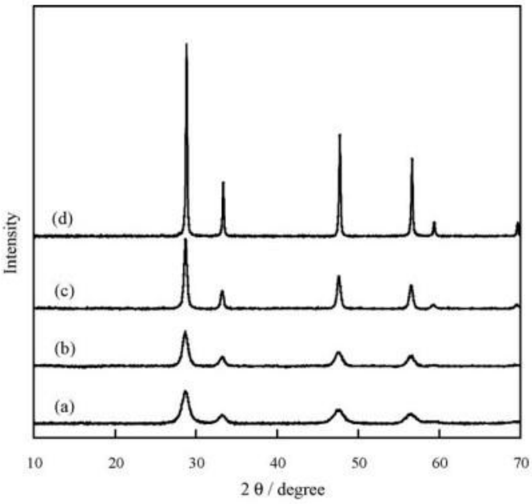
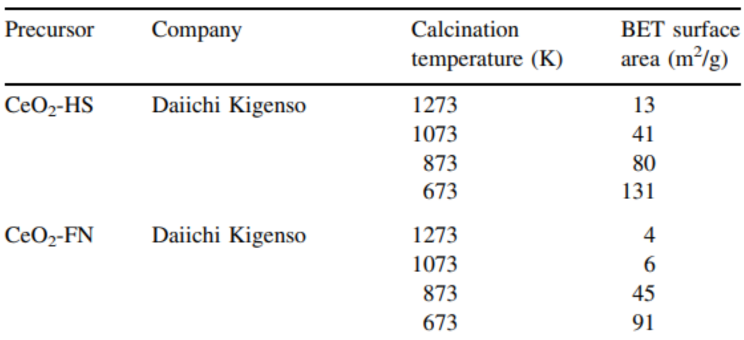


Figure 17 - XRD patterns of CeO2-HS calcined at (a) 673 K, (b) 873 K, (c) 1073 Kα[84]



Precursor	Company	Calcination temperature (K)	BET surface area (m^2/g)
CeO_2-HS	Daiichi Kigenso	1273	13
		1073	41
		873	80
		673	131
CeO_2-FN	Daiichi Kigenso	1273	4
		1073	6
		873	45
		673	91

Figure 18 - BET surface area of CeO_2 calcinated at different temperatures[84]

The calcination of the catalyst used in this work was performed through the electric furnace *Advantec FUH312PB*.

Figure 19 - Electric furnace *Advantec FUH312PB*

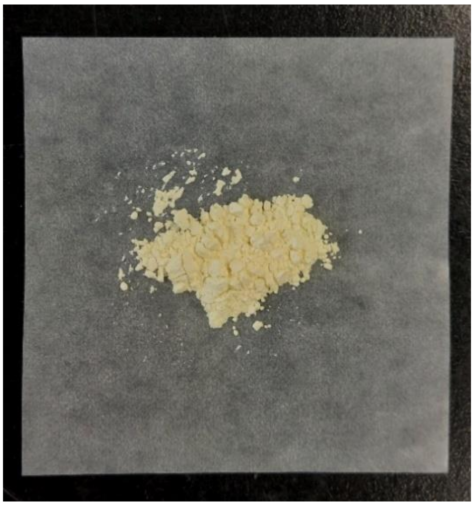
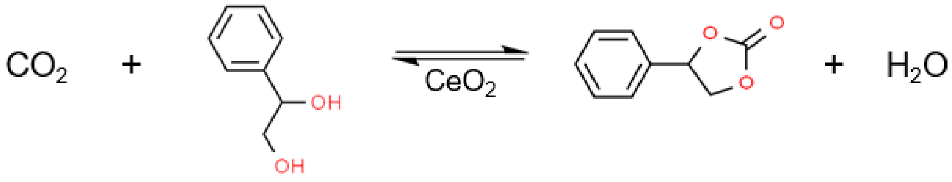


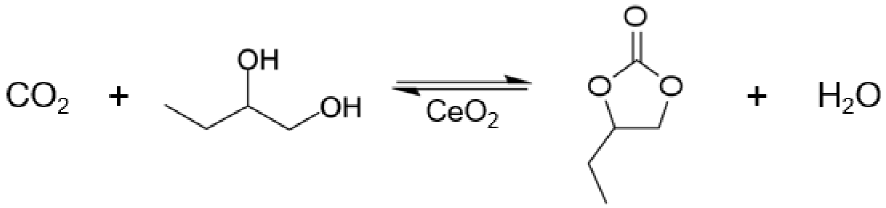
Figure 20 - Calcinated CeO_2

1.6 - Aim of the project

The aim of this project is the investigation and the optimization of the synthesis of two different cyclic carbonates, styrene carbonate and 1,2-butylene carbonate (which will be mentioned simply as butylene carbonate), through the method describe in **1.5**. The whole research is based on the reactions shown below (**R12**, **R13**), in which styrene glycol and 1,2-butanediol react with CO_2 to form 5-membered cyclic carbonates and water. CeO_2 and 2-cyanopyridine were used as catalyst and dehydrating agent, respectively.



R12



R13

In particular, the focus was put on the analysis of the reaction rate and the dependence of the carbonate yield on four main variables: time, temperature, amount of dehydrating agent and pressure.
The last two aspects were investigated at a fixed temperature, chosen from previous results as the best for a proper evaluation of the reaction rate.

To analyze the products, gas chromatography and proton NMR spectroscopy were used.

CHAPTER 2 - MATERIALS AND METHODS

2.1 - Compounds

Substrates:

- *1-phenyl-1,2-ethandiol* or *styrene glycol*. Purity: > 98%. Company: *Tokyo Chemical Industry*.
- *1-phenyl-1,2-ethandiol* or *styrene glycol*. Purity: 97%. Company: *Sigma-Aldrich*.
- *1,2-butanediol*. Purity: > 98%. Company: *Tokyo Chemical Industry*.

Dehydrating agent:

- *2-cyanopyridine*. Purity: > 99%. Company: *Tokyo Chemical Industry*.

Catalyst:

- CeO_2 or *ceria*, HS grade, calcinated at 873 K for 3 h. Company: *Daichi Kingenso Kagaku Kogyo Co*.

Solvents:

- *Acetonitrile super dehydrated*. Purity: > 99,5%. Company: *Fujifilm Wako Chemicals*.
- *Methanol-*d_4. Purity: 99,8%. Company: *Fujifilm Wako Chemicals*.

Internal standards:

- *1-hexanol*. Purity: > 98%. Company: *Tokyo Chemical Industry*.
- *Dimethyl sulfoxide super dehydrated*. Purity: > 99%. Company: *Fujifilm Wako Chemicals*.

Products:

- *2-picolinamide*. Purity: 98%. Company: *Tokyo Chemical Industry*.
- *4-ethyl-1,3-dioxolan-2-one* or *butylene carbonate*. Purity: > 98%. *Combi-Blocks*.

2.2 - Analytic techniques

2.2.1 - Gas chromatography (GC)

Gas chromatography is an analytic technique which is widely used in different fields besides chemistry, such as petrochemical industry or forensic.[97,98] It is based on the partitioning of analytes due to their different affinity with a stationary phase located inside a column, depending on properties like polarity or boiling points.[99] Modern capillary columns are coated with a thin film of static phase and the sample is carried through it by a carrier gas, usually inert like nitrogen or helium. Important parameters for GC columns are length, internal diameter and film thickness, and they have influence on retention time and peak clearness. Another important factor for the efficiency of a gas chromatography analysis is the temperature ramping rate.[100]
At the end of the column is located a detector, which is the component able to detect the substances inside the sample. The most common one is the flame ionization detector (FID). The effluent goes into a flame created by air and hydrogen, which allows the formation of ions and, therefore, a current, which can be amplified and converted into a signal.

For this research, the quantitative analysis of the products of reactions was performed using the gas chromatograph *Shimadzu GC-2014*, equipped with a flame ionization detector. The following column was used:

- *CP-Sil 5* capillary column. Length: 50 m. Internal diameter: 0,25 mm. Film thickness: 0,25 μm.

To determine the retention time of each substance, commercially available agents were used. The spectra of pure substances are reported in **APPENDIX A**.
Analyses were performed two times for each sample in order to calculate an average value ad increase the accuracy.

Figure 21 - Gas chromatograph *Shimadzu GC-2014*

Figure 22 - Capillary column *CP-Sil 5*

2.2.2 - Proton nuclear magnetic resonance spectroscopy (NMR)

Nuclear Magnetic Resonance spectroscopy or NMR is an instrumental analytic technique which allows to obtain structural or quantitative information about substances detecting the behavior of the nuclei inside a magnetic field.
Since this analysis exploits the magnetic momentum, the NMR is able to detect only atoms which have an odd number of protons or neutrons, otherwise the overall spin of the nuclei is zero.
The projection of the magnetic momentum of a nucleus with a not null spin, in presence of a magnetic field, tends to be aligned to the field. The allowed orientations are ruled by the magnetic quantic number (m), which can assume values from -I to +I, where I is the spin quantic number.
In case of the hydrogen nucleus, with spin ½, m can assume values of +1/2 and -1/2 and there is a slight difference between the energy of the two configurations, which is proportional to a frequency called Larmor frequency, linked to the magnetic field. Different energies lead to a different number of nuclei in each level. The ^{1}H nucleus is the one exploited by ^{1}H-NMR, used for this work.

Irradiating the sample with a magnetic radiation of frequency equal to the Larmor one, it is absorbed by the nuclei and the resonance phenomenon is induced. After the interruption of the impulse, excited nuclei keep emitting signals, called free induction decay. These signals are then converted through the Fourier transform and a spectrum in function of frequencies is obtained.

To perform a quantitative analysis two concepts are crucial. The first one is the chemical shift. Hydrogen atoms, depending on which element are bonded to, absorb at different frequencies, hence the resonance is not the same but depends on the electronegativity. Since electrons are charged particles, in presence of an external magnetic field another induced one is generated, and this leads to a different frequency of resonance. This variation is called chemical shift and usually is evaluated respect a reference atom which is considered as zero. This is the hydrogen of tetramethylsilane (TMS), which is highly shielded due to the low electronegativity of Si, so all the chemical shifts will be positive. In particular, the relative chemical shift is used, since it does not depend on the applied magnetic field and is defined as follows:

$$\delta = \frac{Hz_{H} - Hz_{H\,TMS}}{Hz_{H\,TMS}}\ [ppm] \tag{E1}$$

For proton NMR, values of δ run from 0 to 12 ppm.

Therefore, every functional group have a particular chemical shift.
The second useful property is that for ^{1}H-NMR the intensity of the signal is proportional to the number of hydrogens which generate it, so the peak area is proportional to the concentration.[101]
This is the fundamental phenomenon which allows to perform quantitative analysis through NMR spectroscopy following the internal standard method.

For this work, the NMR spectrometer *Bruker Ultrashield 400* was used. It provides a magnetic field of 9.4 T (400 MHz).

Figure 23 - NMR spectrometer *Bruker Ultrashield 400*

For the analysis, dimethyl sulfoxide (DMSO) was used as internal standard, since it has 6 protons which give a unique peak with a chemical shift of 2.71 ppm, as can be seen in **Figure 54** reported in **APPENDIX B** and also in literature.[102]
Deuterated methanol, methanol-d_4, instead, was used as solvent. It is a diffuse solvent for NMR and it gives a unique peak with a chemical shift of about 4.9 ppm.[103]
To determine the area of the peaks, the software *Delta 5.3.3* was used.

CHAPTER 3 - EXPERIMENTAL SECTION

3.1 - Reaction procedure

All the reactions were performed inside an autoclave with an internal volume of 190 mL and a magnetic spinner inside.
In the autoclave the following amounts of substances were charged: 2 mmol (0,34 g) of CeO_2, 12,5 mmol of substrate, 100 mmol of solvent and variable quantities of dehydrating agent. As reaction solvent, acetonitrile was used on the basis of previous results and the fact that the hydration of acetonitrile is suppressed under the high CO_2 pressure conditions over CeO_2 catalysts.[104,105,106,107]
Afterwards, the reactor was purged and pressurized with CO_2 at room temperature. Subsequently, the autoclave was stirred at 250 rpm and heated up to the desired reaction temperature. For this operation the *EYELA ChemiStation Personal Synthetizer PPV* was used. The time at which the inner temperature of the autoclave, monitored by a thermocouple, reached the designated one, was defined as 0 h reaction time.

Figure 24 - Autoclave

Figure 25 - *EYELA ChemiStation Personal Synthetizer PPV*

After the specific reaction time, the reactor was cooled to room temperature in a water bath. Therefore, ethanol (20 g) was used for collecting the reaction mixture.

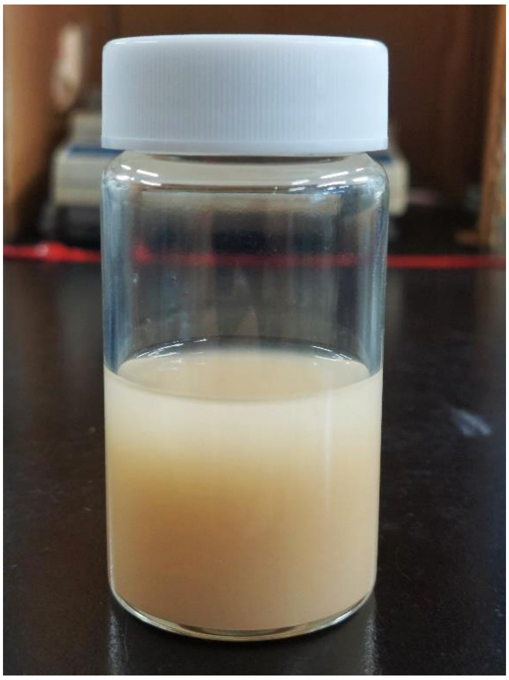


Figure 26 - Recovered reaction products

1-hexanol was added as internal standard for quantitative GC analysis (about 0,4 g) and then the solution was filtrated for separating the catalyst.
For NMR analysis, DMSO was added as internal standard (about 0,15 g). Then, after filtration, about 0,3 g of solution were mixed with about 0,5 g of solvent, methanol-d_4.

While for the synthesis of styrene carbonate it was possible to detect all the substances through gas chromatography, for butylene carbonate the introduction of NMR was necessary since its retention time and the one of 2-cyanopyridine were similar and the peaks resulted overlapped, even using different capillary columns (*Inert Cap for Amine*s, *DB1* and *TC Wax*) and various heating ramp. A spectrum of a reaction using *CP-Sil 5* column is reported in **Figure 53** (**APPENDIX A**). The use of two different methods decreased the reliability of the study but to ensure the robustness of the final results, the amounts of 1,2-butanediol and picolinamide evaluated with NMR were compared with the ones derived from GC analysis and the differences were acceptable, nearly always under 5%. Spectra of all the compounds involved and of a reaction product are reported in **APPENDIX B**.

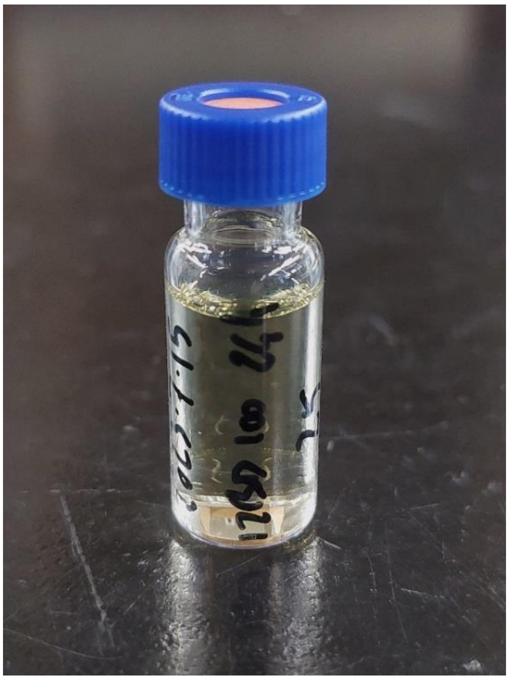


Figure 27 - Sample for gas chromatography

Figure 28 - Sample for NMR spectrometry

3.2 - Internal standard method

Neither of gas chromatography nor NMR analysis give directly the amount of substances as result, instead the areas of the peaks are shown. Hence, to obtain a useful value, the internal standard method was used. It consists of adding to each sample a known amount of a compound, called internal standard, which has its own peak in the spectrogram. Since the area is directly proportional to the moles, by doing a proportion between the two values it is possible to calculate the amount of the target compounds in the sample.
As internal standard the following substances were used:

- 1-hexanol for gas chromatography.
- Dimethyl sulfoxide super dehydrated for NMR.

Standards must have the following characteristics for obtaining a reliable analysis:

- never found in sample, otherwise the real amount would be different from the one added;
- well-resolved, in order to obtain a clear and independent peak;
- stable, to avoid degradation during the analysis;
- available in pure form or with a high purity to avoid interferences;
- structure similar to analyte, in order to have similar retention times or detector response.[108]

The dependency between the moles and the area of the peaks is not the same for all the substances, therefore the evaluation of the amount of substances needs a sort of correction for taking into account the difference with the interna standard (IS). For NMR analysis, the dependency is strictly correlated to the number of protons, as explained in the chapter **2.2.2**. Hence, the final equation for evaluating the amount of the target analytes is:

$$n_{analytes} = \frac{Area_{analytes} * n_{IS}}{Area_{IS} * NoP} \qquad \textbf{E2}$$

Where:

- n is the number of moles;
- $Area$ is the area of the peak;
- NoP is the number of protons of the analytes.

For gas chromatography, relationships are similar but instead of the number of protons, each substance has its own constant, which is linked to the way the instrument responds to it. To evaluate these constants, calibration curves were built for all the compounds involved in the reactions, both reactants and products.

The procedure consists in preparing samples containing a known amount of the pure substance mixed with the solvent, at different concentrations. Usually, at least three samples are required. Analyzing them, is possible to evaluate a correlation between the amount of substance respect to the one of the internal standards and the area of the peaks shown by the instrument. Often, there is a linear dependency which leads to a constant coefficient, characteristic for each analyte. If the pure sample is not available, the parameter can be approximated starting from the ones of substances which have similar structures, like in the case of picolinate. Since it is the reaction product between the diol and picolinamide, the constant used for the calculation was the sum of the two.

The final equation for evaluating the amount of compounds through the gas chromatography is the following:

$$n_{analytes} = \frac{Area_{analytes} * n_{IS}}{Area_{IS} * k} \qquad \textbf{E3}$$

Where:

- n is the number of moles;
- $Area$ is the area of the peak;
- k is the linear coefficient of the calibration curve.

To be sure of the reliability of the calibration curves, concentrations similar to the ones we could have during our tests were chosen. In particular, four concentrations were set starting from the general stoichiometric reaction between a diol and CO_2 with the following parameters:

- 12,5 mmol of diol;
- 50 mmol of 2-cyanopyridine;
- 12,5 mmol of carbonate;
- 12,5 mmol of picolinamide.

Setting the conversion of the diol equal to 20, 40, 60 and 80%, the corresponding amount of substances was calculated.

The calibration curves for the compounds involved in this work are shown below.

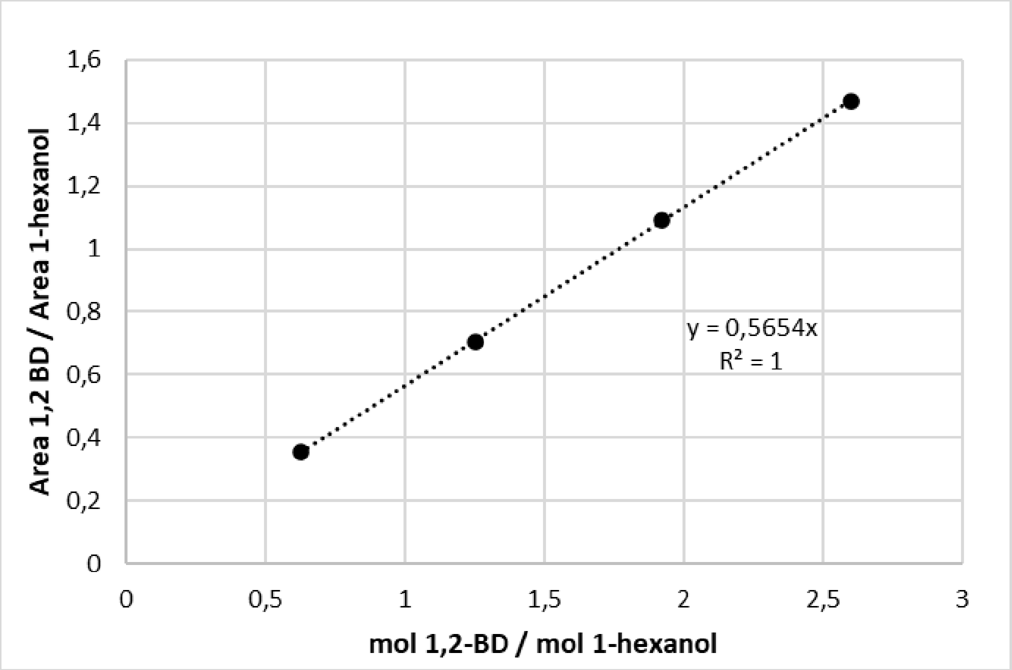


Figure 29 - Calibration line for 1,2-butanediol

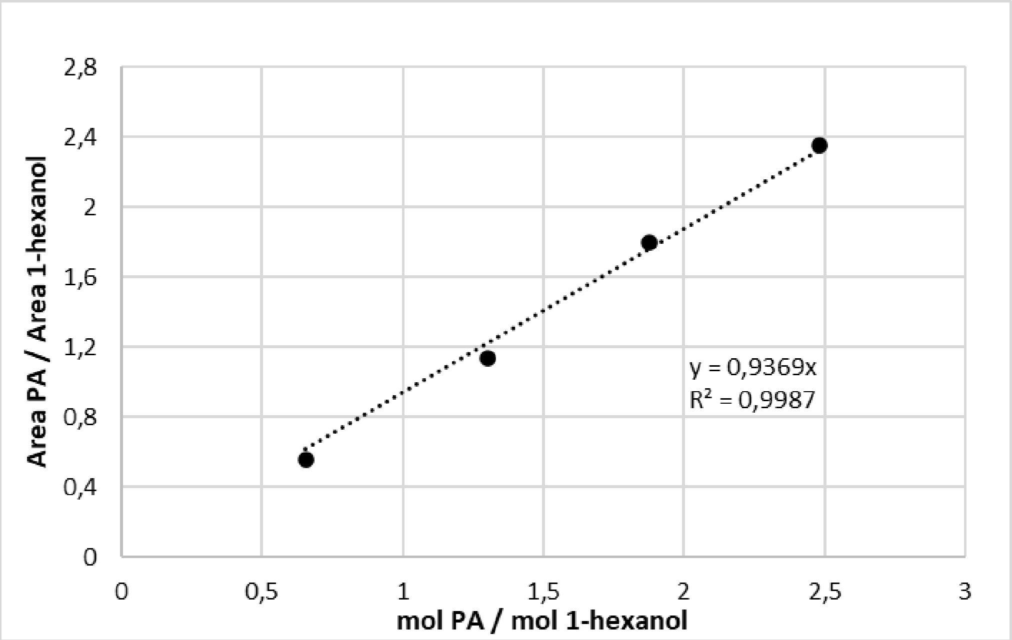


Figure 30 - Calibration line for picolinamide

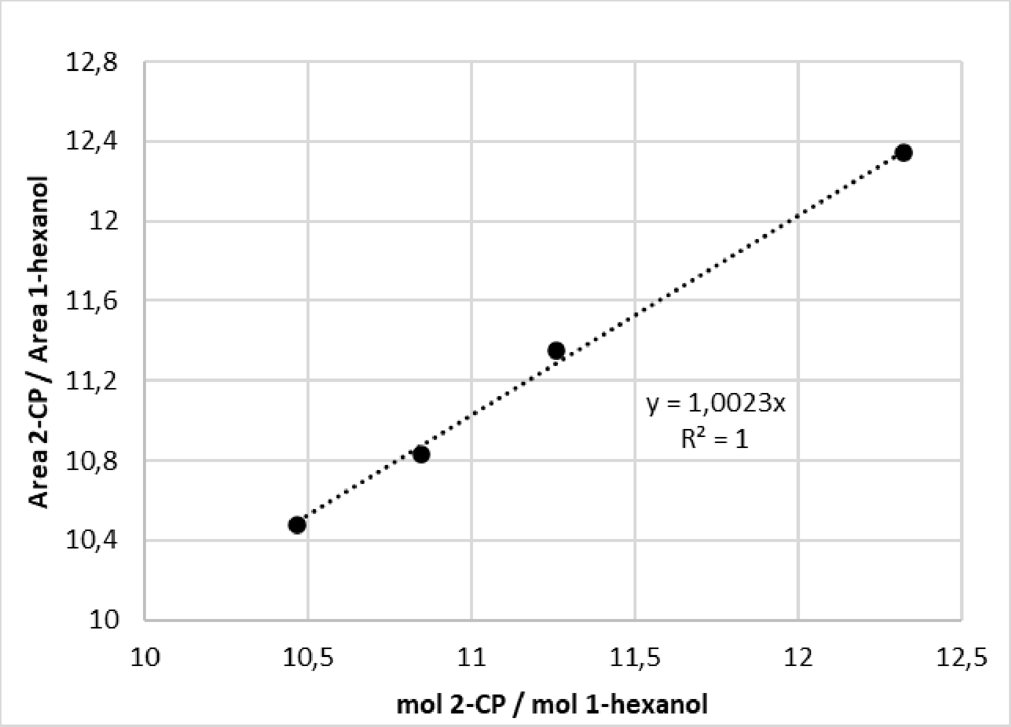


Figure 31 - Calibration line for 2-cyanopyridine

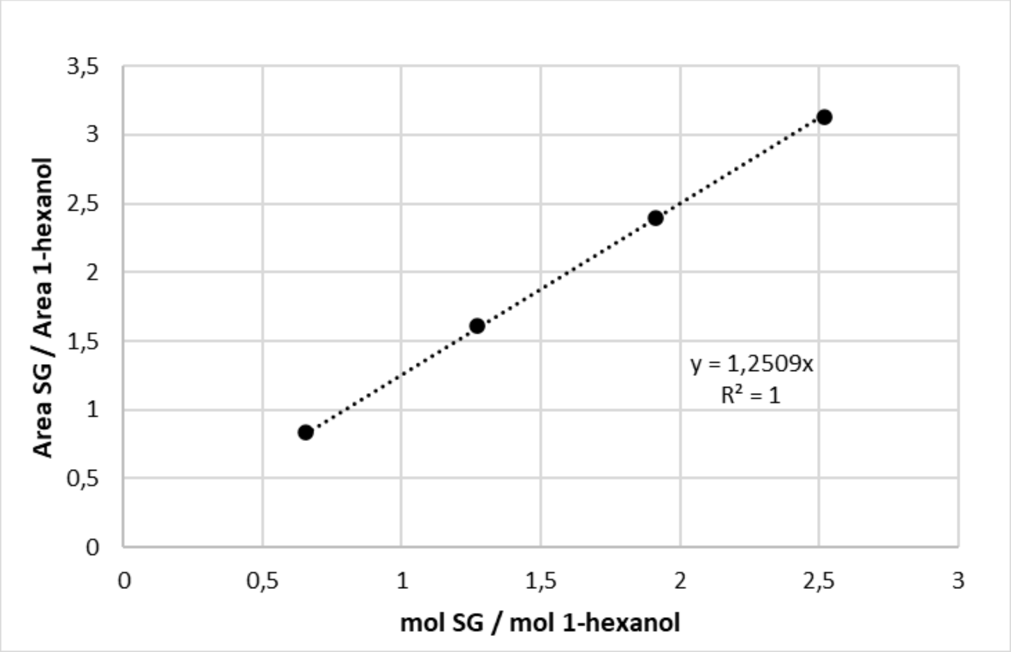


Figure 32 - Calibration line for styrene glycol

3.3 - Synthesis of by-products

As mentioned in chapter **1.5**, some side reactions can take place, leading to the formation of undesired by-product. To detect their presence and evaluate the amount, two reactions related to the synthesis of butylene carbonate were performed:

- synthesis of picolinate, starting from 1,2-butanediol and picolinamide in stoichiometric quantity (1:1, 12,5 mmol);
- synthesis of carbamate, starting from 1,2-butanediol and urea in stoichiometric quantity (1:1, 12,5 mmol).

Both the reactions were performed with the same conditions of the main one in terms of catalyst and solvent. Different pressure and gas, instead, were used: argon at 3 MPa.
The analysis of products through GC was mainly qualitative, since the only information needed were the retention times of the mentioned substances.
Gas chromatography was performed also for a pure sample of acetamide, reaction product of the hydration of acetonitrile.

Results of gas chromatography allowed to exclude an identifiable amount of acetamide and carbamate.
A peak with the same retention time of picolinate, instead, was found also in the main reactions, in a very small amount. The product may be 2-hydroxybutyl picolinate. Even if it was not possible to confirm the structure of the substance through GG-Mass spectrometry, it was considered for the calculation. In lack of a calibration line due to the unavailability of the pure substance, an approximated constant was used, obtained by the summation of the ones of 1,2-butanediol and picolinamide.
Since unknown peaks were not detected for the synthesis of styrene carbonate, the reactions previously mentioned resulted unnecessary.

3.4 - Calculation

Conversion of substrate, carbon and nitrogen balance, yield and selectivity of each product were calculated as represented by the following equations, where *n* are the moles of each component. Note that neither acetonitrile nor acetonitrile-derived compounds, such as acetamide and methyl acetate, were involved in these calculations.

$$\text{Conversion of diol [\%]} = \frac{\sum n_{Diol-derived\ product}}{\sum n_{Diol-derived\ product} + n_{Unreacted\ diol}} \qquad \textbf{E4}$$

$$\text{Yield of carbonate [\%]} = \frac{n_{Carbonate}}{\sum n_{Diol-derived\ product} + n_{Unreacted\ diol}} \qquad \textbf{E5}$$

$$\text{Carbon balance [\%]} = \frac{\sum n_{Diol-derived\ product} + n_{Unreacted\ diol}}{n_{Charged\ diol}} \qquad \textbf{E6}$$

$$\text{Conversion of nitrile [\%]} = \frac{\sum n_{Nitrile-derived\ product}}{\sum n_{Nitrile-derived\ product} + n_{Unreacted\ nitrile}} \qquad \textbf{E7}$$

$$\text{Yield of amide [\%]} = \frac{n_{Amide}}{\sum n_{Nitrile-derived\ product} + n_{Unreacted\ Nitrile}} \qquad \textbf{E8}$$

$$\text{Nitrogen balance [\%]} = \frac{\sum n_{Nitrile-derived\ product} + n_{Unreacted\ nitrile}}{n_{Charged\ nitrile}} \qquad \textbf{E9}$$

$$\text{Selectivity [\%]} = \frac{Yield}{Conversion} \text{ x } 100 \qquad \textbf{E10}$$

For evaluating both the conversion and the yield, equations different from the classic ones were used. The calculation was based on the amount of reactants and products since no unknown peaks were present on the GC results.

CHAPTER 4 - RESULTS

4.1 - Styrene glycol

For a first investigation of the synthesis of styrene carbonate, different reactions were performed changing the two most important parameters: temperature and reaction time.

Reactions were performed using substrates produced by two different companies, *Tokyo Chemical Industry* (*TCI*) at first and *Sigma-Aldrich* (*SA*) in the second place. This choice was induced by the unavailability on the market of the original compound at the moment of the research. This unforeseen event had an impact on the research work and obviously all the data are shown in the following pages, including a comparison between the results given by the two reactants for the same conditions.

4.1.1 - Temperature course

The initial tests were performed to investigate the influence of temperature on the process and to find suitable conditions for the proceeding of the study. The very first reaction was taken at 110 °C for 24 h. Since the yield was not so high, two additional tests were performed increasing the temperature and keeping the reaction time constant. In particular, 130 and 150 °C were selected. The same set of experiments was repeated for both the substrates mentioned before, in order to make a comparison and evaluate the effect of the manufacturer. An additional temperature, 180 °C, was set for the *Sigma-Aldrich* reactant.

The amount of 2-cyanopiridine and the CO_2 pressure were 50 mmol and 5 MPa, respectively.

Table 1 - Temperature course for 24 h reactions with *TCI* substrate

T [°C]	Amount [mmol]		Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	SC	Unreacted SG	SG	SC	SC	Carbon
110	0,51	12,17	3,99	3,99	100,00	101,43
130	0,67	11,85	5,35	5,35	100,00	100,12
150	0,92	11,10	7,68	7,68	100,00	96,18

T [°C]	Amount [mmol]		Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	Unreacted 2-CP	2-CP	PA	PA	Nitrogen
110	1,76	48,85	3,47	3,47	100,00	101,16
130	1,80	48,82	3,55	3,55	100,00	101,55
150	2,93	48,20	5,72	5,72	100,00	102,50

CeO_2 (873 K, 3h): 0,34 g. Styrene glycol (*TCI*): 12,5 mmol. 2-cyanopyridine: 50 mmol. Acetonitrile: 100 mmol. CO_2 pressure: 5 MPa. Reaction time: 24 h.

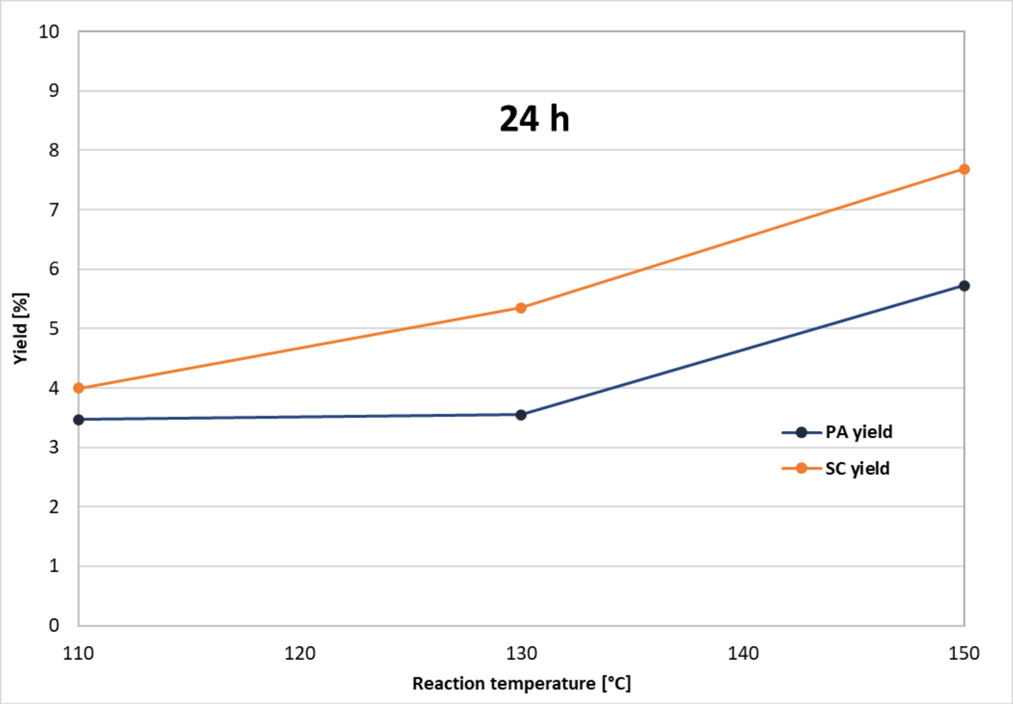


Figure 33 - Temperature course for 24 h reaction time with *TCI* substrate

For the *TCI* substrate a certain kind of pattern can be recognized, with the yield for the 130 °C reaction slightly lower than the one related to a linear dependency. The most important result, anyway, is not the influence of temperature but the efficiency of the process. The yield of styrene carbonate after a considerable reaction reaches almost 8% for the 150 °C test and it is a very low value comparing to the energy request for maintaining those conditions.

A second set of reactions was performed with the *Sigma-Aldrich* substrate and the results are shown below.

Table 2 - Temperature course for 24 h reactions with *Sigma-Aldrich* substrate

T [°C]	Amount [mmol]		Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	SC	Unreacted SG	SG	SC	SC	Carbon
110	0,05	10,88	0,46	0,46	100,00	87,44
130	0,09	11,01	0,77	0,77	100,00	88,68
150	0,62	7,50	7,67	7,67	100,00	64,95
180	0,75	4,99	13,07	13,07	100,00	45,88

T [°C]	Amount [mmol]		Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	Unreacted 2-CP	2-CP	PA	PA	Nitrogen
110	3,01	45,71	6,18	6,18	100,00	97,42
130	2,34	50,91	4,40	4,40	100,00	106,66
150	5,19	40,13	11,46	11,46	100,00	90,52
180	7,31	38,77	15,86	15,86	100,00	91,93

CeO_2 (873 K, 3h): 0,34 g. Styrene glycol (*SA*): 12,5 mmol. 2-cyanopyridine: 50 mmol. Acetonitrile: 100 mmol. CO_2 pressure: 5 MPa. Reaction time: 24 h.

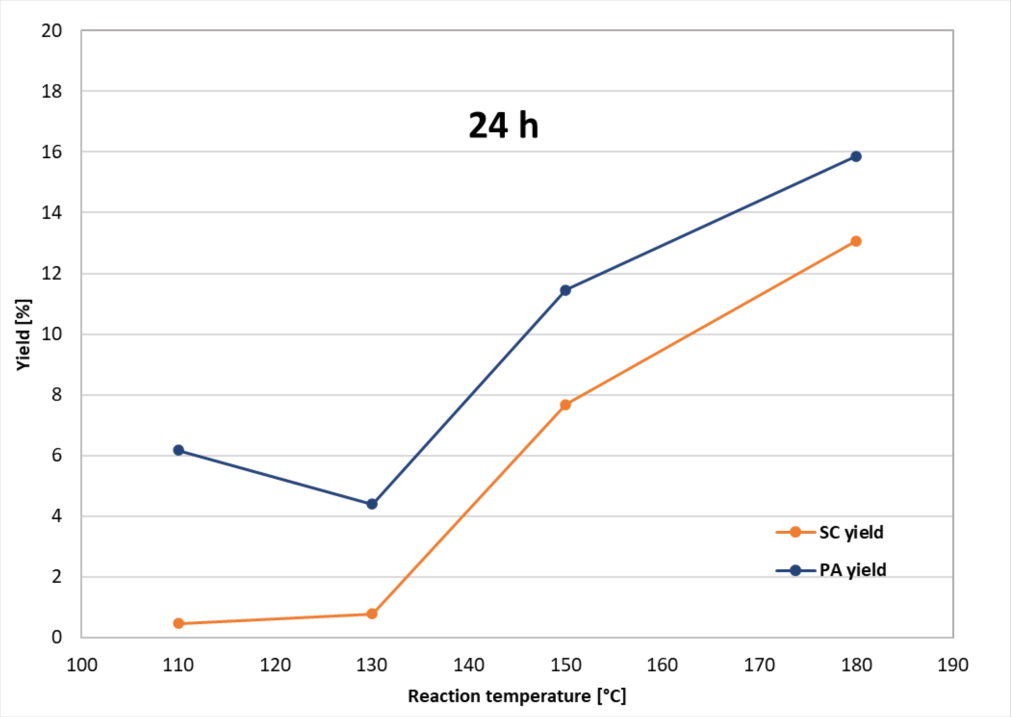


Figure 34 - Temperature course for 24 h reaction time with *Sigma-Aldrich* substrate

For the *Sigma-Aldrich* reactant, an additional test at 180 °C was performed to evaluate the influence of temperature, since the first two values probably were not enough high according to the yields obtained. Looking at the last two points, instead, an improvement linked to the increase of the temperature can be appreciated, even though the better value of the carbonate yield is still low.

Looking at the data, it is clear that the manufacturer of styrene glycol has an influence on the process. In this case, the yields obtained for the tests at the two lowest temperatures are almost null, equal to 0,46% and 0,77% respectively, while with the *TCI* compound are 4% and 5,3% approximately. This not negligible difference disappears for the 150 °C reaction, for which the value of the yield becomes the same, almost 7,7%.
A possible explanation for the different behaviour at lower temperature is linked to the purity of the substrate. Even if the substance was the same, the higher purity of the *TCI* reactant (>98% against 97%) allowed the beginning of the reaction also for lower values of temperature.
The difference between the tests can be appreciated on **Figure 35**.

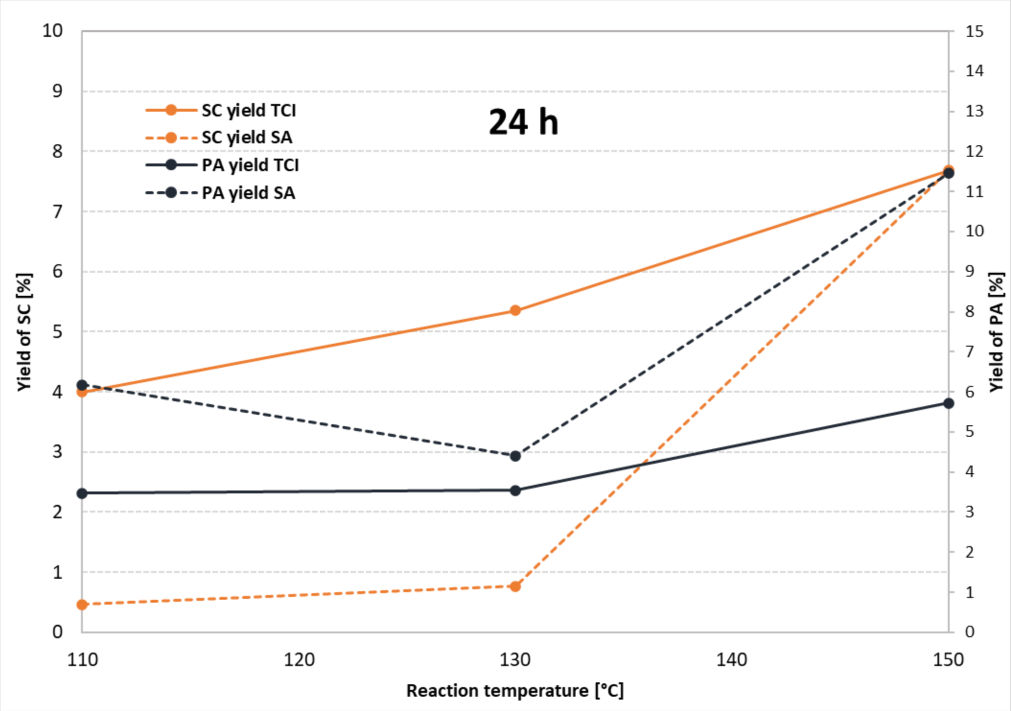


Figure 35 - Comparison of the temperature course for the two substrates

4.1.2 - Time course

To increase the yield of the process, longer reactions were performed in order to verify if the limiting factor was the reaction time. Temperature was fixed at 130 °C and the experiments were stopped after 36 and 48 hours, maintaining the same conditions of the first tests both for the amount of dehydrating agent and the CO_2 pressure. The substrate used was the *Sigma-Aldrich* one.

Table 3 - Time course for 130 °C reaction temperature with *Sigma-Aldrich* substrate

Reaction time [h]	**Amount [mmol]**		**Conversion [%]**	**Yield [%]**	**Selectivity [%]**	**Balance [%]**
	SC	**Unreacted SG**	**SG**	**SC**	**SC**	**Carbon**
24	0,09	11,01	0,77	0,77	100,00	88,68
36	0,30	9,91	2,93	2,93	100,00	81,63
48	0,21	5,52	3,70	3,70	100,00	45,87

Reaction time [h]	**Amount [mmol]**		**Conversion [%]**	**Yield [%]**	**Selectivity [%]**	**Balance [%]**
	PA	**Unreacted 2-CP**	**2-CP**	**PA**	**PA**	**Nitrogen**
24	2,34	50,91	4,40	4,40	100,00	106,66
36	3,63	47,27	7,14	7,14	100,00	101,54
48	3,10	45,38	6,39	6,39	100,00	97,12

CeO_2 (873 K, 3h): 0,34 g. Styrene glycol (*SA*): 12,5 mmol. 2-cyanopyridine: 50 mmol.
Acetonitrile: 100 mmol. CO_2 pressure: 5 MPa. Reaction temperature: 130 °C.

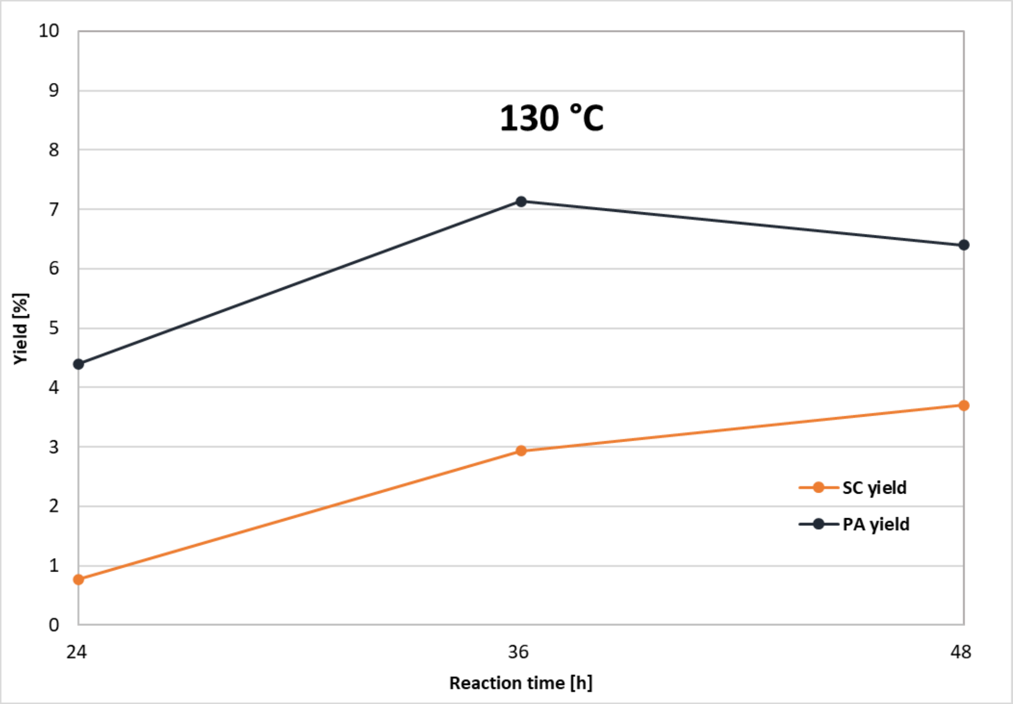


Figure 36 - Time course for 130 °C reaction temperature with *Sigma-Aldrich* substrate

Also these tests did not give positive results. The yield of styrene carbonate slightly increases with the reaction time, but the values are lower than 4% for the longer experiment. Hence this parameter has a negligible impact on the process.

The data previously reported led to the decision of not pursuing deeply the study of styrene glycol as a reactant. The yield reached were not good enough even though the condition of temperature and time were significant in terms of energy demand, therefore the process would be prohibitive and absolutely not convenient.

4.2 - Butane diol

4.2.1 – Time and temperature course

As for styrene glycol, the first approach for the study of the reaction was to perform a preliminary investigation for understanding which range of temperature could give interesting feedback. Hence, at first, a reaction time of 1 h was selected for 70, 90, 110 and 130 °C. Results showed that at 70 °C the reaction does not take place and at 130 °C, instead, it is too quick and does not allow a proper study of the dependencies on other variables. The remaining temperatures showed suitable results, and this led to the decision of introducing an intermediate value of 100 °C.

Therefore, for the analysis of temperature and time course, experiments for the mentioned temperatures were performed with the following reaction times: 1, 2, 4, 8 and 24 hours. Amount of 2-cyanopiridine and pressure were 50 mmol and 5 MPa, respectively.

Results are shown in the following pages.

Table 4 - Time course for reactions at 90 °C

Reaction time [h]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	BC	**Unreacted 1,2-BD**	**Picolinate**	**1,2-BD**	**BC**	**BC**	**Carbon**
1	1,05	10,26	0,00	9,27	9,27	100,00	91,44
2	1,60	9,89	0,00	13,93	13,93	100,00	92,47
4	2,38	9,31	0,00	20,40	20,38	99,87	93,52
8	3,02	8,83	0,00	25,54	25,51	99,88	94,55
24	7,59	4,47	0,02	62,99	62,81	99,71	96,64

Reaction time [h]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	**Unreacted 2-CP**	**Picolinate**	**2-CP**	**PA**	**PA**	**Nitrogen**
1	2,14	47,61	0,00	4,69	4,30	100,00	99,59
2	2,73	47,11	0,00	5,49	5,49	100,00	99,93
4	3,41	47,38	0,00	6,71	6,70	99,91	101,61
8	4,09	45,56	0,00	8,25	8,24	99,91	99,24
24	8,67	40,52	0,02	17,66	17,62	99,75	98,69

CeO_2 (873 K, 3h): 0,34 g. 1,2-butanediol: 12,5 mmol. 2-cyanopyridine: 50 mmol. Acetonitrile: 100 mmol. CO_2 pressure: 5 MPa. Temperature: 90 °C.

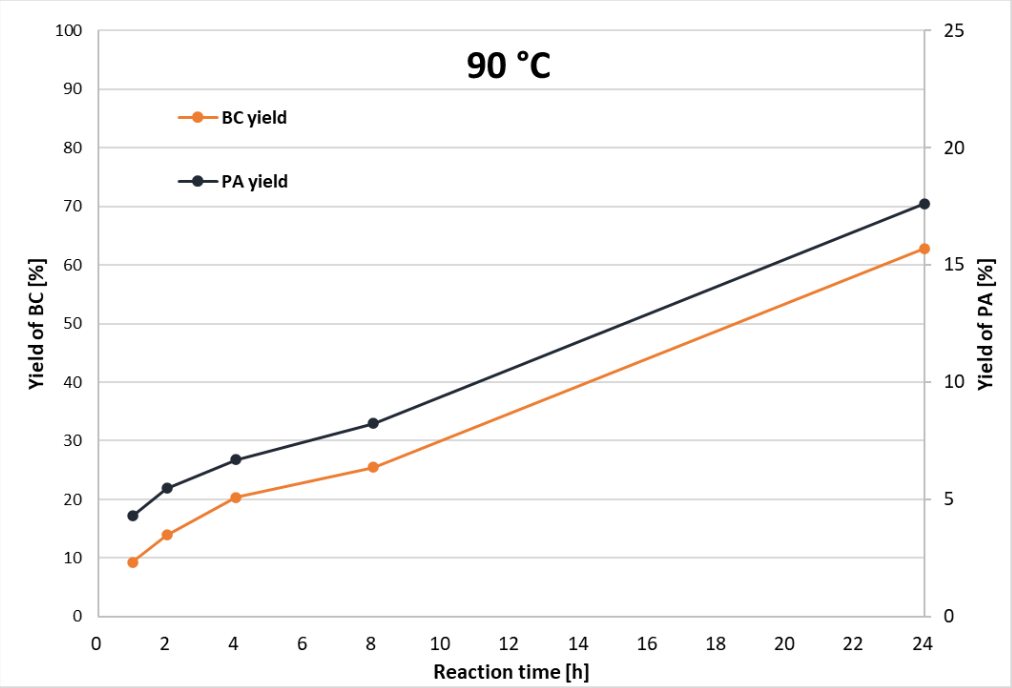


Figure 37 - Time course for reactions at 90 °C

At 90 °C the increase of the yield of both the compounds is almost linear with the reaction time and using different scales for axis allows to see the similarity of trends. This means that the removing of water proceeded with the same rate of the main reaction, confirming the effectiveness of 2-cyanopyridine as dehydrating agent.

Nevertheless, even the 24 hours reaction is not very interesting in terms of productivity of carbonate, since the yield is about 63%, which is not enough thinking to a potential large-scale process. This means that the influence of reaction time on the synthesis is not so significant and the reaction rate at 90 °C is still low.

Table 5 - Time course for reactions at 100 °C

Reaction time [h]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	BC	Unreacted 1,2-BD	Picolinate	1,2-BD	BC	BC	Carbon
0	1,20	10,23	0,00	10,48	10,48	100,00	92,52
1	4,31	7,58	0,01	36,29	36,21	99,79	94,88
2	5,75	6,24	0,02	48,04	47,89	99,69	96,67
4	6,63	5,72	0,03	53,81	53,58	99,57	99,63
8	8,60	3,86	0,02	69,09	68,89	99,71	100,16
24	11,55	0,50	0,05	95,85	95,46	99,59	97,67

Reaction time [h]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	Unreacted 2-CP	Picolinate	2-CP	PA	PA	Nitrogen
0	3,62	44,78	0,00	7,48	7,48	100,00	96,71
1	6,77	41,36	0,01	14,08	14,06	99,87	96,07
2	7,01	41,75	0,02	14,41	14,37	99,74	97,84
4	7,30	40,75	0,03	15,25	15,19	99,61	96,30
8	8,61	40,83	0,02	17,45	17,40	99,71	98,97
24	11,65	36,18	0,05	24,43	24,34	99,60	95,69

CeO_2 (873 K, 3h): 0,34 g. 1,2-butanediol: 12,5 mmol. 2-cyanopyridine: 50 mmol. Acetonitrile: 100 mmol. CO_2 pressure: 5 MPa. Temperature: 100 °C.

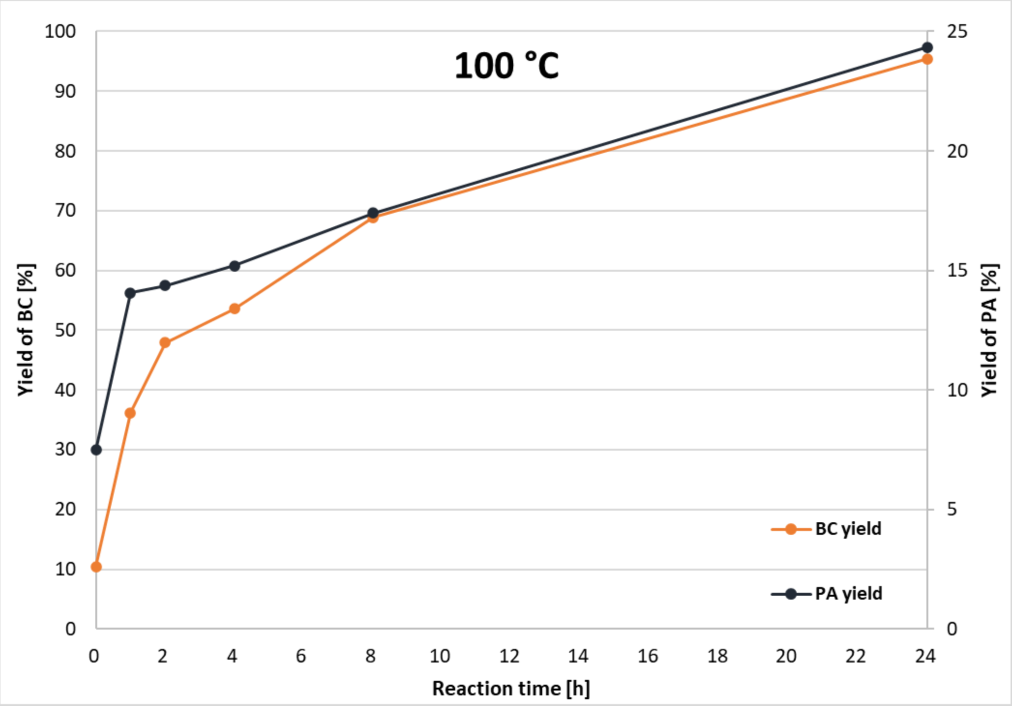


Figure 38 - Time course for reactions at 100 °C

0 h reaction at 100 °C was added at the end of the evaluation. The autoclave was cooled as soon as it reached the target temperature.

The trend in this case is not linear, but the reaction rate is very high at the beginning, particularly for the main reaction. After the second hour, instead, it become more linear as in 90 °C case, and again the yields of butylene carbonate and picolinamide, observed on different scales, resulted similar. This means that a higher temperature allows a fast synthesis of the cyclic carbonate in a short time, but later the rate decreases.

The main difference with the first case is the amount of target product synthesized. At 90 °C, after 24 hours, less than 8 mmol of carbonate were produced. With an increase of only 10 °C, a better result was obtained in one third of the time. The observation of these values is sufficient to affirm that temperature is the crucial parameter for this kind of reaction, and it will be clearer with the following data, related to 110 °C experiments.

Table 6 - Time course for reactions at 110 °C

Reaction time [h]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	BC	**Unreacted 1,2-BD**	**Picolinate**	**1,2-BD**	**BC**	**BC**	**Carbon**
1	10,40	2,05	0,04	83,58	83,27	99,63	100,19
2	10,60	1,43	0,04	88,14	87,85	99,67	95,59
4	11,25	0,92	0,04	92,47	92,12	99,63	98,06
8	11,91	0,27	0,04	97,83	97,52	99,69	98,71
24	12,17	0,06	0,04	99,54	99,22	99,69	98,51

Reaction time [h]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	**Unreacted 2-CP**	**Picolinate**	**2-CP**	**PA**	**PA**	**Nitrogen**
1	10,55	37,31	0,04	22,11	22,03	99,63	95,70
2	10,56	37,16	0,04	22,19	22,12	99,67	95,67
4	10,42	37,35	0,04	21,89	21,80	99,60	95,73
8	10,72	35,57	0,04	23,22	23,13	99,65	92,66
24	10,32	34,97	0,04	22,86	22,77	99,63	90,54

CeO_2 (873 K, 3h): 0,34 g. 1,2-butanediol: 12,5 mmol. 2-cyanopyridine: 50 mmol. Acetonitrile: 100 mmol. CO_2 pressure: 5 MPa. Temperature: 110 °C.

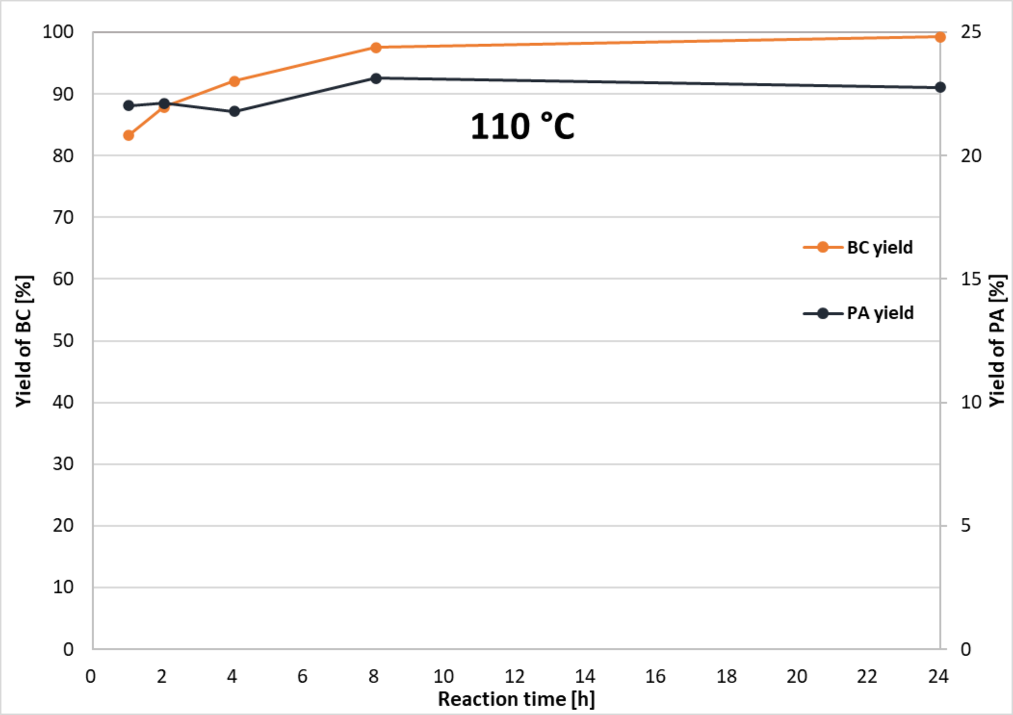


Figure 39 - Time course for reactions at 110 °C

At 110 °C, also after 1 hour the yield of carbonate is very high, above 80%, confirming the influence which temperature has on the synthesis. Doing a comparation on the amount of target product obtained for the 100 °C test, it is possible to see that almost the same quantity was synthesized in one sixth of the time, increasing the temperature of only 10 °C.

On a point of view of efficiency, is clear that 110 °C reaction temperature would be the more likely for a productive process, in which the synthesis of the carbonate is the main purpose. The high amount of product obtained also with short reaction times would allow a lower energy consumption, which is a crucial aspect both in terms of costs and environmental impact.

In the following tables are reported the same data shown before but in a different structure, designed to underline the dependence of the main reaction on temperature.

Table 7 - Temperature course for 1 hour reactions

T [°C]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	BC	Unreacted 1,2-BD	Picolinate	1,2-BD	BC	BC	Carbon
70	0,00	11,44	0,00	8,16	0,00	0,00	91,84
90	1,05	10,26	0,00	9,27	9,27	100,00	91,44
100	4,31	7,58	0,01	36,29	36,21	99,79	94,88
110	10,40	2,05	0,04	83,58	83,27	99,63	100,19
130	11,90	0,26	0,05	97,84	97,44	99,59	99,12

T [°C]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	Unreacted 2-CP	Picolinate	2-CP	PA	PA	Nitrogen
70	1,68	48,02	0,00	3,97	3,39	100,00	99,40
90	2,14	47,61	0,00	4,69	4,30	100,00	99,59
100	6,77	41,36	0,01	14,08	14,06	99,87	96,07
110	10,55	37,31	0,04	22,11	22,03	99,63	95,70
130	12,00	37,55	0,05	24,29	24,19	99,59	99,23

CeO_2 (873 K, 3h): 0,34 g. 1,2-butanediol: 12,5 mmol. 2-cyanopyridine: 50 mmol. Acetonitrile: 100 mmol. CO_2 pressure: 5 MPa. Reaction time: 1 h.

Table 8 - Temperature course for 2 hours reactions

T [°C]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	BC	Unreacted 1,2-BD	Picolinate	1,2-BD	BC	BC	Carbon
90	1,11	10,45	0,00	9,62	9,59	99,72	93,84
100	5,75	6,24	0,02	48,04	47,89	99,69	96,67
110	10,60	1,43	0,04	88,14	87,85	99,67	95,59

T [°C]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	Unreacted 2-CP	Picolinate	2-CP	PA	PA	Nitrogen
90	2,91	47,32	0,00	5,80	5,79	99,89	100,77
100	7,01	41,75	0,02	14,41	14,37	99,74	97,84
110	10,56	37,16	0,04	22,19	22,12	99,67	95,67

CeO_2 (873 K, 3h): 0,34 g. 1,2-butanediol: 12,5 mmol. 2-cyanopyridine: 50 mmol. Acetonitrile: 100 mmol. CO_2 pressure: 5 MPa. Reaction time: 2 h.

Table 9 - Temperature course for 4 hours reactions

T [°C]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	BC	Unreacted 1,2-BD	Picolinate	1,2-BD	BC	BC	Carbon
90	2,38	9,31	0,00	20,40	20,38	99,87	93,52
100	5,70	6,29	0,01	47,59	47,48	99,78	96,20
110	11,25	0,92	0,04	92,47	92,12	99,63	98,06

T [°C]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	Unreacted 2-CP	Picolinate	2-CP	PA	PA	Nitrogen
90	3,41	47,38	0,00	6,71	6,70	99,91	101,61
100	6,34	41,38	0,01	13,31	13,28	99,80	95,42
110	10,42	37,35	0,04	21,89	21,80	99,60	95,73

CeO_2 (873 K, 3h): 0,34 g. 1,2-butanediol: 12,5 mmol. 2-cyanopyridine: 50 mmol. Acetonitrile: 100 mmol. CO_2 pressure: 5 MPa. Reaction time: 4 h.

Table 10 - Temperature course for 8 hours reactions

T [°C]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	BC	Unreacted 1,2-BD	Picolinate	1,2-BD	BC	BC	Carbon
90	3,02	8,83	0,00	25,54	25,51	99,88	94,55
100	8,60	3,86	0,02	69,09	68,89	99,71	100,16
110	11,91	0,27	0,04	97,83	97,52	99,69	98,71

T [°C]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	Unreacted 2-CP	Picolinate	2-CP	PA	PA	Nitrogen
90	4,09	45,56	0,00	8,25	8,24	99,91	99,24
100	8,61	40,83	0,02	17,45	17,40	99,71	98,97
110	10,72	35,57	0,04	23,22	23,13	99,65	92,66

CeO_2 (873 K, 3h): 0,34 g. 1,2-butanediol: 12,5 mmol. 2-cyanopyridine: 50 mmol. Acetonitrile: 100 mmol. CO_2 pressure: 5 MPa. Reaction time: 8 h.

Table 11 - Temperature course for 24 hours reactions

T [°C]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	BC	Unreacted 1,2-BD	Picolinate	1,2-BD	BC	BC	Carbon
90	7,59	4,47	0,02	62,99	62,81	99,71	96,64
100	11,55	0,50	0,05	95,85	95,46	99,59	97,67
110	12,17	0,06	0,04	99,54	99,22	99,69	98,51

T [°C]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	Unreacted 2-CP	Picolinate	2-CP	PA	PA	Nitrogen
90	8,67	40,52	0,02	17,66	17,62	99,75	98,69
100	11,65	36,18	0,05	24,43	24,34	99,60	95,69
110	10,32	34,97	0,04	22,86	22,77	99,63	90,54

CeO$_2$ (873 K, 3h): 0,34 g. 1,2-butanediol: 12,5 mmol. 2-cyanopyridine: 50 mmol. Acetonitrile: 100 mmol. CO$_2$ pressure: 5 MPa. Reaction time: 24 h.

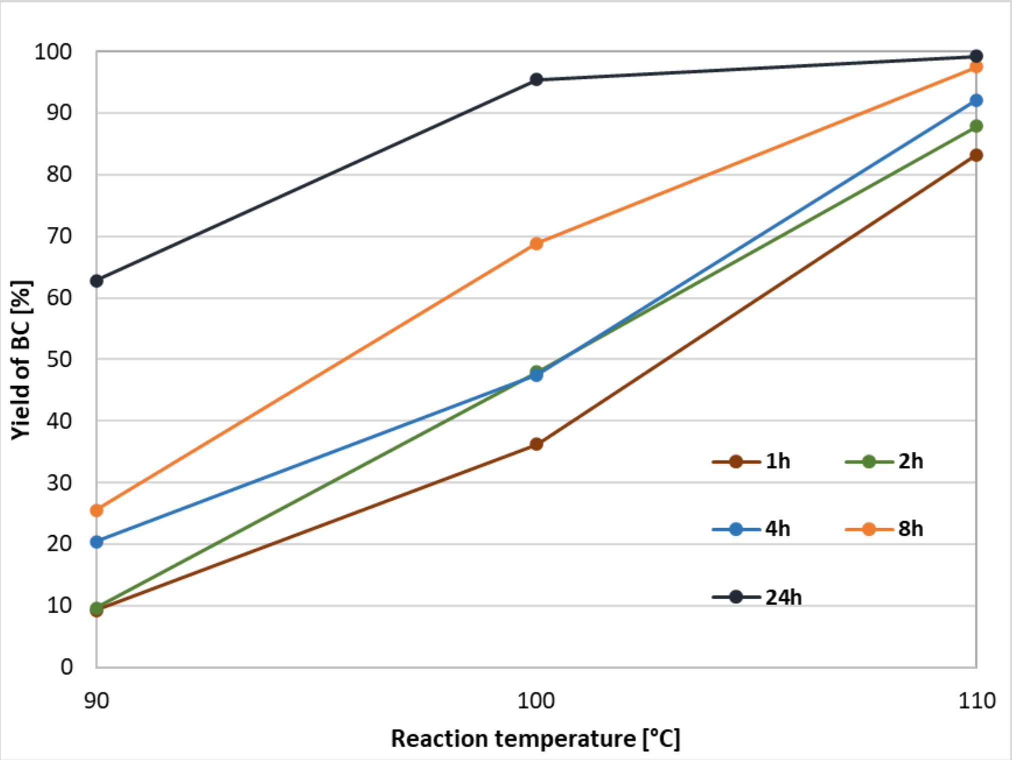


Figure 40 - Temperature course of butylene carbonate yield for different reaction times

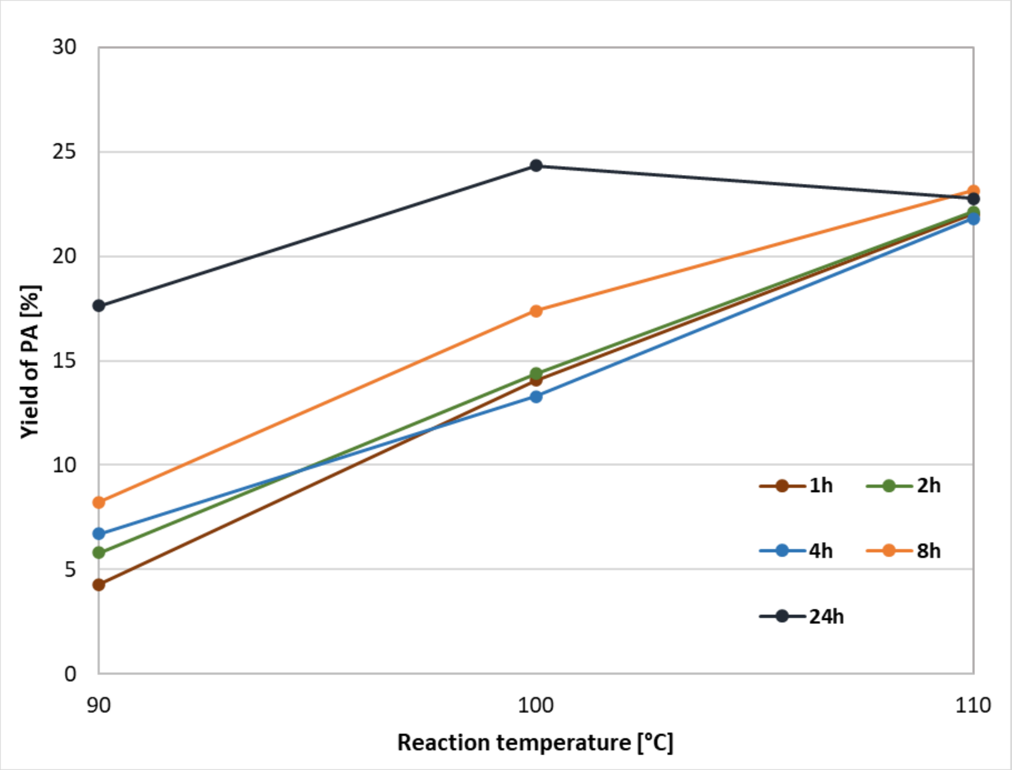


Figure 41 - Temperature course of picolinamide yield for different reaction times

Values of yield at 110 °C are very close to each other, confirming the huge influence of temperature. Nevertheless, since the analysis of the overall reaction and study of the dependence on other variables were requested, the fast reaction rate would have not allowed a proper evaluation. Therefore, the reaction temperature chosen for the continuation of the research was 100 °C.

4.2.2 - Dependence on dehydrating agent

Another crucial aspect of the synthesis is the dehydrating agent, as mentioned before. It ensures the consuming of water and the increase of the carbonate yield, avoiding an equilibrium limitation. Anyway, for the reactions shown in the previous section, the amount of 2-cyanopiridine was much higher than the diol one, even if the stoichiometry is 1:1. In addition, this substance could have a great impact on the economic point of view speaking of an overall large-scale process. For these reasons, the feasibility of the synthesis using lower amounts of dehydrants was investigated, decreasing it of 50% and 75%, respectively. As said before, reaction temperature was fixed at 100 °C.

Results are shown in the following tables.

Table 12 - Time course for reactions with 25 mmol of 2-cyanopyridine

Reaction time [h]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	BC	Unreacted 1,2-BD	Picolinate	1,2-BD	BC	BC	Carbon
1	3,60	8,14	0,02	30,79	30,60	99,38	93,94
2	4,38	7,12	0,02	38,20	38,01	99,50	92,87
4	5,85	6,22	0,03	48,59	48,32	99,45	96,64
8	7,54	4,03	0,05	65,35	64,89	99,30	92,98
24	10,62	0,88	0,09	92,38	91,59	99,15	94,37

Reaction time [h]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	Unreacted 2-CP	Picolinate	2-CP	PA	PA	Nitrogen
1	5,16	18,23	0,02	22,14	22,04	99,56	93,91
2	6,07	17,36	0,02	25,98	25,89	99,64	93,31
4	6,73	17,25	0,03	28,18	28,04	99,52	96,56
8	8,38	14,80	0,05	36,31	36,08	99,37	92,85
24	11,34	12,02	0,09	48,75	48,36	99,20	94,12

CeO_2 (873 K, 3h): 0,34 g. 1,2-butanediol: 12,5 mmol. 2-cyanopyridine: 25 mmol. Acetonitrile: 100 mmol. CO_2 pressure: 5 MPa. Temperature: 100 °C.

Table 13 - Time course for reactions with 12,5 mmol of 2-cyanopyridine

Reaction time [h]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	BC	Unreacted 1,2-BD	Picolinate	1,2-BD	BC	BC	Carbon
1	1,43	10,13	0,02	12,45	12,31	98,91	93,24
2	3,44	8,36	0,02	29,24	29,09	99,50	94,04
4	4,81	6,75	0,03	41,75	41,51	99,43	93,60
8	6,28	5,71	0,05	52,58	52,16	99,19	97,68
24	6,35	5,85	0,15	52,59	51,40	97,74	99,47

Reaction time [h]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	Unreacted 2-CP	Picolinate	2-CP	PA	PA	Nitrogen
1	3,04	9,24	0,02	24,83	24,70	99,49	97,16
2	3,99	7,71	0,02	34,18	34,03	99,57	93,16
4	5,24	6,41	0,03	45,12	44,89	99,48	93,66
8	6,63	5,07	0,05	56,87	56,43	99,23	93,79
24	9,06	2,30	0,15	80,03	78,76	98,41	91,34

CeO_2 (873 K, 3h): 0,34 g. 1,2-butanediol: 12,5 mmol. 2-cyanopyridine: 12,5 mmol. Acetonitrile: 100 mmol. CO_2 pressure: 5 MPa. Temperature: 100 °C.

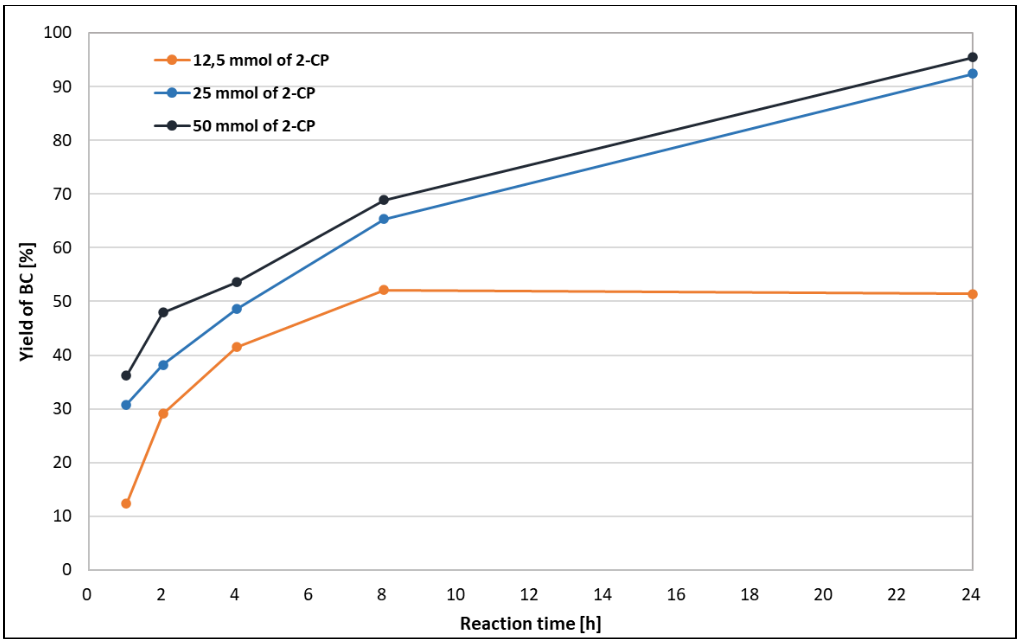


Figure 42 - Time course of butylene carbonate yield for different amounts of dehydrant

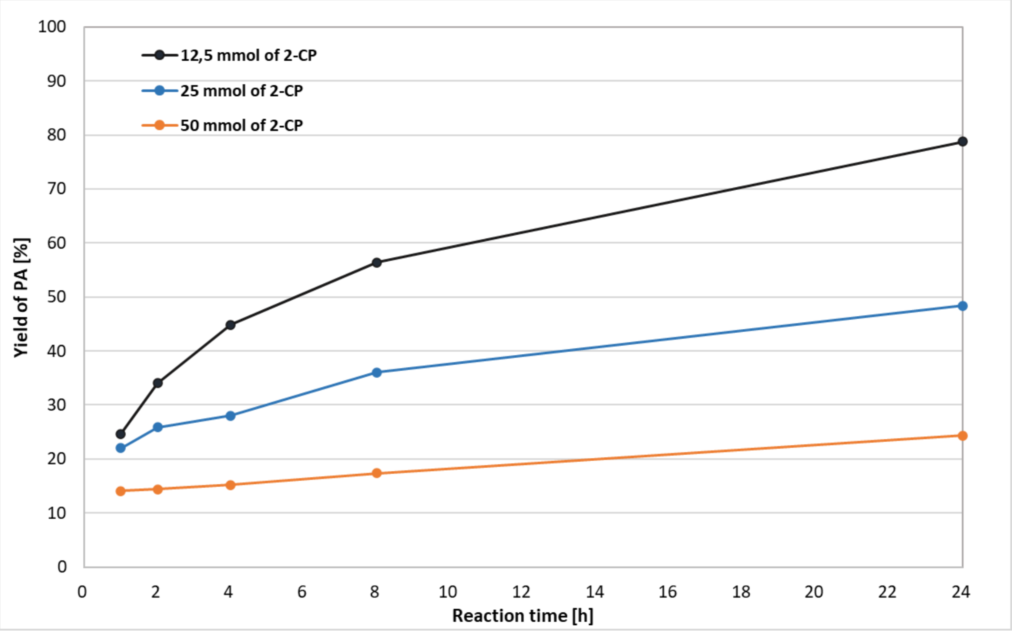


Figure 43 - Time course of picolinamide yield for different amounts of 2-cyanopyridine

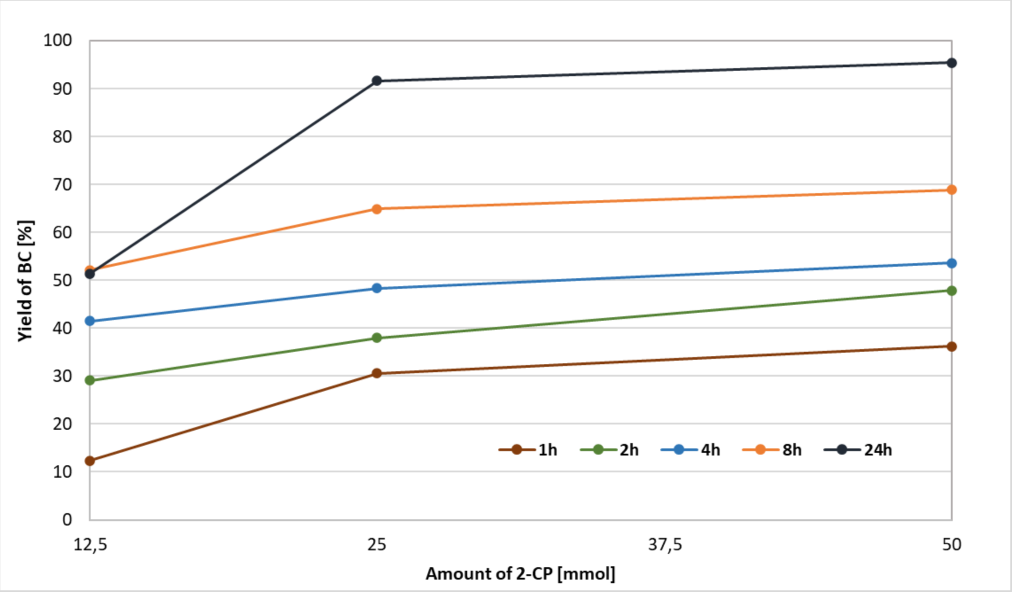


Figure 44 - Variation of butylene carbonate yield with the amount of 2-cyanopyridine

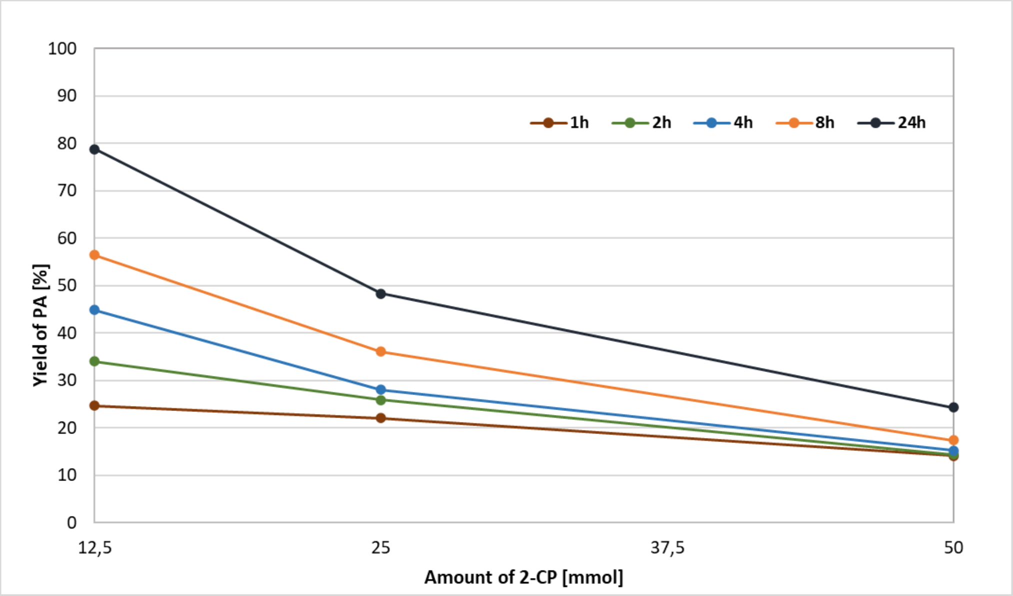


Figure 45 - Variation of picolinamide yield with the amount of 2-cyanopyridine

Looking at the first graphs (**Figure 42-43**), it is possible to identify two different trends. For the tests with 25 and 50 mmol of dehydrating agent, the pattern is very similar. The carbonate yield increased almost linearly with the reaction time up to 8 hours, while for the 24 hour test, the reaction rate became slightly lower. In terms of product synthesized, the difference between the two conditions is not significant, around 1,2 mmol for each step. This is clearer in **Figure 44**, where is possible to observe that between 25 and 50 mmol the line is almost flat, proving only a slight increase. Hence the utilization of a huge excess of 2-cynaopyridine is not justified because does not imply real advantages.

For which concerns experiments with a stoichiometric amount of dehydrant, instead, the difference in terms of yield is not negligible and is possible to observe that after 8 hours the reaction did not proceed anymore, since the yield of carbonate remained the same, about 51-52%. In **Figure 44** this result is clear since 8 and 24 hours curves start almost from the same point.

It is important to underline that the behavior of picolinamide in **Figure 45** has an opposite trend respect to the carbonate one only because the yield was evaluated on the amount of 2-cyanopyridine and this led to not comparable values.

4.2.3 - Dependence on CO_2 pressure

The last parameter detected was the pressure of CO_2 in the reactor, hence its amount. All the tests shown in the previous sections were conducted at a pressure of 5 MPa of carbon dioxide, as suggested from previous studies. But this condition corresponds to an amount of CO_2 of about 300 mmol, using the ideal gas law, and this is a huge excess respect to the amount of diol (12,5 mmol). In addition, a high value of pressure would imply significant costs in a potential large scale process. Therefore, reactions at lower pressure were performed. Temperature and time were fixed at 100 °C and 1 hours. In addition, also the amount of 2-cyanopyridine was fixed at 25 mmol, based on previous tests.

Results are shown in the following tables.

Table 14 - Data for reactions at different CO_2 pressure

CO_2 Pressure [MPa]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	BC	Unreacted 1,2-BD	Picolinate	1,2-BD	BC	BC	Carbon
0,1	2,22	9,40	0,01	19,16	19,06	99,51	93,36
0,5	3,92	7,67	0,01	33,86	33,78	99,77	93,96
1	6,13	5,55	0,03	52,61	52,35	99,50	94,21
2	4,49	7,98	0,03	36,12	35,92	99,44	99,11
3	4,23	7,32	0,01	36,68	36,60	99,80	93,08
4	3,94	7,72	0,02	33,91	33,76	99,56	93,18
5	3,60	8,14	0,02	30,79	30,60	99,38	93,94

CO_2 Pressure [MPa]	Amount [mmol]			Conversion [%]	Yield [%]	Selectivity [%]	Balance [%]
	PA	Unreacted 2-CP	Picolinate	2-CP	PA	PA	Nitrogen
0,1	3,91	20,96	0,01	15,75	15,70	99,72	99,45
0,5	4,79	19,52	0,01	19,73	19,69	99,81	97,18
1	7,22	16,27	0,03	30,82	30,69	99,58	93,71
2	5,27	19,03	0,03	21,78	21,68	99,52	97,64
3	4,92	19,79	0,01	19,94	19,90	99,82	98,41
4	5,25	19,05	0,02	21,65	21,58	99,67	97,40
5	5,16	18,23	0,02	22,14	22,04	99,56	93,91

CeO_2 (873 K, 3h): 0,34 g. 1,2-butanediol: 12,5 mmol. 2-cyanopyridine: 25 mmol. Acetonitrile: 100 mmol. Reaction time: 1 h. Temperature: 100 °C.

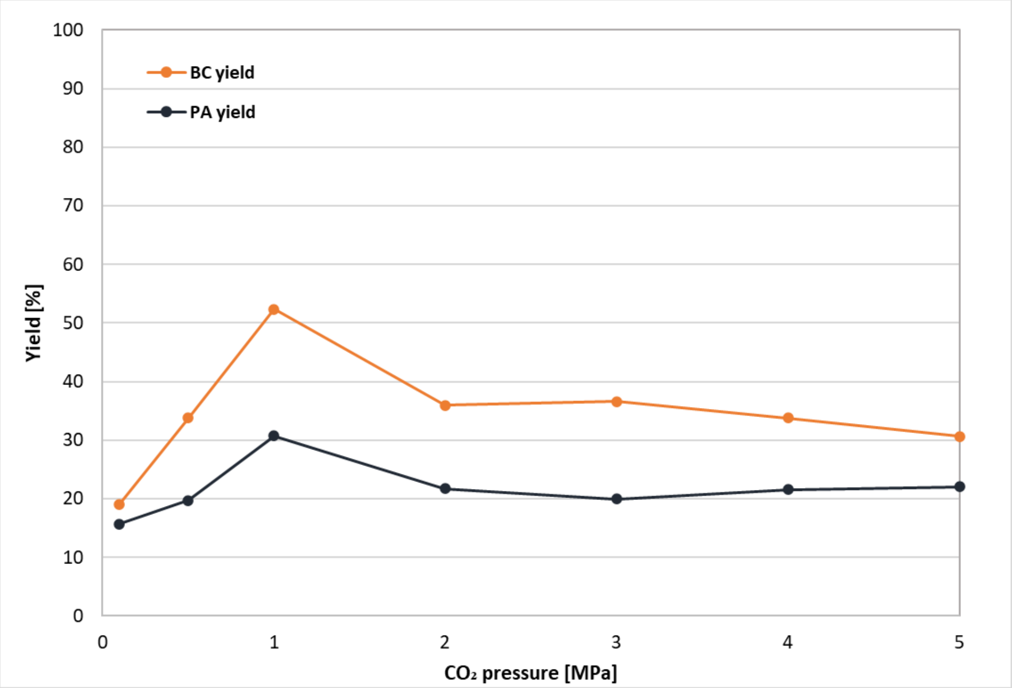


Figure 46 - Variation of butylene carbonate and picolinamide yield with CO_2 pressure

This last set of experiments showed very interesting results, opposite respect to previous studies.[109] High pressure of CO_2, in addition to imply an excess in terms of moles and to create more favorable thermodynamic conditions, has also a third effect. It increases the amount of gas dissolved in the liquid, hence it should make easier the contact with the substrate, leading to a better efficiency.

From the plot is evident, instead, that a decrease of the pressure had a positive influence on the yield of carbonate. It is almost negligible at 2, 3 and 4 MPa, but become significant at 1 MPa. For this last condition, the yield increased from about 36% to 52%, which corresponds to a raise of the amount of product of more than one third. This can be a promising scenario thinking of a real process, since a lower amount of carbon dioxide and a lower pressure are required for producing a larger quantity of target product, resulting in an optimization of the synthesis with a simultaneous reduction of costs.

The cause of this phenomenon is not clear and needs more investigations. One hypothesis is the effect of pressure on the concentration of the reactants in the two phases. The reaction takes place mainly in the liquid phase where the catalyst is dispersed, hence an increase of pressure has two opposite effects. As previously said, it leads to a higher solubility of CO_2 in the liquid phase, which favors the reaction. On the other hand, it causes an increase of the concentration of 1,2-butanediol in the upper phase, reducing the substrate available for the carboxylation process. Probably, at higher pressure this last effect is dominant and leads to a lower yield of carbonate.[110]

Another explanation is linked to the efficiency of the catalyst. At high pressure, the huge amount of carbon dioxide may have caused an undesired occupation of the ceria surface, not allowing the substrate to reach the sites and leading, therefore, to a lower reaction rate. At 1 MPa, instead, the amount of CO_2 (about 61 mmol), still in excess respect to the diol, could have allowed a better performance of the catalyst, resulting in a larger yield of target product.

A progressive reduction of the pressure brings back the yield to lower values. At 0,5 MPa results like the ones of the high pressure tests, instead at 0,1 MPa falls to 19%. This last result is linked to the stoichiometry, since the corresponding amount of carbon dioxide is about 6,1 mmol, against 12,5 mmol of 1,2-butanediol.

Anyway, this ambiguous effect of CO_2 pressure on the reaction rate was reported in various works in literature.[110,111,112,113]

CHAPTER 5 – CONCLUSION

This research work helped to achieve an overall knowledge of the synthesis of styrene carbonate and butylene carbonate from vicinal diols and carbon dioxide, particularly about the dependence on some of the test conditions.

For the former compound, a nearly linear dependency on temperature was detected, in particular for the *TCI* substrate. The *Sigma-Aldrich* one, instead, gave a yield almost null at 110 and 130 °C, underlying that a high purity is necessary for the beginning of the reaction at lower temperature. Increasing the time, instead, the improvement was negligible. However, all the tests were not satisfactory in terms of carbonate yield and the research on this substrate was stopped at the preliminary phase.

A completely different scenario was found for the butylene carbonate synthesis. Reaction time resulted to be influent on the yield of the target product. This behavior was clearer for tests at lower temperatures, for which the increase of the amount of carbonate was proportional to the time.

Nevertheless, the parameter which really determines the efficiency of the synthesis is the reaction temperature. Results showed that an increase of 10 °C, from 90 to 100 °C, allowed the formation of an equal amount of carbonate in about one third of the time. An additional increase, up to 110 °C, ensured a yield higher than 90% after only 4 hours, one sixth of the time needed for the 100 °C reaction. Therefore, on a point of view of efficiency, temperature influence resulted very significant and a potential application in a large-scale process was confirmed, since a high conversion can be reached in relative short times with the preservation of a huge selectivity.
Anyway, an intermediate reaction temperature, 100 °C, was chosen for analyzing the dependence on two more parameters: the amount of dehydrating agent and the CO_2 pressure inside the reactor.

Tests for studying the former factor were performed with an amount of 2-cyanopyridine of 12,5 and 25 mmol, 75% and 50% lower than previous experiments respectively. The first condition resulted insufficient for providing a good yield and the reaction stopped after 8 hours. The second one, instead, showed results similar to the ones of 50 mmol tests, hence a ratio 2:1 between dehydrant and diol is enough for obtaining a great efficiency.

The influence of CO_2 pressure showed very interesting results. A better yield was expected at higher pressure, due to the excess of moles and the easier dissolution inside the liquid. An increase of the conversion, instead, was ensured at lower pressures, particularly at 1 MPa, for which the yield went from about 30% to 52%. The reason of this behavior is not clear but can be linked to a decrease of the catalyst efficiency due to an excess of carbon dioxide on the active sites or to an increase of the diol concentration in the gaseous phase. Anyway, it is an interesting result in terms of a potential industrial application, since a lower pressure leads to a huge decrease of operative costs.

The research work described was a first approach to this kind of processes and a lot of new studies can be performed.

Investigations on the synthesis of styrene carbonate would help to understand which are the limitations on the efficiency and find a way to reach a better yield could be very interesting considering the incredibly high value of this compound, both on the industrial and the economic point of view.

As concerns butylene carbonate, instead, further analyses are necessary to understand the effect of CO_2 pressure, to reach a better knowledge of the overall reaction and to optimize the synthesis, also thinking to a scale-up for industrial applications. For this purpose, performing more tests combining the optimal conditions identified in terms of temperature, amount of dehydrant and pressure, would give more realistic information about the real feasibility of this process.
In addition, it is necessary to find a proper way to determine the nature of by-products.

BIBLIOGRAPHY

(1) Mac Dowell, N.; Fennell, P. S.; Shah, N.; Maitland, G. C. The Role of CO2 Capture and Utilization in Mitigating Climate Change. *Nat. Clim. Chang.* **2017**, *7* (4), 243–249. https://doi.org/10.1038/nclimate3231.

(2) Liu, Z.; Deng, Z.; Davis, S.; Ciais, P. Monitoring Global Carbon Emissions in 2022. *Nat. Rev. Earth Environ.* **2023**, *4* (4), 205–206. https://doi.org/10.1038/s43017-023-00406-z.

(3) Lindsey, R.; Dahlman, L. *Climate Change: Global Temperature*. https://www.climate.gov/news-features/understanding-climate/climate-change-global-temperature.

(4) *THE SCIENCE OF CLIMATE CHANGE*. https://dnr.wisconsin.gov/climatechange/science#:~:text=Since 1880%2C average global temperatures,7.2 degrees Fahrenheit) by 2100.

(5) UNFCCC. The Paris Agreement - Publication. In *Paris Climate Change Conference - November 2015*; 2018.

(6) *IEA (2022), Chemicals, IEA, Paris*; 2022. https://www.iea.org/reports/chemicals, License: CC BY 4.0.

(7) Gabrielli, P.; Gazzani, M.; Mazzotti, M. The Role of Carbon Capture and Utilization, Carbon Capture and Storage, and Biomass to Enable a Net-Zero-CO2 Emissions Chemical Industry. *Ind. Eng. Chem. Res.* **2020**, *59* (15), 7033–7045. https://doi.org/10.1021/acs.iecr.9b06579.

(8) Wang, S.; Yan, S.; Ma, X.; Gong, J. Recent Advances in Capture of Carbon Dioxide Using Alkali-Metal-Based Oxides. *Energy Environ. Sci.* **2011**, *4* (10), 3805–3819. https://doi.org/10.1039/c1ee01116b.

(9) Fu, L.; Ren, Z.; Si, W.; Ma, Q.; Huang, W.; Liao, K.; Huang, Z.; Wang, Y.; Li, J.; Xu, P. Research Progress on CO2 Capture and Utilization Technology. *J. CO2 Util.* **2022**, *66* (July), 102260. https://doi.org/10.1016/j.jcou.2022.102260.

(10) Gao, W.; Liang, S.; Wang, R.; Jiang, Q.; Zhang, Y.; Zheng, Q.; Xie, B.; Toe, C. Y.; Zhu, X.; Wang, J.; Huang, L.; Gao, Y.; Wang, Z.; Jo, C.; Wang, Q.; Wang, L.; Liu, Y.; Louis, B.; Scott, J.; Roger, A. C.; Amal, R.; He, H.; Park, S. E. Industrial Carbon Dioxide Capture and Utilization: State of the Art and Future Challenges. *Chem. Soc. Rev.* **2020**, *49* (23), 8584–8686. https://doi.org/10.1039/d0cs00025f.

(11) Cheah, W. Y.; Ling, T. C.; Juan, J. C.; Lee, D. J.; Chang, J. S.; Show, P. L. Biorefineries of Carbon Dioxide: From Carbon Capture and Storage (CCS) to Bioenergies Production. *Bioresour. Technol.* **2016**, *215*, 346–356. https://doi.org/10.1016/j.biortech.2016.04.019.

(12) Pires, J. C. M.; Martins, F. G.; Alvim-Ferraz, M. C. M.; Simões, M. Recent Developments on Carbon Capture and Storage: An Overview. *Chem. Eng. Res. Des.* **2011**, *89* (9), 1446–1460. https://doi.org/10.1016/j.cherd.2011.01.028.

(13) Drage, T. C.; Smith, K. M.; Pevida, C.; Arenillas, A.; Snape, C. E. Development of Adsorbent Technologies for Post-Combustion CO2 Capture. *Energy Procedia* **2009**, *1* (1), 881–884. https://doi.org/10.1016/j.egypro.2009.01.117.

(14) Serafin, J.; Ouzzine, M.; Cruz, O. F.; Sreńscek-Nazzal, J.; Campello Gómez, I.; Azar, F. Z.; Rey Mafull, C. A.; Hotza, D.; Rambo, C. R. Conversion of Fruit Waste-Derived Biomass to Highly Microporous Activated Carbon for Enhanced CO2 Capture. *Waste Manag.* **2021**, *136* (May), 273–282. https://doi.org/10.1016/j.wasman.2021.10.025.

(15) Davarpanah, E.; Armandi, M.; Hernández, S.; Fino, D.; Arletti, R.; Bensaid, S.; Piumetti, M. CO2 Capture on Natural Zeolite Clinoptilolite: Effect of Temperature and Role of the Adsorption Sites. *J. Environ. Manage.* **2020**, *275* (August). https://doi.org/10.1016/j.jenvman.2020.111229.

(16) Younas, M.; Rezakazemi, M.; Daud, M.; Wazir, M. B.; Ahmad, S.; Ullah, N.; Inamuddin; Ramakrishna, S. Recent Progress and Remaining Challenges in Post-Combustion CO2 Capture Using Metal-Organic Frameworks (MOFs). *Prog. Energy Combust. Sci.* **2020**, *80*. https://doi.org/10.1016/j.pecs.2020.100849.

(17) Pfaff, I.; Kather, A. Comparative Thermodynamic Analysis and Integration Issues of CCS Steam Power Plants Based on Oxy-Combustion with Cryogenic or Membrane Based Air Separation. *Energy Procedia* **2009**, *1* (1), 495–502. https://doi.org/10.1016/j.egypro.2009.01.066.

(18) de Kleijne, K.; Hanssen, S. V.; van Dinteren, L.; Huijbregts, M. A. J.; van Zelm, R.; de Coninck, H. Limits to Paris Compatibility of CO2 Capture and Utilization. *One Earth* **2022**, *5* (2), 168–185. https://doi.org/10.1016/j.oneear.2022.01.006.

(19) Orr, F. M. J.; Taber, J. J. Use of Carbon Dioxide in Enhanced Oil Recovery. *Science (80-.).* **1984**, *224* (4649), 563–569.

(20) Adu, E.; Zhang, Y.; Liu, D. Current Situation of Carbon Dioxide Capture, Storage, and Enhanced Oil Recovery in the Oil and Gas Industry. *Can. J. Chem. Eng.* **2019**, *97* (5), 1048–1076. https://doi.org/10.1002/cjce.23393.

(21) Seyyedsar, S. M.; Farzaneh, S. A.; Sohrabi, M. Experimental Investigation of Tertiary CO2 Injection for Enhanced Heavy Oil Recovery. *J. Nat. Gas Sci. Eng.* **2016**, *34*, 1205–1214. https://doi.org/10.1016/j.jngse.2016.08.020.

(22) Perry, S.; Perry, R. H.; Green, D. W.; Maloney, J. O. *Perry's Chemical Engineers' Handbook*; 2000; Vol. 38. https://doi.org/10.5860/choice.38-0966.

(23) Razzak, S. A.; Hossain, M. M.; Lucky, R. A.; Bassi, A. S.; De Lasa, H. Integrated CO2 Capture, Wastewater Treatment and Biofuel Production by Microalgae Culturing - A Review. *Renew. Sustain. Energy Rev.* **2013**, *27*, 622–653. https://doi.org/10.1016/j.rser.2013.05.063.

(24) Douskova, I.; Doucha, J.; Livansky, K.; MacHat, J.; Novak, P.; Umysova, D.; Zachleder, V.; Vitova, M. Simultaneous Flue Gas Bioremediation and Reduction of Microalgal Biomass Production Costs. *Appl. Microbiol. Biotechnol.* **2009**, *82* (1), 179–185. https://doi.org/10.1007/s00253-008-1811-9.

(25) Lackner, K. S.; Butt, D. P.; Wendt, C. H. Progress on Binding CO2 in Mineral Substrates. **1997**, *38*, 259–264.

(26) Liu, W.; Teng, L.; Rohani, S.; Qin, Z.; Zhao, B.; Xu, C. C.; Ren, S.; Liu, Q.; Liang, B. CO2 Mineral Carbonation Using Industrial Solid Wastes: A Review of Recent Developments. *Chem. Eng. J.* **2021**, *416* (November 2020), 129093. https://doi.org/10.1016/j.cej.2021.129093.

(27) Chauvy, R.; De Weireld, G. CO2 Utilization Technologies in Europe: A Short Review. *Energy Technol.* **2020**, *8* (12), 1–17. https://doi.org/10.1002/ente.202000627.

(28) O'Connor, W. K.; Dahlin, D. C.; Rush, G. E.; S.J. Gerdemann, A.; Penner, L. R. ENERGY AND ECONOMIC CONSIDERATIONS FOR EX-SITU AQUEOUS MINERAL CARBONATION U.S. Department of Energy, Albany Research Center, Albany, Oregon. **2004**.

(29) Turvey, C. C.; Wilson, S.; Hamilton, J. L.; Tait, A. W.; McCutcheon, J.; Beinlich, A.; Fallon, S. J.; Dipple, G. M.; Southam, G. Hydrotalcites and Hydrated Mg-Carbonates as Carbon Sinks in Serpentinite Mineral Wastes from the Woodsreef Chrysotile Mine, New South Wales, Australia: Controls on Carbonate Mineralogy and Efficiency of CO2 Air Capture in Mine Tailings. *Int. J. Greenh. Gas Control* **2018**, *79* (October 2018), 38–60. https://doi.org/10.1016/j.ijggc.2018.09.015.

(30) Zhang, Z.; Pan, S. Y.; Li, H.; Cai, J.; Olabi, A. G.; Anthony, E. J.; Manovic, V. Recent Advances in Carbon Dioxide Utilization. *Renew. Sustain. Energy Rev.* **2020**, *125* (September 2019), 109799. https://doi.org/10.1016/j.rser.2020.109799.

(31) Ravindranathan Thampi, K.; Kiwi, J.; Gratzel, M. Methanation and Photo-Methanation of Carbon Dioxide at Room Temperature and Atmospheric Pressure. *Nature* **1987**, *327* (158), 506–508. https://doi.org/https://doi.org/10.1038/327506a0.

(32) Olah, G. A. Beyond Oil and Gas: The Methanol Economy. *Angew. Chemie - Int. Ed.* **2005**, *44* (18), 2636–2639. https://doi.org/10.1002/anie.200462121.

(33) Alper, E.; Yuksel Orhan, O. CO2 Utilization: Developments in Conversion Processes. *Petroleum* **2017**, *3* (1), 109–126. https://doi.org/10.1016/j.petlm.2016.11.003.

(34) An, B.; Zhang, J.; Cheng, K.; Ji, P.; Wang, C.; Lin, W. Confinement of Ultrasmall Cu/ZnOx Nanoparticles in Metal-Organic Frameworks for Selective Methanol Synthesis from Catalytic Hydrogenation of CO2. *J. Am. Chem. Soc.* **2017**, *139* (10), 3834–3840. https://doi.org/10.1021/jacs.7b00058.

(35) Ganesh, I. Conversion of Carbon Dioxide into Methanol - A Potential Liquid Fuel: Fundamental Challenges and Opportunities (a Review). *Renew. Sustain. Energy Rev.* **2014**, *31*, 221–257. https://doi.org/10.1016/j.rser.2013.11.045.

(36) Aresta, M. *Carbon Dioxide as Chemical Feedstock*, 1 edition.; Wiley-VCH, Ed.; 2010.

(37) Lieuwen, T. C.; Yang, V.; Yetter, R. *Synthesis Gas Combustion - Fundamentals and Applications*; CRC Press - Taylor & Francis Group, 2010.

(38) James, O. O.; Mesubi, A. M.; Ako, T. C.; Maity, S. Increasing Carbon Utilization in Fischer-Tropsch Synthesis Using H2-Deficient or CO2-Rich Syngas Feeds. *Fuel Process. Technol.* **2010**, *91* (2), 136–144. https://doi.org/10.1016/j.fuproc.2009.09.017.

(39) Uner, D.; Oymak, M. M.; Ipek, B. CO2 Utilization by Photocatalytic Conversion to Methane and Methanol. *Int. J. Glob. Warm.* **2011**, *3* (1/2), 142. https://doi.org/10.1504/ijgw.2011.038376.

(40) Della Monica, F.; Kleij, A. W. Mechanistic Guidelines in Nonreductive Conversion of CO2: The Case of Cyclic Carbonates. *Catal. Sci. Technol.* **2020**, *10* (11), 3483–3501. https://doi.org/10.1039/d0cy00544d.

(41) Nakibuule, F.; Nyanzi, S. A.; Oshchapovsky, I.; Wendt, O. F.; Tebandeke, E. Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide Catalyzed by Talc and Other Phyllosilicates. *BMC Chem.* **2020**, *14* (1), 1–14. https://doi.org/10.1186/s13065-020-00713-2.

(42) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Ray Stults, B.; Tumas, W. Catalysis Research of Relevance to Carbon Management: Progress, Challenges, and Opportunities. *Chem. Rev.* **2001**, *101* (4), 953–996. https://doi.org/10.1021/cr000018s.

(43) Shaikh, A. G. Organic Carbonates. **1996**.

(44) Rounce, P.; Tsolakis, A.; Leung, P.; York, A. P. E. A Comparison of Diesel and Biodiesel Emissions Using Dimethyl Carbonate as an Oxygenated Additive. *Energy and Fuels* **2010**, *24* (9), 4812–4819. https://doi.org/10.1021/ef100103z.

(45) Huang, S.; Yan, B.; Wang, S.; Ma, X. Recent Advances in Dialkyl Carbonates Synthesis and Applications. *Chem. Soc. Rev.* **2015**, *44* (10), 3079–3116. https://doi.org/10.1039/c4cs00374h.

(46) Schäffner, B.; Schäffner, F.; Verevkin, S. P.; Börner, A. Organic Carbonates as Solvents in Synthesis and Catalysis. *Chem. Rev.* **2010**, *110* (8), 4554–4581. https://doi.org/10.1021/cr900393d.

(47) Mamparambath Dharman, M.; Choi, H. J.; Park, S. W.; Park, D. W. Microwave Assisted Synthesis of Cyclic Carbonate Using Homogeneous and Heterogeneous Ionic Liquid Catalysts. *Top. Catal.* **2010**, *53* (7–10), 462–469. https://doi.org/10.1007/s11244-010-9473-0.

(48) Clements, J. H. Reactive Applications of Cyclic Alkylene Carbonates. *Ind. Eng. Chem. Res.* **2003**, *42* (4), 663–674. https://doi.org/10.1021/ie020678i.

(49) Lang, X. D.; Li, Z. M.; He, L. N. Protic Ionic Liquid-Catalyzed Synthesis of Oxazolidinones Using Cyclic Carbonates as Both CO2 Surrogate and Sustainable Solvent. *Catal. Today* **2019**, *324* (July 2018), 167–173. https://doi.org/10.1016/j.cattod.2018.09.019.

(50) Hargrove, G. L.; Maruvada, S. FERTILIZER GRANULES HAVING POLYMERC COATING WITH ORGANIC CARBONATE. US 2014 / 0332121 A1, 2014. https://patents.google.com/patent/US20140331942A1/en.

(51) North, M.; Pasquale, R.; Young, C. Synthesis of Cyclic Carbonates from Epoxides and CO2. *Green Chem.* **2010**, *12* (9), 1514–1539. https://doi.org/10.1039/c0gc00065e.

(52) Nohra, B.; Candy, L.; Blanco, J. F.; Guerin, C.; Raoul, Y.; Mouloungui, Z. From Petrochemical Polyurethanes to Biobased Polyhydroxyurethanes. *Macromolecules* **2013**, *46* (10), 3771–3792. https://doi.org/10.1021/ma400197c.

(53) Delledonne, D.; Rivetti, F.; Romano, U. Developments in the Production and Application of Dimethylcarbonate. *Appl. Catal. A Gen.* **2001**, *221* (1–2), 241–251. https://doi.org/10.1016/S0926-860X(01)00796-7.

(54) Srivastava, R.; Srinivas, D.; Ratnasamy, P. Zeolite-Based Organic-Inorganic Hybrid Catalysts for Phosgene-Free and Solvent-Free Synthesis of Cyclic Carbonates and Carbamates at Mild Conditions Utilizing CO2. *Appl. Catal. A Gen.* **2005**, *289* (2), 128–134. https://doi.org/10.1016/j.apcata.2005.04.055.

(55) Honda, M.; Tamura, M.; Nakao, K.; Suzuki, K.; Nakagawa, Y.; Tomishige, K. Direct Cyclic Carbonate Synthesis from CO2 and Diol over Carboxylation/Hydration Cascade Catalyst of CeO2 with 2-Cyanopyridine. *ACS Catal.* **2014**, *4* (6), 1893–1896. https://doi.org/10.1021/cs500301d.

(56) Jehanno, C.; Demarteau, J.; Mantione, D.; Arno, M. C.; Ruipérez, F.; Hedrick, J. L.; Dove, A. P.; Sardon, H. Synthesis of Functionalized Cyclic Carbonates through Commodity Polymer Upcycling. *ACS Macro Lett.* **2020**, *9* (4), 443–447. https://doi.org/10.1021/acsmacrolett.0c00164.

(57) Takeuchi, E. S.; Leising, R. A.; Hong, G. Alkali Metal Electrochemical Cell Having an Improved Cathode Activated with Nonaqueous Electrolyte Having a Carbonate Additive. US 6,221,534 B1, 2001.

(58) Onyenkeadi, V.; Saha, B. Greener Synthesis of Styrene Carbonate from CO2 Using Heterogeneous Catalyst. In *ChemEngDayUK. Better Life, Better World*; Birmingham, 2017.

(59) Sun, J.; Yao, X.; Cheng, W.; Zhang, S. 1,3-Dimethylimidazolium-2-Carboxylate: A Zwitterionic Salt for the Efficient Synthesis of Vicinal Diols from Cyclic Carbonates. *Green Chem.* **2014**, *16* (6), 3297–3304. https://doi.org/10.1039/c4gc00279b.

(60) Lombardo, V. M.; Dhulst, E. A.; Leitsch, E. K.; Wilmoth, N.; Health, W. H.; Gies, A. P.; Miller, M. D.; Torkelson, J. M.; Scheidt, K. A. Cooperative Catalysis of Cyclic Carbonate Ring Opening: Application towards Non-Isocyanate Polyurethane Materials. *Chem. Eur.* **2015**, *2015* (13), 2791–2795.

(61) Jasiak, K.; Krawczyk, T.; Pawlyta, M.; Jakóbik-Kolon, A.; Baj, S. One-Pot Synthesis of Styrene Carbonate from Styrene and CO2 over the Nanogold-Ionic Liquid Catalyst. *Catal. Letters* **2016**, *146* (5), 893–901. https://doi.org/10.1007/s10562-016-1703-z.

(62) *PubChem.* https://pubchem.ncbi.nlm.nih.gov/compound/1_3-Dioxolan-2-one_-4-phenyl#section=3D-Conformer.

(63) Aresta, M.; Dibenedetto, A. Carbon Dioxide as Building Block for the Synthesis of Organic Carbonates. *J. Mol. Catal. A Chem.* **2002**, *182–183*, 399–409. https://doi.org/10.1016/s1381-1169(01)00514-3.

(64) Sun, J.; Fujita, S. I.; Bhanage, B. M.; Arai, M. One-Pot Synthesis of Styrene Carbonate from Styrene in Tetrabutylammonium Bromide. *Catal. Today* **2004**, *93–95*, 383–388. https://doi.org/10.1016/j.cattod.2004.06.105.

(65) Rehman, A.; Gunam Resul, M. F. M.; Eze, V. C.; Harvey, A. A Kinetic Study of Zn Halide/TBAB-Catalysed Fixation of CO2 with Styrene Oxide in Propylene Carbonate. *Green Process. Synth.* **2019**, *8* (1), 719–729. https://doi.org/10.1515/gps-2019-0042.

(66) Qiao, K.; Ono, F.; Bao, Q.; Tomida, D.; Yokoyama, C. Efficient Synthesis of Styrene Carbonate from CO2 and Styrene Oxide Using Zinc Catalysts Immobilized on Soluble Imidazolium-Styrene Copolymers. *J. Mol. Catal. A Chem.* **2009**, *303* (1–2), 30–34. https://doi.org/10.1016/j.molcata.2008.12.025.

(67) Biosinth. https://www.biosynth.com/p/EAA42792/4427-92-3-4-phenyl-13-dioxolan-2-one.

(68) Fujinaga, K.; Kobayashi, Y.; Shimizu, N.; Kawano, S.; Oshima, S.; Sakamoto, M.; Komatsu, Y. The Effect of Solvent on the Liquid – Liquid Extraction of Lanthanides Using DODGAA as an Extractant. *J. Ion Exch.* **2018**, *29* (3), 76–82. https://doi.org/10.5182/jaie.29.76.

(69) Regel-Rosocka, M.; Szymanowski, J. Direct Yellow and Methylene Blue Liquid-Liquid Extraction with Alkylene Carbonates. *Chemosphere* **2005**, *60* (8), 1151–1156. https://doi.org/10.1016/j.chemosphere.2005.01.019.

(70) Schäffner, B.; Andrushko, V.; Bayardon, J.; Holz, J.; Borner, A. Organic Carbonates as Alternative Solvents for Asymmetric Hydrogenation. *Chirality* **2009**, *21*, 857–861.

(71) Behr, A.; Bahke, P.; Klinger, B.; Becker, M. Application of Carbonate Solvents in the Telomerisation of Butadiene with Carbon Dioxide. *J. Mol. Catal. A Chem.* **2007**, *267* (1–2), 149–156. https://doi.org/10.1016/j.molcata.2006.11.043.

(72) Nambu, N.; Kobayashi, D.; Sasaki, Y. Physical and Electrolytic Properties of Different Cyclic Carbonates as Solvents for Electric Double-Layer Capacitors. *Electrochemistry* **2013**, *81* (10), 814–816. https://doi.org/10.5796/electrochemistry.81.814.

(73) Hess, L. H.; Balducci, A. 1,2-Butylene Carbonate as Solvent for EDLCs. *Electrochim. Acta* **2018**, *281*, 437–444. https://doi.org/10.1016/j.electacta.2018.05.168.

(74) Chiba, K.; Ueda, T.; Yamaguchi, Y.; Oki, Y.; Saiki, F.; Naoi, K. Electrolyte Systems for High Withstand Voltage and Durability II. Alkylated Cyclic Carbonates for Electric Double-Layer Capacitors. *J. Electrochem. Soc.* **2011**, *158* (12), A1320. https://doi.org/10.1149/2.038112jes.

(75) Huang, Y.; Qi, L.; Wang, H. Intercalation of Anions into Graphite Electrode from Butylene Carbonate in Activated Carbon/Graphite Hybrid Capacitors. *Electrochim. Acta* **2017**, *258*, 380–387. https://doi.org/10.1016/j.electacta.2017.11.066.

(76) Yanfei, L.; Kelong, H.; Dongming, P.; Suqin, L.; Hong, W. Preparation of Poly(Butylene-Co-e-Caprolactone Carbonate)and Their Use as Drug Carriers for a Controlled DeliverySystem. *Wiley Intersci.* **2006**. https://doi.org/0.1002/pola.21981.

(77) *PubChem*. https://pubchem.ncbi.nlm.nih.gov/compound/4-Ethyl-1_3-dioxolan-2-one#section=3D-Conformer.

(78) Büttner, H.; Steinbauer, J.; Werner, T. Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide by Using Bifunctional One-Component Phosphorus-Based Organocatalysts. *ChemSusChem* **2015**, *8* (16), 2655–2669. https://doi.org/10.1002/cssc.201500612.

(79) Onyenkeadi, V.; Kellici, S.; Saha, B. Greener Synthesis of 1,2-Butylene Carbonate from CO2 Using Graphene-Inorganic Nanocomposite Catalyst. *Energy* **2018**, *165*, 867–876. https://doi.org/10.1016/j.energy.2018.09.135.

(80) *BLD pharm*. https://www.bldpharm.com/products/4437-85-8.html.

(81) Tomishige, K.; Nakagawa, Y.; Tamura, M. *Production of Platform Chemicals from Sustainable Resources. Biofuels and Biorefineries*; Springer, Singapore, 2017. https://doi.org/https://doi.org/10.1007/978-981-10-4172-3_11.

(82) Nakagawa, Y.; Kasumi, T.; Ogihara, J.; Tamura, M.; Arai, T.; Tomishige, K. Erythritol: Another C4 Platform Chemical in Biomass Refinery. *ACS Omega* **2020**, *5* (6), 2520–2530. https://doi.org/10.1021/acsomega.9b04046.

(83) Liu, S.; Amada, Y.; Tamura, M.; Nakagawa, Y.; Tomishige, K. Performance and Characterization of Rhenium-Modified Rh-Ir Alloy Catalyst for One-Pot Conversion of Furfural into 1,5-Pentanediol. *Catal. Sci. Technol.*

(84) Yoshida, Y.; Arai, Y.; Kado, S.; Kunimori, K.; Tomishige, K. Direct Synthesis of Organic Carbonates from the Reaction of CO2 with Methanol and Ethanol over CeO2 Catalysts. *Catal. Today* **2006**, *115* (1–4), 95–101. https://doi.org/10.1016/j.cattod.2006.02.027.

(85) Tomishige, K.; Gu, Y.; Nakagawa, Y.; Tamura, M. Reaction of CO2 With Alcohols to Linear-, Cyclic-, and Poly-Carbonates Using CeO2-Based Catalysts. *Front. Energy Res.* **2020**, *8* (June). https://doi.org/10.3389/fenrg.2020.00117.

(86) Sun, W.; Li, P.; Yabushita, M.; Nakagawa, Y.; Wang, Y. Comparative Study between Cyanopyridine as Dehydrants in Direct Synthesis of Dialkyl Carbonates from CO 2 and Monoalcohols over Ceria Catalyst. *2* (111), 1–36.

(87) Tomishige, K.; Tamura, M.; Nakagawa, Y. CO2 Conversion with Alcohols and Amines into Carbonates, Ureas, and Carbamates over CeO2 Catalyst in the Presence and Absence of 2-Cyanopyridine. *Chem. Rec.* **2019**, *19* (7), 1354–1379. https://doi.org/10.1002/tcr.201800117.

(88) Tamura, M.; Kishi, R.; Nakayama, A.; Nakagawa, Y.; Hasegawa, J. Y.; Tomishige, K. Formation of a New, Strongly Basic Nitrogen Anion by Metal Oxide Modification. *J. Am. Chem. Soc.* **2017**, *139* (34), 11857–11867. https://doi.org/10.1021/jacs.7b05227.

(89) Sun, W.; Li, P.; Yabushita, M.; Nakagawa, Y.; Wang, Y.; Nakayama, A.; Tomishige, K. Comparative Study between 2-Furonitrile and 2-Cyanopyridine as Dehydrants in Direct Synthesis of Dialkyl Carbonates from CO2 and Alcohols over Cerium Oxide Catalyst. *ChemSusChem* **2023**, *16* (24). https://doi.org/10.1002/cssc.202300768.

(90) Li, Y.; Zhao, Y.; Wang, S.; Ma, X. Silica Supported Potassium Oxide Catalyst for Dehydration of 2-Picolinamide to Form 2-Cyanopyridine. *Chinese Chem. Lett.* **2019**, *30* (2), 494–498. https://doi.org/10.1016/j.cclet.2018.04.012.

(91) Gregory, G. L.; Ulmann, M.; Buchard, A. Synthesis of 6-Membered Cyclic Carbonates from 1,3-Diols and Low CO2 Pressure: A Novel Mild Strategy to Replace Phosgene Reagents. *RSC Adv.* **2015**, *5* (49), 39404–39408. https://doi.org/10.1039/c5ra07290e.

(92) Bhanage, B. M.; Fujita, S. I.; Ikushima, Y.; Torii, K.; Arai, M. Synthesis of Dimethyl Carbonate and Glycols from Carbon Dioxide, Epoxides and Methanol Using Heterogeneous Mg Containing Smectite Catalysts: Effect of Reaction Variables on Activity and Selectivity Performance. *Green Chem.* **2003**, *5* (1), 71–75. https://doi.org/10.1039/b207750g.

(93) Zhou, Y.; Hu, S.; Ma, X.; Liang, S.; Jiang, T.; Han, B. Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides over Betaine-Based Catalysts. *J. Mol. Catal. A Chem.* **2008**, *284* (1–2), 52–57. https://doi.org/10.1016/j.molcata.2008.01.010.

(94) Alvaro, M.; Baleizao, C.; Carbonell, E.; El Ghoul, M.; García, H.; Gigante, B. Polymer-Bound Aluminium Salen Complex as Reusable Catalysts for CO 2 Insertion into Epoxides. *Tetrahedron* **2005**, *61* (51), 12131–12139. https://doi.org/10.1016/j.tet.2005.07.114.

(95) Zhang, Y.; Chen, H.; Pan, Y.; Zeng, X.; Jiang, X.; Long, Z.; Hou, X. Cerium-Based UiO-66 Metal-Organic Frameworks Explored as Efficient Redox Catalysts: Titanium Incorporation and Generation of Abundant Oxygen Vacancies. *Chem. Commun.* **2019**, *55* (93), 13959–13962. https://doi.org/10.1039/c9cc06562h.

(96) Chang, K.; Zhang, H.; Cheng, M. J.; Lu, Q. Application of Ceria in CO2 Conversion Catalysis. *ACS Catal.* **2020**, *10* (1), 613–631. https://doi.org/10.1021/acscatal.9b03935.

(97) Varlet, V.; Lagroy De Croutte, E.; Augsburger, M.; Mangin, P. Accuracy Profile Validation of a New Method for Carbon Monoxide Measurement in the Human Blood Using Headspace-Gas Chromatography-Mass Spectrometry (HS-GC-MS). *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* **2012**, *880* (1), 125–131. https://doi.org/10.1016/j.jchromb.2011.11.028.

(98) Krupčík, J.; Gorovenko, R.; Špánik, I.; Bočková, I.; Sandra, P.; Armstrong, D. W. On the Use of Ionic Liquid Capillary Columns for Analysis of Aromatic Hydrocarbons in Low-Boiling Petrochemical Products by One-Dimensional and Comprehensive Two-Dimensional Gas Chromatography. *J. Chromatogr. A* **2013**, *1301*, 225–236. https://doi.org/10.1016/j.chroma.2013.05.075.

(99) Ngxangxa, S.; Villiers, A. de; Tredoux, A. Development of GC-MS Methods for the Analysis of Tyre Pyrolysis Oils. **2016**, No. March, 105.

(100) Grail, A.; Leonard, C.; Sacks, R. Peak Capacity, Peak-Capacity Production Rate, and Boiling Point Resolution for Temperature-Programmed GC with Very High Programming Rates. *Anal. Chem.* **2000**, *72* (3), 591–598. https://doi.org/10.1021/ac9911802.

(101) Tonellato, M. Spettroscopia Nmr. *Pianeta Chim.* **2022**, 1–32.

(102) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176–2179. https://doi.org/10.1021/om100106e.

(103) Solvents, M.; Sizes, M.; Solutions, M. Research Products. **2006**, *1174* (June), 8–11.

(104) Tomishige, K.; Yasuda, H.; Yoshida, Y.; Nurunnabi, M.; Li, B.; Kunimori, K. Catalytic Performance and Properties of Ceria Based Catalysts for Cyclic Carbonate Synthesis from Glycol and Carbon Dioxide. *Green Chem.* **2004**, *6* (4), 206–214. https://doi.org/10.1039/b401215a.

(105) Tomishige, K.; Yasuda, H.; Yoshida, Y.; Nurunnabi, M.; Li, B.; Kunimori, K. Novel Route to Propylene Carbonate: Selective Synthesis from Propylene Glycol and Carbon Dioxide. *Catal. Letters* **2004**, *95* (1–2), 45–49. https://doi.org/10.1023/B:CATL.0000023720.39110.4e.

(106) Honda, M.; Suzuki, A.; Noorjahan, B.; Fujimoto, K. I.; Suzuki, K.; Tomishige, K. Low Pressure CO2 to Dimethyl Carbonate by the Reaction with Methanol Promoted by Acetonitrile Hydration. *Chem. Commun.* **2009**, No. 30, 4596–4598. https://doi.org/10.1039/b909610h.

(107) Honda, M; Kuno, S; Begum, N; Fujimoto, K; Suzuki, K; Nakagawa, Y; Tomishige, K. Catalytic Synthesis of Dialkyl Carbonate from Low Pressure CO2 and Alcohols Combined with Acetonitrile Hydration Catalyzed by CeO2. *Appl. Catal. A Gen. ISSN 0926-860X EISSN 1873-3875* **2010**, *384* (1–2), 165–170.

(108) Dolan, J. W. When Should an Internal Standard Be Used. *LCGC North Am.* **2012**, *30* (6), 474–480.

(109) Honda, M.; Tamura, M.; Nakagawa, Y.; Nakao, K.; Suzuki, K.; Tomishige, K. Organic Carbonate Synthesis from CO2 and Alcohol over CeO 2 with 2-Cyanopyridine: Scope and Mechanistic Studies. *J. Catal.* **2014**, *318*, 95–107. https://doi.org/10.1016/j.jcat.2014.07.022.

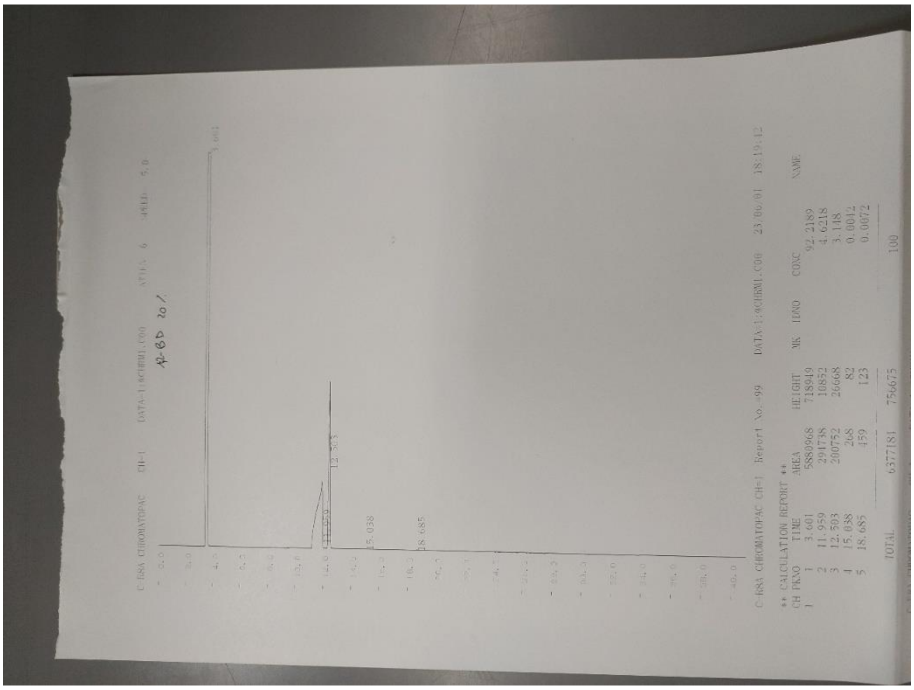
(110) Xiong, Y.; Bai, F.; Cui, Z.; Guo, N.; Wang, R. Cycloaddition Reaction of Carbon Dioxide to Epoxides Catalyzed by Polymer-Supported Quaternary Phosphonium Salts. *J. Chem.* **2013**, *2013*. https://doi.org/10.1155/2013/261378.

(111) Webb, P. B.; Kunene, T. E.; Cole-Hamilton, D. J. Continuous Flow Homogeneous Hydroformylation of Alkenes Using Supercritical Fluids. *Green Chem.* **2005**, *7* (5), 373–379. https://doi.org/10.1039/b416713a.

(112) Onyenkeadi, V. N. Heterogeneous Catalytic Conversion of Carbon Dioxide into 1,2-Butylene Carbonate and Styrene Carbonate, London South Bank University, 2019.

(113) Dai, W. L.; Jin, B.; Luo, S. L.; Yin, S. F.; Luo, X. B.; Au, C. T. Cross-Linked Polymer Grafted with Functionalized Ionic Liquid as Reusable and Efficient Catalyst for the Cycloaddition of Carbon Dioxide to Epoxides. *J. CO2 Util.* **2013**, *3–4*, 7–13. https://doi.org/10.1016/j.jcou.2013.08.002.

APPENDIX A – GC SPECTRA



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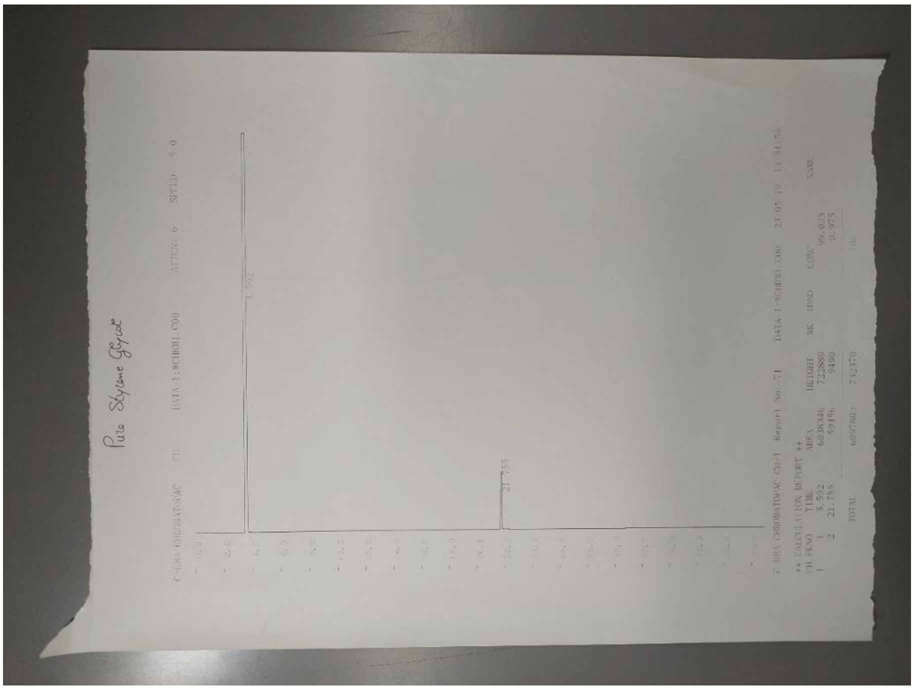
** CALCULATION REPORT **
CH PKNO   TIME      AREA     HEIGHT  MK  IDNO   CONC      NAME
1    1    3.601   5880968   718949              92.2189
     2   11.959    291738    10852               4.6218
     3   12.503    200752    26668               3.148
     4   15.038       268       82               0.0042
     5   18.685       459      123               0.0072
     ----------------------------------------------------
     TOTAL        6377181   756675             100
```

Figure 47 - GC spectrum of 1,2-butanediol



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C-R8A CHROMATOPAC CH=1  Report No.=71   DATA=1:@CHRM1.C00   23/05/19  13:31:58

** CALCULATION REPORT **
CH PKNO   TIME      AREA     HEIGHT  MK  IDNO   CONC      NAME
1    1    3.592   6938346    722880             99.025
     2   21.755     59156      9490              0.975
     ----------------------------------------------------
     TOTAL        6997502    732370            100
```
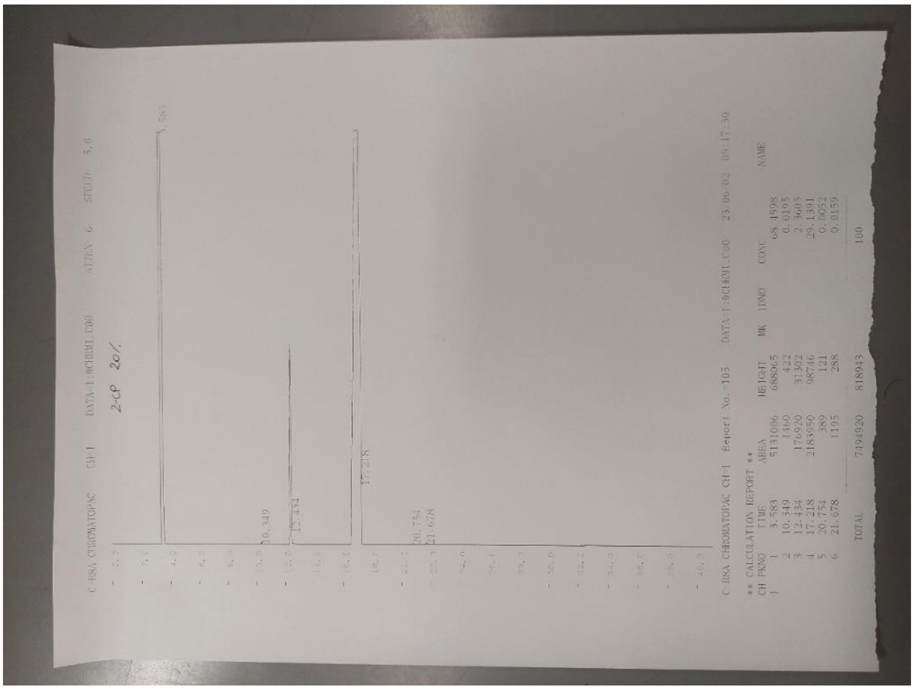

Figure 48 - GC spectrum of styrene glycol



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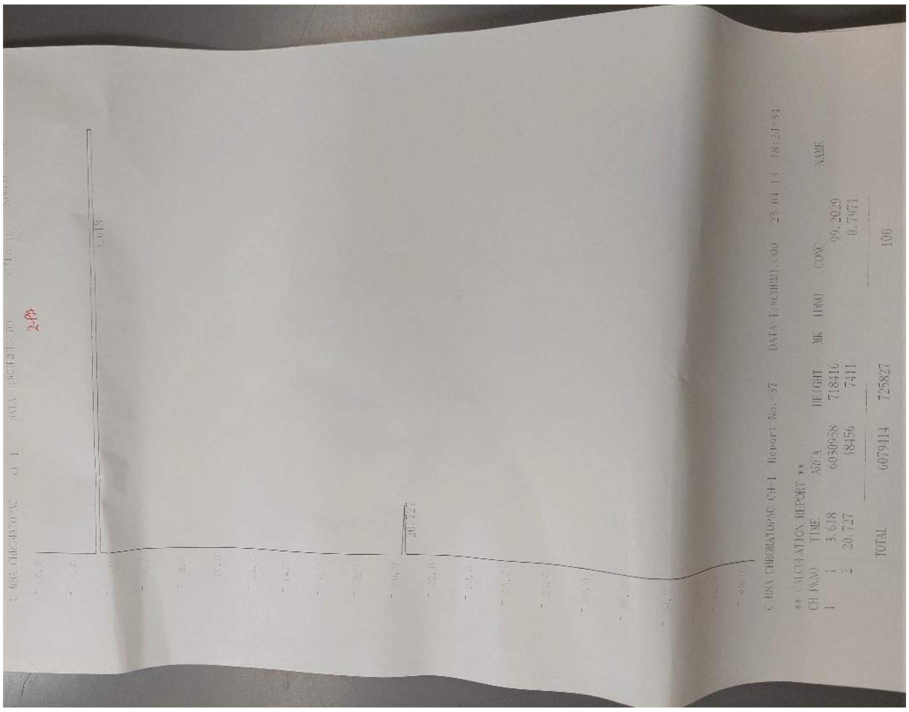
** CALCULATION REPORT **
CH PKNO    TIME      AREA     HEIGHT   MK  IDNO    CONC       NAME
 1    1    3.583   5131006    688065              68.4598
      2   10.349      1460       422               0.0195
      3   12.434    176920     31302               2.3605
      4   17.218   2183950     98746              29.1391
      5   20.754       389       121               0.0052
      6   21.678      1195       288               0.0159
          ─────────────────────────────────────────────
    TOTAL          7494920    818943              100
```

Figure 49 - GC spectrum of 2-cyanopyridine



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C-R8A CHROMATOPAC CH-1  Report No.=37    DATA=1:@CHRM1.C00    23/04/14  18:21:34

** CALCULATION REPORT **
CH PKNO    TIME      AREA     HEIGHT   MK  IDNO    CONC       NAME
 1    1    3.618   6030958    718416              99.2029
      2   20.727     48456      7411               0.7971
          ─────────────────────────────────────────────
    TOTAL          6079414    725827              100
```
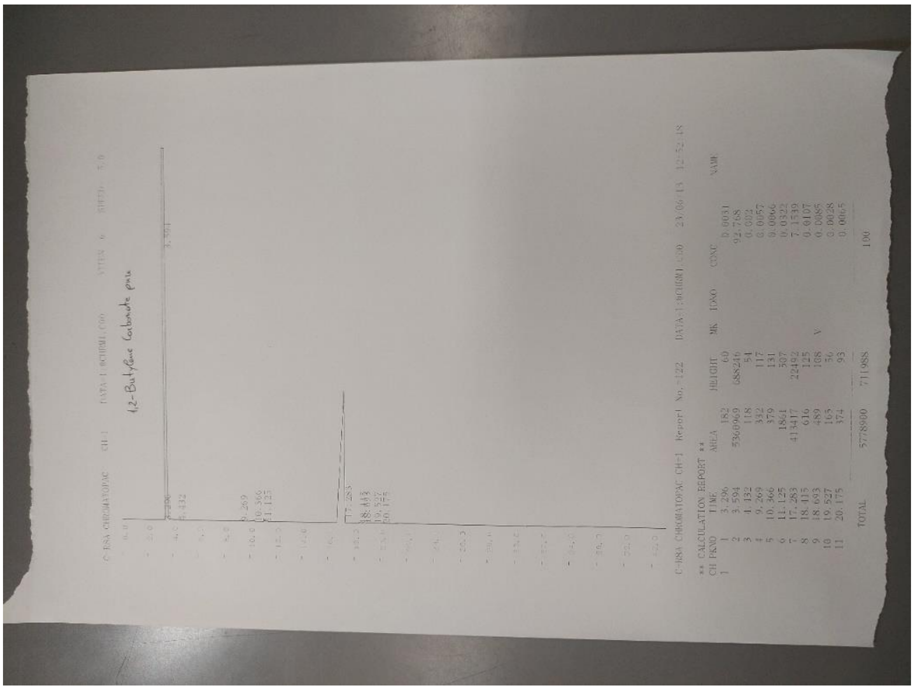

Figure 50 - GC spectrum of picolinamide



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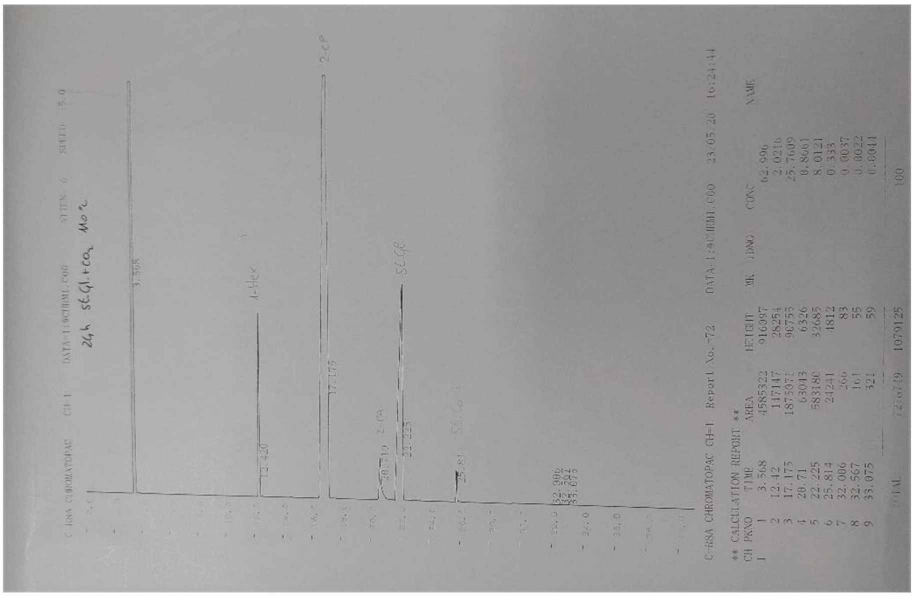
** CALCULATION REPORT **
CH PKNO     TIME        AREA      HEIGHT   MK  IDNO    CONC           NAME
1     1     3.296        182          60                 0.0031
      2     3.594    5360969      688246                92.768
      3     4.132        118          54                 0.002
      4     9.269        332         117                 0.0057
      5    10.366        379         131                 0.0066
      6    11.125       1861         507                 0.0322
      7    17.283     413417       22492                 7.1539
      8    18.415        616         125                 0.0107
      9    18.693        489         108   V             0.0085
     10    19.527        165          56                 0.0028
     11    20.175        374          93                 0.0065
                   ---------   ---------               --------
         TOTAL       5778900      711988               100
```

Figure 51 - GC spectrum of butylene carbonate

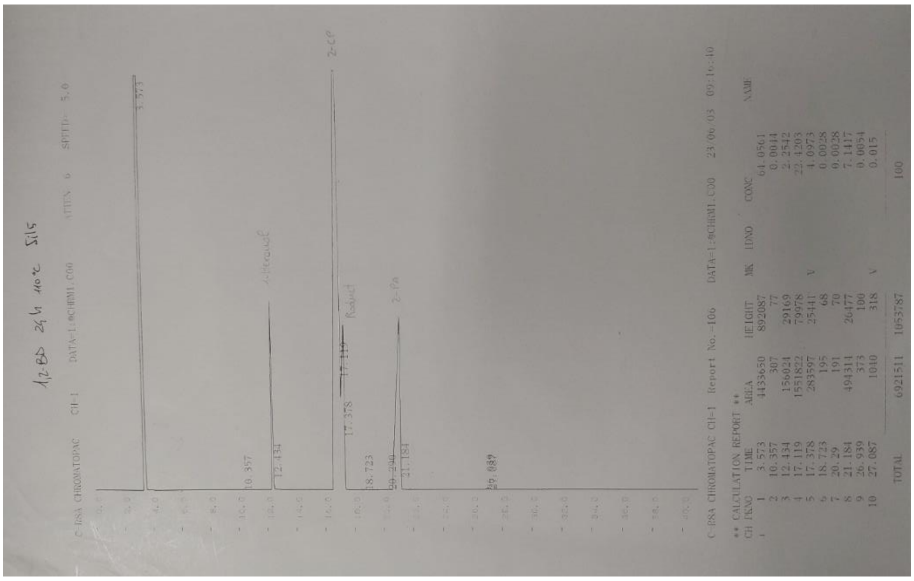


```
C-R8A CHROMATOPAC    CH-1      DATA=1:@CHRM1.C00          ATTEN  6    SPEED  5.0

C-R8A CHROMATOPAC CH=1  Report No.=72    DATA=1:@CHRM1.C00   23/05/20  16:24:44

** CALCULATION REPORT **
CH PKNO     TIME        AREA      HEIGHT   MK  IDNO    CONC           NAME
1     1     3.568    4585322      916097                62.996
      2    12.42      147147       28254                 2.0216
      3    17.175    1875071       90755                25.7609
      4    20.71       63043        6326                 0.8661
      5    22.225     583180       32685                 8.0121
      6    25.814      24241        1812                 0.333
      7    32.006        266          83                 0.0037
      8    32.567        161          55                 0.0022
      9    33.075        321          59                 0.0044
                   ---------   ---------               --------
         TOTAL       7278749     1079125               100
```

Figure 52 - GC spectrum of a reaction between styrene glycol and CO_2



1,2-BD 24h 110°C Si15

```
C-R8A CHROMATOPAC    CH=1    DATA=1:@CHRM1.C00        ATTEN  6    SPEED= 5.0
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```
C-R8A CHROMATOPAC CH=1  Report No.=106    DATA=1:@CHRM1.C00   23/06/03  09:16:40

** CALCULATION REPORT **
CH PKNO     TIME        AREA      HEIGHT    MK  IDNO     CONC            NAME
1     1     3.573     4433650     892087                 64.0561
      2    10.357         307         77                  0.0044
      3    12.434      156024      29169                  2.2542
      4    17.119     1551822      79978                 22.4203
      5    17.378      283597      25441    V             4.0973
      6    18.723         195         68                  0.0028
      7    20.29          191         70                  0.0028
      8    21.184      494314      26477                  7.1417
      9    26.939         373        100                  0.0054
     10    27.087        1040        318    V             0.015
                    ---------  ---------            ---------
         TOTAL        6921511    1053787               100
```

Figure 53 - GC spectrum of a reaction between 1,2-butanediol and CO_2

APPENDIX B – NMR SPECTRA

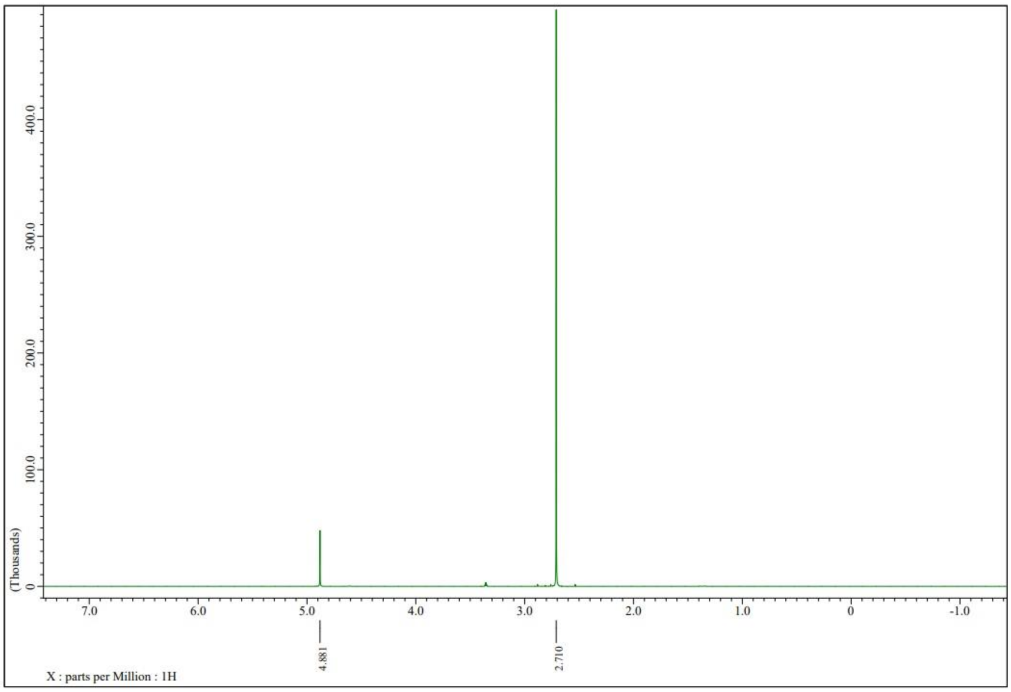

Figure 54 - NMR spectrum of DMSO

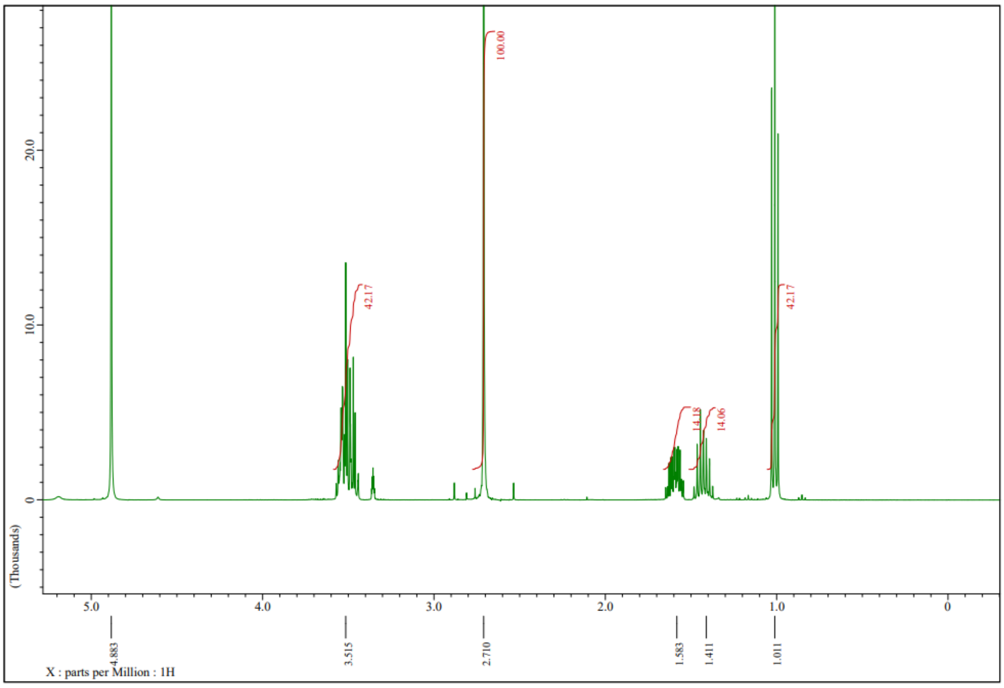

Figure 55 - NMR spectrum of 1,2-butanediol

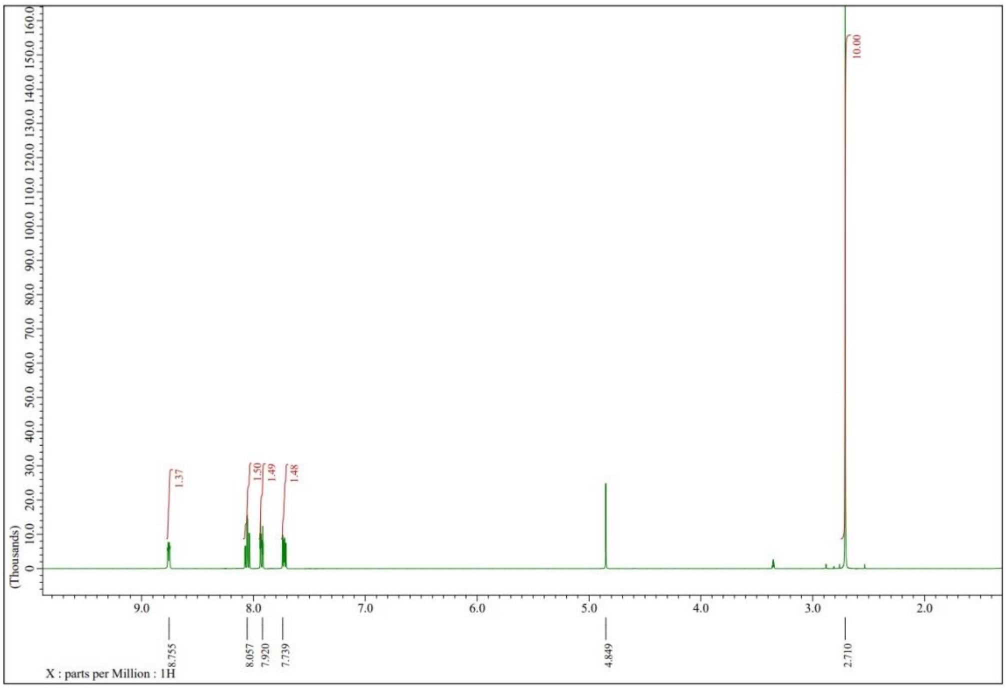

Figure 56 - NMR spectrum of 2-cyanopyridine

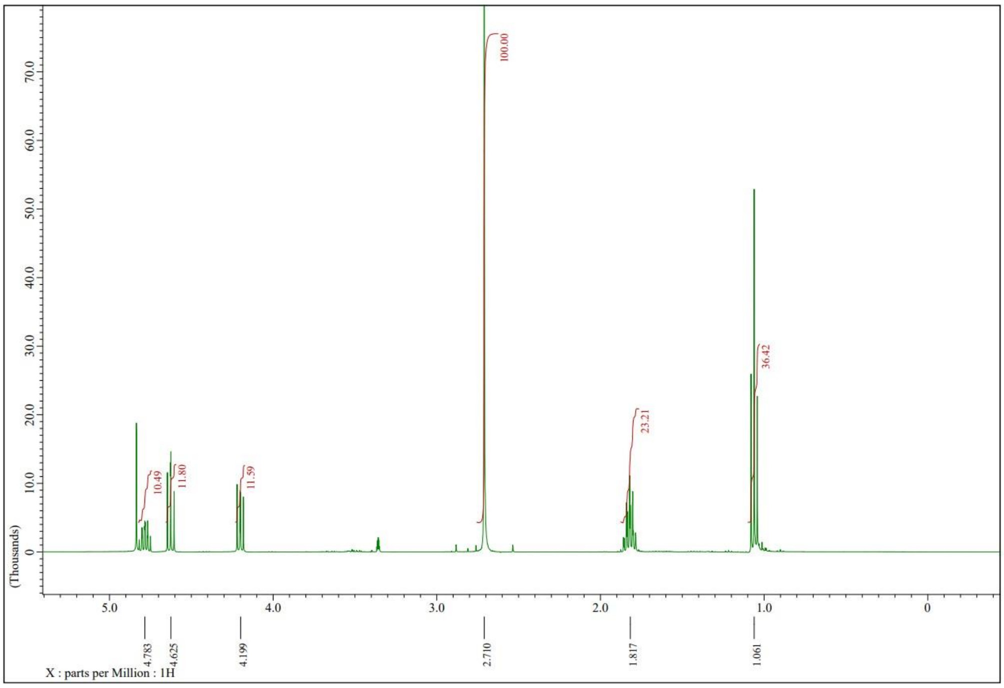

Figure 57 - NMR spectrum of butylene carbonate

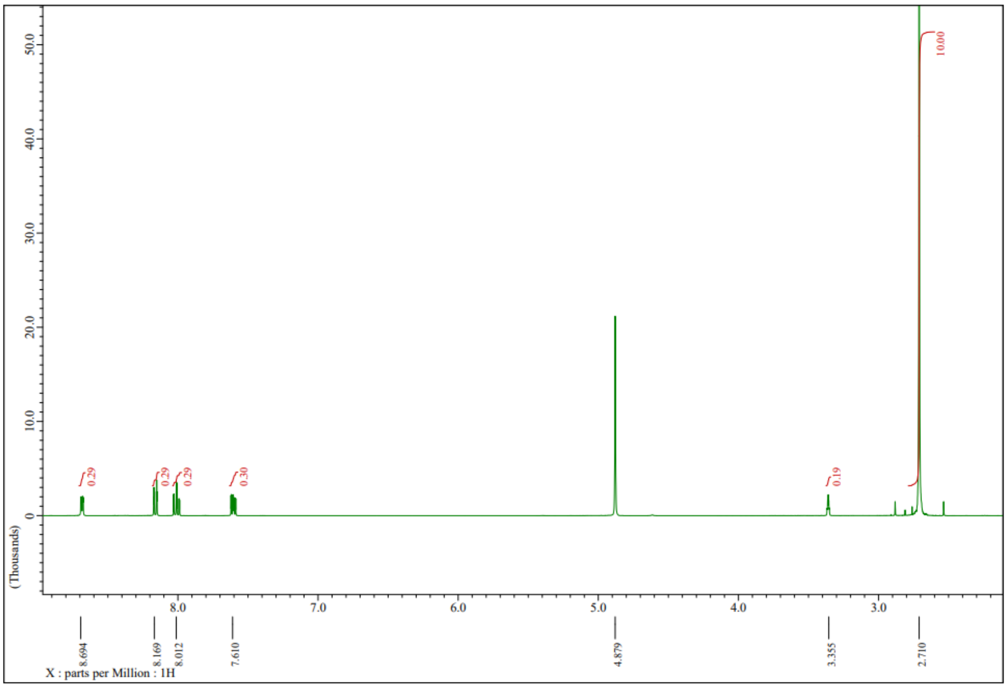

Figure 58 - NMR spectrum of picolinamide

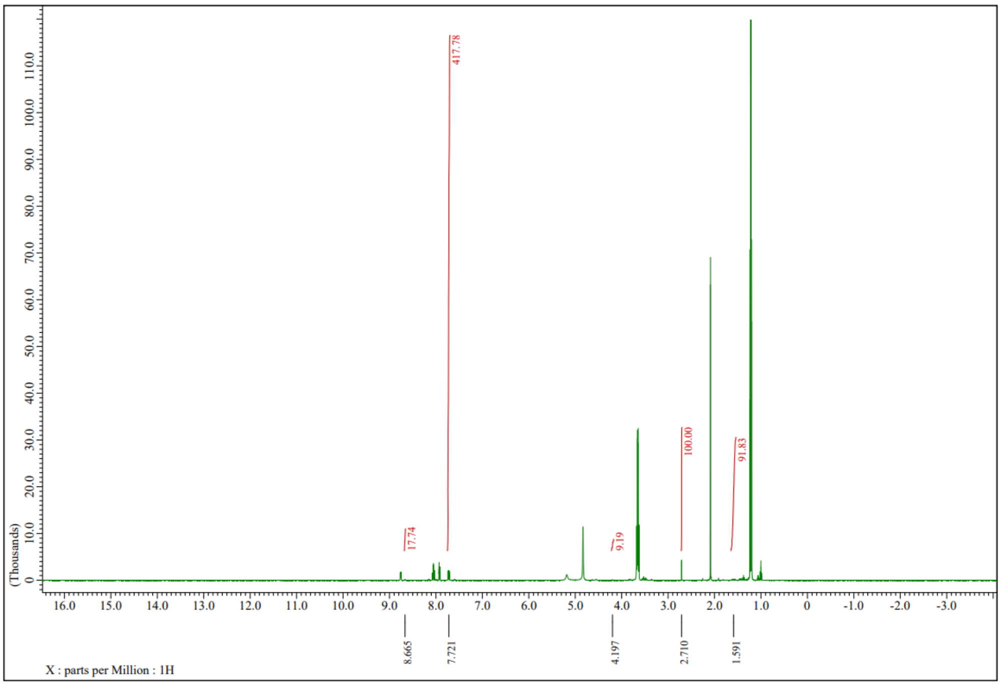

Figure 59 - NMR spectrum of a reaction between 1,2-BD and CO_2

ACKNOLEDGEMENTS

The present thesis work has been carried out during a study abroad semester at Tohoku University, in Sendai (Japan). The whole project has been conducted as a member of the Tomishige Lab, a research group led by prof. Keiichi Tomishige, whose contribution in green chemistry, CO_2 conversion and catalysis is recognized all over the world.

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