FINAL REPORT

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Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 02139

Project Title:

Integrated Electrochemical Processes for CO_2 Capture and Conversion to Commodity Chemicals

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DISCLAIMER

ABSTRACT

The Massachusetts Institute of Technology (MIT) and Siemens Corporations (SCR) are developing new chemical synthesis processes for commodity chemicals from CO_2. The process is assessed as a novel chemical sequestration technology that utilizes CO_2 from dilute gas streams generated at industrial carbon emitters as a raw material to produce useful commodity chemicals. Work at Massachusetts Institute of Technology (MIT) commenced on October 1st, 2010, and finished on September 30th, 2013. During this period, we have investigated and accomplished five objectives that mainly focused on converting CO_2 into high-value chemicals: 1) Electrochemical assessment of catalytic transformation of CO_2 and epoxides to cyclic carbonates; 2) Investigation of organocatalytic routes to convert CO_2 and epoxide to cyclic carbonates; 3) Investigation of CO_2 Capture and conversion using simple olefins under continuous flow; 4) Microwave assisted synthesis of cyclic carbonates from olefins using sodium bicarbonates in a green pathway; 5) Life cycle analyses of integrated chemical sequestration process. In this final report, we will describe the detailed study performed during the three year period and findings and conclusions drawn from our research.

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EXECUTIVE SUMMARY

The Massachusetts Institute of Technology (MIT) and Siemens Corporation (SCR) have explored new chemical processes for the chemical sequestration of CO_2 from dilute gas streams generated at industrial carbon emitters. During the three-year research period on integrated processes for CO_2 capture and conversion to commodity chemicals, MIT research focused on using electrocatalytic and organocatalytic routes to CO_2 transformation. Moreover, the research conducted at SCR focused on placing the carbon capture and utilization technology developed by MIT into context to enable SCR to evaluate the associated environmental and economic impacts, and thereby determine the objectives, scope and boundaries of the Life Cycle Assessment (LCA) study. We have thus achieved:

1) An electrochemical assessment of catalytic transformation of CO_2 and epoxides to cyclic carbonates. Electrochemical properties of quinone were evaluated to elucidate the binding affinity of electrochemically-generated dianion quinones towards CO_2, propylene oxide and propyl bromide.

2) An unprecedented method has been developed for the high yielding continuous synthesis of cyclic carbonates from CO_2 and epoxides. We have demonstrated how a continuous flow apparatus for gas/liquid reactions can greatly enhance the efficiency of the transformation relative to a traditional batch reactor. The catalysts used (NBS and BPO) are commercially available and inexpensive. A series of kinetics experiments have been conducted and support epoxide activation by electrophilic bromine.

3) An efficient flow synthesis of cyclic carbonates starting directly from olefins and CO_2 has been achieved. The flow synthesis was integrated into a hydroxybromination-carboxylation two-step sequential transformation, which represents a successful example of a multi-stage gas/liquid continuous flow process. Specifically, it is possible to introduce incompatible reagents easily without their interacting with each other (such as NBS and DBU), thus significantly enhancing the reaction rate, especially for aliphatic olefins, and we demonstrated the effectiveness of performing sequential reactions in flow. These flow systems enable optimization of individual steps and allow numerous experiments to be conducted at various residence times and temperatures after the initial loading of reagents into the pumps because of the ease with which these operating conditions can be adjusted in real time. Compared to conventional batch

conditions, the flow systems can be operated readily with a broad range of substrates, with enhanced reaction rates and increased product yields without the formation of epoxide or dibromide by-products. Other merits of this gas/liquid flow system include a packed-bed reactor used for carboxylation, which enabled efficient mixing of the phases while stabilizing the flow patterns, i.e., ensuring steady flow. Acetone was applied as the co-solvent with water to achieve a homogenous liquid solution at elevated temperature to avoid the use of phase-transfer reagents.

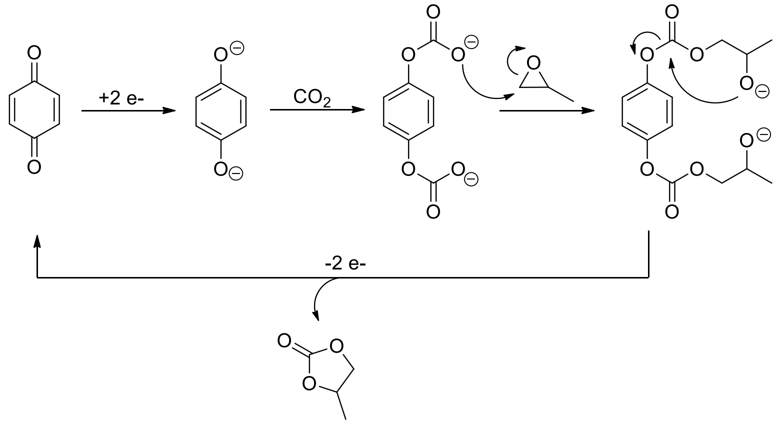
4) An efficient microwave-assisted one-pot synthesis of cyclic carbonates starting from olefins has been achieved with a wide substrate scope. Compared to conventional heating methods, microwave heating resulted in much better selectivity and yield of desired products. $NaHCO_3$ proved to be an excellent substituent for CO_2 gas, thus avoided the high capital cost and related safety issues. This method is also well poised toward green process due to the use of environmental friendly acetone/water solvent.

5) We evaluated the environmental and economic impacts of the novel carbon capture and chemical conversion technology developed by MIT. The analysis was based on publicly available data and experimental data provided by MIT. The LCA models are in parameterized format and can easily be modified to reflect any new scenarios that will be developed in the future. The results from the environmental impacts of CFPP with conventional MEA capture have been verified with existing literature to validate the LCA models. The final results for E-MAR capture show that it has approximately 10% lower impacts than conventional MEA capture system for GWP and PED category. The impacts for the chemical conversion process for carbonate production are quite high even for 15% utilization scenario. The LCC results for CFPP with and without capture have also been presented here. The results are in agreement with previous work done by DOE. The study of scales identified availability of reagent for chemical conversion of CO_2 and demand for the carbonate product as two major limitations for scaling up the system. Solving the optimization equation shows that achieving the DOE set goal of $10/tonne for the final carbonate product is not feasible under current conditions.

REPORT DETAILS

1. Electrochemical assessment of catalytic transformation of CO_2 and epoxides to cyclic carbonates

One of the strategies for effective conversion of CO_2 is to use redox molecules that facilitate the CO_2 capture from a dilute gas stream in its active state and potentially catalyze a subsequent addition reaction with nucleophiles. The reaction product of CO_2 with an electrophilic species should be released on electrochemical oxidation of the products. A chemical transformation of CO_2 that has received a large amount of attention is the reaction of epoxides and CO_2 in the presence of a catalyst to form cyclic carbonates. Successful catalytic systems include Lewis acids[1a-c], *N*-heterocyclic carbenes[2], ammonium salts[3], and organocatalysts[4], to name only a few. Potential electrochemically-active catalysts for our systems described previously are quinones, naturally occurring molecules that facilitate biological transfer reactions in many cellular respiration and photosynthesis cycles. These molecules can be electrochemically reduced to form an aromatic, deprotonated hydroquinone. The dianion can then bind carbon dioxide, even from non-pure, low pressure streams.[5,6,7]



Scheme 1-1: Proposed process for conversion of carbon dioxide to a cyclic carbonate using a quinoidal catalyst.

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[1] (a) Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, H.; Kaneda, K. *J. Am. Chem. Soc.* **1999**, *121*, 4526-4527. (b) Meléndez, J.; North, M.; Villuendas, P. *Chem. Commun.* **2009**, 2577-2579. (c) Lu, X.-B.; Liang, B.; Zhang, Y.-J.; Tian, Y.-Z.; Wang, Y.-M.; Bai, C.-X.; Wang, H.; Zhang, R. *J. Am. Chem. Soc.* **2004**, *126*, 3732-3733.

[2] Zhou, H.; Zhang, W.-Z.; Liu, C-H.; Qu, J.-P.; Lu, X.-B. *J. Org. Chem.* **2008**, *73*, 8039-8044.

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[5] Scovazzo, P.; Poshusta, J.; DuBois, D. L.; Koval, C. A.;Noble, R. D. *Electrochem. Soc.* **2003**, *150*, D91-D98.

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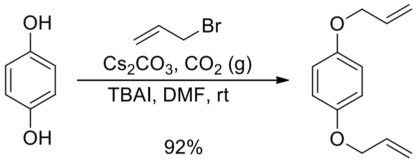
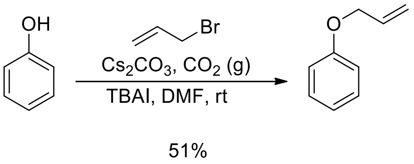
[7] Mizen, M. B.; Wrighton, M. S. *J. Electrochem. Soc.* **1989**, *136*, 941-946.

In order to demonstrate a proof of principle of an electrochemical process for conversion of CO_2 to a cyclic carbonate using a quinoidal catalyst (**Scheme 1-1**), our research began on the actual chemical capture and conversion of carbon dioxide using quinones as catalysts. Jung and co-workers described the synthesis of carbonates from aliphatic alcohols using CO_2 in the presence of base and an ammonium salt.[8] This set of conditions seemed like an appropriate starting point for the incorporation of CO_2 using quinoidal molecules.

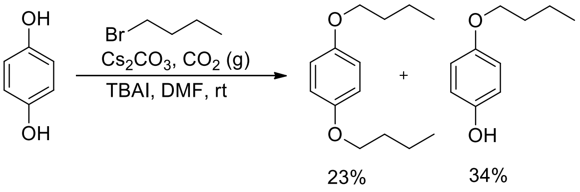
To this end, hydroquinone was treated using allyl bromide as an electrophile (**Equation 1-1**). Unfortunately, no incorporation of CO_2 was observed and the sole product observed arose from the direct alkylation of the aromatic oxygen atoms with the electrophile. To more accurately mimic the conditions employed by Jung, the same reaction was attempted using phenol (**Equation 1-2**). Similarly, alkylated phenol was the sole product observed. Using a less reactive electrophile did not have any effect, on the rate of carbon dioxide incorporation (**Equation 1-3**).



(1-1) *no incorporation of CO_2*



(1-2) *no incorporation of CO_2*



(1-3) *no incorporation of CO_2*

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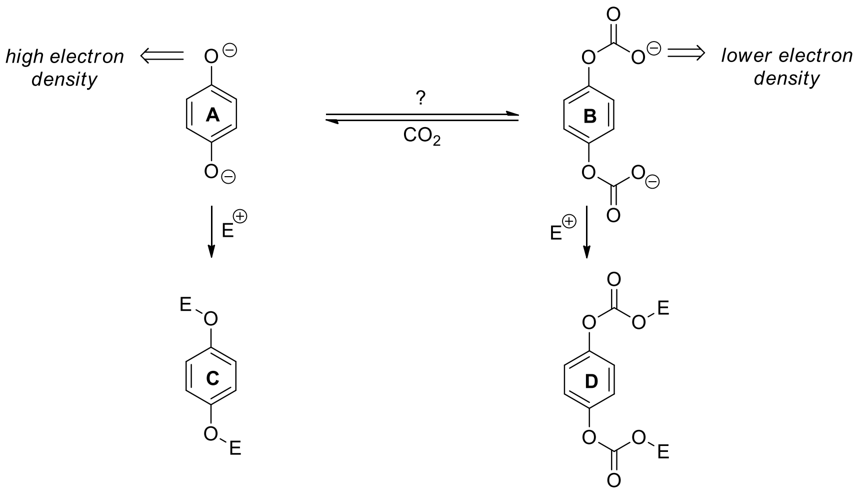
[8] Salvatore, R. N.; Chu, F.; Nagle, A. S.; Kapxhiu, E. A.; Cross, R. M.; Jung, K. W. *Tetrahedron* **2002**, *58*, 3329-3347.

A proposed explanation for the observed products is shown in **Scheme 1-2**. If the binding of carbon dioxide by the quinone is reversible, either dianion **A**, or the dianion carbonate **B** is available to react with an electrophile, "E^{+}". It has been shown using molecular modeling that the electron density on the phenolic oxygen atoms is much greater than that of the oxygen atoms of the carbonate dianion.[9] It is likely then that the electrophile is going to react at a much faster rate with dianion **A** than with the dianion carbonate **B**, giving compound **C** as the sole product.



Scheme 1-2: Proposed explanation of observed product ratios.

Electrochemical properties of quinone has been evaluated for elucidating the binding affinity of electrochemically-generated dianion quinones towards CO_2, propylene oxide and propyl bromide. Under a nitrogen environment, quinones undergo two reversible one-electron transfers. The first reduction occurs at -0.98V vs ferrocene standard potential, and the second occurs at -2.00V. When CO_2 is introduced to the solution, the cathodic current at the first reduction potential at -0.98V is larger than in the absence of CO_2. In addition, the second reduction wave is no longer observed (**Figure 1-1**). These observations suggest the electrochemically generated dianion quinone binds strongly with CO_2 forming bis(carbonate) adducts. Introduction of propylene oxide does not affect the cyclic voltammogram of quinone that indicates weak binding affinity of this molecule toward propylene oxide (**Figure 1-2**). Addition of propyl bromide decreases both oxidation currents that suggest an irreversible nucleophilic addition of propyl bromide to electrochemically generated dianion quinone (**Figure 1-3**). This initial

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[9] Molecular modeling was carried out by Mike Stern. Chemical Engineering, T. A. Hatton Laboratory.

electrochemical experiment suggest the electrochemically generated dianion quinone does react toward nucleophilic addition with both CO_2 and propyl bromide, but it has low reactivity toward propylene oxide.

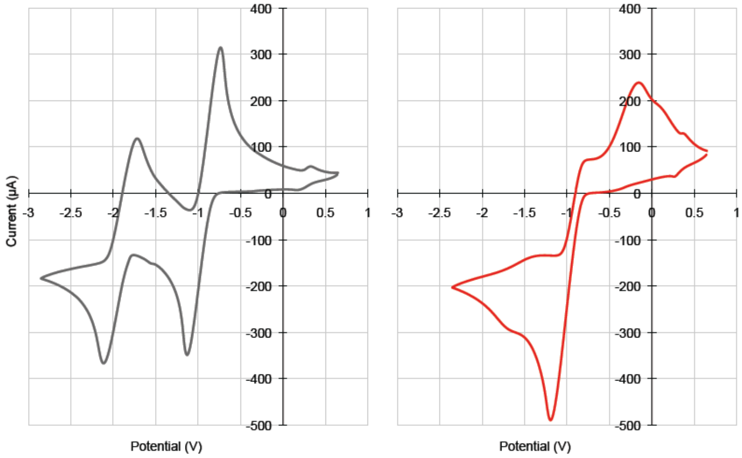


Figure 1-1: Cyclic voltammograms of benzoquinone under nitrogen (left) and carbon dioxide (right).

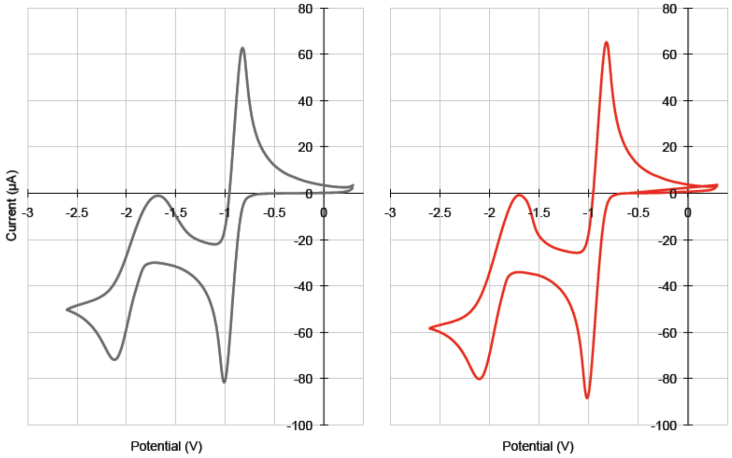


Figure 1-2: Cyclic voltammograms of benzoquinone in the absence (left) and presence (right) of propylene oxide.

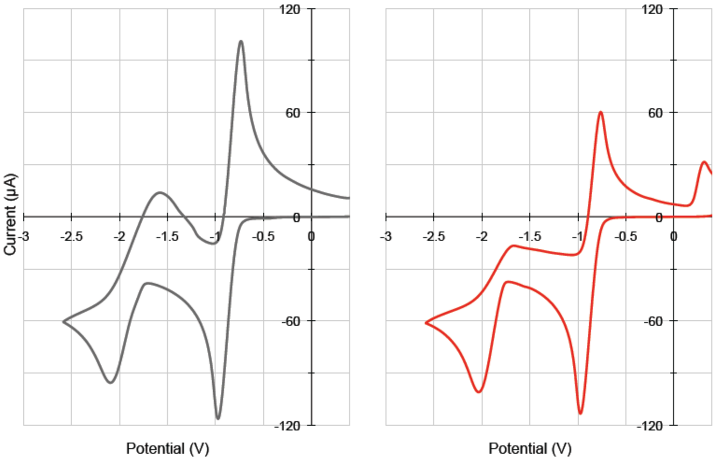
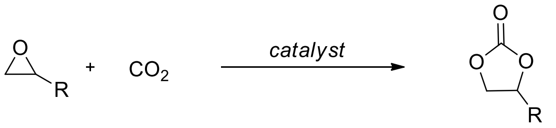


Figure 1-3: Cyclic voltammogram of benzoquinone in the absence (left) and presence (right) of propyl bromide.

2. Investigation of organocatalytic routes to convert CO_2 and epoxide to cyclic carbonates

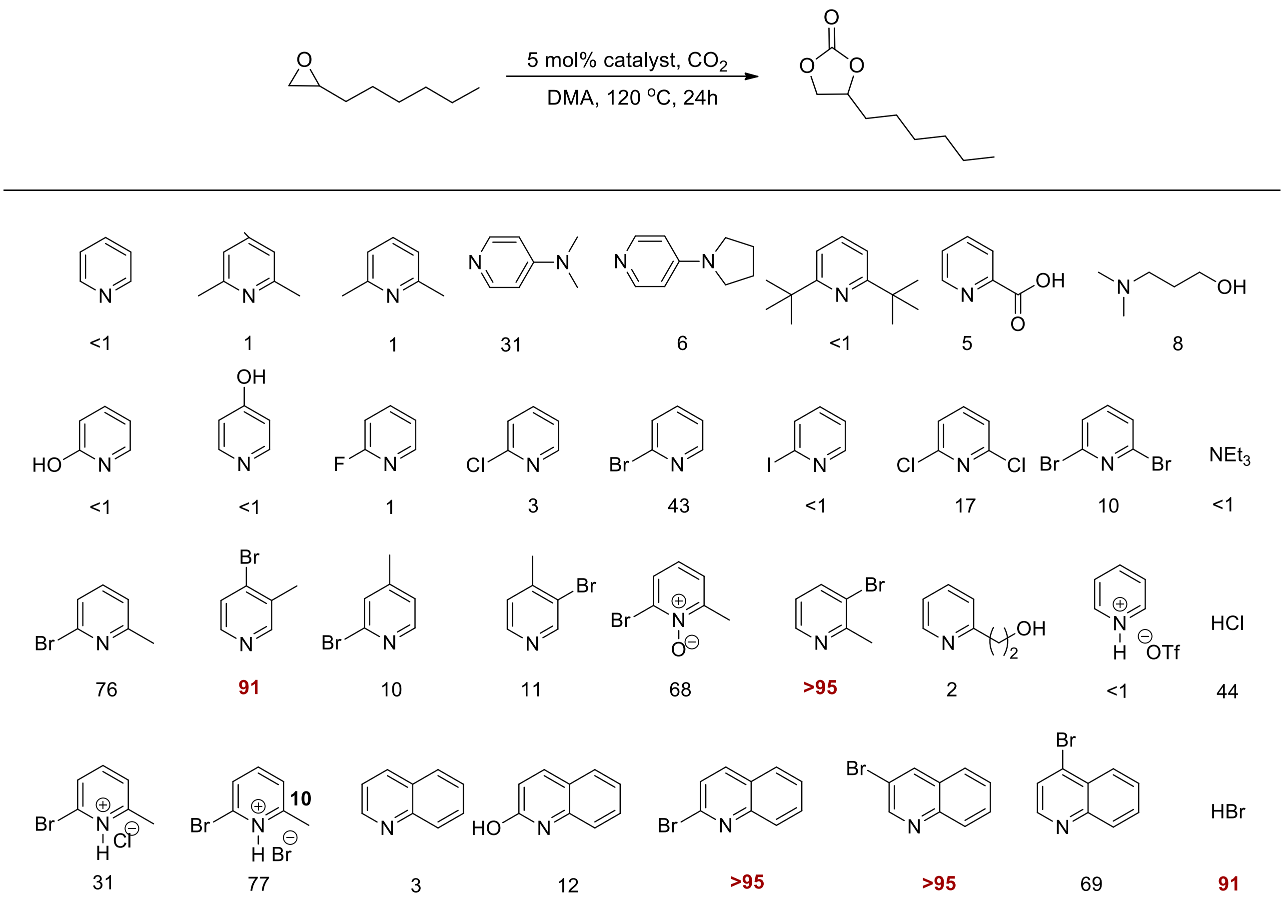
Carbon dioxide (CO_2) is produced abundantly as the by-product from many industrial processes that utilize fossil fuels for their primary energy supply. Even though the conversion of CO_2 to various commodity chemicals is thermodynamically favorable, kinetically the process is slow due to a high activation energy barrier. Employing a catalyst to lower this activation barrier is necessary if CO_2 is to be used as the main carbon source for the synthesis of commodity chemicals. The catalytic reaction of CO_2 and epoxides to form cyclic carbonates has received a large amount of attention recently, and is also the focus of this work (equation 2-1). Recent methods to convert epoxides to cyclic carbonates using CO_2 require high pressures, high temperatures, and specialized equipment to achieve high rates of conversion. We explored organocatalytic routes to react CO_2 at ambient pressure with cyclic oxides to form cyclic carbonates with high yield.



(2-1)

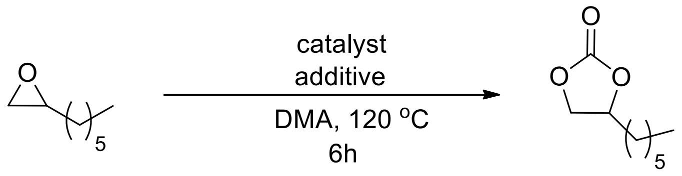
We investigated a number of other catalysts structurally related to pyridine. The results of the screening experiments are shown in **Chart 2-1**. The first reaction was found using 5 mol% of 2-bromopyridine (43% yield). Other bromopyridine catalysts were next evaluated, and the majority of them resulted in good conversion and yields (excluding the bromopyridine catalysts with a methyl substituent at carbon 4). After initial screening, the most promising catalyst in a batch reactor was 5 mol% of 2-bromoquinoline. However the reaction suffered from a long induction period (over 8 hours – refer to Table 5 in the previous progress report). A series of experiments were conducted to determine the active catalyst of the flow system. Unfortunately, the control experiments did not reveal any useful information. A hypothesis was that oxygen or water was a contaminant, thereby causing the active catalyst to form under the reaction conditions. One possibility is the formation of a radical species that is responsible for the catalytic activity. To test this theory, a series of experiments were run using a batch reactor (**Table 2-1**).

Chart 2-1: Summary of Catalysts Tested



The yields reported are for the formation of product based on quantitative GC analysis.

Table 2-1: Investigations into a radical-catalyzed process



entry	catalyst	additive	conv. (%)[a]	yield (%)[a]
1	5% NBS	-	74	81
2	10% NBS	-	73	66
3	5% NBS	***dark***[b]	31	33
4	5% NBS	5% benzoyl peroxide	80	75
5	5% NBS	5% ferrocene	67	57
6	5% NBS	5% AIBN	26	25
7	5% NBS	1 equiv Galvinoxyl	-	0
8	5% NCS	-	19	17
9	5% NIS	-	40	36

[a] Determined by GC analysis. [b] The test-tube reactor was wrapped in aluminum foil.

Each reaction was run for only 6 hours, as opposed to the standard 24 hours, to appropriately observe a possible induction period. *N*-Bromosuccinimide (NBS) is an organic compound that is known to undergo radical as well as ionic processes. Treatment of 1,2-epoxyoctane with 5 mol% of NBS resulted in a surprising 81% yield of cyclic carbonate (entry 1). Increasing the catalyst loading to 10 mol% NBS did not appear to increase the yield further (entry 2). When the reaction was performed in a test tube reactor that was wrapped in aluminum foil to exclude light, only 33 % of the product was formed (entry 3). This suggests that light, an initiator in radical processes, is important for the reaction rate. A series of experiments were run with 5 mol% of NBS in addition to other known radical initiators (entries 4-6). The addition of 5 mol% of benzoyl peroxide resulted in 75% yield of the product. The addition of benzoyl peroxide did not seem to increase the yield of the reaction as compared to using NBS alone, although it appears to be important in continuous flow conditions (*vide infra*). The addition of a known radical inhibitor Galvinoxyl (2,6-Di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy) resulted in complete inhibition of the reaction, again suggesting that a radical mechanism is operative (entry 7). *N*-Chlorosuccinimide (NCS) and *N*-iodosuccinimide (NIS) were also tested, but were inferior to NBS (entries 8 and 9). It is important to note that these reactions all occur in a 6 hour reaction time, therefore do not exhibit the induction period that was observed with 2-bromoquinoline as the catalyst.

The continuous flow apparatus (**Figure 2-1**) was used for the initial testing and development of a method for CO_2 transformation that works well under continuous flow conditions. It was found that 5 mol % of *N*-bromosuccinimide (NBS) and 5 mol % of benzoyl peroxide were successful in catalyzing the reaction of CO_2 with 1,2-epoxyoctane in *N*,*N*-dimethylformamide (DMF, 0.44 M) and at a CO_2 pressure of 100 psi, to form the cyclic carbonate product in excellent yield. The residence time of the transformation was approximately 40 minutes.

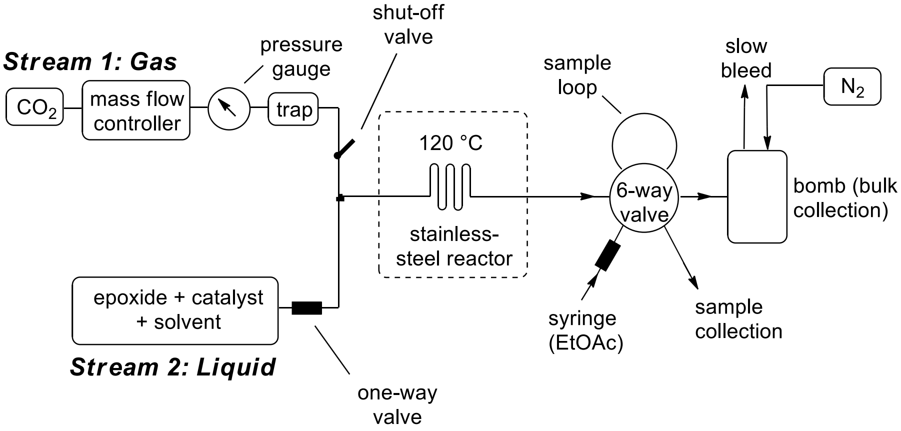
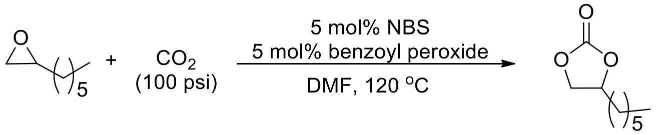


Figure 2-1: Schematic of diagram of our flow reactor

Full conversion of the epoxide and CO_2 occurred with a residence time (t_R) of 40 min. To shorten the residence required for full conversion, different concentrations of the reagents in DMF were investigated at different residence times (**Table 2-2**). We varied the residence times by changing the flow rates of both the liquid in the syringe pump (containing the epoxide, solvent, catalysts, and internal standard), and the CO_2 gas.

Table 2-2: Optimization of the concentration and residence time under continuous flow conditions

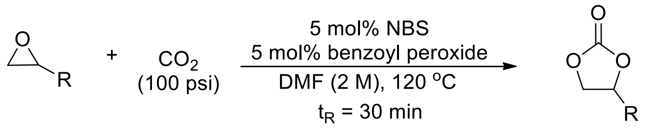


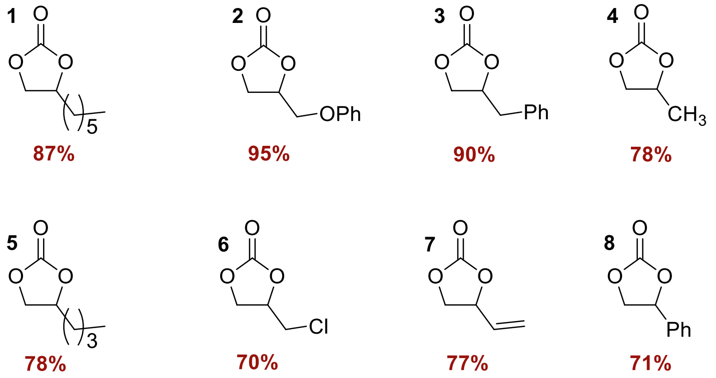
entry	concentration (M)	t_R (min)	conversion (%)[a]	yield (%)[b]
1	0.44	40	100	99
2	1	10	73	73
3	1	20	88	88
4	1	30	96	98
5	2	20	88	84
6	2	10	59	52

[a] Determined by GC analysis using an internal standard. [b] Determined by ^{1}H NMR analysis using an external standard.

The previously observed conditions are described in entry 1. By increasing the concentration of the reagents in DMF to 1 M, nearly full conversion of the epoxide to the cyclic carbonate product was observed after 30 min, a reduction in 10 min (entry 4). Increasing the concentration to 2 M did not help to accelerate the rate of the reaction (entries 5 and 6), but it did not decelerate the rate of reaction at residence times of 20 min. It should be noted that if the concentration was increased to 3 and 4 M, there was a marked decrease in the rate of the reaction. We selected a concentration of 2 M as an optimal condition, given the high environmental and economic cost of DMF as a solvent. A 30 min residence time was also selected as optimal, to ensure full conversion of the epoxide and CO_2 to the corresponding cyclic carbonate. A residence time of 30 min under continuous flow conditions for a kinetically slow reaction such as this one is deemed appropriate.

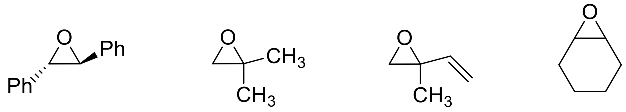
Table 2-3: Using the optimal conditions to convert CO_2 to cyclic carbonate with *different* epoxides



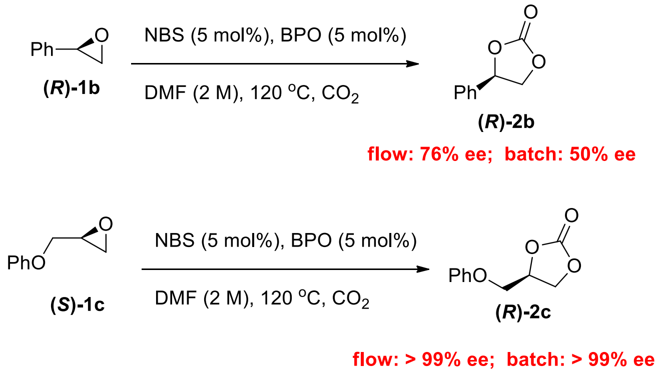


^{a}Yield determined by $_{1}$H NMR analysis using an external standard.

The optimal conditions were then tested on a series of epoxides, to determine the scope of the reaction (**Table 2-3**). The reaction conditions worked for a variety of epoxides. One of the major advantages of the flow reactor is the ability to use low boiling epoxides (such as propylene oxide) without any loss of epoxide due to evaporation from the reactor. This is observed in our flow system as well, by the successful conversion of propylene oxide (entry 4) and 3,4-epoxy-1-butene (entry 7). The reaction tolerated alkyl (entries 1,4, and 5), aromatic (entries 3 and 8), ether (entry 2) and chloride (entry 6) substituents. Unfortunately, the reaction at this stage is limited to *terminal* epoxides. In **Scheme 2-1** is shown examples of epoxides that did not convert to the corresponding cyclic epoxide under the continuous flow, optimal conditions. Enantioenriched pure epoxides were evaluated and compared both in the flow and batch conditions (**Scheme 2-2**). Aliphatic substituted (*S*)-**1c** was converted to (*R*)-**2c** with no loss of ee under both batch and flow conditions. Enantiomerically pure aryl substituted (*R*)**-1b**, on the other hand, was transformed to (*R*)-**2b** with observable ee loss (76% ee) under the flow condition. With the batch condition, product (*R*)-**2b** was achieved with an even lower selectivity (50% ee).



Scheme 2-1: Epoxides that failed to yield cyclic carbonates when reacted with CO_2 under the optimal conditions



Scheme 2-2: Transformations using enantioenriched epoxides

Mechanistic Investigation: The reaction conditions we discovered stand in stark contrast to those previously reported for this transformation; most of the components employed herein are generally considered electrophilic in nature. That is, it was unclear to us how two electrophilic catalysts (NBS and BPO) were mediating the coupling of two electrophiles (epoxide and CO_2). In order to gain mechanistic insight into this apparent paradox, we determined the kinetic parameters of the coupling of 1,2-epoxyoctane (**1a**) and CO_2 catalyzed by NBS and BPO in DMF.

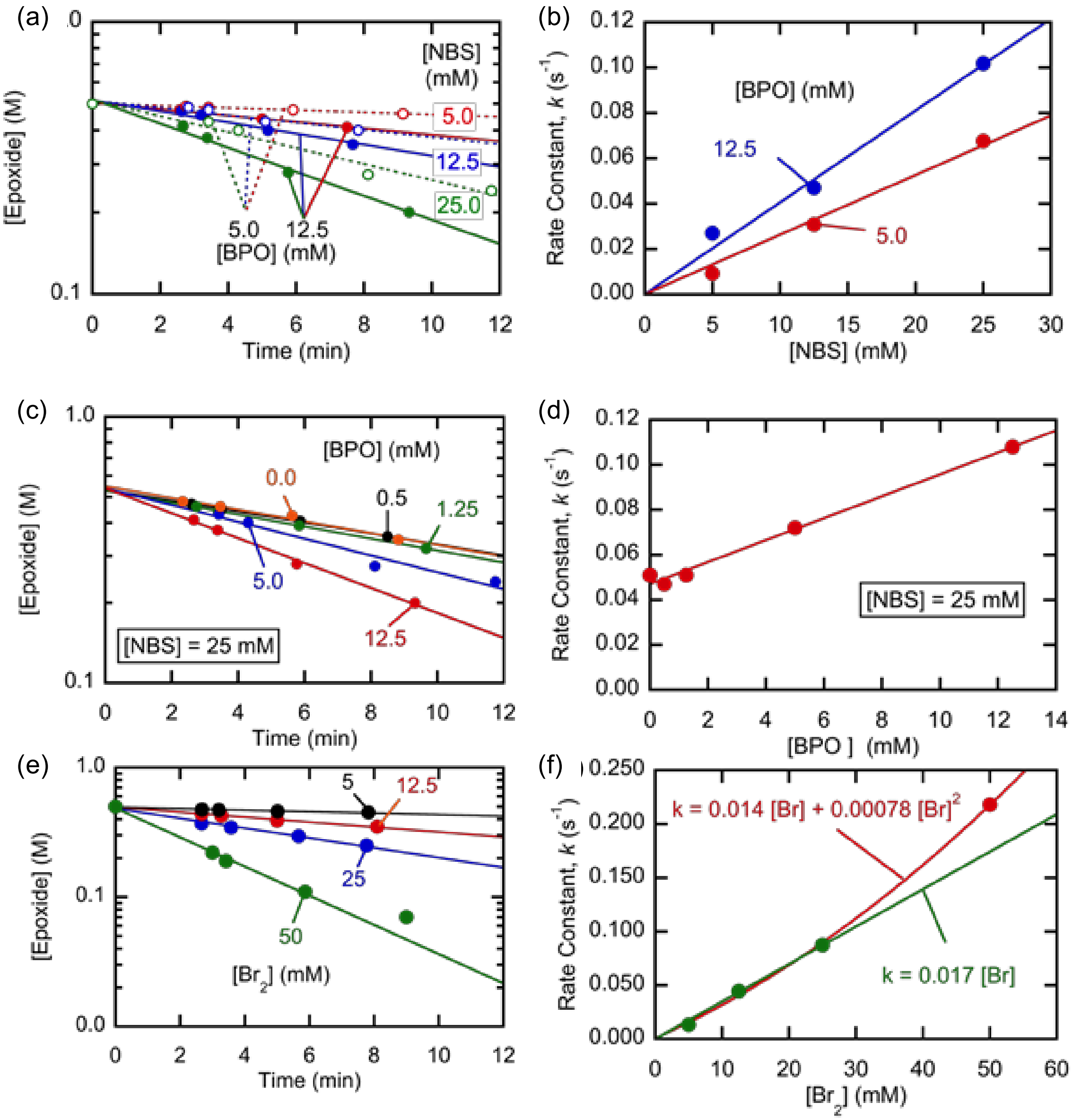
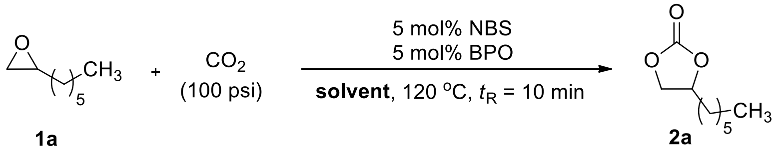


Figure 2-2: Selected kinetic experiment results showing effects of epoxides, NBS, BPO and Br_2 on epoxide coupling with CO_2.

The rate of the reaction displayed a first-order dependence on the epoxide (**Figure 2-2a** and **2-2c**), NBS (**Figure 2-2b**), and BPO concentrations (**Figure 2-2d**) and was independent of CO_2 pressure. Notably, the reaction did not require BPO yet was accelerated by it. These results are easily explained by the following hypothesis: NBS catalysis involves two parallel pathways, one that does not require BPO (with a rate constant k_{10}^{exp}), and one that does (with a rate constant k_1^{exp}). These results can be collected to give the overall rate constant in terms of the initial NBS and BPO concentrations (see **eq 2-2**):

$$\frac{d[Epoxide]}{dt} = -\left(k_{10}^{exp} + k_1^{exp}\,[BPO]_0\right)[NBS]_0[Epoxide] \quad (\mathbf{2\text{-}2})$$

The solvent study has shown that DMF and DMA were critical for the reaction to achieve high conversion and yield, suggesting to us that the solvent may also be a direct promoter of the reaction. Indeed, the Parisi group has reported that *N*,*N*-dimethylamides can convert NBS to Br_2.[10] The Braddock group also demonstrated that DMF and DMA can behavior as nucleophilic organocatalysts for the transfer of electrophilic bromine from NBS.[11] Moreover, highly enantioselective electrophilic brominations catalyzed by peptides and Lewis base-catalyzed alkene halofunctionalizations were recently reported by Miller and Denmark, respectively.[12] On the other hand, CO_2 may be activated by DMF, as has been suggested by Aresta.[13] We verified participation of DMF in the reaction mechanism by carrying out a solvent kinetic isotope effect (KIE) experiment. The relative rate of the reaction in DMF and DMF-d7 (**eq 2-3**) was determined to be 1.3, suggesting a secondary KIE, such as a change of hybridization within DMF.



1a **2a** **(2-3)**

solvent = DMF
DMF-*d7*

rate: ***k*H** = 0.0594 Mmin^{-1}
***k*D** = 0.0458 Mmin^{-1}

$\boxed{\mathbf{kH/kD = 1.3}}$

We suspected that the function of NBS and BPO was the generation of Br_2, which in turn may be the active catalyst, a supposition also consistent with the excellent performance of Br_2 in initial evaluations of preparative conditions. A kinetics experimental study with pure bromine (in the absence of NBS and BPO) confirmed this notion (**Figure 2-2e**). The depletion of the epoxide with time was clearly dependent upon [Br_2]; the observed reaction rate constant is

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[10] Caristi, C.; Cimino, G.; Feriazzo, A.; Gattuso, M.; Parisi, M. *Tetrahedron Lett.* **1983**, *24*, 2685-2688.

[11] Amad, S. M.; Braddock, D. C.; Cansell, G.; Hermitage, S. A. *Tetrahedron Lett.* **2007**, *48*, 915-918.

[12] (a) Gustafson, J. L.; Lim, D.; Miller, S. J *Science* **2010**, *328*, 1251-1255. (b) Pathak, T. P.; Miller, S. J. *J. Am. Chem. Soc.* **2012**, *134*, 6120-6123. (c) Denmark, S. E.; Burk, M. T. *Proc. Natl. Acad. Sci.* **2010**, *107*, 20655-20660. (d) Denmark, S. E.; Burk, M. T. *Org. Lett.* **2012**, *14*, 256-259.

[13] Aresta, M.; Dibenedetto, A.; Gianfrate, L.; Pastore, C. *J. Mol. Catal. A: Chem.* **2003**, *204-205*, 245-252.

shown in **Figure 2-2f** to be essentially linear at low Br_2 concentrations, with a quadratic contribution at higher [Br_2]. The rate constants were similar in magnitude to those obtained when NBS was used as the catalyst, with BPO as a co-catalyst, strongly suggesting that Br_2 produced from NBS was the actual catalyst promoting the reaction.

On the basis of these results, we proposed a mechanism involving an in situ Br_2 generation (**Scheme 2-3**, eq A1-A4) and a bromo-oxonium species (**7**). Given the moderate nucleophilicity of the epoxide oxygen, it is reasonable to propose the intermediacy of this cationic species **7** (eq B1). Moreover, bromine is known to react with other oxygen-containing compounds, such as ethers;[14] in fact, dioxane forms an isolable complex with elemental bromine.[15] Activated CO_2 **9** can react with **7** to give compound **10** (eq B3). It is also possible that bromide ion opens the bromo-oxonium species **7**, followed by activated CO_2 **9** displacement of bromide to give the same intermediate **10**. Epoxide opening at the less hindered (terminal) position was consistent with the observation that enantiomerically pure (*S*)-**1c** was converted to enantiomerically pure (*R*)-**2c** (retention of configuration, **Scheme 2-2**). The lower ee of (*R*)-**2a** was presumably due to increased stabilization of positive charge at the 2-position by the Ph group. The regioselectivity of epoxide opening (with complete inversion of configuration of the minor regioisomer) would be one limiting scenario that would explain this result. It is also possible that the minor enantiomer is the result of an S_N1-like mechanism, followed by stereorandom attack of an activated CO_2 nucleophile (e.g., **9**, **Scheme 2-3**). After epoxide opening, the O–Br bond may be broken by bromide (Br–), regenerating the Br_2 catalyst (eq B4) and liberating an alkoxide anion that undergoes cyclization to form the carbonate product.

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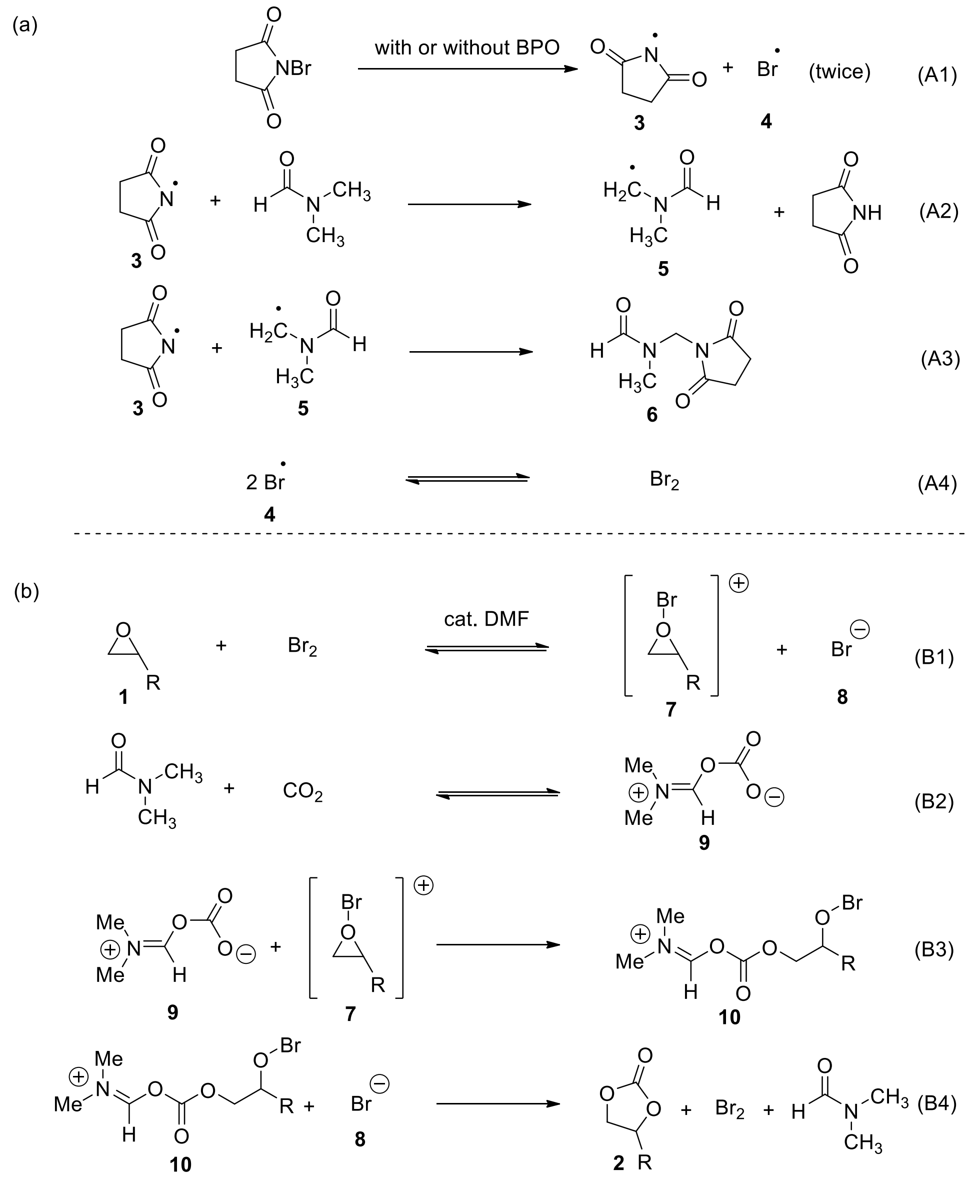
[14] (a) Pajeau, P. *Bull. Soc. Chim.* **1960**, 621. (b) Kratzl, K.; Schubert, K. *Monatsch* **1950**, *81*, 988-995.

[15] Kosolapoff, G. M. *J. Am. Chem. Soc.* **1953**, *75*, 3596-3597.



Scheme 2-3: Proposed mechanism

This kinetic model was further analyzed through mass balances on the reaction intermediates that were assumed to be at pseudo-steady state. The system of algebraic equations was solved for the unknown intermediate concentration [Br•] that was further resolved into **equation 2-4** by considering the homolysis/recombination of Br_2 to be reversible: (note that all rate constants k_i are elementary in eq 4.)

$$r_{overall} = \frac{k_4 k_{r4}[k_{10}+k_1[BPO]][NBS][Epoxide]}{2(k_4^2-k_{r4}^2)} \quad (2\text{-}4)$$

This result is consistent with the experimentally-determined rate expression given by **eq 2-2**. In the derived expression, the BPO concentration is constant due to its role as a co-catalyst.

The NBS concentration is taken to be effectively constant due to the slow rate of Br_2 production relative to the kinetics of carbonate formation. It should be noted that the actual bromine concentration in the liquid phase may be significantly lower than the theoretical maximum because of partitioning of 65-95% of the Br_2 into the gas phase slug (largely CO_2). The exact amount will depend on the relative mass transfer rates between the two phases and Henry's Law constant.

3. Investigation of CO2 Capture and conversion using simple olefins under continuous flow

Continuous flow methods have emerged as enabling technologies for chemical transformations, particularly for gas–liquid biphasic reactions where an exceptionally high surface area-to-volume ratio and enhanced safety with a very small footprint provide significant benefits compared to conventional batch conditions. However, one of the major hurdles in the development of a continuous flow method is reagent incompatibility in multicomponent reactions. Herein we demonstrate that a combination of careful mechanistic investigations and using the results of those experiments to design optimal multi-step continuous flow reactor systems provides a means to solve this problem by making use of the ease of sequential introduction of reagents in flow and optimizing a range of reaction parameters for individual steps.

Following our development of a bromine-catalyzed conversion of CO_2 and epoxides to carbonates in a continuous flow apparatus,[16] a more straightforward and economical approach would be the direct production of cyclic carbonates starting from corresponding olefins. However, in contrast to extensive studies on reactions with epoxides, few reports have documented the direct synthesis of cyclic carbonates from olefins, and most of them entail a one-pot, sequential epoxidation/cycloaddition pathway. Among these reported methods, we were attracted to a “bromohydrin” pathway recently discovered by the Li group with the use of NBS reagents.[17]

In this context, a mechanism-guided design of a sequential flow system has been achieved for the fixation of CO_2 with olefins as the starting material, with results that compare very favorably with reported batch conditions, and avoided the low conversion and reagent incompatibility problems observed in our original flow design (**Scheme 3-1**).

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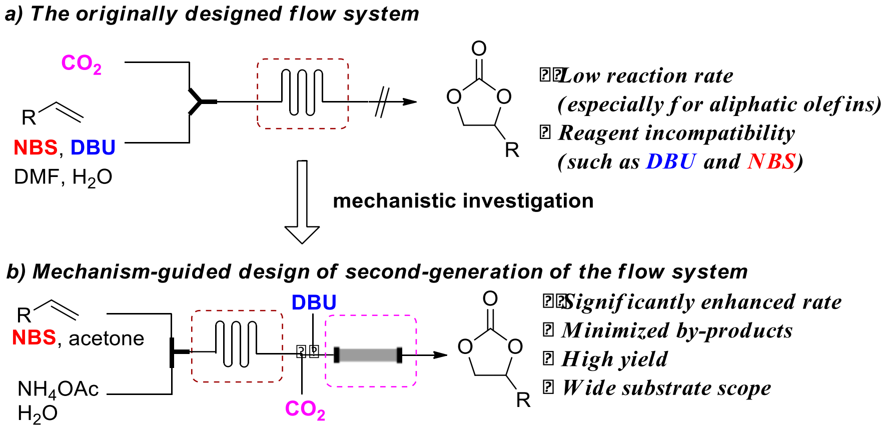
[16] Kozak, J. A.; Wu, J.; Su, X.; Simeon, F.; Hatton, T. A.; Jamison, T. F. *J. Am. Chem. Soc.* **2013***, 135,* 19497-18501.

[17] Eghbali, N.; Li, C.-Li *Green Chem.,* **2007**, *9*, 213-215



Scheme 3-1. Conversion of CO_2 and olefins into cyclic carbonates in flow.

Li proposed a bromohydroxylation pathway (**Scheme 3-2**, path a) for the conversion of olefins to cyclic carbonates using stoichiometric NBS and DBU based on the transformation in which bromohydrins can be generated from olefins and NBS in water. However, when we treated styrene with NBS and DBU in water under pressurized CO_2, dibromide **12a** was obtained as the only byproduct instead of bromohydrin **13a**. By reconsidering the possible mechanism for this transformation, it was argued that different intermediates, such as DBU activated CO_2 (complex **C**, path b),[18] water induced bicarbonate anion **B**, and the epoxide intermediate **14a** (path d) could also play a role in the formation of the cyclic carbonate product.

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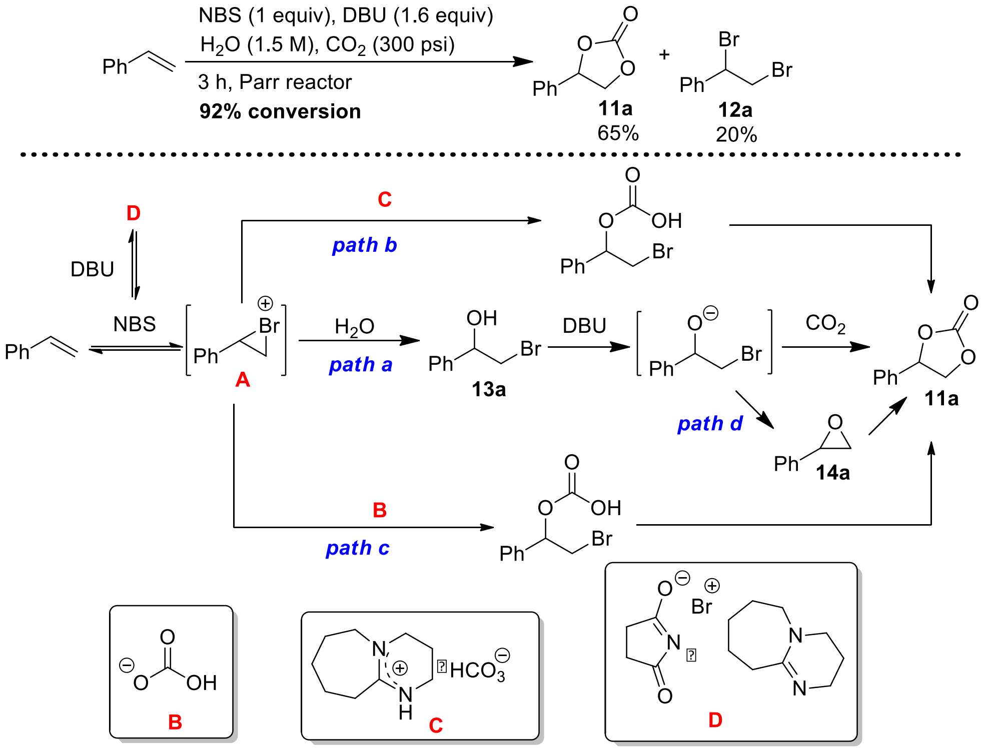
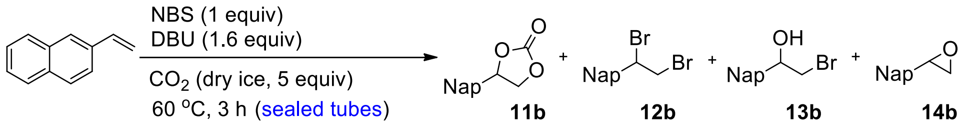
[18] It has been reported that DBU activated CO_2 in H_2O to form a bicarbonate salt of DBU instead of a zwitterionic adduct, which exhibited good reactivity for various CO_2-fixation reactions: (a) Heldebrant, D. J.; Jessop, P. G.; Thomas, C. A.; Eckert, C. A.; Liotta, C. L. *J. Org. Chem.*, 2005, **70**, 5335-5338; (b) Yoshida, M.; Komatsuzaki, Y.; Ihara, M. *Org. Lett.*, 2008, **10**, 2083-2086.



Scheme 3-2. Possible reaction pathways.

Control experiments were first conducted in sealed tubes to explore the reaction mechanism using vinylnaphthalene as the model substrate. As shown in Table 3-1, full conversion was achieved with NBS in water to deliver bromohydrin **13b** in 87% yield (entry 1). However, in the presence of DBU, the reaction rate became exceedingly low (only 26% conversion after 3 hours, entry 2), indicating an interaction between DBU and NBS (complex **D**, **Scheme 3-2**), which hindered the formation of the reactive bromonium ion between NBS and olefins. With the assistance of CO_2, the conversion increased to 84% in a 3 h reaction period (entry 3), probably due to the formation of complex **C** that released NBS to react again with olefin. In the absence of H_2O, only the dibromide by-product 1**2b** was observed (entry 4). Further control experiments indicated that the reaction seemed likely to proceed through DBU activation of CO_2 via pathway b. However, it is highly possible that all the pathways contributed simultaneously to the formation of the final cyclic carbonates during the reaction process.

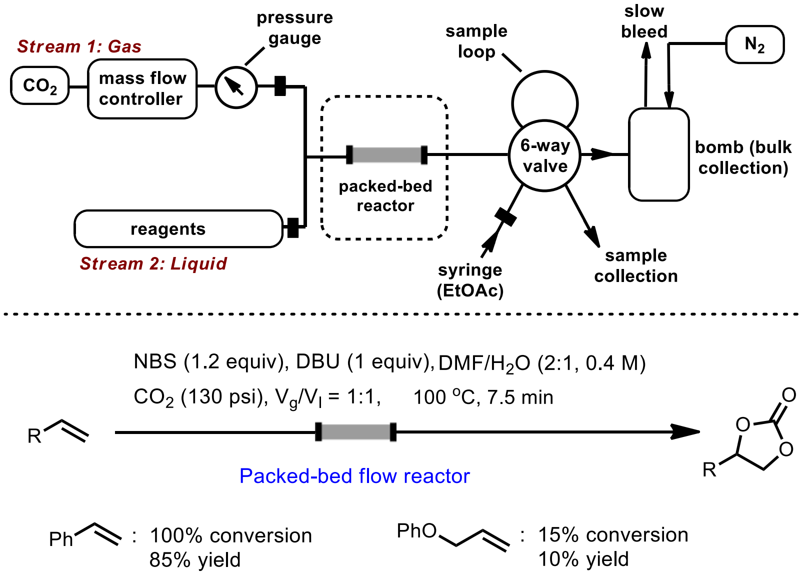


entry	conditions	conversion[a]	yield of **11b**[a]	other products[a]
1	NBS +H_2O	100%	0%	87% **13b**
2	NBS+H_2O+DBU	26%	0%	15% **14b**
3	NBS+H_2O+DBU+CO_2	84%	55%	8% **14b**
4	NBS+DMF+DBU+CO_2	50%	0%	45% **12b**

[a] Conversion and yield based on crude ^1H NMR analysis using trichloroethylene as an external standard.

Table 3-1. Control experiments to explore the reaction mechanism.

With a better understanding of the reaction mechanism, we turned our attention to the flow synthesis. A two-stream gas-liquid continuous flow apparatus was first constructed (**Scheme 3-3**). A screen of water-miscible solvents suitable for use in the flow system was carried out, with DMF emerging as the best solvent to ensure a homogenous reaction solution with retention of good reactivity. A temperature study with styrene in a stainless steel tubing (SS-tubing) reactor (2 mL) indicated that styrene oxide **14a** was the major product at low temperature, and the yield of carbonate **11a** was higher at elevated temperature. However, above 100 °C, diol byproducts were observed, and the flow rate became unsteady. Further optimization of the flow condition revealed that the packed-bed reactor (packed with stainless steel powder, 325 mesh, strem, 1.2 mL space volume) was more efficient than the SS-tubing reactor, and the flow rate became steady even at high temperature probably due to the increased inner diameter of the reactor (0.25 inch vs 0.03 inch).



Scheme 3-3. Transformations in the two-stream gas-liquid flow reactor.

Even though the two-stream flow technique exhibited remarkable efficiency compared with traditional batch conditions in the case of styrene, several limitations with this system were identified. Most importantly, aliphatic olefins showed only sluggish reactivity under the optimal conditions. Moreover, nonpolar olefins such as 1-octene and vinylnaphthalene had poor solubility in the DMF/H_2O co-solvent. Extensive studies aimed at improving the reaction rate of aliphatic olefins, such as applying phase-transfer-reagents, changing residence time and concentration, and utilizing different brominating reagents and bases, proved fruitless.

Due to the poor solubility and incompatibility of starting materials at high concentration (e.g. olefins and NBS generated dibromide in DMF), multi-stream flow systems (three-stream and four-stream) were introduced. Even though the reaction rate of aliphatic olefins was not significantly improved, it is worth noting that the order of the gas stream can be easily switched in the flow system, which is hard to achieve with pressurized autoclaves.

To overcome the low conversion problem associated with aliphatic olefins, a different design was considered. Based on the mechanistic study, it was concluded that DBU significantly decreased the reaction rate of the oxidative carboxylation due to interaction with NBS. It was envisioned that if NBS and DBU were introduced into the flow system at different stages during the reaction, an enhanced reaction rate should be achievable. Furthermore, the formation of bromohydrins in the first stage of the process could also avoid the dibromide by-products observed in batch conditions (**Scheme 3-2**).

In this regard, we first tested the sequential transformation of 1-octene as the model substrate in the continuous flow system. Acetone/H_2O (1:1), which was the only solvent mixture found to provide a homogenous solution in both the bromohydroxylation and cyclization steps, precluded the need to use phase-transfer-reagents. The addition of a catalytic amount of NH_4OAc facilitated conversion of olefins to bromohydrins.[19] In order to achieve complete consumption of starting olefins, a temperature of 40 ^{o}C was maintained during the bromohydroxylation step. In the flow setup, after the system reached the appropriate pressure (130 psi of CO_2), an acetone solution of 1-octene and NBS, and an aqueous NH_4OAc solution were introduced by a Syrris Asia pump. The organic and aqueous streams met at a T-mixer, and were introduced into a PFA tubing reactor for 30 minutes. Then the CO_2 stream was metered into the system using a mass flow controller, which met the liquid flow at a Y-mixer, and a 1:1 (v:v) liquid/gas slug flow stream was observed at the outlet. The aqueous DBU solution was introduced last and combined with the gas/liquid flow in a stainless steel T-mixer at 100 ^{o}C; in this way possible epoxide formation was avoided. The resulting gas/liquid segmented flow was passed through a packed-bed reactor (filled with SS-powder) at 100 ^{o}C for 10 minutes. The acetone/water co-solvent could be heated above the boiling point at 130 psi while maintaining a steady flow. N_2 was employed for back pressure and a slow bleed was utilized to regulate the overall pressure of the system. After steady state was achieved (~ 4 x t_R, 2 h), the final eluent stream was sampled using a 6-way valve, which showed 75% yield of product **11c**.

With the optimized flow conditions in hand, we investigated the substrate scope (**Scheme 3-4**). A variety of aliphatic olefins were converted into the corresponding cyclic carbonates with good yield. Interestingly, the flow conditions not only tolerated functionalities such as ether, nitrile, silane and ester (**11d** to **11g**), but also allowed for conversion of even more challenging substrates like ketone and alcohol that had potential to undergo cyclization under basic conditions (**11h**, **11i**). The reaction of ethylene proceeded efficiently to furnish **11j** in good yield, which stated a successful example of sequential introduction of different gas reagents into a continuous flow system. Aromatic carbonates were generated effectively at a slightly lower temperature to avoid diol formation. Electron-poor aromatics appeared to afford higher yield

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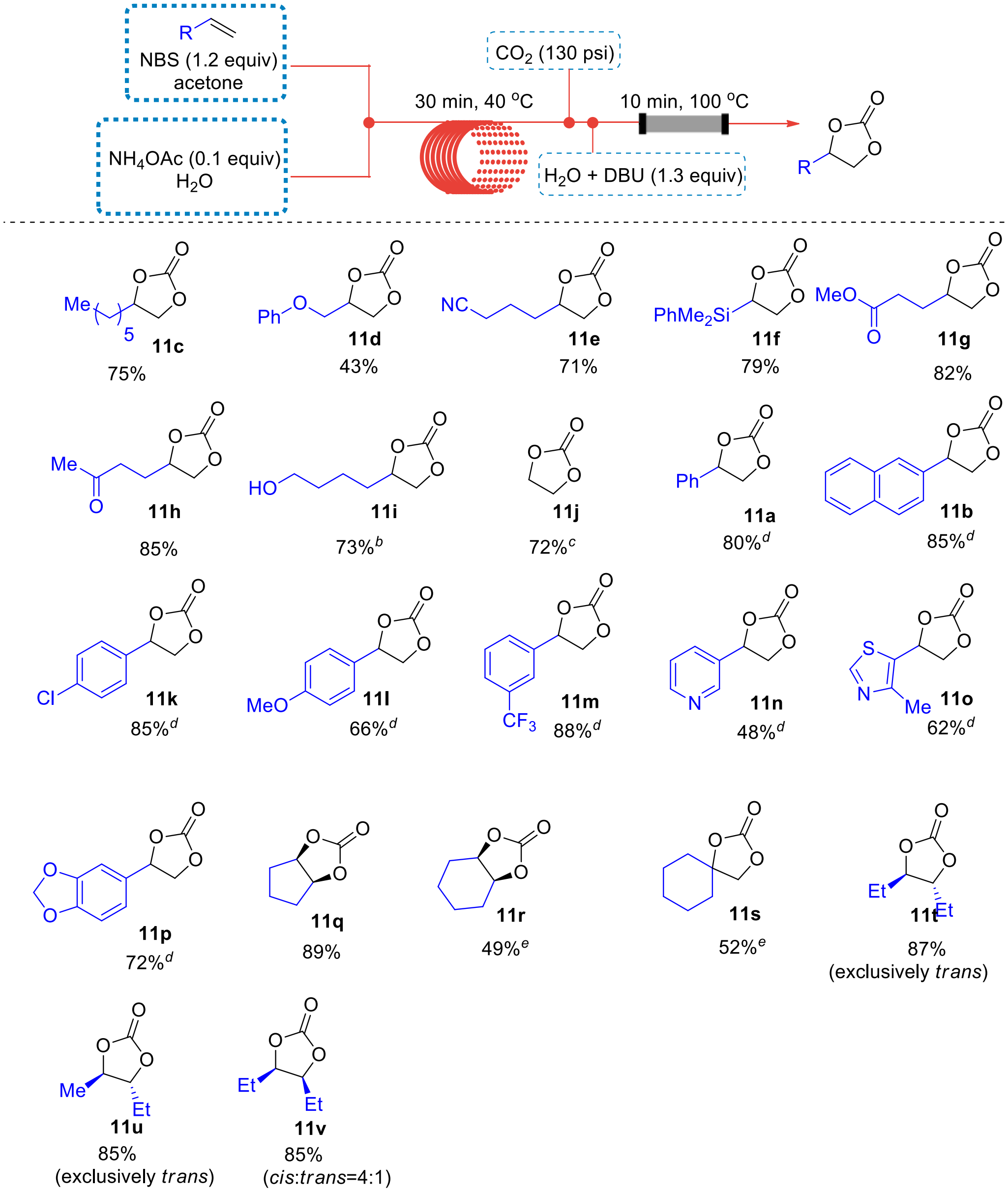
[19] Das, B.; Venkateswarlu, K.; Damodar, K.; Suneel, K. *J. Mol. Catal. A: Chem.,* 2007, 17-21.

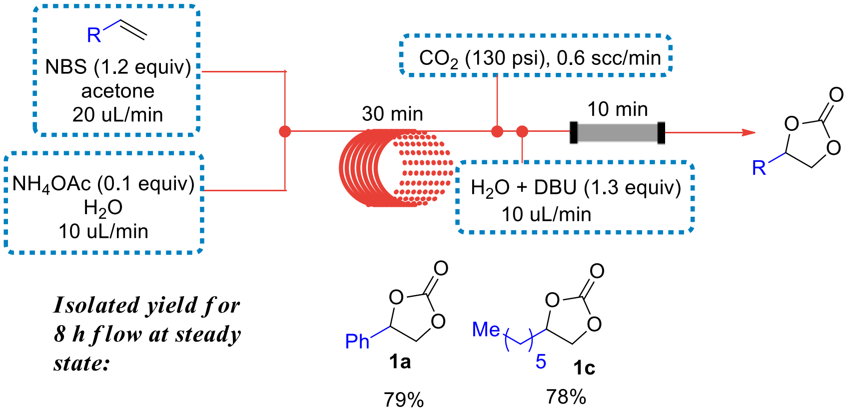
than electron-rich ones (**11k** to **11l**). Notably, some heteroaryl olefins were also amenable substrates for our flow reactors (**11n** to **11p**). No epoxide or dibromide by-product was observed in these cases.



[a]Yield based on crude ^{1}H NMR analysis using trichloroethylene as an external standard. [b]Using 2.3 equiv DBU. [c]CO_2 and ethylene were both introduced at 90 psi, residence time 9 min + 6 min, yield based on NBS. [d]Bromohydroxylation conducted at 30 °C; cyclization conducted at 85 °C. [e]Less H_2O (totaly 10 mL) and higher CO_2 pressure (180 psi) were applied.

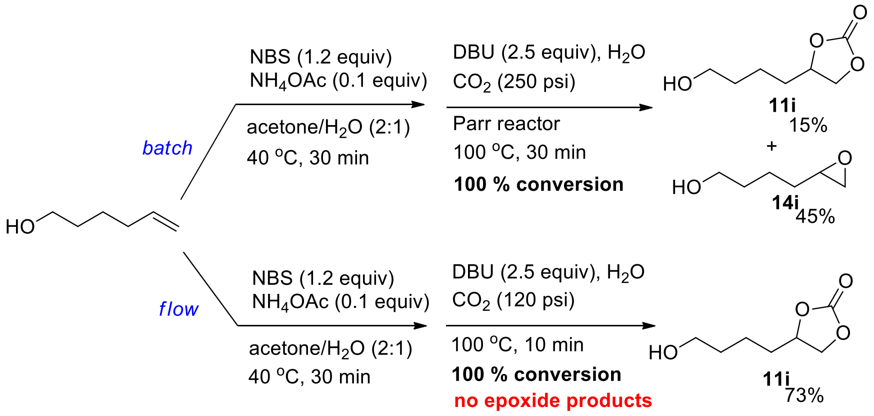
Scheme 3-4. Sequential transformation in flow.[a]

To further challenge the newly developed flow conditions, internal olefins with increasing steric bulk were chosen as reaction partners. Cyclopentene was a good candidate for this transformation and product **11q** was obtained in high yield. Reaction of cyclohexene proceeded at a slower rate to give the desired product **11r** in approximately 20% yield along with the *trans*-diol by-product. With increased CO_2 pressure and a lower amount of H_2O, the yield of **11r** was improved to 49%. Importantly, *trans*-3-hexene afforded the desired carbonate **11t** stereospecifically with high yield. Moreover, even though two different bromohydrins were formed when alkenes contained different substituents, they ended up with the same cyclic product (**11u**). *Cis*-3-hexene was transformed to carbonate **11v** in a similar yield, with the observation of partial isomerization. It should be noted that this is the first report of a direct synthesis of cyclic carbonates from acyclic disubstituted olefins, which were widely considered to be difficult substrates for epoxide cycloaddition. Gem-disubstituted olefins were also amenable to this transformation, delivering product **11s** in moderate yield.



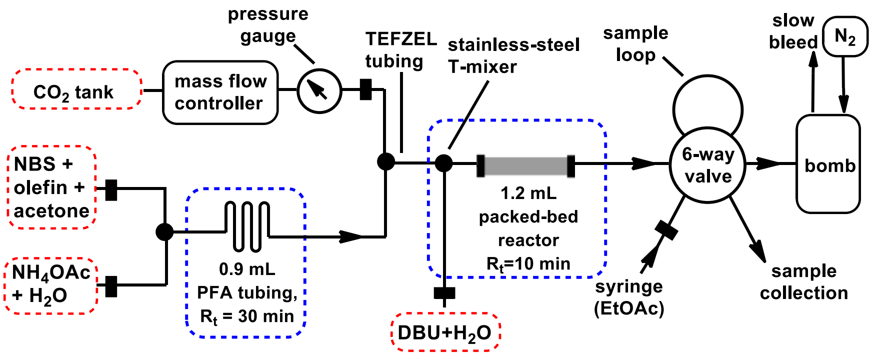
Scheme 3-5. Long term flow at the steady state.

Based on data presented in **Scheme 3-4** and the residence times investigated, approximately products could be synthesized at a rate of 0.6 mmol/h. To test this, experiments were repeated using the optimal conditions, and the product stream was collected for 8 hours at steady state. As shown in **Scheme 3-5**, the isolated product yields were comparable with those in **Scheme 3-4**.



Scheme 3-6. Comparison between batch and flow sequential reactions.

Thus, both aromatic and aliphatic olefins, as well as mono-substituted and disubstituted olefins were converted to cyclic carbonates in the continuous flow system within 40 minutes with full conversion and moderate to good yield. On balance, our sequential transformation in the flow reactor compared very favourably with reported conditions in batch (which required > 3 h for aromatic olefins, > 5 h for aliphatic olefins, and dibromide byproducts were detected). Batch reactions of the sequential transformation were also conducted in pressurized autoclaves (**Scheme 3-6**). In all cases, the products were accompanied by a large amount of epoxides, which were not observed under the flow condition.



Design features	Impacts
sequential reactions	significantly enhances the reaction rate; avoids reagent incompatibility
excellent surface-to-volume ratio	accelerates synthesis; minimizes byproduct formation
packed-bed reactor	increases the reaction rate; enhanced mixing
acetone as co-solvent	avoids phase-transfer-reagents
elevated temperature and pressure	provides rate enhancement
no headspace	reduced equipment footprint (safety)

Scheme 3-7. Function of each reactor feature.

4. Microwave assisted synthesis of cyclic carbonates from olefins using sodium bicarbonates in a green pathway

Since the discovery of significant rate enhancement of microwave irradiation in organic chemical transformations by the Gedye and Giguere/Majetich groups in 1986,[20] microwave heating has become a fast-moving and exciting field in synthetic community.[21] Spectacular accelerations, high yields, and good selectivity (chemo-, regio- and stereoselecitivty) under milder conditions have often been described using microwave compared to conventional heating.[22] The effect of microwave irradiation is a combination of thermal effects, arising from the volumetric heating nature, superheating and the selective absorption of radiation by polar substances. On the other hand, the non-thermal effect of highly polarizing radiation, which is still a controversial topic, provides additional benefits for microwave as an impressive applicable new energy source.[23] However, it was found that hot spots, thermal runaway and explosions were often produced during the microwave assisted on heterogeneous reactions.[24] In addition, due to high pressure generated from heated gas, conducting gas/liquid heterogeneous reactions in microwave is difficult in practical.

Even though transformation of CO_2 into useful organic chemicals attracts ever-increasing attention as CO_2 is an easily available, non-toxic and economical carbon resource, there is a general reluctance for using it in conventional batch conditions largely owing to problems related to the containment of pressurized CO_2, associated safety factors, high capital costs, and infrastructure requirements of large scale reactors. Moreover, it is difficult to apply the microwave-actuated system in conversion of CO_2 because of the requirement of complicated design and control for the whole system. In this context, bicarbonate salts, especially $NaHCO_3$, can be utilized as a substituent for CO_2 as a cheap and clean candidate of C1 sources, thus avoid

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[20] (a) Gedye, R. N.; Smith, F.; Westaway K. *Tetrahedron Lett*., **1986**, *27*, 279. (b) Giguere, R. J.; Bray, T. L.; Duncan, S. M.; Majetich, G. *Tetrahedron Lett*., **1986**, *27*, 4945.

[21] (a) Polshettiwar V.; Varma, R. S. *Chem. Soc. Rev.,* **2008**, *37*, 1546. (b) Kappe, C. O. *Chem. Soc. Rev*. **2008**, *37*, 1127. (c) Kiddle, J. J. *J. Am. Chem. Soc*., **2006**, *128*, 1771. (d) David, A. *Nature*, **2003**, *421*, 571.

[22] (a) Mingos, D. M. P. *Blackwell, Oxford,* **2005**. (b) Loupy, A. 2nd edn., *Wiley-VCH, Weinheim*. (c) Kappe, C. O.; Stadler, A. **2005**, *Wiley-VCH, Weinheim*.

[23] (a) Metaxas, A. C. *Wiley-VCH, Weinheim*. **1996**. (b) Hoz, A.; Díaz-Ortiz A.; Moreno, A. *Chem. Soc. Rev.*, **2005**, *34***,** 164. (c) Baig, R. B. N.; Varma, R. S. *Chem. Soc. Rev.*, **2012**, *41***,** 1559.

[24] (a) Horikoshi, S.; Osawa, A.; M.; Serpone, N. *J. Phys. Chem. C*, **2011**, *115*, 23030. (b) Kappe, C. O. *Angew. Chem. Int. Ed*., **2004**, *43*, 6250.

the using of giant pressurized autoclaves and the waste of excess CO_2, and providing a convenient "CO_2" substitution in case where CO_2 is hard to be applied. Thus, we investigated an microwave-assisted synthesis of cyclic carbonates from olefins and bicarbonate salts (**Figure 4-1**).

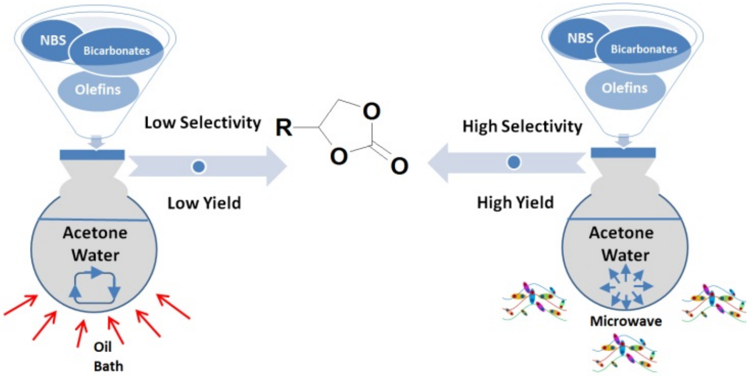
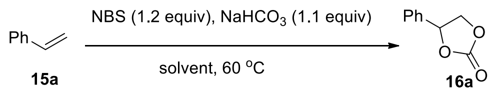


Figure 4-1 Syntheses of cyclic carbonates using $NaHCO_3$ and olefins

Our study was initiated with a solvent study in both conventional oil bath and microwave conditions (**Table 4-1**). Styrene and sodium bicarbonate were chosen from the economical aspect in the model reaction to screen the optimized reaction condition. A poor but encouraging yield (25%) of carbonate **16a** was obtained using water alone as the solvent under microwave heating (entry 1). To our delight, polar solvents such as acetone, MeCN and DMF mixed with water exhibited remarkable enhancement of reactivity and selectivity of the desired transformation (entries 3, 5 and 7). Other solvents like dioxane, THF, and DMSO resulted in strikingly decreased yield (entries 8-10). No reaction was observed with the unpolar solvent and water mixture (entry 11). Notably, the results of comparative tests between microwave and oil bath heating clearly demonstrated the superior of microwave heating, no matter which solvent system was using (entries 1-6). Normally, oil bath reactions resulted in lower yield of cyclic carbonates compared with microwave heating, generating significant diol and epoxide by-product even with an 18 hour reaction period. Considering the economic effect and easy-removal of acetone than DMF and MeCN, acetone/water mixture was chosen as the solvent system for our further study. Even though epoxide by-products were detected in a 3 hour period reaction, the amount of by-product was totally depressed with a prolonged reaction time (entry 3).

Table 4-1 Evaluation of solvents with different loss factor

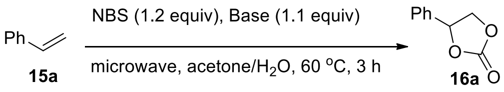


entry	solvent	loss factor [b]	time	microwave[a]		oil bath[a]	
				yiled (%)	conversion (%)	yiled (%)	conversion (%)
1-2	H_2O	0.122	3 h	25	76	10	78
3-4	Acetone/H_2O	0.09	18 h	86	100	55	100
5-6	DMF/H_2O	0.142	3 h	88	100	80	100
7	MeCN/H_2O	0.092	3 h	56	100	-	-
8	Dioxane/H_2O	0.079	3 h	23	100	-	-
9	THF/H_2O	0.085	3 h	15	70	-	-
10	DMSO/H_2O	0.467	3 h	37	100	-	-
11	Hexanes/H_2O	0.071	3 h	0	0	-	-

[a] Conversion and yield based on crude ^1H NMR using trichloroethlene as the external standard.

[b] The measurement of microwave vector network analyzer of Agilent E8362B combined with the calculation by Genetic algorithms was used to obtain loss factors of different mixture solvents.

Table 4-2 Base evaluation



entry	base	conversion[a]	yiled[a]
1	$NaHCO_3$	100%	62%
2	$CsHCO_3$	100%	60%
3	K_2CO_3	65%	24%
4	$KHCO_3$	83%	48%
5	NH_4HCO_3	58%	0%

[a] Conversion and yield based on crude ^1H NMR using trichloroethlene as the external standard.

To evaluate the effect of bicarbonate salts, a quick screening of various bicarbonates was carried out, which indicated most bicarbonate salts were effective to achieve good conversion and yield (**Table 4-2**). $NaHCO_3$ was chosen from the economic aspect. Thus, the optimal condition was: 1 equiv olefin, 1.2 equiv NBS, 1.1 equiv $NaHCO_3$, acetone (1 M), and H_2O (1 M) stirred at 60 °C for 18 hours in microwave.

In order to understand the reaction process, we investigated the product distribution at different time scales both in microwave (**Figure 4-2**) and oil bath heating (**Figure 4-3**). With the optimized condition, the starting olefins were totally converted into bromohydrins within 10 minutes. With the reaction going on, bromohydrins were converted to epoxides and cyclic carbonates, and epoxides were transformed to cyclic carbonates at the same time. In microwave, the epoxide reached a maxim yield at approximate 1 hour reaction time and the amount started decreasing after that. Eventually, all epoxide intermediates were converted to cyclic carbonate products in microwave. Evidently, microwave accelerated the transformation of epoxides to carbonates compared to oil bath heating, probably due to the "hot spot" caused by insoluble $NaHCO_3$ particles and the specific effects associated with microwave heating.

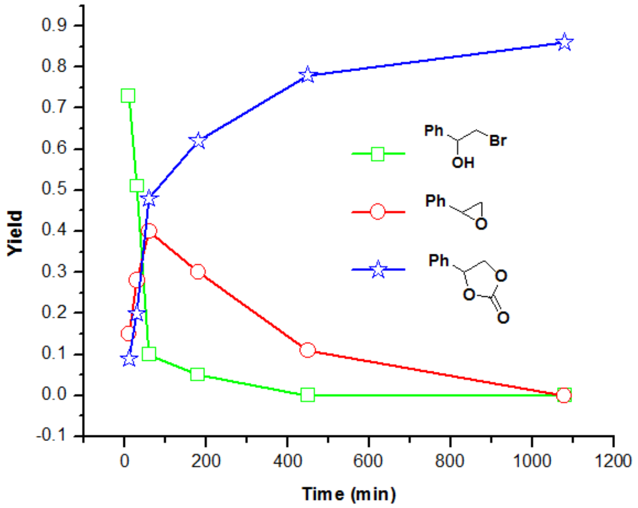


Figure 4-2 Products distribution at different time scales under the microwave heating

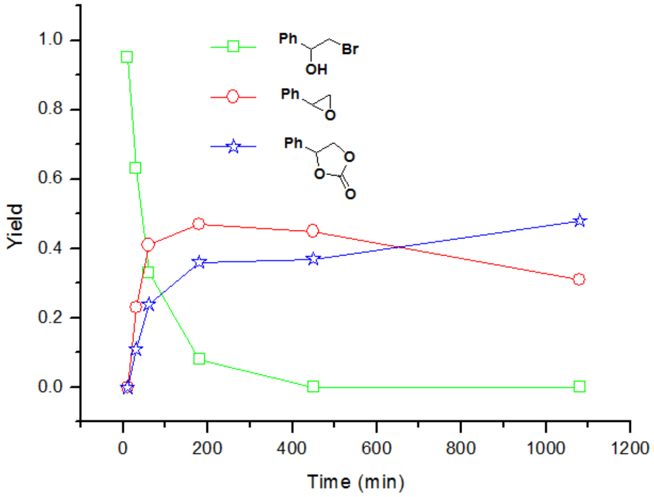
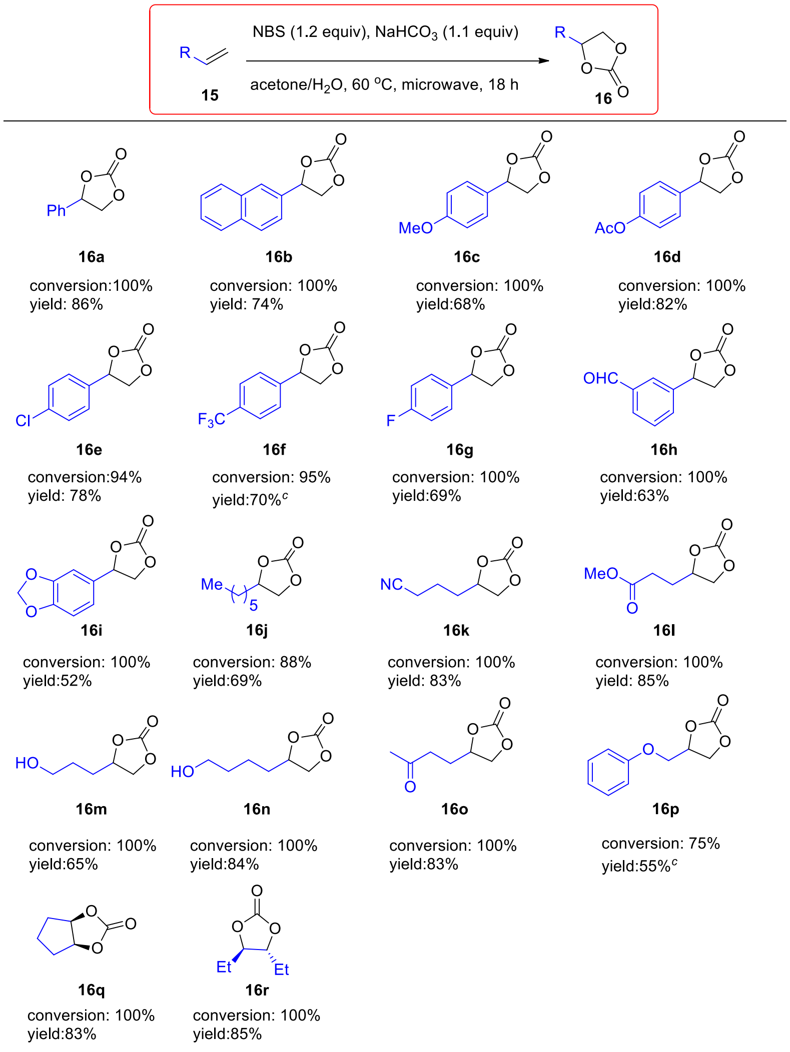


Figure 4-3 Products distribution at different time scales using the oil bath heating

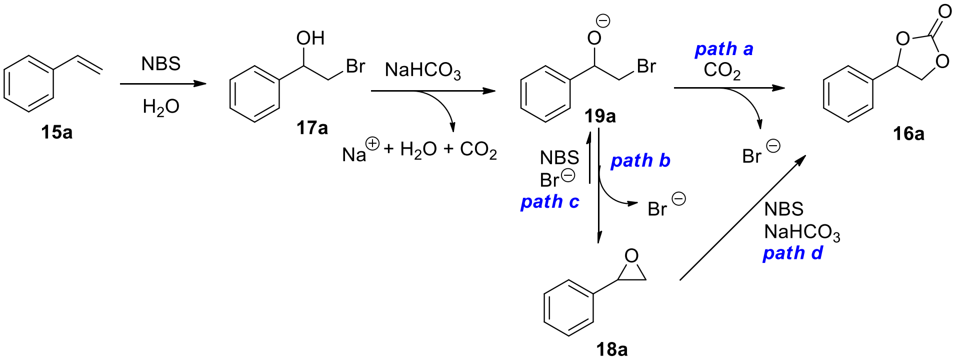
Using the optimal conditions in the microwave apparatus, we investigated olefins bearing different functional groups (**Scheme 4-1**). All electron-rich aromatic olefins (**16c**, **16d**, **16i**), electron-rich aromatic olefins (**16e-16h**) and terminal aliphatic olefins (**16j-16p**) were converted to the corresponding cyclic carbonates in moderate to good yields. The microwave-assisted conditions not only tolerate functionalities such as halide, trifluoromethyl, ether, nitrile, and ester, but also allowed for conversion of even more challenging substrates like aldehyde, ketone, and alcohol that had potential to undergo cyclization under basic conditions (**16h**, **16m-16o**). Notably, disubstituted olefins were also amenable substrates for this transformation to achieve good yield of products (**16q**, **16r**). In some cases, it was necessary to use DMF/H_2O as solvent instead of acetone/H_2O to improve the reaction efficiency (**16f**, **16p**). All the products were converted into the corresponding carbonates with no or little epoxide formation, indicating the high versatility of the microwave-assisted transformation utilizing sodium bicarbonate as C1 source.

A plausible mechanism was proposed based on the product distribution study (**Scheme 4-2**). Bromohydrin **17a** was generated first with stoichiometric NBS and olefins followed by deprotonation of the hydroxyl group to deliver anion **19a** and in situ generation CO_2. The subsequent intramolecular cyclization of **19a** (path b) is more favoured than the intermolecular cycloaddition with CO_2 (path a), which resulted in a significant amount of epoxide **18a** within a relatively short reaction period. Two reaction pathways may contribute the conversion of epoxide **18a** to cyclic carbonate **16a** including regeneration of intermediate **19a** path c) and direct transformation to achieve cyclic product **16a** (path d).



[a]Conversion based on ^1H NMR using trichloroethylene as the internal standard, isolated yield. [b]H_2O was reduced to 2 M concentration. [c]Reactions conducted in DMF/H_2O instead of acetone/H_2O.

Scheme 4-1 Substrate scope



Scheme 4-2 Plausible mechanism

5. Life Cycle Analyses of Integrated Chemical Sequestration Process

Goals & Objectives of Analyses

The goal of the study is to evaluate the environmental and economic performance of the electrochemical capture and chemical sequestration process developed by MIT. The MIT prototype will capture CO_2 from flue gas at a Coal Fired Power Plant (CFPP) and convert CO_2 into commercially-desirable chemical feedstock.

This goal will be achieved by performing the following:

i. **Evaluate** the environmental impacts associated with the Electrochemically Mediated Amine Regeneration (E-MAR) CO_2 capture system and chemical sequestration process developed by MIT.

ii. **Study** different scenarios that involve a combination of:

   - Post-combustion carbon capture via either monoethanolamine (MEA) absorption or E-MAR process
   - Carbon sequestration via deep saline aquifers.
   - Carbon utilization via catalytic conversion of CO_2 into organic carbonates

iii. **Interpret** results in terms of environmental impact and economic performance.

Life Cycle Assessment

Methodology

Life cycle assessment is an analysis tool that follows a “cradle-to grave” approach for assessing systems; including products or processes. In ISO 14040, LCA is defined as the “compilation and evaluation of the inputs, outputs and potential environmental impacts of a product system throughout its life cycle”[25]. ISO also distinguishes four stages of an LCA study: goal and scope definition, inventory analysis, impact assessment and interpretation or improvement analysis (**Figure 5-1**). The goal and scope definition stage is vital in determining the system boundaries and objectives of the LCA. The system boundaries are the limits placed on data collection for the study and can influence the outcome of the LCA. This first stage also

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[25] Guinée, J.B., **2002** Handbook on life cycle assessment: Operational guide to the ISO standards. Kluwer Academic, The Netherlands.

specifies the functional unit (FU) of the LCA. The choice of correct functional unit is important for meaningful comparison. One of the main purposes for a functional unit is to provide a reference to which the input and output data are normalized.

Inventorying the inputs (e.g., raw materials and energy) and outputs (e.g., products, byproducts, waste and emissions) comprises the second stage of an LCA. This is usually the most time consuming and data intensive stage.

The life cycle impact assessment (LCIA) can be defined as the "quantitative and/or qualitative process to characterize and assess the effects of the environmental interventions identified in the inventory table". This process is generally divided into three parts: the *Classification* stage links the inputs and outputs distinguished during the inventory process to corresponding environmental impacts. *Characterization* stage quantifies impacts and determines the potency of the effect of inputs and outputs on the impact categories and the final stage *valuation* weighs impacts giving relative importance to each category so that a single index indicating environmental performance can be calculated[26].

The LCIA seeks to establish links between a system's inputs and outputs (in terms of energy and material requirements identified during the life cycle inventory) and potential environmental impact categories as illustrated in **Figure 5-1**[27].

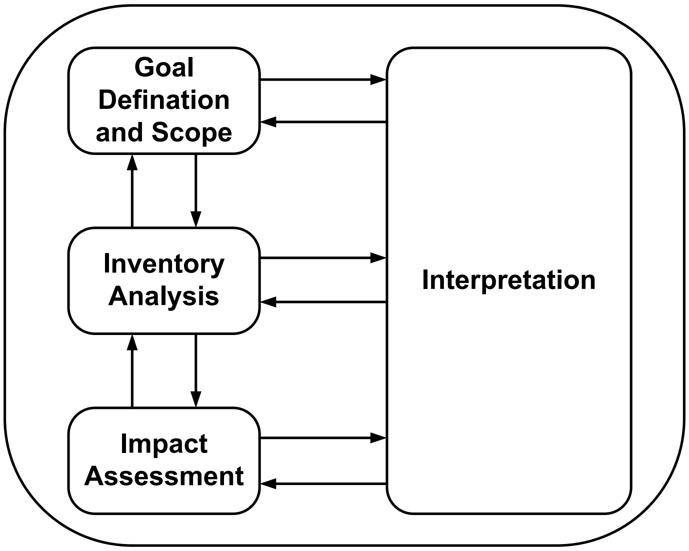

Figure 5-1: Framework of Life Cycle Assessment methodology as defined by ISO 14040[28]

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[26] Allen, D.T. and Shonnard, D.R., **2002** Green engineering: environmentally conscious design of chemical processes. Prentice Hall PTR. Upper Saddle River, NJ.

[27] Curran, M. A. **2006** Life cycle assessment: principles and practice. EPA, National Risk Management Research laboratory

There are several impact assessment categories available for performing a LCA. Some of the most common examples are: Cumulative Energy Demand, Global Warming Potential, Acidification & Eutrophication potentials, Ozone layer depletion, photochemical ozone creation potential, Resource depletion, Eco-toxicity (e.g. aquatic life), Human toxicity potential etc.

Depending on the nature of product, system or process under consideration, the choice of impacts to be calculated is made. The impact method used for this study is CML2001- Nov 09[29] as available in GaBi LCA software and database. For this study the most relevant impact categories are as follows:

1. Global Warming Potential (GWP)
2. Acidification Potential (AP)
3. Eutrophication Potential (EP)
4. Ozone Layer Depletion Potential (ODP)
5. Primary Energy Demand (PED)

These categories are explained in details in Appendix A

Allocation and Credits

An industrial or energy production system can produce multiple products. The ISO 14040/44 standards[30] provide guidance on how to allocate the environmental burdens between the different products. The preferred approach by ISO is to avoid allocation by either (a) dividing the unit processes such that input and output flows can be segregated between products or (b) to expand the product system boundary to include additional functions of the co-products (this is usually achieved by giving the system a credit for the co-product produced through an alternative industrial route). In case allocation cannot be avoided, it is recommended allocation is done on the basis of either physical or economic relationships between products.

The two specific examples from this study are explained below:

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[28] ISO, **2006**. Environmental Management -Life cycle assessment – Principles and framework. International Standard ISO 14040:2006 (E). International Organization for Standardization. Geneva.

[29] Guinée, J.B.; et al. Handbook on life cycle assessment. Operational guide to the ISO standards. I: LCA in perspective. IIa: Guide. IIb: Operational annex. III: Scientific background. Kluwer Academic Publishers, ISBN 1-4020-0228-9, Dordrecht, **2002**, 692 pp.

[30] ISO, **2006**. Environmental Management -Life cycle assessment – Requirements and guidelines. International Standard ISO 14044:2006. International Organization for Standardization. Geneva.

(i) CFPP produces three byproducts (fly ash, bottom ash and gypsum). All three products can be used for different applications instead of being dumped into landfill. Hence the CFPP system boundary is expanded to include these applications and it is assumed that the virgin material that might have been used for this application otherwise will be replaced by the CFPP by products. This credit reduces the total impacts produced by the system. One example of the gypsum byproduct is shown in **Figure 5-2**,

(ii) Another example is for the ethylene carbonate production. In this case the goal is to compare the impacts of producing ethylene carbonate through the conventional route vs through organocatalytic chemical conversion process. This is achieved again through system expansion methodology as explained previously.

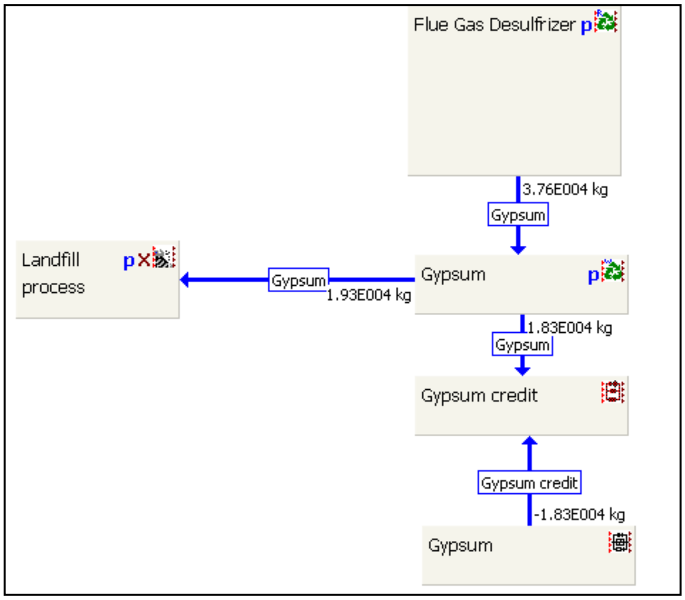
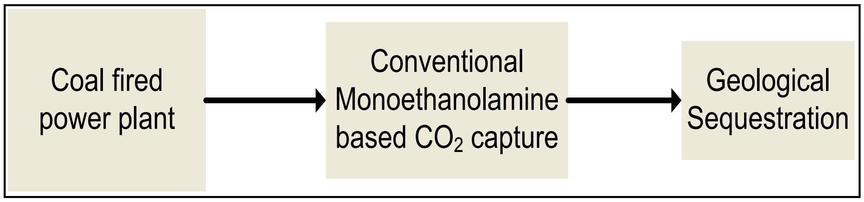


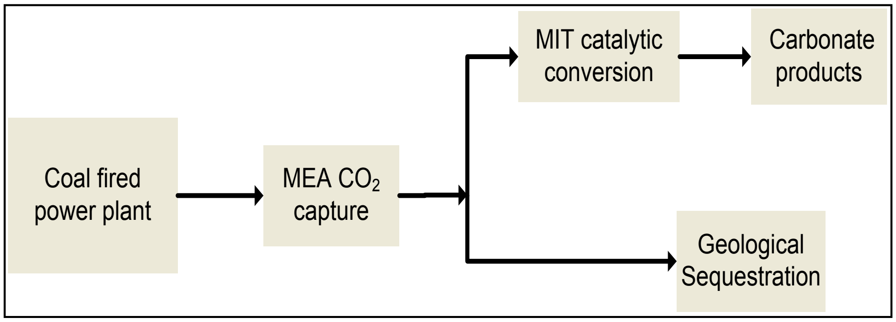
Figure 5-2: System expansion for application of credit to gypsum production in CFPP

System Boundaries

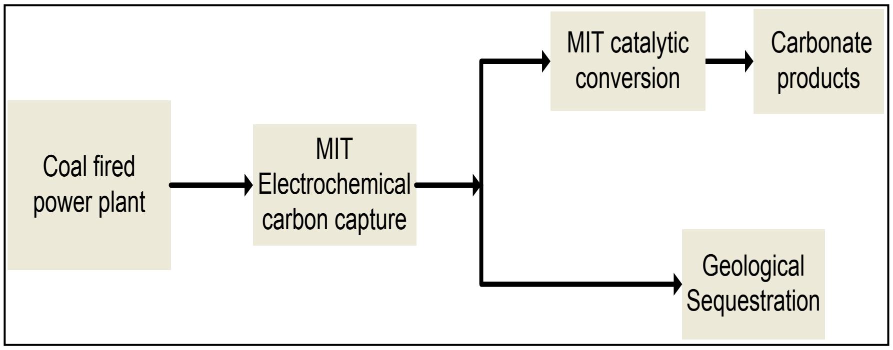
The system boundary of the study is illustrated in **Figure 5-3**. It includes three scenarios as illustrated by (a), (b) and (c) sections of the figure. The reference scenario (a) includes coal fired power plant (CFPP) with MEA based carbon capture system and a geological sequestration system. Scenario (b) includes the reference scenario coupled with the chemical sequestration process for organocatalytic conversion of CO_2 into carbonate product. And finally scenario (c) illustrates the CFPP coupled with E-MAR capture system developed by MIT with chemical and geological sequestration.



(a) Reference CFPP with MEA capture scenario



(b) CFPP with MEA capture coupled with chemical sequestration process



(a) CFPP with E-MAR capture coupled with chemical sequestration process

Figure 5-3: Block diagrams illustrating system boundary

Data Sources

The data were obtained from publicly available information and from primary sources (i.e. Experimental work performed at MIT).

1. CFPP and MEA
    a. IECM, 2011. Integrated Environmental Control Model (IECM) developed by Carnegie Melon University in collaboration with NETL, DOE (http://www.cmu.edu/epp/iecm/)
2. Geological Sequestration
    a. Koornneed,J.,van Keulen T., Faaij A., and Turkenburg W., 2008. “Life cycle assessment of a pulverized coal power plant with post combustion capture, transport and storage of CO_2”, Int J. GHG control, pp. 448-467.

    b. Intergovernmental Panel on Climate Change. 2006 Guidelines for National Greenhouse Gas Inventories, Volume 2: Energy, Chapter 4 Fugitive Emissions. <http://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/2_Volume2/V2_4_Ch4_Fugitive_Emissions.pdf

3. Electrochemically Mediated Amine Regeneration (E-MAR)
    a. Stern, M.C.; Simeon, F.; Hatton, T. A. Methods and systems for carrying out a pH-influenced chemical or biological reaction, U.S. Provisional Application No.: 61/528,449, submitted 08/29/2011
    b. Stern, M.C.; Simeon, F.; Hammer, T.; :Landes, H.; Herzog, H.J.; Hatton, T.A. electrochemically mediated separation for carbon capture, Energy Procedia, Vol 4, 2011, 860-867.
    c. Stern, M.C.; Simeon, F.; Herzog, H.J.; Hatton T.A. Amine Sorbent for use in the electrochemically mediated gas scrubbing of carbon dioxide. Energy Procedia, accepted for GHGT-11 conference in Kyoto, Japan, 2012.
    d. Stern, M.; Herzog, H.; Hatton, T. Technological and Economic Analysis of Electrochemical Gas Scrubbing of CO_2 from Post-combustion Flue Gas.(Unpublished manuscript)
    e. Personal Communications with Fritz Simeon (MIT)
    f. The LCI Nafion membrane dataset was not available in the GaBi database, hence it was ordered from PE international through their Data-on-demand service.
4. Chemical conversion
    a. Personal Communications with Jennifer A. Kozak and Fritz Simeon (MIT)
    b. The LCI datasets for N-Bromosuccinimide and Benzoyl Peroxide were unavailable in the GaBi database and were ordered from PE international through their Data-on-demand service

Modeling

Multiple sub-systems were modeled in GaBi 4.4 (LCA software from PE International[31]) and represent:

1. The reference CFPP with the typical flue gas treatment options
    a. Selective Catalytic Reduction (SCR) and in-furnace low NOx burner to control NOx emissions
    b. Electrostatic Precipitation (ESP) for controlling particulate matter
    c. Flue Gas Desulfurizer (FGD) for SOx control
2. MEA-based post-combustion carbon capture system,
3. E-MAR post-combustion carbon capture system
4. CO_2 geological sequestration, and
5. Chemical sequestration process based on organocatalytic transformation of CO_2 to useful carbonate product.

The detailed life cycle inventory used for all the above mentioned models [1-5] is presented in Appendix B. The following considerations were taken into account with respect to the system boundaries:

1. Direct and indirect impacts of materials and energy use were included. An example of indirect material and energy use is in the modeling of flue gas desulfurizer (FGD), the energy and materials required for manufacturing the lime that is used for SO_2 control was considered as part of the system.
2. The infrastructure required for any component of the system was not included e.g. materials and energy required to build a coal fired power plant or retrofit it with the monoethanolamine CO_2 capture system were not a part of this study. These assumptions can be backed up by literature[32,33]that clearly shows that the use phase outweighs the construction of the power plant and materials extraction for construction is negligible compared with operation of the power plant. The same is true for the geological sequestration system modeled in this study.

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[31] PE, LPB. GaBi 4 Software-System and Databases for Life Cycle Engineering (Version 4.4). 1992-2008. <http://www.gabi-software.com/>

[32] Odeh N. L.; Cockerill, T. T. *Energy Policy* **2007**, *36*, 367-380

[33] M. Pehnt and J. Henkel, *International Journal of Greenhouse Gas Control* **2009**, *3*, 49-66.

3. End of Life (EoL) treatment for wastes for CFPP is included in the study (explained in details in the CFPP LCA modeling section. The EoL treatment for MEA waste is not included in the system boundary.

The modeling considered various parameters that characterize each flue gas treatment option in the CFPP sub-system e.g. flow rate, flue gas composition etc. By switching on/off different parameters in the CFPP sub-system, environmental impacts associated with the following combinations can be quantified:

1) CFPP with SCR, ESP without FGD
2) CFPP with SCR, ESP, FGD without carbon capture
3) CFPP with SCR and carbon capture without FGD
4) CFPP with SCR, ESP, FGD, and carbon capture

The configuration 4) with MEA capture has been used in this study as the baseline scenario

LCA model for CFPP

In the first step, the model of the base plant for standard subcritical 500 MW[34] pulverized coal power plant with control devices for NO_x, particulate matter and SO_2 and recirculating cooling tower was built (**Figure 5-4**). Efficiency of the plant is 35.81% without carbon capture and 20.14% with carbon capture using a monoethanolamine system. CO_2 removal efficiency was assumed to be 90%. The LCA model is parameterized to simulate different scenarios – with and without FGD and CO_2 capture rate of 0% and 90%. The carbon dioxide emission from the power plant can then be split into an intermediate product feeding into another LCA sub-system model and emission to air depending upon the capture rate.

Co-product credit has been applied for utilization of fly ash, bottom ash and gypsum. To correctly represent the byproduct credit for utilization and the disposal burdens, the utilization data from the American Coal Ash Association (ACAA)[35] were taken into consideration. From these data only about 38% of fly ash, 42.4% of bottom ash and 48.7% of gypsum were used for various end-use applications such as construction, mining, agriculture and the rest is assumed to be transferred to landfill.).

Another version of the CFPP model was built to account for the novel E-MAR capture system developed by MIT. The main change included was the amount of power that will be diverted to

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[34] Gross electrical output with capacity factor of 75%

[35] ACAA **2011,** 2010 Coal Combustion Product (CCP) Production & Use Survey Report.

the E-MAR capture system. Unlike the MEA system the E-MAR process does not require any steam for the desorption stage hence no additional coal is required. The auxilia$_{r}$y load required for the CO_2 absorption process is obtained from CFPP by reduction in overall efficiency. The electric power requirement for ECGS process is less than the power requirements for MEA capture and will increase the efficiency of the CFPP by approximately 6%.

All data is based on Integrated Environmental Control model developed by Carnegie Melon University in collaboration with NETL, DOE[36]

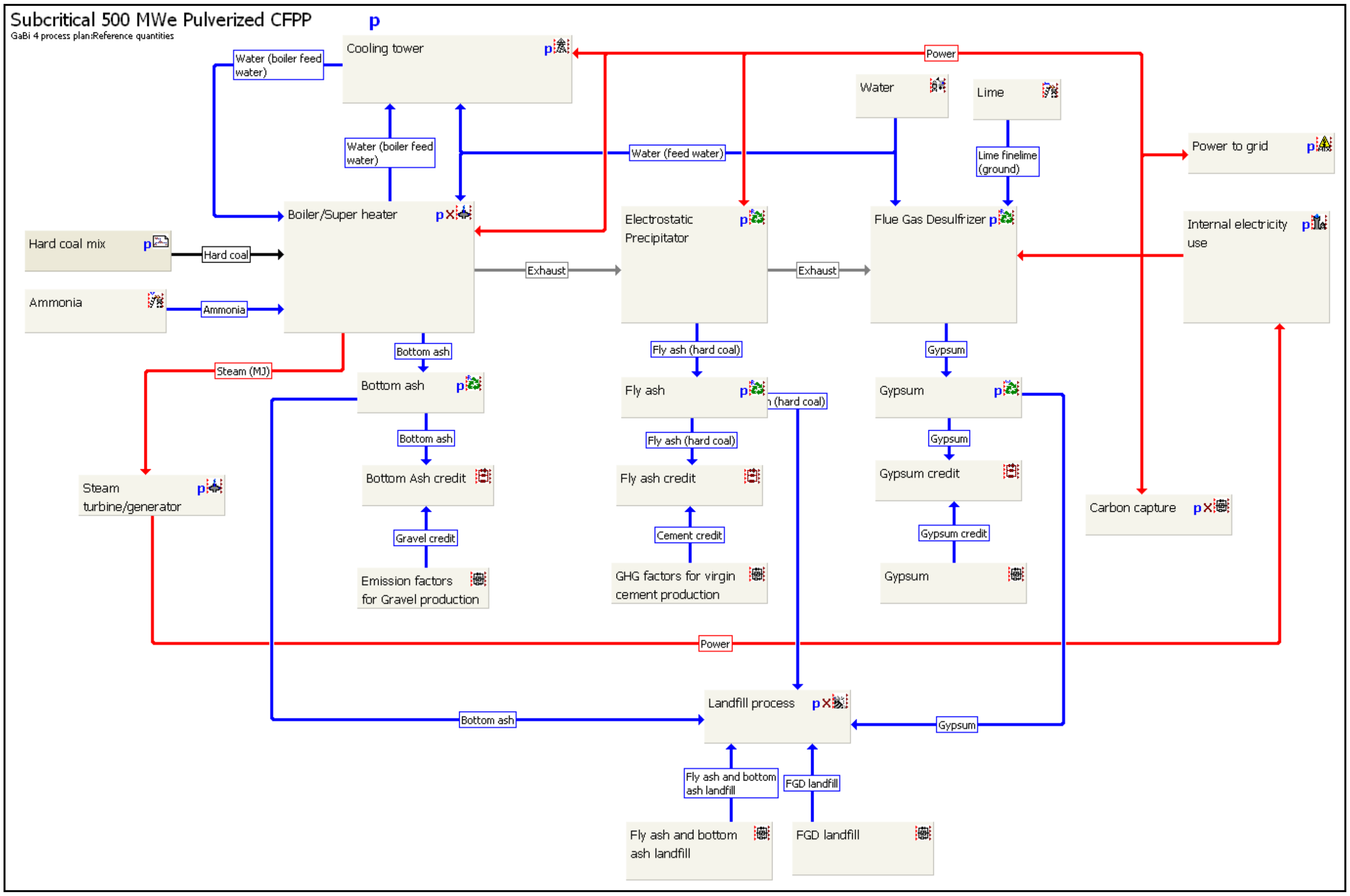

Figure 5-4: Screenshot of LCA model of Coal fired power plant (CFPP) in GaBi 4.4

LCA model for Monoethanolamine (MEA) carbon capture

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[36] IECM, http://www.cmu.edu/epp/iecm/

The monoethanolamine-based carbon capture system was chosen as a baseline process for post-combustion carbon capture. The most common form of carbon capture technology is the sorbent/solvent system. Carbon capture is achieved through the contact of flue gas and a liquid absorbent or solid sorbent that is capable of capturing carbon dioxide. Monoethanolamine is commonly employed as the liquid absorbent and was thus chosen as the baseline system for this study.

The screenshot of the LCA model in GaBi is presented in **Figure 5-5**. The model consists of an absorber, stripper and a compressor. The carbon dioxide-loaded sorbent in the absorber vessel is heated in the stripper to release carbon dioxide. The sorbent is hence regenerated and can be cycled back to the absorber to react with the incoming flue gas. The underlying principle of the MEA capture/release process is the exothermic, reversible reaction between a weak acid (e.g., CO_2) and a weak base (e.g., MEA) to form a soluble salt. The inlet flue gas is passed through the absorber and brought in contact with MEA solvent (aqueous MEA). The flue gases are absorbed by the MEA to form MEA carbamate as shown in the reaction **Scheme 5-1** below.

Scheme 5-1: Chemical equation describing the formation of MEA carbamate[37]

This carbamate is then passed through the desorption process where thermal energy in the form of steam is applied to separate MEA and CO_2. During the desorption process approximately 1% MEA is lost and make-up MEA needs to be added to the system

Similar to the CFPP model all data is based on Integrated Environmental Control model developed by Carnegie Melon University in collaboration with NETL, DOE[38]. The MEA model includes mass and energy flows associated with SO_2 polishing, CO_2 capture, desorption, compression, MEA makeup and MEA regeneration unit processes.

The following assumptions were made when creating the monoethanolamine CO_2 capture model:

1. CO_2 removal efficiency is assumed to be 90%. And efficiency of the coal fired power plant after adding the capture system is reduced to 20.14%.

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[37] Davis J., Rochelle G. Energy Procedia. **2009**, *1*, 327-333.

[38] IECM, http://www.cmu.edu/epp/iecm/

2. The CO_2 desorption process to regenerate MEA requires thermal energy in the form of steam. This steam energy is taken from the CFPP resulting in a drop of the power plant's efficiency.
3. For the amine process to function properly, SO_2 emissions are required to be at or below 10 ppm . Even when the CFPP is equipped with FGD, the SO_2 concentration is not reduced to such a low value. Hence the amine CO_2 capture system is equipped with an additional SO_2 polisher and direct contact cooling (DCC) which reduces the SO_x concentration before going into the amine system. If higher concentration of SO_x goes into the MEA solution it binds with the sorbent more strongly and is very difficult to be desorbed. As a result, SO_2 will build up in the MEA and decrease the effectiveness of CO_2 removal. This reduces the regeneration rate of MEA[39].

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[39] National Energy Technology Laboratory. 2009. Database and Model of Coal-fired Power Plants in the United States for Examination of the Costs of Retrofitting with CO2 Capture Technology. DOE/NETL-402/030809, April 2009. <http://www.netl.doe.gov/energy-analyses/pubs/Carbon_Capture_Enegis_Clearwater_Report_and_Presentation.pdf>

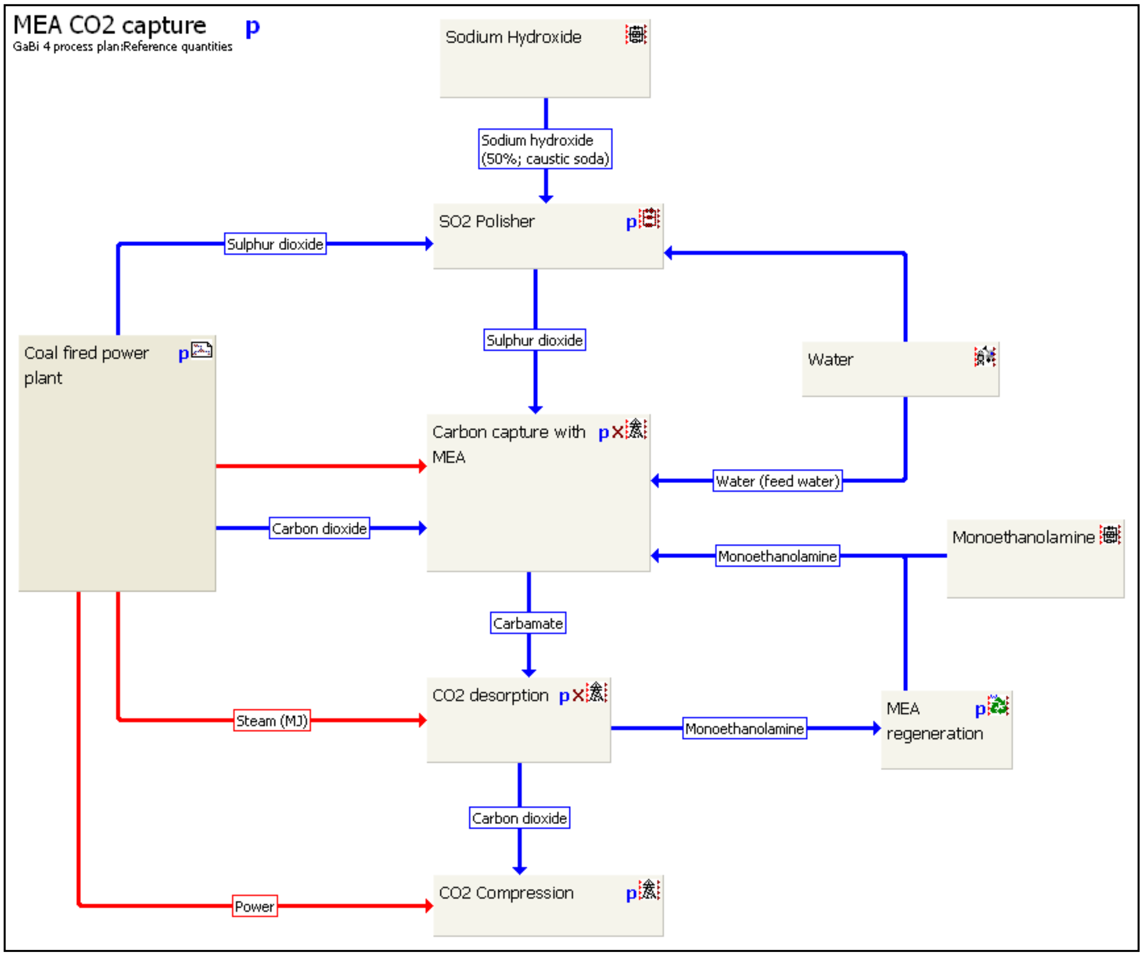

Figure 5-5: Screenshot of LCA model of Monoethanolamine based capture system in GaBi 4.4

<u>LCA model for geological sequestration system</u>

After CO_2 is separated from the flue gases of a power plant, it must be compressed for geological sequestration at a pressure suitable for pipeline transportation which is about 15 MPa[40]. The model for geological sequestration is created based on literature[41]. In order to remain consistent with the LCA models of the other sub-systems i.e. CFPP, MEA, the infrastructure for sequestration was not included. Assumptions for fugitive CO_2 during pipe transportation were

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[40] McCollum D., Ogden J., **2006**. Techno-Economic Model for Carbon Dioxide Compression, Transportation, and Storage & Correlation for Estimating Carbon Dioxide Density and Viscosity, University Of California, Davis.

[41] Koornneef, J.; van Keulen, T.; Faaij, A.; Turkenburg W. *International Journal of Greenhouse Gas Control* **2008**, *2*, 448 – 467

made based on IPCC guidelines[42]. A schematic of the GaBi model for CFPP with MEA system and geological sequestration is shown in **Figure 5-6**.

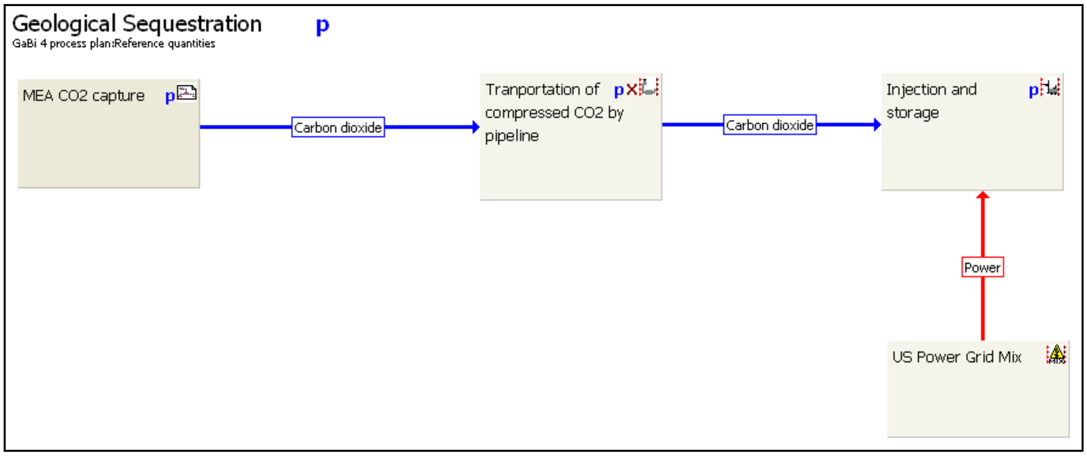

Figure 5-6: Screenshot of LCA model of geological sequestration system in GaBi 4.4

<u>LCA model for Electrochemically-Mediated Amine Regeneration (E-MAR) system</u>

E-MAR is a new way of performing CO_2 capture with the help of an electrochemical cell which performs both desorption and regeneration of the loaded amine solution under isothermal conditions using targeted electrical energy instead of heat[43]. The LCA model for this novel E-MAR capture technology developed by MIT was built based on the techno-economic data provided by the MIT team[44]. The model is illustrated in **Figure 1-7**. This model is linked to the modified coal fired power plant model (as explained in the CFPP modeling section above) to correctly represent the power requirements for the E-MAR process. Additional assumptions were made to fill in the data gaps:

i. Sorbent recovery rate was assumed same as that for MEA system (approximately 1%)
ii. Work of capture was calculated as 0.253 MWh/tonne of CO_2 captured.
iii. The compression energy used for the E-MAR model is the same as that for MEA system.
iv. Since no copper is consumed in the process and 100% recovery is achieved, the environmental burdens of copper are not included in the model.

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[42] Intergovernmental Panel on Climate Change. 2006 Guidelines for National Greenhouse Gas Inventories, Volume 2: Energy, Chapter 4 Fugitive Emissions. <http://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/2_Volume2/V2_4_Ch4_Fugitive_Emissions.pdf

[43] Stern, M. et al. *E-MAR (Electrochemically-Mediated Amine Regeneration)* Poster presented at 2012 NETL CO2 capture Technology Meeting, July 9-12, 2012. Pittsburgh, PA.

[44] Stern, M.; Herzog, H.; Hatton, T. *Technological and Economic Analysis of Electrochemical Gas Scrubbing of CO2 from Post-combustion Flue Gas*.(Unpublished manuscript)

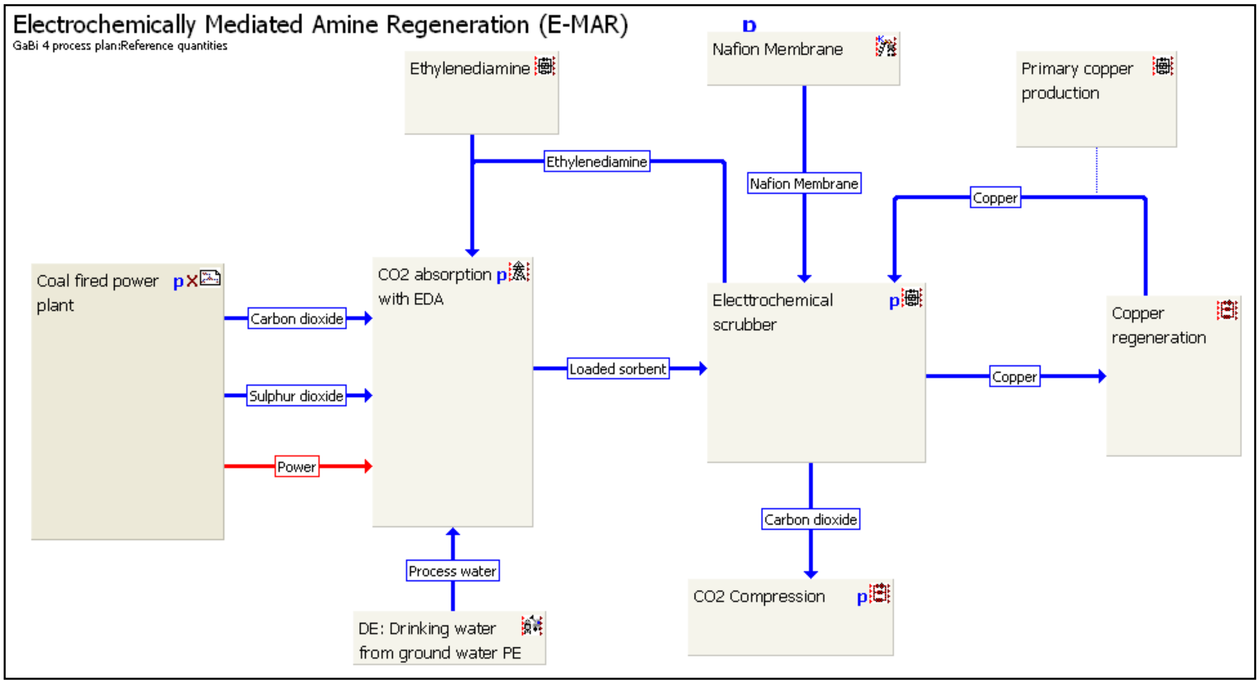
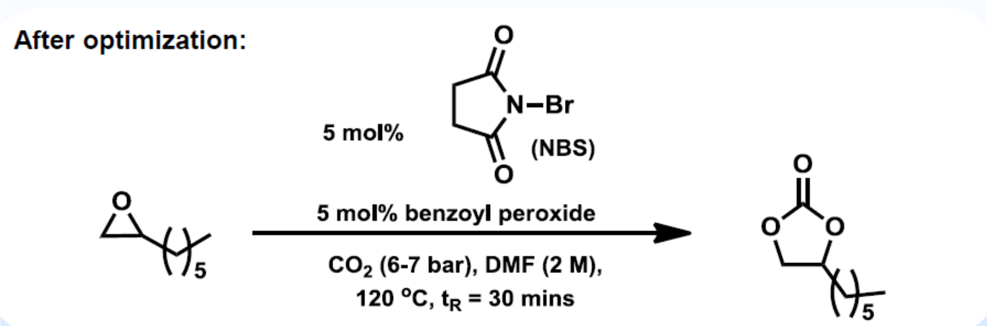


Figure 5-7: Screenshot of LCA model of E-MAR capture system in GaBi 4.4

<u>LCA model for Chemical Conversion system</u>

A novel catalytic method for the continuous chemical conversion of carbon dioxide into organic carbonates was developed by MIT (**Scheme 5-2**).



Scheme 5-2: Chemical conversion of CO_2 into organic carbonate

The corresponding LCA model (**Figure 5-8**) was created based upon the following reaction conditions provided by MIT:

Reagents

1. Epoxide: 2M concentration in N,N-Dimethylformamide. Several mono-substituted epoxides were tested during the optimization of the reaction conditions. As an example,

the following quantities are provided for 1,2-epoxyoctane: 1.53 ml (128.21 g/mol, density = 0.839 g/ml)

2. N-Bromosuccinimide: 5 mol % = 89.1 mg (177.98 g/mol)
3. Benzoyl peroxide: 5 mol % = 121.3 mg (242.23 g/mol)
4. N,N-Dimethylformamide: 3.38 ml (73.09 g/mol, density = 0.948 g/ml)

Conditions:

1. The reaction was carried out in a continuous flow reactor at 120 °C for 30 minutes under a CO_2 atmosphere at 100 psi.
2. As an example, the conversion of 1,2-epoxyoctane into the corresponding cyclic carbonate is approximately 90% mole and the yield is approximately 83%.

In order to model the reaction in GaBi 4.4., ethylene oxide was selected as the epoxide of choice for two reasons. Firstly, the LCI data related to ethylene carbonate (reaction product) was readily available within the GaBi database, thus enabling us to build a complete cradle-to-grave model including reagents, manufacturing, product utilization credits etc… Secondly, ethylene oxide is ranked #36 in the list of top 50 chemicals produced in the US[45], thus inferring a relatively high annual demand associated with a commodity chemical.

The reaction conditions were optimized by MIT at lab scale (mmol or mg range). No studies were performed to simulate and extrapolate these conditions to industrial scale (kg or ton) to match, at best, the scale of CFPP carbon dioxide emissions. Therefore, several assumptions were made to create the LCA model

1. All reagent mass values were calculated based on stoichiometry from the reaction conditions provided by MIT and described above.
2. The mass of each reagent was scaled up linearly from lab scale to industrial scale i.e. 1 mol of ethylene oxide reacts with 1 mol of carbon dioxide to form 1 mol of ethylene carbonate corresponding to # tons of ethylene oxide needed to react with # tons of CO_2 in the CFPP flue gas.
3. Both N-bromosuccinimide and benzoyl peroxide are used as catalysts and are not recovered from the reaction medium.

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[45] Bhown, A.; Freeman, B. *Environ. Sci. Technol.* **2011,** *45,* 8621-8623

4. N,N-Dimethylformamide is used as the solvent and can be recovered (99%) from the reaction medium.
5. The conversion rate was set to 90% i.e. for every mole of ethylene oxide, 90 mol % of ethylene oxide is produced.
6. Based on the reaction temperature, the thermal energy required was calculated using the following equation:

$$\Delta H = mC_p\Delta T$$

Where, m = mass of ethylene oxide, kg

Cp = Specific heat capacity of ethylene oxide in gas phase calculated from data obtained from NIST website[46] , J/mol*K

ΔT = Temperature difference between atmospheric conditions and reaction conditions, K.

7. The conversion efficiency for the electricity consumption was assumed to be 70%.
8. The LCI datasets for N-Bromosuccinimide and Benzoyl Peroxide were unavailable in the GaBi database and were ordered from PE international through their Data-on-demand service.
9. Credit was allocated for ethylene carbonate based on the industrial production route as explained in the methodology section

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[46] NIST (2012) Ethylene Oxide: Constant pressure heat capacity of gas. (http://webbook.nist.gov/cgi/cbook.cgi?ID=C75218&Mask=1#Thermo-Gas)

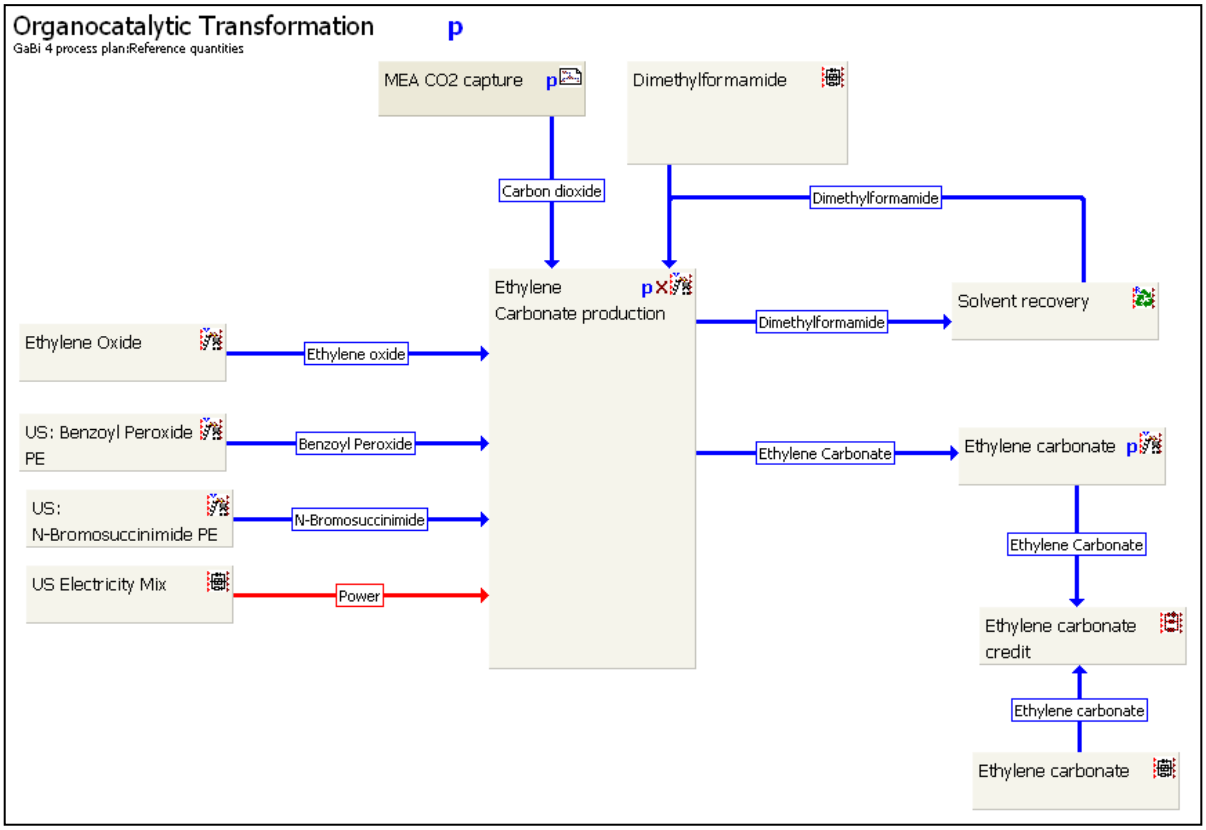

Figure 5-8: Screenshot of LCA model of Organocatalytic transformation system in GaBi 4.4

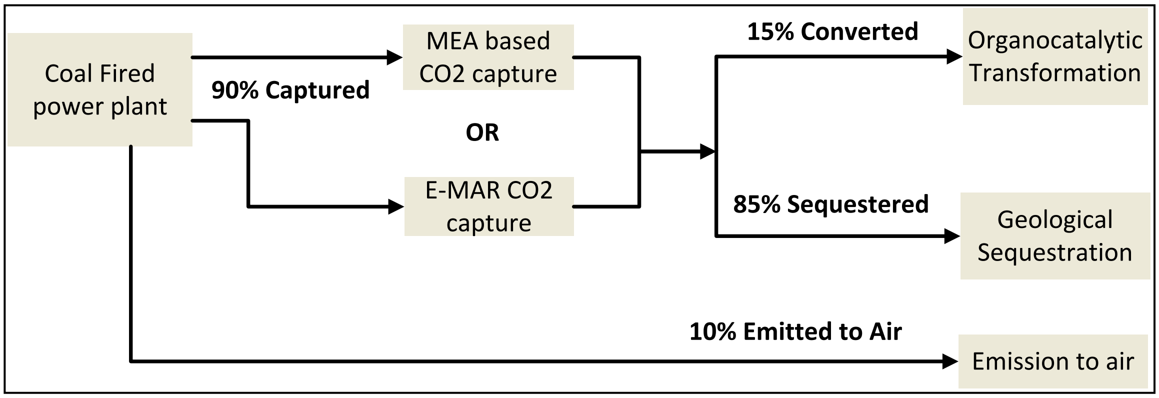

Figure 5-9: Block diagram indicating the amount of CO_2 (%) diverted to each of the subsystems.

All results are presented for the functional unit of 500 MWe subcritical pulverized coal fired power plant and different scenarios. **Figure 5-9** illustrates the percent amount of CO_2 utilized by each system. 90% of the total amount of CO_2 in the CFPP's flue gas is captured and 10% emitted to air. It is then assumed that only 15% of the captured CO_2 is diverted to the chemical conversion system and the rest is sequestered in ground.

Life Cycle Impact Analysis Results for CFPP with and without MEA Carbon Capture followed by Geological Sequestration

The impact results for all the categories are shown in **Table 5-1.** For all environmental impact categories except global warming potential, the scenario with MEA carbon capture and sequestration has higher values. This can be attributed mainly to the reduction in efficiency associated with the MEA capture system, in terms of energy use required for the CO_2 desorption and compression for sub-sequent transportation for geological sequestration.

Table 5-1: Comparative impact analysis results for CFPP with and without carbon capture system

Impact Category[47]	**Units**	**CFPP without capture**	**CFPP with capture and geological sequestration**
PED	MJ	5.32E+06	6.70E+06
AP	kg SO_2 eqiv.	2.54E+02	8.30E+02
EP	kg phosphate eqiv.	1.03E+02	2.67E+02
GWP	kg CO_2 eqiv.	4.65E+05	1.37E+05
ODP	kg R-11 eqiv.	2.45E-04	1.10E-03

Only the PED and GWP results for comparison of CFPP with and without capture are shown in **Figures 5-10 (a)** and **(b)**, respectively. Carbon capture and sequestration (CCS) using MEA reduces the global warming potential by 71% but increases the primary energy demand by 27%. These values are consistent with previous studies[48]. This increase in PED can be attributed to the parasitic energy requirement for post combustion carbon capture. Out of the 27% approximately 98% increase in PED is due to the increased coal combustion in CFPP and only 2% can be attributed to MEA capture and geological sequestration. The thermal energy required to recover CO_2 from the amine solution (desorption) reduces the CFPP efficiency by at least 5 percentage

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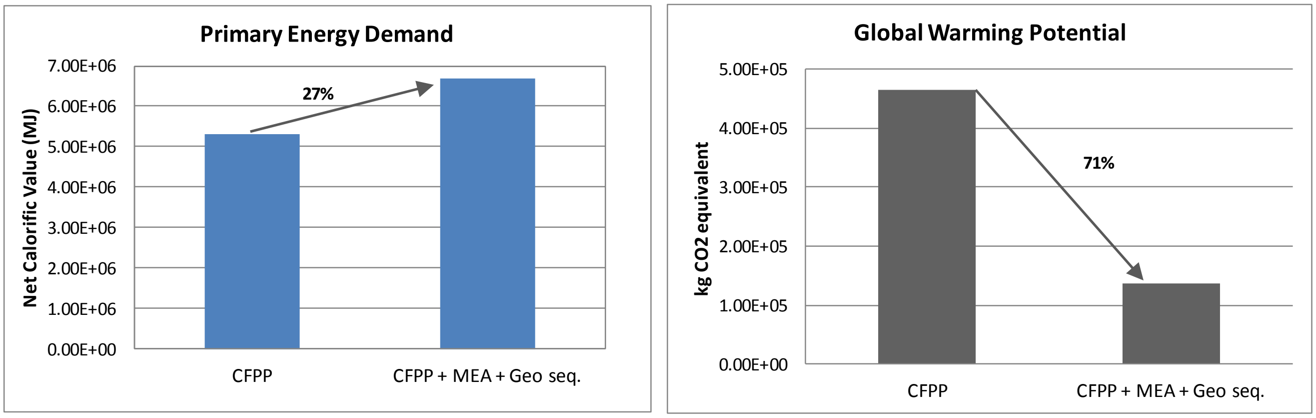
[47] Global Warming Potential (GWP); Acidification Potential (AP); Eutrophication Potential (EP); Ozone Layer Depletion Potential (ODP); Primary Energy Demand (PED)

[48] Viebahn, P *et al*. in *Int. J. Greenh Gas. Con.* **2007**, *1*, 121-133

points and the remaining drop comes from power requirements of MEA absorber and CO_2 compressor[49].



(a) Primary Energy demand **(b)** Global Warming potential

Figure 5-10: LCA results for coal fired power plant with and without conventional CCS

Life Cycle Impact Analysis Results for comparison between MEA and E-MAR capture system: CFPP with either EMAR or MEA Capture followed by Geological Sequestration

Comparative impact analysis results for the E-MAR and MEA capture systems are presented in **Table 5-2**. Except for ODP category, E-MAR has lower impacts than MEA in all other categories.

Table 5-2: Comparative impact analysis results for CFPP with MEA and E-MAR carbon capture system

Impact Category	Units	CFPP with MEA capture and Geological Sequestration	CFPP with E-MAR capture and Geological Sequestration
PED	MJ	6.70E+06	6.12E+06
AP	kg SO_2 equiv.	8.30E+02	5.82E+02
EP	kg phosphate equiv.	2.67E+02	2.02E+02
GWP	kg CO_2 equiv.	1.37E+05	1.28E+05
ODP	kg R-11 equiv.	1.10E-03	1.65E-03

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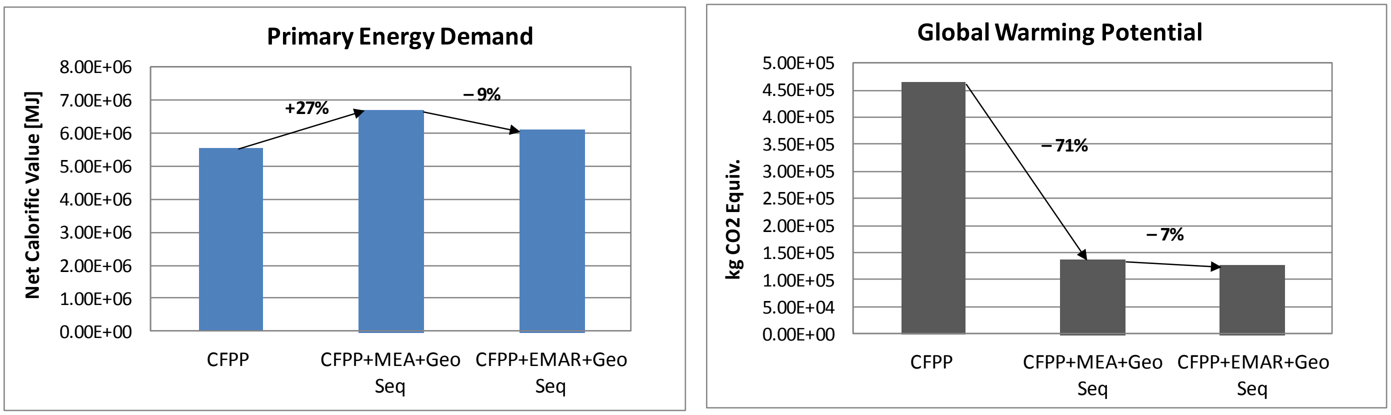
[49] MIT *The future of coal* – Report 2007

The GWP and PED impact categories are presented in graphical format in **Figure 5-11 (a)** and **(b)**. It can be seen that for both categories, E-MAR process has lower impacts; 9% lower in PED and 7% lower in GWP. These lower values are directly related to the amount of amine used for CO_2 capture as explained below.



(a) Primary Energy demand potential

(b) Global Warming

Figure 5-11: LCA results comparing Impacts from MEA and E-MAR capture

Noteworthy observations from this analysis:

1. The amount of amine (Ethylenediamine or EDA) required in the E-MAR capture is lower than the amount of amine (Monoethanolamine or MEA) required in the MEA capture resulting in lower overall impacts for E-MAR than MEA capture system, despite the per kg impacts for EDA being higher than MEA as seen in **Tableb5-3**.

Table 5-3: Comparative impacts for EDA and MEA

Impact Category	Units	Ethylenediamine (EDA)	Monoethanolamine (MEA)	Difference
PED	MJ	2.26E+02	1.40E+02	61%
AP	kg SO_2 equiv.	2.49E-02	1.33E-02	88%
EP	kg phosphate equiv.	1.88E-02	7.69E-03	145%
GWP	kg CO_2 equiv.	5.61	3.44	63%
ODP	kg R-11 equiv.	2.53E-06	3.24E-07	680%

2. The ODP impacts are much higher for EDA than MEA compared to all other categories. This can be explained by the associated high ODP impact ethylene dichloride used in the production of EDA.

Life Cycle Impact Analysis Results for Chemical Conversion

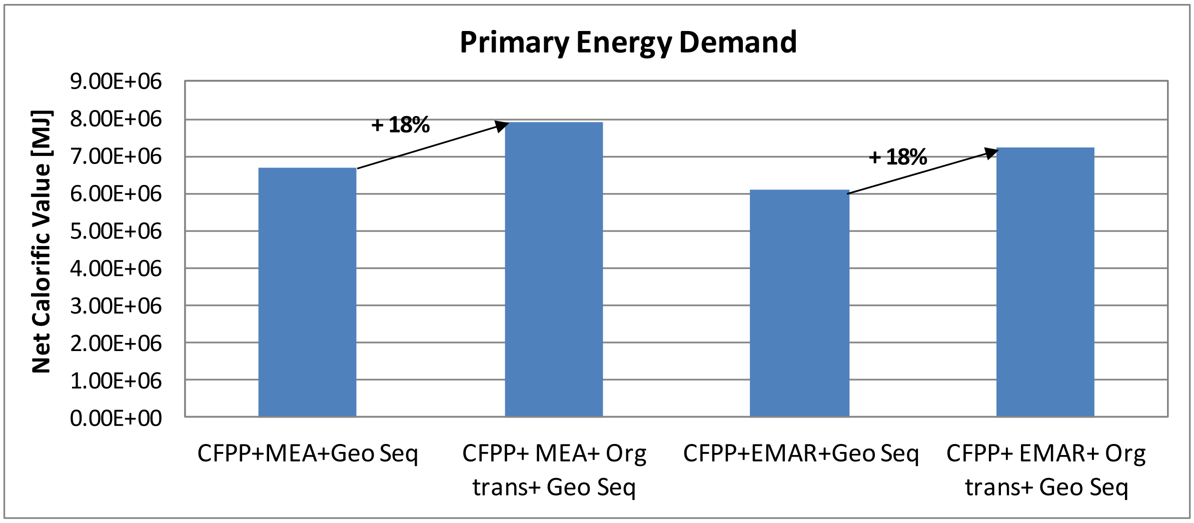
The entire system including capture, utilization and sequestration is analyzed here. Results for all five categories are presented in **Table 5-4**.

Table 5-4: Comparative impact analysis results for CFPP with capture and utilization system

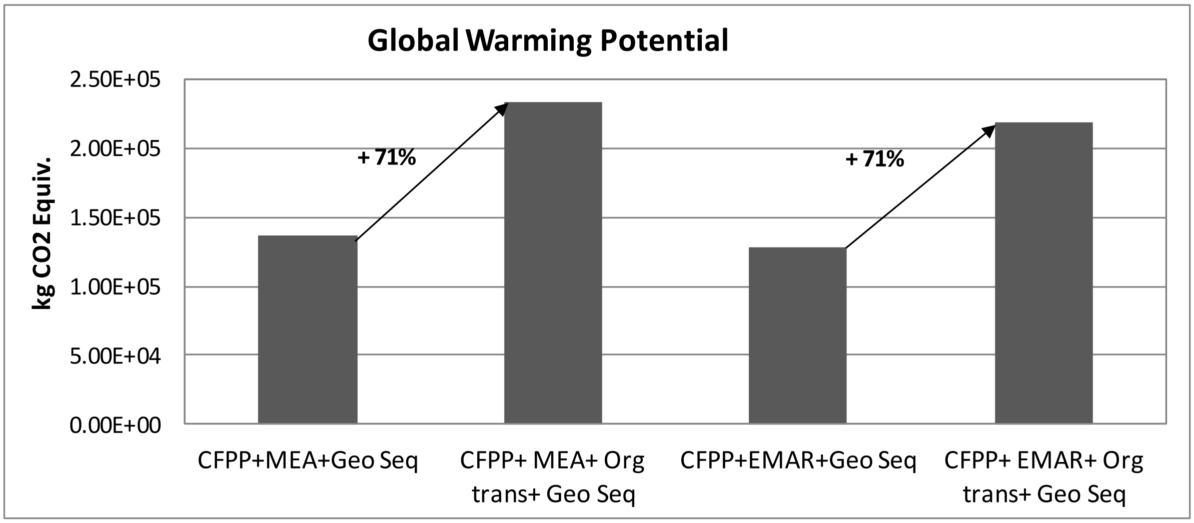
Impact Category	**Units**	**CFPP with MEA capture, Geological Sequestration and Chemical Conversion**	**CFPP with E-MAR capture , Geological Sequestration and Chemical Conversion**
PED	MJ	7.90E+06	7.25E+06
AP	kg SO_2 equiv.	3.20E+03	2.81E+03
EP	kg phosphate equiv.	3.27E+02	2.59E+02
GWP	kg CO_2 equiv.	2.34E+05	2.19E+05
ODP	kg R-11 equiv.	-1.98E-04	4.27E-04

The chemical conversion system includes the credit for the final carbonate product. This credit affects only the ODP category, because the ODP impacts from the conventional production of ethylene carbonate are very high and the application of this credit into the system offsets the ODP impacts of the organocatalytic chemical conversion. Credit produces negative impact which means that the current method of production of the carbonate (using MEA capture and chemical conversion) is environmentally superior in the ODP category than the conventional method (which could be combination of different industrial rotes). Although the credits make the total impacts in the ODP category for the system with MEA capture negative, they are not high enough to make the total impacts for the E-MAR system negative due to the higher ODP impacts of the E-MAR system itself as explained in previous section.

Figure 5-12 (a) and **(b)** illustrates the comparative LCA results for PED and GWP categories. The addition of the chemical conversion system increases the PED impacts by 18% and GWP impacts by 71%.



(a) Primary Energy demand



(b) Global Warming potential

Figure 5-12: LCA results for complete MIT system explained in Figure 8.

The percentage contribution analysis of the complete system is presented in **Figure 5-13**. The chemical conversion contributes to approximately 80% of the total acidification impacts and 40% of the total GWP impacts. The contribution of the chemical conversion to the PED and EP categories is less than 20%. The credit of the final carbonate is responsible for the negative values in the ODP category.

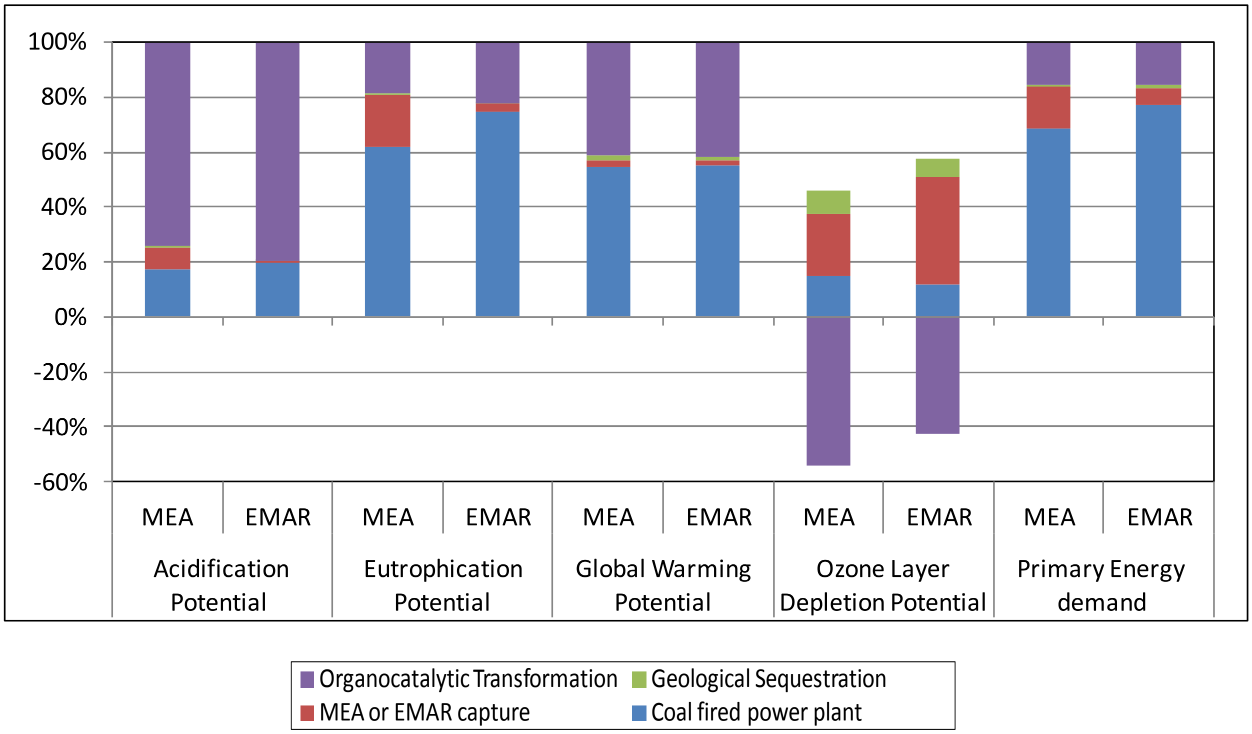


Figure 5-13: LCA results for complete MIT system explained in Figure 8.

Life Cycle Cost Analysis

Goal

The objective of the funding opportunity from the U.S. Department of Energy was to fund the development of technologies that would produce useful products from CO_2 at a net cost of less than \$10 per metric tonne. For the carbon capture and conversion technology developed by MIT, the \$10/tonne cost for the commodity product i.e. cyclic organic carbonate, can be determined based upon the life cycle costs (LCC) of the CFPP, EMAR and chemical conversion systems. However, it is important to note that This study is not a rigorous assessment to determine the overall techno-economic feasibility of the MIT carbon capture and conversion process vis-à-vis the conventional MEA based capture technology but an attempt to estimate the approximate range of difference in terms of environmental and economic burdens for the prototype technology.

Scope

The scope of LCC for each system includes the cost elements of the included sub-systems as per the respective system boundary for the LCA analysis described in the previous sections, except for the following:

- Life cycle costs associated with infrastructure elements are included (LCA had excluded environmental burdens associated with infrastructure)
- LCC are determined over the 30 year life of the CFPP (in addition, costs of geological sequestration include monitoring cost for 50 years after CFPP closure)

The life cycle costs are estimated for newly constructed facilities only[50].

Methodology

The life cycle costs can be broadly categorized into the following components:

- Capital costs (also referred as CAPEX)
- Operation and maintenance (O&M) costs (also referred as OPEX)

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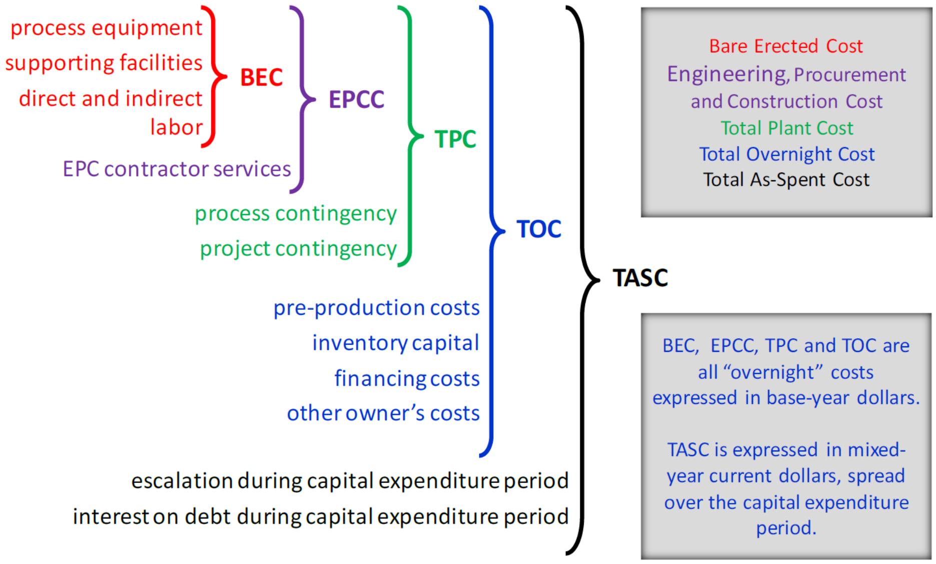
[50] Although DOE has published cost estimates for retrofitting existing unit with carbon capture technologies, but this was outside the scope of this study.

The capital costs are associated with the initial purchase, acquisition and construction, and the associated charges for financing a project. The operation and maintenance costs include labor, consumables, repair and replacement. The U.S. Department of Energy (DOE) has developed a capital cost estimation methodology for power plants and carbon capture systems[51,52] .The categorization of CAPEX adopted by DOE is illustrated in **Figure 1-14**. The detailed description of each CAPEX element is included in Appendix C. The OPEX can be categorized into the following components:

- Operating labor
- Maintenance – material and labor
- Administrative and support labor
- Consumables
- Fuel
- Waste disposal
- Co-product or by-product credit

The first three components of OPEX can be termed as Fixed O&M costs, since they are independent of the amount of power generated at the facility. The rest of the OPEX components are termed as Variable O&M costs.



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[51] DOE (2011a). Cost Estimation Methodology for NETL Assessments of Power Plant Performance (DOE/NETL-2011/1455). http://www.netl.doe.gov/energy-analyses/pubs/QGESSNETLCostEstMethod.pdf (Accessed 11th January, 2012)

[52] DOE (2010). Cost and Performance Baseline for Fossil Energy Plants. Volume 1: Bituminous coal and Natural gas to Electricity, Revision 2, November 2010. (DOE/2010/1397). http://www.netl.doe.gov/energy-analyses/pubs/BitBase_FinRep_Rev2.pdf (Accessed 11th January, 2012)

Figure 5-14: Capital cost structure adopted by U.S. Department of Energy for power plants (Source: DOE, 2011a)

The processes associated with the geological sequestration of carbon dioxide are as follows:

- Compression of carbon dioxide at outlet of capture process
- Transportation via pipeline
- Injection of super critical carbon dioxide into a geologic reservoir
- Monitoring of the storage site

The life cycle costs associated with geological sequestration have been estimated as per the guidelines published by U.S. Department of Energy (DOE)[53,54]. The DOE guidelines assume the following in modeling the transport, storage and monitoring (TS&M) of carbon dioxide:

- Cost and energy burdens associated with the compression of captured CO_2 are borne by the power plant operating entity
- CO_2 is compressed to high pressure (15.3 MPa) to ensure that it is in super critical state during transportation and at point of injection
- Compressed CO_2 is transported 80 km via pipeline. Appropriate pipeline diameter is selected such that pressure loss during transportation is limited to 6.9 MPa and outlet pressure at pipeline is 8.4 MPa (above the super critical state pressure). This also ensures that there is no requirement of recompression along the length of the pipeline. A 14 inch pipeline was selected for this study.

The detailed description of parametric equations provided by DOE to estimate TS&M costs of carbon dioxide are provided in Appendix D.

Data sources

The estimation of CAPEX and OPEX requires a detailed understanding of power plant design, engineering, construction and operational parameters. This type of comprehensive analysis is outside the scope of this study. Therefore, the cost analysis for the CFPP, carbon

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[53] DOE (2010a). Estimating Carbon Dioxide Transport and Storage Costs (DOE/NETL-2010/1447). http://www.netl.doe.gov/energy-analyses/pubs/QGESStransport.pdf (Accessed 15th February, 2012)

[54] DOE (2010b). Cost and Performance Baseline for Fossil Energy Plants. Volume 1: Bituminous coal and Natural gas to Electricity, Revision 2, November 2010. (DOE/2010/1397). http://www.netl.doe.gov/energy-analyses/pubs/BitBase_FinRep_Rev2.pdf (Accessed 11th January, 2012)

capture systems, geological sequestration and chemical conversion process is based upon publicly available CAPEX and OPEX estimates provided by DOE[55] and U.S. Energy Information Administration (EIA)[56]. The DOE CAPEX and OPEX cost data are derived from other data sources such Worley Parson, EPRI, AACE International etc. The CAPEX and OPEX were used to estimate the Cost of Electricity (COE) with and without CO_2 emission price ($20/tonne) using the Power Systems Financial Model (PSFM) tool developed by DOE[57]. The DOE CAPEX data on Total Overnight Cost (TOC) was used to estimate the Total as Spent Cost (TASC) in the PSFM tool prior to COE estimation. The variable component of OPEX was modified to incorporate the revenues to the power plant operator from the sale of CFPP residues (i.e. fly ash, bottom ash and gypsum). The DOE estimates assume 100% disposal of these by-products. The rate of utilization of coal combustion by-products was based upon the data published by the ACAA[58]. The utilization data are summarized in Appendix E. The market price for each by-product (excluding FGD gypsum) was based upon ACAA data[59], personal communication with DOE[60] and informed estimates. The price of FGD gypsum was based upon personal communication with U.S. Geological Survey[61]. The estimated price of fly ash, bottom ash and FGD Gypsum (in constant 2007 dollars per metric ton) used in this analysis are $ 20.5, $12.3 and $1.4, respectively. The DOE estimate of Fixed OPEX and the estimated variable OPEX were the other inputs to the PSFM tool. The IECM model used to develop the LCA as described previously also reports CAPEX and OEPX results for CFPP and MEA based capture system. However, it does not provide the corresponding COE estimate whereas DOE has published the COE estimates for the CFPP with and without MEA based capture system. Therefore, this study used only the DOE cost data and PSFM tool to ensure consistency with the background assumption and enable direct comparison with DOE COE estimates. These DOE

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[55] DOE (2010). Cost and Performance Baseline for Fossil Energy Plants. Volume 1: Bituminous coal and Natural gas to Electricity, Revision 2, November 2010. (DOE/2010/1397). http://www.netl.doe.gov/energy-analyses/pubs/BitBase_FinRep_Rev2.pdf (Accessed 11th January, 2012

[56] EIA (2010). Updated capital cost estimates for electricity generation plants. http://www.eia.gov/oiaf/beck_plantcosts/pdf/updatedplantcosts.pdf (Accessed 13th January, 2012)

[57] DOE (2011b). Power Systems Financial Model Version 6.6 User's Guide (DOE/NETL-2011/1492). http://www.netl.doe.gov/energy-analyses/refshelf/PubDetails.aspx?Action=View&PubId=382 (Accessed 11th January, 2012)

[58] ACAA (2010). http://acaa.affiniscape.com/associations/8003/files/2010_CCP_Survey_FINAL_102011.pdf (Accessed 29th March, 2012)

[59] http://acaa.affiniscape.com/displaycommon.cfm?an=1&subarticlenbr=5#Q5 (Accessed 30th March, 2012)

[60] Personal communication, William Aljoe, U.S. Department of Energy

[61] Personal communication, Robert Crangle, U.S. Geological Survey.

cost estimation guideline for carbon dioxide storage and transport are based upon previous DOE studies and available research data from other sources.

Results

LCC of CFPP with or without MEA carbon capture and sequestration

The CAPEX and OPEX estimates for a new 550 MWe sub-critical pulverized coal (SCPC) power plant without and with MEA based carbon dioxide capture are illustrated in **Table 1-5** and **Table 5-6**, respectively.

Table 5-5: CAPEX and OPEX estimates for a new 550 MWe SCPC power plant without carbon dioxide capture (All costs in constant 2007 ‘000 US dollars) (Source: DOE, 2010)[3]

Power plant unit	**BEC**	**EPCC**	**TPC**
Coal & sorbent handling	31894	2862	39969
Coal & sorbent preparation and feed	15076	1321	18857
Feed water & misc BOP systems	58767	5390	74675
PC boiler & accessories	221528	21582	267421
Flue gas cleanup	112288	10748	135340
Combustion turbine/accessories	0	0	0
HRSG, Ducting & Stack	31679	2909	39104
Steam turbine generator	93508	8675	114005
Cooling water system	32190	3029	40003
Ash/spent sorbent handling system	10832	1042	13096
Accessory electric plant	42691	3765	52202
Instrumentation & control	17451	1582	21370
Improvements to site	10678	1053	14078
Buildings and structures	45726	4125	62314
TOTAL	**724308**	**68803**	**892434**
Owner’s costs			
Pre-production cost			28543
Inventory capital			18266
Initial cost for chemicals and catalysts			0
Land			900
Financing cost			24096
Other owner’s cost			133865
TOC			**1098124**
TASC (TOTAL CAPEX)			**1245272**
Fixed O&M costs			
Operating labor			5524
Maintenance labor			5842

Administrative and support labor			2841
Property taxes and insurance			17848
Variable O&M costs			
Maintenance material			8763
Fuel			62176
Water			1425
Chemicals			7736
Waste disposal			2562
Other			593
TOTAL OPEX			**115310**

Table 5-6: CAPEX and OPEX estimates for a new 550 MWe SCPC power plant with carbon dioxide capture (All costs in constant 2007 ‘000 US dollars) (Source: DOE, 2010)[3]

Power plant unit	**BEC**	**EPCC**	**TPC**
Coal & sorbent handling	39541	3546	49551
Coal & sorbent preparation and feed	18985	1664	3097
Feed water & misc BOP systems	78061	7175	99339
PC boiler & accessories	280980	27374	331189
Flue gas cleanup	144350	13816	173982
CO_2 removal and compression	322855	30869	492819
Combustion turbine/accessories	0	0	0
HRSG, Ducting & Stack	33792	3096	41736
Steam turbine generator	105471	9748	128725
Cooling water system	52626	4952	65322
Ash/spent sorbent handling system	13088	1258	15822
Accessory electric plant	68316	1815	25647
Instrumentation & control	20024	1815	25647
Improvements to site	12006	1185	15829
Buildings and structures	50206	4530	62947
TOTAL	**1240301**	**117071**	**1618357**
Owner’s costs			
Pre-production cost			48733
Inventory capital			28281
Initial cost for chemicals and catalysts			2712
Land			900
Financing cost			43696
Other owner’s cost			242754
TOC			**1985432**
TASC (TOTAL CAPEX)			**2263393**
Fixed O&M costs			
Operating labor			6445
Maintenance labor			10430
Administrative and support labor			4219

Property taxes and insurance			32367
Variable O&M costs			
Maintenance material			15644
Fuel			87426
Water			2712
Chemicals			14705
Waste disposal			3602
Other			831
TOTAL OPEX			**178381**

It can be observed that for new SCPC facilities with carbon dioxide capture, the TPC increases by 81% and the total operating costs increases by 55%. The carbon dioxide capture and compression component accounts for approximately 68% of the increase in TPC and the remaining 32% increase in TPC for each power plant unit is illustrated in **Figure 5-15**.

The TS&M CAPEX and OPEX results are summarized in **Table 5-7** and the detailed breakdown is provided in Appendix D. Based upon these results, the cost of geologic sequestration of carbon dioxide is \$1.7 per metric ton CO_2 which is significantly lower than DOE estimate of \$5.5-\$11 per metric ton CO_2.

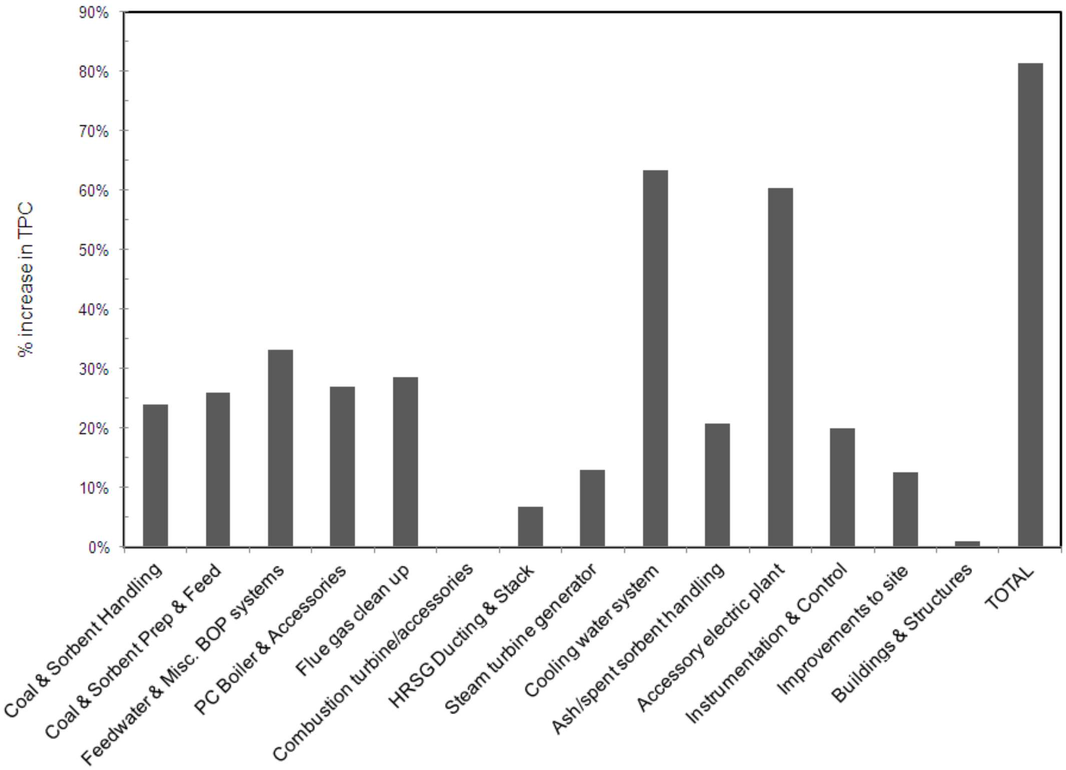

Figure 5-15: Increase in TPC for each power plant unit with addition of carbon dioxide capture unit

Table 5-7: CAPEX and OPEX estimates for CO_2 transport, storage and monitoring

Sequestration process component	**CAPEX (Constant 2007 dollar)**	**OPEX (Constant 2007 dollar)**
Transport	74,923,162	431,600
Storage	55,013,736	286,573
Monitoring	48,872,399	—
TOTAL	**178,809,296**	**718,173**

Cost of electricity estimates for coal fired power plant with and without capture

The COE results for the CFPP with monoethanolamine capture process and without capture are summarized in **Table 5-8**. It should be noted that COE results for CFPP w/ MEA capture do not include the contribution of CAPEX and OPEX associated with CO_2 transport, storage and monitoring. The assumptions for the financing structure for geologic sequestration have not been published by DOE. The DOE estimate is that the COE of geological sequestration is 5.9 mills/kWh. The overall COE results are approximately the same order of magnitude as published by DOE (without capture – 59.4 mills/kWh and with MEA capture – 103.8 mills/kWh). The estimated COE values are used with the COE estimates for MIT capture and chemical conversion systems (described in sections below) to check if the final cost of commodity product is less than $10/tonne.

Table 5-8: COE results for coal fired power plant with and without MEA capture process

Cost element	**Unit**	**CFPP w/o capture**	**CFPP w/ MEA capture**
Total plant cost	2007 '000$	1,098,124	1,985,432
Fixed O&M	2007 '000$	32,057	53,460
Variable O&M	2007 '000$	80,516	122,606
Total-as-spent-cost	2007 '000$	1,252,379	2,264,328
Cost of electricity	mills/kWh	66.9	113.5
Cost of electricity with CO_2 emission price of $20/tonne	mills/kWh	80.1	115.4
Cost of CO_2 avoided	2007 $/tonne	-	73.7
Net present value @ 8% discount rate	'000$	3,78,758	684,766
Net present value @ 10% discount rate	'000$	150,675	272,397

LCC of Electrochemically-Mediated Amine Regeneration (EMAR) system

The lifecycle cost analysis of the EMAR capture system was based on the report by Stern et al[62]. In the report, it has been assumed that the EMAR system is similar to the thermal or the MEA process. The cost data for the MEA process were obtained from the *Future of Coal* report[63]. These data were scaled using the increased size of the power plant due to addition of EMAR system to obtain the cost of the new capture system. The results are presented in **Table 5-9**.

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[62] Stern, M.; Herzog, H.; Hatton, T. *Technological and Economic Analysis of Electrochemical Gas Scrubbing of CO_2 from Post-combustion Flue Gas*.(Unpublished manuscript)

[63] Ansolabehere S., Beer J., Deutch J., Ellerman A. D., Friedmann S. J., Herzog H., Jacoby H. D., Joskow P. L., Mcrae G.,Lester R., Moniz E. J., Steinfeld E., Katzer J., 2007. *"Future of Coal : Options for a carbon-constrained world*" MIT report.

Table 5-9: Cost of Electricity for E-MAR process

	With Capture (mills/kWh)
Fuel	25.1
O & M	23.3
CapEx	59.2
TOTAL	**107.6**

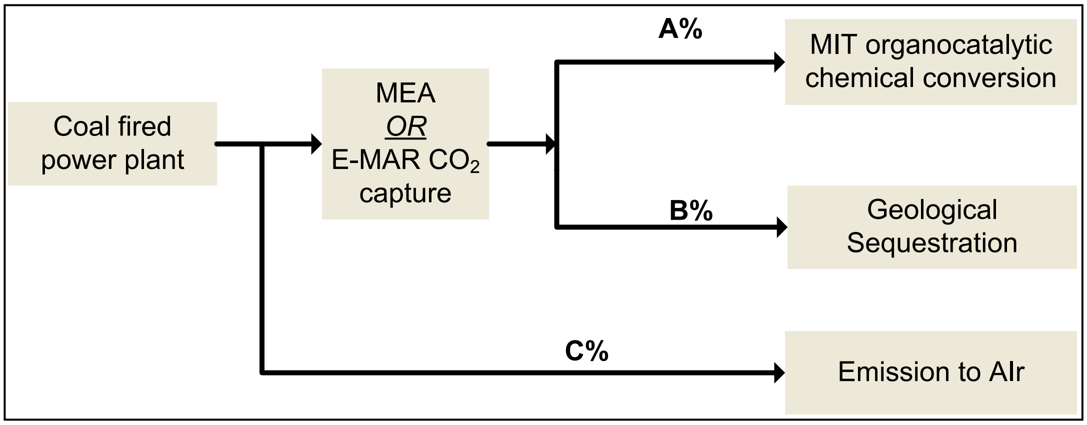
The cost of electricity for MEA capture is approximately 10% higher than that for E-MAR capture which is consistent with MIT's findings[43]

LCC of Chemical Conversion System

The costing analysis for the chemical conversion system developed by MIT falls in the category of cost estimation for emerging technologies and processes in the chemical industry. The reaction conditions for the chemical conversion were optimized by MIT at lab scale (mg - g range). No studies were performed to simulate and extrapolate these conditions to industrial scale (kg - ton) to match, at best, the scale of CFPP carbon dioxide emissions. At this time of development of the reaction protocol, it would be too difficult to estimate with relative accuracy the costs of reagents, equipment as well as associated cost of energy for operation. Instead, a different approach based on optimization technique was used to calculate the cost of the chemical conversion system. The optimization technique is presented in the following section.

Market Research – Study of scales

In order to understand the size to which the chemical conversion system must be scaled up, we first need to understand what are the limiting factors involved. **Figure 5-16** illustrates a simplified view of the system under study. Three values A, B and C are percentages of total CO_2 emitted from CFPP that will be diverted to chemical conversion, geological sequestration or emission to air.



A% — Governed by (a) physical limits of the chemical sequestration process and (b) availability of reagents in US/world market

B% — Governed by (a) geological limits of injection rate in US and (b) availability of injection sites

C% — Minimum value is 10% due to limits on current capture rates. Once the limits of A and B are set, C can be calculated as [100-(A+B)]

Figure 5-16: Conceptual block diagram illustrating various limiting factors in the system under study

Based on **Figure 5-16**, the following sections will discuss the possible values of A, B and C for our study.

1) Scale of Carbonate Production

In the proposed chemical conversion process, an epoxide reacts with CO_2 to form a cyclic carbonate. Two most commonly used organic oxides are listed in **Table 5-10** and ranked based on total annual production in US.

Table 5-10: Total annual production of reagent chemicals for carbonate production[64]

Rank	Chemical	US		World	
		Mt/yr	Gmol/yr	Mt/yr	Gmol/yr
#36	Ethylene oxide (EO)	3.5	17.5	80	367
#46	Propylene oxide (PO)	2.1	6.3	37	108

The scale of CO_2 production from power plants producing electricity in US is presented in **Table 5-11**. Since both EO and PO react with CO_2 in equimolar manner, we can combine

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[64] Bhown, A.; Freeman, B. *Environ. Sci. Technol.* **2011,** *45,* 8621-8623

information from **Table 5-10** and **5-11** to draw conclusions regarding the scale of the system. Approximately 0.05% of CO_2 produced 1from electricity generation with coal will be utilized if it is reacted with all of EO in US. For PO this percentage is even lower (0.016%). If we expand our boundary to include the global supply of epoxides, these percentages will be 0.93% and 0.27% for EO and PO respectively.

Table 5-11: Total annual production of CO_2 from electricity generation in US in 2010[65]

CO_2 emissions from electricity generation	Mt/yr	Gmol/Yr
Coal	1741	39568
Total from electric power sector	2200	50000

For the 500 MWe subcritical pulverized CFPP used in the study, the annual CO_2 emission rate is 3.4 Mt or 77 Gmols. At this scale, approximately 22% of captured CO_2 would exhaust the US production of EO and respectively, 8% would exhaust that of PO, leaving respectively 78% and 92% of CO_2 for sequestration.

For this study, we assumed that only 15% of captured CO_2 from the CFPP could be diverted realistically to the chemical conversion system, Recalculation of the epoxide utilization shows that about 66% of EO produced in the US would be sufficient to react with 15% of CO_2 captured from a single 500 MWe CFPP.

2) Scale of Geological sequestration

Similar scale analysis was performed for the geological sequestration. According to the carbon sequestration Atlas[66], the current estimated total CO_2 storage capacity in US which includes sum of saline formation, oil and gas reservoir and unminable coal area CO_2 storage resource estimate is approximately 1850 (low estimates) to 20470 (high estimates) billion tonnes. These numbers translate to storage potentials of 530 (low estimate) to 5900 (high estimate) years which are calculated based on total annual CO_2 emissions in US. From these estimates it is clear that amount of storage is not the limiting factor in this case.

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[65] http://www.eia.gov/totalenergy/data/annual/pdf/sec11.pdf

[66] NETL (2010) *Carbon Sequestration Atlas of the United States and Canada*, 3rd Ed. Available at http://www.netl.doe.gov/technologies/carbon_seq/refshelf/atlas.

Currently the injection rates range from 274-4000 t/day[67] and this will be the limiting factor at the present day since the CFPP in the study produces approximately 9400 t/day of CO_2. Assuming 10% is emitted to air due to capture efficiency of 90% and 15 % is utilized in the chemical conversion, approximately 7200 t/day CO_2 still needs to be geologically sequestered. Current injection rates are not sufficient to satisfy this flow rate and hence this will be a limiting factor. Further literature review revealed that cumulative maximum injection rates in the US could be of the order of 2300 Mt/yr for short term (25 years) or 1700 Mt/yr for long term (50 years) storage scenarios[68]. Hence future developments could eliminate the injection rate as a limiting factor. These new technological developments in turn would influence the life cycle costing of the geological sequestration process.

Methodology for Optimization

The results from previous section regarding the limits and scale of the study will be used to set up a linear programming problem for optimization. **Figure 5-17** illustrates the block diagram used for setting up the linear programming problem.

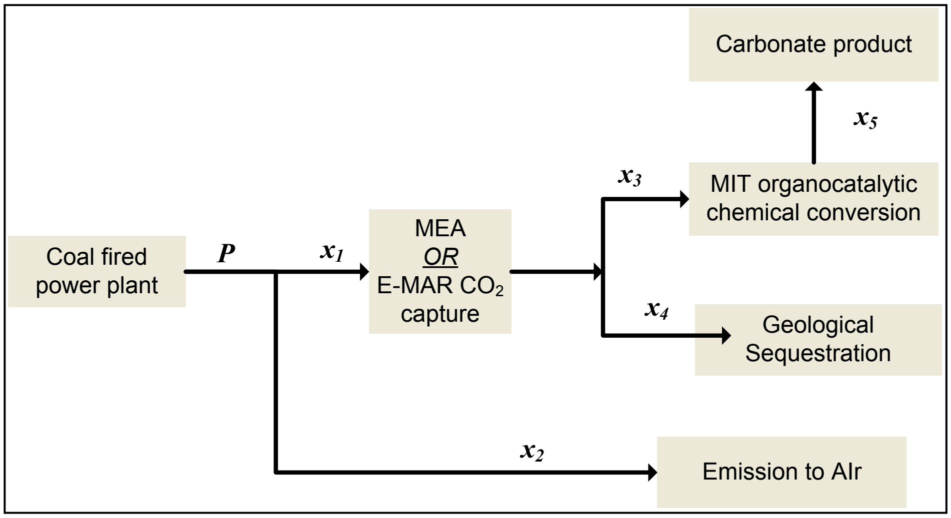

Figure 5-17: Conceptual block diagram for setting up linear programming problem for optimization

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[67] NETL, 2011: Carbon Sequestration, NETL's Carbon Capture and Storage Database – Version 3. http://www.netl.doe.gov/technologies/carbon_seq/global/database/index.html

[68] Szulczewski, M.L. (2009): *Storage Capacity and Injection Rate Estimates for CO2 Sequestration in Deep Saline Aquifers in the Conterminous United States*, Unpublished MS thesis, Massachusetts Institute of Technology.

Table 5-12 lists all the mass flows variables presented in **Figure 5-17** along with their limits as interpreted from the discussion in previous section.

Table 5-12: Description and limits of mass flow variables

Variable	**Description**	**Limited by**
P	Mass of CO_2 emitted from the CFPP	500 MWe Subcritical CFPP
x_1	Mass of CO_2 captured using MEA or E-MAR process	At most 90% of the CO_2 emitted by the power plant
x_2	Mass of CO_2 emitted to air	At least 10% of CO_2 emitted by the power plant
x_3	Mass of CO_2 converted to carbonate using organocatalytic process	(a) Physical Limit of the chemical sequestration process (b) Market demand for organic carbonate commodity (c) Market supply of organic oxide reagent
x_4	Mass of CO_2 geologically sequestered	Injection rate currently available in US
x_5	Mass of carbonate product	—

In addition to the variables listed in **Table 5-12**, cost variables y_1 though y_5 corresponding to the mass variables are also used for setting up the optimization equations. From **Table 5-12**, the mass flow limits were determined. Due to the constraints on the utilization of CO_2 (x_3 and x_4) the mass flow optimization is a single solution problem. The mass flows calculated are presented in **Table 5-13** along with the cost values from previous section.

Table 1-13: Variables used to set-up the linear programming problem

Variable	**Units**	**Limits**	**Values calculated**
P	Tonnes/yr	Max 3.8E6	3.8E6
x_1	Tonnes/yr	Max 3.42E6	1.97E6
x_2	Tonnes/yr	Min 3.8E5	1.83E6
x_3	Tonnes/yr	The lowest of (a) Max 5.13E5 (b) Max 1.73E6 (c) Max 7.7E5	Based on (a) 5.13E5
x_4	Tonnes/yr	Max 1.46E6	1.46
x_5	Tonnes/yr	N/A	5.77E5

y_1	\$/Tonne	N/A	70.55 (MEA capture) 66.88 (E-MAR capture
y_2	\$/Tonne	N/A	20
y_3	\$/Tonne	N/A	Calculated below
y_4	\$/Tonne	N/A	1.7
y_5	\$/Tonne	Max 10	N/A

The cost value for chemical conversion process (y_3) cannot be determined at this stage as explained in the LCC section. According to the FOA from DOE under which this project is funded, the mandated limit on the cost of the final useful product from the CO_2 utilization should be less than \$10/tonne.

Assuming that the system under study satisfies this cost limit, **Equation 5-1** was set up and can be used to calculate the value for y_3.

$$\frac{x_1y_1+x_2y_2+x_3y_3+x_4y_4}{x_5} \leq 10 \qquad \textbf{Equation 5-1}$$

Plugging in the values from Table 13, the cost of chemical conversion is found to be less than or equal to –336.1 S/tonne for MEA capture and –322 \$/tonne for E-MAR capture which is impossible to satisfy. Hence we can draw a conclusion that the target set by DOE for the final carbonate product of \$10/tonne is not a feasible target for this process at the current stage of development. For comparison purposes, the current cost of ethylene carbonate is approximately \$30/kg69, which is 3 orders of magnitude higher than the limit mandated in the FOA.

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[69] Sigma-Aldrich, E26258 ALDRICH: Ethylene Carbonate. http://www.sigmaaldrich.com/catalog/product/aldrich/e26258?lang=en&region=US

EXECUTIVE CONCLUSION

During the three-year period research on integrated electrochemical processes for CO_2 capture and conversion to commodity chemicals, we have focused on using electrocatalytic and organocatalytic routes of CO_2 tranformation. Moreover, the research conducted at SCR focused on placing the carbon capture and utilization technology developed by MIT into context to enable SCR to evaluate the associated environmental and economic impacts, and thereby determine the objectives, scope and boundaries of the Life Cycle Assessment (LCA) study. We have thus achieved:

1) An electrochemical assessment of catalytic transformation of CO_2 and epoxides to cyclic carbonates have been studied. Electrochemical properties of quinone has been evaluated for elucidating the binding affinity of electrochemically-generated dianion quinones towards CO_2, propylene oxide and propyl bromide.

2) An unprecedented method has been developed for the high yielding continuous synthesis of cyclic carbonates from CO_2 and epoxides. We have demonstrated how a continuous flow apparatus for gas/liquid reactions can greatly enhance the efficiency of the transformation relative to a traditional batch reactor. The catalysts used (NBS and BPO) are commercially available and inexpensive. A series of kinetics experiments have been conducted and support epoxide activation by electrophilic bromine.

3) An efficient flow synthesis of cyclic carbonates starting directly from olefins and CO_2 has been achieved. The flow synthesis was integrated into a hydroxybromination-carboxylation two-step sequential transformation, which represents a successful example of a multi-stage gas/liquid continuous flow process. Specifically, it is possible to introduce incompatible reagents easily without their interacting with each other (such as NBS and DBU), thus significantly enhancing the reaction rate, especially for aliphatic olefins, and we demonstrated the effectiveness of performing sequential reactions in flow. These flow systems enable optimization of individual steps and allow numerous experiments to be conducted at various residence times and temperatures after the initial loading of reagents into the pumps because of the ease with which these operating conditions can be adjusted in real time. Compared to conventional batch conditions, the flow systems can be operated readily with a broad range of substrates, with enhanced reaction rates and increased product yields without the formation of epoxide or

dibromide by-products. Other merits of this gas/liquid flow system include a packed-bed reactor used for carboxylation, which enabled efficient mixing of the phases while stabilizing the flow patterns, i.e., ensuring steady flow. Acetone was applied as the co-solvent with water to achieve a homogenous liquid solution at elevated temperature to avoid the use of phase-transfer reagents.

4) An efficient microwave-assisted one-pot synthesis of cyclic carbonates starting from olefins has been achieved with a wide substrate scope. Compared to conventional heating methods, microwave heating resulted in much better selectivity and yield of desired products. $NaHCO_3$ proved to be an excellent substituent for CO_2 gas, thus avoided the high capital cost and related safety issues. This method is also well poised toward green process due to the use of environmental friendly acetone/water solvent.

5) We evaluated the environmental and economic impacts of the novel carbon capture and chemical conversion technology developed by MIT. The analysis was based on publicly available data and experimental data provided by MIT. The LCA models are in parameterized format and can easily be modified to reflect any new scenarios that will be developed in the future. The results from the environmental impacts of CFPP with conventional MEA capture have been verified with existing literature to validate the LCA models. The final results for E-MAR capture show that it has approximately 10% lower impacts than conventional MEA capture system for GWP and PED category. The impacts for the chemical conversion process for carbonate production are quite high even for 15% utilization scenario. The LCC results for CFPP with and without capture have also been presented here. The results are in agreement with previous work done by DOE. The study of scales identified availability of reagent for chemical conversion of CO_2 and demand for the carbonate product as two major limitations for scaling up the system. Solving the optimization equation shows that achieving the DOE set goal of \$10/tonne for the final carbonate product is not feasible under current conditions.

Appendix A

Life Cycle Impact Categories (Based on information from Shonnard et al70)

1) Global Warming Potential (GWP)

The impact assessment for global warming was conducted using a method outlined by Shonnard using “the tier 3 metrics for environmental risk evaluation of process designs”. In this method a dimensionless risk index is calculated by **Equation (A-1)**.

$$Dimensionless\ Risk\ Index = \frac{[(EP)(IIP)]_i}{[(EP)(IIP)]_B} \quad \textbf{Equation (A-1)}$$

Where EP is the exposure potential, IIP is the inherent impact potential, i is the compound being indexed, and B is the benchmark compound. In case of global warming, the benchmark compound is CO_2.The dimensionless risk index for global warming is referred to as global warming potential (GWP) and the values of GWP for CO_2, CH_4, N_2O and NO_x are taken from CML. To evaluate the total index for global warming due to all the air emissions obtained from all the stages of the ethanol production system, **Equation (A-2)** was used:

$$I = \sum_i [(Dimensionless\ Risk\ Index)_i \times m_i] \quad \textbf{Equation (A-2)}$$

2) Acidification Potential (AP)

Acidification results from processes that increase the acidity or H^+ ion concentration of air, water and soil. Acidification has direct and indirect damaging effects (such as nutrients being washed out of soils or an increased solubility of metals into soils). It is expressed in terms of kg SO_2 equivalent.

3) Eutrophication Potential (EP)

Excessive levels of nitrates and phosphorus can cause problems for environment and human health. Main source is runoff and leaching of fertilizers. In general, the characterization factors estimate the eutrophication potential of a release of chemicals containing N or P to air or water, per kilogram of chemical released, relative to 1 kg N discharged directly to surface freshwater. It is expressed in terms of kg PO_4 equivalent

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[70] Allen, D.T. and Shonnard, D.R., 2002. Green engineering: environmentally conscious design of chemical processes. Prentice Hall PTR. Upper Saddle River, NJ.

4) Ozone Layer Depletion Potential (ODP)

ODP is the relative amount of degradation to the ozone layer a chemical compound can cause in reference to R-11 as base compound which has ODP as 1.0. It is expressed in terms of kg R-11 equivalent

5) Primary energy demand (PED)

Cumulative energy demand is the total quantity of primary energy needed throughout the process under consideration. It is represented as the net calorific value in MJ.

Appendix B: Life Cycle Inventory

Table B-1: Mass and Energy inventory for all the components within system boundary

Coal Fired Power Plant			
		Value	Units
Mass IN	Hard coal	2.54E+05	kg/hr
	Ammonia	2.52E+02	kg/hr
	Sodium Hydroxide	1.53E+02	kg/hr
	Water (feed for boiler)	1.86E+06	kg/hr
	Water (for cooling tower)	8.21E+07	kg/hr
	Lime	2.70E+04	kg/hr
Mass OUT	CO_2 (product flow)	5.21E+07	kg/hr
	Bottom Ash	3.21E+03	kg/hr
	Fly ash	1.38E+04	kg/hr
	Gypsum	1.93E+04	kg/hr
Energy IN	Coal (based on HHV)	6.45E+06	MJ/hr
Energy OUT	Power to Grid	1.30E+06	MJ/hr
CO_2 capture using MEA			
		Value	Units
Mass IN	CO_2 (product flow)	5.21E+07	kg/hr
	SO2	3.16E+02	kg/hr
	Sodium Hydroxide	1.53E+02	kg/hr
	Water	1.82E+04	kg/hr
	Monoethanolamine	3.54E+06	kg/hr
Mass OUT	CO_2 (product flow)	5.21E+07	kg/hr
	Monoethanolamine waste	1.59E+03	kg/hr
Energy IN	Electricity	2.71E+05	MJ/hr
	Steam	6.67E+05	MJ/hr

CO_2 capture with E-MAR process			
		Value	Units
Mass IN	CO_2 (product flow)	4.88E+05	kg/hr
	SO2	3.16E+02	kg/hr
	Nafion Membrane	1.25E+01	kg/hr
	Water	3.56E+06	kg/hr
	Copper (recirculated mass)	5.42E+05	kg/hr
	Ethylenediamine	7.12E+05	kg/hr
Mass OUT	CO_2 (product flow)	4.88E+05	kg/hr
	Ethylenediamine waste	3.21E+02	kg/hr
Energy IN	Electricity	3.62E+05	MJ/hr
Geological Sequestration			
		Value	Units
Mass IN	CO_2 (product flow)	4.43E+05	kg/hr
Mass OUT	CO_2 (fugitive emissions during transport)	1.94E+01	kg/hr
Energy IN	Electricity	1.32E+04	MJ/hr
Organocatalytic Conversion Process			
		Value	Units
Mass IN	CO_2 (product flow)	7.81E+04	kg/hr
	Dimethylformamide (Solvent)	1.84E+05	kg/hr
	Ethylene Oxide	7.81E+04	kg/hr
	Benzoyl Peroxide (Catalyst)	7.00E+03	kg/hr
	N-Bromosuccinimide (Catalyst)	5.15E+03	kg/hr
Mass OUT	Dimethylformamide (Solvent)	1.84E+03	kg/hr
	Ethylene Oxide	3.21E+01	kg/hr
	Benzoyl Peroxide (Catalyst)	7.00E+03	kg/hr
	N-Bromosuccinimide (Catalyst)	5.15E+03	kg/hr
Energy IN	Electricity	1.38E+04	MJ/hr

Appendix C

CAPEX and OPEX estimation for CFPP and MEA based capture

The DOE has adopted the following categorization for CAPEX:

- Base Erected Cost (BEC) – This includes material and equipment costs, direct and indirect labor costs during construction, installation and commission, supporting facilities and infrastructure at the plant site (such as offices, roads, laboratories etc.,).
- Engineering, Procurement and Construction Cost (EPCC) – This includes BEC plus cost of services provided by engineering, procurement and construction (EPC) contractors.
- Total Plant Cost (TPC) – This includes EPCC plus process and project contingencies. The process contingencies are included to account for performance uncertainties associated with the development status of a technology and are applied to each power plant component based upon the current technology being used. The DOE has adopted the AACE International[71] recommended guidelines AACE 16R-90[72] for process and project contingencies. In case of carbon dioxide removal system for pulverized coal fired power plants, 20% process contingency is recommended. The project contingency is usually 15% to 30% of the sum of BEC, EPC fees and process contingency. In addition, DOE has also included project contingency estimates from a third party EPC firm – Worley Parsons.
- Total Overnight Cost (TOC) – This is TPC plus owner's cost. The owner's costs included in TOC are as follows[3] and are as per AACE[5] and Electrical Power Research Institute (EPRI) Technical Assessment Guide (TAG) on Power Generation and Storage Technology Options[73] :
    - Prepaid royalties
    - Pre-production (start-up) costs – This includes 6 months operating labor, 1 month maintenance materials and non-fuel consumables, at full capacity,1 month waste disposal, 25% of one month's fuel cost at full capacity and 2% of TPC.
    - Inventory capital – This includes 0.5% of TPC for spare parts, 60 day supply of fuel and non-fuel consumables (such as chemicals and catalysts) at full capacity. Since inventory capital costs are accounted for, DOE does not include additional costs for working capital.

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[71] Formerly known as American Association of Cost Engineering or Association for the Advancement of Cost Engineering. Current official title is AACE International (http://www.aacei.org/mbr/whoWeAre.shtml)

[72] AACE (1991). 16R-90: Conducting Technical and Economic Evaluations: As Applied for the Process and Utility Industries. (Rev. Apr 1991). Morgantown: AACE International.

[73] EPRI updates annually the TAG report but in the DOE (2010) report it is not explicitly stated for which reference year owner's cost estimates were included. Therefore, specific EPRI reference is not cited.

    - Land – DOE considers 300 acres of land requirement for sub-critical pulverized coal (SCPC) power plant at a cost of $3000 per acre.
    - Financing cost – Assumed to be 2.7% of TPC.
    - Other's owner's cost – This additional lumped cost (assumed to be 15% of TPC) includes – preliminary feasibility studies, economic development outside the site boundary, legal fees, permitting fees, owner's engineering services (hired by the owner to oversee EPC services), and owner's contingencies.
- Total As-Spent Cost (TASC) – This includes TOC plus interest on debt and the escalation in costs during the capital expenditure period. DOE have reported the TASC to TOC ratio for different financing structures and capital expenditure periods.

It should be noted that BEC, EPCC, TPC and TOC are considered as overnight costs and are expressed in base year dollars. The base year for DOE estimates is 2007. TASC is expressed in mixed year, current-year dollars spread over the five year capital expenditure period (2007 to 2011) for SCPC power plants. The BEC and EPCC cost estimates reported by DOE are derived from Worley Parsons estimates, for which the estimation methodology is not available publicly. The labor costs are based on a 50 hour work week and are estimated at $34.65 per hour. In addition, the labor burden (assumed to be 30% of base labor rate) and taxes and insurance costs (assumed to be 2% of TPC) are also included in Fixed O&M costs. DOE has not reported the detailed methodology to estimate the maintenance costs (material and labor) but has only indicated it is based upon the relationship with the initial capital cost. The administrative and support labor costs are assumed to be 25% of operating labor and maintenance costs. The variable O&M costs were based upon the prevailing market price for the base year.

Appendix D

CAPEX and OPEX estimation for CO_2 Transport, Storage and Monitoring

Transport costs

The cost elements associated with pipeline transport of CO_2 are summarized in **Table D-1**. The pipeline costs (i.e. materials, direct labor, miscellaneous indirect costs, and right of way acquisition) are estimated as a function of pipeline length and diameter. The pipeline diameter is selected as a function of CO2 flow rate and distance (refer **Figure D-1**).The indirect costs include surveying, engineering, supervision, contingencies, allowances, allowances for funds used during construction, administration and overheads, and regulatory filing fees. In addition, the project and process contingencies of 30% and 20% respectively are also included in the capital costs. The fixed operation and maintenance (O&M) are expressed in terms of dollars per mile per year.

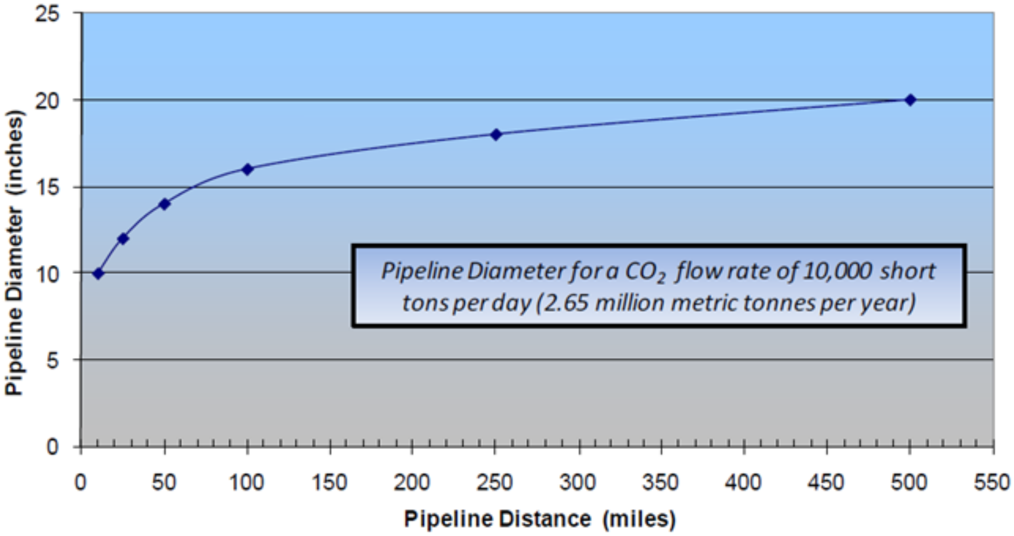

Figure D-1: Minimum pipeline diameter as a function of pipeline length

Table D-1: Cost elements of CO_2 pipeline transport (L = Length of pipeline, D = Diameter of pipeline)

Cost type	Units	Cost
Pipeline costs		
Materials	$	$\$64,632 + \$1.85 * L * (330.5 * D^2 + 686.7 * D + 26,690)$
Labor	$	$\$3,41,627 + \$1.85 * L * (343.2 * D^2 + 2074 * D +170,013)$
Miscellaneous	$	$150,166 + $1.58 * L * (8,417 * D + 7,234)
Right of way acquisition	$	$48,037 + $1.20 * L * (577 * D + 29,788)
Other capital		
CO_2 surge tank	$	$1,150,636
Pipeline control system	$	$110,632
O&M		
Fixed O&M	$/mile/year	$8,632

The characteristics of the deep saline aquifer are provided in **Table D-2**.

Table D-2: Specifications of the deep saline aquifer

Parameter	Units	Average case
Pressure	MPa	8.4
Thickness	m	161
Depth	m	1,236
Permeability	Md	22
Pipeline distance	km	80
Injection rate per well	tonnes CO_2/day	9,360

Storage costs

The breakdown of the storage costs is illustrated in **Table D-3**. These costs reflect the costs associated to determine, develop and maintain a CO_2 storage location, including evaluation of the site, drilling operations and the capital equipment required to distribute and inject CO_2. The site screening and evaluation are fixed capital costs whereas the other capital costs are based on the number of injection wells and the depth of the well. The liability bond of five million dollars is included to pay for any potential damages during CO_2 injection and long term storage of CO_2. The pore space acquisition costs includes the costs to acquire additional rights to store CO_2 within the subsurface area of the aquifer and are estimated for the CO_2 emissions for the complete lifetime of the power plant.

Monitoring costs

The DOE guidelines assume that the CO_2 plume is monitored during operational life time of the plant (i.e. 30 years), and for additional 50 years after the closure of the plant. A capital fund is established to pay for the operational and closure monitoring costs. The present value of the capital fund (using 10% discount rate) is estimated to be \$ 0.377 per short ton of CO_2 to be injected over the operational lifetime of the power plant.

Table D-3: Breakdown of geologic storage costs

Cost type	Units	Cost
Capital		
Site screening and evaluation	\$	\$4,738,488
Injection wells	\$/injection well*	$\$240{,}714 * e^{0.0008 \text{ *well-depth}}$
Injection equipment	\$/injection well	$\$94{,}029 * \left(\frac{7389}{280 * \# \text{ of injection wells}}\right)^{0.5}$
Liability bond	\$	\$5,000,000
Declining capital funds		
Pore space acquisition	\$/short ton CO_2	\$0.334/short ton CO_2

O&M		
Normal daily expenses (Fixed O&M)	\$/injection well	\$11,566
Consumables (Variable O&M)	\$/yr/short ton CO_2/day	\$2.995
Surface maintenance (Fixed O&M)	\$/injection well	\$23,478 * $\left(\frac{7389}{280 * \#\text{ of injection wells}}\right)^{0.5}$
Subsurface maintenance (Fixed O&M)	\$ft-depth/injection well	\$7.08

*- Well depth is expressed in meter

Table D-4: CAPEX and OPEX components of TS&M and other assumptions

Pipeline diameter (inch)	14
Pipeline distance (mile)	50
Number of wells	2
Depth (feet)	4,055
CO_2 emitted/hr (as product flow) (metric ton/hr)	597
Capacity factor	0.75
CO_2 injected/yr (metric ton/yr)	3,919,298
Life of the plant (yrs)	30
Pipeline Transport	**Cost (constant 2007 dollar)**
Materials	9,439,674
Labor	24,975,876
Miscellaneous	10,030,854
Right of Way	2,319,997
CO2 Surge tank	1,150,636
Pipeline Control system	110,632
Total Capital cost	**74,923,162**
Total Fixed O&M cost	**431,600**
Storage	**Cost (constant 2007 dollar)**
Site screening and evaluation	4,738,488
Injection wells	1,294,045
Injection equipment	683,110
Liability bond	5,000,000
Total capital cost	**11,715,643**
Pore space acquisition	**43,298,093**
Normal daily expenses	23,132
Consumables	35,457
Surface Maintenance	170,565
Subsurface Maintenance	57,419
Total Fixed O&M cost	251,116
Total Variable O&M cost	35,457
Total O&M cost	**286,573**
Monitoring	**Cost (constant 2007 dollar)**
Monitoring capital fund	**48,872,399**

Appendix E

Table E-1: Coal combustion by-products utilization data

Utilization category	Fly ash utilization (short tons)	Bottom ash utilization (short tons)	FGD Gypsum utilization (short tons)	Price used in estimation ($/metric ton)	Reference (price data)
Concrete/Concrete Products/Grout	11016097	615332	21045	25	Personal Communication, William Aljoe, US DOE
Blended cement/raw feed for clinker	2045797	949183	1135211	50	ACAA
Flowable fill	135321	52414	0	1	ACAA
Structural fills/embankments	4675992	3124549	454430	1.5	Personal Communication, William Aljoe, US DOE
Road base/sub-base	242952	715357	0	6	ACAA
Soil modifications/stabilization	785552	162065	0	15	ACAA
Snow and Ice control	0	549520	0	4.5	ACAA
Blasting grit/roofing granules	86,484	19914	0	1.5	Assumption
Mining applications	2399837	528881	835536	1.5	Personal Communication, William Aljoe, US DOE
Gypsum panel products	109	0	7661527	1.5	Assumption
Waste stabilization/solidification	3258825	41233	0	20	ACAA
Agriculture	22220	4674	481827	1.5	Assumption
Aggregate	6726	555031	0	6	Assumption
Miscellaneous	1047305	223579	123562	1.5	Assumption
TOTAL utilization	25723217	7541732	10713138		
TOTAL production	67700000	17800000	22000000		
% utilization	38.0%	42.4%	48.7%		

ACAA (2010). http://acaa.affiniscape.com/associations/8003/files/20_CCP_Survey_FINAL_102011.pdf (Accessed 29th March, 2012)