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ARTICLE

Kinetic and Economic Analysis of Reactive Capture of Dilute Carbon Dioxide with Grignard Reagents

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Carbon Dioxide Utilisation (CDU) processes face significant challenges, especially in the energetic cost of carbon capture from flue gas and the uphill energy gradient for CO_2 reduction. Both of these stumbling blocks can be addressed by using alkaline earth metal compounds such as Grignard reagents as sacrificial capture agents. We have investigated the performance of these reagents in their ability to both capture and activate CO_2 directly from dried flue gas (essentially avoiding the costly capture process entirely) at room temperature and ambient pressures with high yield and selectivity. Naturally, to make the process sustainable, these reagents must then be recycled and regenerated. This would potentially be carried out using existing industrial processes and renewable electricity. This offers the possibility of creating a closed loop system whereby alcohols and certain hydrocarbons may be carboxylated with CO_2 and renewable electricity to create higher-value products containing captured carbon. A preliminary Techno-Economic Analysis (TEA) of an example looped process has been carried out to identify the electrical and raw material supply demands and hence determine production costs. These have compared broadly favourably with existing market values.

Introduction

With the looming threats posed by climate change, a key plank in carbon dioxide reduction strategies is to develop new pathways to mitigate and avoid emissions by the production of low carbon, carbon neutral and even carbon negative alternatives to common and bulk chemicals.[1] One route by which this can be accomplished is to incorporate carbon dioxide that would otherwise be emitted into the desired product, delaying or avoiding its release into the atmosphere. In this way, when the product is consumed or degraded, there is reduced change to the atmospheric carbon dioxide levels associated with that product, ideally rendering the product itself carbon neutral. Naturally, if the product has a prolonged life or is recycled effectively this method represents an overall sequestering of the original carbon dioxide from the atmosphere to the solid state in a form of long term storage which would complement geological storage aspirations.[2]

This strategy of Carbon Dioxide Utilisation (CDU) is known by a variety of names and acronyms, but in all cases involves the use of carbon sources, including mixed and dilute ones such as flue gas and biogas, to generate products.[3] The resulting products therefore have a reduced carbon footprint leading to an overall net emissions reduction. While ambitious, if CDU processes can be implemented with atmospheric carbon dioxide (also known as "direct air capture", DAC) this would represent both a key technique to form a sustainable carbon product cycle, analogous to the natural carbon cycles, and potentially allows the creation of useful products irrespective of geographical location.

This generation of products using the carbon dioxide is what sets CDU apart from Carbon Capture and Sequestration (CCS) where carbon dioxide is instead treated as a waste to be dumped in geological storage sites, with only the environmental benefit of net emissions reduction as a motivation. The major benefit of CDU, in contrast, is the addition of value by the carbon dioxide to the product in addition to the environmental benefit associated with shrinking, or eliminating, its carbon footprint.

The extent of the environmental benefit will of course be product-dependent, however recent publications have shown that even modest targets for CDU allow amounts of CO_2 to be mitigated that match or even exceed current CCS targets.[4] Indeed, while it predates this argument, global production of urea from CO_2 and ammonia (which essentially a CDU process) utilises *ca.* 140 million tonnes of carbon dioxide annually.[1] Admittedly when the production of the ammonia and the breakdown of the urea as a fertiliser are taken into consideration, the net emissions of the overall process are

greater than unity. However, urea production acts as an indicator of the scale that CDU processes could hope to achieve, dwarfing even optimistic CCS targets of 102 million tonnes total stored by 2020.[5]

The fact that CDU treats carbon dioxide as a resource rather than a waste also allows traditional economic driving forces to foster innovation. This has already resulted in several examples of economically successful CDU processes.[6] These include the Bayer Dream process[7] where CO_2 is incorporated into polyurethane plastics, Sunfire's synthetic diesel[8] and Carbon Recycling International where cheap Icelandic geothermal energy is used to turn CO_2 into methanol.[9]

Importance of Techno-economic Analysis in CDU processes

Since CDU primarily relies upon the addition of value through using the CO_2, it would therefore seem essential to combine any serious attempt at the development of a CDU process with at least a preliminary or generalised Techno-Economic Analysis/Assessment (TEA) to demonstrate what value, if any, can be added by the process in question.[10]

This is because the likelihood for implementation of existing and new technologies depends on the interest and motivation of private and public investors. Many researchers who develop new technologies have limited knowledge of their economic potentials and pitfalls. Therefore, understanding the investors' needs and the related economic questions enables technology developers to focus their work on the promising options and avoid expending effort in technologies that are fundamentally not economically viable. TEA studies of new technologies and processes, such as CDU systems, allow us to better understand the relationship between process performance (*e.g.* conversion) and costs (*e.g.* production) to help identify the most promising process designs which can provide the highest financial returns for the potential investors. Therefore, in the case of CDU, TEA studies are an invaluable tool which can support policy makers and businesses in their decision-making by establishing whether the production of chemicals and fuels from waste CO_2 is economically feasible; and identifying the modifications and conditions required to improve the economic competitiveness of CDU technologies.

What has already been revealed by these analyses and assessments is that for CDU and CCS strategies that rely on separation of carbon dioxide from dilute sources such as flue gas, this "capture" step is a major energy sink and therefore carries significant costs.[11]

Cost of Capture of CO_2

Separating carbon dioxide from other gases on large scales is one of the largest challenges for CDU and also CCS. This might be surprising as thermodynamically the cost of separation is not large (Table 1). Even the most dilute source of CO_2, such as that which is found in the atmosphere, requires only 521.7

MJ/tonne for separation (approximated from binary $CO_2:N_2$ mixtures).

Table 1 : Minimum thermodynamic energy cost of separating 1 tonne of CO_2 from N_2/CO_2 mixtures at stp

CO_2 Concentration in N_2 (vol %)	Minimum Entropic Demixing Cost per Tonne CO_2 (MJ)
Atmospheric (400ppm)	521.7
1%	340.2
5%	248.0
10%	206.9
15%	182.0
20%	163.6

Despite this, calculated capture energy costs using industrial benchmark capture agents such as monoethanolamine (MEA) and other amines frequently exceed 3,000-4,000 MJ/tonne CO_2 even when starting from relatively concentrated CO_2 sources. This translates into both large capital and large operational costs for carbon capture from power plants, with the cost of the capture plant often exceeding the base plant costs (see Figure 1).[12]
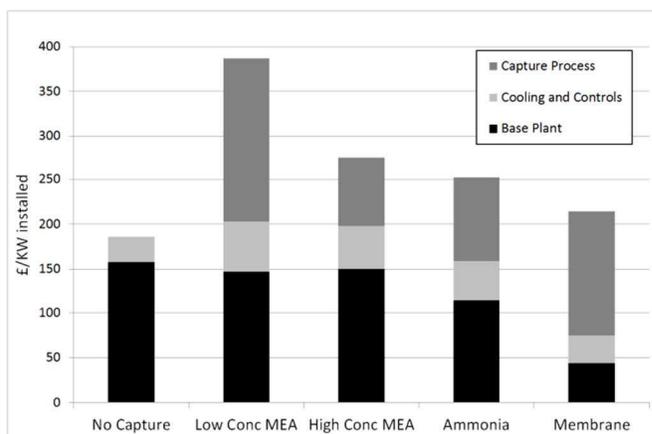
Figure 1 Breakdown of annual Operation and Maintenance (O&M) costs per unit electricity by capture process

The cause of this discrepancy in energy cost, in the case of MEA and other amines, is that the capture process is driven by a chemisorption reaction loop involving the creation and then decomposition of carbamates.[13] The high energy cost of this loop is indicative of the relatively low reactivity of carbon dioxide at standard temperatures and pressures. However, while this reactive capture chemisorption approach has the major advantage of ensuring high carbon dioxide selectivity over the other main component gases, nitrogen and methane (in flue gas and biogas respectively), it actually represents a waste of energy from CDU perspectives as the product carbamate is itself a CDU product. As a result, the decomposition of the post-capture carbamate to create purified CO_2 only to react that CO_2 again to make another product can be seen as an energetic wild goose chase where the carbon dioxide is essentially utilised twice!

Additionally, the chemisorption approach will often allow some of the trace gases in these feed gas streams to react with the sorbent. At best, this is disadvantageous due to the

displacement of CO_2 in the capture step, but at worst the trace gas poisons the sorbent permanently. This is especially problematic when dealing with gas supplies contaminated with sulfur compounds.

While for MEA the carbamate product is a mere intermediate for CO_2 purification, if an analogous process where a valuable carbon-carbon bond is formed instead were developed, it would represent a potentially attractive pathway for direct conversion of flue gas into products without a distinct gas separation step. Naturally the value of this process would be decided by the economic value of the product but it would certainly avoid much of the wasted energetic costs of the carbamate loop.

Any such process would therefore require a stoichiometric reactant of some sort with which the CO_2 must react, however this already the case when using any capture process for generation of CDU products. Considering the reactants that could be used, one prominent example is the Grignard reaction, involving organomagnesium halide reagents.

A Fresh Look at Grignard Chemistry in the Context of Carbon Dioxide Reactive Capture

The classic schoolroom carbon-carbon bond formation process using carbon dioxide is the reaction of a Grignard reagent with a pellet of dry ice. This standard reaction proceeds by the insertion of the carbon dioxide molecule between the carbon-magnesium bond of an organomagnesium halide, formed by the reaction of metallic magnesium with an organohalide.[14]
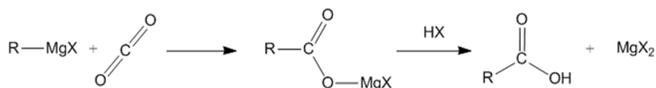
**Scheme 1** Generalised reaction of a Grignard reagent with CO_2

This reaction is exothermic and readily carried out at atmospheric pressure and ambient temperatures. Aside from requiring that all components are stringently dried, due to the rapid and exothermic reaction with water, the reaction also proceeds to typically high yields, dependent on reaction conditions and solvents, with a wide range of possible R-groups. The resulting carboxylic acid product is then readily isolated from the magnesium salt by-product in the majority of cases by solvent extraction, esterification and/or distillation.
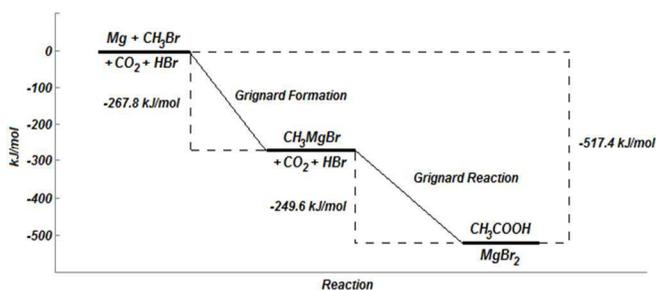
Figure 2 Reaction enthalpy profile of each step of a Grignard reaction to form acetic acid from CO_2 and methyl bromide[16]

The strongly exothermic nature of the reaction is driven by the oxidation of the starting elemental magnesium to the 2+ oxidation state. Coupled with the exothermic nature of the formation of the initial organohalide, (e.g. -42.2 kJ/mol for methyl bromide from methanol), the overall reaction of the parent alcohol with CO_2 becomes facile.

While methanol would be the parent alcohol in the example in Figure 2, the Grignard reaction is well-understood and offers a wide range of potential substrates, allowing a variety of industrially interesting CDU products to potentially be formed, a selection of which is shown in Figure 3.
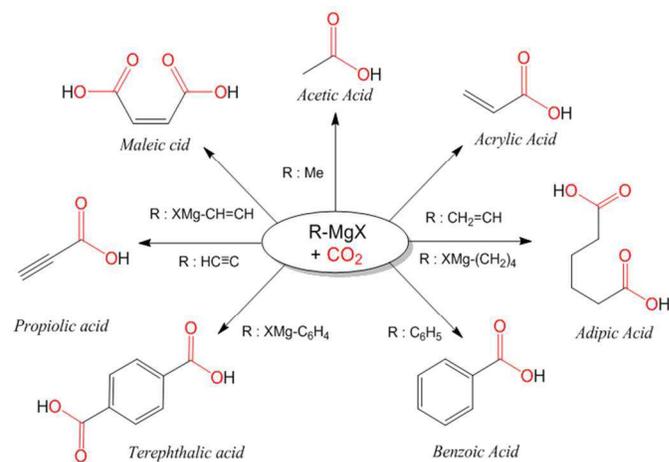
Figure 3 A series of potential CO_2 Grignard products of potentially industrial significance

The substrates for the formation of above products could open new pathways of commercial or environmental interest. The use of CO_2-derived carboxylic acids in polymers especially has already been targeted for large scale CDU applications.[16] For example, adipic acid, used for the synthesis of Nylon, is currently manufactured from petrochemical phenol, cyclohexene or butadiene, but could instead be created from biological 1,4-butanediol and CO_2 via halogenation to 1,4-dihalobutane. Similarly, terephthalic acid which is a key component of polyethyleneterephthalate (PET) plastic, the third most common plastic in use today, is currently derived from p-xylene, about which there has been a long-standing shortage and safety concerns, highlighted by the recent explosions in Zhangzhou, China.[17] Utilising CO_2, the terephthalic acid polymer precursor could be derived directly from the relatively plentiful benzene (via p-dihalobenzene, which is easily synthesised).

Collectively, the products shown in Figure 3 are manufactured on scale of approximately 71 million tonnes per annum worldwide and could potentially utilise over 40 million tonnes of CO_2, much of which would be sequestered into various polymers and other long life products.

However, as previously mentioned, Grignard reactions of carbon dioxide would typically be carried out using dry ice pellets rather than gas phase or dilute CO_2 mixtures. A series of tests were therefore performed to determine whether direct

utilisation of gas phase CO_2 and even simulated flue gas compositions and atmospheric concentrations were in any way suitable for Grignard chemistry. The reaction conditions and reaction rates for different gas compositions would allow a more complete techno-economic analysis of the process to be completed.

Grignard reactions can typically be tracked by titration of the remaining active organomagnesium reagent using 1,10-phenanthroline. The phenanthroline forms a coloured, charge transfer complex in a 1:1 ratio with the reagent that may then be titrated by using a dry alcohol such as 2-butanol.[18] However, it was found that in the case of the reaction of methylmagnesium chloride and CO_2, no colour change was observed when injected into a solution of 1,10-phenanthroline in dry THF. A possible reason for this is that the intermediate product, a magnesium acetate bromide species, acts as a quenching agent for the charge transfer complex, thereby preventing the colour change needed for titration.

Therefore, in order to determine the rate of reaction of CO_2 with methylmagnesium chloride, a high-accuracy pressure transducer (Omega PX409USB) was used to monitor CO_2 consumption within the reaction apparatus (Figure 4). In order to maintain a generally stable CO_2 partial pressure, the pressure drop was monitored intermittently between periods of CO_2 sparging.

As shown in Figure 5, these reactions were found to proceed cleanly when using gas-phase carbon dioxide bubbled through the Grignard reagent solution. Furthermore, this intermittent sparging process demonstrated clear trends in pressure drop rate, despite the exothermic nature of the reaction causing thermal expansion and vapour generation from the ethereal solvent required for Grignard chemistry. This high degree of reactivity with CO_2 prompted tests with increasingly dilute CO_2 mixtures in nitrogen, comparing the rate of change of pressure during the CO_2 interruptions.

The calculated rate of CO_2 consumption from the rate of pressure drop seen in Figure 5 is shown in Figure 6(a). Figure 6(b) plots individual natural log plots at varying gas compositions. These appear initially to be pseudo-first order in the presence of a constant supply of CO_2. However, while they are superficially similar to pseudo-first order kinetics, where a large and essentially constant surplus of one reagent is present, the change in rate constant when varying CO_2 concentration demonstrates that the reaction system is more complex. This is because although CO_2 concentration is static (as found in pseudo-first order reactions), it is not in excess, limiting each rate "constant" to the maximum rate that can be achieved at the given CO_2 concentration under these conditions. As a result, there is a decrease in reaction rate "constant" at lower concentrations. Overall combination of these effects strongly indicates the rate has a dependence on the concentration of both reagents, appearing to be first order with respect to Grignard.
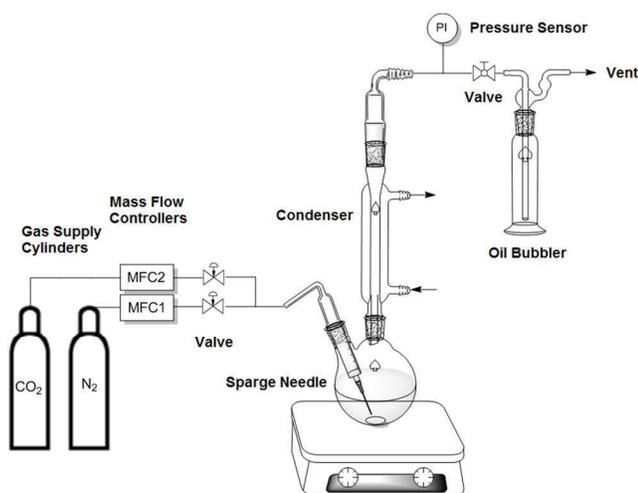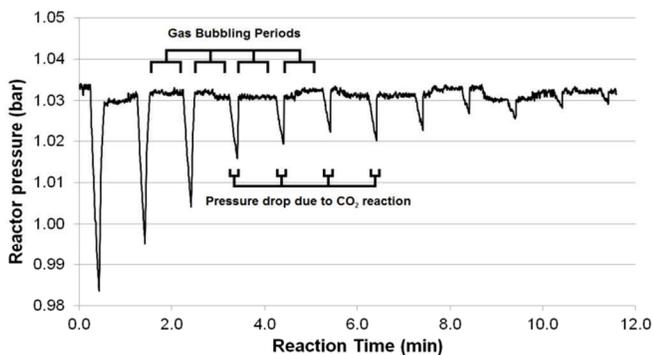

Figure 4 Schematic of the gas sparging reaction system

Figure 5 Typical reaction profile showing rapid pressure drop within the sealed reactor when gas sparging of 50% CO_2/N_2 is paused for 10 seconds every 1 minute

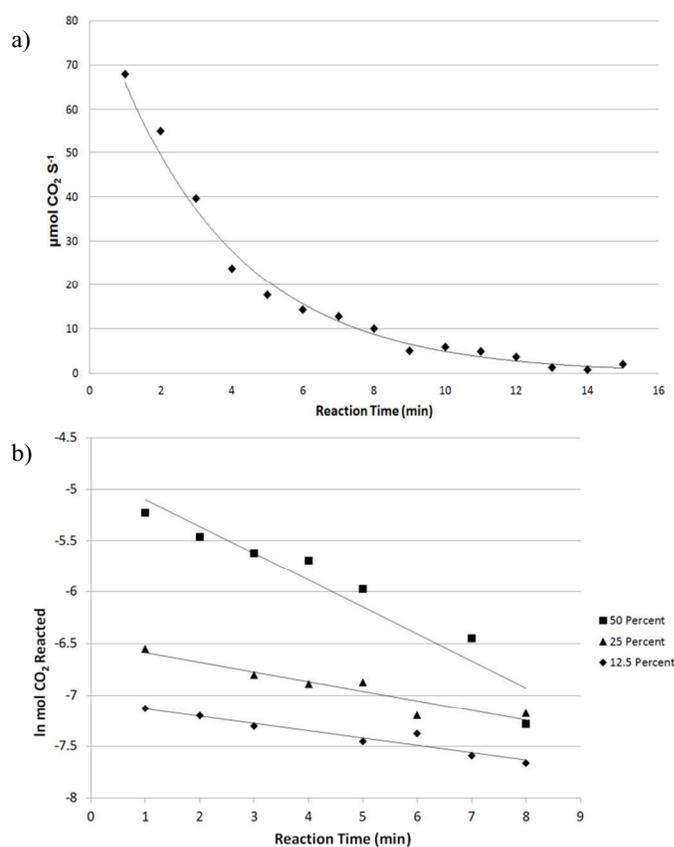**Figure 6** (a) CO_2 consumption in the Grignard reaction of 1M MeMgCl with 100% CO_2 by pressure drop detection. (b) Comparison of reaction rate at decreasing CO_2 compositions by dilution in N_2 with total gas flow rate of 100 mL/min

Table 2   Reaction rate constants of methylmagnesium chloride with CO_2/N_2 gas mixtures

Gas Composition (vol% CO_2)	Pseudo Rate Constants (s^{-1})
100	5.49×10^{-3}
50	4.36×10^{-3}
25	1.56×10^{-3}
12.5	1.19×10^{-3}

Table 3 Comparison of yields using pure CO_2 and dilute CO_2/N_2 mixtures with a selection of Grignard agents

| Entry	R	CO_2 (vol%)	Yield[a] (%)	Time (min)
1	Me-	100	82.5	20
2	CH_3CH_2-	100	91.8	20
3	iPr-	100	78.1	20
4	Ph-	100	92.4	20
5	XMg-Ph-	100	41.2[b]	20
6	$H_2C=CH$-	100	95.2	20
7	$H_2C=C(CH_3)$-	100	89.7	20
8	Me-	50	81.2	25
9	Me-	25	79.2	45
10	Me-	12.5	80.1	60
11	CH_3CH_2-	12.5	88.9	60
12	iPr-	12.5	74.2	60
13	Ph-	12.5	88.4	60
14	XMg-Ph-	12.5	42.1[b]	60
15	$H_2C=CH$-	12.5	95.0	60
16	$H_2C=C(CH_3)$-	12.5	81.1	60
17	Me-	0.05[c]	0.09	360

[a] Yield of isolated sodium carboxylate salt following NaOH quench of product. [b] Monocarboxylated product, *p*-bromobenzoic acid isolated in equimolar yield with terephthalic acid. [c] Dry Compressed air used

Table 3 shows Grignard reaction yields for a selection of alkyl and aryl substituents using different volumetric CO_2 concentrations. Grignard reactions are often dramatically affected by the reaction solvent and conditions so results shown in Table 3 may not be representative of those that *could* be achieved in a dedicated process where optimisation had been carried out. However, yields in almost all cases were high, regardless of the CO_2 concentration used and no other product was detected in work up mixtures other than the desired carboxylate salt (with the exception of the di-Grignard reagents in entries 5 and 14), indicating the expected extremely high selectivity, although longer reaction times naturally were required at lower CO_2 concentrations. Using lower concentrations of CO_2 for the reaction tended to have somewhat reduced yields, however this is likely due to additional exposure to potential contaminants owing to the longer reaction

period. Generation of terephthalic acid from the di-Grignard reagent derived from 1,4-dibromobenzene proceeded in disappointingly modest yield with approximately equimolar generation of the mono-substituted product, 4-bromobenzoic acid. This can be explained by the deactivation of the *para*-position on generation of the mono-substituted version of the starting Grignard reagent. Using more forcing conditions during the synthesis of the Grignard reagent and more reactive magnesium precursors has been found to improve yields of reactions of this type in the past.[19] Once again, optimisation of the reaction conditions and precursor formation will be essential for high yields to be realised.

Potential Side Reactions in a Capture Context

With the exception of the last entry in Table 3, all reactions were carried out in the absence of oxygen. However, in a genuine reactive capture scenario, non-negligible quantities of oxygen would be present and would likely represent the largest threat of unwanted side reactions when using a dried flue gas stream. Commonly quoted figures for such streams usually cite O_2 concentrations of around 3% by volume although this figure can vary dependent on combustion process and fuel.[20]

Oxygen is thought to react with Grignard reagents *via* the formation of peroxides, which disproportionate to form the corresponding alcohols after quenching with aqueous acid (Scheme 2).[21]
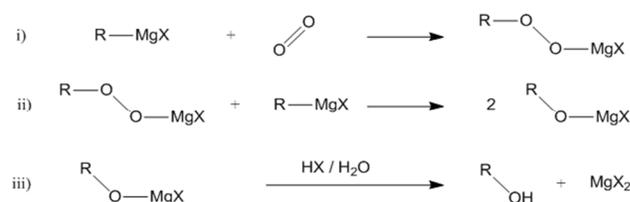
Scheme 2 Generalised reaction of a Grignard reagent with oxygen

Due to their sensitivity and explosive nature, the formation of any organic hydroperoxides, potentially by quenching the product from the first reaction shown above, would be very troublesome to a potential Grignard process. Thankfully, prior investigation of these species has shown that the second reaction in Scheme 2 is extremely rapid in comparison with the first, keeping peroxide concentrations negligible and preventing their isolation except when the reaction mixture is both saturated with oxygen and very cold.[22] Uncatalysed, the overall reaction of Grignard with oxygen at room temperature is generally slow and has a poor yield in comparison with that with CO_2. This is exacerbated when the Grignard reaction is carried out in a volatile ethereal solution such as diethyl ether. The ether is thought to form a protective blanket of solvent vapour at ambient or elevated temperatures.[23] However; this blanket effect may actually be an over-simplification of a more complex process than first thought since, in entry 17, the dry air was sparged through the reaction mixture in the same fashion as the other runs.

Previous literature measurements of reaction rates of simple diethyl ether-solvated akyl Grignards at room temperature with pure oxygen atmospheres demonstrated that over the course of an hour up to 43% of the initial Grignard reagent would react.[23] These results have shown that, with excess oxygen present, this reaction has pseudo-zeroth order characteristics, reacting at a steady rate of 6.67×10^{-7} mol s^{-1}. For comparison, the corresponding pure CO_2 atmosphere experiments demonstrate an initial reaction rate of 0.1087 mol s^{-1}, and an average reaction rate over the course of the reaction of approximately 5.9×10^{-3} mol s^{-1} some 8,850 times faster. Optimised CO_2-liquid contacting would be likely to improve this reaction rate further. The reactions carried out here, shown in Figure 6(b) and Table 2, have demonstrated that even when using 12.5% volume CO_2 gas, the addition of CO_2 is comparatively rapid compared with the literature values for O_2. The discrepancy in the reactivity of the two species is further demonstrated by entry 17 in Table 3, where compressed air, passed through a Drierite^{TM} column, was used as the CO_2 source. In dry air there is more than 500 times more oxygen than carbon dioxide by volume, yet a small yield of the acetate product was isolated. While this by no means demonstrates viability of atmospheric CO_2 utilisation by Grignard reagents, it confirms that under the right reaction conditions, the yield reduction caused by oxidation could be minimised, especially in oxygen-poor environments.

Other trace gases, especially the sulfur oxides, if dry, will also interfere with the reaction, generating the corresponding sulfinic acids.[24]
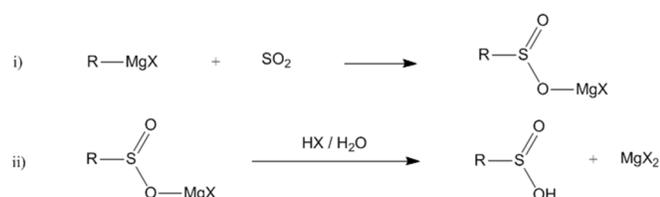
Scheme 3 Generalised reactions of a Grignard reagent with sulfur dioxide

While this process consumes the reagent and would diminish efficiency and selectivity, unlike with some reactive capture agents, such as MEA, there is no irreversible loss of the capture agent by interaction with the sulfur.[25] In the case being explored here, the magnesium chloride product is the same as that found in the reaction with CO_2.

The other major acidic gases, nitrogen oxides, are not known to react particularly with Grignard reagents without the presence of a transition metal catalyst. With these catalysts present, nitrous oxide, and also oxygen as previously mentioned, promote homocoupling of the alkyl or aryl moieties present or form other compounds such as hydrazones.[26]

In general, side reactions of this type are obstacles for all flue gas capture processes. However, as discussed above, the high reactivity of the Grignard reagents throws this into sharp focus. The question remains: in an optimistic scenario where these problems have been overcome or mitigated, what would be the cost of a Grignard CDU process?

Calculating Costs of a Grignard CDU Process

Naturally, the fact that a stoichiometric quantity of the magnesium reagent is required for the capture of the carbon dioxide could lead to the instant conclusion that Grignard reagents are totally unsuitable for CDU from an environmental perspective. However, further consideration of how the Grignard agent may be regenerated by electrolysis, thereby forming an electrolytic magnesium cycle, gives rise to a potentially sustainable, if high-energy, CDU process (Figure 7). Note that any electricity used in such a process must be derived from low-carbon sources or any carbon sequestration potential for the process is immediately reversed as more carbon must be emitted from the electricity production than would be stored in the resultant products.
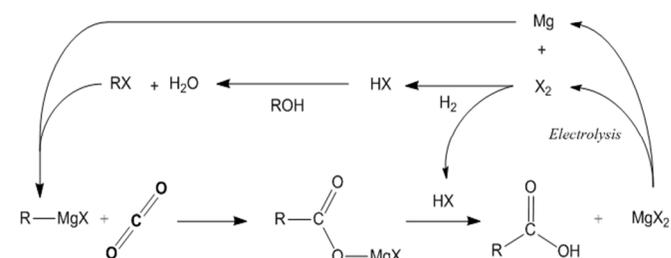
Figure 7 Grignard Reaction with regeneration

The net reaction of such a process would be the dehydration-carboxylation of alcohols using CO_2 and H_2. However, it should be noted that the organohalide reagent required to make the starting Grignard reagent need not be sourced from alcohols. If instead hydrocarbons such as methane or benzene were used, no hydrogen would be required in this process as halogenation of both can be carried out directly from the elemental halide under suitable conditions.

Magnesium and Halide Regeneration

All steps in such a process are readily achievable and exothermic with the exception of the electrolysis step to regenerate the starting magnesium and halogen. Magnesium regeneration from magnesium dihalide, specifically magnesium dichloride, is already a fully established industrial process, and one of the two main ways that metallic magnesium is manufactured.[27]

In this process, the magnesium dihalide (typically dichloride) is heated until molten, at 750-800 °C and then electrolysed requiring a molar electrode potential of 3.74 V. Typically, industrial magnesium production processes are reported to require 10.5–13.2 kWh per kg, including the drying and purification of the starting magnesium dichloride, which is a significantly energy-intensive part of the overall process.[28] In our proposed process, this step could be avoided by using either gaseous or alcoholic HCl (which is available as by-product of the formation of the initial alkylchloride from the parent alcohol) to quench the Grignard product. The resulting

magnesium chloride would then be much more readily dried, reducing electrical costs and opening a reaction pathway to direct formation of potentially valuable esters.

Furthermore, recent advances in the area of magnesium electrolysis particularly focused on rapid removal of the chlorine gas by-product have been able to demonstrate a reduction in the energy cost to just 7.0 kWh per kg.[29] This is very close to the theoretical minimum energy cost of this process of 6.2 kWh per kg magnesium or 542 kJ/mole, and represents an electrical efficiency of nearly 89%.

Even taking the more standard magnesium production process energy consumption figures, magnesium potentially represents an efficient energy vector for the net reduction of carbon dioxide by electricity.

The other product of magnesium electrolysis is naturally the elemental halide, which when using alcohols as reagents must be reacted with hydrogen to regenerate the acid for both the alkyl halide formation and the post reaction quenching. This reaction is also very exothermic. Typical hydrogen chlorine burners reach 2,000-2,500 °C with up to half of the combustion energy being recoverable.[30] It is easily to imagine that this high temperature reaction would further aid the magnesium chloride electrolysis by supplying the temperatures needed to melt the starting magnesium halide salt.

Aspen Plus ® Modelling

The model shown in Figure 8 was constructed and used to derive a preliminary Techno Economic Analysis of the reaction of methanol with CO_2 and H_2 *via* methyl magnesium chloride to generate acetic acid. This example was chosen for its simplicity and to be used as a basis to show just how expensive or otherwise a Grignard-based CDU system would be.

The model assumes a magnesium regeneration energy cost of 10.5 kWh/kg and quantitative yield of HCl from the reaction of H_2 and Cl_2, comparable with industrial processes. The extremely exothermic nature of the latter reaction is modelled

as supplying all the heat requirements of the plant, but no further energy recovery beyond this for the is included in the model.

The methanol chlorination reaction is assumed to be 94% yield, in line with industry performance, however the 5-6% by-product of this reaction, dimethyl ether (DME), is not given a value. The 5%-6% of the HCl that would therefore be expected to remain unreacted from the methanol chlorination step, primarily due to dilution by the by-product water and incomplete chlorination, can still be potentially utilised for quenching the Grignard reaction and so HCl utilization would be expected to be quantitative.

For simplicity, both the formation of the Grignard reagent and the subsequent reaction with CO_2 was assumed to also be quantitative. While this may seem to be rather optimistic, Grignard formation reactions, under appropriate conditions regularly reach extremely high yields.[21] Likewise, optimisation of the CO_2 reaction and workup did not therefore seem to be wholly unreasonable. Furthermore, the absence of any additional heat recovery from the essentially entirely exothermic reaction pathway and the overlooking the valuation of the DME stream will go some way to offset the ignored costs of a true Grignard-based system, which will naturally have some yield limitations, especially if an oxygen-containing gas stream is used.

Tables 4 and 5 summarise the outputs and base conditions of the model shown in Figure 8. At first glance, perhaps unsurprisingly, the production cost of acetic acid using such a process is significantly higher than that of the market value of the product. However, this is primarily an effect of the small production scale of the model, the scale of which is based on large existing Grignard plants in the US and UK.[31] From the point of view of acetic acid, this is an extremely small scale plant, with commercial acetic acid production facilities reaching a scale exceeding 500,000 tonnes per year. This point is emphasised by noting that the labour costs exceed that of the electricity and raw materials costs in Table 4.
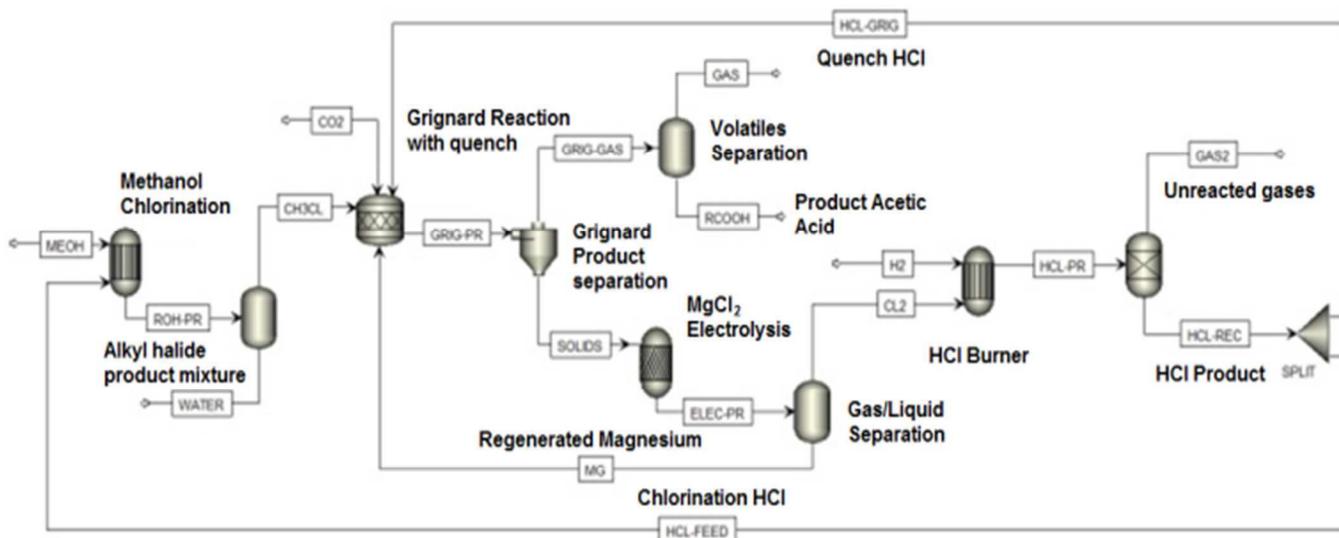

Figure 8 Aspen Plus® Model used for Preliminary Techno Economic Assessment of acetic acid production from Grignard reaction of methanol with CO_2

Table 4   Aspen Plus ® Model Outputs

Model Output	
Total Capital Costs	€4,835,230
Annual Cost of Capital	€567,944
Annual Labour Costs	€482,130
Annual Electricity Costs	€431,161
Annual Raw Materials Costs	€250,444
Total Operating Costs	€1,367,964
Production Cost (per tonne)	€3,217
Current European acetic acid value (per tonne)	€525

Table 5   Model calculation notes

Base Case Conditions, Model Notes and Assumptions	
Methanol	350 €/tonne
Hydrogen	4700 €/tonne
Carbon Dioxide	12 €/tonne
Electricity Supply	17 ¢€/kWh : 170 €/MWh
Plant Lifetime	20 years
Interest Rate	10%
Production Scale	602 tonne/a

Approximating the effect of increasing plant scale on production price from these results was then carried out using the "six-tenths rule".[32] As shown in Figure 9, this demonstrates that dramatic reductions in the production cost to levels comparable with current acetic acid market value could be achieved by increasing reaction scale. For example, a tripling of the reactor linear dimensions (which would increase reactor volumes and therefore production by around a factor of 27) would drop production cost to around €865 per tonne from the base case of over €3,200. Further size increases may even allow for profitable production of acetic acid in this way, however caution must be taken when dealing with extended extrapolations of this sort.
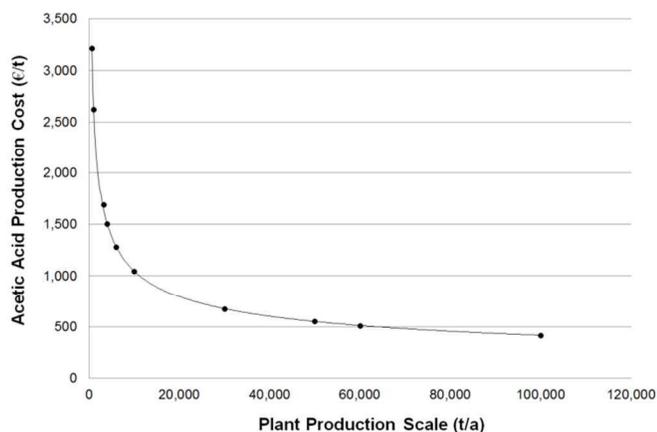
Figure 9   Projected Effect of Process Scale on Production Cost
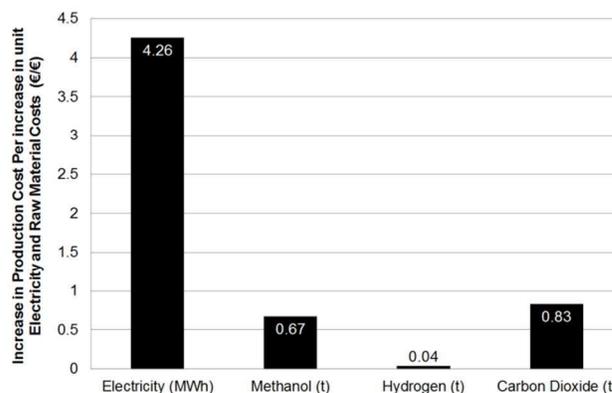
Figure 10 Model electrical and raw material price sensitivity measured as production cost increase per increase in unit price

Sensitivity analysis was also carried out to determine what effect both raw material and electricity price would have on the production cost of the acetic acid (Figure 10). Here, we can see that by far the most important cost is that of the electricity, as might be expected for an electrochemical cycle, with each change in the price per megawatt hour causing more than a four-fold change in production cost. The electricity figure used in the base case model in Table 5 is a relatively high one, representing the requisite renewable electricity, but this figure could easily be halved by more developed lower-cost low carbon sources. Dropping electricity costs in this way to €85 per MWh, within reported ranges for onshore wind and large scale photovoltaic sources, would then decrease production costs by over €360 per tonne.[33]   This effect would proportionally complement any drop in production cost by increasing the reaction scale.

Other Potential Products

As previously mentioned, acetic acid was chosen due to its simplicity; however that same simplicity and acetic acid's market as a bulk chemical makes it an especially difficult target for this process from an economic perspective due to the relatively low value of the product. In comparison, many of the other carboxylic acids show previously in Figure 3 have significantly higher value. This would mean that the value-added by the addition of CO_2 *via* Grignard chemistry would be larger, making the overall process far more economically enticing, even if the process cost is high.

This effect is especially apparent in the polymer precursors; adipic, acrylic and terephthalic acids where the cost differential between the starting material and product in a putative Grignard process is significantly larger than that of acetic acid from methanol (Figure 11).
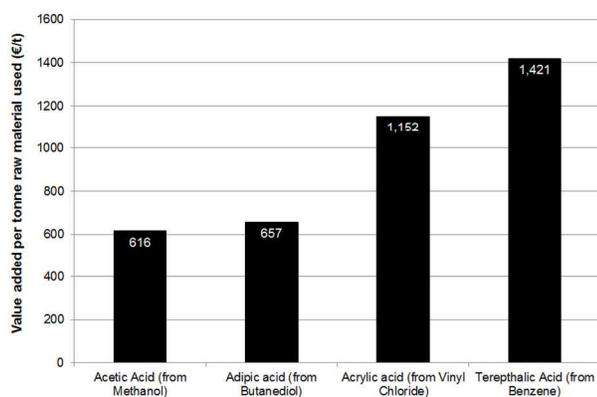
Figure 11 Value added by addition of CO_2 to starting compound (in brackets). Average 2013 prices used

However, it should be noted that no direct comparison between these putative processes and that of the acetic acid model should be carried out due to stark differences in reaction profile, energetics and potential yields.

Experimental

With the exception of the di-grignard product of 1,4-dibromobenzoic acid, all Grignard reagents were purchased in THF solution from Sigma Aldrich and used without further purification. Reactions were performed using Schlenk techniques under inert (N_2) atmosphere unless otherwise indicated. HPLC grade THF was dried by storage over freshly-regenerated 3Å molecular sieves *ca.* 30% by volume. CO_2, N_2 and compressed air were supplied by BOC-Linde. CO_2 and N_2 mixtures compositions were achieved using a pair of Bronkhorst 100mL/min Mass Flow Controllers. Compressed air was dried using a Drierite[TM] 8 Mesh Laboratory Drying Unit. ^{1}H NMR spectra were recorded using a Bruker Avance 400MHz spectrometer with D_2O (99.9% D). Pressure data were recorded using an Omega PX409USB High Accuracy Pressure Transducer. Grignard concentrations were verified by titration with 2-butanol (99+%) and 1,10-phenanthroline (99.5%). Modelling was conducted using Aspen Plus®om AspenTech .

General procedure for kinetic investigation of Grignard reaction with dilute CO_2

An oven-dried 2-neck 100 mL round bottom flask with attached empty cold-finger condenser was charged with THF (20 mL dried over 3Å molecular sieve) under nitrogen using Schlenk techniques. Using a needle adapter the flask was then connected to a sparging needle and a flow of 100 mL/min of selected CO_2 gas mixture, venting through a silicone oil bubbler. To avoid any amount of water condensation within the reactor during set-up, gas flow was carried out for 20 minutes before a freezing salt-ice slurry was added to the cold finger. A normal ice bath was then placed around the reaction vessel and an additional 30 minutes was given to allow the temperature to equilibrate. A measured volume of 3M MeMgCl sufficient to achieve 1M overall concentration of the Grignard solution (10mL) was then swiftly added to the vessel under positive nitrogen pressure, and

reaction timing initiated. Every 60 seconds, the CO_2-containing gas flow in and out of the reactor was paused for a set period of time (10-20 s) before being resumed, as pressure readings were logged every 0.2 seconds. Reaction was deemed complete when no pressure drop was observed during a prolonged gas flow pause. Aqueous HCl (3.5 M) was then slowly added to the reaction mixture until the mixture clarified and gave an acidic reaction on indicator paper. To this mixture aqueous NaOH (1 M) was then added until the reaction mixture became basic, and a cloudy suspension of salts formed. The basic mixture was then evaporated until dry by rotary evaporation. An accurately weighed sample of the dry salt mixture was then dissolved in D_2O (2 mL) with the addition of DMSO (10 μL) as an internal reference for NMR spectroscopy.
^{1}H NMR (400MHz D_2O) δ (ppm): 2.81 (s, 6H, DMSO), 1.94 (s, 3H, CH_3COO). Integration of the individual peaks is then used to determine carboxylate yield.

Conclusions

In summary, a series of experiments were carried out to determine the reaction kinetics and feasibility of the reaction of Grignard reagents with dilute sources of CO_2 in N_2. From these results, it was determined that high yield reactive capture of dilute CO_2 is possible with Grignard agents. Although oxygen concentration in any gas stream will likely hamper yields, the previously-measured rate of reaction with oxygen has been found to be nearly negligible in comparison of that with CO_2.
A preliminary techno-economic analysis was also carried out, to determine the economic feasibility of such a capture process to be used for production of acetic acid from methanol, using industrially-relevant data and a simplified reaction process model. It determined that when scaling factors were taken into account, the production costs of acetic acid by this method were comparable with existing market prices.
While a more complete costing and detailed assessment could very possibly demonstrate the economic infeasibility of the described process under less favourable conditions, the assessment carried out here suggests that the use of a Grignard reaction cycle to generate acetic acid from methanol is not perhaps as absurd as would be expected.

Acknowledgements

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