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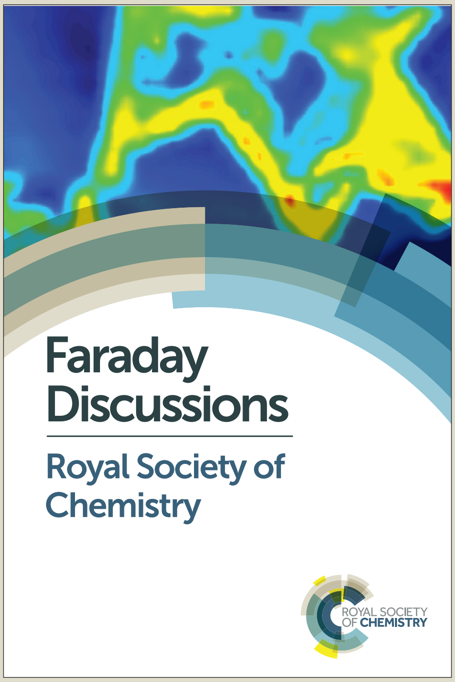

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A framework for the analysis of the security of supply of utilising carbon dioxide as a chemical feedstock

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25th May 2015

Recent developments in catalysts have enhanced the potential for the utilisation of carbon dioxide as a chemical feedstock. Appropriate catalysts make possible and/or energy efficient a range of chemical pathways to desirable products. In doing so, CO_2 provides an economically and environmentally beneficial source of C_1 feedstock while improving security of supply issues related to fossil based feedstocks. However, the dependence on catalysts brings other supply chains into consideration, supply chains that may also have issues of security. The choice of chemical pathways for specific products will therefore entail an assessment not only of economic factors but also security of supply issues for catalysts. This is a multi-criteria decision making problem.

In this paper, we present a modified 4A framework, based on the framework suggested by the Asian Pacific Energy Research centre for macro-economic applications. The 4A methodology is named for the criteria used to compare alternatives: availability, acceptability, applicability and affordability. We adapt this framework for the consideration of alternative chemical reaction processes using a micro-economic outlook. Data from a number of sources are collected and used to quantify each of the 4A criteria. A graphical presentation of the assessments is used to support the decision maker in comparing alternatives. The framework not only allows for the comparison of processes but also highlights current limitations in the CCU processes.

The framework presented can be used by a variety of stakeholders, including regulators, investors, and process industries, with the aim of identifying promising routes within a broader multi-criteria decision making process.

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Keywords: Carbon capture and utilisation; security of supply; catalysis; multi-criteria decision making

1 Introduction

Carbon dioxide (CO_2) is a non-toxic and abundant C_1 (1 carbon atom) feedstock. The release of CO_2 has contributed to global warming and the greenhouse effect making emissions an increasing concern for society and policy makers. In recent years carbon capture and sequestration (CCS) has been mooted as the solution to controlling emissions but has raised the question of what to do with the increasing large amounts of CO_2. A potential solution is to use CO_2 as a chemical feedstock and a raw product in the production of chemicals. This is known as carbon capture and utilisation (CCU).

There are several benefits that arise from the utilisation of carbon dioxide as a chemical feedstock.[1] Firstly, like CCS, CCU is able to mitigate emissions of carbon dioxide through capture. CCU, unlike CCS, may allow for a closed loop recycling system. Secondly, an economic benefit may arise from the generation of economically valuable products. Finally, it may help address an individual country's security of supply for energy.

As C_1 feedstock is currently predominantly sourced from oil derived hydrocarbons, security of supply for oil may be a concern. Most nations depend on foreign oil imports, often from areas of geo-political instability. As a result, market volatility and uncertainty disrupts national sustainability and forward planning. Through a carbon economy, reliance of volatile sources of oil could be mitigated or even eliminated through the use of secure domestic carbon sources.

Currently, there are a few chemical pathways that utilise CO_2 on a commercial scale: the production of urea, salicylic acid and sodium carbonate. However, CO_2 utilisation has a key limitation. CO_2 is a kinetically and thermodynamically stable molecule. This results in a high activation energy and a large quantity of energy may be required to react carbon dioxide. Unfortunately, energy generation currently emits more CO_2 than would be consumed in generating valuable products, leading to an overall net increase in emissions. Although these emissions could be reduced or eliminated through the use of renewable energy generation, any energy requirements could also be ameliorated through the development of suitable catalysts as can the potentially high activation energy. This has led to an increasing level of research and development in the field of catalysis. This research is leading to new potential products that can be derived from CO_2 as a feedstock.

However, the use of catalysts brings up the issue of security of supply yet again. Many catalysts are made from rare materials and these materials may also be sourced from geo-politically unstable regions. Recycling of many of the catalysts may be difficult.[2] This paper presents a methodology for the assessment of alternative CO_2 utilisation routes, incorporating a number of factors that may characterise the security of supply. The methodology provides an attractive graphical visualisation of the characteristics of an individual route which enables the comparison of alternatives. This may help decision makers identify those routes which best achieve the potential benefits of CCU with improved security of supply.

2 Carbon dioxide as a feedstock

The pathways currently utilising CO_2 on an industrial scale are few. Examples include the Solvay process to produce sodium carbonate,[3] the production of urea via the Bosch-Meiser process,[4] and the production of salicylic acid through the Kolbe-Schmitt process.[5] These only account for a fraction of the number of pathways theoretically possible using CO_2 as a C_1 feedstock. Alternative pathways are being considered and a selection of these are summarised in Table 1, grouped according to the compounds used to react with CO_2.

Table 1: Summary of CO_2 pathways

Group	Substrate	Product
Oxygen containing compounds	Epoxides	Cyclic carbonate
		Alternating polycarbonates
		Aromatic polycarbonates
	Alcohols	Acyclic carbonates
Nitrogen containing compounds	Ammonia, amines	Urea
		Carbamic acid esters
		Polyurethanes
Carbon-carbon	Aromatic compounds	Carboxylic acids
Unsaturated compounds	Alkynes	Carboxylic acid esters
	Alkenes	Lactones
Other	Hydrogen	Formic acid
		Methanol

Many of the routes in Table 1 are currently commercially viable. Table 2 illustrates the level of production for some of these processes. The most mature CCU process is the production of urea. The rates for the other CCU routes are orders of magnitude smaller. The level of production of each of these products correlates well with the level of development in terms of technology.[6] A summary of the utilisation levels is presented in Table 3 with polymers separated out into individual products.

Given the level of technological development, current market saturation and potential demand, we can shortlist promising CCU product targets for immediate consideration:

1. methanol
2. urea
3. formic acid
4. polymers, mainly polyalkylene carbonates
5. cyclic carbonates

The promise in technologies for the production of these targets derives predominantly from catalyst development. However, in order to determine commercial viability, the

Table 2: Current levels of production of products showing levels for both CCU and traditional (non CO_2) routes.

Chemical	CO_2 utilising production (kT)	Global Production (kT)	CO_2 % (%)
Cyclic carbonates[7]	80	200	40
Formic acid[8]	0	300	0
Methanol[9]	4	100,000	≈ 0
Polypropylene carbonate[10]	76	≈ 0	0
Polycarbonate[11]	605	3,700	16
Salicylic acid[6]	90	90	100
Urea[12]	157,000	157,000	100

Table 3: Current state of carbon capture & utilisation technologies. A double ✓ indicates significant levels of activity and a single ✓ an area that is showing increasing levels of acitivity.[6]

Technology	Research	Demonstration	Feasibility	Mature Market
Chemical Production				
Acyclic carbonates	✓✓			
Alternating polycarbonates	✓✓	✓		
Aromatic polycarbonates	✓✓	✓		
Carboxylic acids	✓✓			
Carboxylic acid esters	✓✓			
Cyclic carbonates	✓✓			
Lactones	✓✓			
Polyurethanes	✓✓	✓		
Sodium carbonate				✓✓
Urea				✓✓
CO_2 to fuels				
Methanol		✓✓	✓	
Formic acid	✓✓	✓		

security of supply for each overall process must be considered. The next section describes a methodology for assessing the security of supply and presenting this in the context of other factors that decision makers will wish to consider.

3 Methodology

The target products described above illustrate the potential for effective CO_2 utilisation. However, beyond purely economic and technical issues, other aspects may affect the adoption of any particular route to a product. One such aspect is the *security of supply*. This term is most often used in the context of energy and is defined as follows:

> "the ability of an economy to guarantee the availability of energy resource supply in a sustainable and timely manner with the energy price being at a level that will not adversely affect the economic performance of the economy."[13]

In the context of energy, security of supply is dependent on 5 main factors: availability of fuels domestically and externally, the ability to acquire supply to meet demand, level of an economy's diversification, accessibility to fuel resources through sufficient infrastructure, and geo-political challenges in sourcing energy. From these factors the Asian Pacific Energy Research Centre (APERC), proposed the categorisation of these factors into *availability*, *accessibility*, *acceptability* and *applicability*, collectively called *the 4 As of Energy Security.*[13]

We adapt this 4As approach to the security of supply to the case of CO_2 utilisation. The framework proposed by APERC was intended for a macro-economic analysis of the energy system. Each A value was quantified on the basis of macro-energy system characteristics.[13] In the context of CO_2 utilisation, it makes sense to also consider smaller scale analyses, e.g. at the process route level, while still including macro-economic aspects. The key is the suitable re-definition of the 4A categories for their application to CO_2 utilisation. In what follows, we will be defining the parameters that quantify each A with a value between 0 (bad) to 10 (good).

3.1 Availability

The availability of the supply side of the product will be defined by the catalyst. The catalyst is often the limiting factor in the production rate. Further, few of the catalysts used for the products noted above are replaceable because many are tailored for the specific reaction. The availability of the catalyst will be estimated using a combination of parameters:

Crustal abundance is a measure of the scarcity of a metal on a macro scale with the abundance measured in parts per million.[14] For example, the abundance of ruthenium is 0.00057 ppm, which indicates a high risk catalyst, whereas aluminium, with an abundance of 84149 ppm, would be low risk. Each metal within each of the catalysts is given a score based on its abundance, as quantified in Table 4.

Table 4: Crustal abundance Scoring

Abundance (ppm)	Score
≥ 100	4 (low risk)
50-100	3 (medium/low risk)
1-50	2 (medium/high risk)
<1	1 (high risk)

Production concentration is an indicator of the distribution of regions in which the metal is produced and data are provided by the British Geological Survey.[15] A commodity with a limited distribution of production is at a higher risk than one produced in many places around the world. For instance, 91% of iridium is produced in South Africa and the top 3 countries producing iridium control 98% of the global production. In contrast, the cumulative production of the top 3 copper producers accounts for less than half of the global production. A score is allocated to the geographic concentration of metals production concentration as shown in Table 5.

Table 5: Production Concentration Scoring

Concentration (%)	Score
0-25	4 points
25-50	3 points
50-75	2 points
75-100	1 point

Reserves Concentration Reserves concentration is similar to the production concentration but relates to the distribution of the reserves. A score is allocated to the metals reserve concentration as shown in Table 6.

Table 6: Reserves Concentration Scoring

Concentration (%)	Score
0-25	4 points
25-50	3 points
50-75	2 points
75-100	1 point

Political Corruption and Stability Political corruption has become an increasing concern as black-market dealings and market inconsistencies reduce the transparency of what should be a free market. Societal pressure is also increasingly a factor. Whilst corruption has an effect on stability, both factors are included separately. This is because political instability will describe the current situation whilst political corruption could lead to increased instability due to pressures on the system. The measures for corruption and stability are based on data from the World Bank.[16] These data provide an index rating of political corruption and stability in [1,100] where 1 is the most corrupt/unstable and 100 the least. We have mapped the index rating to scores for our framework as shown in Table 7. This factor contributes 4 values to the overall availability measure: a value of stability and of corruption separately for each of two countries, the top producer and the country that has the most reserves.

Table 7: Political Corruption & Stability Scoring

Measure	Score
75-100	4 points
50-75	3 points
25-50	2 points
1-25	1 point

The maximum score for availability based on the above is 28 (4×7). A perfect score of 28 means that a metal has high levels of availability where both the production and reserves are not highly concentrated in single regions and the main producers and owners of reserves present low levels of corruption and high levels of stability. A scaled value in the desired range was achieved by dividing the sum of the all of the above by 2.8.

In calculating the availability of the catalyst material, we have firstly assumed that there is an equal weighting between each of the parameters in terms of importance. For example, the extent of corruption in the country where the reserves are held is as important the abundance. Secondly, in measuring the abundance of a mineral, the abundance measure does not take into account the spatial distribution within a region. For example in one region there may be an abundance of zinc although it may be spread uniformly over the whole region. This means the crustal abundance may not necessarily be a realistic measure of the ability to extract the material through mining. Finally, this index is based on results at one point in time and does not including future projections and historical context. These assumptions can, of course, be addressed subsequentaly and the scorings adapted, if desired.

3.2 Affordability

The second A is economic, based on the revenue generated per unit of catalyst:

$$\text{catalyst to evenue ratio} = \frac{\text{catalyst price}}{\text{product price} \times \text{product amount}} \tag{1}$$

This assumes an equal turnover frequency for all catalysts which is not typically the case. For instance, cheaper catalysts may have a shorter life than a more expensive or robust catalyst. However, the measure should be appropriate as an indication of affordability. Other measures of affordability could be used, of course. In any case, the mapping of ratio to score is shown in Table 8.

Table 8: Affordability Score System

Catalyst to revenue ratio	Score
0-0.001	10 points
0.001-0.0025	9 points
0.0025-0.005	8 points
0.005-0.01	7 points
0.01-0.025	6 points
0.025-0.05	5 points
0.05-0.1	4 points
0.1-1	3 points
1-10	2 points
10-20	1 points
20+	0 points

It is worth noting that the process cost is not considered, only the cost of any catalyst required. This is based on the assumption that the general plant cost is comparatively less volatile and hence affects security of supply negligibly. It is also assumed that other raw materials will have lower costs than the catalyst, which is generally the case.

3.3 Applicability

Applicability has been defined according to the technological readiness level[17] (TRL) of the process. The TRL rating is a systematic approach that assesses the level of maturity for a given technology, allowing for consistency in comparison. The TRL method classifies a technology into one of 9 levels from level 1 indicating that the basic principles are understood through to level 9 indicating commercial operations exist. The TRL is incorporated by scaling by 10/9.

3.4 Acceptability

The final A value is dependent on two main parameters: a life cycle assessment (LCA) in terms of CO_2 emissions (Table 9) and a measure of the lifetime of storage of CO_2 in the product (Table 10). The use of these factors is motivated by one of the key motivations for CCU: the need to reduce the impact of CO_2 emmisions on the global climate. The life storage measure for carbon dioxide in a product is included to mitigate the lack of comparable LCA data in some cases. For example, methanol may have only have temporary storage due to its use as a combustible fuel whereas polyalkylene presents a long term store for the CO_2. The scores from the two factors are combined with equal weighting after scaling to yield a score in the range [1,10].

Table 9: LCA Score System based on the ratio of amount of CO_2 emissions to the amount of CO_2 utilised in the process.

Ratio	Score
0-0.5	10 points
0.5-1	9 points
1-1.5	8 points
1.5-2	7 points
2-2.5	6 points
2.5-3	5 points
3-3.5	4 points
3.5-4	3 points
4.5-5	2 points
5+	1 point

Table 10: CO_2 life storage in the final product.

Storage Life	Score
No Storage	1 point
Temporary Storage	2 points
Permanent Storage	3 points

3.5 Visualising the 4As

The 4As framework described above generates a quantitative assessment of the individual factors. Displaying this multi-dimensional information can be done in variety of ways. We have chosen to use star charts, otherwise known as *radar charts* and *spider charts*, to present this multi-dimensional information. This is a simple graphical representation that facilitates comparing different alternatives and is illustrated in Figure 1.

Each of the 4 measures is itself an indicator of the security of supply for a given process but it is the overall combination these factors that needs to be compared when looking at alternative catalysts and products. A perfect rhombus is an illustration of a technology that would be considered to have a secure supply.

3.6 Assumptions

There have been 5 key assumptions made in this framework:

1. The catalyst is the limiting factor for the success of the process. Given that overcoming the thermodynamic constraints of carbon dioxide based reactions is the key, this is assumption is reasonable.

2. A second assumption is that the availability and the affordability are dependent solely on the catalyst. We assume that the general plant cost and material sourcing is comparatively less volatile given known knowledge of developing chemical

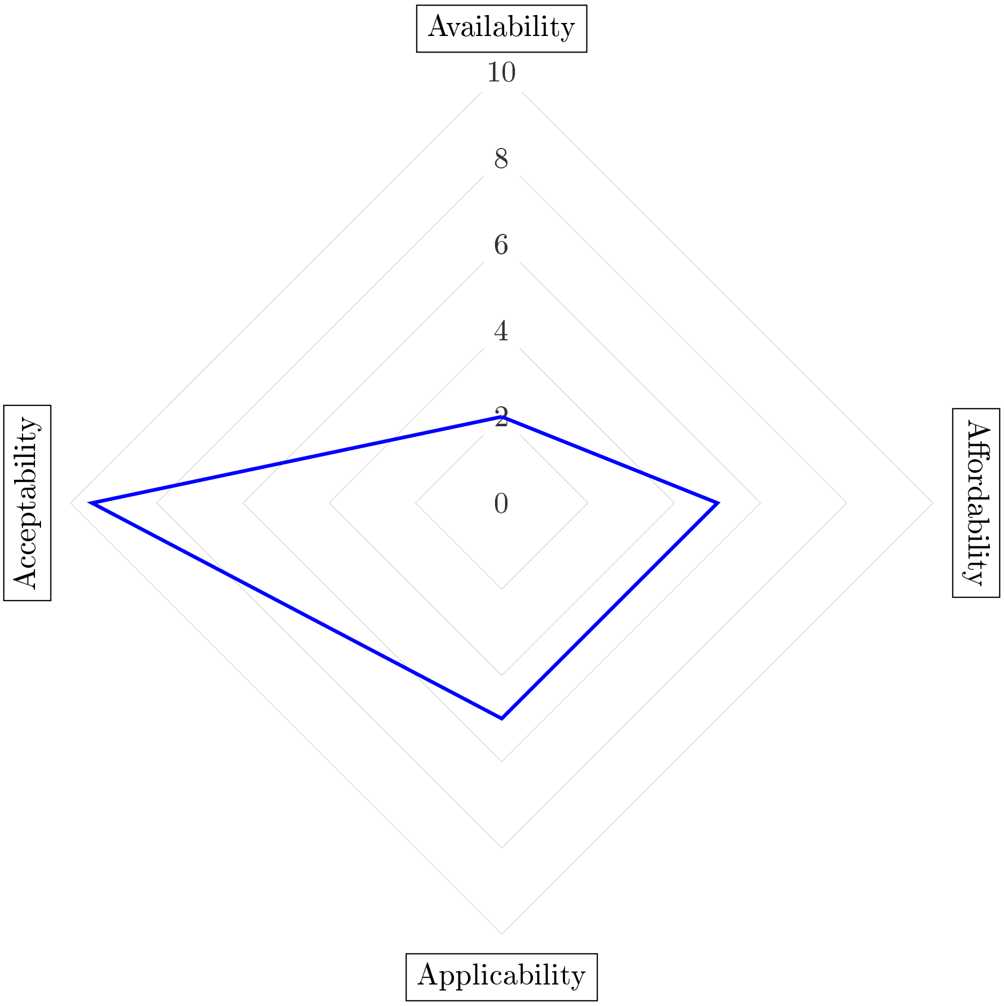


Figure 1: Example radar chart for visualising the 4A measure showing a case with high acceptability (score of 9.5), low availability (2) and average applicability (5) and affordability (5).

process. For example, in processing polyalkylene carbonates, the majority of the processing units will be similar if not the same for a process without CCU and one with CCU. However, the catalytic reactor and the capture cost are the key differences in the processes.

3. The turnover frequency (TOF) is assumed to be the same for different catalysts. This is not true in general but we believe is sufficient for an initial comparison. A more accurate approach would involve a full economic analysis, including product revenue and catalyst costs. These data are often proprietary and therefore difficult to obtain generally.

4. Equal weighting is given to sub-items within each category, e.g. corruption versus stability within the availability category. For specific cases, it may be useful to have non-equal weightings. This would be straightforward to implement should it be desirable.

5. The results presented below are based on current estimates for each of the categories with no attempt at projecting into the future. For instance, the political situation in relevant countries may change, new sources of raw materials may be discovered or improved mining operations could change the affordability of a specific catalyst. Also, historical context could be useful in estimating the values of some of the sub-items, especially in terms of the impact of stability or corruption on availability. However, updating individual inputs to the framework is straightforward.

It is also worth noting that the framework need not be limited to 4 categories. In fact, it is highly likely that further economic considerations for the particular product, e.g. process cost and market demands, would be included to define a 5As framework. We have not included such elements as the data required are often sensitive and company specific. The overall methodology, however, does not preclude such an extension.

4 Carbon utilisation targets and processes

The information required for the assessment of each target, on the basis of the methodology described above, is given in this section. The various processes, including both chemistry and actual processing, are described and any catalysts required specified.

4.1 Urea

Urea accounts for approximately 50% of global nitrogen fertiliser production. Urea has the highest concentration of nitrogen of all solid nitrogenous fertilisers which are widely used in agriculture.[18] Ammonia, a key reactant for the production of urea, and urea plants are often combined as one plant.[19]

The basic synthesis of urea has been established since 1922, a process known as the Bosch-Meiser process.[4] The process consists of two main equilibrium reactions. The first is carbamate formation in a fast exothermic reaction which is then followed by urea conversion, a slow endothermic decomposition of the ammonium carbamate into urea and water.

$$\begin{aligned} 2\,\mathrm{NH_3} + \mathrm{CO_2} &\rightleftharpoons \mathrm{NH_2COONH_4} \\ 2\,\mathrm{NH_2COONH_4} &\rightleftharpoons \mathrm{H_2O} + \mathrm{NH_2CONH_2} \end{aligned}$$

The synthesis of urea is a non-catalytic process and therefore does not require any catalyst material.

Interestingly, historically, the production of ammonia has often exceeded the amount required stoichiometrically when compared with the amount of CO_2 readily available for the production of urea. Combined ammonia and urea plants would sell the surplus ammonia because the cost of CO_2 to meet the deficiency was not economically justified. However, with the potential increase in CCS, there would be an opportunity to boost urea production economically in these plants. This is known as the KM-CDR process, which is used to enhance the yield in urea production.[19] This aligns well with the desire to increase CCU.

4.2 Polyalkylene Carbonate

Polyalkylene carbonates are polymers that have a range of uses from biodegradable polymers in medical use to high temperature tolerance polymers. Polypropylene carbonate, a polyalkylene derivative, is amongst the most promising polymer products. The synthesis of polyalkylene carbonates is through the reaction between epoxides and CO_2. The process conditions determine the generated product. Conditions can vary from 30-40 °C for polymers obtained from polypropylene oxide and up to temperatures of 110-120 °C for polymers from cyclohexene epoxide. Pressure also has an impact on the reactions.[20] Current methods utilise biomass feedstocks. If CO_2 were used to generate these polymers, competition with food production would be reduced (which highlights that security of supply is also an issue for food and water, but out of scope for this paper).

Various catalysts have been researched for the co-polymerisation process. Inoue *et al.*[21] discovered that the combination of $ZnEt_2$ and water allowed viable catalyst performance for the co-polymerisation of carbon dioxide and propylene oxide. Further validation on the performance of a zinc catalyst was made when Kawachi *et al.*[22] demonstrated high catalytic activity for polymerization of epoxides and CO_2. Previous varieties include aryl, alkyl, diimines, Schiff bases and zinc compounds. More recently, researchers have focused on 3 main catalysts: chromium, cobalt and zinc. For example, Noh et al.[23] discuss the reaction between carbon dioxide and propylene oxide in the presence of Co(salen). The cobalt catalyst showed a superior turnover number at 22,000 g/gcat[23] whilst zinc only yields a turnover value of 1441 g/gcat. The catalyst proved to be highly active in the reaction for CO_2 and propylene oxide co-polymerization although commercial viability of the process has yet to be demonstrated.

4.3 Formic Acid

Formic acid, HCOOH, has a wide range of uses including silage, additives to pharmaceutical intermediates, and as a fundamental feedstock in the chemicals industry to produce aldehydes, ketones and carboxylic acids.[24] More recently there has been strong interest in utilising formic acid within fuel cells due to its strong electrochemical oxidation ability for Pt-Ru electrodes. Formic acid is traditionally produced through the reaction of methanol and carbon monoxide which produces an intermediate, methyl formate:

$$CH_3OH + CO \longrightarrow HCOOCH_3$$

Hydrolysis then produces formic acid and methanol:

$$HCOOCH_3 + H_2O \longrightarrow HCOOH + CH_3OH$$

However, the hydrogenation of CO_2 is also possible using both transition and non-transition metal compounds as catalysts with a resulting benefit in a reduction of the cost of raw materials:

$$CO_2 + H_2 \longrightarrow HCOOH \tag{2}$$

Farlow[25] investigated the reaction in the presence of a nickel catalyst under high pressure, 20-40 MPa, and high temperature, 353-423 K. This eventually progressed to favourable conditions (298 K) through catalyst complexes of Ru or Pd combined with halides and hydrides.[26] Simultaneously, there has been research in homogeneous catalysts, such as supercritical CO_2, water and ionic liquids. This can achieve comparable reaction rates to transition complexes in the supercritical phase. However, the heterogeneous catalysts proved more attractive as the separation of the formic acid from the catalyst is easier. An activated carbon supporting ruthenium through impregnation is preferred as it does not use hazardous and expensive reagents used in other approaches.[8] Using ruthenium as the active component results in high activity and selectivity.

4.4 Methanol

Methanol is widely used as a fuel for transport and as a chemical feedstock.[27] There are over 90 process plants worldwide producing 75 million tons of methanol annually.[9] Methanol has traditionally been produced through fossil fuels via syngas chemistry. Therefore, elements of energy security of supply come into play in global methanol production from C_1 feedstocks. However, recently, new pathways and catalysts have been developed.

Olah[27] devised an approach to produce methanol through what is known as "metgas". Metgas is composed of CO and H_2 at a 1:2 ratio through a single step by reacting CO_2, 3 CH_4 and steam. This is known as *bireforming*. The temperature is high, 1073-1273 K, whilst pressure is held between 0.5-4 MPa in the presence of a nickel based catalyst:

$$3CH_4 + CO_2 + 2\,H_2O \longrightarrow 4\,CO + 8H_2 \longrightarrow 4\,CH_3OH \tag{3}$$

The hydrogenation of CO_2 has become an increasingly promising solution given an appropriate catalyst. The conversion has favourable thermodynamics although the high activation energy barrier remains a challenge.[28] Heterogeneous catalysts have therefore been widely investigated. Copper has proven to be the most favourable catalyst. With the use of copper catalysts, such as Cu/ZnO, CuO/ZnO and $CuO-ZnO/ZrO_2$, the hydrogenation proceeds at lower temperatures and under higher pressures.

4.5 Cyclic carbonates

Cyclic carbonates are commonly used as degreasing agents, polar aprotic solvents and electrolytes for lithium ion batteries.[7;29] Cyclic carbonates can also be converted into dimethyl carbonate which is used as a quality oxygenating additive for both petrol and aviation fuel. The main chemical pathway for cyclic carbonates is the reaction between epoxides and carbon dioxide.

The development of the catalysts and the mechanisms for this reaction has been well documented over several permutations of catalysts, including organic bases,[30] zeolites, metal oxides,[31] alkali metal halides[32] and metal complexes.[7] Whilst the synthesis has been applied to industry with a variety of such catalysts, the recovery and stability of the catalysts itself has yet to be improved. More recently, research has focussed on using ionic liquids as the catalyst due to advantageous negligible vapour pressures.[33] The use of ionic liquids as a clean catalytic form has proven to improve reaction rate and reaction selectivity. However, the use of ionic liquids exhibits low catalyst stability and activity and requires a co-catalyst. Whilst Dai *et al.*[34] suggested that the performance was substantiated through the use of Lewis acidic compounds as co-catalysts, it still held industrial limitations due to challenges in separation. Recent research has begun to tackle this by immobilising the ionic liquid onto solid supports.

A further form of catalyst proposed for this reaction has been through using metal complexes such as Co, Cr, Ni, Al, Zn and Re mounted onto supports. North & Young[7] have proposed a catalyst based on bimetallic aluminium (acen) complexes. This allows the reaction to take place at room temperature and at atmospheric pressure.

5 Assessing carbon utilisation targets

The 4As methodology has been applied to the processes described above. Table 11 summarises the results which are also presented using radar charts in Table 12 for easy comparison. Data from a number of sources,[15;16;14;18;6;27] along with those cited in the discussion above and below, were used to determine these scores. For all the categories, except for acceptability, the scores cover almost the full range of values possible, indicating that the scoring system for these categories is able to discriminate between alternatives. The acceptability scores cover only half of the range. This is due mostly to the energy requirements of each process. Currently, energy sources are typically not carbon neutral and so there is significant impact on emissions in each case. What these scores show, besides the possibility of comparing the alternatives, is that there is scope for improvement, in this category in particular.

The results can be used to identify which processes show the most promise, in comparison with the others, in the context of security of supply. For each individual case, the

Table 11: Summary of scores for each process/catalyst combination. The maximum score in each category is 10.

Product	Catalyst	Avail.	Afford.	Applic.	Accept.	Average
Cyclic carbonates	Al	5	9	2	4	5
Formic acid	Ir	5	1	3	2	3
Formic Acid	Ru	5	2	3	2	3
Methanol	Cu	7	8	6	4	6
Polyalkylene carbonates	Co	3	5	9	4	5
Polyalkylene carbonates	Zn	7	9	9	4	7
Urea	Ru	5	2	10	5	5
Urea	none	10	10	10	5	9

different factors can help focus the attention on any aspects that could be addressed by stakeholders to reduce supply risks. The benefit of the 4As model for a process is that the nature of future and current challenges can be efficiently identified.

Some discussion about each target process follows.

5.1 Urea

Urea overall is the most promising target with maximum values for three of the criteria. First of all, the applicability is high because the process has been used for a long time and is well established. With respect to availability and affordability, the process requires no catalyst. It is useful to compare this process for the production of urea with an alternative that is based on the use of ruthenium as a catalyst.[35]

In either case, the acceptability score ranked second overall. This is due to unfavourable CO_2 emissions by the processes.

5.2 Polyalkylene carbonate

Two different catalysts, cobalt and zinc, have been considered for the production of polyalkylene carbonates. The radar charts for the two options (second row of Table 12) show significant differences, particularly in availability and affordability. Zinc is more easily available and also more affordable when compared with cobalt (see Table 13). In both cases, the relatively low score for acceptability was mostly due to CO_2 emissions.

For availability, a zinc catalyst is preferred for both economic and geo-political factors. Cobalt is 3 times less abundant than zinc and the production levels of zinc are 84 times that of cobalt. The ability to source the catalyst is also a consideration: 81% of cobalt production is concentrated in 3 producing countries whilst only 49% of zinc production is in its top 3 producing countries. The risk to supply is lower for zinc, i.e. were there to be instability in one of the top producing regions, a large amount will be available from other sources. The political considerations of production and of reserve distribution lead to the low score for cobalt: the top producing country for cobalt (Democratic Republic of

Table 12: Star charts for the 8 CCU process alternatives.

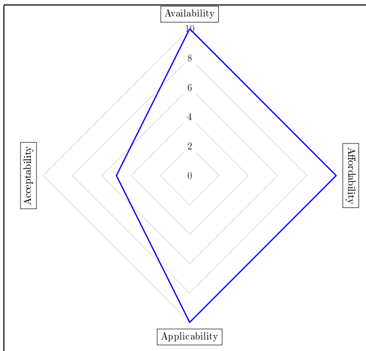
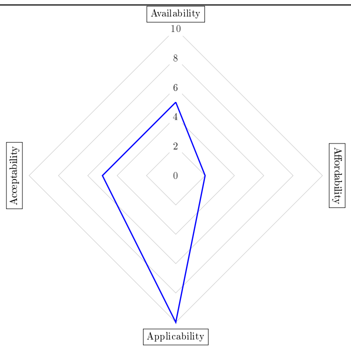
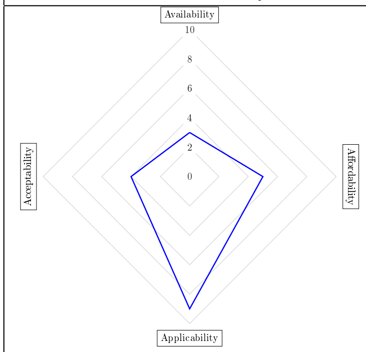
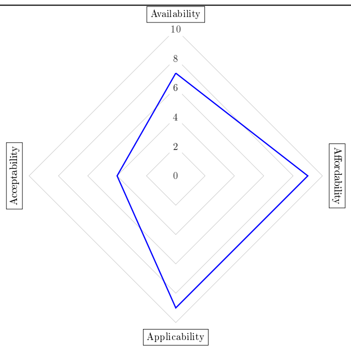
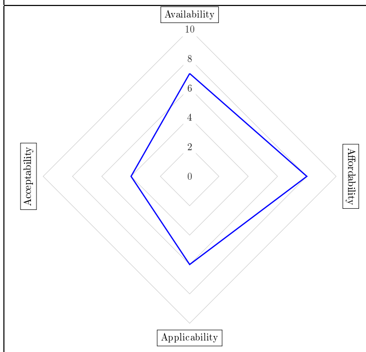
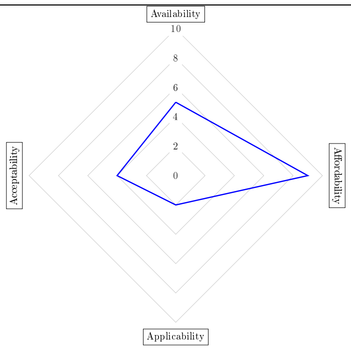
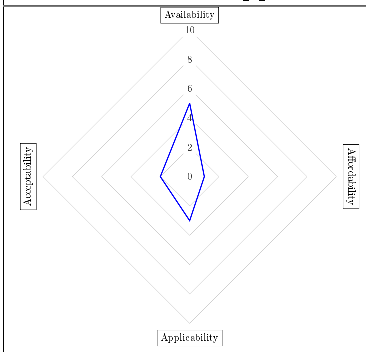
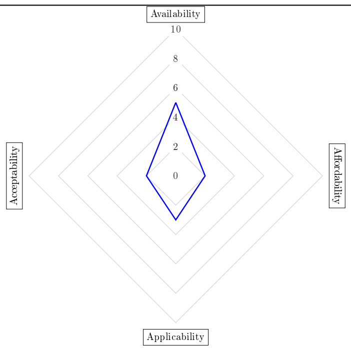
 Urea with no catalyst	 Urea with ruthenium
 Carbonate with cobalt	 Carbonate with zinc
 Methanol with copper	 Cyclic carbonates
 Formic acid with iridium	 Formic acid with ruthenium

Table 13: Price of catalyst relative to the price of aluminium

Material	Relative Cost
Al	1
Zn	1.14
Cu	4
Co	18
Ru	1529
Ir	11418

the Congo) is ranked high in global corruption levels whereas, for zinc, the top producing country (P. R. China) has a better ranking for both corruption and political stability.

The high score for applicability is based on the fact that existing technologies can be used for the production of these polymers. Also, current production is based on food based feedstocks such as corn. Replacing these with CO_2 will help address food security and therefore increase the applicability of this CCU alternative.

5.3 Methanol

Methanol rates reasonably well in availability and affordability, with applicability average. Acceptability is low, again mostly due to emissions of CO_2 due to energy requirements for the process. There are no particular concerns beyond this and so methanol can be considered a good choice as a target, especially if CO_2 neutral energy sources are available.

5.4 Cyclic carbonates

The key factor in the production of cyclic carbonates is the low applicability score. This is primarily due to the low TRL value of 2. Although there has been significant research into catalysts for the production of cyclic carbonates, no commercial implementations exist.[7] The existing processes for cyclic carbonates, not based on CO_2 utilisation, perform well enough that the incentive to develop CO_2 based processes is not there currently. As pressure, financial and regulatory, on utilising CO_2 increases, there will be increasing incentives to take existing lab-scale processes into pilot and eventually plant scale. This will increase the applicability score and, depending on the energy requirements, may also lead to an increase in the acceptability score.

The availability score of 5 is the same as for urea with ruthenium. Although aluminium has a much higher abundance, the overall score is the same due to the political and corruption assessments of the countries with greatest production and reserves. The overall security of supply is deemed to be similar although this is a function of the weighting of the different criteria that form the basis for the availability score.

5.5 Formic acid

The progress of formic acid production through CO_2 utilisation is the least mature of all the processes presented, leading to low applicability scores. Further, both of the catalysts considered are costly, having significant impact on the affordability scores. However, because of the potential applications, e.g. the use of formic acid in fuel cells, there is an incentive to develop and to improve the processes; see, for instance, this press release from Market Wired.[36]

6 Conclusion

This paper presents a framework for the analysis of the security of supply for carbon dioxide utilising processes. Development in CCU has concentrated on catalysis to ameliorate the energy requirements for reactions involving CO_2. At these early stages of CCU development, gaining insight into any potential limitations that arise from security of supply issues is of value to various stakeholders, including industry, governments and potential end-users of the products.

The 4As approach, proposed by the Asian Pacific Energy Research Centre for energy security, has been adapted to CCU, combining micro- and macro-economic criteria with process considerations. The framework enables us to compare and contrast alternative products and processes through the analysis of the impact of catalyst choice. It also highlights those aspects which could benefit from further development. The cases considered show that urea production is currently the most secure while formic acid is at the other end of the scale. The reasons for the differences amongst the various target products range from geopolitical through to the stage of development of the individual processes.

A number of assumptions have been made. These are all subject to change as the framework is fundamentally extensible. Of primary concern to industrial users of the framework would be the addition of process and market economics beyond the impact of the catalysts. However, economics will necessarily trade-off with security of supply and eventual decisions will be based on the stakeholders' own perceptions of relative importance.

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