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Closing the loop: captured CO_2 as a feedstock in the chemical industry

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The utilization of 'captured' CO_2 as a feedstock in the chemical industry for the synthesis of certain chemical products offers an option for preventing several million tons of CO_2 emissions each year while increasing independence from fossil fuels. For this reason, interest is increasing in the feasibility of deploying captured CO_2 in this manner. Numerous scientific publications describe laboratory experiments in which CO_2 has been successfully used as a feedstock for the synthesis of various chemical products. However, many of these publications have focused on the feasibility of syntheses without considering the ancillary benefits of CO_2 emissions reduction if the CO_2 is sourced from effluent or the potential profitability of this process. Evaluating these environmental and economic benefits is important for promoting the further development of benign CO_2 applications. Given the multitude of CO_2 utilization reactions in the laboratory context, an initial assessment must be undertaken to identify those which have the most potential for future technical exploration and development. To achieve this, 123 reactions from the literature were identified and evaluated with the help of selection criteria specifically developed for this project. These criteria incorporate both the quantitative potential of reducing CO_2 and possible economic benefits of these syntheses. The selected reactions are divided into bulk and fine chemicals. Of the bulk chemicals, formic acid, oxalic acid, formaldehyde, methanol, urea and dimethyl ether, and of the fine chemicals, methylurethane, 3-oxo-pentanedioic acid, 2-imidazolidinone, ethylurethane, 2-oxazolidone and isopropyl isocyanate, mostly fulfil the selection criteria in each category.

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Broader context

In order to achieve global greenhouse gas reduction targets, in addition to increasing the deployment of renewable energy technologies and improving efficiency, carbon capture and storage (CCS) will be an important means of CO_2 reduction in the future. However, even with the complete decarbonization of electricity generation through the widespread implementation of renewable power, huge amounts of CO_2 from process emissions will still be emitted by the cement, steel and chemical industries, which can be greatly reduced with CCS. The utilization of a portion of the collected CO_2 as a feedstock in the chemical industry in turn presents a means of reusing, rather than merely disposing of it. Additionally, the sourcing of CO_2 as a feedstock would reduce the chemical industry's dependence on fossil fuels. In the scientific literature, numerous experiments have successfully demonstrated the viability of CO_2 as a feedstock. However, not all CO_2 utilization reactions have the potential to utilize significant amounts of CO_2 or be profitably implemented. Therefore, the present study focuses on those CO_2 based reactions which do and thus merit further study and compares these to conventional process routes.

1. Introduction

Currently, only a handful of commercial processes use CO_2 as a feedstock for the production of organic chemical products. These processes synthesize urea, methanol, salicylic acid, organic carbonates and polycarbonates (see Table 1). Globally, these processes entail approximately 116 million tons of CO_2 consumption per year, 94% of which goes toward the production of urea. Although urea production currently accounts for the most quantitatively significant utilization of CO_2 as a feedstock, it should also be noted that this process produces more CO_2 than it consumes. The reason for this is that the origin of the CO_2 utilized constitutes only part of the resulting CO_2 emissions, which arise during the synthesis of the necessary co-reactant, ammonia.[1]

Notwithstanding of this, the current use of CO_2 as a feedstock for chemicals corresponds to only 0.36% of global CO_2 emissions, which amounted to 32.3 billion tons in 2014.[8] In its World Energy Outlook 2012,[9] the International Energy Agency (IEA) outlines the "450 Scenario", that the growth of average global temperature could be limited to 2 °C if CO_2 emissions total no more than 22 billion tons a year by 2035. To achieve this aim, in addition to improvements in efficiency, renewable

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Table 1 Industrial production volume of products made of CO_2, utilized mass of CO_2 per mass product and bounded CO_2 in the product

Product	Production volume (million tons per annum)	Bounded CO_2 in product (million tons per annum)	Ref.
Urea	150	109.5	2
Methanol[a]	4.4	6	3
Methanol[b]	0.004	0.00548	4
Salicylic acid	0.17	0.054	4
Organic carbonate	0.1	0.043–0.049	5
Bisphenol-A polycarbonate	0.6	0.102	6
Polypropylene carbonate	0.07	0.03	7
		Sum ≈ 116	

[a] Admixing of CO_2 to synthesis gas. [b] Direct hydrogenation of CO_2 with H_2.

energy technology and electricity saving, Carbon Capture and Storage (CCS)[10–12] will be an important CO_2 reducing option in the future.[13,14] The IEA states that by 2035, 2.1 billion tons of CO_2 per year should be prevented from atmospheric emission by means of CCS. In a green paper, the German DECHEMA (Society for Chemical Engineering and Biotechnology)[15] estimates the future potential of CO_2 as a feedstock for polymers and basic chemicals to be at least 178 million tons per year, a tenfold potential for synthetic fuels. Compared to the huge demand for geological storage that CCS entails (see above), the utilization of CO_2 as a feedstock for chemicals therefore has less quantitative potential for mitigating CO_2 emissions by comparison to that of reusing CO_2 as a feedstock for the synthesis of fuels. Moreover, in the future, there is potential for new applications of CO_2 as a feedstock, for example in the context of so-called power-to-gas technologies. These technologies are primarily for the purpose of storing temporary excess wind and solar power through the production of hydrogen *via* water electrolysis, followed by the conversion of hydrogen, with CO_2, into fuels like synthetic methane.[16,17] However, these technologies will only consume large amounts of CO_2 in conjunction with the expansion of renewable power and a high degree of capacity utilization by the electrolyzers.

Although the reuse potential of captured CO_2 as a feedstock for the synthesis of chemicals is limited, it offers other benefits, such as increasing the chemical industry's independence from fossil feedstock such as naphtha, natural gas, oil and coal. Additionally, if the CO_2 utilization process is located directly at the emission source, the energy and costs required for CO_2 transport and the need for storage can be avoided. In the literature contains numerous scientific publications that deal with the utilization of carbon dioxide as a feedstock, but usually concerning the feasibility of the syntheses, new catalysts or research into the reaction mechanism, without paying attention to CO_2 reduction potential or the profitability of these reactions. Furthermore, there are several reviews concerning the kind of reaction mechanisms and products that can be produced, depending on the reactant of CO_2 (*e.g.*, ref. 3, 18–21). For the present study, 123 chemical reactions that utilize CO_2 as a feedstock were identified. The synthesis of polymers or fuels will not be considered, as the focus is on the conversion of CO_2 into organic products that can substitute conventional chemical products. To evaluate the CO_2 reduction and economic potential of the identified chemicals, special selection criteria were developed. These criteria should identify the most suitable products with the greatest potential for a detailed direct comparison of the CO_2 based and conventional manufacturing process, without incurring enormous expenditure for the evaluation of each published reaction. Using these selection criteria, it was possible to rank the numerous reactions in the literature into a list to determine their potential for CO_2 re-utilization.

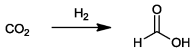
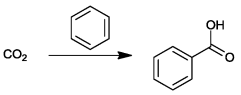
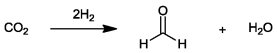
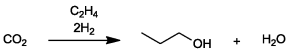
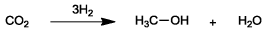
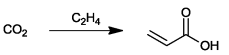
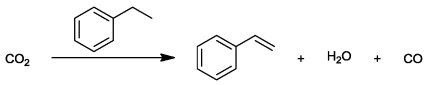
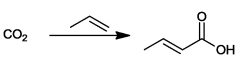
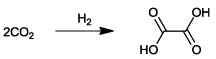
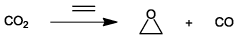
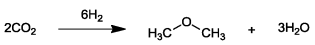
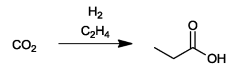
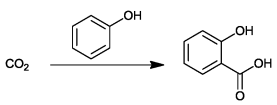
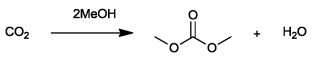
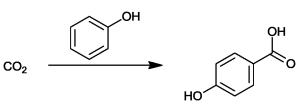
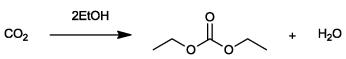
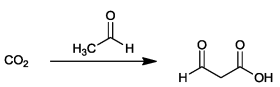
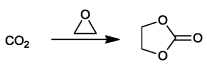
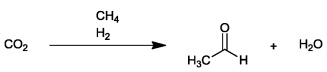
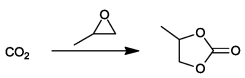
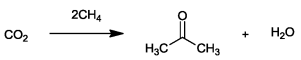
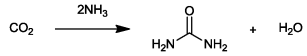
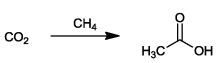
2. Identification of CO_2 utilization reactions

For the identification of CO_2 utilization reactions in the literature, the knowledge of the possible synthesis products is a basic requirement. For this reason, Table 2 displays an overview of important substance groups that can be synthesized with CO_2 as a feedstock, depending on the nature of the reactants. On this basis, a search was conducted in the online database SCI-Finder[22] for reactions that, when combined with the particular reactants, lead to the substance groups described (see Tables 3 and 5). For the purpose of this research, 123 CO_2 utilization reactions were collected. The products of the registered reactions were divided into 23 bulk chemicals (Table 3) and 100 fine chemicals (Table 5).

Table 2 Possible producible substance groups with CO_2 as a feedstock, depending on the nature of the reactants

Reactant	Substance groups	Examples in
Organic compounds with "active hydrogen"	Carboxylic acids and coumarins	18 and 25
Organometallic compounds	Carboxylic acids	18 and 26
Alkenes	Unsaturated carboxylic acids	19, 20 and 27
Conjugated dienes	Lactones and unsaturated ester	19, 20 and 27
Allenes	Pyrones and unsaturated ester	19, 20 and 27
Methylcyclopropane	Lactones und pyrones	19, 20 and 27
Alkynes	Lactone und pyrones	19, 20 and 27
Hydrogen	Carboxylic acids, ether, alcohols and aldehydes	19 and 28
Epoxides or dioles	Cyclic carbonates	29 and 30
Alcohols	Linear carbonates	31–33
Ammonia	Urea	18 and 19
Amines	Linear urea derivatives and isocyanates	25 and 34
Diamines	Cyclic urea derivatives	35
β-Amino alcohols or aziridines	Cyclic carbamates	36–39
Amines or ammonia + alcohols	Linear carbamates	40

Table 3 Catalogue of the 23 bulk chemicals considered

Product name	Reaction	Ref.	Product name	Reaction	Ref.
Formic acid		42–48	Benzoic acid		19 and 25
Formaldehyde		49	Propanol		19 and 25
Methanol		50–55	Acrylic acid		19, 25 and 56
Styrol		57	Methacrylic acid		19
Oxalic acid		58	Ethylene oxide		19 and 25
Dimethyl ether		59–63	Propanoic acid		19 and 25
Salicylic acid		18 and 64	Dimethyl carbonate		31, 32 and 65
p-Salicylic acid		18 and 64	Diethyl carbonate		32 and 66
Formylformic acid		67	Ethylene carbonate		68
Acetaldehyde		19 and 25	Propylene carbonate		69 and 70
Acetone		19 and 25	Urea		2, 19 and 64
Acetic acid		19, 25 and 67			

By definition, a bulk chemical is a substance with a global production volume of over 10 000 tons per annum, while a fine chemical constitutes less.[23] In the present study, the production rates of chemicals related to the production of the 27 states of the European Union in 2011. As no exact information on the boundary between bulk and fine chemicals in the EU could be found in the literature, the boundary is estimated on the basis of the fact that approximately 17%[24] of chemicals produced worldwide are produced in the EU at a volume of approximately 1700 tons per annum. With respect to the next order of magnitude, this value is rounded to 1000 tons per annum, which is defined as the boundary between bulk and fine chemicals for the purposes of this work. The division of the resulting reaction products is necessary, as the later defined selection criteria for the bulk and fine chemicals are different. Therefore, the evaluation of CO_2 based reaction products is separated for each category. In Table 3, the 23 bulk chemicals considered with their respective gross reactions and the reference is listed.

Table 5 shows the 100 fine chemicals identified with their identification number (ID), gross reaction, European Union Community Production (ProdCom)[41] number and the reference that reported these reactions. The individual products or product groups are registered in the database by their ProdCom number. Table 4 displays the ProdCom numbers of product groups to which the fine chemicals considered could be allocated.

3. Definition of the selection criteria

This section outlines the selection criteria for the evaluation of the above collected CO_2 utilization reactions (Tables 3 and 5) to identify the most suitable reactions relating to quantitative potential to reduce CO_2 and the possible economic interests of the industry in these reactions.

3.1 Bulk chemicals

For the evaluation of CO_2 utilization reactions on each other, following selection criteria for bulk chemicals were defined:

3.1.1 Specific mass of CO_2 as a feedstock. The specific mass of CO_2 as a feedstock is the mass of CO_2 necessary to produce,

Table 4 Description of the ProdCom numbers 2011[71]

ProdCom no.	Explanation
20143475	Carboxilic acid with alcohol, phenol, aldehyde or ketone functions
20143440	Aromatic polycarboxylic acids, their anhydrides, halides, peroxides, peroxyacids and their halogenated, sulphonated, nitrated or nitrosated derivatives (excluding esters of orthophthalic acid, phthalic anhydride, terephthalic acid)
20143370	Aromatic monocarboxylic acids, (anhydrides), halides, peroxides, peroxyacids, derivatives excluding benzoic acid, phenylacetic acids their esters, benzoyl peroxide, benzoyl chloride
20145210	Heterocyclic compounds with oxygen only hetero-atom(s) (including coumarin; methylcoumarins and ethylcoumarins) (excluding other lactones)
21103110	Lactones (excluding coumarin, methylcoumarins and ethylcoumarins)
20143310	Unsaturated acyclic and alicyclic monocarboxylic acids, their anhydrides, halides, peroxyacids (excluding fomic acid, acetic acid, butyric acid)
20143383	Acyclic and alicyclic polycarboxylic acids
20145225	Heterocyclic compounds with oxygen only hetero-atom(s) (excluding other lactones)
20144310	Urea and their derivatives
21102070	Cyclic amides and their derivatives-(including cyclic carbamates)
21102060	Acyclic amides and their derivatives-(including acyclic carbamates)
20144450	Isocyanates

Table 5 Catalogue of the 100 fine chemicals considered

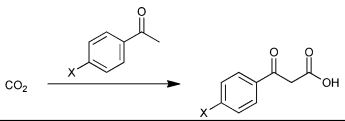
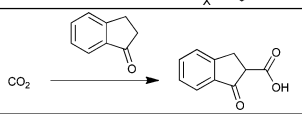
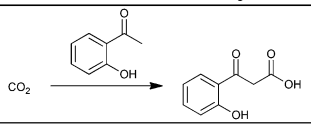
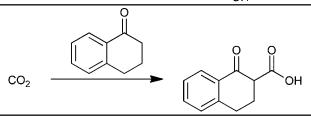
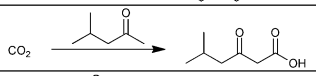
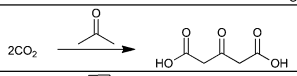
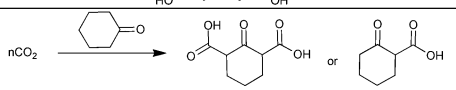
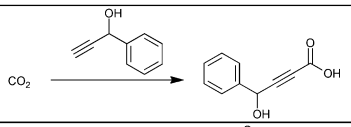
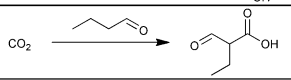
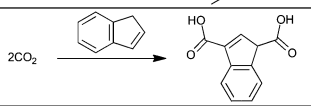
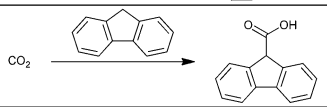
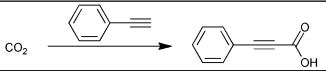
ID	ProdCom No.	CAS	Product name	Reaction	Ref.
1	20143475	614-20-0	3-Oxo-3-phenylpropanoic acid (X= H)		25
2		13422-78-1	p-Methylbenzoylacetic acid (X= CH_3)		
3		17589-68-3	4-Chlorobenzoylacetic acid (X= Cl)		
4		64929-35-7	p-Bromobenzoylacetic acid (X= Br)		
5		13422-77-0	p-Methoxybenzoylacetic acid (X= O-CH_3)		
6		6742-29-6	Indanone-2-carboxylic acid		25
7		17392-16-4	2-Hydroxybenzoylformic acid		19
8		62952-26-5	2-Carboxy-α-tetralone		25
9		131991-42-9	5-Methyl-3-oxohexanoic acid		19
10		542-05-2	3-Oxo-pentanedioic acid		25
11		22775-31-1	2-Oxo-1,3-cyclohexanedicarboxylic acid		25
12		18709-01-8	2-Carboxycyclohexanone		
13		62952-24-3	4-Hydroxy-4-phenyl-2-butynoic acid		25
14		4442-98-2	2-Butyraldehyde		67
15	20143-440	82947-33-9	1,3-Indenedicarboxylic acid		25
16	20143370	1989-33-9	9H-Fluorene-9-carboxylic acid		25
17		637-44-5	3-Phenylpropynoic acid		25

Table 5 (*continued*)

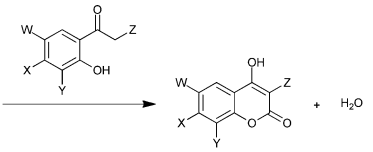
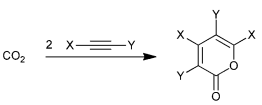
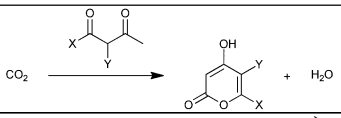
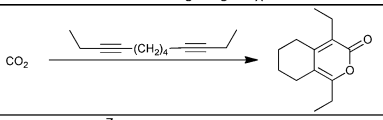
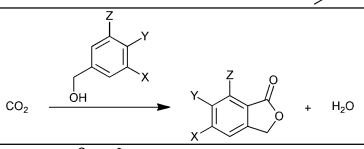
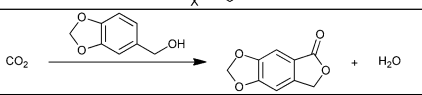
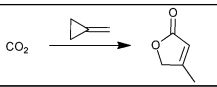
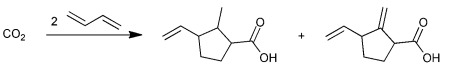
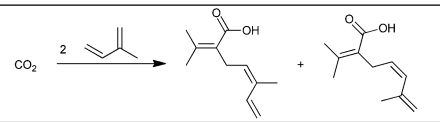
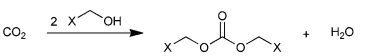
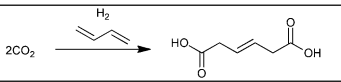
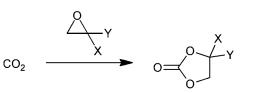
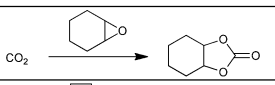
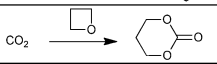
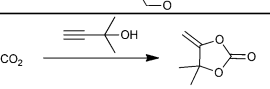
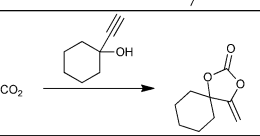
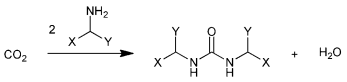
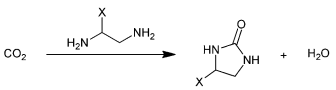
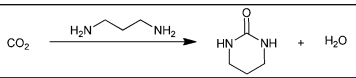
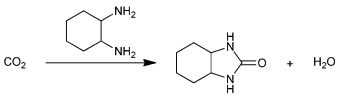
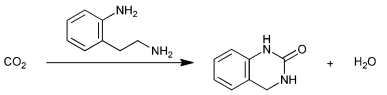
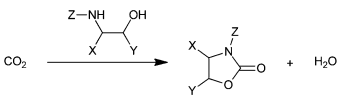
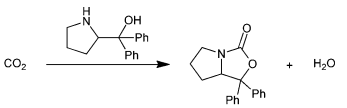
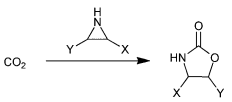
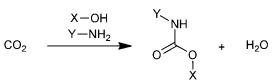
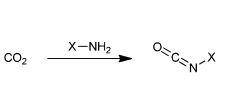
ID	ProdCom No.	CAS	Product name	Reaction	Ref.
18	20145210	1076-38-6	4-Hydroxycoumarin (W= X= Y= Z= H)		25, 72
19		18692-77-8	7-Methyl-4-hydroxycoumarin (W=H; X= CH_3; Y= H; Z= H)		25
20		24631-83-2	8-Methyl-4-hydroxycoumarin (W= X= H; Y= CH_3; Z= H)		25
21		15074-17-6	4-Hydroxy-3-methylcoumarin (W= X= Y= H; Z= CH_3)		25, 72
22		21315-28-6	3-Ethyl-4-hydroxycoumarin (W= X= Y= H; Z= CH_2-CH_3)		72
23		1786-05-6	3-Phenyl-4-hydroxycoumarin (W= X= Y= H; Z= Ph)		72
24		17575-15-4	7-Methoxy-4-hydroxycoumarin (X= O-CH_3; W= Y= Z= H)		72
25		118157-94-1	3,6-Dimethyl-4-hydroxycoumarin (W=CH_3; X= Y= Z= H)		72
26	21103110	65095-32-1	4,6-Dibutyl-2-pyrone (X=C_4H_9; Y=H)		73
27		67530-99-8	Tetraethyl-2-pyrone (X= Y=C_2H_5)		74, 75
28		77664-31-4	Tetrapropyl-2-pyranone (X= Y=C_3H_7)		76
29		675-09-2	4,6-Dimethyl-2-pyrone (X=CH_3; Y=H)		27, 77
30		675-10-5	4-Hydroxy-6-methyl-2H-pyran-2-one (X= CH_3; Y=H)		78
31		50405-45-3	4-Hydroxy-5,6-dimethyl-2H-pyran-2-one (X=Y=CH_3)		78
32		5526-38-5	4-Hydroxy-6-phenylpyran-2-one (X= Ph; Y= H)		79
33		111395-92-7	1,4-Diethyl-5,6,7,8-tetrahydro-3H-2-benzopyran-3-one		80
34		87-41-2	1(3H)-Isobenzofuranone (X=Y=Z=H)		81
35		28281-58-5	7-Methoxy-3H-isobenzofuran-1-one(X= H; Y= H; Z= O-CH_3)		
36		569-31-3	6,7-Dimethoxyphthalide (X= H; Y= O-CH_3; Z= O-CH_3)		
37		3465-69-8	5,7-Dimethoxyphthalide (X= O-CH_3; Y=H; Z= O-CH_3)		
38		4741-65-5	Furo[3,4-e]-1,3-benzodioxol-8(6H)-one		81
39		6124-79-4	4-Methyl-2(5*H*)-furanone		82
40		108451-44-1	3-Ethenyl-2-methyl-cyclopentane-carboxylic acid		83
41		108451-43-0	3-Ethenyl-2-methylene-cyclopentane-carboxylic acid		
42	20143310	134226-08-7	5-Methyl-2-(1-methylethylidene)-4,6-heptadienoic acid		84
43		134226-09-8	6-Methyl-2-(1-methylethylidene)-4,6-heptadienoic acid		
44		15022-08-9	Diallyl carbonate (X=C_2H_5)		33
45		3459-92-5	Dibenzyl carbonate (X=Ph)		
46		64057-79-0	Bis(methallyl) carbonate (X=C_3H_5)		
47	20143383	29311-53-3	3-Hexenedioic acid		25
48	20145225	4437-85-8	4-Ethyl-1,3-dioxolan-2-one (X=C_2H_5; Y=H)		69, 70
49		66675-43-2	n-Butylethylene carbonate (X=n-C_4H_9; Y=H)		69, 70
50		4427-92-3	4-Phenyl-1,3-dioxolan-2-one (X=Ph; Y=H)		69, 70
51		931-40-8	3-Hydroxypropylene carbonate (X=CH_2OH; Y=H)		85
52		4437-69-8	4,4-Dimethyl-1,3-dioxolan-2-one(X= CH_3; Y=CH_3)		70
53		4427-96-7	4-Ethenyl-1,3-dioxolan-2-one (X= C_2H_3; Y=H)		70
54		4389-22-4	Cyclohexene carbonate		86
55		2453-03-4	2-Oxo-1,3-dioxane		85
56		4437-80-3	4,4-Dimethyl-5-methylene-1,3-dioxolan--2-one		87, 88
57		92474-80-1	4-Methylene-1,3-dioxaspiro[4.5]decan-2-one		88

Table 5 (*continued*)

ID	ProdCom No.	CAS	Product name	Reaction	Ref.
58		6744-64-5	N,N'-Bis(benzhydryl)urea (X= Ph; Y=Ph)		89
59		2387-23-7	N,N'-Dicyclohexylurea (X= cHex; Y=H)		34, 35, 89, 90
60		102-07-8	1,3-Diphenylurea (X= Ph; Y=H)		35, 89
61		1466-67-7	N,N'-Dibenzylurea (X=Bn; Y=H)		35, 89
62		4128-37-4	1,3-Diisopropylurea (X=CH_3; Y=CH_3)		35, 89
63		623-95-0	N,N'-Dipropylurea (X=C_2H_5; Y=H)		35, 89
64		1792-17-2	Dibutylurea (X=C_3H_7; Y=H)		35
65		1189-23-7	N,N'-Diisobutylurea (X=iPr; Y=H)		35
66		869-79-4	N,N'-Di-sec-butylurea (X=CH_3; Y= C_2H_5)		35
67		2763-88-4	N,N'-Dihexylurea (X=n-C_5H_{11}; Y= H)		35
68		1801-72-5	1,3-Diallylurea (X=C_2H_3; Y= H)		35
69		6849-92-9	1,3-Bis(2-methoxyethyl)urea (X=CH_2-0-CH_3;Y= H)		35
70	20144310	120-93-4	2-Imidazolidinone (X=H)		35
71		6531-31-3	4-Methyl-2-imidazolidinone (X=CH_3)		
72		1852-17-1	Tetrahydro-2-pyrimidone		35
73		1123-97-3	Hexahydro-2-benzimidazolinone		35
74		66655-67-2	3,4-Dihydro-1H-quinazolin-2-one		91
75	21102070	102029-44-7	(R)- 4-(Phenylmethyl)-2-oxazolidinone (X=Bn; Y=H; Z=H)		91, 92
76		90319-52-1	(4R)-4-Phenyl-1,3-oxazolidin-2-one (X=Ph; Y=H; Z=H)		92
77		17016-83-0	(4S)-(-)-4-Isopropyl-2-oxazolidone (X=iPr; Y=H; Z=H)		91, 92
78		7693-77-8	5-Phenyl-2-oxazolidone (X=H; Y= Ph; Z=H)		36, 37
79		19836-78-3	N-Methyl-2-oxazolidone (X=H; Y=H; Z=CH_3)		38
80		497-25-6	2-Oxazolidone (X=H; Y=H; Z=H)		35 92
81		17016-83-0	(4S)-(-)-4-Isopropyl-2-oxazolidone (X=iPr; Y=H; Z=H)		92
82		160424-29-3	Diphenyl-5,6,7,7a-tetrahydropyrrolo [1,2-c]oxazol-3(1H)-one		91
83		16112-59-7	4-Methyl-2-oxazolidone (X= CH_3; Y=CH_3)		39
84		497-25-6	2-Oxazolidone (X= H; Y=H)		
85		51-79-6	Ethylurethane (X= Et; Y=H)		
86		598-55-0	Methylurethane (X= Me; Y=H)		93
87	21102060	592-35-8	Butyl carbamate (X= Bu; Y=H)		
88		5817-70-9	Methyl benzylcarbamate (X= Me; Y=Bn)		
89		2621-78-5	Ethylbenzylurethane (X= Et; Y=Bn)		
90		500912-98-1	Ethyl N-(cyclohexylmethyl)carbamate (X= Et; Y=cHex)		40
91		2603-10-3	Methyl N-phenylurethane (X= Me; Y=Ph)		
92		101-99-5	O-Ethyl N-phenylcarbamate (X= Et; Y=Ph)		
93	20144450	103-71-9	Isocyanatobenzene (X= Ph)		94
94		1795-48-8	2-Isocyanatopropane (X= iPr)		94
95		111-36-4	n-Butyl isocyanate (X= nBu)		94
96		1609-86-5	t-Butylisocyanate (X= tBu)		94
97		3173-53-3	Cyclohexyl isocyanate (X= cHex)		94
98		*2525-62-4*	n-Hexyl isocyanate (X= nHex)		94
99		624-83-9	Methyl isocyanate (X= Me)		95
100		622-58-2	p-Tolyl isocyanate (X= p-Tolyl)		95

for instance, one kilogram of a product. This can be calculated using eqn (1) and the information from Table 3.

$$\frac{m_{CO_2}}{m_P} = \frac{|\nu_{CO_2}| \cdot M_{CO_2}}{|\nu_P| \cdot M_P} \quad (1)$$

m_{CO_2} = mass of carbon dioxide, kg; m_P = mass of product, kg; ν_{CO_2} = stoichiometric coefficient of carbon dioxide; ν_P = stoichiometric coefficient of the product; M_{CO_2} = molar mass of carbon dioxide (0.04401 kg mol^{-1}); M_P = molar mass of the product.

The specific mass of CO_2 as feedstock for the synthesis of the product is of interest, as this can vary over a wide range, depending on the resulting product and byproduct. The greater the specific mass of CO_2 used is, the more CO_2 can be inserted as feedstock for the production of a given amount of a chemical.

3.1.2 CO_2 avoidance potential. CO_2 avoidance is an important selection criterion, as it defines the maximum quantitative potential for the utilization of CO_2 as a feedstock for the complete substitution of the conventional synthesis of a chemical with the CO_2 based method. At this point, CO_2 avoidance potential is defined as the product of the specific mass of CO_2 per mass of product (eqn (1)) and the production volume of the synthesis product within the 27 states of the European Union (EU), as of 2011. In this manner, the CO_2 avoidance potential expresses the mass of CO_2 that can be theoretically used without regard to power emissions, heat or reactant allocation by the wholesale substitution of the conventional process within the EU. The required data on the production volumes were primary determined using the ProdCom database[41] of the Statistical Office of the European Union (EUROSTAT) and, secondarily, with the database of the European Chemical Agency (ECHA).[96]

3.1.3 Relative added value. The criterion "relative added value" is a measure of profit and considers the economic aspect of the evaluation. The higher the relative added value is, the more attractive the reaction is for industrial implementation. The relative added value is defined as the difference between the value of the product and price of the necessary educts (CO_2 and reactants) divided by the product's value according to eqn (2).

$$\text{Relative added value} = \frac{(m_p \cdot W_p) - \sum_i^n (m_{E,i} \cdot W_{E,i})}{\sum_i^n (m_{E,i} \cdot W_{E,i})} \quad (2)$$

m_P = mass of product, kg; $m_{E,i}$ = mass of educt i, kg; W_P = specific value of product, € per kg; $W_{E,i}$ = specific price of educt i, € per kg.

The starting substances and products considered refers to the gross reaction equation (see Table 3). Catalysts and auxiliary reagents were not considered with the calculation of relative added value. As a reason for the multitude of reactions and the missing thermodynamic data values of most of the considered chemicals, it is assumed that the educts react to 100% of the desired product. At this point, therefore, the relative value added is only a theoretical number for an evaluation of the reactions. For the calculation of the "real" relative value added, it is necessary to consider all manufacturing costs entailed in the process. At this point, this is not possible because most CO_2 based reactions for industrial processes are not yet extant and must first be designed, which is beyond the scope of this article. The specific values of the product and specific prices of the educts were at first determined by the ProdCom database and secondly with the online trading platform Alibaba.com.[97]

3.1.4 Independence from fossil reactants. A special criterion for the bulk chemicals is the evaluation of whether it is possible to avoid fossil carbon as a feedstock for the production of the reactants. This means that the carbon in the synthesis product results exclusively from the captured CO_2 molecule. This selection criterion highlights the fact that after the disposal of the product at the end of its lifetime through combustion, the amount of CO_2 released is equivalent to the amount which was used as a feedstock for the synthesis. By reusing captured CO_2, no additional CO_2 is emitted through the use of other fossil sources. As a result of the reuse of the carbon source, the disposal of the product generates no additional CO_2 emissions or fossil feedstock demand compared to a synthesis of the complete product or the reactants using fossil sources. An example for the possible independence of fossil reactants is the reaction of CO_2 with hydrogen to methanol under the condition that the hydrogen is produced by water electrolysis.

3.2 Fine chemicals

In some cases, the selection criteria for fine chemicals are different than for those of bulk chemicals. For example, the independence criterion of fossil reactants will be eliminated, as the fine chemicals are generally relatively large molecules with only a small part of carbon deriving from CO_2. Moreover, for the fine chemicals, some new selection criteria were defined to achieve a more sensitive relative evaluation amongst the products considered. The following selection criteria for fine chemicals were therefore defined:

3.2.1 Specific mass of CO_2 as feedstock. The criterion of specific mass of CO_2 as feedstock is defined similarly to the bulk chemical (see Section 3.1.1). By using the information of Table 5 and eqn (1), its value can be calculated.

3.2.3 Production volume of the substance groups. In terms of fine chemicals, the criterion production volume of the substance groups defined by the ProdCom database replaces the selection criterion of CO_2 avoidance potential of the bulk chemicals. The reason for this is that in the context of this study, it was not possible to detect individual production volumes for all of the fine chemicals. However, the ProdCom database also contains the production volumes of the chemical substance groups (see Table 4), in which the 100 fine chemicals considered, displayed in Table 5, can be allocated. However, it must be noted that the substance groups of the ProdCom database do not only contain the fine chemicals discussed in this study. Nevertheless, the production volumes of the substance groups were used to evaluate the relative quantities of the chemicals. As a result, this selection criterion is not tailored to a special reaction product and will only be respected by the total evaluation at one quarter.

3.2.3 Technical availability. The criterion "technical availability" expresses which of the 100 fine chemicals can be bought in industrial-scale volumes. This only considers chemical products

that are produced in larger quantities and have the potential to be produced over a new technology, such as with CO_2 as feedstock. For chemicals with a very small production volume only for research applications, a modification of the conventional production route is generally neither economical nor represents a significant contribution for the avoidance of CO_2 emissions by using CO_2 as feedstock. The technical availability of the chemicals was determined using the inventory of the online trading platform, Alibaba.com,[97] and the online directory of manufacturers and suppliers Chemical Register.[98]

3.2.4 Relative added value. The relative added value is defined in similar terms to the bulk chemicals (see Section 3.1.3). This value can be calculated using the information from Table 5 and eqn (2). Similarly to the selection criterion outlined above though, it was not possible to identify the individual market value of all educts and products of the 100 fine chemicals considered in this study. Therefore, if no individual price could be determined, the average prices from the ProdCom database for the substance groups were used for calculation. As with the selection criterion above, this selection criterion will only be observed by the total evaluation for one quarter, as the prices could not be determined for every chemical.

3.2.5 Scientific relevance. In this study, the criterion of "scientific relevance" is defined as the number of related references of a certain chemical, which is determined by the database SCI-Finder (compare Section 3). This selection criterion should differentiate chemicals with relatively rare applications, which are a part of the basic research or are specially synthesized and substances with a multitude of publications which can be used in many applications or which are constituents of the feedstock of many other products. Only for the second kind of chemicals might a new synthesis route with CO_2 as feedstock be of interest from an ecological and economic point of view. The number of references to the 100 fine chemicals considered was determined during January and April 2014.

4. Evaluation of the CO_2 utilization reactions

The aim of this section is to identify the most suitable CO_2 utilization reactions from the above (Tables 3 and 5) listed reactions from the literature relating to the potential of CO_2 reduction and profitability. The basis for the evaluation is the selection criteria defined in Section 3. Using a point system, for certain value ranges, points between 1 and 5 will be assigned increasing numbers of which indicate that the significance or potential of CO_2 utilization reactions is higher. The value ranges for the points are distributed in such a way, that there is a homogeneous distribution over all of the determined values. Finally, all points from the different selection criteria will be added and a ranking list for bulk and fine chemicals created separately.

4.1 Evaluation of the bulk chemicals syntheses

4.1.1 The specific mass of CO_2 as a feedstock. Fig. 1 illustrates the specific mass of CO_2 as a feedstock, as well as the value ranges of the points for evaluation. The specific consumed mass of CO_2 varies between 0.31 for the synthesis of salicylic acid and 1.91 for the synthesis of dimethyl ether. The low value for salicylic acid is a result of the relatively low content of CO_2 in the molecule, as 68 wt% of the acid is provided by the reactant phenol (see Table 3). In contrast, two CO_2 molecules and six light hydrogen molecules lead to dimethyl ether. Therefore, dimethyl ether consists of 87 wt% of CO_2, while at the same time three oxygen molecules of the two CO_2 molecules react to water. In all four cases, the conversion to water led to the high specifically used mass of CO_2, but with the disadvantage that a part of the reactive hydrogen reacts to unreactive water and is not bounded in the product.

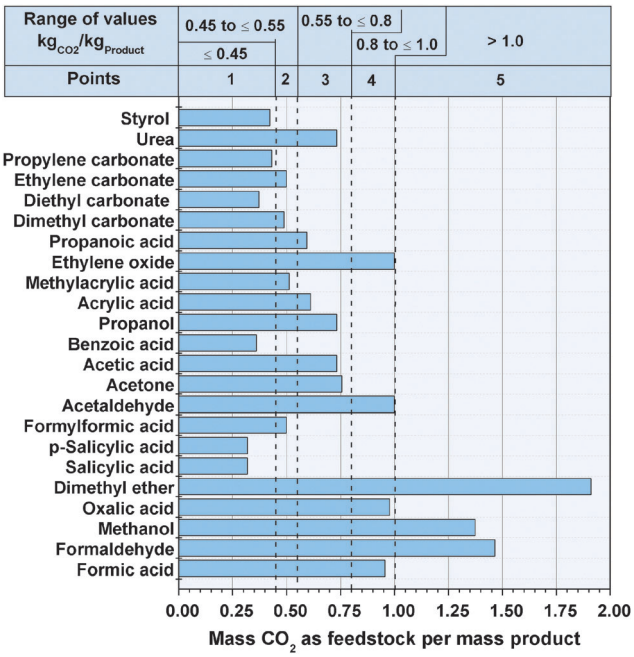


Fig. 1 Specific mass of CO_2 as feedstock for the synthesis of the bulk chemicals, as well as the value ranges of the points.

4.1.2 CO_2 avoidance potential. The CO_2 avoidance potential of the bulk chemicals and value ranges for the points for the evaluation are illustrated in Fig. 2. The CO_2 avoidance potential for the entire substitution of the conventional production processes by the CO_2 based route within the 27 states of the EU is for the most considered bulk chemicals below one million tons per year. A significantly higher CO_2 avoidance potential achieves a synthesis of urea with $\sim$40 million tons CO_2 per year. However the synthesis of urea *via* CO_2 as feedstock is already the only conventional process route.[2] Therefore, no substitution potential exists.

4.1.3 Relative added value. At this point, it is necessary to determine the relative added value of the 23 bulk chemicals. For the calculation of the relative added value (eqn (2)) for the reactions with hydrogen, the hydrogen price was defined at 5.22 € per kg_{H_2}. This value corresponds to the average manufacturing costs of hydrogen produced by alkaline water electrolysis operated with wind power.[99] Although the average cost of

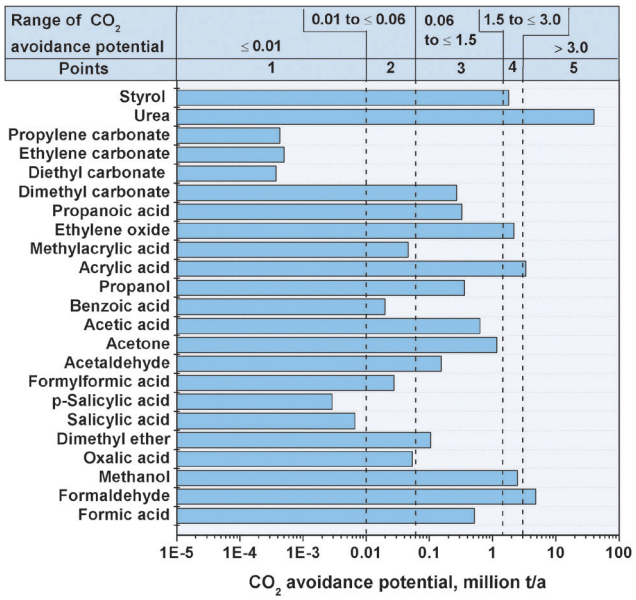


Fig. 2 CO_2 avoidance potential for bulk chemicals within the EU for 2011.

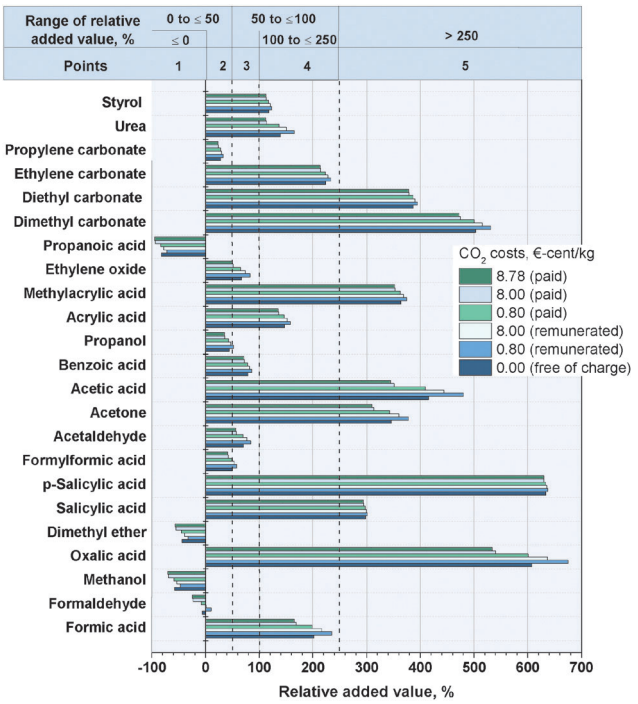


Fig. 3 Relative added value by the synthesis of the bulk chemicals for different CO_2 prices.

conventional hydrogen from natural gas reforming is much lower ($\sim$1.22 € per kg_{H_2}[99]), the specific reaction-dependent CO_2 emissions for hydrogen production from natural gas are $\sim$5.5 kg_{CO_2} $kg_{H_2}^{-1}$. Consequently, the process-dependent CO_2 emissions of conventional hydrogen production are in the range of the CO_2 used as feedstock in the reactions, despite the relatively low specifically used masses of hydrogen. As a reason for this, the utilization of CO_2 under these conditions will not lead to the aim of a reduction in CO_2 emissions. Hydrogen derived from alkaline water electrolysis operated by renewable energy technologies is an opportunity to produce hydrogen with very low CO_2 emissions. For the feedstock price of CO_2, different cases (see Fig. 3) are considered, like the assumption that CO_2 is free of charge or that the market price of 8.78 €-cent per kg[41] has to be paid. In another case it is assumed that a CO_2 emitter pays the average CO_2 certificate price (8.0 €-cent per kg, May 2015[100]) for the consumption or sale of CO_2 for this price. As Fig. 3 illustrates, the different prices of CO_2 considered have no significant influence on the relative added value. The reason for this is that even for the highest considered price of 8.78 €-cent per kg, the prices for the other reactants and the resulting product are generally ten times higher. The relative added value for the synthesis of propionic acid, dimethyl ether, methanol and formaldehyde is negative because the prices of the reactants are higher than the value of the products. All of these reactions have in common the fact that only hydrogen is a reactant of CO_2, the price for which was set to 5.22 € per kg_{H_2} for the afore-mentioned reason. Therefore, the synthesis of these products is only profitable if the manufacturing costs of hydrogen, produced by water electrolysis operated with renewable energies, decreases in the future. An exception is the synthesis of formic acid, although hydrogen is used as a reactant. The necessary amount of hydrogen is very low (0.04 kg_{H_2} kg_{HCOOH}^{-1}), because no hydrogen is consumed for the formation of water.

4.1.4 Independence from fossil reactants. In the condition where hydrogen is produced by water electrolysis operated with renewable energy, for the synthesis of propionic acid, dimethyl ether, methanol, formaldehyde and formic acid, there is an opportunity for complete independence on fossil sources as feedstock, as the only carbon feedstock is CO_2. For the CO_2 based synthesis of dimethyl carbonate, diethyl carbonate and urea, an indirect independence of fossil sources as feedstock is possible (see Table 6). For the synthesis of dimethyl carbonate, the necessary reactant methanol (see Table 3) can be produced over the CO_2 based route with renewable hydrogen and for the synthesis of diethyl carbonate, bio-ethanol can serve as the reactant. The conventional synthesis of urea occurs with ammonia and CO_2, at which point the ammonia is produced *via* the reforming of natural gas with ambient air.[2,101] At this point, it is possible to produce urea directly using renewable hydrogen and CO_2 without the previous steps utilizing fossil sources. Table 6 illustrates the points allocated for the evaluation of the criterion, ''independence from fossil reactant,'' for the 23 bulk chemicals considered.

4.1.5 Ranking of bulk chemical synthesis. With the addition of all points of the selection criteria from Sections 4.1.1–4.1.4, it is possible to create a ranking list. The synthesis with the most points is favored CO_2 utilization reactions regarding the potential to reduce CO_2 emissions and their economic feasibility. Formic acid, oxalic acid and formaldehyde achieve 16 of the maximum achievable 20 points.

For formaldehyde as well as for methanol, urea and dimethyl ether (see Table 7) point deduction occurs as a result of the negative relative added value (see Fig. 3) because of the high

Table 6 Evaluation of the independence of fossil sources of the reactants

Name	Independent of fossils	Points
Formic acid	Yes	5
Formaldehyde	Yes	5
Methanol	Yes	5
Styrol	No	1
Oxalic acid	Yes	5
Dimethyl ether	Yes	5
Salicylic acid	No	1
p-Salicylic acid	No	1
Formylformic acid	No	1
Acetaldehyde	No	1
Acetone	No	1
Acetic acid	No	1
Benzoic acid	No	1
Propanol	No	1
Acrylic acid	No	1
Methacrylic acid	No	1
Ethylene oxide	No	1
Propanoic acid	No	1
Dimethyl carbonate	Indirect	2.5
Diethyl carbonate	Indirect	2.5
Ethylen carbonate	No	1
Propylen carbonate	No	1
Urea	Indirect	2.5

price of renewable hydrogen. Formic acid and oxalic acid do not achieve the maximal score due to the relatively low CO_2 avoidance potential.

4.2 Evaluation of the fine chemicals synthesis

4.2.1 Specific mass of CO_2 as feedstock. Analogous to the bulk chemicals, Fig. 5 (see Appendix) illustrates the specific mass of CO_2 as feedstock, as well as the value ranges for the points for the evaluation of the fine chemicals. The specific consumed mass of CO_2 varies between 0.11 for *N*,*N*′-bis(benzhydryl)urea (ID 58) and 0.77 for methyl isocyanate (ID 99). All in all, 46% of the fine chemicals achieve a specific CO_2 consumption higher than 0.3 and 4% higher than 0.5. The reason for this is that the reactants of CO_2 are generally large molecules and CO_2 only contributes to a small portion of the final products.

4.2.2 Production volume of the substance groups. Fig. 4 illustrates the production volumes of the substance groups (see Table 4) referred to in the ProdCom database, into which the 100 fine chemicals considered were assigned. The production

Table 7 Ranking list of the 23 bulk chemicals after the accumulation of points of the selection criteria from Sections 4.1.1–4.1.4

Name	Points	Name	Points
Formic acid	16	Methylacrylic acid	10
Oxalic acid	16	Styrol	10
Formaldehyde	16	Diethyl carbonate	9.5
Methanol	15	Propanol	9
Urea	14.5	Ethylene carbonate	8
Dimethyl ether	14	Salicylic acid	8
Acrylic acid	13	*p*-Salicylic acid	8
Dimethyl carbonate	12.5	Propionic acid	8
Acetone	12	Formylformic acid	7
Acetic acid	12	Benzoic acid	7
Ethylene oxide	12	Propylene carbonate	5
Acetaldehyde	11		

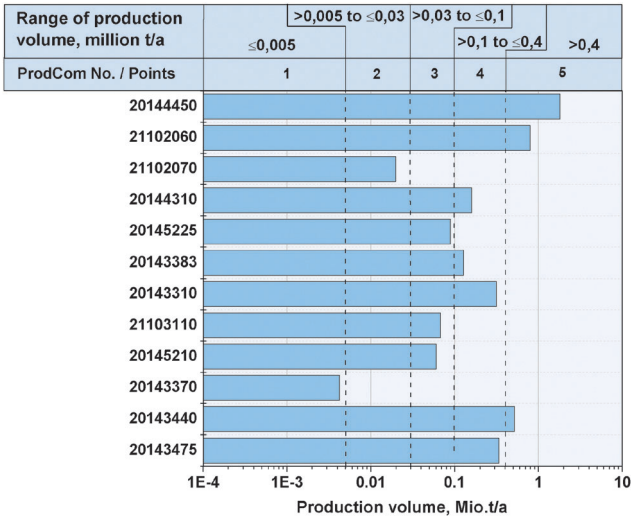


Fig. 4 Production volume of the substance groups referred to in the database, in which the 100 considered fine chemicals are assigned.

Table 8 IDs of technically unavailable products

2; 4–6; 8–9; 11–15; 20; 22; 28; 33; 37; 38; 42; 43; 58; 59; 66; 67; 74

volumes of the substance groups vary between 0.004 and 1.8 million tons per year. It should be remembered though that Fig. 4 not only shows the production volume of the 100 fine chemicals, but also includes the production volume of all chemicals within the EU which belong to these substance groups. Nevertheless, the production volumes of the substance groups are used to evaluate the relative quantities of the chemicals amongst each other. Because of the inexact availability of the database, this selection criterion is only included in one quarter of the total evaluation.

4.2.3 Technical availability. In Table 8, the IDs (compare Table 5) of the CO_2 utilization reaction, which leads to products that are not technically available, are summarized. These 25 reactions get only one point for the criterion. All of the other 75 reactions receive 5 points for the evaluation.

4.2.4 Relative added value. The relative added value for the fine chemicals according eqn (2) and illustrated in Fig. 6 (see Appendix) was calculated under the assumption that CO_2 as a feedstock is free of charge. This assumption is justified because the low CO_2 price does not significantly influence the relative added value to the bulk chemicals in Section 4.1.3. The relative added value for 41 of the CO_2 utilization reactions is over 500% and, for 27, over 1000%. The fine chemicals which belong to the substance group of lactones (ProdCom No. 2110311) achieve almost all of the highest values of the 100 fine chemicals.

4.2.5 Scientific relevance. The selection criterion of "scientific relevance" was determined by the number of references relating to the product in the SCI-Finder database. Fig. 7 shows that of the 100 fine chemicals considered, the number of references vary between one (*e.g.*, 5-methyl-2-(1-methylethylidene)-4,6-heptadienoic acid) and 12 293 (*e.g.*, isocyanatobenzene). In general, the 10 considered isocyanate have a high number of references, with

Table 9 Ranking list of the 100 fine chemicals after accumulation of the points of the selection criteria from Sections 4.2.1–4.2.3

ID	Points	ID	Points	ID	Points
86	17.5	87	14.75	12	11
10	17.25	92	14.75	27	11
70	17.25	44	14.25	40	11
85	17.25	1	14	41	11
80/84	16.75	50	14	25	10
94	16.75	52	14	26	10
95	16.75	56	14	82	9.5
99	16.75	68	14	90	9.5
55	16.5	81	14	69	9.25
96	16.5	88	14	11	9
47	16.25	77	13.75	15	9
30	16	60	13.5	59	8.25
39	16	64	13.5	9	8
48	16	31	13	14	8
51	16	35	13	20	8
53	16	36	13	37	8
72	15.75	89	13	65	7.5
79	15.75	24	12.75	66	7.5
93	15.75	76	12.75	8	7.25
97	15.75	78	12.75	74	7.25
17	15.5	16	12.5	2	7
98	15.5	73	12.25	5	7
100	15.5	19	12	6	7
18	15	21	12	22	7
29	15	23	12	38	7
34	15	32	12	67	6.25
49	15	57	12	42	6
54	15	75	12	43	6
91	15	61	11.5	58	6
62	14.75	45	11.25	28	5
63	14.75	46	11.25		
71	14.75	3	11		
83	14.75	7	11		

more than one quarter of the fine chemicals having over 500 references. Similarly to the other selection criteria, the value range for the award of points is shown in the figure.

4.2.6 Ranking of fine chemical synthesis. The addition of the points from Sections 4.2.1–4.2.6 lead to the ranking list shown in Table 9. Only the synthesis to methylurethane achieves the maximum number of 17.5 points and completely fulfils all of the selection criteria. The CO_2 utilization reactions to 3-oxo-pentanedioic acid, 2-imidazolidinone and ethylurthane almost achieve the maximal score, with 17.25 points.

5. Conclusions

The utilization of captured CO_2 as a feedstock in the chemical industry for the synthesis of organic products offers an opportunity to mitigate CO_2 emissions and increase independence from fossil fuels. In the scientific literature, numerous reactions are described that use CO_2 as a feedstock to synthesize various chemical products, but most of these publications have focused on the feasibility of the syntheses without considering the CO_2 reduction potential or potential profitability of these reactions. The present study pre-evaluated 23 reactions to bulk and 100 reactions to fine chemicals that use CO_2 as feedstock, relating to the CO_2 reduction and economic potential with specially developed selection criteria. The aim was to identify the most suitable products for further, detailed analysis within a reasonable period. Of the examined bulk chemicals, formic acid, oxalic acid, formaldehyde, methanol, urea and dimethyl ether and, of the fine chemicals, methylurethane, 3-oxo-pentanedioic acid, 2-imidazolidinone, ethylurethane, 2-oxazolidone and isopropyl isocyanate, mostly fulfil the selection criteria in each category. Therefore, these reactions represent useful CO_2 utilization options with high potential for future technical, ecological and economic analysis that compares their viability to conventional processes.

In addition to the pre-evaluation of the CO_2 utilization reactions, some conclusions can be drawn: Amongst the top six bulk chemicals, there are five for which hydrogen is the only reactant of CO_2. The advantage of these hydrogenation reactions is that a large amount of CO_2 is consumed and the resulting products are simple molecules with a high production volume. For these products, a complete synthesis without fossil feedstock is possible, which would increase their manufacturers' degree of independence from fossil sources. Through the synthesis of oxalic acid, formaldehyde, methanol, urea and dimethyl ether, some of the oxygen atoms of the CO_2 react with water, increasing the consumption of CO_2 in the reactions. As a result of the conversion of oxygen into water, these reactions are highly exothermic and in most cases exergonic. At the same time though, the generation of water is the main disadvantage undermining the economic feasibility of the syntheses, as it leads to negative relative added value. The prior highly energy- and cost-intensively-produced hydrogen by electrolysis – preferably operated with renewable power – further reacts to the starting material, water. Future developments and cost reductions in the production of renewable hydrogen could lead to decreasing hydrogen prices and therefore to the economical utilization of CO_2 as a feedstock for these products. In the event that hydrogen is produced by steam reforming, the manufacturing costs are significantly lower, but then there is no potential to effectively reduce CO_2 emissions through the utilization of CO_2 as a feedstock. If CO_2 is used as feedstock, the bulk chemicals considered, other than urea, which is already exclusively produced using CO_2, have the potential to avoid the emission of $\sim$20 million tons of CO_2 per year if all conventional processes in the EU were to be substituted. This corresponds to $\sim$0.43% of the EU's greenhouse gas emissions. Therefore, the synthesis of bulk chemicals could be a suitable additional route for the avoidance of CO_2 emissions alongside other, already existing options, even if the possible quantities are, at this time, limited. To avoid the emission of larger quantities of CO_2 through CO_2 re-utilization, the synthesis of fuels or power-to-gas technologies, for example, must also be taken into account.

Of the fine chemicals, four syntheses fulfil or nearly fulfil the maximum of all of the selection criteria. In general, the advantage of these reactions is that in most cases, there is high added value. However, the potential of CO_2 consumption is more limited than for the bulk chemicals and distributed over many individual reactions. The CO_2 avoidance potential is, for all substances, significantly lower than 1.3 million tons per year, which corresponds to $\sim$0.029% of EU greenhouse gas

emissions. Therefore, the utilization of CO_2 as a feedstock for fine chemicals is not a CO_2 avoidance option for large amounts of CO_2. Nonetheless, as a basis for the highly achievable relative added value, the synthesis of fine chemicals can be an economical option for reducing small amounts of CO_2, for instance if a CO_2 source is under the control of a manufacturer that already produces the necessary reactants for one of the syntheses.

Appendix

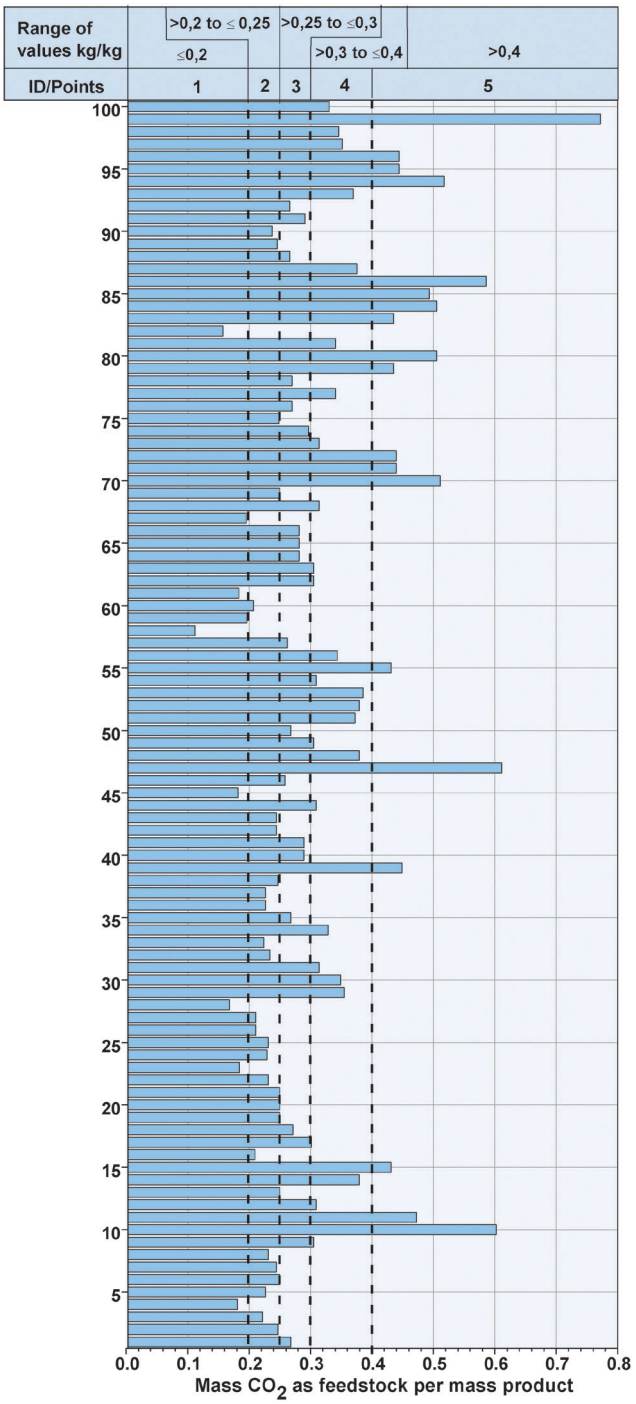


Fig. 5 Specific mass of CO_2 as a feedstock for the syntheses of the fine chemicals and value range of the points.

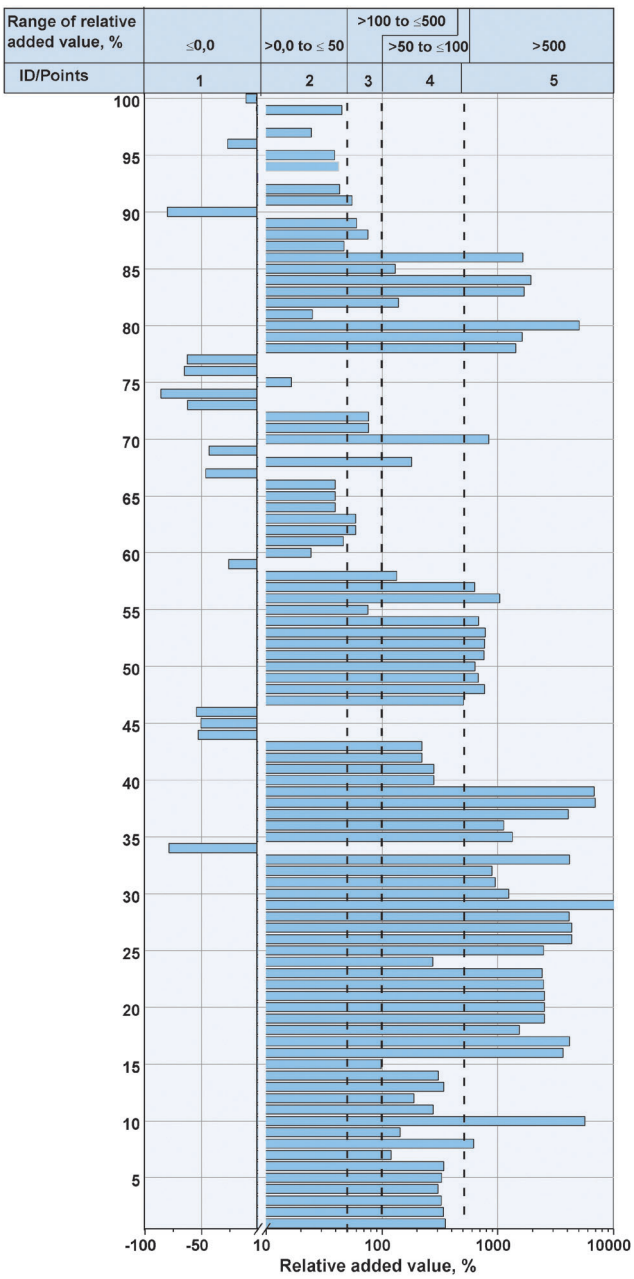


Fig. 6 Relative added value by the synthesis of the fine chemicals.

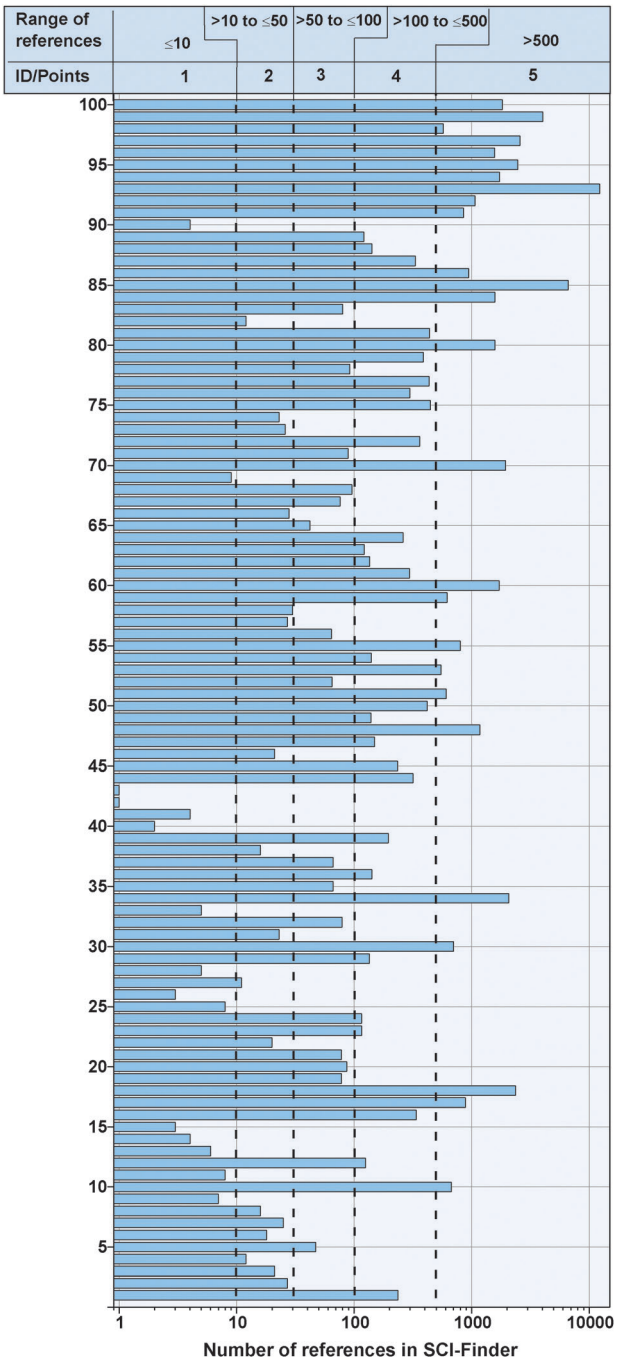


Fig. 7 Number of references of the fine chemicals in the online database SCI-Finder.

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