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Potential of commodity chemicals to become bio-based according to maximum yields and petrochemical prices

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Abstract: Carbohydrates are the prevailing biomass components available for bio-based production. The most direct way to convert carbohydrates into commodity chemicals is by one-step conversion at maximum theoretical yield, such as by anaerobic fermentation without side product formation. Considering these hypothetical yields and petrochemical prices in Europe in 2010–2014, a ranking of 58 commodity chemicals was made using a simple model with ethanol as a base case. It was concluded that base chemicals such as lower olefins and benzene-toluene-xylene (BTX) are too cheap and require too much carbohydrate to be produced competitively compared to bioethanol. However, more oxidized products that require multiple conversion steps in petrochemical production, such as adipic acid, acrylic acid, acrylate esters, and 1,4-butanediol, can be produced competitively from carbohydrates if theoretical yields are approached and if processing is efficient. Instead of carbohydrate fermentation, hypothetical photochemical production from CO₂ was also considered. Using again a simple model, the same commodity chemicals remained the most attractive ones. © 2017 The Authors. *Biofuels, Bioproducts, and Biorefining* published by Society of Chemical Industry and John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: commodity chemicals; carbohydrates; prices; yields; petrochemical production; carbon dioxide

Introduction

Dependence on fossil carbon sources as well as greenhouse gas (GHG) emissions might be reduced by using biomass as feedstock for the fuels and chemicals industry. Many options exist to produce chemicals from biomass. Commodity chemicals especially receive a lot of attention.^{1–6} These commodity chemicals are

categorized either as drop-ins or as candidate commodity chemicals. If produced competitively, either type might replace existing petrochemical commodity chemicals, but candidate commodity chemicals have properties unknown to the market. Therefore, in the case of competitive production, drop-in chemicals have a higher chance of quickly reaching the market. However, there is no good overview of which drop-in commodity chemicals are the

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most attractive ones to develop. For example, Werpy and Peterson's influential study¹ focuses on identifying candidate commodity chemicals. About drops-ins, they merely state that economic hurdles would be difficult to overcome.

The aim of the current study is to rank existing commodity petrochemicals based on economic potential of bio-based production.

It is useful to consider the situation in which bio-based production competes with petrochemical production on product price without taking into account potential tax incentives and carbon credits. Then, a simple model can be used with only a few variables: feedstock prices (carbohydrate vs. crude oil), number of conversion steps to product, maximum yields per conversion step, and typical feedstock contribution to product price.

Methods

Selection of commodity chemicals

From a useful starting list (https://en.wikipedia.org/wiki/Commodity_chemicals), compounds were taken that are derived from fossil carbon sources, thus eliminating compounds such as sorbitol. Also, compounds containing Cl atoms, and their derivatives, were excluded, because neither fossil nor lignocellulosic sources are preferred sources of Cl atoms. The main source of Cl is NaCl, leading to co-production of sodium compounds, which would diverge the discussion from the sources of C, H, and O atoms. N₂ can be taken as source of N-atoms, though, so N-containing chemicals were included. Some mixtures from the starting list were considered as individual compounds: methyl, ethyl, butyl, and ethylhexyl acrylate rather than acryl esters; 1-butanol, isobutanol, and 2-ethylhexanol rather than oxo alcohols; monoethanolamine, diethanolamine, and triethanolamine rather than ethanolamines; and toluene diisocyanate and methylene di(phenylene isocyanate) rather than isocyanates. Because of their commodity nature, isopropanol, MTBE, *o*-xylene, and *p*-xylene were added. Some more complex mixtures of compounds were not considered: glycol ethers, polyols, naphtha, and white spirit.

Source price data

Usually, prices of commodity chemicals are difficult to find in public information, and cannot be shared by companies. They are heavily influenced by local and temporal conditions, such as fluctuating crude oil prices. We assumed that such fluctuations could be largely eliminated if prices of different chemicals could be compared

over several years for the same location. Therefore, publicly available prices for commodity chemicals were collected from www.ICIS.com, for northwestern Europe as a location. Monthly prices were obtained for many chemicals. For some others, quarterly prices were found, and in some cases, there were gaps up to a year. For ammonia, partly prices from marketrealist.com were taken, to fill the dataset. Linear interpolation was done between the found prices to obtain a dataset (Supporting Information) with the prices (€/kg) for the 50 months from January 2010 to February 2014, for each of 54 commodity chemicals. The average prices are given in Table 1. Standard deviations are about 5 to 35%, indicating rather large price fluctuations.

Table 1. Average prices from January 2010 to February 2014 with standard deviations.

Commodity chemical	Price (€/kg)
Acetic acid	0.50 ± 0.10
Acetone	0.91 ± 0.08
Acrylic acid	1.80 ± 0.26
Acrylonitrile	1.77 ± 0.30
Adipic acid	1.84 ± 0.32
Ammonia	0.41 ± 0.07
Benzene	0.88 ± 0.14
Bisphenol A	1.56 ± 0.15
Butadiene	1.54 ± 0.58
1,4-Butanediol	2.00 ± 0.17
1-Butanol	1.10 ± 0.07
Butanone	1.52 ± 0.34
Butyl acetate	1.11 ± 0.12
Butyl acrylate	1.84 ± 0.32
Caprolactam	2.10 ± 0.14
Cyclohexane	1.03 ± 0.14
Diethanolamine	1.06 ± 0.08
Dimethyl terephthalate	0.99 ± 0.08
Ethanol	0.82 ± 0.09
Ethyl acetate	0.93 ± 0.08
Ethyl acrylate	2.04 ± 0.31
Ethylene	1.03 ± 0.08
Ethylene glycol	0.86 ± 0.10
Ethylene oxide	1.33 ± 0.14
2-Ethylhexanol	1.37 ± 0.14
2-Ethylhexyl acrylate	2.14 ± 0.23
Hexane	0.81 ± 0.08
Isobutanol	1.15 ± 0.06
Isopropanol	1.03 ± 0.08

Table 1. Continued

Maleic anhydride	1.64 ± 0.15
MDI (Methylene diphenyleneisocyanate)	1.95 ± 0.17
Melamine	1.28 ± 0.17
Methanol	0.31 ± 0.06
Methyl acrylate	1.82 ± 0.25
Methyl methacrylate	1.81 ± 0.29
MIBK (Methyl isobutyl ketone)	1.46 ± 0.19
Monoethanolamine	1.38 ± 0.12
MTBE (Methyl <i>tert</i> -butyl ether)	0.82 ± 0.13
Nylon-6	2.23 ± 0.20
PET (Polyethylene terephthalate)	1.29 ± 0.14
Phenol	1.25 ± 0.18
Phthalic anhydride	1.23 ± 0.18
PMM (Poly methyl methacrylate)	2.67 ± 0.43
Polyethylene	1.26 ± 0.10
Polypropylene	1.22 ± 0.11
Polystyrene	1.54 ± 0.18
Propylene	0.98 ± 0.08
Propylene glycol	1.30 ± 0.11
Propylene oxide	1.54 ± 0.09
Styrene	1.08 ± 0.14
Terephthalic acid	0.91 ± 0.10
Toluene	0.83 ± 0.14
Toluene diisocyanate	2.09 ± 0.14
Triethanolamine	1.44 ± 0.08
Vinyl acetate	0.88 ± 0.10
<i>o</i> -Xylene	1.00 ± 0.15
<i>p</i> -Xylene	1.02 ± 0.13
Xylenes (mixed)	0.85 ± 0.11

In the considered interval, the Brent oil price was between 0.38 and 0.72 €/kg according to recalculation of the FOB (free on board) price, which was 102 ± 15 \$/barrel (https://en.wikipedia.org/wiki/Price_of_oil). The US dollar to euro ratio was 1.33 ± 0.05 \$/€, with extremes of 1.23 and 1.45 \$/€ (www/x-rates.com). These variations were considered mild as compared to the extreme variations in some earlier and later intervals. Natural gas prices were from http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=nrg_pc_203&lang=en.

Linear regression

Correlation between monthly prices of products and precursors was done by linear regression using the 'Linest' function in Microsoft Excel 2010. This minimized the sum

of squared differences between actual and model value of product price.

Results and discussion

The cost of a conversion step

Petrochemical commodity chemicals are ultimately derived from fossil feedstocks such as crude oil and natural gas. The prices of these fossil feedstocks are linked to each other because they are both mainly used as source of energy (for heating, power generation, and transportation) rather than as source of chemicals and materials. A variety of refining and conversion steps is used to convert a relatively modest part of the fossil feedstocks into seven main base chemicals: ethylene, propylene, butenes, benzene, toluene, xylene, and syngas/methanol.⁷ Ammonia was added to this set of compounds. Their prices, on mass basis, correlate very strongly with those of their feedstock, as shown in Table 2.

The base chemicals are stepwise used to produce other commodity chemicals. For almost each of these other chemicals, one or two compounds can be identified as precursor for the dominating industrial process (Table 3).

The petrochemical industry is a mature industry, and the prices of the products are largely determined by the costs of their direct precursor(s).⁸ Other important factors are capital investment costs, energy costs, and profit. If cumulated for multiple sequential conversion steps, capital investment and energy costs may exceed the costs of primary petrochemical feedstock used in the pathway,⁹ but the subsequent analysis is per conversion step.

In case of a single precursor, the simplest relation between product price $P_{prod,i}$ (€/kg) and precursor price $P_{prec,i}$ in month i is $P_{prod,i} = \alpha P_{prec,i}$. A somewhat more

Table 2. Slope α of a plot through the origin of base chemical vs. feedstock prices (€/kg) from the used database.

Base chemical	Feedstock	α (€ _{base chemical} /€ _{feedstock})
Ethylene	Crude oil	1.73 ± 0.04
Propylene	Crude oil	1.66 ± 0.03
Butadiene ^a	Crude oil	2.63 ± 0.14
Benzene	Crude oil	1.51 ± 0.03
Toluene	Crude oil	1.42 ± 0.02
Xylenes (mixed)	Crude oil	1.45 ± 0.01
Methanol	Natural gas	0.68 ± 0.01
Ammonia	Natural gas	0.89 ± 0.15

^a No prices were available for the other butenes.

Table 3. Commodity products and α' values for formation from the indicated precursors.

Product	Precursor(s)	α'
Acetic acid	Methanol + CO	1.94 ± 0.09
Acetone ^a	Cumene ^c + O ₂	1.24 ± 0.01 ^b
Acrolein ^c	Propylene + O ₂	1.77 ± 0.02 ^b
Acrylic acid	Acrolein ^c + 0.5 O ₂	1.77 ± 0.02 ^b
Acrylonitrile	Propylene + NH ₃ + 1.5 O ₂	1.93 ± 0.06
Adipic acid	Cyclohexanol ^c + O ₂ ^d	1.75 ± 0.03 ^b
Bisphenol A	Acetone + 2 Phenol	1.22 ± 0.03
1,4-Butanediol	Maleic anhydride + 5 H ₂	0.97 ± 0.04
1-Butanol	Butyraldehyde ^c + H ₂	1.23 ± 0.01 ^b
2-Butanol ^c	Butene ^c	n.d.
Butanone	2-Butanol ^c	n.d.
Butyl acetate	1-Butanol + Acetic acid	1.15 ± 0.02
Butyl acrylate	1-Butanol + Acrylic acid	1.12 ± 0.02
Butyraldehyde ^c	Propylene + CO + H ₂	1.23 ± 0.01 ^b
Caprolactam	Cyclohexanone ^c + Hydroxylamine sulfate ^c	n.d.
Cumene ^c	Benzene + Propylene	1.24 ± 0.01 ^b
Cyclohexane	Benzene + 3 H ₂	1.08 ± 0.01
Cyclohexanol ^c	Cyclohexane + 0.5 O ₂	1.75 ± 0.03 ^b
Cyclohexanone ^c	Cyclohexane + O ₂	n.d.
Diethanolamine	2 Ethylene oxide + NH ₃	0.89 ± 0.01
Dimethyl terephthalate	2 Methanol + Terephthalic acid	1.12 ± 0.01
Ethanol	Ethylene	1.32 ± 0.02
Ethyl acetate	Ethanol + Acetic acid	1.20 ± 0.01
Ethyl acrylate	Ethanol + Acrylic acid	1.22 ± 0.02
Ethylbenzene ^c	Benzene + Ethylene	1.07 ± 0.01 ^b
Ethylene diamine ^c	Monoethanolamine + NH ₃	n.d.
Ethylene glycol	Ethylene oxide	0.91 ± 0.01
Ethylene oxide	Ethylene + 0.5 O ₂	2.02 ± 0.04
2-Ethylhexanol	2 Butyraldehyde ^c + 2 H ₂	1.30 ± 0.01
2-Ethylhexyl acrylate	2-Ethylhexanol + Acrylic acid	1.28 ± 0.01
Formaldehyde ^c	Methanol + O ₂	1.56 ± 0.01 ^b
Isobutyrinaldehyde ^c	Propylene + CO + H ₂	1.25 ± 0.01 ^b
Isopropanol	Propylene	1.49 ± 0.01
Maleic anhydride	Butane ^c + 3.5 O ₂	n.d.
MDI	Diamine ^c + Phosgene ^c	n.d.
Melamine	Urea ^c	n.d.
Methyl acrylate	Methanol + Acrylic acid	1.12 ± 0.01
Methyl methacrylate	Methyl propionate ^c + Formaldehyde ^{c,e}	1.83 ± 0.02 ^b
Methyl propionate ^c	Methanol + Ethylene + CO	1.83 ± 0.02 ^b

Table 3. Continued

MIBK	2 Acetone + H ₂	1.33 ± 0.02
Monoethanolamine	Ethylene oxide + NH ₃	1.29 ± 0.01
MTBE	Methanol + Isobutene ^c	n.d.
Nylon-6	Caprolactam	1.06 ± 0.01
PET	Ethylene glycol + Terephthalic acid	1.20 ± 0.02
Phenol ^a	Cumene ^{a,c} + O ₂	1.24 ± 0.01 ^b
Phthalic anhydride	<i>o</i> -Xylene + 3 O ₂	1.71 ± 0.01
PMM	Methyl methacrylate	1.46 ± 0.03
Polyethylene	Ethylene	1.23 ± 0.02
Polypropylene	Propylene	1.24 ± 0.01
Polystyrene	Styrene	1.42 ± 0.02
Propylene glycol	Propylene oxide	1.10 ± 0.01
Propylene oxide	Propylene + H ₂ O ₂ ^c	n.d.
Styrene	Ethylbenzene ^c	1.07 ± 0.01 ^b
Terephthalic acid	<i>p</i> -Xylene + 3 O ₂	1.39 ± 0.01
Toluene	Diaminotoluene ^c + Phosgene ^c	n.d.
Triethanolamine	3 Ethylene oxide + NH ₃	1.17 ± 0.01
Vinyl acetate	Ethylene + Acetic acid + 0.5 O ₂	1.28 ± 0.01
<i>o</i> -Xylene	Xylenes (mixed)	1.18 ± 0.01
<i>p</i> -Xylene	Xylenes (mixed)	1.20 ± 0.01

^a Acetone and phenol are jointly made from propylene and benzene via cumene. ^b For two consecutive conversions involving this one, the price of an intermediate product was not known (Table 1). The given α' value is only correct if it is the same for the consecutive conversion steps. ^c Compound for which no price data were available for regression. ^d Via regeneration of HNO₃. ^e Not the precursors in the dominant process, which has stoichiometric coproducts that could not be considered.

complicated relation is $P_{prod,i} = \alpha P_{prec,i} + \beta$. The model parameters α and β were regressed by minimizing the sum of square errors between predicted and real $P_{prod,i}$ values, for each product with a single precursor, if they were both covered by the price database. Model discrimination using the F-test showed that the second model, including the β term, was not significantly better considering this extra parameter. Therefore, the analysis was continued without a β term. From the found values of α (on mass basis), values of α' (on mole basis) were calculated. This calculation involved the mass yield Y of product on precursor when assuming 100% molar yield for the product formation reaction.

$$Y_{prod/prec,j} = \frac{\text{mass product}}{\text{mass precursor } j} \quad (1)$$

On average for these cases with a single precursor, α' was 1.41, with an average standard error of 0.02 per case.

In case of two precursors, with prices $P_{prec1,i}$ and $P_{prec2,i}$, different mass yields $Y_{prod/prec.1}$ and $Y_{prod/prec.2}$ apply, according to the stoichiometry of Table 3. We tried the two-parameter model $P_{prod,i} = \alpha'_1 \cdot P_{prec1,i}/Y_{prod/prec.1} + \alpha'_2 \cdot P_{prec2,i}/Y_{prod/prec.2}$, but regressed α'_1 and α'_2 values had a large error and were widely different for different products. When using a one-parameter model, $P_{prod,i} = \alpha'(P_{prec1,i}/Y_{prod/prec.1} + P_{prec2,i}/Y_{prod/prec.2})$, these problems disappeared. Therefore, it was decided to use one general equation for each conversion with j precursors:

$$P_{prod,i} = \alpha' \sum_j \frac{P_{prec,j,i}}{Y_{prod/prec.j}} \quad (2)$$

The number of conversions for which regressions could be performed was increased significantly by assuming prices for H₂ and CO as second or third precursor. A relatively low accuracy was acceptable for these prices, because of their low price and modest mass contribution to the product. The natural gas price in €/kg was multiplied by 4 for H₂ and by 0.4 for CO to obtain in the considered time interval on average 1.81 €/kg H₂ and 0.18 €/kg CO, which has a reasonable correspondence with occasional prices seen elsewhere.^{10, 11}

Sometimes the price of an intermediate of two consecutive conversions was not available in the database. Then, regression was performed using the prices of the precursor of conversion 1 and the product of conversion 2. The regressed $\alpha'_{1,2}$ value is the multiplication of α'_1 and α'_2 . For simplicity, these were assumed to be the same, so that an α' value could be obtained from the square root of the $\alpha'_{1,2}$ value.

Table 3 shows that all individual α' values have low standard errors, demonstrating strong correlations between product and precursor prices. When dividing all monthly product prices by those for stoichiometric mass amounts of precursor, on average $\alpha' = 1.34 \pm 0.24$. This suggests that a product is on average 34% more expensive than the stoichiometric amount of its precursors, which makes sense. However, some individual conversions deviate significantly from the average. For example, ethylene oxide shows a relatively high α' value for its production and relatively low α' value for its conversion. A potential explanation is that its shipping is very expensive as compared to those of the conversion product (ethylene glycol) such that this conversion product may face much stronger price pressure from other continents. Also, some other α' values are unexpected, in particular $\alpha' = 0.97$ for maleic anhydride (MA) to 1,4-butanediol (BDO), maybe

because BDO is produced from crude MA which is not traded (https://en.wikipedia.org/wiki/Maleic_anhydride) whereas the correlations were performed with available prices of higher quality MA. Detailed discussions on the background of all individual α' values are not within scope of this paper, however.

The strong correlations suggest that the price of a commodity chemical for which no price is available can be estimated by taking the costs for its precursor(s) while assuming 100% molar yield, and multiplying by a factor of about 1.34 to cover all other costs, such as capital investments and utility consumption, and to cover profit. Many conversions are performed at less than this 100% molar yield of product on precursor. Then, a model assuming 100% molar yield might still be applicable because unconverted precursor can be recycled and valorization of side products originating from unselective conversion of the precursor can be very successful.

If differences in efforts required to recover different main products would be dominating, more scatter in α' values would have been found.

The model implies that a chemical would become cheaper if fewer conversion steps would be required to obtain it from a particular fossil carbon source.

Most error ranges in Table 3 do not overlap, indicating that using in the model the individual α' value of a conversion is more accurate than using the average value of $\alpha' = 1.34$. The relevant individual α' value or otherwise the average value was used to predict some prices not available from the used source (Table 4).

Carbohydrate feedstock

It is assumed here that, in biomass-based chemical industry, the biomass will be decomposed into building block mixtures such as monosaccharides or bio-syngas, and that a range of consecutive conversion steps will use these building blocks. There is a lot of debate about what will be the most attractive building blocks. Here we assume monosaccharides and disaccharides. Currently, fermentation of glucose or sucrose (originating from first-generation biomass) to ethanol is used at very large scale. Most of the produced ethanol is used as biofuel, and this bioethanol has also largely replaced petrochemical ethanol as a commodity chemical. In future scenarios, second-generation carbohydrates may become the dominant fermentation feedstock, and butanol or terpene-derived compounds, for example, may become the dominant biofuel.¹² When a carbohydrate-based biofuel industry exists (as it does currently), the biochemical industry can obtain carbohydrates

Table 4. Prices predicted using relevant α' from Table 3 or otherwise $\alpha' = 1.36$.

Commodity product	Average model price (€/kg)	Conversion used for calculation
Acrolein	1.30	Propylene → Acrolein → Acrylic acid
2-Butanol	1.15	2-Butanol → Butanone
Butyraldehyde	0.85	Propylene → Butyraldehyde → 1-Butanol
Cumene	1.14	Benzene → Cumene → Phenol
Cyclohexanol	1.51	Cyclohexane → Cyclohexanol → Adipic acid
Cyclohexanone	1.54	Cyclohexane → Cyclohexanone → Adipic acid
Ethylbenzene	0.99	Benzene → Ethylbenzene → Styrene
Ethylene diamine	2.07	Monoethanolamine → Ethylene diamine
Ethyl <i>tert</i> -butyl ether (ETBE)	1.08	Ethanol + Isobutene → ETBE
Formaldehyde	0.60	Methanol → Formaldehyde
Isobutene	0.77	Methanol + Isobutene → MTBE
Isobutyraldehyde	0.87	Propylene → Isobutyraldehyde → Isobutanol
Methyl propionate	0.91	Ethylene → Methyl propionate → Methyl methacrylate

for the price that the biofuel industry is willing and able to pay. This statement is derived from the situation on the petrochemical market, where the feedstock prices for the chemicals are determined by what the transportation industry is willing and able to pay.¹³

Thus, the chemical industry will not get feedstock for lower prices than the fuel industry, because carbohydrate-based chemicals production must compete with the carbohydrate-based biofuel production.

Maximum anaerobic production yields from glucose

Carbohydrate-based production of the aforementioned commodity products will be analyzed in more detail, except for the aforementioned polymers. To produce these polymers at desired quality, it is assumed that polymerization of the current purified monomers will

remain and only the source of the monomers might change.

For convenience, glucose is taken here as the default monosaccharide for chemicals production. Other monosaccharides and sucrose can be expressed in glucose equivalents.

For each commodity chemical $C_aH_bN_cO_d$ in the selected set, a product reaction stoichiometry can be formulated according to:



Thus, N_2 is taken as nitrogen source, to avoid that fossil carbon sources enter the equation via petrochemical production of NH_3 . No costs were taken for N_2 as feedstock.

Calculation of coefficients x , y , and z was done using the three elemental balances of C, H, and O. For maleic anhydride, phthalic anhydride and terephthalic acid a negative coefficient for CO_2 was found, because these products are more oxidized than glucose. For simplicity, no costs for CO_2 co-consumption with glucose were considered, though. In another scenario, these three chemicals are candidate for anaerobic co-production with a reduced commodity product.¹⁴

The maximum mass yield Y of product on glucose was derived using coefficient x in Eqn (3). Oxidized products have a more advantageous mass yield than reduced products, which in many cases is due incorporation of O atoms with a high atomic mass relative to C and H. Similar observations have been made before.⁴

On the basis of this model, and in line with other studies,⁹ anaerobic fermentation of carbohydrates directly to a target commodity chemical is attractive, considering that one conversion step is the minimum number and that maximum theoretical yields are achievable with anaerobic conversion. Aerobic fermentation is known to be less attractive.¹⁴ Product yields are lower if O_2 is included as co-substrate in the product formation reaction. Energy requirements for air compression and stirring are avoided, as well as oxygen transfer limitations. Besides, a complication of aerobic fermentation is that growth does not depend on the energy that the microorganism gains from product formation. Mutations that decrease product formation are favored, rendering continuous fermentation with cell retention impossible. Re-growing cells becomes unavoidable. If one cannot avoid that a significant amount of glucose is consumed by cell growth, the maximum theoretical product yield on glucose cannot be approached.

Check for thermodynamic constraints

The maximum theoretical yield according to anaerobic reaction stoichiometry might also be unachievable according to kinetic and thermodynamic constraints.⁵ Basic thermodynamic constraints can be identified early on. The value of $\Delta_r G^\circ$, the standard Gibbs energy of reaction, was calculated for each product reaction (Eqn (3)) using values of the standard Gibbs energies of formation, $\Delta_f G^\circ$, from both a biochemical database¹⁵ and a chemical database.¹⁶ These use as standard state for the products 1 mol/L aqueous solution and ideal gas, respectively, at 25 °C and 1 atm. Most $\Delta_f G^\circ$ values were available from both databases and did not differ much. Also $\Delta_f G^\circ$ values for gaseous or liquid standard states do not differ much.¹⁷ The found $\Delta_r G^\circ$ values typically showed small differences as compared to required values as discussed subsequently. Only for MDI no values were found.

It has been estimated¹⁸ that for industrially relevant rates the $\Delta_r G^\circ$ value for formation of product from glucose should be more negative than about -27 kJ/mol glucose. Then, sufficient energy in the form of ATP or membrane potential can be provided for cell production, maintenance, and product excretion. For almost all considered products, this constraint was easily satisfied. Exceptions were maleic anhydride, melamine, formaldehyde, when using the chemical database ethylene oxide, and when using the biochemical database ethylene glycol. The $\Delta_f G^\circ$ value of ethylene oxide from the biochemical database¹⁵ was assumed to be unreliable because epoxides have not been used for establishing biochemical databases. On the other hand, the chemical database¹⁶ was assumed to lead to unreliable results for ethylene glycol. Calculations using the $\Delta_f G^\circ$ value obtained for ethylene glycol via another chemical database¹⁷ gave results consistent with the biochemical database results, and also with the expectation that ethylene glycol would show, like related alcohols, no thermodynamic constraint for anaerobic production. Maleic anhydride, melamine, formaldehyde, and ethylene oxide, on the other hand, were left out from further analysis, like the diisocyanates, which are very reactive in water.

Comparison to glucose fermentation into ethanol

From industrial white sugar prices in the EU in the considered time interval (http://ec.europa.eu/agriculture/sugar/presentations/price-reporting_en.pdf) an equivalent glucose price was calculated. On basis of the theoretical

yield of ethanol on glucose, and the ethanol prices, $\alpha' = 1.22$ was calculated using a similar equation as before.

$$P_{EtOH,i} = \alpha'_{Glc \rightarrow EtOH} \frac{P_{Glc,i}}{Y_{EtOH/Glc}} \quad (4)$$

This value would be higher for cheaper, lower-quality carbohydrate. To eliminate discussions about carbohydrate type and quality, a similar equation is taken for alternative fermentation products:

$$P_{prod,i} = \alpha'_{Glc \rightarrow prod} \frac{P_{Glc,i}}{Y_{prod/Glc}} \quad (5)$$

Now the price P_{Glc} of glucose can be eliminated, such that the price of fermentation products is linked to that of ethanol, which is available in the used database:

$$P_{prod,i} = \frac{\alpha'_{Glc \rightarrow prod}}{\alpha'_{Glc \rightarrow EtOH}} \frac{Y_{EtOH/Glc}}{Y_{prod/Glc}} P_{EtOH,i} \geq \frac{Y_{EtOH/Glc}}{Y_{prod/Glc}} P_{EtOH,i} \quad (6)$$

The right-hand side of Eqn (6) has been derived from the judgement that the bioethanol production is a competitive market using well-developed and efficient processes, leading to the relatively low $\alpha'_{Glc \rightarrow EtOH} = 1.22$, while fermentative production of other commodity chemicals is not expected to reach even lower α' values.

The Y -values can be calculated from achievable yields. The maximum theoretical yield for ethanol (0.51 kg per kg glucose) is closely approached in practice, whereas for most other commodity chemicals their theoretical maximum is not approached (Table 5), because the processes are aerobic or not well developed yet. Besides, in the ethanol fermentation process α' is in the same range as for bulk chemicals production, and it is not likely that for production of other chemicals by fermentation the values will become lower. Therefore, the latter equation gives a minimum achievable price of commodity chemicals when produced from carbohydrates by fermentation, or similarly by catalytic conversion. Like for ethanol, is it assumed that the commodity chemicals are produced in one conversion step with the highest yield possible according to basic stoichiometric and thermodynamic limitations, and all costs besides carbohydrate are assumed to be as low as in ethanol production.

For each commodity chemical, the difference Δ between the minimum price, when produced from carbohydrate (Table 5), and the current petrochemical price was calculated. A ranking was made (Fig. 1) based on the Δ -values. According to this analysis, commodity chemicals that are lower ranked than ethanol would not be able to

Table 5. Production in one conversion step from glucose.

Commodity product	Max. yield theoretical (g _{prod} /g _{glc})	Min. price theoretical (€/kg _{prod})	Yield reported (g _{prod} /g _{glc})
Acetic acid	1.000	0.42	0.8 ⁵
Acetone	0.483	0.87	0.11 ⁵
Acrolein	0.533	0.79	
Acrylic acid	0.800	0.53	<0.01 ²⁶
Acrylonitrile	0.471	0.89	
Adipic acid	0.749	0.56	0.05 ²⁷
Benzene	0.347	1.21	
Bisphenol A	0.422	1.00	
Butadiene	0.327	1.29	
1,4-Butanediol	0.545	0.77	>0.40 ²⁸
1-Butanol	0.411	1.02	0.36 ⁵
2-Butanol	0.411	1.02	0.02 ²⁹
Butanone	0.436	0.96	0.01 ³⁰
Butyl acetate	0.483	0.87	
Butyl acrylate	0.474	0.89	
Butyraldehyde	0.436	0.96	
Caprolactam	0.457	0.92	
Cumene	0.333	1.26	
Cyclohexane	0.311	1.35	
Cyclohexanol	0.392	1.07	
Cyclohexanone	0.408	1.03	
Diethanolamine	0.609	0.69	
Dimethyl terephthalate	0.616	0.68	
ETBE	0.378	1.11	
Ethanol	0.511	0.82	0.50 ⁵
Ethyl acetate	0.587	0.72	0.20 ³¹
Ethyl acrylate	0.556	0.76	
Ethylbenzene	0.337	1.25	
Ethylene	0.311	1.35	<0.01 ⁵
Ethylene diamine	0.500	0.84	
Ethylene glycol	0.827	0.51	0.27 ^{5,a}
2-Ethylhexanol	0.361	1.17	
2-Ethylhexyl acrylate	0.409	1.03	
Hexane	0.302	1.40	
Isobutanol	0.411	1.02	0.35 ⁵
Isobutene	0.311	1.35	
Isobutyraldehyde	0.436	0.96	0.18 ⁵
Isopropanol	0.444	0.95	0.24 ⁵

Table 5. Continued

Methanol	0.711	0.59
Methyl acrylate	0.637	0.66
Methyl methacrylate	0.556	0.76
Methyl propionate	0.587	0.72
MIBK	0.392	1.07
Monoethanolamine	0.626	0.67
MTBE	0.391	1.08
Phenol	0.448	0.94
Phthalic anhydride	0.658	0.64
Propylene	0.311	1.35
Propylene glycol	0.633	0.66
Propylene oxide	0.483	0.87
Styrene	0.347	1.21
Terephthalic acid	0.738	0.57
Toluene	0.341	1.24
Triethanolamine	0.602	0.70
Vinyl acetate	0.637	0.66
o-Xylene	0.337	1.25
p-Xylene	0.337	1.25

^a From xylose, not glucose

compete with bioethanol production for the carbohydrate feedstocks. The base chemicals mentioned in Table 2 are all too low ranked. Their petrochemical production does not require many conversion steps and has much higher yields than would be possible by production from carbohydrate. Carbohydrate contains a lot of oxygen which is useless for production of these base chemicals. Indeed, ethylene production from carbohydrate, for example, was found to be economically infeasible in Europe,¹⁹ although more favorable situations might be obtained elsewhere.²⁰ Unfortunately, the base chemicals dominate the market with respect to production volume.

Among the best ranked candidates for carbohydrate-based production are adipic acid, acrylic acid, 1,4-butanediol, and methyl methacrylate. These are relatively oxidized (containing much oxygen) and require several petrochemical conversion steps starting from the base chemicals, with each step leading to a price multiplication by a factor α' . Thus, these relatively oxidized commodity chemicals might be produced competitively from carbohydrates. High-yield one-step conversion (e.g. by anaerobic fermentation) in combination with efficient processing (to obtain $\alpha' < 1.5$, e.g.) will favor this. Low capital investment, thus achieving

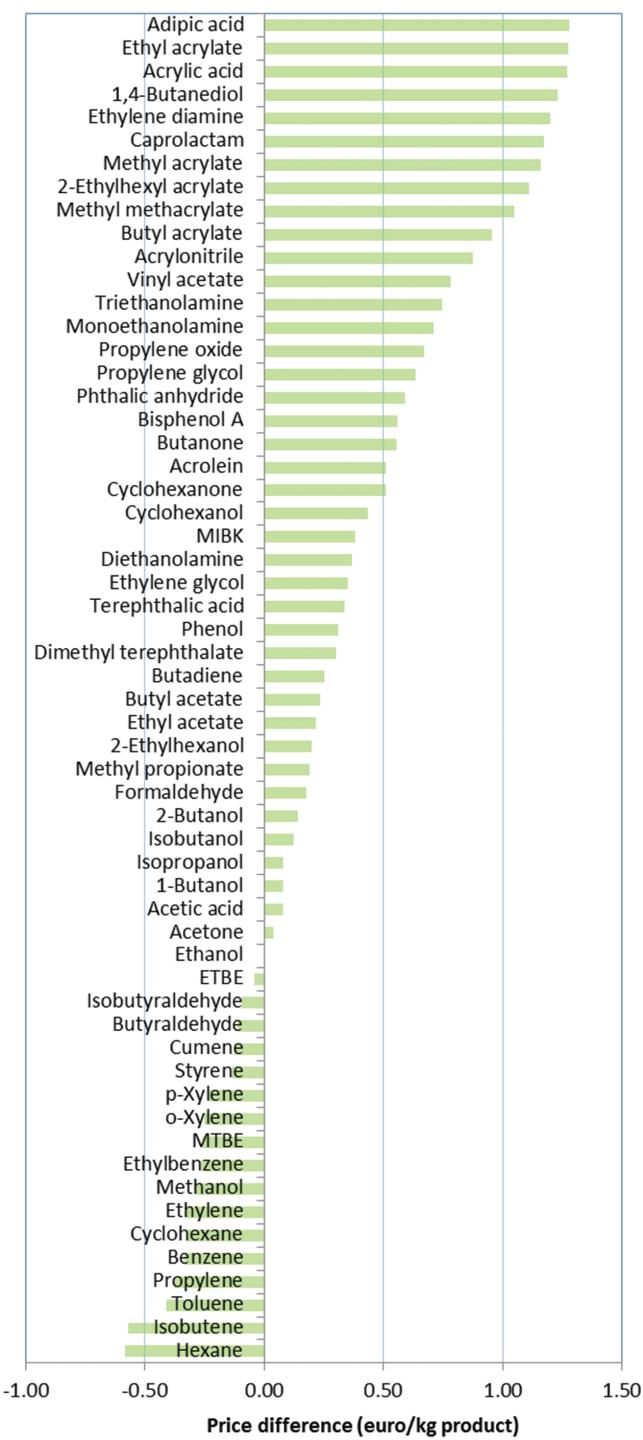


Figure 1. Ranking of commodity chemicals with respect to the difference between petrochemical price and predicted minimum price in production from carbohydrate.

economy of scale such as in bioethanol production, is an important factor for efficient processing.

Some nitrogen-containing products (e.g. caprolactam, ethylene diamine) rank high despite a low degree of

oxidation. This is not due to high maximum theoretical yields on glucose (because those are low, due to their low degree of oxidation) but because of their relatively high petrochemical price. That high price originates from the high number of required petrochemical conversion steps, which include producing ammonia from N₂. But fermentative conversion of N₂ into N-containing commodity chemicals while using carbohydrate as energy source is still a challenge, even though micro-organisms can be engineered to obtain the genes required for N-fixation.²¹

In the cases in which Fig. 1 shows a large positive value, there is room for suboptimal processing. The margin for bio-based production can be recalculated using a lower anticipated yield and higher α' value. If more than one conversion step is required to obtain a particular product from carbohydrate, Eqn (6) can be multiplied by α' values of the additional conversions. For example, production of acrylic acid by direct fermentation is difficult because of its toxicity, but if fermentation of 1 mole glucose into 2 moles of lactic acid²² would be followed by selective catalytic dehydration,²³ theoretically $Y = 0.8$ could be achieved. Supposing a realistic value of 0.5 and taking a suboptimal value ($\alpha' = 2$) for the extra step, the bio-based price for acrylic acid is calculated to be 1.42 €/kg, which still is well below the petrochemical price of 1.77 €/kg.

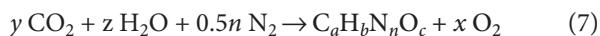
Production of commodity chemicals from CO₂

The aforementioned fermentative production from carbohydrates has to be preceded by photochemical (agricultural) processes to convert CO₂ into plants, by harvesting, transportation, and by biorefining up to fermentable carbohydrates. Algae are also a potential source of fermentable carbohydrates. Alternatively, CO₂ might be converted into chemicals more directly, for example using recombinant algae that use solar energy to drive this conversion.²⁴ The same question may be raised as before: which chemicals could become the more profitable ones if ideal metabolic pathways and ideal process technology would be established.

Energy costs and CO₂ costs are major contributions to overall production costs from CO₂.²⁵ In algal production, harvesting solar energy requires transparent reactor surface, which is one of the main costs. The costs of CO₂ will be lower, especially at locations where it is freely available. For simplicity, we assume that all other cost factors are in some way proportional to energy and CO₂ costs. At current algal research standards, high product recovery costs due to low product titers might easily

be prohibitive. However, we imagine ideal production conditions with high titers.

The absolute minimum amount of energy required for such production is the negative of the standard Gibbs energy of reaction for photochemical synthesis of the commodity chemical $C_aH_bO_c$ from CO_2 ; while including N_2 in case of N-containing products:



Analogous to the carbohydrate-based cases, one-step microbial conversion is taken as example, but the same reasoning may be valid for catalytic conversion. It is assumed that CO_2 and Gibbs energy required to produce the microorganisms that should perform the conversion can be neglected. Thus, perfect cell retention would have to be approached and product must be secreted.

Using Eqn (7), per product the stoichiometric coefficients and the Gibbs energy of reaction were calculated as explained for carbohydrate-based production. Gibbs energy values are given in Table 6. Coefficient y in Eqn (7), indicating the absolute minimum amount of required CO_2 , simply equals the number of carbon atoms in the target product. It is positively correlated with the required Gibbs energy (Fig. 2). So, there is no need for a separate evaluation of the effect of the required amount of CO_2 per chemical product. An initial ranking can be based merely on Gibbs energy requirement per chemical product.

Two scenarios were evaluated. A minimum anticipated price for solar energy of 98 \$/MWh (http://www.eia.gov/forecasts/aeo/electricity_generation.cfm) was used. Supposing that such energy would be converted into the minimum Gibbs energy required for the photochemical product synthesis and that all other costs would be neglected, the 'low' scenario prices for chemicals were found, which are in the range of petrochemical prices (Table 6). Also 'high' scenario prices are given, multiplying the low prices by 5. These high prices range clearly above petrochemical prices. The difference Δ between petrochemical prices and low scenario CO_2 -based prices was used for ranking (Fig. 3). Like for carbohydrate-based production, more oxidized products are more favorable. Generally, less solar energy (and less CO_2) will be required per kg of chemical product if the product is more oxidized. When taking the high scenario prices, all Δ values became negative, but the ranking of products changed only marginally (not shown). So, not knowing which scenario will be valid for the presented model should not affect a choice between potential target products.

Table 6. Production from CO_2 considering only Δ_rG° costs.

Commodity product	Δ_rG° (kJ/ $mol_{product}$)	Price in "low" scenario (€/kg _{prod})	Price in "high" scenario (€/kg _{prod})
Acetic acid	881	0.36	1.80
Acetone	1744	0.74	3.68
Acrolein	1605	0.70	3.50
Acrylic acid	1388	0.47	2.36
Acrylonitrile	1731	0.80	3.99
Adipic acid	2868	0.48	2.40
Benzene	3209	1.01	5.03
Bisphenol A	7808	0.84	4.19
Butadiene	2441	1.11	5.53
1,4-Butanediol	2488	0.68	3.38
1-Butanol	2616	0.86	4.32
2-Butanol	2598	0.86	4.29
Butanone	2382	0.81	4.04
Butyl acetate	3480	0.73	3.67
Butyl acrylate	3954	0.76	3.78
Butyraldehyde	2412	0.82	4.10
Caprolactam	3603	0.78	3.90
Cumene	5113	1.04	5.21
Cyclohexane	3825	1.11	5.57
Cyclohexanol	3675	0.90	4.49
Cyclohexanone	3465	0.86	4.32
Diethanolamine	2671	0.62	3.11
Dimethyl terephthalate	4659	0.59	2.94
ETBE	3909	0.94	4.69
Ethanol	1334	0.71	3.55
Ethyl acetate	2200	0.61	3.06
Ethyl acrylate	2677	0.65	3.27
Ethylbenzene	4474	1.03	5.16
Ethylene	1333	1.16	5.82
Ethylene diamine	1843	0.75	3.76
Ethylene glycol	1205	0.48	2.38
Ethylene oxide	1148	0.64	3.19
2-Ethylhexanol	5176	0.97	4.87
2-Ethylhexyl acrylate	6526	0.87	4.34
Formaldehyde	530	0.43	2.16
Hexane	4031	1.15	5.73
Isobutanol	2611	0.86	4.31
Isobutene	2587	1.13	5.65

Table 6. Continued

Isobutyraldehyde	2412	0.82	4.10
Isopropanol	1961	0.80	4.00
Maleic anhydride	1460	0.36	1.82
Melamine	2156	0.42	2.09
Methanol	708	0.54	2.70
Methyl acrylate	2033	0.58	2.89
Methyl methacrylate	2681	0.66	3.28
Methyl propionate	2217	0.62	3.08
MIBK	3658	0.89	4.47
Monoethanolamine	1514	0.61	3.03
MTBE	3281	0.91	4.56
Phenol	3047	0.79	3.96
Phthalic anhydride	3302	0.55	2.73
Propylene	1959	1.14	5.70
Propylene glycol	1830	0.59	2.94
Propylene oxide	1781	0.75	3.75
Styrene	4321	1.02	5.08
Terephthalic acid	3269	0.48	2.41
Toluene	3834	1.02	5.10
Triethanolamine	3849	0.63	3.16
Vinyl acetate	2062	0.59	2.93
<i>o</i> -Xylene	4466	1.03	5.15
<i>p</i> -Xylene	4465	1.03	5.15

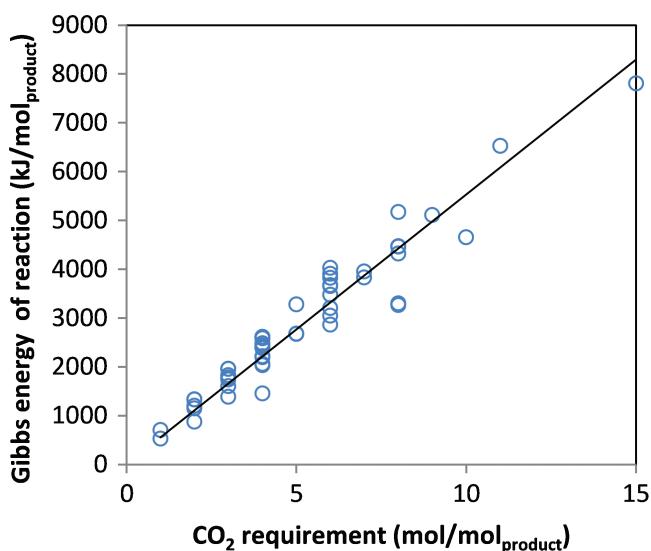


Figure 2. Correlation between $\Delta_r G^\circ$ and stoichiometric coefficient y in ideal photochemical production. Markers indicate products from Table 6.

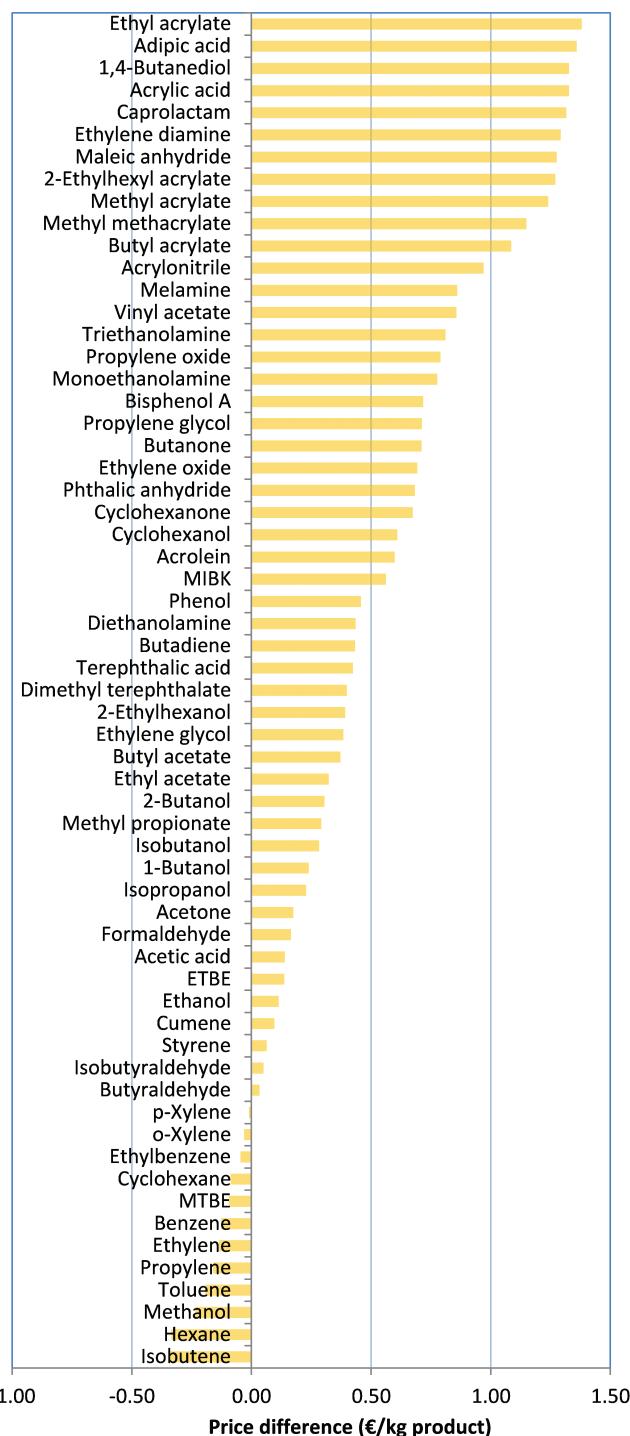


Figure 3. Ranking of commodity chemicals with respect to the difference between petrochemical price and predicted price for production from CO₂ in the 'low' scenario.

Sensitivity analysis

This study has many assumptions. Readers with different assumptions can often directly quantify the impact of their assumptions.

The presented rankings rely heavily on the used petrochemical prices, which are from northwestern Europe in 2010–2014. Prices will be different at other locations and times, and will also depend on product purity. Recent changes in the petrochemical industry due to the use of shale gas are not yet reflected in the used prices. The petrochemical prices mentioned in Table 4 are model-derived prices, therefore less reliable than those in Table 1, making the Δ -values of the products involved less reliable.

The use of ethanol production as base-case makes the absolute values of calculated Δ -values (but not their ranking) sensitive to explicit and implicit assumptions about ethanol production such as not considering the ethanol purity as variable in production costs.

Feedstocks that are more reduced than carbohydrate, for example glycerol or fatty acids, if available at sufficiently large scale and low price, will lead to higher theoretical yields for most commodity chemicals, and bio-based production of lower olefins and benzene-toluene-xylene (BTX) might still be considered using such feedstocks.

The practical feasibility to achieve the optimum values for carbohydrate-based and CO₂-based production will be different per target product and should be considered in the next evaluation stage.

Conclusions

Price correlations between commodity chemicals and maximum yield calculations can be used to predict which production routes may be competitive. Production from carbohydrates is not competitive for platform chemicals such as ethylene, propylene, and BTX. Based on prices in Europe in 2010–2014, these chemicals can be produced more cheaply from petrochemical resources. This situation may remain if bioethanol is a profitable destination for available carbohydrates. When production of a petrochemical requires more steps and more oxidation, such as for adipic acid, acrylates, and diols, production from carbohydrates can be competitive. This requires that maximum theoretical yields are approached in the minimum number of steps, for example by anaerobic fermentation.

Also for photochemical production from CO₂ it seems more attractive to focus on production of relatively oxidized commodity chemicals.

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