Rules for the bio-based production of bulk chemicals on a small scale

- Can the production of bulk chemicals on small scale be competitive?

E.L. Scott, M.E. Bruins, J.P.M. Sanders

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Colophon

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Abstract

The goal of this desktop study was to define what products conversions/technologies/processes (currently used in the petrochemical industry) have intensive variable (feedstock and energy) and high investment aspects. What biomass raw materials could be used and what alternative conversions could be carried out (chemical, enzymatic and/or fermentative) to reduce capital costs and allow the production of bulk chemicals on a small scale.[1]

It is reported that the costs (for production) for a wide range of petrochemicals can be broken down, albeit with assumptions, into variable (feedstock and energy) and capital (investment) costs. The assumptions used were related to total energy and costs.

- Variable costs were determined from total energy inputs (@€4/GJ) derived from life cycle analysis data and estimations (where data was incomplete) from the calorific inputs of the amount of original feedstocks of the process chain.
- Capital costs were determined from the cost (of production) price minus the variable costs.

From the wide range of chemicals (processes) analysed a trend in the relationship of investment and variable costs emerged. A large number of chemicals displayed a heavy capital investment cost. In general these are summarised as:

- More functionalised chemicals, that have undergone multiple process steps that have large energy inputs and losses, have higher investment and variable costs. The effects on costs are indicated to be cumulative.
- Chemicals (produced and used elsewhere) where safety issues, such as explosion and toxicity, have a major influence on the costs of subsequent products.

Biomass offers potential to reduce heavy capital investments as described above thereby allowing production in a smaller production facility. The functionality present in biomass facilitates the formation of the desired end product in less steps under milder, less capital intensive conditions thereby allowing competitive cost of production.

- An example is the formation of ethanolamine by decarboxylation of serine at ambient conditions. This allows not only the elimination of fossil ethylene feedstock, but also a number of production steps and use of co-reagents e.g. ammonia.

As well as this, there are possibilities to eliminate the need for the production or use of hazardous intermediate.

- Examples include the conversion of amino acids to nitriles and amino alcohols under ambient conditions using enzymes avoiding the use of hydrogen cyanide and ethylene oxide.

The use of microorganisms would allow multiple transformations to take place in one reactor, while anaerobic fermentation to products would lead to high yield, higher productivities and lower reactor costs. Therefore costs of production of bulk chemicals will be attractive, because even on second generation raw materials, the total investment for a competitive factory is much lower than one that is producing transportation fuels. However, more research is required to establish a range of systems.

A focus area in general is the isolation and purification of sources of biomass molecules. Cost and energy efficient isolation of starting materials from complex environments as well as product isolation from e.g. aqueous media are required if success is to be achieved.

[1] Original proposal, Appendix 1

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1. Evolution of the chemical industry

During the last century the oil and petrochemical industry has grown and expanded and led to a contribution in both national and global prosperity. For example Houston, USA, saw an increase in population from ca. 2500 to ca. 1.6mln allied with a boom in economic prosperity between 1890 and 1980 as the oil industry established itself.[2] Such a relationship can also be seen with regards to the history of the OPEC and other oil and petrochemical producing countries in the early 1970's. During the oil boom the petrochemical industry enjoyed wide availability at low cost of the raw materials for commodity chemicals (naphtha, derived from oil cracking and refinery processes). As well as this other energy sources such as gas and coal were also abundant at low cost.

During this period a steep learning curve with regards to technology takes place. In general low demand/production volume products have higher unit costs while high demand/production volume products have lower unit costs (Figure 1). Therefore as products and processes have been designed and improved to optimize yields with fast reactions (often benefiting from large enthalpy differences between reagents and products) the result is a lowering in the price per volume. For example, in the 1940s the scale of operation of and ethylene plant was 10's of thousand tonnes per annum. By the 1990s this had increased 15 fold. As can be seen from Table 1, this figure has now reached capacities on millions tonnes per year.[3] However, this expansion process can (depending on timing of the expansion) lead to overcapacity and result in loss in returns of investment.[4]

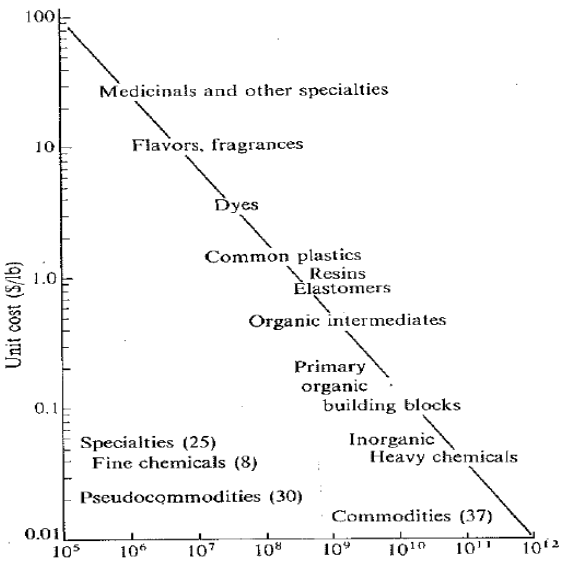

Figure 1 Unit costs versus demand of different categories of chemicals (taken from Organic Building Blocks of the Chemical Industry, Szmant H)

[2] *Feagin JR (1985) The Global Context of Metropolitan Growth : Houston and the Oil Industry, American Journal of Sociology, 90(6), 1204-1230*
[3] *http://www.ogj.com/articles/print/volume-109/issue-27/special-report-ethylene-reprot/global-ethylene-producers-add-record.html*
[4] *Henderson J, Cool K (2003) Learning to time capacity expansions: an empirical analysis of the worldwide petrochemical industry, 1975-1995. Strategic Management Journal (24), 393-413.*

Table 1 Capacities for Top 10 ethylene production complexes (Jan 2011)

Company	Location	Capacity (mln tonnes per annum)
Formosa Petrochemical Corp.	Mailiao, Taiwan	2.9
Nova Chemicals Corp.	Joffre, Alta	2.8
Arabian Petrochemical Co.	Jubail, Saudi Arabia	2.3
ExxonMobil Chemical Co.	Baytown, Texas	2.2
ChevronPhillips Chemical Co.	Sweeny, Texas	1.9
Dow Chemical Co.	Terneuzen, Netherlands	1.8
Ineos Olefinsa and Polymers	Chocolates Bayou, Texas	1.75
Equistar Chemicals LP.	Channelview, Texas	1.75
Yanbu Petrochemical Co.	Yanbu, Saudi Arabia	1.7
Equate Petrochemical Co.	Shuaiba, Kuwait	1.65

The petrochemical industry has been developed as a tree of products (Figure 2), where more and more functionality is introduced step by step to obtain the properties of the wide variety of products that we nowadays use in polymers and other chemical products. As the number of reaction steps that have to be performed, the more important the cost of the raw materials for each subsequent step/process becomes.

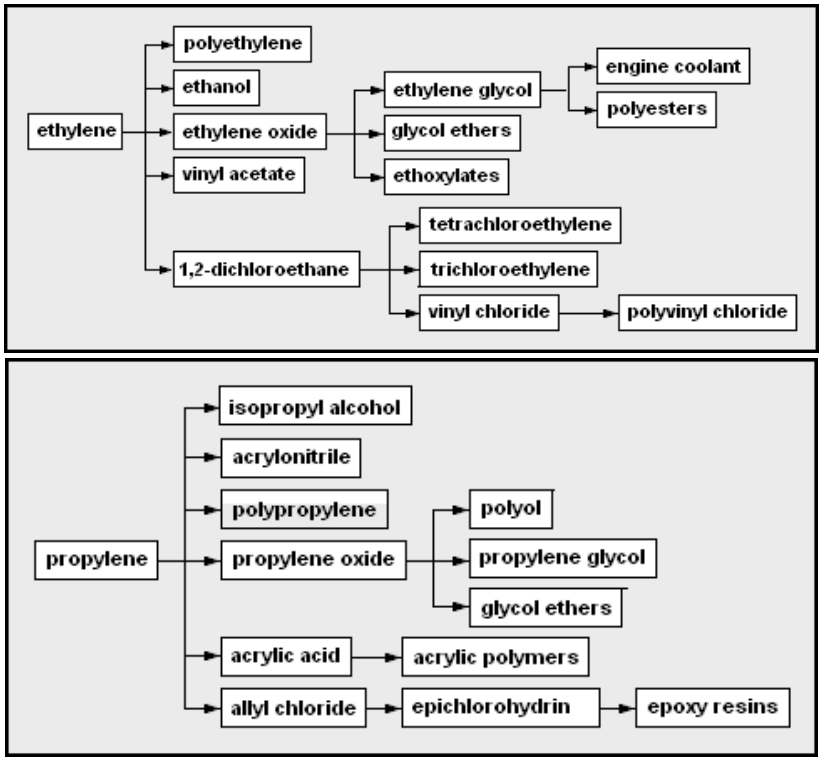

Figure 2 The product tree from ethylene and propylene.[5]

[5] Diagrams obtained from Wikipedia

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1.1 Cost of production and the economy of scale

The cost of production of a chemical broken down into a set of contributing costs 1) **variable costs** (raw materials and utilities etc..), 2) **fixed costs** (*direct* [labor, maintenance and overhead] and *allocated* [which is linked to capital investment]), 3) **depreciation** (on the **capital investment**). The major contributions to the cost of production are attributed to variable and capital costs. The market price of the product is higher as it included the return on the capital investment.

1.1.1 Variable costs

Maximising product yield and selectivity of reactions, as well as atom efficient processes, to obtain the highest output from the process raw materials has been a focus area in the petrochemical industry. The major scientific and technical developments here have revolved around the use of catalytic processes which facilitate otherwise unobtainable reactions, reduces the temperature and pressure required for reaction as well as allowing increased selectivity to the desired product. It also allows for faster reactions to occur under the reactor conditions. In a large number of processes (although not all) higher temperatures (>150°C) and elevated pressure are still employed.[6] However the most influence on the variable cost is the cost of the raw material due to fluctuations of the oil and energy price itself. When historical data of chemical prices are examined the market price (and hence the cost of production) ebbs and flows with the corresponding commodity (e.g. oil, benzene, ethylene, propylene etc). For example ICIS reports describe the changes in a chemical price in relation to the activities in the price of the corresponding commodity raw material.[7] To reduce the costs with regards to energy new or alternative (less expensive) feedstocks can be considered. However, this usually requires the development of new processes and therefore a capital injection.[8] However, the author hints that the greatest impact on reduction in energy use will be by the development of new processes and not incremental changes in technology with investments.

1.1.2 Fixed costs

While the contribution of the fixed costs to the overall cost of production contributes less than the other aspects, it is still significant (typically 20%). Unlike the variable costs, this value is not readily influenced by changing to less expensive feedstocks or improving energy efficiency. However *fixed costs are related to the capital investment.*

1.1.3 Capital costs

In a number of chemical processes the formation and/or use of toxic or explosive products and/or intermediates can be generated. Examples here include the production of hydrogen

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[6] *An overview of some process and reaction conditions are given in Appendix 2.*

[7] *An example is given for styrene in Appendix 3*

[8] *Ten, T (2009) Barriers and drivers for process innovation in the petrochemical industry: a case study. J. Eng. Technol.285-304*

Omdat de grondstofkosten overheersend zijn in de algehele balans is het voor de hand liggend om hierop te besparen en te zoeken naar goedkope varianten. Methanol, dat vroeger uit kool geproduceerd werd, wordt nu uit gas gemaakt. Voorheen gingen deze grondstofveranderingen vaak hand in hand met een verlaging van de reactiewarmte, wat daardoor ook zorgde voor een vermindering in warmte verlies en dus verminderde investeringskosten (voor warmtewisseling). Echter, momenteel wordt ook veel onderzoek gedaan naar grondstoffen, die wel goedkoper zijn, maar een toename in de reactiewarmte hebben, waardoor de winst die je op grondstofgebied maakt, tenietgedaan wordt door verhoogde investeringskosten.

cyanide (toxic) by ammoxidation of methane (at 1000-1200°C) and the oxidation of ethylene to ethylene oxide (explosive). In order to fulfil safety conditions more capital costs are required to contain the toxic chemical (intermediates) or risk of explosion. As well as this, the use or formation of corrosive acidic materials (e.g. acetic and chlorinated acetic acid) can lead to decreased reactor lifetimes or the application of more expensive alloys need to be applied. Lange has described the cost build-up of chemical processes and has given approaches to further reduce the cost prices.[9] Capital costs are correlated to the degree of energy transfer that is required in the process. This includes the heat generated during reaction, the energy supplied to overcome thermodynamic barriers as well as various downstream operations such as distillation. While effort to develop new processes based on new feedstocks to reduce energy costs, improvement in technology e.g. distillation columns allied with the required investment, is used to reduce energy use and hence costs.[7]

In order to further reduce the cost of production, chemical industries have benefited from the Economy of Scale (EoS), which actually became the most important competition factor for the chemical commodities that were sold on price. Some parts of the process equipment are able to take advantage of the EoS such as reactors. However some process equipment have little, or no, EoS such as pumps, centrifuges, and various auxiliary units. Lange included fuel, chemical and power processes to identify the scaling factors for the overall factories as determined by these individual parameters. The heat transfer duty, the capacity of heat exchange had the highest influence on EoS with a scaling factor of 0.55 on the overall investment cost relating to a number of different industries with different characters.[10] This observation should be regarded with care, because heat exchangers themselves will not have low scaling factors since heat exchange is surface limited.[11]

1.2 Characteristics of the costs of the petrochemical industry

The costs of production = variable + fixed + capital costs. The feedstock and energy and capital cost. contribute significantly to the overall costs. As a result lower cost feedstocks with new processes and existing processes with more energy efficiency have been extensively investigated. In this desktop study we intend to define what conversions/technologies/processes (currently being carried out) have intensive, high investment aspects and could biomass raw materials could be used and what alternative conversions could be carried out to reduce capital costs and allow the production of bulk chemicals on a small scale.

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[9] *Lange J-P (2001) Fuels and chemicals manufacturing. Cattech 5: 82-95*

[10] *Investment (million$)= 2.9* [energy losses (MW)]$^{0.55}$ Lagere investeringskosten kunnen verwezenlijkt worden door een minimalisatie van het warmtewisselend oppervlak. Warmtewisselaars bepalen namelijk voor een groot deel de investeringskosten en zijn de reden voor schaalvergroting (R=0.55)*

[11] *Het gaat hier echter om het totale aantal warmtewisselaars, dus inclusief alle tussenstappen. Het totale energie transport wordt gedomineerd door de warmtewisseling als gevolg van de reactiewarmte gecombineerd met de warmtewisseling tussen grondstof en product. Als je enkel de begin en eind energie waardes (=energieverlies) neemt zie je wel de correlatie met de investeringskosten, maar niet meer het schaaleffect (R=0.84). Ook moet erbij gemeld worden dat als de fabrieken kleiner worden, de andere kosten meer invloed krijgen en dat energie transport niet langer een goede maat is voor de investeringskosten.*

2 Cost of production and the contribution of variable and capital costs in petrochemical production: an analysis

As described earlier the cost of production of a chemical can be broken down into variable and fixed costs (which includes some capital aspects) and depreciation and interest related to the capital investment. From an analysis of a (limited) number of process economic reports it was found that the cost of production accounts for ca.70-85% of the market price.[12] As the information pertaining to the cost of production is more limited with respect to market price, this provides useful insight when it comes to estimating the variable and capital costs. This will be discussed later. Depending on location, less expensive feedstocks prices may be obtained. While this will reduce cost prices a lowering of the market price.

Assumption #1

The cost price is 80% of the market price of a chemical product

Although fixed costs are present, currently we assume that the cost price consists of variable costs (for raw materials and energy) and (depreciation and interest related to) capital investment. In assumption #2 no labour costs are included.

Assumption #2

Cost price = variable + capital investment costs

It must be noted that this is not an impregnable approach. Changes in feedstock costs as well as supply and demand may change margins to different amounts which will lead to fluctuation of the cost of production. As well as this many factories will have been repaid financially, and *de facto* the capital costs and contribution to cost of production from depreciation are reduced. This latter fact may later be compensated as when a new factory has to be constructed, these capital costs will end back in the cost price which then determines the market price.

At the (very) large scale of processes that are currently operated for many bulk chemicals, the capital cost contribution is still highly significant. If new processes based on biomass feedstock's have to compete with petrochemical processes that are only competitive with huge investments (e.g.>€100 Mln), there will not be many companies that will take that step, or at least not without many years of research and development. This study wants to address the question whether biomass raw feedstock's would enable to lower the relative cost from capital while allowing for the higher costs of the feedstock? If this were the case, faster innovations with lower financial and feedstock supply risks can occur, thereby increasing the probability of building a competitive process on a smaller scale.

[12] *Cost of production in relation to market price - Appendix 4*

Initially over 40 bulk and commodity chemicals were identified.[13] They include commodity raw materials such as ethylene and propylene, as well as products from an initial conversion and products produced by multiple conversion processes. After obtaining the market price (all are expressed in € per tonne) it was possible to estimate the cost of production using assumption 1. Later we suggest how to reduce capital costs and still stay competitive changing to biomass (components) as feedstock's. Which feedstock's and processes are anticipated to be more successful?

Finally there might be other reasons to be more competitive at small factory sizes because of logistical reasons in the case of very dangerous chemicals such as ethylene oxide or chlorine, that required significant cost of transportation, that might no longer be needed if their production could be done on small scale.

2.1 Analysis of capital costs and raw material costs

In recent years a wide variety of studies have been carried out examining the use of fossil raw materials and chemical processes that has resulted in a number of detailed life cycle analysis (LCA) studies or concise footprint analyses. By utilising these it is possible to gain insight as to the total fossil energy use and resources used to prepare 1 tonne of chemical. In some cases specific data is available as to the type and amount of (fossil) energy source: oil, natural gas, coal, or that it is electricity possibly derived from nuclear or water power sources. However in a number of cases it was not possible to find the total energy used.
If the total energy is known it is still not clear what contribution arises from the feedstock and what portion is attributed to the associated process energies. Therefore a calculation was performed in order to determine the calorific value of the feedstocks used for the production of 1 tonne product.[14]

In order to calculate this all the process steps used to prepare that product starting from the base commodity (ethylene, propylene etc..) were identified. Where co-reagents (e.g. chlorine, ammonia etc..) were used, the process steps to prepare they were also identified. The overall stoichiometric amounts required for the process were determined and then expressed as an amount per tonne product together with corresponding the calorific value.

Interestingly it was observed that when this was carried out that the calorific value was ca. 50% of the total GJ (from LCA data) know for certain chemicals (Figure 3).

Assumption #3

Where LCA data was not present, the total feedstock (raw materials and energy) for the production was estimated as x2 the calorific value of the feedstocks used for the production of 1 tonne product

[13] *List of chemicals, with market and cost price – Appendix 5*
[14] *Energy inputs and dissipation and cost, variable and investment prices - Appendix 6*

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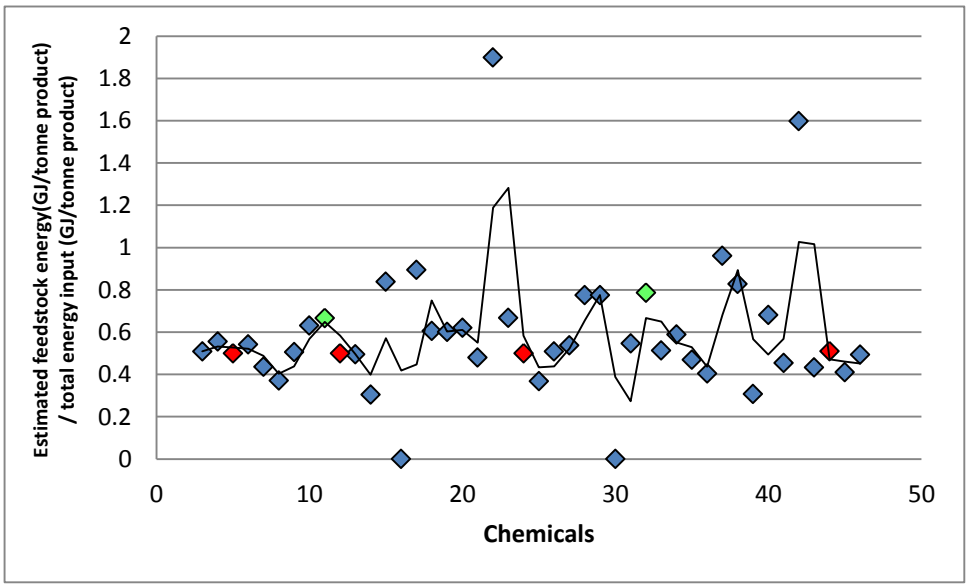

Figure 3 Estimated feedstock energy (GJ/tonne products) / total energy input in (GJ/tonne product) for +40 different chemicals. Red points were based on assumption #3. Green points, not all data found.

The raw material and energy costs have been described as €2/GJ for fuel, €4/GJ for steam and €10 /GJ for electricity with an average of €3/GJ[15]. Here €4/GJ was used as the average for all inputs to calculate the raw material and energy cost.[16]

Assumption #4

Variable costs (raw materials and energy) =

€4/GJ * total raw material and energy input per tonne product

While raw material and energy inputs are reasonably well documented in literature, capital costs are not. Only a limited amount of information on this topic is published e.g. in a press release when a new factory are announced. As well as this the precise production process is not specified. Since we do not need accurate capital costs, estimations of these capital costs have been made by assuming that the capital costs can be calculated by subtraction of the costs for raw materials from the overall cost price.[17]

Assumption #5

Capital investment costs =

Cost price (Assumption #1) - Variable costs (Assumption #4)

[15] *Lange J-P (2001) Fuels and chemicals manufacturing. Cattech 5: 82-95*
Chauvel A, Lebebvre G (1989) Petrochemical processes:1. Synthesis gas derivatives and major hydrocarbons and 2. Major oxygenated, chlorinated and nitrated derivatives Ed Technip)
[16] *€4/ GJ as opposed to €3/ GJ did not change the general trend/correlation to a great extent. At (much) higher average raw material costs, a more diffuse trend was seen.*
[17] *Energy inputs and dissipation and cost, variable and investment prices - Appendix 6*

A correlation between capital investment costs and energy losses for single factories performing a specific process had also been shown.[15] Based on the cumulative processes investigated here, it was also shown that investments increased with energy losses (cumulative total feedstock and energy to produce 1 tonne product – calorific value of 1 tonne product) , Figure 4.

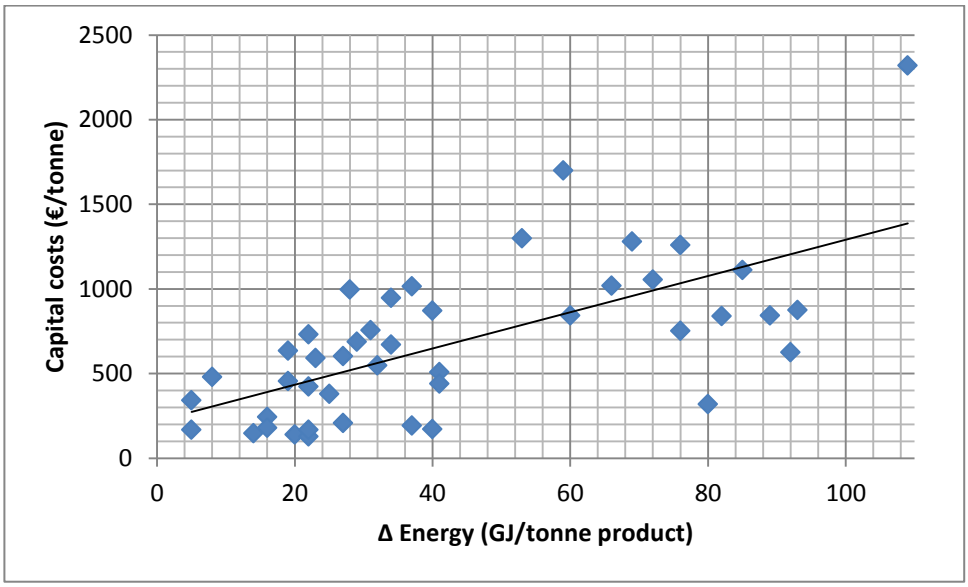

Figure 4 Capital investment cost v dissipated heat (GJ/tonne product)

Lange investigated the correlation of investment costs with the heat transfer in separate processes (factories). Here the cumulative total energy (in GJ, electricity also calculated in GJ thermal energy) that is used in along the whole production chain starting from naphtha and resulting in 1 tonne of the product indicated is used. The cumulative raw material and energy inputs of more functionalised chemicals should be higher than the chemicals that actually serves as the feedstock. For example ethanolamine has a higher cumulative total energy input as compared to ethylene oxide which is higher than ethylene.

Example

Chemical	***Total input GJ/tonne chemical***	***Total GJ / tonne product***
Ethylene	*72*	*33*
Ethylene oxide	*63*	*45*
*Ethanolamine (**product**)*	*89*	*89*

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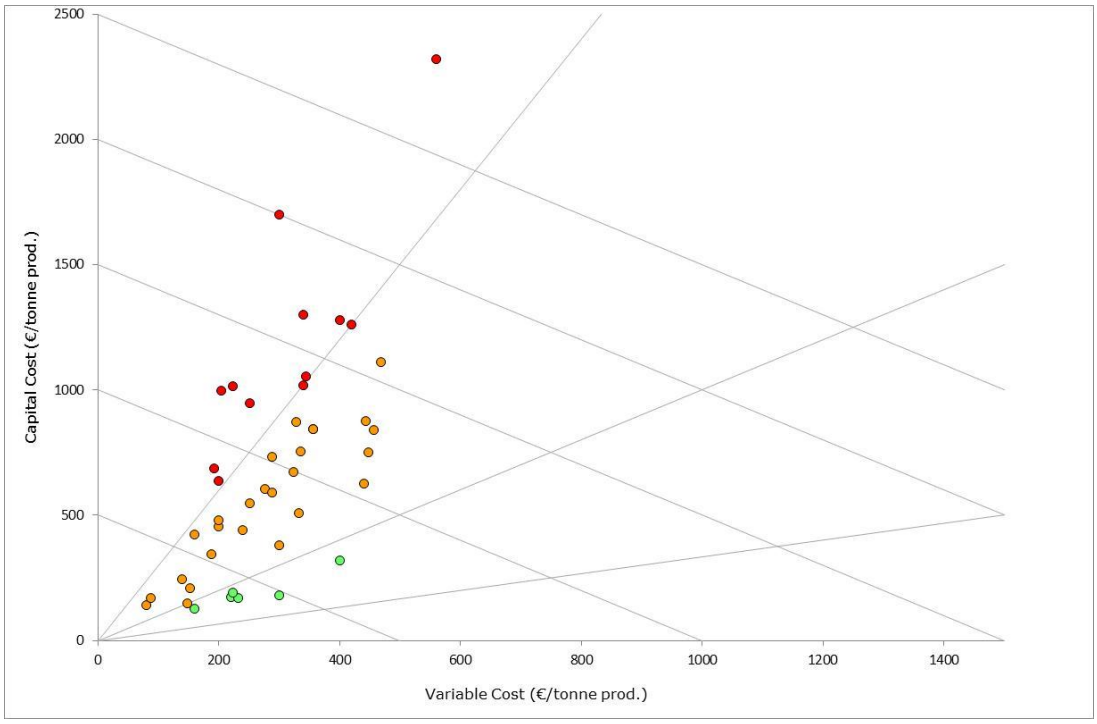

Figure 5 Capital vs raw material feedstock (variable) cost for a number of different chemicals.[18]

Figure 5 and Table 2 shows over data about 40 chemicals analysed. For the vast majority of the chemicals (86%) the capital costs were higher than the raw material (variable) costs. For 75% of the chemicals analysed the capital cost was >1.5 higher than the variable costs. Indeed 25% had a capital/raw material (variable) cost ratio larger than 3.

Table 2 What is the proportion of investment for +40 chemicals: Lower, higher, highest

Capital cost/ Variable cost	Number of chemicals	Chemical Product
Ca. 0.7-0.9	6	Acetic acid, crude glycerol, isoprene, natural gas, vinyl acetate, vinyl chloride
1-1.5	5	Benzene, butane, ethylene dichloride (EDC), ethylene vinyl acetate (EVA), methanol,
1.5-2.0	7	Ammonia, butanol, chlorine, oil, phenol, sodium hydroxide, terephthalic acid (TPA)
2.0-3.0	13	Acetone, butadiene, caprolactam, ethanol, ethyl benzene, ethylene, hydrogen, methyl methacrylate (MMA), monoethylamines (MEA), naphtha, xylene, butanediol, glycerol, propylene, styrene
3.0-4.0	6	Acrylonitrile, adipic acid epichlorohydrin, ethanol (fossil), ethylene glycol (MEG), ethylenediamine, ethylene oxide (EO),
4.0-6.0	4	Acrylic acid, butanediamine, hydrogen cyanide, methionine
Total	***41***	

[18] *The scale of operation of each process is not known. The exact process is not known. Where estimations were made on energy, these were based in on the calculation from well-established routes/methods.*

Although by no means without error (due to the assumptions), it appears that the costs are cumulative and estimations can be made.[19] Logically the cost of a raw material for a process will have had a cost/market price with variable and investment costs, therefore this is also ultimately included in a given process step.

In some cases the chemical produced is toxic or explosive (ethylene oxide and hydrogen cyanide) and has been shown to very heavy investment costs in relation to variable costs. The use of these will therefore increase the price of other products that use them. This can be seen clearly from Table 2 where butanediamine and methionine have high capital costs and both use HCN during their production. A similar observation can also be seen with regards to ethylene oxide. In some cases these more dangerous chemicals need to be transported to another production facility. The costs for transportation of hazardous goods are high.[20]

2.2 Conclusions of analysis

Petrochemical processes involve overcoming the large thermodynamic barriers that are associated in converting hydrocarbons to other more functionalised molecules. This requires large amounts of energy and the use of catalysts to perform such specific reactions under demanding conditions. As a result investment costs and scales are high. It is recognised that energy costs contribute significantly to the cost of production and therefore people have investigated improving process efficiency by carrying out the required investments. However others approach it differently by turning to new low cost feedstocks and developing new processes.
The costs (for production) for a wide range of petrochemicals can be broken down, albeit with assumptions, into variable (feedstock and energy) and capital (investment) costs. The assumptions used were related to total energy and costs.

- Variable costs were determined from total energy inputs (@€4/GJ) derived from life cycle analysis data and estimations (where data was incomplete) from the calorific inputs of feedstocks from first principles.
- Capital costs were determined from the cost (of production) price minus the variable costs.

From the wide range of chemicals (processes) analysed a trend in the relationship of investment and variable costs emerged. A large number of chemicals displayed a heavy capital investment cost. In general these are summarised as:

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[19] *Are costs cumulative? - Appendix 7*

[20] *With regards to issues surrounding the transportation of chlorine (toxic) - Akzo Nobel in cooperation with Italian machine manufacturer Uhdenora has started building small scale chlorine factories for a maximum production of 15.000 tonnes per year. The factories produce chlorine, sodium hydroxide and hydrogen from NaCl and water by membrane electrolysis. The unit is modular based and skid mounted. The production is on-site of users, but controlled centrally from the control room at AkzoNobel. They claim that this process is not more expensive than current centralized mercury based chlorine plants, and is certainly safer.*
Hazardous transport conditions e.g. ethylene oxide costs are around 400€/ tonne (personal communication Willem van de Zande 2012)

- More functionalised chemicals, that have undergone multiple process steps that have large energy inputs and losses, have higher investment and variable costs. The effects on costs indicate them to be cumulative.
- Chemicals (produced and used elsewhere) where safety issues, such as explosion and toxicity, have a major influence on the costs of subsequent products.

To be able to reduce the high costs associated with large use and loss of energy and use of hazardous materials can only significantly be realised by developing new processes that eliminate these issues. Thereby new biobased feedstocks can contribute by virtue of their functionality (next section). In this phase of new developments, opportunities for lower cost, smaller scale and innovative chemical process may be designed.

This study wants to address the question whether biomass raw feedstock's would enable to lower the relative cost from capital while allowing for the higher costs of the feedstock. If this were the case, faster innovations with lower financial and feedstock supply risks can occur, thereby increasing the probability of building a competitive process on a smaller scale.

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3. The application of biomass in the production of industrial chemicals

Which chemicals have the best chance of being produced from biomass at smaller scales?

- Probably chemicals with the current highest absolute capital costs.
- More functionalised chemicals currently produced by multiple steps that tend to have high cumulative costs.
- Chemicals that are currently produced with the aid of hazardous reagents (that have high costs).

The most likely chemicals are from the red and orange categories in Table 2.

Which biomass building blocks combined with which conversion steps will enable the same (or lower) cost prices as current petrochemicals with a lower scale of production?

- Biomass building blocks that contain certain functionality: either similar to the final product or easily converted to the final products using suitable conversions (below).
- Conversion processes that do not lead to large losses in energy.
- Conversions that allow the formation of the desired products but eliminate the need to use hazardous reagents or intermediates.
- As few separate conversion steps as possible.

Below is discussed a number of biomass building blocks and conversions strategies that aim to tackle these points.

Table 3 Estimation on costs for reactors and conversion rates

Reactor costs (€/m^3.hr)	**Suitable conversion**	**Optimised Productivity (kg/m^3.hr)**
2.5	Aerobic fermentation	4
0.5	Anaerobic fermentation	10-15
0.2	Simple, no heating or heat dissipation	1
0.1	*Simple, no stirring, heating or heat dissipation*	1

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1. Amino acids using (bio)catalysis

Due to the chemical functionality present and generic similarity to a number of industrial chemicals, such as aliphatic (di)amines and carboxylic acids, amino acids may be suitable feedstocks. Indeed a number of amino acids have been reported in the open literature as building blocks for the synthesis of chemicals. For example, glutamic acid[21] can be used to synthesis N-methylpyrrolidone, acrylonitrile and succinonitrile (precursor to 1,4-butanediamine for nylon 4-6) while arginine[22] can result in the formation of 1,4-butanediamine in a 2 step enzymatic reaction. If we assume that amino acids can be isolated from inexpensive protein streams such as dried distillers grains and solubles (DDGS) at €140 per tonne (available in volumes of 15 Mln tonnes per annum from corn to ethanol processes in the USA) and that the essential amino acids (lysine, methionine, phenylalanine, threonine, valine and (iso)leucine) can command a price of ca. €1500 per tonne, this would allow the other amino acids to be obtained for *€600 per tonne (and potentially even lower)*. Amino acids will loss mass due to e.g. decarboxylation etc.. during conversion. In some cases this will present a small mass loss and others somewhat more. On average, *33% reduction in the molecular weight* is estimated. Therefore the raw material costs are estimated to be *€800 per tonne product*. From literature (see footnotes) enzyme costs can vary (from low to high) depending on the activity and productivity. Development in this area is still required. However we assume *€100 for other materials*[23] *per tonne of product* (for conversion and product recovery). **Variable costs are estimated at ca. €900 per tonne product**. If a simple reactor is used for the (immobilized) enzyme conversion (Table 3) capital costs could be modest €100 per tonne of product. To allow for capital relating to product recovery a further €100 per tonne of product is assumed (**total capital estimated at ca.€200 per tonne product**).

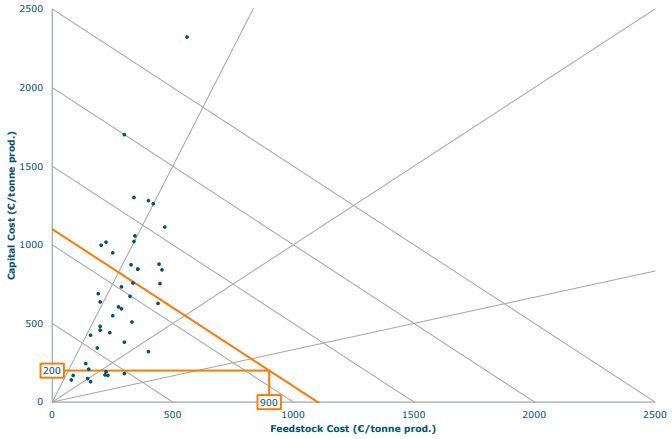

Figure 6 Capital and feedstock costs for chemical production from amino acids(• are petrochemicals previously described)

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[21] *Lammens TM, Franssen MCR, Scott EL, Sanders JPM (2010) Synthesis of biobased N-methyl pyrrolidone from γ aminobutyric acid Green Chem 12, 1430-1436.*
Lammens TM, Le Notre J, Franssen MCR, Scott EL, Sanders JPM (2011) Synthesis of biobased succinonitrile from glutamic acid and glutamine ChemSusChem 4, 785-791.
Le Notre J, Scott EL, Franssen MCR, Sanders JPM (2011) Green Chem 13, 807-809
[22] *Konst PM, Turras PMCCD, Franssen MCR, Scott EL, Sanders JPM (2010) Advanced Synthesis and Catalysis 352, 1493-1502*
Konst PM, Franssen MCR, Scott EL, Sanders JPM (2011) Green Chem 13, 1167-1174
[23] *Lammens TM, De Biase D, Franssen MCR, Scott EL, Sanders (2009) 11:10, 1485-1704*

Potentially other reactions may be required to produce the desired compound. In the case of the formation of succinonitrile from glutamic acid, as described earlier, the use of hypochlorite as an oxidant in the oxidative decarboxylation reaction is required. From a techno-economic assessment the use of the oxidant was found to be prohibitive.[24] As well as this it was found to negatively contribute to the environmental footprint and the authors recommend finding alternative oxidants.[25] Later it was demonstrated that the same oxidative decarboxylation reaction could be performed enzymatically in the presence of hydrogen peroxide as the oxidant.[26] While in this case a petrochemically derived hydrogen peroxide was used, it does open up the possibility to generate peroxide *in situ* using a tandem enzymatic reaction (e.g. conversion of glucose with glucose oxidase to gluconic acid and peroxide). The ability to therefore produce nitriles (e.g. succinonitrile) which does not require the use HCN, and its associated capital costs (highly temperature, toxicity considerations), becomes an area with potential for lower investment, smaller scale activities.
Another amino acids, serine, opens up the possibility to produce ethanolamine. This may be carried out using an enzymatic decarboxylation reaction under ambient conditions. Here the reaction offers the opportunity to not only reduce the fossil raw material (in this case ethylene), but allows the elimination for the need to produce ethylene oxide. As described earlier, ethylene oxide is explosive and has a high capital investment in the cost price. Allied to this the use of ammonia is eliminated.

2. Aerobic Fermentation using crude (beet or cane) sugar concentrates

We have assumed best practices.

- Aerobic industrial fermentation has a volumetric productivity of 4kg/m3.h (e.g. lysine by Corrynebacterium) and the resulting product concentration in the broth has been assumed to be 150 kg/m3.
- An industrial aerobic fermenter costs about 2.5 €/m3.h including operational costs as well as capital costs without the raw materials.
- Although components such as citric acid and other organic acids from the Krebs cycle can be produced at high C/C yield even under aerobic conditions while the energy yields are often far below 100% , we have assumed a 50% C/C yield as well as energy yield (J/J(for chemical compounds that are more distant from the Krebs cycle such as amino acids, aromatic components etc…

To calculate the cost price of 1 tonne of a chemical.

- The fermenter cost will be €625/tonne.
- The substrate costs will be 2 tonnes of sugar taken as €200/tonne which is low in Europe. In Brazil sugar can be available at €150 certainly at industrial quality. World white sugar prices are

[24] *Lammens, T.M.; Gangarapu, S.; Franssen, M.C.R.; Scott, E.L.; Sanders, J.P.M. (2012) Techno-Economic assessment of the production of biobased chemicals from glutamic acid BioFPR* 6 (2). - p. 177 - 187.
[25] *Lammens TM, Potting J, Sanders JPM, De Boer IJM (2011) Environmental Science and Technology 45, 8521-8528*
[26] *But, A.; Le Notre, J.E.L.; Scott, E.L.; Wever, R.; Sanders, J.P.M. (2012) Selective Oxidative Decarboxylation of Amino Acids to Produce Industrially Relevant Nitriles by Vanadium Chloroperoxidase* ChemSusChem 5 (7). - p. 1199 - 1202

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volatile. The global sugar prices in 2013 have been very high, though even at €400/tonne white sugar. For this study we should mention here that part of the sugar price is capital cost for harvesting equipment but certainly also the sugar factory. These capital costs are estimated between €50-100/tonne of sugar depending on how allocation of costs are done for the different side products.

- Recovery costs have been assumed at €100 capital and €100 raw materials. There might be chemicals that require higher costs for their recovery, certainly if high purity is required (e.g. for polymerisation). Sometimes we might benefit from phase separations, e.g by precipitation that might lower the costs for specific chemicals.

The total production costs are estimated at 625+ 100+100+ 400=1250€/ tonne
The total investment costs at an annual production of 15 000 tonne of chemical product are estimated at € 55 Mln. This small scale factory benefits form the existing sugar production infrastructure on large scale (> 100 000 tonnes/year and higher). For very similar reasons, we are developing sugar factories of <10 000 tonnes of sugar , that can be competitive with the existing large scale factories.

3. Anaerobic Fermentation using lignocellulosic substrates

Second generation raw materials are hoped to be available at lower costs than the sugar or starch derived from first generation raw materials. This will only be the case however using the currently developed technology, at certain boundary conditions - large scale factories and availability of low cost lignocellulosic materials. It seems that these conditions can only be fulfilled in the USA and Brazil. This will not enable the production of bulk chemicals at small scale unless the pre-treated lignocelluloses are used for several different products, each being small scale. The logistics of the raw material supply would then be similar as in the case described above when a large scale sugar factory supplies the raw materials to the small dedicated fermentation factory. A major difference being the purity and concentration of the raw materials, which probably will cause a lot of additional costs for recovery and purification of the chemical product. In addition to this, we do not see the possibility of a small scale 2nd generation process as is being developed for beet sugar. If we take the capital costs as published for the POET ethanol factory as $ 300mln for the production of 175 000 tonnes of ethanol as the reference. This factory produces about 350 000 tonnes of fermentable sugars (C5 and C6). This factory includes the fermentation and the product recovery.

Table 4 Capital costs per tonne of fermentable sugar and per tonne of product assumed that there is 50% yield.

Sugars capacity (tonne/y)	Investment (M$)	Annual Capital cost (M$) (on 20% basis)	Capital per tonne of sugar (€/tonne)	Capital;(€/tonne of product 50% yield
370 000	300	60	120	240
75 000	100	20	200	400
37 000	60	12	240	480
15 000	33	6.5	330	660
7 500	25	5	500	1000

These costs include the costs for ethanol production under anaerobic conditions. We calculate these fermentation capital cost therefore to be €50/tonne, assuming €0.5/m3.hr while productivity will be 5-10 tonnes/m3.hr . Since the ethanol production itself is not very scale dependent, we can subtract €50-100 from the last column in the table here above if we want to have the basis for the pre-treatment investment. For anaerobic fermentations actually taking the capital cost for ethanol would be helpful. For the aerobic fermentation (see below) we first subtract the capital for ethanol fermentation and then add the fermenter capital costs for the aerobic case again.
Also the capital costs for the recovery of ethanol have to be subtracted to obtain the capital costs just for the obtaining the raw materials. This will also give the basis of calculation for the aerobic fermentation case based on 2nd generation raw materials.

In ethanol fermentations the costs of recovery are relatively low: capital €50/ tonne + raw materials €25 /tonne.

To calculate the capital cost for raw materials and an anaerobic fermenter at a capacity of 15 000 tonnes of fermentable sugar per year the capital cost will be 240-50= €190/ tonne of sugar.
If we still assume that the recovery costs for bulk chemicals are €100 per tonne for the capital and €100 for raw materials, in case of second generation fermentation broths the overall capital costs will be 190+ 100= **€290/ tonne** of product. The total investment at 20% capital costs will be between €25-40 mln

Here below we will calculate the capital costs for the aerobic fermentation. We need about twice as much sugars. From table 4, 37 000 tonnes of sugar leads to €240-100 per tonnne of sugar, which leads to €280 / tonne for the pre-treatment. Adding €100 capital costs for the recovery will lead to a total capital cost of **380€/ tonne** of product excluding the fermentation costs. **The raw material costs** for the fermentation given that 2 tonnes of lignocellulose give 1 tonne of fermentable C5+C6 sugars(assuming 90% yield on sugars, raw material costs are €110 (@ €50/tonne of straw) + €100 for the recovery= **€210.**

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Table 5 cost of raw materials for lignocellulose fermentations

Cost of straw (€/tonne dw0	Cost of C5+ C6 sugars (€/tonne)	Cost of raw materials at 50% yield (€/ tonne product)
25	50	100
50	100	200
100	200	400

4. Aerobic fermentation using lignocellulose

For the **aerobic** fermentation much higher costs will result assuming 50% yield. Furthermore the fermenter costs are 625€/ tonne and thereby much higher than in case of the anaerobic fermentation

At an annual production volume of 18 500 tonne of product, the capital costs will be 380+625-100+50= €950 while the raw materials cost 200+100= €300 per tonne of product (at straw prices of €50/ tonne).

The total investment is estimated around €60- 80mln

5. Anaerobic Fermentation using crude (beet or cane) sugar concentrates

Best practices:

- Volumetric productivity of 10 kg/m3.h
- Final product concentration in the fermenter 150 kg/m3;
- Cost of the fermenter at €0.5/m3/hr; yield 90% J/J yield;

Therefore the fermenter costs are €50/ ton excluding the raw materials, which costs €200*1.1= €220, recovery costs assumed at €100 capital and €100 raw materials; capital costs: €50+100=150; raw material costs 220+100= €320.Total costs €470 / tonne of product. Total capital cost at 15 000 tonnes of product per year is around 12 M€ excluding the capital costs for the sugar (see above).

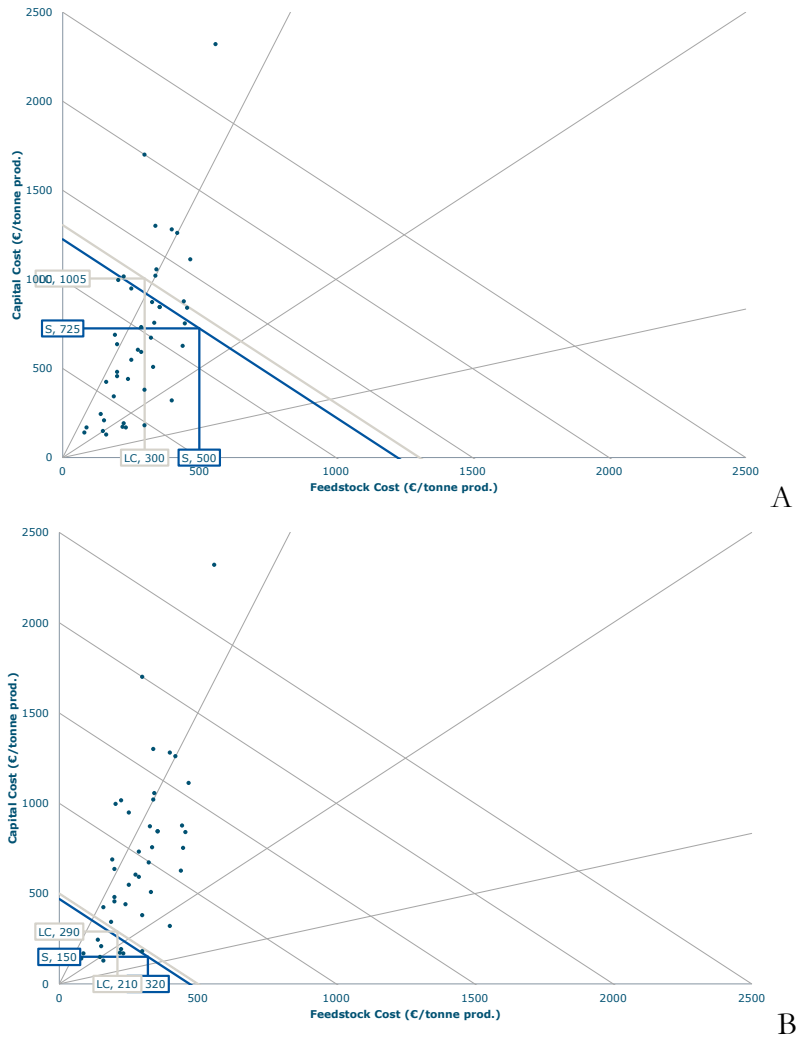

Figure 7 A: capital and feedstock costs using sugar (S) or lignocellulose (LC) as feedstocks in aerobic fermentations.
B: capital and feedstock costs using sugar (S) or lignocellulose (LC) as feedstocks in anerobic fermentations.

6. Other building blocks including carbohydrates using (bio)catalysis

Solvay started the production of Epichlorhydrin on glycerol. HCl and hypochloride are required. Furthermore the glycerol from the 'traditional' biodiesel production has to be prurified. Enzymatic biodiesel processes produces high quality glycerol that can be used in animal feed. It is not known which quality will suit the epichlorhydrin reaction with HCl and Hypochloride. About 1 tonne of glycerol[27] is required for the synthesis of 1 tonne of epichlorohydrin. Obviously Solvay, now building its third factory again at a scale of 100 000 tonnes per annum in China swiftly after the pilot in Taveaux, France (10 000 tonnes) and the factory in Thailand (100 000

[27] *Purified glycerol is available at ca.€700 per tonne while crude glycerol is available for. €350 per tonne.*

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tonnes per annum). The process is competitive with the existing fossil process based on propylene.

Avantium[28], have focused not in "drop in" chemicals but have developed new chemicals and materials from biomass. In this case the synthesis of furans from carbohydrates has been developed. These monomers can be used as a suitable alternative to terephthalates in poly(ethylene terephthalate) (PET). Tonne scale pilot production is currently under way.

7. Direct plant production by Genetic modification (GMO)

If we can produce bulk chemicals directly in plants like beet, cane, corn or other plants then the cost of production will be modest depending on how the cost fo the components obtained are distributed over the different biorefinery components. If the allocation is on weight than the cost of the primary production will be around €150 – 200 /tonne. Recovery and purification might add another €150-200 so that the actual cost price could become €400. Since many bulk chemicals will be toxic for the plant, it would be advisable to produce a precursor. That strategy will require an another conversion step that in the same time might contribute to the purification of the product. In that case we should be able to manufacture many different bulk chemicals, at a cost below €600/ tonne. There will be a long development period required as well as quite some investment in the approval of the production, certainly in Europe, where at least fr food crops, there has been a difficult atmosphere cause by NGO's and farmers initially. The capital costs for such products will be modest, mainly in the fractionation and purification of the product. The capital costs including the additional conversion step are estimated to be €150- 250 / ton on the scale of a potato starch or sugar factory. There is no reason why such processes should not be feasible in the future on smaller scale as we have published (Kolfschoten, R. , Bruins, M., Sanders, J.P.M. submitted to BioFPR 2013).

[28] *Avantium - Appendix 8*

Table 6 Cost breakdown and investment estimations for a factory of 15 000 tonnes/annum Capacity

€/ tonne product	Raw material cost €/tonne end product	Capital (pre-treatment +recovery) €/tonne end product	Capital fermentation €/tonne end product	Total cost (€/tonne end product)	Overall investment (M€) at around 15 000 ton/y
Second generation					
aerobic	300	380	625	1300	60-80
anaerobic	210	290	50	500	25-40
First generation					
Aerobic	500	100	625	1250	55
anaerobic	320	100	50	470	12
Amino acids	900	200+	--	1100	15
Plant production	150-250	250-350		400-600	20-25 (+20 M€ legislation costs)

n.b. exclusive the recovery of amino acids in enough concentration and purity. If this should be included the costs can be at least €200 higher per tonne, while the investment cost is difficult to estimate because this will be required for all or most of the amino acids.

3.1 Conclusions

Which biomass building blocks combined with which conversion steps will enable the same (or lower) cost prices as current petrochemicals with a lower scale of production? Was the original proposition together with some suggested guidelines. Based on these it has been described how a great number of functional biomass sources have functionality not dissimilar to current petrochemical products produced with the use of high investment cost. These include chemicals containing nitrogen such as (di)amines and nitriles. In the case of amino acids, their use allows the formation of the required functionality using conversion methods operated under mild(er) conditions and eliminates the need for hazardous reagents. The higher costs associated with dissipation of energy and hazardous compounds can therefore be avoided. Although the biomass feedstock costs are higher, the estimated lower investments allow for an encouraging cost price to be achieved.

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Fermentations based on sucrose, glucose but more often also xylose as derived from hemicellulose, can benefit from the 'metabolic engineering' of microorganisms that are selected to perform well in fermentative production. This metabolic engineering technology has been developed during the past 10 years and has shown to be powerful for several products yet. The development time and costs can be quite considerable, especially when the synthesis pathway is long and 'far away' from the central metabolic routes such as the Krebs cycle. Apart from the development costs also the performances of such 'distant' chemicals will give a lower economic performance as well.

It is expected, but not proven yet, that different approaches will be suitable for specific aims, while other routes will give better results for other chemicals.
These approaches lead to the need to develop or improve processes for the recovery and purification of industrial chemicals. In some cases chemical and physical changes take place during reaction (e.g. change in vapour pressure, solubility, phase behaviour etc..) which can aid not only the recovery process but also the conversion where product inhibition is an issue. Such aspects could also aid process intensification.

Table 7 Comparison of the different strategies to come to small scale production of bulk chemicals: boundary conditions, development cost

	Amino acid	**Aerobic Sugar**	**Anaerobic LC**	**Aerobic LC**	**Anaerobic Sugar**	**Carbohydrate conversion**	**In Plant**
Capital	low, unless	high	medium	high	low	low, if	low
Pre-conditions	Limit steps and heat transfer		raw material availability	raw materials availability*		Limit steps and heat transfer	Non toxicity for plants
Challenge to overcome	purification					purification	
Introduction (years)	>3-5Y	>4Y	>6Y	>5Y	>5Y	>3Y	>10Y
Development costs	low	Medium	high	high	high	Medium	High initial regulato ry costs

*Availability of raw lignocellulosic materials will be a problem in Europe as long as the electricity sector is pushed on wood generated power by European Directives.

Can a factory of 15 000 tonnes/y be competitive? What will be the investment costs?
The production of bulk chemicals by traditional petrochemical routes is (very) capital intensive. Using a variety of biomass components, the relative capital costs can be reduced considerable. In some strategies the cost of raw materials will increase) considerable, while in other strategies both capital and raw material costs can be reduced drastically, however at the cost of long or costly development projects. We have investigated the capital costs for factories of 15 000 tonne bulk chemicals on an annual basis. Anaerobic fermentation processes on sugar but even on

lignocellulose will need an investment of €12mln and €25-40mln respectively. The latter capital costs can be even reduced on the condition that the pre-treatment is done on a larger scale.
Also if amino acids can be obtained in rather pure form, they offer good opportunity for the production of chemicals on small scale. An investment of around €15mln would do, but this will be considerably higher if also the amino acids should be purified from waste protein streams.
The production of (intermediate) bulk chemical in plants is another potential route with limited investment costs. There is opportunity for the production by several small units spread in different (inland) countries in order to recover the costs for legislation.

Summary of work group meeting and acknowledgements

Thank you to Martin Patel and to the industrial members[29] that participated in an afternoon work group discussion about our goals, methodology and assumptions. The methodology and assumptions were found to be reasonable and acceptable and the small scale aspect would be an intrinsic advantage for the logistics of using biomass. It was discussed that the cost of energy of €4/GJ is reasonable in Europe, but it will differ in the US and we should bare this in mind. It was pointed out that in the case of some petrochemicals chemicals, the current prices can vary significantly in a short time frame and may influence the outcome of the assumptions in specific cases. Thus it was suggested to look at costs and technologies for each product individually in the study. This was indeed carried out to gain a broad knowledge of different products and processes and to determine trends of costs and conversion.

Where intensive or hazardous processes are used it was suggested to try and avoid them in suggesting alternative, biobased routes. We found that such process contribute significantly to the costs and therefore we have tried to avoid them in the examples highlighted in this report.

When using biomass (derived molecules), the issue of isolation of purification was raised a number of times. Having less separation operations and production of an intermediate (for further conversion and isolation elsewhere) were discussed. In some cases centralised activities will allow more constant quality of the product. Especially for amino acids, isolation costs might be significant and have an impact on the variable cost.

Some assumptions regarding fermentation may vary for specific products. However, the higher general yield of anaerobic fermentation coupled with lower reactor costs will be advantageous compared to aerobic fermentation.

Some other suggestions have been taken into account during the study. The work group discussion was very constructive with regards to the rounding off of this desk study.

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[29] *Prof J Moulijn (Catalysis Engineering Consultancy), Dr J Tsou (Akzo Nobel), Dr H Noorman (DSM), Dr K Biesheuvel (Dow), Dr T Runneboom (BioRenewables Business Platform)*

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Appendix 1 Proposal / offerte

Rules for the biobased production of bulk chemicals on a small scale

Background

The petrochemical industry has developed to produce (commodity) chemicals in large scale production facilities. This is related to several factors including the investment required to build facilities that have to deal with the high energy/heat transfer requirements of the processes developed and the (price of) bulk acquisition of raw materials in order to minimise the price per unit product. Due to requirements to improve and maintain energy efficiency heat transfer will continue as will the required large scale production. Only fundamental changes in practice can break this cycle where reactions can take place under less intensive conditions (e.g. lower temperatures, pressure, toxicity and corrosiveness etc..) and will allow lower investment costs and therefore implementation of economically viable small scale production. These fundamental changes have hindered or delayed new developments in alternative production routes (from biomass), as have the number of "new" chemicals/monomers for alternative products.

The lowering of costs in small scale (agro based) process has been described by Bruins and Sanders.[30] However, what are the rules in order to be able to perform the biobased production of bulk chemicals on a small scale and how could this be achieved?

Goal

In this desktop study we intend to define what conversions/technologies/processes (currently being carried out) have intensive, high investment aspects. What biomass raw materials could be used (based on the functionality) and what alternative conversions could be carried out (chemical, enzymatic and/or fermentative) to reduce capital costs and allow the production of bulk chemicals on a small scale. Not only the transformation process will be important, but what are the influences of upstream and downstream issues on the production chain.

Approach

- Initially a literature survey will be carried out for a range of industrial chemical process (e.g diols, diamines, nitriles, (meth)acrylates, etc…).
    - Break down a (chemical) process into smaller sections determining what intermediates, technologies or conversion steps are prohibitive in terms of energy use, reactor requirements, investment, toxicity, safety etc..
    - Define what are the conversions/technologies that should be avoided if small scale production was to be achieved.

From the literature, and from our own expertise, are there potential (functionalised) biomass raw materials in order to avoid these prohibitive aspects (above).

[30] *Bruins M.E., Sanders J.P.M. (2012) Small-scale processing of biomass for biorefinery Biofuels, Bioprod. and Bioref. DOI:10.1002/bbb1319*

- Define of the general features that link biomass functionality in the raw material and the final product and its influence on the investment and scale of production.
- Offer potential (alternative) conversion route(s) which could be used in order to avoid the prohibitive aspects in a new process chain with lower investment, smaller scale. During this phase a focus group will be created to obtain ideas and opinions. This will also include representation from the chemical industry.
    - Careful matching of chemical functionality of raw material and product to circumvent processes/reduce process steps, reagents and energy. Can alternative reactions be carried out (using enzymes) at lower temperatures reducing the need for heat exchange and high capital investment? Can (bio)catalytic processes be identified which allows the circumvention of the use of corrosive, energy intensive chemicals/reagents such as chlorine and ammonia and toxic intermediates?
    - Which product or process developments will be most influenced?
    - What are the down sides/restrictions to small scale production (biomass availability, biomass processing, lack of technology?
    - Are there other issues? For example, a company may wish to use ethylene but is not connected to a gas pipeline. However decentralised production of ethanol in the vicinity may be possible, transported to the site and converted to ethylene for further use. Alternatively ethylene oxide may be required and to avoid transport of toxic ethylene oxide, harmless ethanol could be transported and converted on site. Such an approach is already described for the production of chlorine gas.[31]

- From the above, what is the response of the chemical sector in general? Where are there chances, what bottlenecks need to be overcome, what is a strategy for development? Here a workshop will be held.

Result:

Report describing the issues addressed in the approach/activities. An overview of chances and opportunities as well as potential bottlenecks. The activities of the assignment will be completed by 30 September 2013. An initial draft will be submitted to the Biorenewable Business Platform and from their remarks a final version will be submitted.

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[31] *AkzoNobel in cooperation with Italian machine manufacturer Uhdenora has started building small scale chlorine factories for a maximum production of 15.000 tons per year. The factories produce chlorine, sodium hydroxide and hydrogen from NaCl and water by membrane electrolysis. The unit is modular based and skid mounted. The production is on-site of users, but controlled centrally from the control room at AkzoNobel. They claim that this process is not more expensive than current centralized mercury based chlorine plants, and is certainly safer.*

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Details of the organisation and applicants:

The **Biobased Commodity Chemistry** group at **Wageningen University** (WUR-BCH) has developed a reputation in the field of biomass, conversion technology and applications, and in particular the (enzymatic and chemical) conversion of biomass into industrial chemicals, materials and products. WUR-BCH is/has been involved in a number of projects that are related to biomass conversion from renewable resources (NWO: ASPECT, STW-GSPT, ECHO. SenterNovem EOS LT projects, *N-ergy* and *Lignovalue* and SmartMix - CatchBio) and has strong links with industry, both within the context of these projects (BASF, DSM, Huntsman) as well as bilateral studies.

Prof. **Johan Sanders** is Professor within the *Biobased Commodity Chemistry* chair with the focus on producing bulk chemicals fromplant raw materials by enzymatic, chemical or fermentative approaches. Biorefinery process technologies for both large- and small-scale application are also being investigated. From 1977 to 1983, he worked at Gist Brocades, starting the Genetic Engineering group and working on various projects in the field of enzyme research; he became Associate Director of Food Research. From 1993 to 2001, Sanders worked at AVEBE as R&D Director focusing on the enzymatic and genetic modification of starch. From 2001 to 2002, he held a management function at Wageningen UR. He holds a PhD in Molecular Biology from the University of Amsterdam for researching the physical map of yeast mitochondrial DNA.

Dr. E.L. Scott is Assistant Professor at the chair of *Biobased Commodity Chemistry,* Wageningen University. She obtained her PhD at Heriot-Watt University, UK. Between 1993-1997 she carried out both academic and industrial post-doc fellowships in the chemical synthesis of polymeric monomers and materials. Since 1997 she has been working in the area of biomass conversion to industrial products, and more specifically been concerned with economic and ecological chemical conversions and processes of biomass to industrial chemicals at WUR.

Dr. M. Bruins is Assistant Professor at the chair of *Biobased Commodity Chemistry,* Wageningen University. She specialises in bioprocessing and biorefinery.

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Appendix 2 Chemical processes[32],[33]

Chemical	Examples of process steps	Example of process conditions /remarks
Acetic acid	Carbonylation of methanol	T=150-200oC, P=ca. 30 bar, use of catalyst
Acetone	Oxidation of propylene	T=110-120oC, P=ca. 15 bar, catalyst
Acrylic acid	Oxidation of propylene	T=200-500oC, P=ca. 10 bar, catalyst
Acrylonitrile	Ammoxidation of propylene	T=450oC, P=ca.2 bar, catalyst + other
Adipic acid	Oxidation of cyclohexane via cyclohexanone	1.T=125-165oC, P=ca. 10 bar, catalyst 2.T=ca. 80oC, catalyst
Ammonia	Hydrogenation of nitrogen	Insufficient information
Butadiene	Dehydrogenation of butane/butane	T=450-600oC, use of catalyst
Butanediamine	Reaction of hydrogen cyanide with acrylonitrile	Not known
Caprolactam	1.Dehydrogenation of phenol 2. Oxime formation with hydroxylamine 3.Beckmann rearrangement	1.T=ca.400oC, catalyst 2. T=ca.485oC, other reagents 3.T-90-120oC, other reagents
ethlyene glycol (MEG)	Hydration of ethylene oxide (EO)	T=50-70oC, catalyst
ethyl benzene	Alkylaltion of benzene with ethylene	T=ca.90oC, P-ca. 5bar, catalyst
ethylene diamine	Amination of ethylenedichloride (EDC) or amination of ethanolamine (MEA)	Insufficient information
ethylene dichloride (EDC)	Various including the chlorination of ethylene	T=ca. 50oC, P-ca. 5 bar, catalyst
ethylene oxide (EO)	Direct (partial) oxidation of ethylene	Insufficient information, catalyst, exothermic reaction
Hydrogen cyanide	Oxidative or dehydrative amination with methane	T=1000-1300oC, catalyst
Methanol	Hydrogenation of CO	T=300oC-400oC, P=340bar, catalyst
Methionine	1.Reaction of methyl mercaptan with acrolein. 2. Reaction with sodium cyanide and ammonium carbonate	Insufficient information
Monoethyl amines (MEA)	Amination of ethylene oxide (EO)	T=60-150oC, P=30-150bar
Phenol	Various including the sulphonation and hydration of benzene	Insufficient information
Styrene	Dehydrogenation of ethylbenzene	T=ca. 550oC, catalyst
Terephthalic acid (TPA)	Oxidation of p-xylene	Various. T=140-280oC, P=40-100bar, catalyst
Vinylchloride	Various including elimination of HCl from ethylene dichloride (EDC)	T=400-600oC, P=ca. 30bar, catalyst

[32] *Most of the processes presented here are used as the basis for the calculation of estimated feedstocks (GJ/tonne product)*
[33] *Weissermel K, Arpe H-J (1993) Industrial Organic Chemistry, VCH*

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Appendix 3 E.g. price of styrene and discussion with respect to feedstock[34]

Sample Report

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ICIS pricing

1st March 2013

Styrene (Europe)

Editor Truong Mellor, Truong.Mellor@icis.com

Correction: *In the Styrene (Europe) report dated 01 March 2013, please read ...CIF RDAM (+) MAR n/c $1685.00-1730.00 n/c... instead of ...CIF RDAM (+) MAR n/c $1685.00-1725.00 n/c.... A corrected report now follows.*

CONTRACT PRICES					
Click for Price History			Price Range		US CTS/LB
FD BARGE NWE MAR	EUR/TONNE	+27.00	**1475.00-1475.00**	+27.00	86.86-86.86
AVERAGE FD BARGE NWE MAR	EUR/TONNE	+27.00	**1475.00-1475.00**	+27.00	86.86-86.86
FD TRUCK NWE MAR	EUR/TONNE	+27.00	**1500.00-1500.00**	+27.00	88.33-88.33
FCA RDAM FEB	EUR/TONNE	-40.00	**1448.00-1448.00**	-40.00	85.27-85.27

SPOT PRICES						
Click for Price History			Price Range		Four weeks ago	US CTS/LB
FOB RDAM (*) MAR	USD/TONNE	-55.00	**1685.00-1710.00**	-40.00	1720.00-1735.00	76.43-77.56
FOB RDAM (+) MAR	USD/TONNE	-40.00	**1695.00-1740.00**	-8.00	1710.00-1748.00	76.88-78.92
FOB RDAM (#) MAR	USD/TONNE	n/c	**1685.00-1760.00**	n/c	1700.00-1755.00	76.43-79.83
FOB RDAM (*) APR	USD/TONNE	n/c	**1690.00-1725.00**	n/c	1730.00-1750.00	76.66-78.24
FOB RDAM (+) APR	USD/TONNE	n/c	**1710.00-1740.00**	n/c	1735.00-1745.00	77.56-78.92
CIF RDAM (+) MAR	USD/TONNE	n/c	**1685.00-1730.00**	n/c	1700.00-1738.00	76.43-78.47
FCA RDAM (TRUCKS)	EUR/TONNE	+35.00	**1335.00-1350.00**	+30.00	1300.00-1330.00	78.61-79.49

Note: **(*)= Price range at close of business Friday.**
(+)=Price range for the week.
(#)=Bid/offer range for the week.

NOTE: for full details on the criteria ICIS pricing uses in making these price assessments visit www.icispricing.com and click on "methodology".

Subscriber note: ICIS is changing the monthly FD Barge NWE and FD Truck NWE contract quotes to FOB ARA, in light of changing market circumstances. Any comments or queries should be directed to the editor of the Styrene (Europe) report.

March barge CP agreed up €27/tonne

The European styrene barge contract price for March has settled at €1,475/tonne FOB ARA, an increase of €27/tonne from the previous month, several producers and consumers confirmed this week.

According to one of the consumers involved, the €27/tonne increase reflected higher raw material costs, with benzene up €14/tonne for March and ethylene settled €50/tonne higher. Although spot values have started to drop this week and derivative offtake remains slower than expected, the commencement of the turnaround season is keeping upward pressure on the European market.

Market softens with upstream losses

Styrene spot values gradually declined this week in line with falling benzene and energy numbers. The upcoming tightness for March and April did initially help mitigate some of the downward movement, but by the week's end, the market was back below $1,700/tonne.

The contango between March and April also started to narrow as the week progressed, although this later widened amid falling prompt upstream values and an ongoing bullish outlook for pricing over the turnaround season.

Spot activity was reasonably subdued in the week ahead of the March barge settlement. March opened the week with offers at $1,760/tonne, initially buoyed by firmer benzene numbers. The market was valued at $1,740-1,760/tonne, while April was higher on the bid side at $1,750/tonne.

As the week progressed, March offers crept down as benzene fell below the $1,400/tonne mark. March was offered at $1,750/tonne and then later at $1,730/tonne. Bids were at $1,720/tonne, although one buyer said it was expecting further price erosion. Deals were done at $1,740/tonne, $1,735/tonne and $1,720/tonne.

April maintained a slight contango, at least on the buy side, with bids at $1,730/tonne. Midweek saw two April deals done at $1,740/tonne. There was a March deal done at $1,725/tonne.

As the week drew to a close, upstream benzene and naphtha saw more bearishness on pricing. Styrene sellers were largely attempting to resist the downtrend, with March offers at $1,730/tonne. April was firmer with offers at $1,740/tonne. The spot market was quiet, however, in anticipation of the monthly contract settlements on benzene and styrene for March.

[34] *ICIS March 2013*

Appendix 4 Derivation of cost price from market price[35]

Chlor-alkali **Process A**	**$ / tonne**	**%**
Variable costs	66.7	29.5
Direct fixed costs	17.4	7.5
Allocated fixed costs	15.7	7
Depreciation on capital investment	58.6	25.5
Cost of production (cost price)	**158.4**	**69.5**
Return on capital investment (ROC)	69.5	30.5
Cost of production + ROC (market price)	**227.9**	**100**
Syn gas (steam methane reforming) **Process B**[1997]	**$ / tonne**	**%**
Variable costs	21.1	52
Direct fixed costs	2.5	6
Allocated fixed costs	2.4	6
Depreciation on capital investment	7.3	18
Cost of production (cost price)	**33.3**	**82**
Return on capital investment (ROC)	7.3	18
Cost of production+ROC (market price)	**40.6**	**100**
Formalin **Process C**	**$ / tonne**	**%**
Variable costs	74	58
Direct fixed costs	11	9
Allocated fixed costs	8	6
Depreciation on capital investment	17	13
Cost of production (cost price)	**110**	**85**
Return on capital investment (ROC)	21	15
Cost of production +ROC (market price)	**127**	**100**
Ethanolamine **Process D**	**$ / tonne**	**%**
Variable costs	872	82
Direct fixed costs	25.5	2
Allocated fixed costs	30	3
Depreciation on capital investment	56	5
Cost of production (cost price)	**983**	**92**
Return on capital investment (ROC)	81	8
Cost of production +ROC (market price)	**1064**	**100**
Methanol **Process E**	**$ / tonne**	**%**
Variable costs	25.7	28.4
Direct fixed costs	3.3	3.6
Allocated fixed costs	3.8	4.2
Depreciation on capital investment	25.9	28.6
Cost of production (cost price)	**58.7**	**64.8**
Return on capital investment (ROC)	31.7	35.2
Cost of production+ROC (market price)	**90.4**	**100**

[35] *Via Nexant, ChemSystems (PERP 01/02S4, PERP 00/01-8, PERP 01/02S2, PERP 03/04-4)*

Appendix 5 Chemical market price and related cost price (estimate: market price*0.8)[36]

Product	Market price (€/tonne)	Cost price (€/tonne)
acetic acid	490	392
acetone	1000	800
acrylonitrile	2050	1640
adipic acid	1700	1360
ammonia	480	384
benzene	1050	840
butadiene	1365	1092
butane/raffinate 1	850	680
butanediamine	3600	2880
caprolactam	1975	1580
chlorine	275	220
crude oil	531	531
epichlorhydrin	1750	1400
ethanol (bio)	820	656
ethanol (fossil)	1044	835
ethlyene glycol (MEG)	1100	880
ethyl benzene	1100	880
ethylene	1275	1020
ethylene diamine	2100	1680
ethylene dichloride (EDC)	450	360
ethylene oxide (EO)	1500	1200
Ethylene vinyl acetate (EVA)	1333	1066
Glycerol (crude)	730 (360)	584 (288)
Hydrogen	1500	1200
Hydrogen cyanide	3200	2560
isoprene	600	480
Methanol	370	296
methionine	1500	1200
Methyl methacrylate (MMA)	1650	1320
Monoethyl amines (MEA)	1500	1200
naphtha	nvt	680
natural gas	nvt	400
phenol	1620	1296
propylene	1100	880
sodium hydroxide	320	256
styrene	1500	1200
Terephthalic acid (TPA)	850	680
Vinyl acetate	900	720
Vinyl chloride	520	416
xylene	1245	996

[36] *ICIS 2013, estimated based on the price of other amino acids, market reports*

Appendix 6 Energy input and dissipation and cost price, variable and capital costs (hypothesis)

Product	*Total GJ / tonne product*	*⊿GJ / tonne product*	*Cost price (€/tonne)*	*Variable cost (€/tonne)*	*Capital cost (€/tonne)*
acetic acid	55	40	392	220	172
acetone	63	32	800	252	548
acrylonitrile	85	53	1640	340	1300
adipic acid	85	66	1360	340	1020
ammonia	35	16	384	140	244
benzene	83	41	840	332	508
butadiene	84	31	1092	336	756
butane	75	25	680	300	380
butanediamine	140	109	2880	560	2320
butanediol	105	76	1680	420	1260
butanol (iso)	112	76	1200	448	752
caprolactam	117	85	1580	468	1112
chlorine	20	20	220	80	140
epichlorhydrin	86	72	1400	344	1056
ethanol (bio)	50	19	656	200	456
ethanol (fossil)	50	19	835	200	635.2
ethlyene glycol (MEG)	48	29	880	192	688
ethyl benzene	69	27	880	276	604
ethylene	72	22	1020	288	732
ethylene diamine	100	69	1680	400	1280
ethylene dichloride (EDC)	38	27	360	152	208
ethylene oxide (EO)	63	34	1200	252	948
glycerol (crude)	40 (40)	22 (22)	584 (288)	160 (160)	424 (128)
Hydrogen	89	89	1200	356	844
Hydrogencyanide	75	59	2000	300	1700
isoprene	75	16	480	300	180
methionine	51	28	1200	204	996
Methyl methacrylate (MMA)	111	93	1320	444	876
Monoethyl amines (MEA)	89	60	1200	356	844
phenol	114	82	1296	456	840
propylene	72	23	880	288	592
styrene	82	40	1200	328	872
Terephthalic acid (TPA)	60	41	680	240	440
Vinyl acetate	100	80	720	400	320
vinylchloride	56	37	416	224	192
xyleen	81	34	996	324	672

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Appendix 7 Are costs cumulative (from hypothesis)?

Ethanolamine (cost price €1200/tonne: €356 (variable), €844 (capital))

Inputs per tonne final product	*Moles*	*Tonnes*	*Variable costs (€)*	*Capital costs (€)*
Ethylene	1639	0.46	132	336
0.5 O2	820	0.26	-	-
Ethylene oxide	1639	0.72	181	682
Ammonia	1639	0.28	95	68

Ethylene diamine (cost price €1680/tonne: €400 (variable), €1280 (capital))

Inputs per tonne final product	***Moles***	***Tonnes***	***Variable costs (€)***	***Capital costs (€)***
Ethylene	1666	0.47	135.4	344
Cl2	1666	1.18	94	165
Ethylene dichloride	1666	1.65	250	343
Ammonia	3333	0.57	79	139

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Appendix 8 Details Avantium

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Avantium and Danone sign development partnership for Next Generation bio-based plastic: PEF

Danone Research joins the development of 100% bio-sourced PEF bottles for water

Today Avantium announced its second major partnership for its YXY technology to produce PEF bottles. Danone Research and Avantium have entered into a Joint Development Agreement for the development of PEF bottles for Danone, number two worldwide in bottled water business. The agreement forms another cornerstone of Avantium's commercialization strategy to further co-develop the YXY technology for producing PEF bottles.

"The agreement with Danone Research is a fantastic step forward on our path to commercialize PEF bottles" says Avantium's CEO Tom van Aken. Today, Danone Research is at the forefront in contributing to the development of next generation bio-based plastic bottle. Our YXY solution for the packaging industry creates a new bio-sourced material delivering superior functional properties versus conventional PET technology (for example light weighting potential, barrier and thermal properties). We believe that the process economics and carbon footprint of PEF make it a suitable PET alternative. A recent study done by the Copernicus Institute at Utrecht University, showed that PEF has a 50-60% lower carbon footprint than oil-based PET. Finalizing the LCA study is part of the Joint Development Agreement. Avantium is currently validating the use of existing supply and recycling chains, enabling a full transition to bio-based PEF bottles in three to five years from now.

"Based on the YXY technology, the Avantium and Danone Research joint objective is to contribute to the emergence of a new renewable material generation which will not be in direct competition with food. YXY is used as a fast and efficient chemical-catalytic technology to convert carbohydrates produced from plants, grains, energy crops, lignocellulosic matter, waste streams, waste paper or agricultural residues, into a wide variety of bio-based polymers. Based on ongoing R&D programs, Avantium will also continue to develop PEF from renewable feedstock not competing with food.

Avantium has recently opened its pilot plant in Geleen, the Netherlands, with the capacity of producing 40 tons of PEF for application development. The collaborations with Danone and The Coca-Cola Company are key to secure a smooth transition into the mass production phase of PEF bottles. Avantium is in active discussion with other leading brand owners to develop PEF bottles, fibers and film. In the longer term Avantium will license its YXY technology to enable large scale, world-wide production and use of its bio-sourced plastic materials.

About Danone

Danone is one of the fastest-growing food companies in the world. Its mission is to bring health through food to as many people as possible.The group, whose products are sold on five continents, has more than 180 production plants and around 100,000 employees. In 2011, Danone generated sales of €19 billion, of which more than half were in emerging markets. The group holds top positions in healthy food through four businesses: Fresh Dairy Products, Baby Nutrition, Bottled Water, and Medical Nutrition. Listed on Euronext Paris, Danone is a component stock of leading social responsibility indexes including the Dow Jones Sustainability Indexes, ASPI Eurozone and the Ethibel Sustainability Index.

About Avantium

Avantium is a leading technology company specialized in the area of advanced high-throughput R&D. The company develops and commercializes YXY - its brand name for chemical building blocks for making green materials with superior product properties at a competitive price. Combined with the significant reduction in carbon footprint, Avantium's lead application PEF, fulfills key criteria to become

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