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# C123 – Methane oxidative conversion and hydroformylation to propylene

## Raw material sources and Market analyses of the modular route C3 products

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**ABSTRACT**

The C123 project will develop two scenarios for the production of $C_3$ products from unutilized natural gas sources. The add-on route targets propylene production in large, established petrochemical facilities. The modular route targets the production of a set of other $C_3$ products from remote, stranded methane sources such as marginal gas or biogas. Potential sites for the exploitation of the C123 technology are investigated. A market study of the potential $C_3$ products from the modular route,




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propanal, 1-propanol and propionic acid is then provided, which indicates that a smaller, local production process for these chemicals may have economic viability.

## INTRODUCTION

Conversion of methane to ethylene through oxidative coupling has been investigated since the 80's. One of the limitations of the oxidative coupling reaction is the difficulty to increase the selectivity and the conversion to $C_2$ products, hence new technologies that are better able to convert methane to valuable chemical commodities are needed. This is the goal of the C123 project, which aims to couple the Oxidative Conversion of Methane (OCoM) and hydroformylation to produce $C_3$ products. OCoM is a suite of reactions that aims to improve the overall atom economy of methane coupling reactions to produce an optimum ratio of CO:ethylene:$H_2$ for hydroformylation. Depending on the amount of $H_2$, the catalyst and the process, the hydroformylation reaction will produce a mixture propanal and propanol. Propanal  can then be hydrogenated to 1-propanol, and further dehydrated to propylene. A paper detailing the technical challenges faced by the C123 European consortium was presented in parallel by the partners in C123, the reader is directed there for further details (1). The present paper constitutes an extensive technoeconomic and viability review.

The C123 project will develop two exploitation scenarios known as the add-on route, for a capacity of 200 kt/yr propanol for its conversion to propylene, and the modular route, for a capacity of 10 kt $C_3$ products/yr. Propylene has a very large market, and this is thus the focus of larger add-on units where the C123 technology would be integrated into an existing petrochemical site, taking benefit of existing infrastructures and gas networks. Currently, propionaldehyde and 1-propanol have a


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much smaller market as chemical intermediates. They are therefore suitable for the smaller modular units, where the C123 technology would operate on a stand-alone basis. These are specifically useful for utilising either smaller feed sources, such as biogas, or natural gas feed sources at highly remote locations far from existing infrastructure, such as flared gas. To this end, C123 technologies have the potential to reduce global warming emissions by utilizing flared methane.

Potential sites appropriate for the commercial implementation of both the add-on and modular C123 technologies are being investigated. The market potential of propanal (such as for propionic acid) and 1-propanol, through identifying their current technologies, market players, product values and qualities, is therefore relevant for determining the best exploitation strategies.



**Methane sources for C123**

The large-scale add-on process concept and smaller-scale modular concept have different value chains. The add-on route, to be co-located with an existing (petro)chemical facility, is expected to be more economically viable due to the benefit of economies of scale, the possibility to produce high-value propylene, and the possibilities to use existing facilities and infrastructure. The main advantage of the modular unit is that it can be placed at remote locations where stranded natural gas or associated gas resources are available, but with logistical challenges for exploiting existing infrastructure such as pipelines, liquefied natural gas (LNG) plants or refineries. The modular unit can also be applied to valorise biogas, which is typically produced in decentralized smaller-scale units. The use of biogas will result in bio-based products, contributing to a more sustainable chemical industry. For this


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feedstock, Germany has been earmarked as a suitable location. Of all the European countries, Germany produced the most energy from biogas in 2015, contributing 329 PJ of the 662 PJ biogas produced in Europe (49.7 %) through 185 biomethane plants (2).

Marginal and associated gas are two examples of stranded natural gas. Associated gas is natural gas found with oil reserves and flared at several locations. A world map with detected flaring sites in 2012 is shown in Figure 1 (3). There is an effort to decrease flaring, because it negatively affects local air quality and releases carbon dioxide, a greenhouse gas, which has a significant impact on global warming and climate change. Consequently, the application of C123 technology for flared gas reduces greenhouse gas emissions, contributing to a more sustainable process and lower environmental impact. Marginal gas includes explored, but unused underground gas reserves. A specific marginal gas field of interest to the C123 project is the Absheron gas field (Figure 2). It is estimated to contain 350 billion $m^3$ of gas and covers an area of 270 $km^2$, 500 m under water (4). It is operated by a C123 project partner, Total, and located in the Caspian Sea approximately 100 km from Azerbaijan capital Baku where C123 project partner ANAS (Azerbaijan National Academy of Sciences) is located.




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Fig. 1.: World map with red dots indicating the 100 spots with the largest annual gas flaring emissions of between 0.2 - 1 billion $m^3$/yr. (KLM-file in Google Earth from (3))


Fig. 2.: Location of marginal gas resource Absheron in the Caspian Sea close to Azerbaijan (Redrawn from Gotev, 2016 (5)).

There can be several reasons why natural gas remains unused or stranded, such as the distance of the resource to existing infrastructure and markets, unfavourable gas composition or a small gas reserve volume. All of these factors


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contribute to a lack of economic incentive to utilise stranded natural gas resources. However, the application of the C123 technology aims to address these challenges, by providing an energy and carbon efficient process that will enable the transport of higher-value products than natural gas, and using tailored process design for the resource's composition and available volume. Therefore, it may be profitable to valorise these stranded natural gas reserves. The economic and environmental viability will be determined by performing a techno-economic assessment (TEA) and a life cycle analysis (LCA), respectively, on the two C123 processes, products and their value chains. Successful implementation of this technology is expected to ensure a secure supply of C3 products that is not dependent on the available oil reserves. An iterative approach between the LCA, TEA and process design will ensure a well-integrated project to reach the overall goals with regards to the TRL, economic viability and sustainability. The development of stranded gas or biogas is also expected to trigger economic development and the growth of a petrochemical industry to accompany market development.



**Market analyses of the modular route C3 products**

The add-on route aims to produce large volumes of propylene, a gas that is an important chemical commodity for the production of plastics (polypropylene) and other chemicals. The economic viability of the modular route is conversely dependent on the transportation from remote locations of liquid $C_3$ products. Fortunately, these products, propanal, 1-propanol and propionic acid, already have market applications and a value that could be superior to propylene.


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**Propanal**

Propanal, also known as propanaldehyde or propionaldehyde, is a liquid, with an ethereal pungent odour (6). Propanal is mainly used as a chemical intermediate in the production of n-propanol and propionic acid, for example. The market for propanal itself is not large and the annual quantity imported and/or manufactured in Europe is in the range of 100 – 1,000 tons according to ECHA (7). Main producers consume it internally. Hydroformylation of ethylene with syngas is the usual process to produce propanal. An alternative route, through isomerization of allylic alcohol, would nevertheless also be possible (i.e. enol reaction).

According to the trade data, there was a significant volume of exports of propanal in 2019 (8,9), amounting to 286 thousand tons worth 725 million US $:

- Germany had 22 % in value of the world exports or about 83 000 tons (BASF, Oxea).
- The United-States had 22 % or about 54 000 tons (Dow Chemical, Eastman).
- China had 14 % or about 39 000 tons (Zibo Nalcohol Chemistry, which represents a production of 2 million tons per year) (10).

Trade data are accessible through the HS code (numbers used to classify traded products), e.g. 291219 which includes "acyclic aldehydes, without other oxygen function (excluding methanal, ethanal, butanal, benzaldehyde)". Therefore, it is not possible to isolate propanal in the trade data, but because it is the main product share under this code, general trends are relevant.

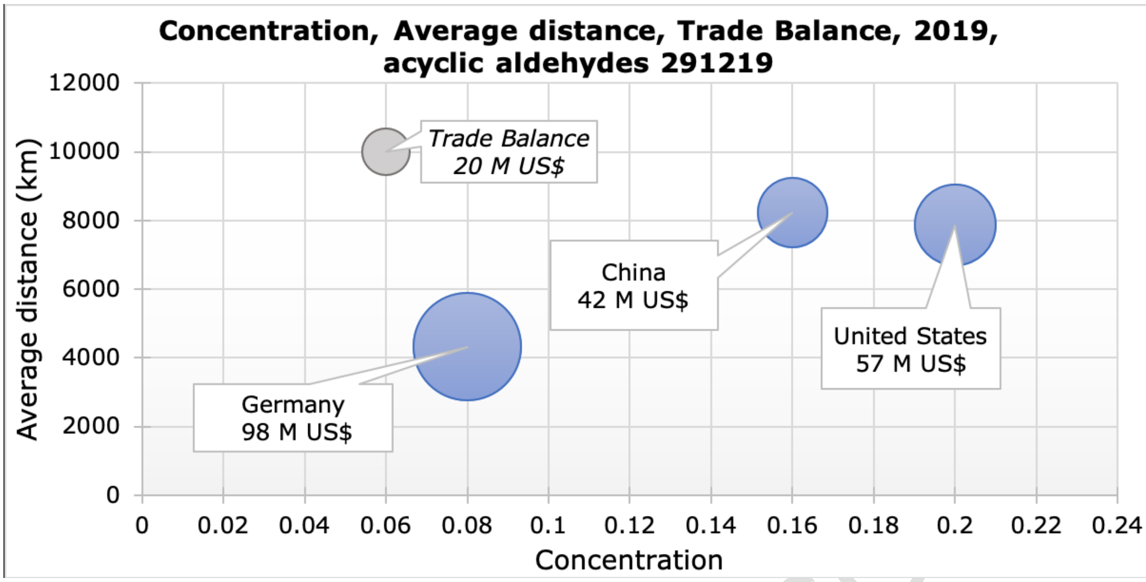


Fig. 3.: Concentration of exporting countries of products 291219 (acyclic aldehydes) and average distance with their destination countries in 2019. Data have been computed from TradeMap (9).

The data in Figure 3 are computed from the export volumes and take into account the average distance travelled by the product weighted by the trade value. The concentration parameter is an indication of the diversity of customers (importing countries); a concentration value of 1 means export to a single country. The trade balances (exports-imports) are used as the indicator, but the distance is based on exports only. Chinese and US products travel longer distances than products made in Germany. The data illustrate that for this product (propanal), there would certainly be a demand for small/local production, with small units, avoiding long distance transports and representing a potential market of 100 M US$. Stranded gas, complemented with biogas, make methane an ubiquitous resources for small plants. Taking into account the higher cost for importing small volumes of products and other logistics costs, a local small production cost compares more favourably than with a world market prices. In addition, production on-site and on-demand contributes to the reduction of other associated costs such as inventory, safety… and require specific local investigation.


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**1-Propanol**

1-Propanol is a colourless liquid whose odour and flavour are alcoholic/earthy (11). Due to its excellent solvent properties, 1-propanol is used in various applications, including lubricants, coating products, dispersing agents, pesticides, surface agents, cleaning products, and adhesives. This material is also used for packaging and food-contact applications and was recently also used in some sanitizer gels in combination with isopropanol.

Due to the wide range of potential applications, the market is more developed, and the annual quantity imported and/or manufactured in Europe is in the range of 10,000 – 100,000 tons according to the REACH registrations (12). 1-propanol has 85 % of the propanol market, with 15 % for isopropanol (2-propanol). 1-propanol can be produced through hydrogenation of propanal, or directly from syngas through the Fisher-Tropsch process developed by Sasol, in which it is separated from the mix of products. Interestingly, there does not seem to be a commercial fermentation route to produce biobased 1-propanol.

The propanol HS trade code is 290512, including both 1-propanol and 2-propanol. Because 1-propanol represents 85 % of the market, the trade data mostly represent the targeted product. Asian countries produce mostly 2-propanol (for example by Tokuyama, Isu, Lcy, Zhejiang Xinghua Chemical, LG Chem). For the readers who would be interested in 2-propanol trade and productions, we suggest to look at the phenol trade data. Acetone is coproduced with phenol, and 2 propanol can be produced either by hydrogenation of acetone, or direct hydration of propylene, or fermentation (just starting). So if acetone is the main source for 2-propanol, it would be linked with phenol production. But this is not the scope of the present paper.


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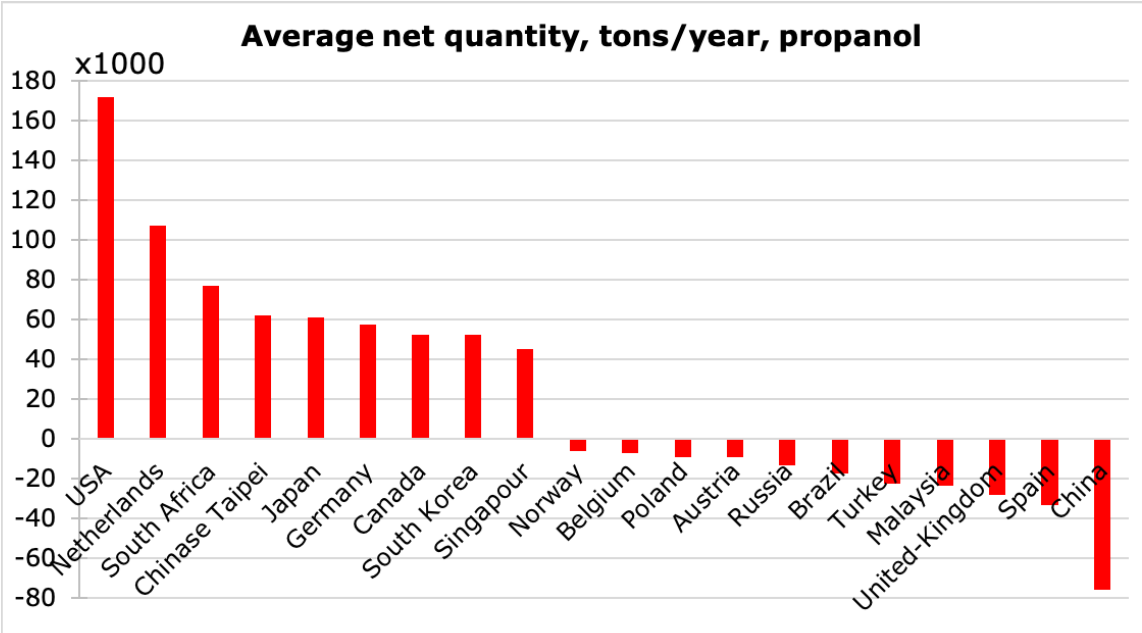


Fig. 4.: Calculated average of annual differences between exported and imported quantity, in each country, for the 2010-2018 period (tons per year), for products 290512 (1- and 2-propanol). Data computed from TradeMap database (9).

The net difference between exports and imports has been computed from the annual data available from TradeMap between 2010 and 2018 and is shown in Figure 4. This was done to identify where the main producers are located and to eliminate the countries only involved in trading. Imports and exports are based on the HS trade codes for both propanol isomers.

According to the trade data, there was a significant volume of 1- and 2-propanol exports in 2019 (9,13):

- The United-States had 24 % of the world exports in value – or 307 000 tons (Dow Chemical, Oxea). Oxea produces around 100 000 ton per year (14).
- China had 10 % -or 183 000 tons (Zibo Nalcohol Chemistry which products 1 million ton per year) despite a negative trade balance (imports larger than exports) in 2019 (-2.1 M US$) (10).
- Germany had 9.2 % - or 101 000 tons (Sasol Germany, Oxea).


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- The Netherlands had 7.8 % - or 93 000 tons (Eastman Chemical).
- South Africa had 6.3 % - or 103 000 tons (Sasol, which claims 30 % of the 1-propanol market) (15).

These data illustrate the market activity. The same country can be an exporter and an importer of the same chemical compound. It is obvious for large countries like China, Russia or USA, where the east/west coast can more easily import from other countries than to transfer product from the other side of the country. Therefore export volumes/value from major producers are more relevant to assess potential for other production units in other countries. In addition the volume produced is not necessarily in line with the exported volume, since a lot of captive use can exist. However, the share of exports to the production capacity, is an important indicator, to identify the potential risks linked with a specific producer or producing country.

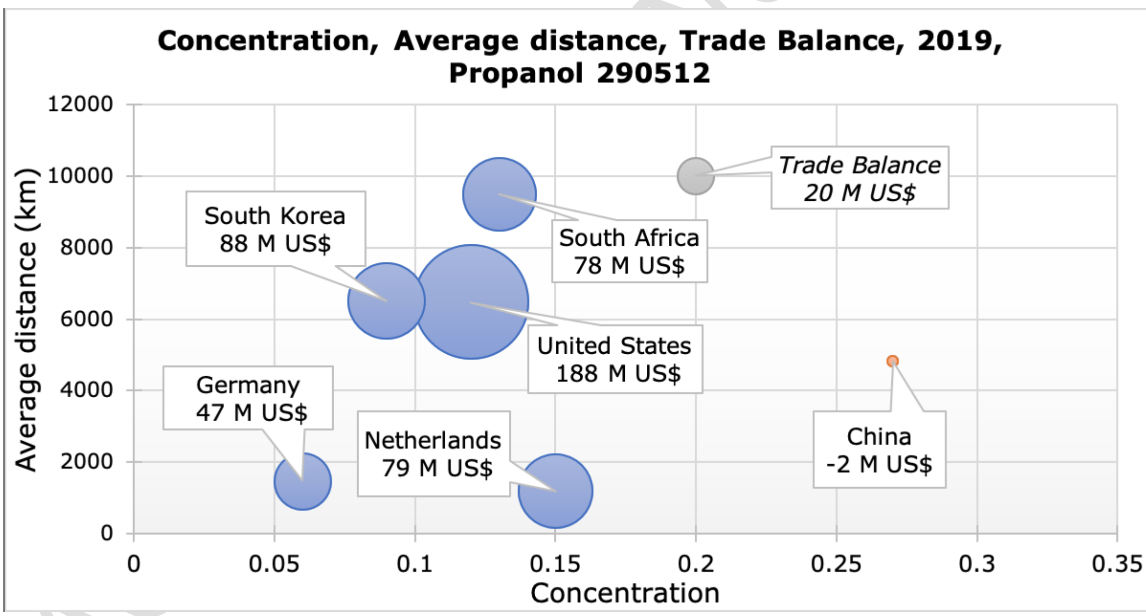


Fig. 5.: Concentration of exporting countries of products 290512 (1 and 2- propanol) and average distance with their destination countries in 2019. Computed from TradeMap (9).


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Exporting countries sell the product in many countries (low concentration factor), Figure 5. Moreover, the average distance is similar to that of propanal. Germany and the Netherlands export to Europe, while South Africa, South Korea and USA export at longer distances. The largest shares of export values are in the USA, where products travel on average 6000 km. This supports the notion that smaller, modular C123 plants for local production should have a commercial interest, with a cumulated value of 350 M US$ (this value is calculated based on the export values from South Africa, USA and South Korea from which the product travel more than 6000 km). When products travel on long distance, they not only consume a lot of energy for transport, but also contribute that way to global warming but are also more sensitive to energy price variations, and as seen recently to unpredictable events like the COVID19, and country resilience.

### Propionic Acid

Propionic acid is a colourless pungent odorous liquid (16). Propionic acid is manufactured to be used as preservative and anti-mold agent in animal feed and grain (17). It is also used as a chemical building block for the production of herbicides, pharmaceuticals, dyes, textile and rubber products, plastics, cosmetics and perfumes. In addition, propionic is a preservative and flavouring agent in packaged foods.

The annual quantities imported and/or manufactured in Europe is in the range of 100 000 – 1 000 000 tons, according to ECHA (18). The calculated average of annual differences between exported and imported quantities are shown in Figure 6. Propionic acid is produced either by oxidation of propionaldehyde or by a Reppe process, i.e. the hydroxy-carboxylation of ethylene (19). The HS trade code 291550 includes propionic acid, its salts and esters. Because propionic acid is needed for the creation of its salts, the traded volumes are relevant for discussion.

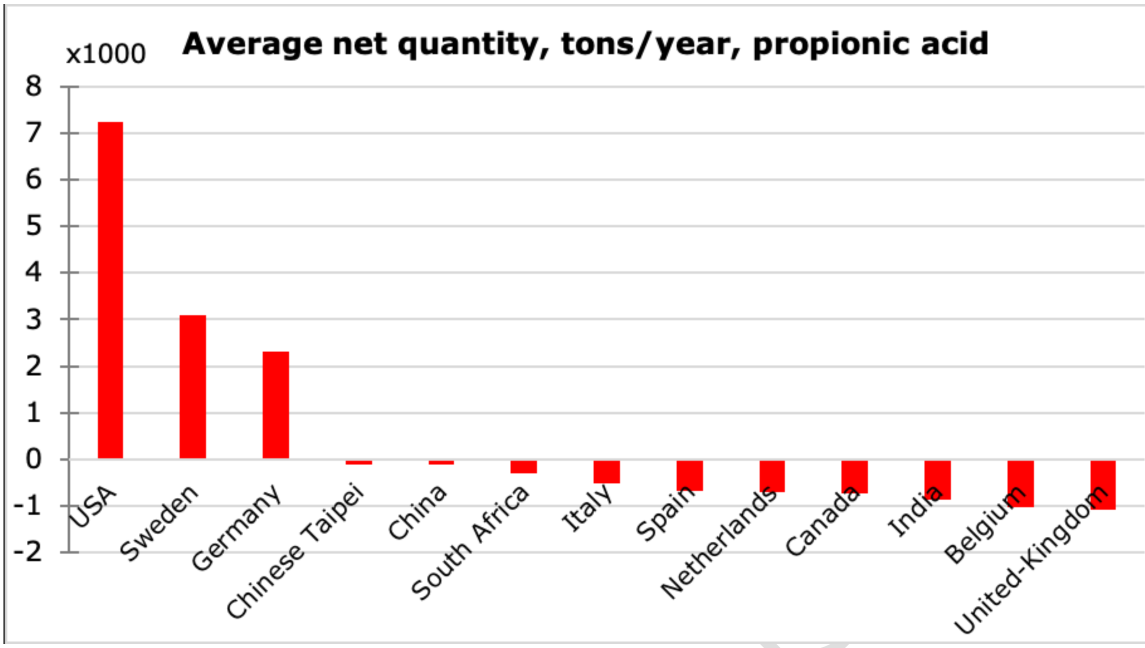


Fig. 6.: *Calculated average of annual differences between exported and imported quantity for the 2010-2018 period (tons per year), for product 291550 (propionic acid, its salts and esters). Data computed from TradeMap (9).*



According to the trade data, propionic acid export volumes in 2019 were as follows (9,20):

- The United-States had 25 % in value of the world exports – or about 135 000 tons (Dow Chemical which increased its capacity of production in 2017) (21).
- Germany had 14% - or 46 000 tons (BASF, and Oxea which expanded its capacity in 2017) (22).
- The Netherlands had 14 % - or 39 000 tons (Eastman) despite a negative trade balance in 2019 (-4.1 M US$).
- China had 6.8 % - or about 20 000 tons (BASF-YPC which increased its production in 2019 to 69 000 tons per year) (23).
- Sweden had 9.6 % -or about 35 000 tons (Perstorp) (24).

The capacity expansion which have been made recently by several producers are a good sign that the market demand is growing, whether the growth is for captive use or to satisfy customer demands.


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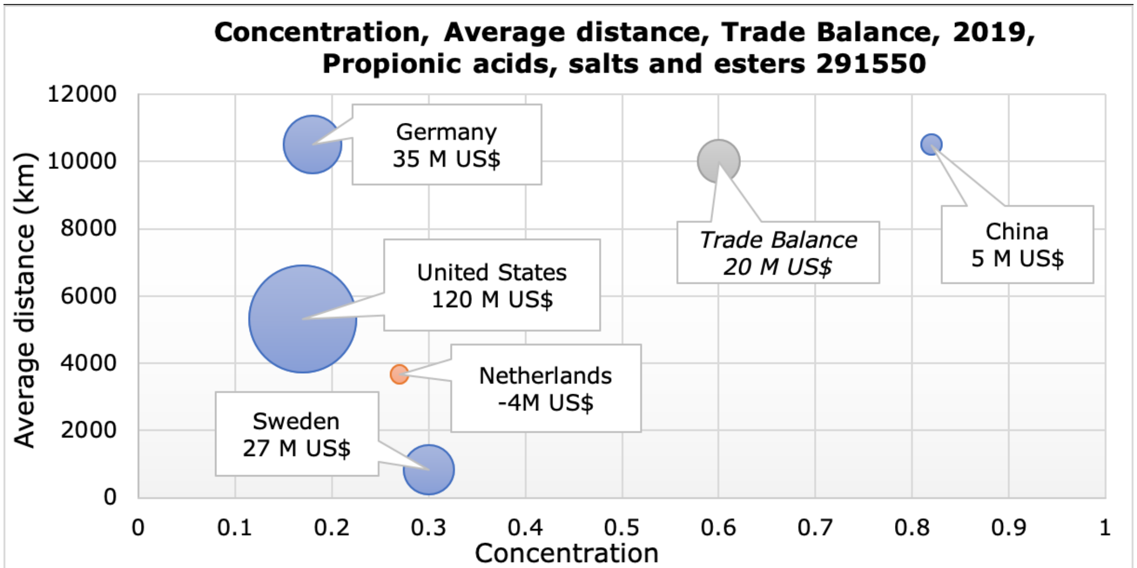


Fig. 7.: Concentration of exporting countries of products 291550 and average distance with their destination countries in 2019. Data computed from TradeMap (9).

In contrast with the exporting countries of the two previous products, the export concentration (Figure 7) is higher for propionic acid, and is above 0.8 in case of China. This means that exporters have a limited number of customers in targeted regions. Nevertheless, the average distance from a given exporting country to their markets is similar. Sweden appears as an exporting country to neighbouring northern Europe, while Germany exports worldwide. Again, the USA has the largest share in export value, with products traveling more than 5000 km. Once again this supports the notions that it would make sense to have more localized production of this C3 chemical.



## Influences of prices

### Energy

The variation of the trading value (import/export prices) for 1- and 2-propanol from the United States (9), together with the price of crude oil (Brent is selected as a better world price reference than WTI) (25),  US ethylene (26) and propylene (9),


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the traditional feedstocks for the $C_3$ products, is shown in Figure 8. It illustrates that the value of propanol replicates the price of crude oil, ethylene, and propylene, and the dependence between the prices of the raw material and products of interest. When propanol is at the same price per ton than propylene, there is more value in propanol, since the dehydration to propylene also corresponds to a weight loss in material.

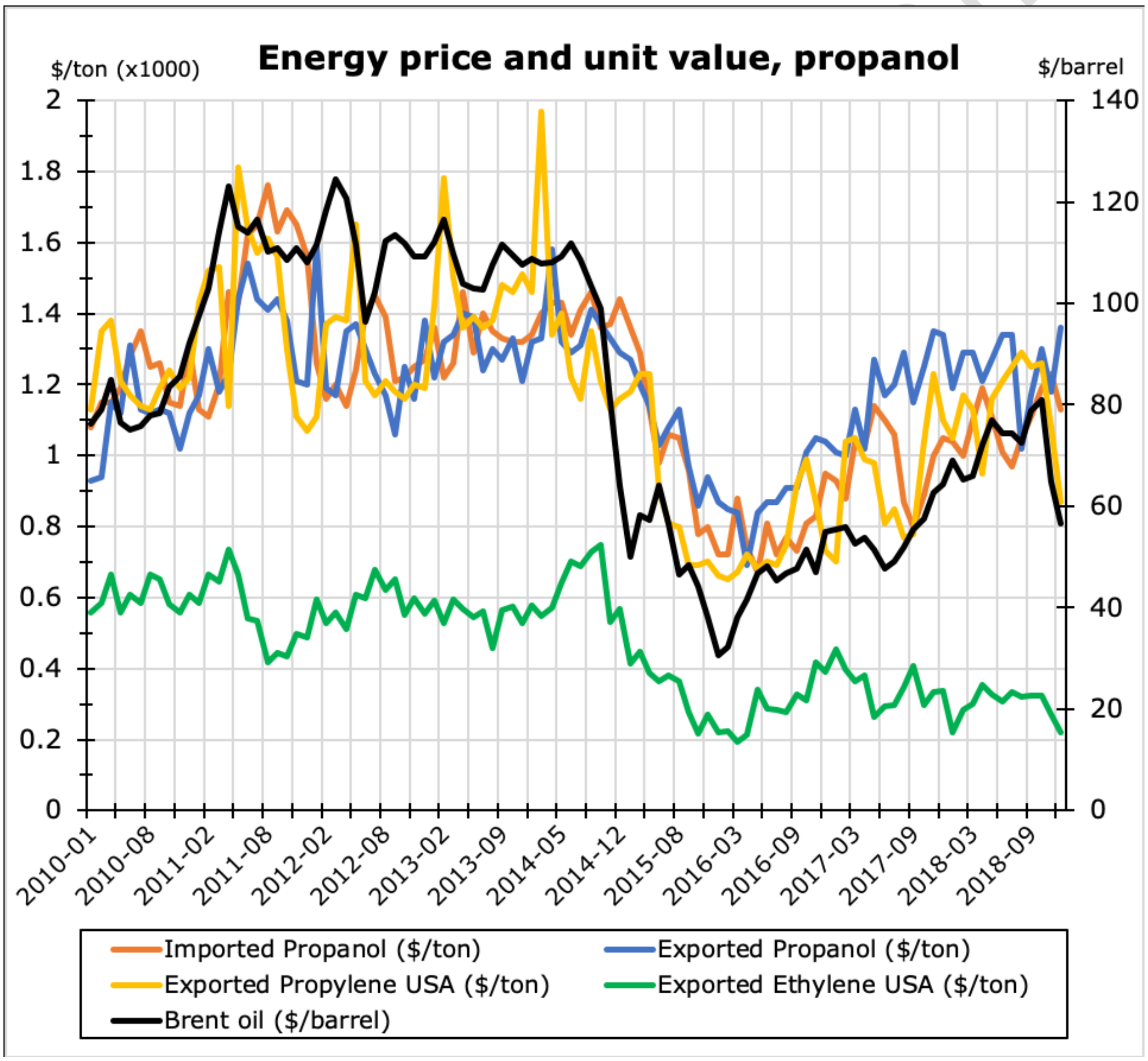


Fig. 8.: Evolution of energy (crude oil), ethylene, propylene and propanol prices in the USA between 2010 and 2018. Data from TradeMap (9) and IHS Market (26).

Importantly, the price of the product depends on the production process as well. In South Africa propanol is produced by Sasol via the Fischer-Tropsch process, which resulted in an average export price of 765 $/ton (9), compared to the United States where propanol is produced through the hydrogenation of propionaldehyde, resulting in an export unit value (calculated as a ratio between the exported value and the volume exported) at around 1008 $/ton (9). For more details on the way the values are calculated, the reader can refer to the website in reference.

### Correlation matrix

**Table I: Correlation Matrix between unit values for exports from the USA, monthly data in the period 2010-2018. Data from TradeMap (9) and IHS Market (26).**

| | Propanol | Propanal | Propionic Acid | Crude Oil | Ethylene | Propylene |
|---|---|---|---|---|---|---|
| Propanol | 1 | | | | | |
| Propanal | 0.16 | 1 | | | | |
| Propionic Acid | 0.04 | 0.21 | 1 | | | |
| Crude Oil | 0.67 | 0.48 | 0.07 | 1 | | |
| Ethylene | 0.53 | 0.52 | 0.17 | 0.76 | 1 | |
| Propylene | 0.71 | 0.36 | 0.09 | 0.82 | 0.71 | 1 |

In a correlation matrix, values can be between -1 and +1. A positive value means that 2 parameters vary in the same direction. A value close to 0 means that the parameters are relatively independent, while a value close to 1 means that the parameters are highly dependent on each other.

The influence of raw material costs on final product prices in a process can be analyzed with the help of a correlation matrix. The correlation matrix in Table 1 is




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made for the United States exports, because the country is producing the three targeted products in large quantities. Thus, we can isolate the price fluctuations of the geo-economic environment to reflect the connections to raw materials.

The value of exported ethylene correlates less with the value of crude oil (value of 0.76) than with the value of propylene (value of 1). This is most probably due to the fact that recently, ethane crackers have increased ethylene production in the US. Propanal, which is produced through ethylene hydroformylation, correlates poorly with ethylene (value of 0.52), because most of the production is consumed internally, and only part of it is sold on the market. Propanol correlates with the price of crude oil (0.67) and ethylene (0.53), as this is the major market; while propionic acid, used in feed additives, has a rather small market and therefore poorly correlates with feedstocks (values of 0.07 - 0.17). Products correlate poorly between themselves (e.g. propanol and propionic acid has a value of 0.04). This shows that there are opportunities for each product, and that a balanced product portfolio is probably a wise strategy. In addition, the targeted products have a high growth potential (Pre-COVID estimates), of around 6-8% CAGR (compounded annual growth rate). Therefore, propylene, propanal, n-propanol and propionic acid are deemed good C3 candidates for the C123 technology.

**Conclusions:**

In the C123 project, opportunities to valorise low-value stranded gas such as marginal or flared gas, and biogas for the production of bio-based C3 chemicals, are investigated. Two process design routes are considered: a larger add-on unit to an existing petrochemical site(s) or a smaller modular unit for remote feedstock locations.

In this market study it is shown that there is a fair market potential, with good opportunities for modular units focusing on local production, for the three primary products derived from the C123 modular route: propanal, n-propanol, and propionic acid. Other products derived from propionaldehyde and propanol will be also investigated in C123, with the objective to identify other market opportunities.

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