

Environmental Performance Assessment of a Novel Process Concept for Propanol Production from Widely Available and Wasted Methane Sources

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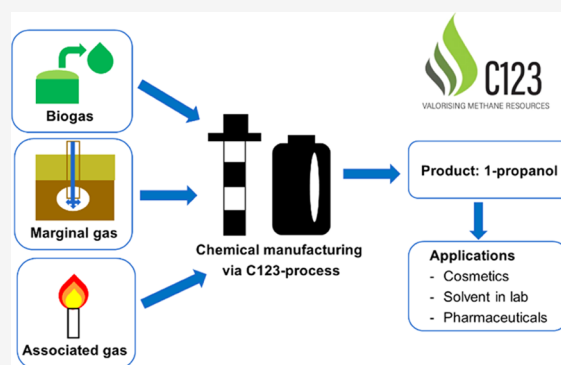
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ABSTRACT: Currently, propanol production highly depends on conventional fossil resources. Therefore, an alternative production process, denoted as “C123”, is proposed and evaluated in which underutilized and methane-rich feedstocks such as biogas (scenario BG), marginal gas (scenario MG), and associated gas (scenario AG) are converted into propanol. A first modular-scale process concept was constructed in Aspen Plus, based on experimental data and know-how of the C123 consortium partners. The environmental performance of the considered scenarios was compared at the life cycle level by calculating key performance indicators (KPIs), such as the global warming burden. The results showed that scenario BG is the least dependent on fossil fuels for energy use. Scenario AG seems the most promising one based on almost all selected KPIs when taking into account the avoided gas flaring emissions. The performance of the C123 process concept could be improved by applying heat integration in the process concept.



1. INTRODUCTION

Propanol is an added-value chemical with a growing market. An annual growth rate of 4.0% was forecasted between 2018 and 2023 and its market size is estimated to reach USD 4.3 billion by 2023.¹ This alcohol is mainly used as a solvent and as a precursor for the production of amines, ethers, and esters.² 1-Propanol can be dehydrated to form propylene.² It is also used as an additive in printing inks, cosmetics, and pharmaceuticals.³ The production of 1-propanol heavily relies on conventional fossil resources. Currently, this chemical is produced via ethylene hydroformylation followed by propanol hydrogenation.^{2,4} Ethylene is usually obtained by steam cracking of naphtha, which is a very energy-intensive process. Due to an impending shortage of fossil resources, alternative feedstocks and production methods are pursued. Microbial production routes such as the Wood–Werkman pathway and the acrylate pathway also deliver 1-propanol.² However, these fermentation processes are still under development: the propanol yields are still low, the production strains only have a low tolerance for propanol, and the use of glucose-based feedstocks, which achieve the highest productivity at this moment, causes competition with food purposes.²

To replace conventional propanol production, an alternative technology, denoted as C123 throughout this work, is developed as part of an EU Horizon 2020 integrated project.⁵ C123 refers to the carbon number of the crucial species involved in this specific propanol production process. First,

feedstocks containing methane (C1) are converted into ethylene (C2) via a so-called oxidative conversion of methane (OCOM). Second, ethylene is transformed into propanol (C3) via hydroformylation followed by hydrogenation.⁶ Hydroformylation is typically applied to produce aldehydes by the reaction of ethylene with CO/H₂ via homogeneous catalysis.^{7,8} Rh complexes are often selected as catalysts due to their high activity and selectivity.⁷ More details on the process design (e.g., purification and separation steps) will follow in Section 3.1.

Apart from the C123 process, other conversion technologies involving methane activation are well known. These processes are becoming economically more attractive because of the increasing supply of natural gas (e.g., exploitation of shale gas reserves).⁹ Nevertheless, they exhibit several disadvantages. For instance, methane can be used to produce methanol (methane to methanol, MTM) and liquid hydrocarbons.¹⁰ In the case of MTM, low conversion and production rates as well as overoxidation were reported, the reactivity of methanol

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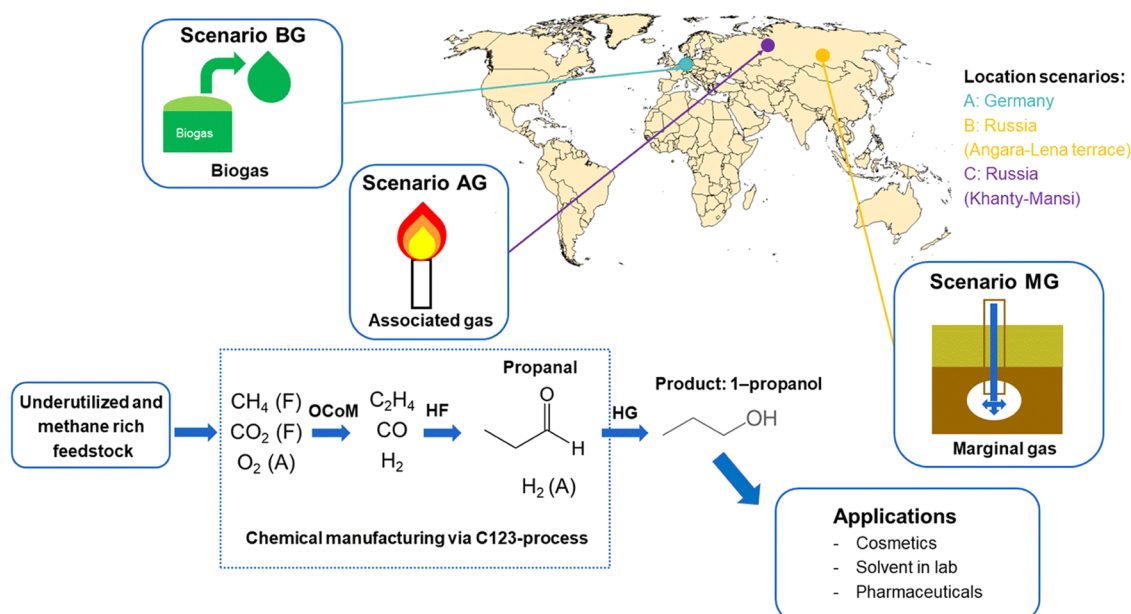


Figure 1. Illustration of selected feedstocks and locations for propanol production in C123 project (C123 scenarios). BG = biogas, MG = marginal gas, AG = associated gas, (F) = in feed, (A) = added, OCoM = oxidative conversion of methane, HF = hydroformylation, HG = hydrogenation.

being higher than that of methane.¹⁰ In the case of liquid hydrocarbons production, syngas is first obtained by methane reforming followed by Fischer–Tropsch synthesis. This technology also has important disadvantages such as the pronounced endothermicity of the reforming step and the associated high cost.¹⁰ Methanol can be further converted into olefins (MTO). However, this process requires higher economies of scale compared to propanol production to be economically attractive.¹¹ Methane liquefaction for transportation is another strategy, which is hampered, however, by the pronounced energy need for cooling (temperature must be below 111 K) and methane losses through leakages.¹⁰ Finally, the oxidative coupling of methane (OCM) is a promising reaction to convert low-value methane feedstocks into ethylene.^{12,13} However, the obtained C²⁺ yield, comprising ethane and ethylene, is too low (maximum 30%) and temperature control is difficult due to the pronounced exothermicity of the OCM. In the C123 technology, this reaction is combined with other reactions to improve its performance, resulting in the OCoM reaction (see Section 2.2).

In this work, three alternative and underutilized methane-rich feedstocks are proposed to produce propanol via the C123 technology, namely, biogas (scenario BG), marginal gas (scenario MG), and associated gas (scenario AG). These possible production routes (C123 scenarios) are illustrated in Figure 1.

Separate variants of the C123 technology are evaluated for each of the considered feedstocks. Biogas is typically obtained via anaerobic digestion of manure, sewage sludge, organic waste, energy crops such as maize, etc.¹⁴ At present, this methane source is mostly used as feedstock for combined heat and power (CHP) installations or is purified to bio-methane, which can be injected into the gas grid.¹⁴ Hydrogen production from biogas via steam reforming is also commercially applied.¹⁵ However, to the authors' best knowledge, its conversion to propanol has not yet been investigated. Marginal gas is natural gas that is present in

unexploited underground reservoirs. Several conditions must be met before being called a marginal gas field: at least one exploration well is drilled in the last 10 years, the field contains large gas and small oil reserves, and the field is not exploited because of the limited economic viability and no gas is extracted in the last three years.¹⁶ Associated gas is a byproduct of oil production, which is often flared for economic and technical reasons.¹⁷ Gas flaring has many consequences for the environment such as global warming by CO₂, CH₄, and black carbon emissions, human health effects (e.g., respiratory problems), acidification of the soil in the neighborhood of the flare, etc.^{17,18} Pipeline transportation of marginal gas and associated gas is not feasible due to the long distance from remote areas to the market.¹⁸ Conversion of these raw materials into a liquid such as propanol could be more convenient to make its storage and transportation more environmentally friendly and economically viable. Additionally, flaring emissions can be avoided using associated gas for the production of propanol.

This work aims at comparing the C123 scenarios at the life cycle level via key performance indicators (KPIs), e.g., global warming burden. Therefore, a preliminary process concept for the C123 technology was proposed at a modular scale, starting from underutilized methane-rich feedstock (biogas, marginal gas, and associated gas) and converting it separately into propanol. Aspen Plus V11 was used to construct a process configuration based on experimental data and know-how of the C123 consortium partners and to evaluate its environmental performance based on simulation data (e.g., mass and energy flows). This analysis also resulted in a mass balance and dataset for each C123 scenario.

2. METHODOLOGY

2.1. C123 Scenarios as a Function of the Geographical Location. Modular units (small scale, stand-alone) were conceptually designed to produce propanol via the C123 technology with a capacity of 10 ktonnes per year. The location was determined for each scenario because of its

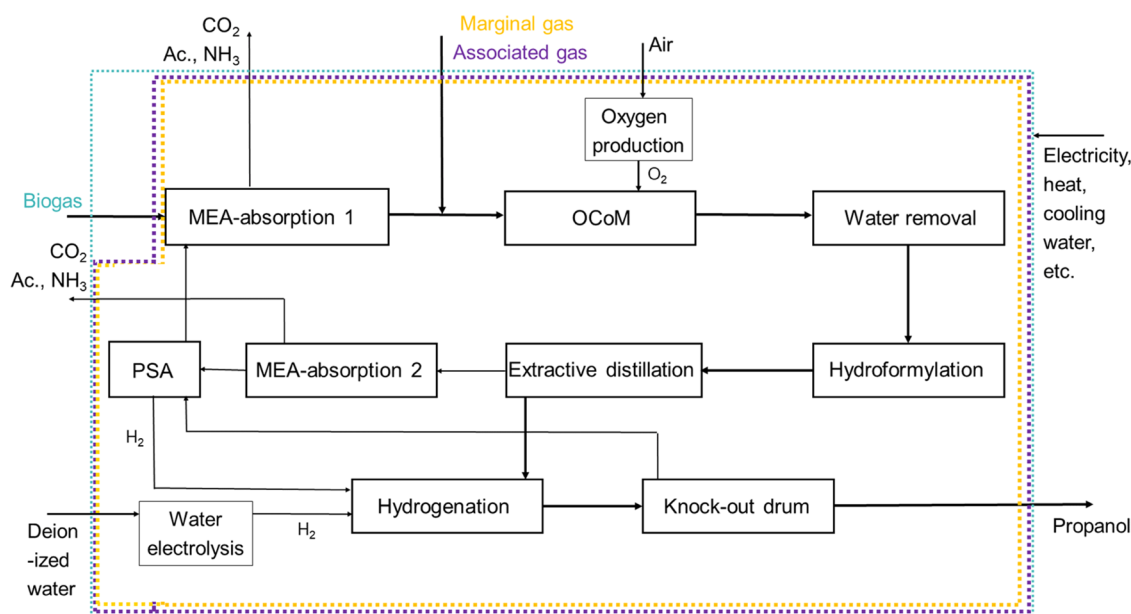


Figure 2. Flow chart of preliminary process concept for C123 technology. The system boundaries of scenarios BG, MG, and AG are indicated in apple blue sea green, orange, and purple, respectively. MEA-absorption 1 is only applicable for scenario BG, and MEA-absorption 2 is only applicable for scenarios MG and AG. OCoM = oxidative conversion of methane, MEA = mono-ethanolamine, Ac. = acetaldehyde.

impact on the preliminary process concept (see Figure 1). For instance, the composition of the gas is location dependent. The supply of utilities (e.g., electricity) may also be more complicated in remote areas. For scenario BG, Germany was selected as the location, which is a populated area with established infrastructure and one of the biggest biogas producing countries in the world.¹⁹ Scenario MG is proposed for Russia, because large marginal gas reservoirs (e.g., Angara-Lena terrace), that meet the demand for propanol production, are situated in this country.²⁰ Finally, Russia and USA (North Dakota) were targeted for scenario AG. Ultimately, only Russia was chosen because flaring spots over the North Dakota region are more dispersed and the gas flaring volume of each spot is quite small, which complicates the gas transportation and processing. Russia accounts for 17% of the global gas flaring volume. Hence, it is the country with the biggest flaring emissions in the world.²¹ Many flaring spots are located in Khanty-Mansi, a region in Russia where flaring is concentrated. Moreover, the gas flaring volume related to the selected spots (50 million m³ per year for each spot) is sufficiently high to produce the desired propanol yield: 31 million m³ of associated gas per year is needed on an annual basis if an efficiency of approximately 50% is considered for the conversion of methane to propanol.²² Production processes for scenarios MG and AG were located in remote areas. Transportation of marginal gas and associated gas is not profitable from these places, as the distance to the market exceeds 750 km, favoring conversion of gas into liquids (e.g., propanol).²³

2.2. Description of Modular C123 Process Concept. In this section, a preliminary C123 process concept at technology readiness level 4 (TRL 4) and at small scale is described for the production of propanol. It should be emphasized that this process is a first design, which is still susceptible to improvements as a result of advancing insights in the ongoing C123 project (see Section 4.2). In scenario BG, biogas is supposed to be produced on-site via anaerobic digestion of maize silage and cattle manure. These feedstocks are usually co-digested in Germany.²⁴ The feed consists of 70% maize

silage and 30% cattle manure.²⁵ A co-digestion of these feedstocks typically has a higher efficiency than a mono-digestion. However, the separate mono-digestion of both feedstocks was assumed due to a lack of data for this specific co-digestion.²⁵ Biogas generally contains a higher fraction of CO₂ compared to marginal gas and associated gas.²⁶ Considering scenario BG, the feed consists of 50 mol % CH₄ and 50 mol % CO₂. Therefore, CO₂ is largely removed from this feed before entering the OCoM section using chemical absorption with mono-ethanolamine as solvent. Scenarios MG and AG took into account the marginal gas extraction and the separation of associated gas from oil, respectively. In those scenarios, the feed contains 90 mol % CH₄ and 10 mol % CO₂. Excess CO₂ in the recycling loop is also removed via chemical absorption. The removal of impurities in the feed, such as H₂S and natural gas liquids, was not considered in any scenario. In addition, electricity must be produced locally (e.g., from natural gas via a gas turbine) as no electricity grid is assumed to be available in the considered remote areas.

A flowsheet of the preliminary C123 process concept is given in Figure 2. The production steps explained in the next paragraphs apply to each scenario. All considered chemical reactions, together with the corresponding fractional conversion, are listed in Appendix S1. The OCoM section is intended to be split into three reactions in series to obtain the optimal ratio of ethylene, CO, and H₂ (1:1:2) for hydroformylation.²⁷ The stoichiometric ratio for hydroformylation only amounts to 1:1:1, but auxiliary H₂ can be needed for hydrogenating propanal into propanol. Additional information about the modeling of these three reactors can be found in Appendix S2. First, an OCM reaction takes place to produce ethylene. Pure oxygen, obtained from cryogenic air separation (local production), is added in the first reactor.²⁸ The yield of C₂-hydrocarbons (i.e., ethane and ethylene), CO, and CO₂ was not high after OCM (8.0, 4.8, and 5.0 mol %, respectively), and the selectivity toward ethane within the C₂-fraction was relatively high (the ratio of ethylene to ethane was 1:1 on a

molar basis). Therefore, OCM can be followed by post bed cracking (PBC) to convert excess ethane into ethylene and hydrogen. Finally, CO₂-induced oxidative dehydrogenation (CO₂-ODH) of ethane can reduce the amount of CO₂ (formed in OCM) simultaneously yielding more ethylene, CO, and H₂ to further adjust the ratio of these three compounds and to meet the requirements for hydroformylation. Recovering products as a C₃ species allows for a much more straightforward separation from the product stream.²⁹ All reactions in the OCoM section take place at 1 bar. In this section, water is also formed as a result of the OCM and CO₂-ODH reactions. To avoid an azeotrope between propanal and water, the latter is removed via a knockout drum and water trap before hydroformylation. Since this reaction ideally takes place at 20 bar, multistage compression is required after OCoM.

During hydroformylation, only propanal is formed as no propanol was detected in the experimental work.²⁷ Moreover, not all ethylene is converted into propanal. A partial conversion of 0.90 was considered.³⁰ The unreacted ethylene is separated from propanal by extractive distillation and returned to the OCoM section. Through hydrogenation, propanal is converted into propanol with 99% efficiency.³¹ A pressure swing adsorption (PSA) is proposed to remove excess hydrogen gas from the recycle loop to avoid build-up. The removed hydrogen can be utilized in the hydrogenation step. A small quantity of hydrogen must still be added because the amount from the recycle loop is not sufficient. This small fraction can be produced via water electrolysis. Excess propanal is removed via a knockout drum, and this stream is also recycled to the extractive distillation. A product purity of 99.5 wt % was aimed at. This high purity for propanol is required for certain applications e.g., use as a solvent.³² Cooling is needed for the OCM reaction, hydroformylation, and hydrogenation. A cooling water circuit was assumed for this, including cooling towers. Only 1.8% of the total flow rate of cooling water in the process must be added to compensate for the losses by evaporation, blowdown, and drift losses.³³

2.3. Data Collection, System Boundaries, and Functional Unit of C123 Scenarios. The software Aspen Plus V11 was used to construct a C123 process model based on experimental work, know-how of the C123 consortium partners, and the assumptions presented in Section 2.2. It allowed collecting the necessary data such as mass and energy flows, composition of all flows, purity, utility requirement, etc. via simulations. More details about the Aspen simulations can be found in Appendix S3. Only the conversion of the produced feedstocks into propanol was included in the simulations. Data for the production of the raw materials, such as the energy requirement, was retrieved from Boulamanti et al.,²⁵ Skone et al.,³⁴ and the Ecoinvent database version 3.6. The simulation data were used to set up mass balances in Section 3.1 and to calculate the selected KPIs (see Section 2.4), allowing the comparison of the C123 scenarios at the life cycle level. The system boundaries for each scenario, indicated with the dotted lines in Figure 2, show which production steps are included. The production of the feedstocks, the utilities (e.g., heat and electricity), and auxiliary chemicals (e.g., mono-ethanolamine) were also taken into account in the analysis. For the production of biological feedstocks, carbon neutrality was assumed (emitted CO₂ by the C123 process is equal to CO₂ uptake by biomass). The removal of H₂S and natural gas liquids from the feedstocks was not included in this analysis

due to a lack of data in this stage of the process development. The infrastructure, maintenance, and catalyst production for the preliminary C123 process were also not considered. The functional unit was 1 kg of propanol with a purity of at least 99.5 wt %. This means that all data and results are mentioned as a function of 1 kg propanol.

2.4. Key Performance Indicators. The performance of the various C123 scenarios was compared at the life cycle level based on KPIs, which were retrieved from the sustainability metrics of IChemE.³⁵ The C123 project aims to reduce the dependence on conventional fossil fuels and the greenhouse gas emissions associated with 1-propanol production. Therefore, the energy input (in MJ/kg propanol) and the global warming burden (in kg CO₂ equiv/kg propanol) were selected as indicators. For the energy input, the energy contained in the feedstock and the energy need for all production steps were calculated and separately reported. The percentage of the energy obtained from fossil fuels was also indicated. Due to an increasing risk of water scarcity (e.g., in Northeast Germany) and decreasing water availability worldwide, water consumption (in tonnes/kg propanol) was also investigated.^{36,37} Finally, human health damage due to carcinogenics (in comparative toxic units for humans (CTUh)/kg propanol) was evaluated because acetaldehyde was identified as a carcinogenic emission in the CO₂-removal stage of the C123 technology.³⁸ According to the National Research Council (2008), adverse effects such as eye irritation have already been reported at 50 ppm, and it is expected that the emitted acetaldehyde concentration will be much higher.³⁹

3. RESULTS

3.1. Preliminary C123 Process Concept and Associated Mass Balances. Figure 2 illustrates the preliminary design of the C123 process for the three scenarios in a block flow diagram. The main difference between scenario BG and scenarios MG and AG is the position of chemical absorption with mono-ethanolamine. In scenario BG, this is the first step due to the excess CO₂ in the feed that must be removed (MEA-absorption 1) since biogas typically contains 50 mol % CO₂. In scenario MG and AG, only additional CO₂ created in the OCoM section is removed in the recycling loop before PSA (MEA-absorption 2). Appendix S4 shows the dataset for scenario BG and a mass balance check. The data for scenarios MG and AG is represented in Appendix S5. Additional information can be found in Appendix S6. The conversion of biogas into propanol is less efficient than its production from marginal gas or associated gas because 3.57 kg biogas is needed to obtain 1 kg propanol, while only 1.25 kg marginal gas or associated gas is required. After OCoM, the ethylene/CO/H₂ molar ratio amounts to 1:0.93:1.7 for all scenarios. This corresponds closely to the optimal 1:1:2 ratio for hydroformylation. The excess of H₂ can be used for the subsequent hydrogenation after PSA. In the product stream of the hydroformylation, 1 mol % of ethylene and 74.3 mol % methane are still detected. This high fraction of methane can be explained by the relatively low methane conversion in the OCoM section. Therefore, the recycling stream to OCoM is methane-rich (88 mol %). Hydrogenation does not convert all propanal into propanol because 0.4 mol % of propanal is still present in the product stream. In each scenario, the weight fraction of propanol amounts to 0.995, which is in line with the predetermined purity target. In Appendix S7, the detailed

Table 1. Comparison between Propanol Production via C123 Process and Conventional Propanol Production and between the C123 Processes among Themselves Based on Energy Input, Global Warming Burden, Water Consumption, and Human Health Damage as a Function of 1 kg Propanol^{a,b}

propanol production method		scenario BG	scenario MG	scenario AG	conventional propanol production
energy input (MJ/kg)	feedstock	47.7 (0)	52.9 (100)	52.9 (100)	16.5 (100)
	utilities/chemicals	55.2 (72.8)	29.8 (100)	29.3 (100)	62.5 (64.7)
	total	102.9 (39.0)	82.7 (100)	82.2 (100)	79.0 (72.0)
global warming burden (kg CO ₂ equiv/kg)		6.0	7.1	6.6/2.0*	3.1
water consumed (ton/kg)		0.05	0.03	0.03	0.16
human health damage (CTUh/kg) ($\times 10^{-10}$)		26.7	6.6	5.7/−46.8*	4.2

^aFor the energy input, the percentage of the energy obtained from fossil resources is also mentioned within parentheses. ^bNote: *first value does not consider avoiding flaring; second value takes avoidance of flaring into account.

composition after OCoM, hydroformylation, and hydrogenation can be consulted.

3.2. Results of Key Performance Indicators. Table 1 lists the results of the key performance indicators for the different C123 scenarios. Scenario BG requires more energy (102.9 MJ/kg propanol) than scenario MG (82.7 MJ/kg propanol) and AG (82.2 MJ/kg propanol) due to the high electricity demand for the biogas production (42% of total energy need), e.g., for stirring. For scenarios MG and AG, the energy requirement is high in the OCoM section due to the needed oxygen for the OCM reaction and in the post-treatment stage after hydroformylation due to the hydrogen production and the PSA. Scenario BG is the least dependent one on fossil energy (39.8 MJ/kg propanol versus 82.7 and 82.2 MJ/kg propanol in scenarios MG and AG, respectively). The global warming burden is the highest for scenario MG (7.1 kg CO₂ equiv/kg propanol). When including the avoided flaring emissions for scenario AG, 2.0 kg CO₂ equiv/kg propanol are obtained (for details, see Appendix S8). This scenario achieves the lowest global warming burden among all other C123 scenarios. Scenario BG requires 2 times more water due to biogas production (53% of total water demand for this scenario). Finally, the score for human health damage amounts to 26.7×10^{-10} CTUh for scenario BG which is 4 times higher than for scenario MG. However, a negative value (-46.8×10^{-10} CTUh) was found for scenario AG when the avoided gas flaring emissions are included. This last scenario seems the most promising when all indicators, except energy consumption from fossil fuels, are taken into consideration.

4. DISCUSSION

4.1. Comparison of C123 Scenarios Based on KPIs.

The results from Section 3.2 show that scenario AG performs better than the other C123 scenarios when considering energy requirement. The production and upgrading of biogas require a lot of energy for stirring and pumping and regeneration of the absorption solvent, respectively. The extraction of marginal gas and associated gas has a much smaller impact on the total energy consumption. In addition, the conversion of biogas into propanol is less efficient than the conversion of marginal gas and associated gas. Despite the higher energy need in this scenario (BG), the global warming burden is lower compared to scenario MG. This is due to the more significant emissions related to electricity production from fossil fuels for the latter, given the considered locations. In Germany, 61% of electricity is obtained from renewable sources, while in remote places in Russia, electricity is exclusively produced from natural gas via gas turbines. Scenario AG has a lower global warming burden than scenario MG due to the low contribution of the

associated gas extraction. The largest part of the CO₂ emissions, at least 99% both on a mass, energy, and economic basis, is related to oil production. Associated gas is only a byproduct accounting for 1% of the total emissions on a weight basis. In all C123 scenarios, oxygen (for OCoM), heat, and electricity production contribute the most to the global warming burden. Electricity is mainly needed for biogas production (only in scenario BG), compression after OCoM, and post-treatment after hydroformylation (compression of hydrogen gas, pumping, and pressure swing adsorption). Heat is needed to bring the feed stream of the OCoM section, the hydroformylation, and the hydrogenation to the desired temperature. Scenario BG has the highest score for human health damage. This can be explained by the emission of acetaldehyde during the regeneration of the solvent from the chemical absorption and by the oxygen, electricity, and maize silage production. Concentrations around 2000 ppm were found for scenario BG (5.79×10^{-3} kg emitted/kg propanol) in the gas released from chemical absorption, while the threshold value is set at 25 ppm.⁴⁰ More CO₂ must be removed in scenario BG compared to the other scenarios. The value for human health damage of scenario MG and AG is mainly caused by the emission of acetaldehyde in the CO₂ removal stage, the oxygen production for OCoM, and the heat production for the post-treatment of the hydroformylation. The environmental performance of the C123 scenarios has not been compared to the conventional propanol production in this paper (see Section 4.3 for more details).

4.2. Process Challenges. In the C123 project, some challenges have not yet been solved. On the one hand, some pretreatment steps, e.g., the removal of H₂S, are not included in the preliminary process concept. On the other hand, the C123 process can be improved by replacing some production steps or by changing the production method of some chemicals and utilities. These items will be discussed in the following paragraphs. However, these potential changes are not expected to affect the comparison of the C123 scenarios from the environmental point of view.

4.2.1. Feedstock Pretreatment. Biogas usually contains levels of H₂S between 100 and 3000 ppm after co-digestion of manure and energy crops.¹⁴ This compound must be removed to avoid corrosion of the installations, catalyst deactivation, and human health effects.^{14,41} Additionally, H₂S can be used to produce sulfur or sulfuric acid to prevent the emission of this toxic compound.⁴² Biological treatments with sulfur-oxidizing bacteria are often applied for this desulfurization.¹⁴ Biogas can also contain siloxanes and sulfur compounds other than H₂S such as COS and CS₂.⁴³ The highest levels of siloxanes were found in biogas from wastewater treatment facilities and

landfill gas.⁴³ Inorganic SiO₂ can be formed from this contaminant in gas burners causing clogging.⁴³ These compounds can be effectively removed via adsorption (e.g., with activated carbon) and chemical absorption.^{44,45} Marginal gas and associated gas can also contain H₂S depending on the location. For instance, 11 360 ppm H₂S is detected on average in the Bakken formation (North Dakota/USA).⁴⁶ H₂S is usually converted into sulfur by a Claus reaction in the oil and gas industry, but this process would not be profitable in this case (daily production of sulfur is too low).⁴⁷ The removal of H₂S with scavengers such as ZnO and ZnCO₃ or the liquid redox process in combination with the conversion of sulfur into sulfuric acid is a more suitable option.^{47,48} However, no major changes are expected for the KPI results when taking into account H₂S removal. In contrast, many costs can be saved in the long term by the longer shelf life of the equipment.

In marginal gas and associated gas, natural gas liquids such as ethane, propane, butane, etc. are present. In Appendix S9, an example of the composition for both feedstocks is given. For example, in the Bakken formation (North Dakota), 66% of the feed consists of natural gas liquids on a weight basis.⁴⁶ The behavior of these higher hydrocarbons in the OCoM section is not fully understood yet. On the one hand, if these compounds are not recovered before the OCoM section, impurities such as butanol and pentanol may be formed in the C123 process reducing the propanol purity. On the other hand, these may have been combusted by the OCoM reactions. Two strategies need to be further investigated. First, propane and butane can be removed before the OCoM section via a cryogenic separator and a de-ethanizer. Second, propanol can be processed downstream when impurities are created. Ethane must not necessarily be removed because this compound is even more reactive than methane under oxygenated conditions in OCoM.⁶

4.2.2. Change of Production Steps. The regeneration of the solvent in the mono-ethanolamine absorption stage requires a lot of heat. Therefore, it is useful to investigate alternatives such as membrane technologies. No heat is needed for the removal of CO₂ via membranes and they are easier to operate. A lower methane recovery and a higher electricity need are disadvantages of this technology.³⁸ Next, the OCM reaction can be modeled as a plug flow reactor. Currently, a stoichiometric reactor was considered due to an incomplete kinetic model. According to Farrell et al. (2016),⁴⁹ the C2 selectivity, methane conversion, and C2 yield could be maximized to 57, 29, and 16%, respectively. Using membrane reactors instead of the conventional packed bed reactors could also rise the C2 selectivity and yield.⁵⁰ However, the improved performance of membrane reactors has not yet been proven on an industrial scale. Furthermore, the pressure in the hydroformylation reactor currently amounts to 20 bar. This value could potentially be reduced to 10 bar because it is intended to use a heterogeneous catalyst for the hydroformylation reactor and operate it as a gas-phase reactor. Consequently, the electricity need for compression would also decrease. However, as the catalyst performance is not stable at high temperatures, the reaction temperature should not exceed 100 °C. Therefore, operating the reactor at 20 bar may result in condensation of some of the products on the catalyst, which may adversely impact the catalyst performance. Finally, a small amount of the recycled gas is purged to avoid a build-up of gases. Purge streams are necessary to ensure there is little to no accumulation in the system from the recycle stream feeding

back into the fresh feed, preventing dilution of reactants due to waste chemicals. The purge can be sent to a flare system. The flare gas mainly contains CH₄ (88 mol %) and CO₂ (6 mol %). Flares burn flammable gases that would otherwise be released into the atmosphere. It also wastes a lot of valuable energy resources that could be used. Flaring seems a better option than gas purging (conversion of CH₄ into CO₂ via combustion) because CH₄ has a higher global warming potential than CO₂. However, when the combustion is incomplete, harmful components for humans such as CO, black carbon particles, etc. can be formed.

4.2.3. Production of Utilities and Auxiliary Chemicals. CO and H₂ are produced in the OCoM section together with ethylene. Therefore, only a small amount of H₂ must be added to the hydrogenation. From an environmental point of view, this is a great advantage of the C123 process since H₂ is mostly produced from fossil resources nowadays and its energy consumption is high.⁵¹ However, the OCoM reactions can be tuned slightly in favor of hydrogen production so that no additional hydrogen needs to be produced. O₂ must still be fed to the OCM reactor. This gas can be produced via cryogenic air separation or water electrolysis. In the latter case, an excess of hydrogen is created, which cannot be transported in remote areas. Therefore, air separation is preferred to electrolysis. The impact of the oxygen production can be lowered by combining this with renewable electricity production e.g., from wind power. Nevertheless, this approach is only realistic for scenario BG at this moment due to the challenging integration of renewable electricity production in remote areas (scenario MG and AG), for example, due to pricing and unfavorable climatic conditions.⁵² Pressure swing adsorption of air to produce enriched air (95% oxygen in stream) is another possibility. However, the effect of adding N₂ with enriched air to the C123 process must be studied. A substantial amount of heat is needed for the conversion of the feedstocks into propanol (e.g., for the regeneration of mono-ethanolamine in the chemical absorption stage). Heat integration can further reduce the heat demand. For example, heat from the exothermic OCM reaction in the OCoM section and the exothermic hydroformylation and hydrogenation can be recovered. Steam with an energy content between 25 and 30 MJ per kg propanol can be produced via a steam boiler with an efficiency of 70%. Afterward, the steam can be sent to the chemical absorber, the distillation columns, etc. Heat integration could hence lower the energy consumption, the global warming burden, and the human health damage in scenario BG by 26.8, 24.0, and 41.0%, respectively. In scenario MG, the decrease in the indicators is less pronounced (14.5, 11.7, and 30.0%). However, this heat integration must still be performed in more detail to substantiate these numbers. Finally, when all electricity comes from wind power, the energy consumption, global warming burden, and human health damage by carcinogenics may be reduced by 17.6, 38.0, and 2.6%, respectively, in scenario BG and 8.6, 42.2, and 0.8% in scenario MG.

4.3. Comparison C123 Scenarios with Conventional Propanol Production. The comparison between the C123 scenarios and the conventional propanol production is currently not straightforward. First, the C123 process has not yet the same maturity level, e.g., no detailed heat integration has been applied in the preliminary process concept yet. Second, the production scale of the conventional propanol production in Europe can be 10 times higher than the targeted production scale for the C123 process (10 ktonnes per year)

depending on the market demand.⁵³ Further research on the C123 process is needed to increase its maturity level and allow for a fair comparison between conventional propanol production and the C123 process concept.

Nevertheless, when the C123 scenarios are compared to conventional propanol production (reference) based on the KPIs (see Table 1), the former does not perform better for all indicators. For example, the global warming burden of scenario BG and MG is higher than that for the reference. In contrast, water consumption is 3–5 times lower in all C123 scenarios. For scenario AG, when the avoided gas flaring emissions are taken into account, all indicators are better than that for the conventional propanol production, with the exception of the energy need. Using associated gas for propanol production would therefore be a good alternative for conventional propanol production. At the same time, gas flaring could be reduced.

5. CONCLUSIONS

In this paper, a preliminary modular scale process concept was proposed to produce propanol from different methane rich feedstocks (biogas, marginal gas, and associated gas). Simulations in Aspen Plus were performed to generate the necessary data (mass and energy flows, utility data, etc.). Subsequently, KPIs (e.g., the energy requirement and global warming burden) were selected to evaluate the new design. The results showed that the energy consumption was the highest for scenario BG. However, the propanol production from biogas was the least dependent on fossil fuels for energy consumption. The global warming burden was the highest for scenario MG. Scenario AG could be the best alternative for the conventional propanol production due to its lower global warming burden, water consumption, and impact of carcinogenic substances on human health compared to scenario BG and MG. Scenario BG had the highest score for human health damage due to the biogas upgrade (chemical absorption). Future research could also consider the pretreatment of the feedstocks. For example, biogas, marginal gas, and associated gas can contain H₂S. This compound should be removed to avoid corrosion of installations and human health effects. Including renewable electricity production and applying heat integration in the design can further reduce the global warming burden and the heat demand, respectively.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.2c00808>.

Additional information for Aspen simulation and data collection for calculation of key performance indicators (PDF)

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■ ABBREVIATIONS

Ac.	acetaldehyde
AG	associated gas
BG	biogas
CHP	combined heat and power
CO ₂ -ODH	CO ₂ assisted oxidative dehydrogenation
HF	hydroformylation
HG	hydrogenation
ICChemE	Institute of Chemical Engineers
KPIs	key performance indicators
MEA	mono-ethanolamine absorption
MG	marginal gas
OCM	oxidative coupling of methane
OCoM	oxidative conversion of methane
PBC	post bed cracking
PSA	pressure swing adsorption

■ REFERENCES

(1) Propanol Market by Type (N-Propanol, Isopropanol), Application (Direct Solvent, Chemical Intermediate, Pharmaceutical),

- Household & Personal Care), and Region (North America, APAC, Europe, Middle East & Africa, and South America) - Global Forecast to 2023. <https://www.marketsandmarkets.com/Market-Reports/isopropyl-alcohol-and-n-propanol-market-1113.html> (accessed 2022-01-04).
- (2) Walther, T.; François, J. M. Microbial production of propanol. *Biotechnol. Adv.* **2016**, *34*, 984–996.
- (3) Propanols. https://onlinelibrary.wiley.com/doi/abs/10.1002/14356007.a22_173.pub2 (accessed 2022-05-08).
- (4) Nanda, S.; Rana, R.; Vo, D. V. N.; Sarangi, P. K.; Nguyen, T. D.; Dalai, A. K.; Kozinski, J. A. In *Biorefinery of Alternative Resources: Targeting Green Fuels and Platform Chemicals*. 1th ed.; Springer, 2020.
- (5) C123 – Methane oxidative conversion and hydroformylation to propylene. <https://www.sintef.no/projectweb/c123/> (accessed 2022-01-04).
- (6) Fonseca, A. A.; Heyn, R. H.; Frøseth, M.; Thybaut, J. W.; Poissonnier, J.; Meiswinkel, A.; Zander, H. J.; Canivet, J. A Disruptive Innovation for Upgrading Methane to C3 Commodity Chemicals: Technical challenges faced by the C123 European consortium. *Johnson Matthey Technol. Rev.* **2021**, *65*, 311–329.
- (7) Franke, R.; Selent, D.; Börner, A. Applied hydroformylation. *Chem. Rev.* **2012**, *112*, 5675–5732.
- (8) Rodriguez, B. A.; Tenn, W. J., III Direct formation of propanol from a dilute ethylene feed via reductive-hydroformylation using homogeneous rhodium catalysts at low feed pressures. *Appl. Catal., A* **2012**, *421–422*, 161–163.
- (9) Tang, P.; Zhu, Q.; Wu, Z.; Ma, D. Methane activation: the past and future. *Energy Environ. Sci.* **2014**, *7*, 2580–2591.
- (10) Sun, L.; Wang, Y.; Guan, N.; Li, L. Methane activation and utilization: Current status and future challenges. *Energy Technol.* **2020**, *8*, No. 1900826.
- (11) Onel, O.; Niziolek, A. M.; Floudas, C. A. Optimal production of light olefins from natural gas via the methanol intermediate. *Ind. Eng. Chem. Res.* **2016**, *55*, 3043–3063.
- (12) Keller, G. E.; Bhasin, M. M. Synthesis of ethylene via oxidative coupling of methane: I. Determination of active catalysts. *J. Catal.* **1982**, *73*, 9–19.
- (13) Kiatkittipong, W.; Tagawa, T.; Goto, S.; Assabumrungrat, S.; Silpasup, K.; Praserttham, P. Comparative study of oxidative coupling of methane modeling in various types of reactor. *Chem. Eng. J.* **2005**, *115*, 63–71.
- (14) Weiland, P. Biogas production: current state and perspectives. *Appl. Microbiol. Biotechnol.* **2010**, *85*, 849–860.
- (15) Kapoor, R.; Ghosh, P.; Tyagi, B.; Vijay, V. K.; Vijay, V.; Thakur, I. S.; Kamyab, H.; Nguyen, D. D.; Kumar, A. Advances in biogas valorization and utilization systems: A comprehensive review. *J. Cleaner Prod.* **2020**, *273*, No. 123052.
- (16) Ministry of Petroleum Resources. Guidelines for farmount and operation of marginal fields. <http://africaoilgasreport.com/wp-content/uploads/2013/12/GUIDANCENOTES-FOR-NIGERIAN-2013-MARGINAL-FIELDS-BID-ROUND.pdf> (accessed 2022-01-04).
- (17) Soltanieh, M.; Zohrabian, A.; Gholipour, M. J.; Kalnay, E. A review of global gas flaring and venting and impact on the environment: Case study of Iran. *Int. J. Greenhouse Gas Control.* **2016**, *49*, 488–509.
- (18) Fawole, O. G.; Cai, X. M.; MacKenzie, A. R. Gas flaring and resultant air pollution: A review focusing on black carbon. *Environ. Pollut.* **2016**, *216*, 182–197.
- (19) Scarlat, N.; Dallemand, J. F.; Fahl, F. Biogas: Developments and perspectives in Europe. *Renewable Energy* **2018**, *129*, 457–472.
- (20) Role of stranded gas in increasing global gas supplies: U.S. Geological Survey Open-File Report 2013–1044. <http://pubs.usgs.gov/of/2013/1044> (accessed 2021-01-15).
- (21) Global Gas Flaring Reduction Partnership (GGFR). <https://www.worldbank.org/en/programs/gasflaringreduction#7> (accessed 2020-08-30).
- (22) Elvidge, C. D.; Ziskin, D.; Baugh, K. E.; Tuttle, B. T.; Ghosh, T.; Pack, D. W.; Erwin, E. H.; Zhizhin, M. A fifteen year record of global natural gas flaring derived from satellite data. *Energies* **2009**, *2*, 595–622.
- (23) Khalili-Garankani, A.; Iravaninia, M.; Nezhadfar, M. A review on the potentials of flare gas recovery applications in Iran. *J. Cleaner Prod.* **2021**, *279*, No. 123345.
- (24) Lansche, J.; Müller, J. Life cycle assessment of energy generation of biogas fed combined heat and power plants: Environmental impact of different agricultural substrates. *Eng. Life Sci.* **2012**, *12*, 313–320.
- (25) Boulamanti, A. K.; Maglio, S. D.; Giuntoli, J.; Agostini, A. Influence of different practices on biogas sustainability. *Biomass Bioenergy* **2013**, *53*, 149–161.
- (26) Bharathiraja, B.; Sudharsana, T.; Jayamuthunagai, J.; Praveenkumar, R.; Chozhavendhan, S.; Iyyappan, J. Biogas production—A review on composition, fuel properties, feed stock and principles of anaerobic digestion. *Renewable Sustainable Energy Rev.* **2018**, *90*, 570–582.
- (27) Siradze, S.; Poissonnier, J.; Frøseth, M.; Stensrød, R. E.; Heyn, R. H.; Thybaut, J. W. Kinetics Assessment of the Homogeneously Catalyzed Hydroformylation of Ethylene on an Rh Catalyst. *Ind. Eng. Chem. Res.* **2021**, *60*, 16665–16681.
- (28) Adhikari, B.; Orme, C. J.; Klaehn, J. R.; Stewart, F. F. Technoeconomic analysis of oxygen-nitrogen separation for oxygen enrichment using membranes. *Sep. Purif. Technol.* **2021**, *268*, No. 118703.
- (29) Thybaut, J. W.; Marin, G. B.; Mirodatos, C.; Schuurman, Y.; van Veen, A. C.; Sadykov, V. A.; Pennemann, H.; Bellinghausen, R.; Mleczo, L. A novel technology for natural gas conversion by means of integrated oxidative coupling and dry reforming of methane. *Chem. Ing. Tech.* **2014**, *86*, 1855–1870.
- (30) OXO PROCESS: Applications, Catalytic Activity and Recycling. https://hero.epa.gov/hero/index.cfm/reference/details/reference_id/8697875 (accessed 2022-03-08).
- (31) Fache, E.; Santini, C.; Senocq, F.; Basset, J. M. Homogeneous catalysis in water Part III. The catalytic hydrogenation of propionaldehyde with (RuCl₂L₂)₂, RuHClL₃, RuH(OAc)L₃, RuH₂L₄, RuHIL₃, RuCl₂(CO)₂L₂ and [Ru(OAc)(CO)₂L]₂, (L = P(C₆H₄-mSO₃Na)₃-3H₂O): A kinetic investigation of the salt effect in water. *J. Mol. Catal.* **1992**, *72*, 337–350.
- (32) BASF. N-Propanol. BASF-CPI_1018e_n-Propanol%20(1).pdf (accessed 2021-08-30).
- (33) Cooling Towers. Continuing Education and Development, Inc. <https://www.cedengineering.com/userfiles/Cooling%20Towers%20R1.pdf> (accessed 2022-01-04).
- (34) Skone, T. J.; Littlefield, J.; Marriott, J.; Cooney, G.; Jamieson, M.; Jones, C.; Demetron, L.; Mutchek, M.; Chungyan, S.; Curtright, A. E.; Schivley, G.; Yost, A.; Krynock, M. *Life Cycle Analysis of Natural Gas Extraction and Power Generation*, (No. DOE/NETL-2015/1714), U.S. Department of Energy, Office of Scientific and Technical Information: United States; 2016. DOI: DOI: 10.2172/1480993.
- (35) IChemE. The sustainability metrics. <https://www.greenbiz.com/sites/default/files/document/O16F26202.pdf> (accessed 2022-01-04).
- (36) Lischeid, G.; Nathkin, M. The Potential of Land-Use Change to Mitigate Water Scarcity in Northeast Germany – a Review. *Journal of the Geographical Society of Berlin* **2011**, *142* (1-2), 97–113.
- (37) Orłowski, B.; Hoekstra, A. Y.; Gudmundsson, L.; Seneviratne, S. I. Today's virtual water consumption and trade under future water scarcity. *Environ. Res. Lett.* **2014**, *9*, No. 074007.
- (38) Collet, P.; Flottes, E.; Favre, A.; Raynal, L.; Pierre, H.; Capela, S.; Peregrina, C. Techno-economic and Life Cycle Assessment of methane production via biogas upgrading and power to gas technology. *Appl. Energy* **2017**, *192*, 282–295.
- (39) National Research Council. *Emergency and Continuous Exposure Guidance Levels for Selected Submarine Contaminants*, 1st ed.; National Academies Press, 2008; Vol. 2.
- (40) New Jersey Department of Health. Hazardous substance fact sheet. <https://www.nj.gov/health/eoh/rtkweb/documents/fs/0001.pdf> (accessed 2022-01-04).

- (41) Agbroko, O. W.; Piler, K.; Benson, T. J. A comprehensive review of H₂S scavenger technologies from oil and gas streams. *ChemBioEng Rev.* **2017**, *4*, 339–359.
- (42) King, M.; Moats, M.; Davenport, W. G. Sulfuric acid manufacture: analysis, control and optimization. In *Newnes*, Elsevier, 2013.
- (43) Dannesboe, C.; Hansen, J. B.; Johannsen, I. Removal of sulfur contaminants from biogas to enable direct catalytic methanation. *Biomass Convers. Biorefin.* **2021**, *11*, 1823–1834.
- (44) Shen, M.; Zhang, Y.; Hu, D.; Fan, J.; Zeng, G. A review on removal of siloxanes from biogas: with a special focus on volatile methylsiloxanes. *Environ. Sci. Pollut. Res.* **2018**, *25*, 30847–30862.
- (45) Bak, C. U.; Lim, C. J.; Lee, J. G.; Kim, Y. D.; Kim, W. S. Removal of sulfur compounds and siloxanes by physical and chemical sorption. *Sep. Purif. Technol.* **2019**, *209*, 542–549.
- (46) Gaspar, J.; Davis, D.; Camacho, C.; Alvarez, P. J. Biogenic versus thermogenic H₂S source determination in Bakken wells: considerations for biocide application. *Environ. Sci. Technol. Lett.* **2016**, *3*, 127–132.
- (47) Linde. Sulfur process technology. https://www.linde-engineering.com/en/images/Sulfur%20Process%20Technology_tcm19-111155.pdf (accessed 2021-09-20).
- (48) Aмоса, M. K.; Mohammed, I. A.; Yaro, S. A. Sulphide scavengers in oil and gas industry—a review. *Nafta* **2010**, *6*, 18598. <https://hrcak.srce.hr/49124>.
- (49) Farrell, B. L.; Igenegbai, V. O.; Lincic, S. A viewpoint on direct methane conversion to ethane and ethylene using oxidative coupling on solid catalysts. *ACS Catal.* **2016**, *6*, 4340–4346.
- (50) Kao, Y. K.; Lei, L.; Lin, Y. S. A comparative simulation study on oxidative coupling of methane in fixed-bed and membrane reactors. *Ind. Eng. Chem Res.* **1997**, *36*, 3583–3593.
- (51) Wang, M.; Wang, Z.; Gong, X.; Guo, Z. The intensification technologies to water electrolysis for hydrogen production—A review. *J. Renewable Sustainable Energy Rev.* **2014**, *29*, 573–588.e.
- (52) Phuangpornpitak, N.; Tia, S. Opportunities and challenges of integrating renewable energy in smart grid system. *Energy Procedia* **2013**, *34*, 282–290.
- (53) Dubois, J. L.; Nieder-Heitmann, M.; Letoffet, A.; Vleeming, H. C123—Methane oxidative conversion and hydroformylation to propylene: Raw material sources and market analyses of the modular route C3 products. *Johnson Matthey Technol. Rev.* **2021**, *65*, 301–310.