

### **Ultra-Low Carbon Methanol Applications**

### **Acetic Acid and Derivatives**

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Application of blue methanol in the production of acetic acid and derivative resins results in significant reductions of product CO<sub>2</sub>e.

### 27.1% for Acidic Acid and 12.5% for Vinyl Acetate Monomer

### Fundamental

Acetic acid (CH<sub>3</sub>COOH), also known as ethanoic acid, is a colorless organic compound. The diluted form of acetic acid is called vinegar, which is the most common chemical substance available in the market. It kills microbes and fungus, it is commonly used for general disinfecting and combating mildew and is found in several conventional cleaning products, such as mold and mildew cleaners, floor cleaners, window cleaners, surface cleaners, cleaning and dusting sprays, and roof cleaners, in the form of vinegar or as an ingredient by itself.

Industrially acetic acid is used in the processing of cellulose acetate, vinyl acetate, metal acetates, and volatile organic esters (such as butyl and ethyl acetates), as well as widely used as solvents for paints, resins, and lacquers. Acetic acid is also used as a solvent in polyester fiber production and in the manufacturing of synthetic fibers and resins. Apart from these, the acid is popularly used in the making of perfumes, manufacturing of dyes and inks, and rubber and plastic. Acetic acid has various uses in the healthcare and pharmaceutical including antiseptic against streptococci, enterococci, pseudomonas, staphylococci and others. It is also used for the treatment of infections and cervical cancer screening. Further, it has wide usage as an agent to lyse red blood cells before white blood cells are examined.

### Commercial

As per the report published by The Brainy Insights, the global acetic acid market is expected to grow from USD 10.25 billion in 2020 to USD 18.27 billion by 2028, at a CAGR of 7.85% during the forecast period 2021-2028.<sup>1</sup>

The acetic acid market is segmented on the basis of industry applications, such as vinyl acetate monomer, purified terephthalic acid, acetic anhydride, and ester solvents (ethyl acetate & butyl acetate).

In terms of volume, the Vinyl Acetate Monomer (VAM)<sup>2</sup> consumes a majority of the acetic acid produced worldwide in 2020. This is attributed to the widespread demand for the product from rapidly growing industrial and cosmetics manufacturing sectors across the globe. VAM is a colorless liquid that possesses a pungent odor which is preferably stored in reconditioned steel drums and is typically transported in tank trucks and bulk vessels. Rising demand by VAM producers worldwide is projected to remain a key driving factor for the market growth. VAM is traditionally produced by reacting acetic acid with ethylene and oxygen along with a palladium

<sup>&</sup>lt;sup>1</sup> Acetic Acid Market Analysis, Share, Growth, Trends, and Forecast 2021 to 2028, The Brainy Insights (2021)

<sup>&</sup>lt;sup>2</sup> Vinyl acetate monomer (VAM) is a significant intermediate used in the production of a wide range of resins and polymers for paints & coatings, adhesives, glues & sealants, elastomers, textile finishes, paper coatings, binders, films, and a myriad of other industrial and consumer applications.



catalyst which is typically conducted in the gas phase. A large portion of VAM produced is used in paint and coating formulations, wherein VAM is polymerized to form polyvinyl acetate or other polymers which are key ingredients in the paints industry.

The major use of VAM is in producing polyvinyl alcohol and polyvinyl acetate (PVA)<sup>3</sup>, which cumulatively accounts for more than 80% of its utilization on a global level. PVA is majorly used in water-soluble packaging, coatings, adhesives, and textile warp sizing among others. Furthermore, polyvinyl acetate is predominantly utilized in textile treatment, adhesives, paints, and paper coatings worldwide.

Purified Terephthalic Acid (PTA) is majorly utilized to formulate polyester coating resins used to produce automotive, appliances, coil coatings, general metal applications, and more. Eastman Corporation is one of the largest producers of PTA worldwide. It is also used for applications such as fiberglass reinforced plastics in unsaturated polyesters. Key attributes of PTA include good stain and chemical resistance, excellent weathering, the ideal temperature range for glass transition, and good flexibility balance among others.

Acetic acid in its liquid form is hydrophilic which makes the substance apt for a wide array of applications. Other applications include the formulation of acetate esters, acetic anhydride, and more. The usage of acetate ester is increasing in printing ink applications as well as in adhesives and sealant space, wherein it is majorly used as a solvent. However, acetic anhydride is largely utilized for oil spill cleanup, synthesizing aspirin, acetylation of salicylic acid, wood preservation applications, and more.

The substance is categorized as hazardous to human health by harmonized classification and labeling of the European Chemicals Agency (ECHA) as it causes severe eye damage, skin burns, and more. However, according to the U.S. Environmental Protection Agency (EPA), the substance is categorized as safe to use as a food additive under permissible limits as cited by the agency in accordance with 21 CFR 184.1 regarding substances added directly to human food. The chemical finds application in the food industry as a condiment and acidity regulator.

Asia Pacific dominated the market and accounted for 62.0% of the global revenue in 2020. This is attributed to the increasing penetration of polymer formulators in the region. Acetic acid is a key substance used across an array of industries across China, Japan, and India. The region is witnessing high construction activities due to increased mergers and acquisitions. Since the past decade, the region has been home to a number of multinational companies from all business domains and has reflected multiple manufacturing expansion projects.

The European region reflected significant progress in the food & beverage industry in 2020, with a turnover generation of USD 1,194 billion. It is recognized as the largest manufacturing industry in the European Union employing over 4.57 million people. Increasing requirements for packaged food across countries such as Germany, France, Italy, and the U.K., led to increasing demand for acetic acid in the region significantly. Moreover, the growing food industry also led to high demand for packaging which is anticipated to fuel the demand for acetic acid.

<sup>&</sup>lt;sup>3</sup> Poly(vinyl alcohol) (PVOH, PVA, or PVAI) is a water-soluble synthetic polymer. It has the idealized formula [CH<sub>2</sub>CH(OH). It is used in papermaking, textile warp sizing, as a thickener and emulsion stabilizer in PVAc adhesive formulations, in a variety of coatings, and 3D printing. It is colorless (white) and odorless. It is commonly supplied as beads or as solutions in water. Without an externally added crosslinking agent, PVA solution can be gelled through repeated freezing-thawing, yielding highly strong, ultrapure, biocompatible hydrogels which have been used for a variety of applications such as vascular stents, cartilages, contact lenses, etc.



The market has the presence of multiple key established players globally which are constantly focusing on enhancing their product offerings in order to cater to broader market space.

British Petroleum Chemicals and Celanese Corporation are the largest producers of the chemical globally.

Celanese Corporation and British Petroleum are the two largest manufacturers of the chemical worldwide. Major players in the global acetic acid market are Mitsubishi Chemical Corporation, Wacker Chemie, GNFC Limited, Saudi International Petrochemicals, DuPont, Eastman Chemical Company, Daicel Corporation, Jiangsu Sopo (Group), and LyondellBasell among others.

In August 2018, BP and Eastman Chemical Company announced that both companies had signed an agreement, in which BP will take over sales and marketing of the US acetic acid made by Eastman Chemical.

In October 2019, BP signed a memorandum of understanding (MoU) with China's Zhejiang Petroleum and Chemical Corporation (ZPCC) to establish a joint venture. Under the joint venture, the companies are planning to open an acetic acid plant in Zhoushan, China, with a production capacity of one million tonnes per annum (Mtpa).

A high level of market competition ensures competitive product development and quality coupled with competitive pricing and product placement. Some of the prominent players in the acetic acid market include:

Eastman Chemical Company <u>https://www.eastman.com/Products/Pages/ProductList.aspx?categoryName=Acids</u> British Petroleum <u>https://www.argusmedia.com/en/news/2118871-bp-sells-to-ineos-65mn-tyr-of-petchem-output-in-asia</u>

LyondellBasell <u>https://www.lyondellbasell.com/en/products-technology/chemicals/chemical-type/acetyls/</u> Celanese Corporation <u>https://www.celanese.com/en/intermediate-chemistry/products/Acetic-Acid/Grades</u> Gujarat Narmada Valley Fertilizers & Chemicals <u>https://www.indiamart.com/gujarat-narmada-valley-fertilizers-chemicals-limited-bharuch/</u>

Helm AG https://www.helmag.com/business-lines/chemicals/products

Pentoky Organy <a href="http://www.pentokey.com/">http://www.pentokey.com/</a>

Dow Chemicals <u>https://www.dow.com/en-us/pdp.glacial-acrylic-acid-gaa.133200z.html</u> Indian Oil Corporation <u>https://iocl.com/</u>

## Production

Methanol carbonylation, acetaldehyde oxidation, ethylene oxidation, oxidative fermentation, and anaerobic fermentation are among the widely practiced production process for acetic acid.

Acetic acid is produced naturally when excreted by certain bacteria such as Acetobacter genus and Clostridium acetobutylicum. These bacteria are found in foodstuffs, water, and soil. Acetic acid is also produced naturally when fruits and other foods spoil. It is also commercially produced from bacterial fermentation that accounts for roughly 10% of the overall production worldwide and is anticipated to grow as it remains crucial for the production of vinegar since it is explicitly mentioned by many food purity laws.

Synthetic production routes accounted for 81.6% in 2020 of production with 75% made by the carbonylation of methanol.



The first process for carbonylation of methanol in homogenous phase was commercialized by the BASF in 1960. This process used cobalt as catalyst and iodide as co-catalyst to produce acetic acid to perform carbonylation reaction at high temperature (250°C) and pressure (680 bar) required. In 1973 process based upon use of rhodium catalyst and iodide co-catalyst, named Monsanto process, commercialized. This process operated at relatively mild conditions (150–200°C and 30–60 bar of pressure).<sup>4 5</sup> In the purification stage the Monsanto process due to low CO partial pressure, rhodium catalyst participated, therefore to establish high catalyst stability and high methane formations, high water concentration in reactor composition required. These restrictions imposed more distillation columns in the later purification stage, to remove considerable amounts of water in product stream [6]. To overcome Monsanto limitation and significant price difference between iridium and rhodium, in 1996 BP Chemicals developed Cativa process based upon iridium catalyst and iodide co-catalyst.

Carbonylation process is a most employed commercial route for synthesis of acetic acid, also known as Monsanto process. Methanol and carbon monoxide are reacted in liquid phase in the presence of rhodium (Rh)-based catalyst at 150–200°C temperature and 30–50 bar pressure to produce acetic acid with 95% selectivity and 5% side products such as formic acid and formaldehyde. Small quantities of hydrogen iodide are used as an alkali promoter in this process.

 $CH_3OH + CO \rightarrow CH_3COOH \Delta H = -137.6kJ/mol$ 

The reaction proceeds in liquid phase with methyl acetate as solvent using homogeneous catalyst. Controlled amount of water is required for the reaction, which is generated in situ by reaction of methanol with hydrogen



Figure 1 - Simplified process flowsheet for acetic acid plant

iodide. The rate of reaction in the Monsanto process depends on the concentration of water. CO<sub>2</sub>, H<sub>2</sub> and methanol are obtained as byproducts in the reaction. The generated methanol in the reaction is recycled. The process has evolved with time and different strategies have been adopted to separate pure acetic acid from a mixture of water and by-products. This process was modified by BP chemicals replacing rhodium-based catalyst with iridium (Ir) catalyst known as Cavita process. The choice of Ir as a coordination

metal is relatively more economic process than rhodium. The use of an iridium catalyst improves the overall rate of reaction. It has been shown that increased pressure and methyl iodide concentration reduced CO<sub>2</sub> formation.<sup>6</sup> An issue that must be addressed in facility design is the source of CO. The most practical solution is to co-locate

<sup>&</sup>lt;sup>4</sup> Sunley GJ, Watson DJ. High productivity methanol carbonylation catalysis using iridium The Cativa™ process for the manufacture of acetic acid. Catal Today 2000; 58: 293–307.

<sup>&</sup>lt;sup>5</sup> Thomas CM, Suss-Fink G. Ligand effects in the rhodium-catalyzed carbonylation of methanol. Coord Chem Rev 2003;243:125–142.

<sup>&</sup>lt;sup>6</sup> M. Kazemeinia, V. Hosseinpour. "Minimizing CO2 formation in Ir-catalyzed methanol carbonylation process" Procedia Engineering 42 (2012) 1179 – 1188 (2012)



with a facility that can supply over-the-fence CO. If the project needs to produce its own CO either a SMR calibrated for minimum  $H_2$  production:

 $CH_4 + H_2O (+heat) \rightarrow CO + 3H_2 \Delta + 206 \text{ kJ/mol}$ 

or a dry methane reformer if a source of CO<sub>2</sub> is available:

 $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H + 247 \text{ kJ/mol}$ 

In either of the options the CO will carry with it the CO<sub>2</sub>e associated with its production.

Acetic acid can also be produced from CO<sub>2</sub>, but state of the art routes have encountered difficulties, especially in reaction selectivity and activity. The reaction can be efficiently catalyzed by Ru–Rh bimetallic catalyst using imidazole as the ligand and Lil as the promoter in 1,3-dimethyl-2-imidazolidinone (DMI) solvent. It is confirmed that methanol is hydrocarboxylated into acetic acid by CO<sub>2</sub> and H<sub>2</sub>, however, this is not commercial. The reaction is:

CH<sub>3</sub>OH + CO<sub>2</sub> + H<sub>2</sub> → CH<sub>3</sub>COOH + H<sub>2</sub>O 
$$\Delta$$
H = -137.6kJ/mol

The growing use of acetic acid in manufacturing of various products such as vinyl acetate monomers (VAM) and purified terephthalate acid is projected to boost the market size during the assessment period. Acetic acid is widely used to produce VAM, which is in turn used to manufacture various resins and polymers for adhesives, films, paints, coatings, textiles and other end-user products. Industry statistics estimate that approximately 80% of global VAM production is used to manufacture PVA and PVOH, with most of the remaining volume being used in the production of PVB, EVA copolymers and EVOH resins.<sup>7</sup> <u>Acetic acid is about 70 wt% in the end product</u>.<sup>8</sup>

Three main routes for VAM (C<sub>4</sub>H<sub>4</sub>O<sub>2</sub>) manufacturing are:

1. Acetic acid and acetylene - The process is based on the reaction:

 $\text{HC=CH} + \text{CH3COOH} \rightarrow \text{H2C=CH-O-(CO)CH3} \quad \Delta\text{H} \text{-118 KJ/mol}$ 

The operating conditions are gas phase at 170-250 °C and  $Zn(OAc)_2$  catalyst impregnated on charcoal. Per-pass acetylene conversion is 60-70% with a selectivity of 93% acetylene and 99% acetic acid. High acetylene cost and safety problems make this process less competitive.

2. Acetaldehyde and acetic anhydride - The process takes place in two stages. Firstly acetaldehyde and acetic anhydride form ethylidene diacetate in liquid phase at 120–140 °C with FeCl3 as a catalyst:

 $CH_3CHO + (CH_3CO)_2 O \rightarrow CH_3CH(OCOCH_3)_2$ 

In the second step the intermediate decomposes at 120 °C with acid catalyst:

$$CH_3CH(OCOCH_3)_2 \rightarrow H_2C=CH-O-(CO)CH_3 + CH_3COOH$$

<sup>&</sup>lt;sup>7</sup> Alyaa Aboud Almanssoor, "Planning of Petrochemical Industry under Environmental Risk and Safety Considerations", University of Waterloo (2008)

<sup>&</sup>lt;sup>8</sup> Weissermel, K., Arpe, H. J., Industrial Organic Chemistry, 4th edn, Wiley-VCH, Weinheim, Germany, 2003



3. Acetic acid, ethylene and oxygen - This route dominates today. In older technologies the reaction was conducted in liquid phase at 110–130 °C and 30–40 bar in the presence of a redox catalyst PdCl2/CuCl2, but



corrosion raised problems. Modern processes operate in gas phase with Pdbased catalysts. A highly undesired secondary reaction is the combustion of ethylene to CO<sub>2</sub>. With modern Pd/Au catalysts the selectivity may reach 94%, based on ethylene and 98–99% based on acetic acid. The removal of CO<sub>2</sub> – usually by a wash with hot KOH solution –negatively affects the overall economics. Hoechst/Celanese and Bayer/DuPont are the most widespread processes, the main difference being in

the formulation of the catalyst. With respect to reaction engineering a multi-tubular fixed-bed reactor is employed, where the operational difficulty is mastering the occurrence of excessive temperature rise.<sup>9</sup>

 $C_2 H_4 + C_2 H_4 O_2 + \frac{1}{2} O_2 \rightarrow C_4 H_6 O_2 + H_2 O \Delta H + 42.1 \text{ Kcal/mol}$ 

 $C_2H_4 + 3O_2 \rightarrow 2CO + 2H_2O \quad \Delta H - 316 \text{ Kcal/mol}$ 

A modeled 5,000 kg/d VAM plant (330 kg/h) would require 2,145kg/d or 89.4kg/h ethylene, 345 kg/d or 14.4 kg/h oxygen, 1,380 kg/d or 57.5 kg/h acetic acid and 1,130 kg/d or 47.1 kg/h nitrogen.<sup>10</sup>

Polyvinyl acetate (PVA) and polyvinyl alcohol (PVOH) are the major derivatives manufactured using VAM. PVA is widely employed in textiles, adhesives, packaging films, photosensitive coatings and thickeners whereas, PVOH finds its applications in paper coatings, paints and industrial coatings owing to their excellent adhesion properties. Moreover, the rising application of acetic acid in production of terephthalic acid is also set to aid in the market growth during the forecast period. Terephthalic acid forms a major building block in manufacturing of polyester resins which is extensively used in polyester films, Polyethylene Terephthalate (PET) resins and polyester fibers. Additionally, terephthalic acid also finds its application in home furnishing and in manufacturing of textiles such as bed sheets, clothes, and curtains.

# **Carbon Footprint**

The LCA for acetic acid that on the methanol selected and the source of the carbon monoxide. While there are several methods for producing carbon monoxide the most widely is the partial oxidation of methane through a steam methane reforming (SMR) or if a source of  $CO_2$  is available dry reforming with methane. In the emissions are primarily from the natural gas required to heat the catalysts tubes where the steam and methane are converted to  $CO + 3H_2$ . Dry reforming with  $CO_2$  and  $CH_4$  but careful control is required to avoid the  $H_2$  from reacting via the water-gas shift reaction to for reform  $CO_2$ . Since as noted above the most likely solution is to colocate with a process that is already producing a CO stream. If more than one product is produced in a process,

<sup>&</sup>lt;sup>9</sup> Luyben, W., Tyreus, B., An industrial design/control study for vinyl acetate monomer plant, Comput. Chem. Eng., 22, 867, 1998

<sup>&</sup>lt;sup>10</sup> Chemical Process Design: Computer-Aided Case Studies. Alexandre C. Dimian and Costin Sorin BildeaCopyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, WeinheimISBN: 978-3-527-31403-4



it is necessary to divide the environmental impacts between the products according to ISO 14040 (International Organization for Standardization (ISO), 2006a. Praxair, one of the world's largest producers of hydrogen, has broken down the carbon footprint associated with the individual SMR process steps. Since each 3 H2 result in one CO it allows the assessment of; combustion for reforming energy =  $5.07 \text{ g CO}_2/\text{mol CO}$ , combustion for steam =  $3.42 \text{ g CO}_2/\text{mol CO}$ , power for separation and compression =  $0.13 \text{ g CO}_2/\text{mol CO}$ ; for a total of  $8.62 \text{ g CO}^2/\text{mol CO}$  additionally since each mol CO results in one mol CH<sub>3</sub>COOH this provides an estimate for the CO portion of the acetic acid. Each kg of acetic acid contains 16.6 mol acetic acid there are the same number of mol CO equal to 0.464 kg CO which result in  $0.143 \text{ kg CO}_2/\text{kg}$  acetic acid.

In developing the LCI for VAM the only the acetic acid, ethylene and oxygen process was considered as it represents 80%+ of the production. The values for ethylene has three sources from naphtha, from ethane and from ethanol. Production from ethanol involves highly energy-intensive steps in the overall life cycle resulting in the highest  $CO_2e$  value of 268 g  $CO_2e/kg$  with naphtha at 198 g  $CO_2e/kg$  and ethane at 167g  $CO_2e/kg$ .<sup>11</sup> Lacking a relative distribution between the feedstocks or this analysis we use and central value of 198g/kg and assign 115 g  $CO_2e/kg$  for the required power.<sup>12</sup>

A modeled 5,000 kg/d VAM plant (330 kg/h) would require 2,145kg/d or 89.4kg/h ethylene, 345 kg/d or 14.4 kg/h oxygen, 1,380 kg/d or 57.5 kg/h acetic acid and 1,130 kg/d or 47.1 kg/h nitrogen.<sup>13</sup>

Utilizing the modeled VAM plant above each kg of VAM would have 0.270 kg ethylene and 0.175 kg acetic acid which consumed 0.095 kg methanol.

<sup>&</sup>lt;sup>11</sup> Ghanta, M., Fahey, D. & Subramaniam, B. Environmental impacts of ethylene production from diverse feedstocks and energy sources. Appl Petrochem Res 4, 167–179 (2014). https://doi.org/10.1007/s13203-013-0029-7

 $<sup>^{12}</sup>$  US EPA states that in 2020, total U.S. electricity generation by the electric power industry of 4.01 trillion kWh from all energy sources resulted in the emission of 1.55 billion metric tons—1.71 billion short tons—of carbon dioxide (CO<sub>2</sub>). This equaled about 0.85 pounds (385g) of CO<sub>2</sub> emissions per kWh.

<sup>&</sup>lt;sup>13</sup> Chemical Process Design: Computer-Aided Case Studies. Alexandre C. Dimian and Costin Sorin BildeaCopyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, WeinheimISBN: 978-3-527-31403-4



Acetic Acid Production									
Input	kg/kg	%		GHG <sup>a</sup>					
Carbon Monoxide	0.5088	3 45%		kg CO₂e/					
Methanol <sup>b</sup>	0.5394	1 54%		1.551					
Methyl lodide	0.0135	5 1%							
Stoichiometr	ic Product 1.0617	7 106%	_						
Acetic Ac	id at Gate 1.0000	) 100%	]						

GHG <sup>a</sup>					
kg CO₂e/kg					
1 551					

Fugitive Byproducts <sup>c</sup>	0.0617	6%
Carbon Dioxide	0.0035	
Methane	0.0013	
Propionic Acid	0.0000	
Methyl Acetate	0.0013	
Hydrogen Iodide	0.0081	
Acidic Acid	0.0007	
Methanol	0.0019	
Carbon Monoxide	0.0440	
Water Vapor	0.0009	

Modeled Acetic Acid Production								
Product CO₂e	1.551	kg CO2e/kg						
IGP Ultra-Low Carbon CO₂e Improvement	0.421	kg CO2e/kg						
Improved Acetic Acid CO <sub>2</sub> e	1.130	kg CO2e/kg	27.1%					

Methanol in Acetic Acid <sup>d</sup>								
Grey SMR Methanol	0.704	kg CO2e/kg						
IGP Ultra-Low Carbon Methanol	0.283	kg CO2e/kg						
Improvement	0.421	kg CO2e/kg	60%					

Note: The improvement in the product is proportional to the methanol content of the product.

a: BP's CATIVA process GHG value from the GaBi 6 database https://sphera.com/product-sustainability-gabi-data-search/

b: Felix Adom, Jennifer B. Dunn, "Material and Energy Flows in the Production of Macro and Micronutrients, Buffers, and Chemicals", Argonne National Laboratory (2015)

c: US EPA, "Coupling Computer-Aided Process Simulation and Estimations of Emissions and Land Use for Rapid Life Cycle c: US EPA, "Coupling Computer-Aided Process Simulation and Estimations of Emissions and Land Use for Rapid Life Cycle

d: CO2e adjusted for methanol portion of product.



Vinyl Acetate Monomer (VAM) Resin Production <sup>a</sup>							
	Reaction	Mass	Macc				
	Ratio	Ratio	1VIASS %				
	Mole	grams	70				
Ethylene	0.5070	43.63	50.7%				
Oxygen	0.0700	6.02	7.0%				
Acetic Acid <sup>d</sup>	0.1600	13.77	16.0%				
Nitrogen	0.2630	22.63	26.3%				
	1.0000	86.06	100.0%				
VA	86.06						

a: A molar composition of 0.5 of ethylene, 0.07 of oxygen, 0.15 acetic acid and 0.263 of nitrogen have to be fed. An excess of ethylene over acetic acid (3:1) must be guaranteed. The concentration of oxygen must be kept below 8 % molar because at higher concentrations it breaches the explosive limit of the mixture. (Luyben , W. , Tyreus , B. , An industrial design/control study for vinyl acetate monomer plant , Comput. Chem. Eng. , 22 , 867)

b: In developing the LCI for VAM only the acetic acid, ethylene and oxygen process was considered as this represents 75%+ of world production.

c: The values for ethylene was devloped from three feedstocks; naphtha, ethane and ethanol. Production from ethanol has highly energyintensive steps in the overall life cycle resulting in the highest CO<sub>2</sub>e value of 268 g CO<sub>2</sub>e/kg with naphtha at 198 g CO<sub>2</sub>e/kg and ethane at 167g CO<sub>2</sub>e/kg. Lacking a relative distribution between the feedstocks or this analysis we use and central value of 198g/kg and assign 115 g CO<sub>2</sub>e/kg for the required power for a value of 313 g CO<sub>2</sub>e/kg.

d: Basing upon the values modeled in a 5,000 kg/d VAM plant (330 kg/h) would require 2,145kg/d or 89.4kg/h ethylene, 345 kg/d or 14.4 kg/h oxygen, 1,380 kg/d or 57.5 kg/h acetic acid and 1,130 kg/d or 47.1 kg/h nitrogen. Utilizing the modeled VAM plant above each kg of VAM would have 0.270 kg ethylene and 0.175 kg acetic acid which consumed 0.095 kg methanol. This validates the 54% content on methanol in Acetic Acid. (Ghanta, M., Fahey, D. & Subramaniam, B. Environmental impacts of ethylene production from diverse feedstocks and energy sources. Appl Petrochem Res 4, 167–179 (2014). https://doi.org/10.1007/s13203-013-0029-7)

Modeled VAM Resin Production <sup>b</sup>							
	Ethylene <sup>c</sup>	0.313	kg CO2e/kg				
	Oxygen	-	-				
	Acetic Acid	1.551	kg CO2e/kg				
	Nitrogen	-	-				
	Product CO <sub>2</sub> e	1.864	kg CO2e/kg				
	IGP Ultra-Low Carbon CO <sub>2</sub> e Improvement	0.233	kg CO2e/kg				
	Improved Product CO <sub>2</sub> e	1.631	kg CO2e/kg	12.5%			
Methanol in Acetic Acid <sup>d</sup>							
	Grey SMR Methanol	0.390	kg CO2e/kg				
IGP Ultra-Low Carbon Methanol		0.157	kg CO2e/kg				
	CO <sub>2</sub> e Improvement	0.233	kg CO2e/kg	60%			

Note: The improvement in the product is proportional to the methanol content of the product.



**Determining Methanol Carbon Intensity** – It is important to understand how a methanol's carbon intensity is determined. IGP follows the ISCC approach for well to gate emissions. Well to Gate grey methanol using SMR technology is 1.305 kg CO2e/kg CH3OH with IGP Blue methanol being 0.0525 kg CO2e/kg CH3OH. Life cycle emissions of SOx, NOx, CO2, CH4, and N2O are considered for methanol. Calculations include natural gas extraction and transpiration, along with methanol production

Many LCI calculations focus on gate-to-gate that is the production process itself. IGP has made an attempt to represent the values that would come from a applying the ISCC Plus accounting by including well to gate. The post gate has not been estimated as that will depend upon the next step in the value chain which has not yet been determined. The full LCA will be made once the transport from the IGP site to the customer and what the customer does along with the end of life estimates.

Detailed Well to Gate (kg Co₂e/kg methanol)											
							_				
		Natural Gas Production	÷	Gathering & Boosting	÷	Natural Gas Processing	→	Natural Gas Storage, Pipleing → & Compression	Conversion to Methanol	÷	TOTAL
Traditonal SMR	100 year GWP	0.07		0.055		0.085		0.09	0.83		1.130
MeOH	20 year GWP	0.14		0.085		0.115		0.135	0.83		1.305
IGP Ultra-Low	100 year GWP	0.07		0.055		0.085		0.09	0.05		0.350
Carbon MeOH	20 year GWP	0.14		0.085		0.115		0.135	0.05		0.525