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Microbial electrosynthesis and anaerobic fermentation: An economic evaluation for acetic acid production from CO₂ and CO

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ABSTRACT

Microbial electrosynthesis (MES) and anaerobic fermentation (AF) are two biological processes capable of reducing CO₂, CO and water into acetic acid, an essential industrial reagent. In this study, we evaluated investment and production costs of acetic acid via MES and AF, and compared them to industrial chemical processes: methanol carbonylation and ethane direct oxidation.
Production and investment costs were found high-priced for MES (1.44 £/Kg, 1770 £/t) and AF (4.14 £/Kg, 1598 £/t) due to variable and fixed costs and low production yields (100 t/y) compared to methanol carbonylation (0.26 £/Kg, 261 £/t) and ethane direct oxidation (0.11 £/Kg, 258 £/t). However, integrating AF with MES would reduce the release of CO₂, double production rates (200 t/y) and decrease investment costs by 9% (1366 £/t). This resulted into setting the production costs at 0.24 £/Kg which is currently market competitive (0.48 £/Kg). This economically feasible bioprocess produced molar flow rates of 4550 moles per day from MES and AF independently. Our findings offer a bright opportunity towards the use and scale-up of MES and AF for an economically viable acetic acid production process.

INTRODUCTION

Chemicals have had a fivefold increase in global demand from 1980 to 2010 and it is projected to reach 3,500 Billion USD by 2020 only in developed countries. As a result, energy demand and greenhouse gas emissions are exponentially growing. Acetic acid is one of the most valuable chemicals as it is an essential raw material for many petrochemical intermediates and products. Its derivatives and applications include latex emulsion resins for paints, adhesives, paper coatings, textile finishing agents, cellulose acetate fibres, cigarette filter tow and cellulosic plastics. Acetic acid’s global demand is expected to grow 4.9% per year and reach 16 million tonnes by 2020. Acetic acid is mainly synthesized chemically via methanol carbonylation, acetaldehyde oxidation, oxidation of naphtha and n-butane, fermentation of hydrocarbons, and ethane direct oxidation. However, all these processes form a noteworthy amount of by-products making their separation and recovery complex and expensive. As corrosive chemical catalysts are used, reaction vessels are made of expensive materials. Chemical reactions take place at high temperatures and
pressures using considerable water, energy and releasing CO$_2$. Hence, the development of alternative production routes from renewable feedstocks which can reduce greenhouse gas emissions while meeting acetic acid’s demand is highly desired.

Anaerobic fermentation (AF) is a biological process capable of reducing carbon monoxide (CO) and water into acetic acid using *Clostridium* bacteria, but it releases CO$_2$. Suitably, studies on microbial electrosynthesis (MES) have shown the feasibility of reducing CO$_2$ and water into acetic acid using acetogenic bacteria. Although the biological conversion of gaseous substrates into chemicals by using microorganisms as biocatalysts shows great potential, both processes (i.e. AF and MES) are limited by energy demand and low production rates which cap their efficiency.

Currently, methanol carbonylation is the most important process for large scale acetic acid production as it is responsible for the 65% of the world’s stock. On the other hand, ethane direct oxidation became very attractive for acetic acid production as ethane costs as low as £0.75 per million BTU and is commercialized in Saudi Arabia from 2012. Economic evaluations between methanol carbonylation and ethane oxidation demonstrated that methanol carbonylation requires higher investment costs compared to ethane oxidation caused by the special materials used for the construction of the plant. Despite that, production costs of methanol carbonylation were lower mainly due to conversion rates (higher product formation). The features of ethane direct oxidation showed its capability to compete with methanol carbonylation and allowed reduction projections using process design optimization.

There is no comprehensive evaluation on investment and production costs for biological processes, however, an economic analysis on lysine production from sucrose was recently published on bulk electricity prices for MES compared to fermentation. It was demonstrated that a sensible market potential for MES could be anticipated if higher yields up to 24.7 mM are
achieved per reactor (Total yield \( \approx 444 \text{ mM} \)). In regards to AF, no economic evaluation was found other than using AF of organic wastes to generate renewable energy; i.e. biogas \(^{13}\) where it was shown that using reverse osmosis as a green fertilizer would lower environmental burden but incur high investment costs. These findings confirm the importance of performing economic evaluations for demonstrating the features and benefits of new technologies.

To the authors’ knowledge, the production of acetic acid via biological processes has not been economically assessed because of the early stage of the technologies’ development. In this study, we evaluate investment and production costs of acetic acid bioproduction via MES and AF compared to methanol carbonylation and ethane direct oxidation. We further assess the economic viability of integrating MES as a recycle plant for AF.

METHODS

Process description. The analysis for MES and AF was calculated based on a plant producing 100 tonne per year (t/y) as per productivity rates reported in the literature \(^{8,9c}\). A recent study in MES showed a 11.4 moles per day production of acetic acid with a 94% conversion rates by increasing product specificity with well – acclimatized and enriched microbial cultures along with the use of an optimized electrode material \(^{14}\). The study used sodium carbonates as a source of carbon indirectly derived from CO\(_2\) instead of gaseous CO\(_2\) as used here. Using sodium carbonates will add up operating costs as capturing CO\(_2\) and processing it into carbonates require process steps embedding high temperatures and raw materials such as sodium chloride and ammonia (by Solvay process) \(^{15}\). This route is not evaluated here but should also be assessed in the future.

Figure 1A illustrates a flowsheet of MES and AF plants which includes major equipment excluding storage tanks. Figure 1B shows the process mass fraction throughout the flowsheet.
Liquid reaction medium and gaseous substrates, CO$_2$ in case of MES and CO for AF, are mixed prior their entry to the reactor and are fixed to 30°C. For MES, the reactants enter the large scale bioelectrochemical systems which include the biocatalyst in the form of a biofilm on graphite granular electrodes. The reaction occurs by applying a specific potential, -0.393 V vs. SHE $^9c$, to achieve the preferred product. Assuming that only conversion of CO$_2$ was converted to acetic acid, with the occurrence of water and O$_2$, the liquid mixture passes to a biocatalyst separator where any remaining biocatalyst is filtered and collected. A vacuum pump is used to draw the output gas mixture from the reactor to the membrane to separate O$_2$ from CO$_2$. The CO$_2$/O$_2$ selectivity of the membrane was assumed to be 50% with a capture efficiency of 99%. Any CO$_2$ excess will be recycled back to the reactor were O$_2$ produced would be released in the atmosphere. After the removal of the biocatalyst, the liquid mixture undergoes distillation to separate water from acetic acid. Similar process is used for AF using large scale bioreactors. Here, CO is converted to acetate and CO$_2$, the liquid mixture moves to the biocatalyst separator followed by distillation. Any excess of CO is recycled back to the bioreactor.

The analysis for methanol carbonylation and ethane direct oxidation was calculated based on a plant producing 200 thousand tonnes per year (kt/y) which run a continuous process as described in Smejkal, et al. $^{11}$. All the values in the study were converted to UK pounds per tonne (£/t) for reliable comparisons unless stated differently using equations stated in Sinnott $^{16}$. 


**Figure 1.** Bioprocess flowsheet of acetic acid production for a 100 t/y plant. (A) Process flowsheet schematic of MES and AF with main equipment. Code letters and numbers; S: separator, R: reactor, C: rectification column, 1: Microbial electrosynthetic reactor (or anaerobic
fermenter), 2: bacterial filter, 3: rectification of water-acetic acid (acetic acid purification), 4: CO\textsubscript{2} separation. \textbf{(B) Mass fraction representation throughout the flowsheet.} Stream numbers show the mass fraction of the reactants, products and biocatalysts.

\textbf{Economic analysis based on fixed capital costs.} Estimation of purchased equipment costs for methanol carbonylation and ethane direct oxidation were projected from Smejkal, et al. \textsuperscript{11} and Soliman, et al. \textsuperscript{5c} respectively. For biological processes, the price of major equipment was estimated using an educational software cost estimator tool \textsuperscript{17}. Costs of standby equipment, storage and surge tanks were not within the scope of this economic analysis and were excluded. Equipment cost analysis for MES included the electrode (£380 per half a tonne of carbon granulars) as in \textsuperscript{9c}. Fixed capital costs were estimated by summing up the bare erected and external costs (e.g. piping, instrumentation etc.) using Lang factors \textsuperscript{16}, and operating costs were calculated as detailed in Supplementary information S2 (Table S2). The working capital accounts for receivable, operating expenses cash and taxes and was estimated as 5\% of the fixed capital cost. To obtain the total investment cost: operating and working capital costs were summed up.

\textbf{Economic analysis based on variable costs.} The amount of raw materials was calculated only using the main reaction materials, and assuming that the formation of by-products is insignificant (Table 1). Raw material prices were taken from Sinnott \textsuperscript{16} and converted to 2015 prices using CPI index. Selectivity and conversion rates of chemical processes were used as in Smejkal, et al. \textsuperscript{11} and Soliman, et al. \textsuperscript{5c}, whereas the rates for biological processes were used as in Jia, et al. \textsuperscript{8} and Marshall, et al. \textsuperscript{9c} (see Supplementary Information S1 – Table S1).
Table 1. Acetic acid process, reaction conditions and chemical and bacterial catalyst costs.

Chemical catalysts costs were taken from a Smejkal, et al. 11 and b Soliman, et al. 5c. c Anaerobic fermenters’ costs were estimated from 18. d Anaerobic bacteria costs were estimated from 19.

<table>
<thead>
<tr>
<th>Processes</th>
<th>Main reaction</th>
<th>Reaction conditions</th>
<th>Catalyst costs (£/year)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol Carbonylation</td>
<td>$CH_3OH + CO \xrightarrow{[Ir(CO_2)I_3]} CH_3COOH$</td>
<td>190 30-40 -133.82</td>
<td>20334582</td>
<td>11, 20</td>
</tr>
<tr>
<td>Ethane Oxidation</td>
<td>$CH_3CH_3 + 1.5O_2 \xrightarrow{[MoVNbPd]} CH_3COOH + H_2O$</td>
<td>277 20 -14.76</td>
<td>260326b</td>
<td>5c</td>
</tr>
<tr>
<td>AF</td>
<td>$4CO + 2H_2O \xrightarrow{Biocatalyst} CH_3COOH + 2CO_2$</td>
<td>30 1 -20</td>
<td>330c</td>
<td>8, 21</td>
</tr>
<tr>
<td>MES</td>
<td>$2CO_2 + 6H_2O + 8e^- \xrightarrow{Biocatalyst} CH_3COOH + 4H_2O + 2O_2$</td>
<td>30 1 216.12</td>
<td>350d</td>
<td>22</td>
</tr>
</tbody>
</table>

Glucose fermentation ran continuously with no need of bacteria enhancement and it is expected that AF and MES will perform similarly.23 Thus, biocatalysts were included as onetime costs in raw materials (Table 1). However, their capabilities of storage and reproducibility at minimum cost should also be noted. Chemical catalysts for methanol carbonylation and ethane direct oxidation were calculated considering 1 year life span.

The economic analysis on utilities (i.e. electricity and cooling water) was based only on the main reaction for product formation. The main reaction of the chemical processes and AF is exothermic thus cooling water was used as their utility value. To calculate the temperature of the reactor Table
1 and equation (1) were used. The process temperature was assumed as 25°C for the chemical
processes and AF. It was assumed that the reactors’ inlet and outlet were maintained isothermally
at operating temperatures.

\[ Q = \Delta H_R = \Delta H_R(T_1) + \int_{T_1}^{T_2} \Delta C_p dT \]  

(1)

Where \( Q \) is the heat required or given out, \( \Delta H_R \) is the heat of reaction, \( C_p \) is the heat capacity, \( T_1 \) is the starting temperature and \( T_2 \) is the reactor temperature. To calculate the amount of cooling water required to control the reaction equation 2 was used.

\[ Heat \ load \ (q) = q_h = q_c \]  

(2)

Where \( q_h \) is the rate of heat loss by hot fluid equal to \( m_hC_p,h\Delta T_h \), \( m_h \) is the mass flowrate, \( C_p,h \) is the mass heat capacity constant and \( \Delta T \) is the difference in the temperature. Where \( q_c \) is the rate of heat gain by cold fluid equal to \( m_cC_p,c\Delta T_c \).

The utility of MES was calculated as the energy needed to activate and control the reaction. The operating temperature of MES was evaluated at 30 °C from -37 °C, due to CO₂ storage requirements. The energy needed for this was also taken into account. The energy balance of the reaction was calculated based on the Coulombic efficiency given by Marshall, et al. ⁹, the amount of electrons (Table 1) needed for the conversion of CO₂ to acetic acid and the activation energy (V).

The Gibbs free energy was calculated using equation (3) and (4).

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]  

(3)

\[ \Delta G^0 = -nFE^0 \]  

(4)
Where $\Delta H^0$ the change in enthalpy (kJ/mol), $T$ is the temperature (in Kelvin), $\Delta S^0$ is the change in entropy (kJ/mol), $n$ is the number of electrons, $E$ is the reactor’s potential and $F$ is the Faraday constant (96485 C/mol).

**Biological processes integrations and processes economics advancement.** AF and MES processes were merged together. MES was used to recycle CO$_2$ produced from AF and increase acetic acid production. Variable, fixed and capital investment costs were re-evaluated using the procedure shown in section 2.2 and 2.3.

**Renewable energy utilization and projected productivity levels.** Different energy sources were used to calculate energy costs of the integrated process for the MES process. Originally, natural gas was used to provide energy to the integrated process, however other energy sources were evaluated such as onshore wind, nuclear, coal, offshore wind and solar photovoltaics $^{24}$ in order to reduce investment and production costs. Costs used are shown in Supplementary information S3 – Table S3. Domestic wastewater was also evaluated as an alternative renewable energy source for the MES process. The energy production was calculated using a wastewater load equivalent to a community of 279 thousand people as described in Logan $^{25}$. However, since MES showed a great potential for becoming an alternative route for the production of not only acetic acid but a range of other chemicals, its optimization was essential. Thus, its potential was assessed using renewable energy to reduce production costs.

Acetic acid production costs were calculated for increased plant capacities of 200, 2000 and 200000 t/y for a more direct comparison with the conventional processes.
All values are reported in British pounds (£) however other currencies are available in Supplementary Information S3 and S4 in Euros (€) and US Dollars ($) using an exchange rate of 1.17 and 1.30, respectively.

RESULTS AND DISCUSSION

**Fixed capital: equipment costs.** Equipment costs of MES (463.12 £/t) and AF (418.32 £/t) were comparable as they use similar equipment (Table 2). However, the increased cost of MES from AF was observed due to electrode costs and large mixing tanks. The MES system evaluated did not use PEM but this would have represented additional costs (£262/m²). Electrode and membrane research is essential for decreasing costs; future work insights should investigate development of high performance carbon electrodes and membrane durability at minimum costs. In terms of the electrode material, positive characteristics, for sustainable operation, are: high electrical conductivity, strong bio-compatibility, chemical stability and large surface area. In this line, recent publications by Jourdin et al. (2015) showed that chemical production was improved ten times due to extended bacterial colonization on 3D electrodes highlighting the importance of high surface area. Furthermore, it is crucial that the electrodes and membranes are obtained from the same region as import and transport contributes 10-20% to their costs. As a result of low production rates and a large amount of reaction medium needed, based on reaction balances (Table 1), MES required larger reactors (total reactor size: 1.8 m³) and mixing tanks (total reactor size: 2 m³) than AF (total reactor size: 0.6 m³) which lead to additional costs.
Table 2. Major purchased equipment costs for acetic acid production for methanol carbonylation (200 kt/y), ethane direct oxidation (200 kt/y), AF (100 t/y), MES (100 t/y) and the integrated process (200 t/y).

<table>
<thead>
<tr>
<th>Cost (£)</th>
<th>Methanol Carbonylation</th>
<th>Ethane direct oxidation</th>
<th>AF</th>
<th>MES</th>
<th>Integrated process</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Main process major equipment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compressor</td>
<td>2201380</td>
<td>5234185</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pre-Heater</td>
<td>113374</td>
<td>75582</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Reactor</td>
<td>425158</td>
<td>132270</td>
<td>17262</td>
<td>13821</td>
<td>17262</td>
</tr>
<tr>
<td>Cooler</td>
<td>-</td>
<td>302334</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mixing tank</td>
<td>-</td>
<td>-</td>
<td>7621</td>
<td>15242</td>
<td>21541</td>
</tr>
<tr>
<td>Tank</td>
<td>1322717</td>
<td>80281</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Distillation column</td>
<td>1150834</td>
<td>1794578</td>
<td>13251</td>
<td>13251</td>
<td>13251</td>
</tr>
<tr>
<td>Gas separator</td>
<td>56669</td>
<td>47224</td>
<td>1700</td>
<td>1700</td>
<td>2000</td>
</tr>
<tr>
<td>Recycle</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13821</td>
</tr>
<tr>
<td>Electrodes</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td><strong>Total (£/year):</strong></td>
<td>13700000</td>
<td>7600000</td>
<td>41832</td>
<td>46312</td>
<td>71495</td>
</tr>
<tr>
<td><strong>Total (£/ton):</strong></td>
<td>68.5</td>
<td>38</td>
<td>418.32</td>
<td>463.12</td>
<td>357.47</td>
</tr>
</tbody>
</table>
Bioprocesses did not require expensive equipment, as they can be fabricated of stainless steel. The material choice is an important parameter for the plants development to ensure long time operation. For example, methanol carbonylation used Hastelloy alloy as equipment material due to the use of high corrosive catalyst mixture \( \text{Rh}(CO)_x \) in the process. This option made the total purchase equipment costs of methanol carbonylation (13.7 million £/y) overpriced in relation to ethane direct oxidation (7.6 million £/y), AF (41.8k £/y) and MES (46.3k £/y). On the other hand, ethane direct oxidation required an expensive compressor when the production capacity was as high as 200 kt/y, making it the main contributor to the purchase equipment cost. Acetic acid purification process of chemical processes were 86 (£1.15 million) and 135 (£1.79 million) times more expensive, respectively, than bioprocesses (£13.2 k) mainly due to the unit size. Another benefit of bioprocesses, is the use of filtration systems (£1998), for separating the biocatalyst, which showed to be 4220 times cheaper than the catalyst separator used for methanol carbonylation (£8.4 million). In addition, in bioprocesses, a membrane system (£1700) was used for gas separation which was 33 and 28 times less expensive than the conventional gas separators used in methanol carbonylation (£56.6 k) and ethane direct oxidation (£47.2 k), respectively. However, showing the cost in relation to unit capacity per tonne (Table 3) made the bioprocesses most expensive as a result of the low production rates. In this study, it was assumed in bioprocesses, that one batch would last for 3.66 days (88 hours) for the production of 1 tonne. Maximizing productivities by increasing residence time could contribute to a further reduction in equipment costs.

**Total investment and operating costs.** Total investment costs for acetic acid production via MES (1770 £/t) and AF (1598 £/t) were about 85% more expensive than methanol carbonylation (261 £/t) and ethane direct oxidation (258.50 £/t) (Table 3). The plant size and number of
equipment is critical for the economics of a process as it is directly related to the investment costs. By increasing the productivities of MES and AF, the investment costs would decrease substantially as the same equipment could be used for larger production quantities.

Table 3. Investment operating costs and production costs for acetic acid production. Total and detailed variable costs are also shown for methanol carbonylation (200 kt/y), ethane direct oxidation (200 kt/y), AF (100 t/y), MES (100 t/y) and integrated process (200 t/y).

<table>
<thead>
<tr>
<th>Costs (£)</th>
<th>Methanol Carbonylation</th>
<th>Ethane direct oxidation</th>
<th>AF</th>
<th>MES</th>
<th>Integrated process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment cost (£/t):</td>
<td>261</td>
<td>258.5</td>
<td>1598</td>
<td>1770</td>
<td>1366</td>
</tr>
<tr>
<td>Operating cost (£/t):</td>
<td>267</td>
<td>115</td>
<td>4147</td>
<td>1447</td>
<td>2379</td>
</tr>
</tbody>
</table>

Detailed variable cost:

| Raw material (£/t) | 127 | 63 | 2927 | 168 | 1547 |
| Utilities (£/t) | 0.67 | 2.41 | 213.1 | 242 | 227 |
| (Bio)catalyst (£/t) | 102 | 13.01 | 3.30 | 3.50 | 3.40 |
| Total variable cost (£/t): | 229.67 | 78.42 | 3143.4 | 413.5 | 1777.4 |
| Total Fixed cost (£/t): | 37.33 | 36.58 | 380.6 | 1033.5 | 601.6 |
Operating costs of bioprocesses resulted to be very costly compared to chemical processes (Table 3). Operating costs are divided into variable (i.e. raw material, utility and (bio)catalyst costs) and fixed (e.g. maintenance, operating labor etc.) costs. For MES, CO$_2$ was the main raw material considered free of charge because of current carbon offset policies. Thus water became the main contributor to raw material costs (168 £/t) in MES. On the contrary, for other processes, water costs were negligible compared to other raw materials used. Raw material costs of AF (2927 £/t) were 46 times more expensive than ethane direct oxidation (63 £/t), 30 times more than methanol carbonylation (127 £/t) and 17 times more than MES (168 £/t). AF uses gaseous carbon monoxide and water as raw materials. Carbon monoxide was the main contributor to the raw material costs of AF as it cost 25 times (18.95 £/t) more than water (0.76 £/t) and is needed 4 times more, in quantity, than methanol carbonylation based on reactions (Table 1). The carbon offset policies do not apply for carbon monoxide as it has an insignificant contributions to the greenhouse gas effect. However, this should be altered as carbon monoxide emissions can have an indirect impact to the environment $^{28}$. Methanol carbonylation was the most expensive acetic acid production chemical route as it used methanol (183.40 £/t) and carbon monoxide. Methanol costs 10 times more than carbon monoxide, resulting in the highest raw material cost. Ethane direct oxidation showed cheaper raw material costs than methanol carbonylation and AF. This is because ethane direct oxidation uses oxygen (33.62 £/t) and ethane (20.17 £/t) as its main raw materials which were almost 2 times higher than carbon monoxide and 9 times less expensive than methanol. This made ethane direct oxidation the cheapest chemical route.

| Acetic acid production costs (£/kg): | 0.26 | 0.11 | 4.14 | 1.44 | 0.24 |

Regarding utilities used for product formation, MES uses CO\(_2\) as the main raw material which is thermodynamically stable and it requires a significant amount of electrons for the synthesis of organic compounds i.e. acetic acid, thus covering more than half (242 £/t) of the variable costs (413.5 £/t)\(^{29}\). On the other hand, AF was found to be the most expensive process for utility costs (213.1 £/t). The amount of cooling water used in AF was 318 and 88 times more compared to methanol carbonylation (0.67 £/t) and ethane direct oxidation (2.41 £/t), respectively. Decreasing the utility costs of MES equivalent to chemical processes would make the technology more competitive. The MES reaction energy barrier does not allow for a further significant reduction on the energetic demand but costs may be depleted by exploring the use of renewable energies to drive reactions as initially discussed by Nevin et al.\(^{9b}\).

Biocatalysts cost showed to be negligible due to their nature of reproducibility and ability of long term storage in laboratories. In contrast, chemical plants have catalyst costs added every year due to catalyst design. Methanol carbonylation had the highest cost based on catalysts as it required a mixture of iridium, ruthenium, methyl acetate and methyl iodide which are expensive and less available. The use of biocatalysts offers unique characteristics over chemical catalysts\(^{30}\). Their high selectivity is a key advantage as it can reduce side reactions and simplify downstream processes. Biocatalysts also offer environmental benefits compared to chemical catalysts as they operate under mild conditions (temperature range of 20°C – 40°C and typically in a pH range of 5-8) and completely degrade in the environment.

Chemical processes had the cheapest fixed costs around 37 £/t; 10 and 28 times less than AF (380 £/t) and MES (1033 £/t), respectively. In addition, it was revealed that 60% of MES’ operating costs were covered by fixed costs suggesting that the maintenance and operating labor of the plant had a higher cost than the actual process. In this line, further detailed evaluation should be
performed to explain this trend. In contrast, the fixed cost of AF was only 12% from the total operating cost, mainly due to the raw material costs (2927 £/t).

**Acetic acid production costs.** Methanol carbonylation and ethane direct oxidation have a cost of 0.26 and 0.11 £/kg, respectively (Table 3). According to the latest purchasing prices, the commercial acetic acid price was set at 0.48 £/kg in December 2015. Production costs of acetic acid were 1.8 times lower for methanol carbonylation and 4.36 times lower for ethane direct oxidation than the commercial price, revealing the advantages of their use in industry. On the other hand, the acetic acid production costs for AF and MES were calculated at 4.14 and 1.44 £/kg, respectively which is 88% and 33% more expensive than the commercial price. As production costs were highly related to operating costs, a high production cost was expected for bioprocesses. For this reason, in this current state, bioprocesses are currently inappropriate to serve as acetic acid production plants and compete with the already existing technologies. However, the optimization of such processes in terms of productivity levels and energy management might improve their feasibility.

**Integration of AF and MES.** Low production rates restrict the commercial application of MES and AF. Producing small volumes of acetic acid per year results in an expensive product as the production cost is calculated in terms of annual production cost (variable, fixed costs and sales expenses) over production rate (i.e. 1 t/y). Increasing production rates at this point of research is a technical challenge. One way to achieve increased product yields in MES is by using several reactors in series, as shown in the case of microbial fuel cells for energy production. Doing this for MES would require a significant amount of land and electrode material, as in this study, one system can only produce 17.25 mM per day, which is unfeasible. AF can easily increase its conversion rates by providing higher residence times using larger reactors (in this study we used...
an 120 m³ reactor volume). This allows AF to be scaled up easier compared to MES. Additionally, to further improve the process economics, selling of other byproducts from biological processes should be experimentally analysed and economically explored.

AF has a better potential of scale up than MES. However, it produces CO₂ as a byproduct which is released to the atmosphere contributing to greenhouse gas emissions. Even that MES cannot compete economically with existing processes, its ability of using CO₂ as raw material allows it to serve as a recycle plant. Integrating MES with AF, could offer complementary advantages and increase the production rates. As well as to avoid the release of CO₂, increase the process efficiency and result in lower investment costs as the same refining equipment will be used for both. Since MES is not only capable of producing acetic acid from CO₂ but a range of other carbohydrates, this principle could be applied to any plant that produces CO₂. Reusing the CO₂ stream in chemical reactions have been previously applied for the production of syngas, hydrogen etc. MES integration could help AF to achieve a full polygeneration potentials.

Figure 2 shows the integrated process. AF was the first stage of the process where liquid water was pumped and preheated at 30°C and gaseous CO was compressed and preheated at the same conditions. Assuming that only the conversion of carbon monoxide to acetic acid occurred, the mixture went through the membrane gas separator (i.e. CO₂/N₂/O₂/CO) where the by-product, CO₂, and excess of carbon monoxide were separated followed by recycle; carbon monoxide was recycled back to the fermenter and the CO₂ was used as raw material. The CO₂ would enter the mixing tank to be prepared and mixed with water prior its entrance in the MES reactor. The MES reactor also included electrodes and the biocatalyst in the form of biofilm. The liquid mixture from both fermenter and MES reactor was filtered to remove any remaining within the mixture. After removing bacteria, the liquid mixture underwent distillation to separate acetic acid and water. Part
of the water production would be then recycled to the fermenter as raw material. By integrating the bioprocesses, the production yield automatically doubled as each of the process would produce 100 t/y of acetic acid.

(A)

(B)

<table>
<thead>
<tr>
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<th>1</th>
<th>2</th>
<th>3</th>
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<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td></td>
<td></td>
<td>66%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100%</td>
<td></td>
<td></td>
<td>48.5%</td>
</tr>
<tr>
<td>Acetic acid</td>
<td></td>
<td>31%</td>
<td></td>
<td></td>
<td>30%</td>
<td>100%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Integrated process</td>
<td>H₂O</td>
<td>34%</td>
<td>65%</td>
<td></td>
<td>70%</td>
<td>100%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dead bacteria</td>
<td>O₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100%</td>
<td></td>
<td></td>
<td></td>
<td>51.5%</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>66%</td>
<td></td>
<td>33%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100%</td>
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</table>
The advantage of integrating both bioprocesses is the use of the same downstream equipment and the increase of productivity rates. By using this approach, the investment cost (1366 £/t) was reduced almost 23% and 14% compared to MES (1770 £/t) and AF (1598 £/t) as alone processes, respectively. This was mainly because of the increase in production rates (200 t/y). On the other hand, the operating costs of the integrated process (2379 £/t) decreased 42% compared to AF (4147 £/t) and increased 61% compared to MES (1447 £/t) as the two alone processes are now sharing material and energy costs for downstream processes. This made the final acetic acid production costs to significantly decrease and set the production cost at 0.24 £/Kg (Table 2) becoming compatible with the conventional routes and the current market (0.48 £/Kg). Further reductions in raw material costs may be achieved by using the water produced from the MES process to be recycled back to the fermenter or the MES reactor.

**Integrated process: Use of renewable energy and increase of acetic acid production rates.**

The evaluation of the integrated process was confirmed as a cheapest production route compared to AF and MES as stand-alone processes. Additionally, the introduction of renewable energy will be vital for the development of a sustainable process; as such the effect of using renewable energy MES process was evaluated. According to the European Wind Energy Association, onshore
wind energy is the cheapest compared to gas, nuclear and coal, offshore wind and solar photovoltaics energy. The difference of acetic acid production costs from the integrated process, when using different energy sources, indicated that powering the MES process with onshore wind energy showed a small reduction in the overall conversion energy costs of 2.7% setting the production cost at 0.23 £/Kg (Supplementary Information – Table S3).

Using wind energy to cover the energy costs for MES as a stand-alone process reduced the acetic acid production cost 6.9% and set it at 1.35 £/t which still remains costly compared to the market. Another source of energy that could be used in the MES is wastewater. An MFC configuration can be used to treat wastewater and harvest the energy in the anode and conduct a MES process in the cathode. It was found that 411 MW per year could be produced from a domestic wastewater which covered the entire cathode energy needs and reduced the acetic acid production cost by 16.6% reaching 1.20 £/Kg; making this source of energy more attractive that wind energy. However, increasing production rates and reducing fixed costs would still be needed in the MES process to achieve production costs compatible to the market price.

In order to accomplish a more direct comparison with the conventional processes, an increase in productivity levels was assessed for the Integrated process (Table 4). Acetic acid production using the integrated process was shown to be viable at 200 t/y plant capacity. When production rates were increased to 2 kt/y and 200 kt/y plants, the acetic acid costs were increased to 1.72 and 1.66 £/Kg which is 7.8 and 7.5 times more expensive, respectively, than the production (0.22 £/Kg) cost of the 200 t/y plant. Operating costs of larger scale plants were expected to increase substantially due to an increase of fixed and variable costs, affecting overall production costs. Compared to methanol carbonylation and ethane direct oxidation for a 200 kt/y plant, the production cost of integrated process (1.55 £/Kg) resulted to be almost 7 (0.26 £/Kg) and 14 (0.11
£/Kg) times more expensive, respectively. In relation to operating costs, integrated process was
set at 334.2 million £/year which was 13 (25 million £/year) and 2.7 (12 million £/year) times more
expensive than methanol carbonylation and ethane direct oxidation mainly to the utilities and fixed
costs. Increasing residence time and production rates would allow the process to decrease
equipment size for the same amount of production capacity and thus decrease purchased equipment
cost and fixed costs. In this line, research must focus on developing methods to increase microbial
product selectivity, thus conversion rates and production yields for optimal scalability of the
process. However, the most economically feasible plant capacity observed from these analyses
was the 200 t/y plant.

Table 4. Acetic acid production costs of integrated process at different production rates

<table>
<thead>
<tr>
<th></th>
<th>Integrated process</th>
<th>Methanol carbonylation</th>
<th>Ethane Direct Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Plant capacity</strong></td>
<td>200 t/y</td>
<td>200 kt/y</td>
<td>200 kt/y</td>
</tr>
<tr>
<td><strong>Total investment costs (£/year)</strong></td>
<td>273250</td>
<td>16898000</td>
<td>17866782</td>
</tr>
<tr>
<td><strong>Operating costs (£/year)</strong></td>
<td>445320</td>
<td>33420000</td>
<td>25488000</td>
</tr>
<tr>
<td><strong>Production costs (£/Kg)</strong></td>
<td>0.22</td>
<td>1.66</td>
<td>0.26</td>
</tr>
<tr>
<td><strong>Production rates per batch (moles per day)</strong></td>
<td>AF 4550</td>
<td>75956</td>
<td>9726048</td>
</tr>
<tr>
<td></td>
<td>MES 4550</td>
<td>75956</td>
<td></td>
</tr>
<tr>
<td><strong>Batch (tonnes)</strong></td>
<td>1</td>
<td>10</td>
<td>1000</td>
</tr>
</tbody>
</table>
The output molar flows should be considered as technical goal in order to ensure process profitability and market compatibility using a biological route. This study used values from Marshall, et al. \(^9c\) which showed the feasibility of MES to produce a maximum of 0.017 moles per day whereas AF has a reported production of 9.25 moles per day \(^8\). Thus future studies should demonstrate the feasibility of a 267k times increase on the molar flow output in MES (4550 moles per day) and 492 times for AF (4550 moles per day). This analysis indirectly suggests that bioprocesses will have better opportunities to be scaled-up for industrial intake as small scale and high value chemicals producers which will reduce the obstacles of competing with large scale chemical plants.

ASSOCIATED CONTENT

**Supporting Information.** Additional material includes: selectivity and conversion rates; variable details of chemical and biological processes; values on energy costs from different energy sources, acetic acid production costs from different energy sources. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

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ABBREVIATIONS

CO₂, carbon dioxide; CO, carbon monoxide; MES, microbial electrosynthesis; AF, anaerobic fermentation; t, tonne; kt, thousand tonnes; t/y, tonnes per year; kt/y, thousand tonnes per year; £/Kg, British pounds per kilo; £/t, British pounds per tonne.

REFERENCES


36. European Wind Energy Association Onshore wind cheaper than coal, gas and nuclear, according to European Comission report. (accessed 16/02/2015).
Table of Contents Graphic

![Diagram showing Anaerobic fermentation and Microbial electrosynthesis processes]

- **CO fixation**: 18198 moles per day
- **Acetic acid**: 4550 moles per day
- **CO₂ fixation**: 9099 moles per day
- **Acetic acid**: 4550 moles per day