



Review

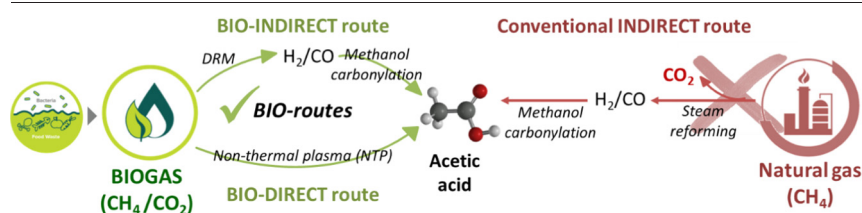
Sustainable routes for acetic acid production: Traditional processes vs a low-carbon, biogas-based strategy

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HIGHLIGHTS

- Biogas conversion to acetic acid represents a circular economy route for chemicals manufacturing.
- Two new BIO-strategies are proposed to obtain acetic acid from CO₂ and CH₄.
- The implementation of plasma technology in dry reforming represents a step-ahead on carbon-neutral processes.
- The state-of-the-art of lab-scale non-thermal plasma dry reforming to value-added products has been reviewed.

GRAPHICAL ABSTRACT



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ABSTRACT

The conversion of biogas, mainly formed of CO₂ and CH₄, into high-value platform chemicals is increasing attention in a context of low-carbon societies. In this new paradigm, acetic acid (AA) is deemed as an interesting product for the chemical industry. Herein we present a fresh overview of the current manufacturing approaches, compared to potential low-carbon alternatives. The use of biogas as primary feedstock to produce acetic acid is an auspicious alternative, representing a step-ahead on carbon-neutral industrial processes. Within the spirit of a circular economy, we propose and analyse a new BIO-strategy with two noteworthy pathways to potentially lower the environmental impact. The generation of syngas via dry reforming (DRM) combined with CO₂ utilisation offers a way to produce acetic acid in a two-step approach (BIO-Indirect route), replacing the conventional, petroleum-derived steam reforming process. The most recent advances on catalyst design and technology are discussed. On the other hand, the BIO-Direct route offers a ground-breaking, atom-efficient way to directly generate acetic acid from biogas. Nevertheless, due to thermodynamic restrictions, the use of plasma technology is needed to directly produce acetic acid. This very promising approach is still in an early stage. Particularly, progress in catalyst design is mandatory to enable low-carbon routes for acetic acid production.

Contents

1.	Introduction	2
2.	Acetic acid: conventional routes and market review	3
2.1.	Applications insight and market overview	3
2.2.	Conventional routes for acetic acid production	3
2.2.1.	Oxidation of acetaldehyde	3
2.2.2.	Oxidation of hydrocarbons	3

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2.2.3. Methanol carbonylation	5
2.3. Research progress and alternative route proposed	6
3. BIO-Indirect approach	7
3.1. Biogas dry reforming	7
3.2. Thermocatalytic DRM	8
3.3. Photocatalytic DRM	9
3.4. Plasma-catalytic DRM	10
3.4.1. Hybrid NTP DRM	10
4. BIO-Direct approach	12
4.1. State-of-the-art of plasma-assisted acetic acid production	12
5. Concluding remarks and outlook	14
CRedit authorship contribution statement	14
Declaration of competing interest	15
Acknowledgements	15
References	15

1. Introduction

In the last two centuries, greenhouse gas (GHG) emissions have significantly increased due to anthropogenic sources. Both CO₂ and CH₄ are considered key contributors of these GHG emissions, representing >90% of the total anthropogenic emissions to the atmosphere (International Energy Agency, 2018). In particular, CO₂ discharges add up to three-fourths of the total anthropogenic GHG emissions. Furthermore, the adverse impact of releasing CH₄ should also be taken into account since its global warming potential (GWP) is 25 times higher than CO₂ (Boucher et al., 2009). Emissions are increasing year by year and some scenarios still project net increments in the near future (International Energy Agency, 2015). Therefore, there is much to be done to meet the target agreed on “Glasgow Climate Pact” about global emissions and temperature rise (United Nations Framework Convention on Climate, 2021). Effective measures, such as CO₂ capture and utilisation (CCU) strategy, are needed to mitigate the environmental impact of GHG emissions.

Most of the GHG emissions come from the consumption of fossil fuels for energy. Notwithstanding, it is less known the relevant contribution of the agriculture, livestock and other organic waste sector, as observed in Fig. 1. Organic waste (e.g., sewage sludge, manure, organic industrial/municipal waste, etc.) greatly contributes to the GHG emissions to the atmosphere due to anaerobic digestion (IPCC Fourth Assessment Report, 2014). These emissions, mainly in the form of biogas (CH₄ and CO₂), were considered a waste rather than a value, but this trend is changing since biogas is now considered a renewable asset. Nowadays, the biogas industry business model is based on two main strategies: (i) the direct conversion into calorific energy and (ii) the production of renewable fuels. These two approaches are not completely sustainable since upgrading of biogas is imperatively required to remove part of the CO₂, thus not achieving the desired carbon neutrality (Le Saché et al., 2019; Navarro Puyuelo et al., 2017). In addition, biogas plants rely on government subsidies due to their lack of competitiveness in the market (Brémond et al., 2021). As an alternative to the current biogas industry business model, new opportunities are blooming through the carbon cycle fixation strategy. The reforming of biogas to fine, value-added chemicals (e.g., acetic acid, methanol, olefins, ammonia, etc.) is deemed a promising way to mitigate GHG emissions, offering an interesting alternative to simply burn it (Liu et al., 2020; Navarro Puyuelo et al., 2017). Biogas upgrading via chemical transformation is an underexplored field which may provide many possibilities for the chemical industry to tackle GHG emissions (Navarro Puyuelo et al., 2017; Puliyalil et al., 2018). Acetic acid (AA) can be an interesting intermediate product generated from biogas which can be later transformed into other valuable products (Tu et al., 2021; Wang et al., 2017a).

Traditionally, acetic acid is industrially produced via an indirect route, carbonylation of methanol, using syngas (primarily formed by CO and H₂). Globally, three main environmental drawbacks are found in this synthesis pathway: a) it is an energy-intensive process, b) syngas is mainly

produced from fossil fuels (e.g., carbon and natural gas) and c) environmental impacts coming from many chemical waste discharges (Cheung et al., 2000; Kalck et al., 2020). Research efforts are now concentrated on promoting alternatives to this process. Furthermore, the current tendency in manufacture is claiming a shift to more sustainable chemical routes to lessen the environmental impacts to the atmosphere and hydrosphere of these large-scale industrial processes. Therefore, the alternative BIO-routes proposed, using biogas as source, could be considered attractive. The general comparison of the traditional route and the alternatives proposed is shown in Fig. 2.

Dry reforming of methane (DRM) can be used to produce syngas from biogas. This process, however, faces a series of disadvantages: it is an energy-intensive process (Bouchoul et al., 2021) and suffer for catalyst's deactivation. Despite the considerable positive environmental potentials, DRM cannot be considered an industrially mature process yet since the development of a robust catalyst is still a challenge (Abiev et al., 2020; Bouchoul et al., 2021; George et al., 2021). Even though, the incorporation of biogas-DRM in acetic acid route represents an innovative low-carbon path taking the edge over the traditional process in terms of sustainability. On the other hand, chemically and stoichiometrically, the direct, one-pot transformation of CH₄ and CO₂ into acetic acid (Eq. 1) is a very appealing atom-efficient process (BIO-Direct route). Nonetheless, this one-step process proposed is quite unfavourable thermodynamically (Liu et al., 2001; Tu et al., 2021).

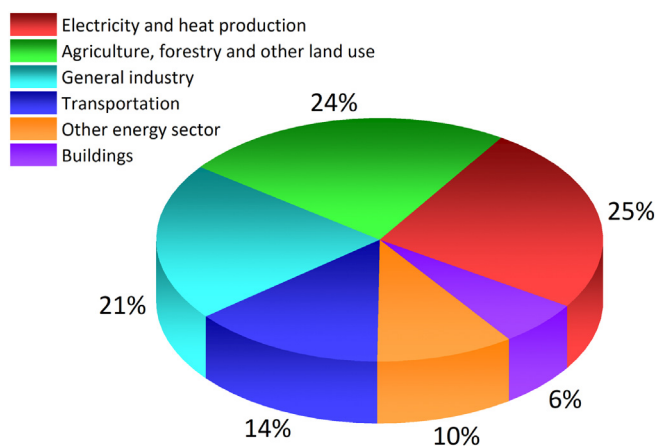
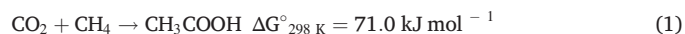


Fig. 1. Global GHG emissions by economic sector, based on the latest IPCC Fourth Assessment Report (2014).

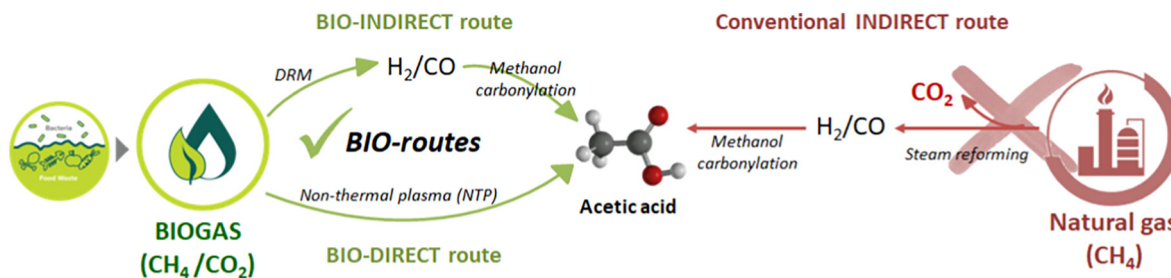


Fig. 2. Traditional acetic acid production (right-sided) versus alternative BIO-routes to acetic acid production from biogas (left-sided).

An ingenious way to overcome these thermodynamic limitations is the use of a non-conventional technology, i.e., non-thermal plasma (NTP). Currently, NTP is considered an enabling green technology for the near future of energy sector inasmuch as it may allow chemical processes to be based on renewable energy sources instead of fossil fuels (Abiev et al., 2020). Indeed, the combination of NTP and a robust catalyst, known as plasma-catalysis or hybrid plasma catalysis, offers a great potential to optimise reaction conditions for the production of acetic acid (Abiev et al., 2020; George et al., 2021; Li et al., 2020).

In this regard, this review frames the new potential opportunities emerged from this cutting-edge strategy herein proposed, the BIO-routes, in contrast to the current position of the chemical industry to produce acetic acid with a high greenhouse gases emission penalty. The historical advances of the industrial production of acetic acid are scrutinised to put in context the current situation. In opposition to this, the BIO-strategy is presented due to the increased environmental concern, focusing on the catalytic performance of the most recent, relevant lab-scale catalytic systems. Specifically, the most promising catalysts are revised in this review. As part of the BIO-strategy, the core of this review, non-thermal plasma is raised to be an enabling technology in order to produce acetic acid, reviewing the most innovative catalytic systems implemented up to now.

2. Acetic acid: conventional routes and market review

Prior to understanding the main chemical routes for synthesising acetic acid, it is relevant to comprehend the importance of this intermediate chemical compound in the chemical industry.

2.1. Applications insight and market overview

Acetic acid is considered a commodity chemical for a wide range of end-user industries (textile, fibre, pharma, foods, etc.) (Cheung et al., 2000; Deshmukh and Manyar, 2021). The broad spectrum of applications is outlined in Fig. 3. More than 65% of acetic acid production participates in the production of polymers derived from the vinyl acetate monomer (VAM) or cellulose acetate. Poly (vinyl acetate) produced is mainly used as a precursor for paints and coatings, or the production of plastics. VAM is one of the principal additives in the polymer industry, employed as an emulsifier, resin, or intermediate for surface coating, acrylic fibre and polymer wires production. On the other hand, cellulose acetate is used to produce acetate fibres (Budiman et al., 2016; Pal and Nayak, 2017). Another prominent application is the production of acetic anhydride (Cheung et al., 2000; Deshmukh and Manyar, 2021).

According to a recent study (Mordor Intelligence, 2020), the 2020 updated global market share by application shows that VAM is the main application of acetic acid, followed by terephthalic acid (TPA), acetate anhydride and acetate esters. On the other hand, the global demand for virgin acetic acid was estimated to be 16.1 million tonnes in 2020, and it is projected to reach 19.6 million tonnes by 2027. Global market analysis forecast a compound annual growth rate (CAGR) around 3% for the period 2020–2027 (IMARC Group, 2021; Zion Market Research, 2021).

The champion EU producer of acetic acid is BP, producing 2.5 million tonnes/year in multiple facilities worldwide. Other relevant producers are

BASF, Chiyoda, Celanese, Dow Chemical, INEOS, LyondellBasell and China Petrochemical (Budiman et al., 2016). All these players produce acetic acid based on different technologies, depending on the route followed. The conventional routes for acetic acid synthesis should therefore be reviewed.

2.2. Conventional routes for acetic acid production

Different chemical processes have been developed in order to produce acetic acid. Traditionally, thermocatalytic routes have been predominant in the chemical industry, prevailing methanol carbonylation (Cheung et al., 2000; Kalck et al., 2020). Nevertheless, there are other routes for large-scale production of acetic acid and are briefly discussed.

2.2.1. Oxidation of acetaldehyde

In this process, petroleum stock-derived acetaldehyde is oxidised to produce acetic acid in the presence of heterogeneous manganese or cobalt acetate catalysts (Eqs. 2 and 3). This process, whose yield exceeds 90%, was widely extended before the discovery of carbonylation of methanol. The use of an organo-mercury catalyst produced an enormous environmental impact due to the toxicity of this material, limiting this route to other alternatives (Pal and Nayak, 2017).



2.2.2. Oxidation of hydrocarbons

The direct synthesis of acetic acid by oxidation of hydrocarbons is recognised as a viable route. It is reported that approximately 9% of acetic acid produced worldwide is synthesised by the oxidation of hydrocarbons. Nevertheless, downstream separation is a complex and energy-consuming process due to its low selectivity. Despite that, direct oxidation processes have been commercialised, for instance, using naphtha, by BP, or using n-butane, by Celanese (Sano et al., 1999).

Direct liquid-phase catalytic oxidation of butane is one of the most preferred routes to acetic acid owing to the low cost of these hydrocarbons. This process undergoes at the critical point of butane (152 °C and 38 bar) (John Wiley & Sons, Inc., 2000), but it fails at given selectively acetic acid. Even though, it is an alluring process for some applications (Budiman et al., 2016; Cheung et al., 2000).

On the other hand, direct vapour-phase catalytic oxidation of ethylene has been of interest to produce acetic acid due to the small generation of non-toxic wastes. This one-step process comprises a single main reaction (Eq. 4) and two side reactions (Eqs. 5 and 6). Its energy-intensive purification is due to the large amount of water required and the number of by-products formed (Budiman et al., 2016). To solve the main problems, Showa Denko K.K. has patented a water-free process by combining a palladium-based catalyst with heteropolyacids. An energy-saving strategy by combining extraction and distillation is included in the intellectual property. This chemical process meets both sustainability requirements and competitiveness. It is reported that little non-toxic waste is generated

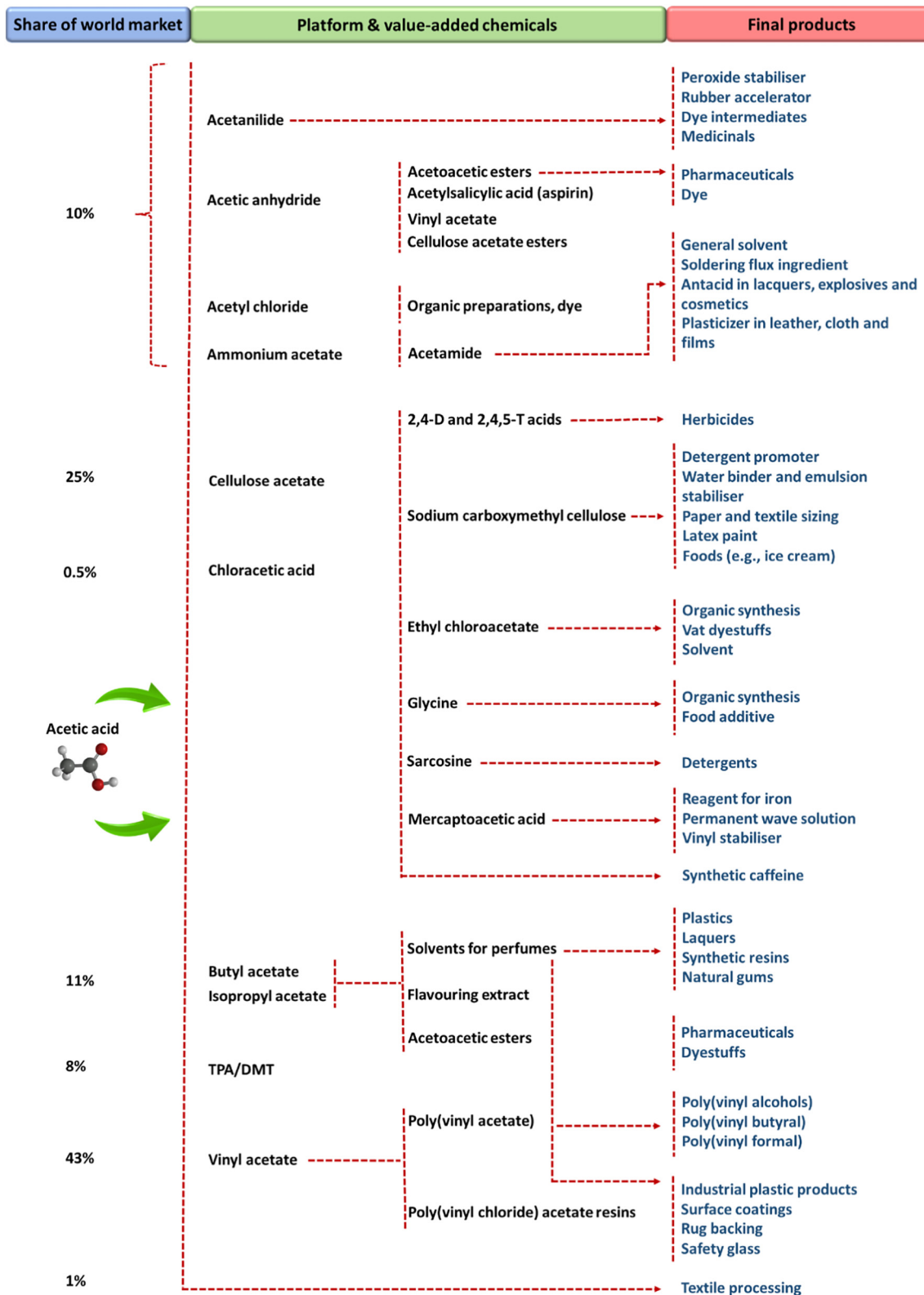
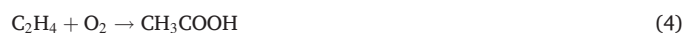


Fig. 3. Applications of acetic acid.
[Adapted with permission from Cheung et al., 2000. Copyright 2002, Wiley-VCH Verlag GmbH & Co. KGaA].

thanks to the high selectivity of the reaction, and small amounts of wastewater are produced. Another great advantage of this process is the use of standard materials since no corrosive compounds are treated except for acetic acid. This route is believed to be competitive with methanol

carbonylation for small plants (100–250 kT year⁻¹), subject to the prices of ethylene (Sano et al., 1999).





Another route is the partial oxidation of ethane (Eq. 7). Molybdenum-vanadium-based catalysts, at 220–300 °C and 12–15 bar, have extensively been researched (Pal and Nayak, 2017). In spite of the research progress, conversion and selectivity are constrained due to oxygen limits in the process for safety reasons, since oxygen should be kept below the explosion limit (Budiman et al., 2016; Cheung et al., 2000).



Despite some of these routes being interesting for acetic acid production, the market production, as mentioned before, is mainly focused on carbonylation of methanol, which represents approximately 80–90% of the total production (Shah, 2014).

2.2.3. Methanol carbonylation

The liquid-phase methanol carbonylation to acetic acid, an exothermic reaction, shown in Eq. 8, is performed using methanol with an excess of carbon monoxide, coming from syngas. Thermodynamically, this route yields acetic acid under ambient conditions. However, an increase in temperature is needed due to the process kinetics, which obliges the operation at medium-high pressures to get high yields.



Several homogeneous metal-organic complexes have been used industrially for the carbonylation of methanol, such as cobalt, rhodium, ruthenium or iridium-based homogeneous catalysts. Such materials operate at temperatures ranging 150–300 °C and pressures below 60 bar (Budiman et al., 2016; Cheung et al., 2000). In general, the presence of high concentrations of water is needed since the catalyst solubility is enhanced, but this situation also facilitates the side water-gas shift (WGS) reaction, which competes with the carbonylation, thus resulting in lower CO uptake for reaction of interest (Haynes, 2006).

Acetic acid was firstly commercialised via methanol carbonylation in 1960. BASF discovered that the presence of methyl iodide was necessary to convert methanol into acetic acid (Ludwigshafen and Friderich, 1957). In its absence, CO tends to insert in the O—H bond of methanol, instead of the C—O bond (Thomas, 2003). Eqs. 9, 10 and 11 show the main reaction steps in the process.



This first approach was improved by the Monsanto process (Schultz, 1973) and the Cativa process (David et al., 1997). Monsanto, in the middle 60s, improved BASF process, obtaining excellent acetic acid selectivity (99%) under milder conditions, around 30–60 bar and 150–200 °C. The Monsanto process involves the use of homogeneous methyl iodide-promoted rhodium-based catalyst in the system, which improves the catalytic activity obtained with the cobalt-based catalyst of BASF. In this process, the most energy-demanding step is the production of CO and H₂ (syngas), used as an intermediate (Thomas, 2003). This step has been traditionally accomplished via steam reforming of natural gas, leading to a heavy carbon fingerprint which is a major environmental burden. The catalytic reaction mechanism of Monsanto process was proposed to be composed by six cyclic steps, as depicted in Fig. 4. Within the six main steps, the oxidative and selective addition of methyl-iodide to the rhodium complex $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ (step 1) seemed to be the rate-determining step, which is consistent with the observed kinetics. This route operates under excess of water of 14–15 wt%, which is needed to (a) enhance the catalytic activity

and (b) maintain the stability of the Rh-based catalyst. Indeed, this optimum water concentration avoids the formation and accumulation of inactive $[\text{Rh}(\text{CO})_2\text{I}_4]^-$ from the unstable intermediate $[\text{Rh}(\text{CO})_2\text{I}_3\text{H}]^-$ and the posterior precipitation of inactive RhI_3 salts (Haynes, 2006; Kalck et al., 2020).

In the late 60s, Monsanto also discovered that iridium was an effective catalyst for methanol carbonylation (Paulik and Roth, 1968). However, this catalytic system was not commercially developed by BP until the early 1990s, under the name of the Cativa process. Iridium clusters act as an active centre using ruthenium species as promoters in the presence of methyl iodide (Ren et al., 2020). The main advantages of this process are its superior stability and the operation using a lower amount of water (~5 wt%) (Sunley and Watson, 2000; Tu et al., 2021). Indeed, compared to rhodium, iridium precipitation IrI_3 is less common due to the stronger metal-ligand bonding for the third-row metal, which inhibits CO loss from the Ir centre (Haynes, 2006). The added $[\text{Ru}(\text{CO})_3\text{I}_2]^-$ complex can react efficiently the iodide from $[\text{MeIr}(\text{CO})_2\text{I}_3]^-$ to fasten the carbonyl coordination step, enhancing the reaction of methyl acetate and hydrogen iodide to acetic acid and methyl iodide. Cativa process is considered a more efficient and greener process than the preceding Monsanto process (Kalck et al., 2020; Ren et al., 2020). In general, the chemistry of BASF, Monsanto and Cativa processes is reported to be similar since the catalyst is promoted by a halogen promoter, methyl iodide or iodide acid (Cheung et al., 2000).

Differently, Chiyoda/Universal Oil Products (UOP) and KBR have commercialised a process called Acetica process. Heterogenised homogeneous rhodium-based catalyst is used, showing high activity as well as long-term stability and insignificant rhodium leaching. The key to the improved features of this process is the use of a novel polymer resin, polyvinyl pyridine (PVP) resin, to immobilise the catalyst, which prevails and also facilitates the separation of the reaction mixture. It is reported that the catalyst activity is maintained after 7000 h and the water content is greatly reduced to 3–8 wt% (Haynes, 2006).

A simplified flowsheet example for the aforementioned processes commercialised by BASF, Monsanto, Cativa and Acetica can be observed in Fig. 5. These processes are designed in three main sections: a liquid-phase slurry reaction, a flash separation tank for the catalyst separation and a separation unit where pure acetic acid is finally obtained. The catalyst remains in the liquid phase and is recycled to the reactor. For all these processes, separation issues of homogeneous catalyst arise (Haynes, 2006; Thomas, 2003).

More recently, in 2010, BP patented a new multi-step vapour-phase process for acetic acid production at a large scale, the so-called SaaBre process. Using the new BP strategy, the only raw material of the process is syngas (Budiman et al., 2016; Deshmukh and Manyar, 2020), industrially produced by steam reforming of natural gas (Cheung et al., 2000). This three-step scheme resembles the one proposed elsewhere by Haldor-Topsøe (Joensen et al., 1997, 1998). The first step is a methanol synthesis by CO hydrogenation using syngas (Eq. 12), which can be further transformed into DME (Eq. 13). The second step consists of DME carbonylation (Eq. 14), obtaining methyl acetate (MA). Finally, intermediate methyl acetate is dehydrated and hydrolysed to an equal molar acetic acid and methanol (Eq. 15). The advantages reported by BP, compared with the other carbonylation routes, are the elimination of the homogeneous precious metal separation and, consequently, lower energy consumption and easier separation, lessening the environmental damage of the process (Budiman et al., 2016). Even though, continuous development of alternative routes, catalysts and strategies is needed in order to reduce the cost production at a large scale as well as the reduction of the environmental burden.



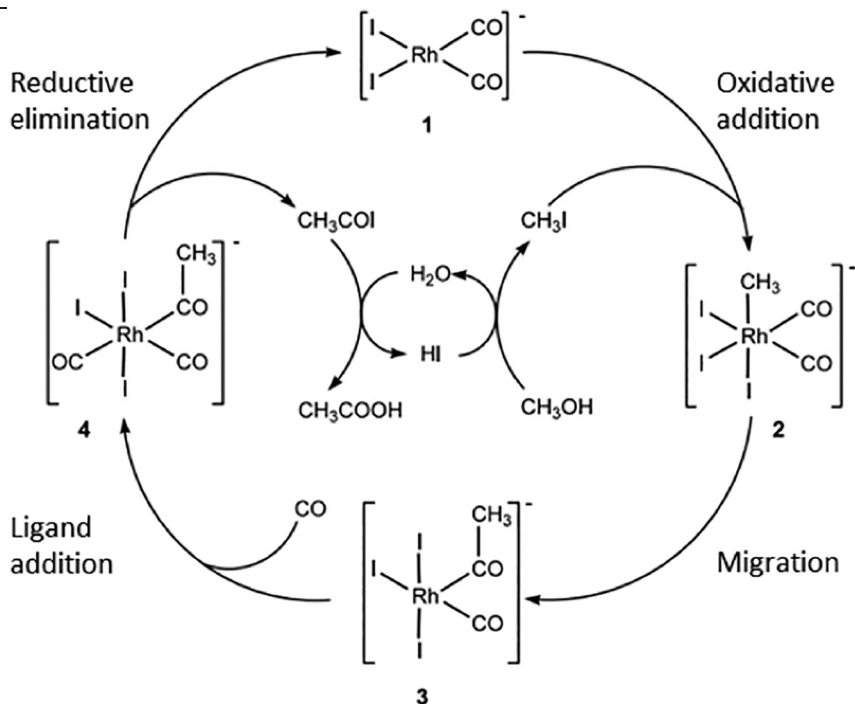


Fig. 4. Catalytic reaction mechanism proposed by Monsanto to produce acetic acid.

[Adapted with permission from Forster, D. Mechanistic Pathways in the Catalytic Carbonylation of Methanol by Rhodium and Iridium Complexes. In *Advances in Organometallic Chemistry*; Academic Press, 1979; Vol. 17, pp. 255–267. Copyright 1979, Elsevier].



The reaction conditions, catalysts and by-products generated in the main conventional routes presented herein can be consulted in Table 1 and Table 2. All the raw materials of these industrial reaction pathways for acetic acid production are derived from petroleum, such as methanol, acetaldehyde, ethylene, butane or syngas. In addition, direct discharges of chemical waste leads to severe environmental issues. Furthermore, most of the catalysts used in these routes are expensive and need continuous regeneration (Pal and Nayak, 2017). Owing to the high operation conditions and the amount of energy needed to synthesise acetic acid, alternatives need to be researched to achieve a novel, greener, environmentally-

friendly process by reducing the energy consumption and improve the integrity & safety of the process with milder conditions.

2.3. Research progress and alternative route proposed

Despite the high efficiency of the homogeneous methanol carbonylation, the issues abovementioned (ecological impact of wastewater discharges and separation) pose strong motivation to shift the research lines into the development of a new generation of catalysts for this process. The focus is on improving the performance of the existing catalysts by adding ligands or on devising new strategies to immobilise the homogeneous systems (Kalck et al., 2020; Ren et al., 2020). On the other hand, heterogenisation is also a direct research line to partially overcome these

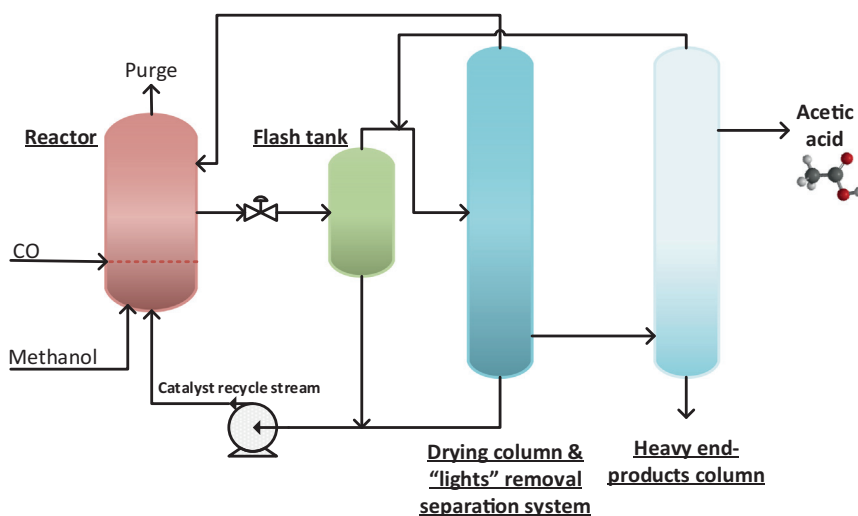


Fig. 5. Simplified process flow diagram (PFD) of a typical liquid-phase methanol carbonylation process for acetic acid production. [Adapted with permission from Haynes, 2006. Copyright 2006, Springer Nature].

Table 1

Key features of conventional oxidation catalytic routes for acetic acid production.

Process	Raw material	Catalyst	T (°C)	P (bar)	Yield (%)	Main by-products
Acetaldehyde oxidation	CH ₃ CHO, O ₂	Co, Mn or Cr-based	150	50–60	90–95	Formic acid, formaldehyde, ethyl or methyl acetate, ethylidene diacetate
Butane oxidation	C ₄ H ₁₀ , O ₂	Co or Mn-based	150–230	50–60	50	Acetone, formic or propionic acid or cracked HC
Ethylene oxidation	C ₂ H ₄ , O ₂	Pb, Pb–Pt or heteropolyacid Pd	160–210	7	87	Water, acetaldehyde or CO ₂
Ethane oxidation	C ₂ H ₆ , O ₂	Mo or V-based	220–300	12	<20	Water

problems. Even though, its potentiality lays on the simplification of the separation procedure and process intensification (Budiman et al., 2016; Tu et al., 2021).

Improvements in methanol carbonylation using heterogeneous catalysts are still under investigation. For instance, Ni et al. (2017) developed a selective, halide-free, noble-metal-free catalyst based on pyridine-modified H-mordenite zeolite for the direct synthesis of acetic acid on vapour phase. Their promising results showed methanol conversions up to 100% while selectivity towards acetic acid is 95% at 250 °C. A recent study by Qi et al. (2020) demonstrated that heterogeneous catalysts based on Rh–Re/SiO₂ are effective in gas-phase carbonylation of methanol. In this catalyst, two different phases of rhenium are found. Atomically-dispersed ReO₄ active sites enhance acetic acid selectivity since they promote CO insertion into the methoxy species, whereas ReO_x cluster promotes DME. However, the presence of dispersed Rh also formed Rh–ReO_x pair-sites which further promote the stable production of acetic acid up to 60 h. The volumetric reaction rate was comparable to the homogeneous processes. Interestingly, other bimetallic catalysts have also demonstrated to enhance the conversion and selectivity due to the synergic effect of both metals. On this premise, Zhang et al. (2020) developed Rh–Ru bimetallic catalyst with an outstanding performance. The mechanism of Rh(I)/Ru(III) for methanol carbonylation is similar to that of the Monsanto process. The methyl iodide oxidation (the rate-determining step) by the Rh(I)/Ru(III) bimetallic catalyst is reported to reduce the energy barrier by 23.88 kJ mol⁻¹. It was found that the 3D structure of Rh/Ru has a bridged dimer space structure which was responsible for the reduction of the energy barrier and increase of the catalyst stability. Differently, in a research line by Park et al. (Bae et al., 2015; Budiman et al., 2016), the synthesis of acetic acid using a series of heterogenised rhodium immobilised in 3-benzoyl pyridine (3BP) over a graphitic carbon nitride catalyst (Rh-3BP/g-C₃N₄) successfully achieved great performance for liquid-phase carbonylation of methanol at 40 bar and 135 °C. Very high conversions (>97%) and yields (75–93%) were obtained using a CO:methanol ratio of 1.5 due to the good dispersion of Rh-3BP complex on the high active surface of carbon nitride. Research is also focused on nickel, copper, gold, cobalt, iridium and ruthenium-based catalyst. However, these homogeneous and heterogeneous catalysts need to be further improved, in general, either in activity, selectivity and stability, to operate under the typical industrial conditions (Kalck et al., 2020; Ren et al., 2020).

On the other hand, other routes, e.g., the direct thermocatalytic transformation of syngas to acetic acid, have being studied. Based on premise, direct conversion of syngas to acetic acid is reported to be selective (67.5%) at extreme conditions of 480 bar and 220 °C using a combination of Ru–Co with promoters, e.g., Zr and Ti (Knifton, 1985). In addition, an unpromoted rhodium-based catalyst over NaY zeolite was used, achieving very low conversions of 1.2% and selectivity of 45–56% (Xu et al., 2000). Using Rh/SiO₂

catalyst, a selectivity of 74.8% to acetic acid and ethyl acetate was reported using H₂:CO ratio 2 at 30 bar and 220 °C, with a meaningless 0.5% conversion (Chen et al., 2006). This thermocatalytic approach does not seem to be the most adequate route due to the severe thermodynamic restrictions of the direct synthesis. Alternatively, the innovative and original route proposed using biogas as feedstock to generate acetic acid is attractive due to the renewable source consideration of biogas. In this approach, two noteworthy alternatives are set (Fig. 6):

- BIO-Direct route. Direct, one-pot production of acetic acid from biogas feedstock. This is a cutting-edge approach to generate acetic acid in one single step. The direct transformation of CO₂ and CH₄ into acetic acid is a 100% atom-efficient process that is thermodynamically unfavourable at ambient conditions. Nevertheless, using a non-equilibrium technology, i.e., NTP, this issue is overcome.
- BIO-Indirect route. Herein, via biogas dry reforming (DRM), syngas is generated from a renewable source. Syngas can be further used in another processes, e.g., methanol carbonylation or BP SaaBre process, lessening the environmental impact of these processes.

In this context, the next two sections present an overview of the state-of-the-art of the BIO-Indirect and BIO-Direct route to produce acetic.

3. BIO-Indirect approach

Alternatives to traditional synthesis of acetic acid are gaining ground due to in the shift in manufacturing practices towards a greener and more sustainable chemical industry. In this context, the proposed BIO-Indirect route to generate acetic acid seems in accordance with this current tendency. Compared to the conventional routes, two main characteristics are changed. Firstly, the use of a different feed. Conventional routes rely on petroleum-derived raw materials, which are known to suffer from a CO₂ penalty, whereas BIO-Indirect route proposes the use biogas. The use of a renewable source is empowered, thus preventing emission of GHGs to the atmosphere. (ii) What is more, CO₂ is partially used instead of being emitted. This strategy synergises bio-resource utilisation and CO₂ utilisation, promoting the circular carbon economy. This original approach is intended to minimise the environmental damage of this large-scale industrial process to achieve carbon neutrality.

Since dry reforming of methane (DRM) is the principal step in the BIO-Indirect route approach, recent tendencies using DRM need to be explored.

3.1. Biogas dry reforming

Dry reforming of methane (DRM), shown in Eq. 16, is a strongly endothermic reaction ($\Delta H^{\circ}_{298K} = 247.3 \text{ kJ mol}^{-1}$ & $\Delta G^{\circ}_{298K} = 170.0 \text{ kJ mol}^{-1}$). The forward reaction is favoured at low pressures, as dictated by

Table 2

Key features of methanol carbonylation routes for acetic acid production.

Process	Catalyst	T (°C)	P (bar)	Yield (%)	Main by-products
BASF	Homogeneous Co-based iodide promoted	230–250	60–80	90	Methane, acetaldehyde, ethanol, propionic acid, CO ₂ and ethers
Monsanto	Homogeneous Rh-based iodide promoted	150–200	30–60	99	Not significant reported
Cativa	Homogeneous Ir-based iodide promoted	190	28	>99	Not significant reported
Acetica	Heterogenized homogeneous Rh-based	160–200	30–60	99	Ester, ether and water

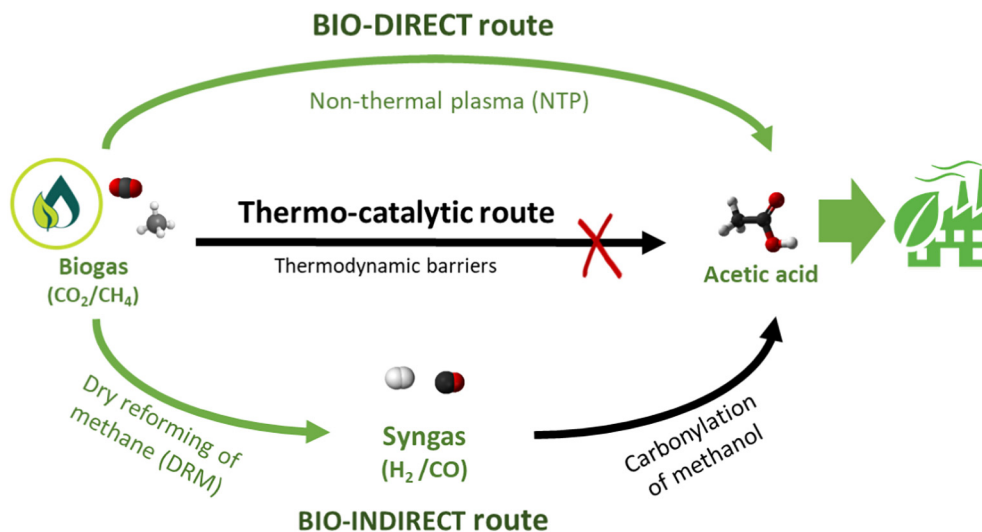


Fig. 6. Acetic acid BIO-routes approach.

stoichiometry. This reaction offers the advantage of using simultaneously two of the major GHG gases to produce syngas (Price et al., 2020).



As a co-reactant on DRM, CO₂ is used as a soft oxidant and can provide an extra carbon source for the conversion. Theoretically, this process generates syngas with a H₂/CO molar ratio ≤ 1, which is suitable for the further generation of oxygenates from syngas (Le Saché et al., 2018; Tu and Whitehead, 2012a). Furthermore, this chemical reaction takes place using biogas without previous separation of CO₂ in biogas feed. On the opposite, CO₂ can be added to the biogas if required (George et al., 2021).

CH₄, having a tetrahedral geometry with four strong C—H bonds (434 kJ mol⁻¹), is chemically more stable than CO₂. CO₂ is considered inert since of the nature of the C=O bond. Co-activation of CO₂ and CH₄, thus, requires high energy input to make the molecules chemically react. Hence, three main ways for the production of syngas using three technologies are presented in Fig. 7: a) thermocatalytic, b) photocatalytic and c) plasma-catalytic DRM (Liu et al., 2020).

3.2. Thermocatalytic DRM

In DRM, due to the endothermic nature and high stability of reactants, high temperatures are needed in order to achieve desirable conversion

levels and yields of syngas. Indeed, researchers conclude that the main reaction is thermodynamically favoured at temperatures above 700 °C (Aramouni et al., 2018; Bradford and Vannice, 1999; Wang et al., 1996). Nevertheless, at these high temperatures, the activity of the catalysts can be compromised due to (i) coke deposition and (ii) sintering, which blocks the access to the active sites (Le Saché et al., 2019; Tu and Whitehead, 2012b). Therefore, a suitable catalyst should be able to overcome deactivation whilst giving high stability and yields.

While performing DRM (Eq. 16), other side reactions can also occur. From all the potential side reactions reported in literature (Aramouni et al., 2018; Nikoo and Amin, 2011), the most representative are illustrated: reverse water-gas shift (RWGS) (Eq. 17); Bourdourad reaction (Eq. 18); CH₄ decomposition (Eq. 19); methanation (Eq. 20); CO and CO₂ reduction (Eqs. 21 and 22) may affect the distribution of products. The thermodynamics of the reactions involved in DRM are explained by Aramouni et al. (2018).

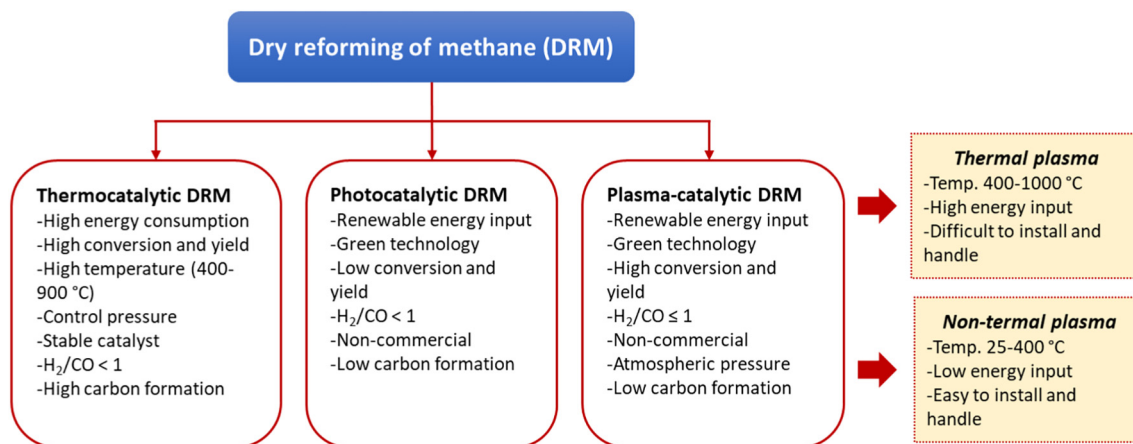
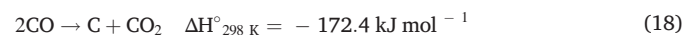
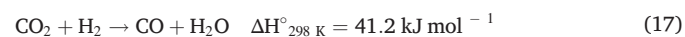
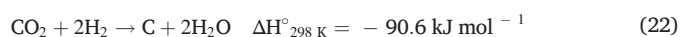
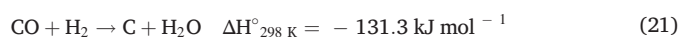


Fig. 7. DRM to syngas main approaches.

[Adapted with permission from Liu et al., 2020. Copyright 2020, American Chemical Society].



In general, noble metals are very active in DRM, exhibiting great performances compared to transition metals (Aramouni et al., 2018; Price et al., 2020). That is because these catalysts partially inhibit the formation of carbon due to the lower equilibrium constants for methane decomposition and reduced dissolution of carbon in their structure. The difference in the performance of noble metals and transition metals may also be ascribed to the ability of noble metals to better disperse on the supporting structures and retain a small particle size (North et al., 2019; Price et al., 2020). Interestingly, the activity of some noble metals was compared with Ni using a MgAl₂O₄ support, showing an activity order at 650 °C of Ru > Rh, Ni > Ir > Pt > Pd, whereas coke deposition behave differently: Ni > Pd > Ir > Pt > Ru, Rh (Rostrupnielsen and Hansen, 1993). Notwithstanding, their scarcity makes them uneconomical for large-scale industrial applications. Transition metals such as Ni, Co, Fe, Mo and Cu are preferred due to their comparable catalytic activity to noble metal, remaining an interesting option concerning manufacturing costs (Le Saché et al., 2021; Stroud et al., 2018). Nickel has especially been researched but, like other transition metal catalysts, suffers from severe coke deposition and sintering, which leads to rapid deactivation. For nickel and the rest of the metals, dispersion is a key parameter favouring stability. Metal particle size is also important to achieve a great catalytic activity and stability as well as avoiding excessive coke formation. Multiple strategies are put into practice in order to engineer brand-new, robust catalysts. The use of a combination of support structures (Al₂O₃-CeO₂, Al₂O₃-La₂O₅ or Al₂O₃-MgO) or other non-typical support structures (K₂O, ZrO₂, MoC, CaO) can upgrade the material. Most catalysts used in reforming industry are supported on aluminium oxides, which tends to catalyse carbon formation reactions, hence making mandatory catalyst's regeneration. The acid-basic properties of alumina are not favourable to CO₂ adsorption (Aramouni et al., 2018). Differently, the addition of promoters (lanthanide or alkali elements, e.g., La, K, Ca, Mg, Zr or Ce) may affect the electronic interactions, tuning the redox properties, stability or dispersion (Abdulrasheed et al., 2019; Jang et al., 2019). It is reported that small amounts of alkali and alkali earth elements minimise coke deposition. For instance, Alipour et al. (2014) has reported that adding small amounts of Ba and Ca over Ni/γ-Al₂O₃ enhances coke resistance due to interaction between the active phase and the support, leading to changes of the basic properties of the catalyst and the adsorption of CO₂. In addition, bimetallic systems (Ni—Co, Ni—Pt, Ni—Mo, Ni—Fe, Co—Mo, etc.) are being explored due to the synergy between two different metals, which provides the ability to fine-tune the properties of the active phases. The combination of transition metals or transition-noble metals seems to be encouraging, demonstrating enhanced activity and stability (Abiev et al., 2020; Yentekakis et al., 2021). Apart from conventional supported-based catalyst formulations, the use of special structures (e.g., core-yolk (Li et al., 2014), sandwich (Zhao et al., 2018), tubular (Coelho et al., 2016), mesoporous (Rodriguez-Gomez et al., 2018), perovskites, fluorites, pyrochlores (Le Saché et al., 2018), hexaaluminates (Gardner et al., 2013) and hydrotalcite (Debek et al., 2016)) are being investigated as catalytic systems owing to their particular properties, which can enhance the performance of DRM (Abdulrasheed et al., 2019; Bhattar et al., 2021). Some literature reviews are highlighted about the most recent advances (Abdulrasheed et al., 2019; Jang et al., 2019; le Saché and Reina, 2022; Yentekakis et al., 2021).

Even though, further investigations are needed in order to solve the shortcomings of the thermocatalytic DRM. Alternative methods, i.e., photo-assisted catalysis and NTP catalysis, are a good choice to promote syngas production while improving the sustainability of the process (Chung et al., 2018).

3.3. Photocatalytic DRM

Harnessing solar energy to enable chemical transformations using photocatalysis is an auspicious strategy to produce value-added products (Muhammad et al., 2020). From the thermodynamic perspective, the use of photo-technology activates CO₂ and CH₄ to generate products. Using UV photo-energy, thermodynamic limitations of unfavourable endothermic reactions can be surpassed at lower temperatures (Shi et al., 2004; Tahir et al., 2015; Yuliati et al., 2008).

In this scenario, photo-assisted DRM has come to the fore. The main advantages of photocatalytic CO₂/CH₄ conversion are: (i) the combination of solar energy utilisation and recycling of GHG emissions to value-added products, (ii) low operating temperatures and, consequently, and (iii) the mild, safer operation (Chung et al., 2018; Tahir et al., 2015). The utilisation of light energy and conversion efficiency is primarily determined by the photocatalyst used, which is the core component of a photocatalytic process. The development of energy-active, stable, cheap photocatalysts is demanded (Muhammad et al., 2020; Wang et al., 2021; Yuliati et al., 2008). Conventional photocatalysis takes place at the fluid-solid interface, and the light intensity decreases along with the thickness of the photocatalytic layer. Hence, the surface area and the capability to capture the sunlight are key parameters in order to enhance the kinetics and performance of the catalysts (Atanda, 2021; Cho et al., 2020).

Generally, in the field of photocatalysis, semiconductors are the state-of-the-art catalysts since these materials are prone to capture sunlight to generate the energy to effectively activate the reactants, in this case CO₂ and CH₄ (Cho et al., 2020). In this context, several semiconductors can be used as photocatalysts for biogas upgrading, e.g., TiO₂, ZrO₂, CdS, ZnO, NbO₅ or CeO₂ (Kulandaivalu et al., 2020). Bimetallic oxides are also under scrutiny, but more research is needed (Zhao et al., 2020). Among all the semiconductor available, titanium dioxide (TiO₂) is the champion photocatalytic material due to its noteworthy properties. Takami et al. (2019) studied various metallic catalysts over different supporting structures at a temperature of 200 °C. Ni/Al₂O₃ showed the highest activity over the other studied systems, Ni/Ga₂O₃ and Ni/TiO₂. Metallic Ni was found to be essential in order to achieve the high activity reported to generate syngas due to the plasmonic excitation of Ni active sites. Conversions of 18% and 17.2% were found for CO₂ and CH₄. Besides, different structures are being studied in photocatalytic DRM systems. A promising study by Muhammad et al. (2020) focused on graphitic carbon nitride nanotubes modified with lanthanum (La/g-CNT). Interestingly, experiments proved effective CO₂ and CH₄ conversion over this catalyst under visible light. The enhancement of the photo-activity reported was due to the efficient transference of electrons over the 1D structure and the separation of charge carriers of La over the supporting g-C₃N₄ structure. In another study, the improvement of H₂/CO ratio was reported using Ni/Ga₂O₃ using photo-assisted catalysis (Rao et al., 2021). The light irradiation provided by a 300 W Xenon lamp improve the H₂/CO ratio from 0.55 to 0.94 while restraining RWGS reaction. The light irradiation boosted the direction of electron transfer to be reversed from Ga₂O₃ to Ni amid the synthesis of H₂. Consequently, more hot electrons from the electronic interband transition of Ni simultaneously stimulated the dehydrogenation of CH₄ and the posterior desorption and formation of H₂. Differently, Chung et al. (2018) assessed a perovskite-type photocatalyst to study its effectiveness. In this study, the combination of plasma-assisted and photo-assisted DRM was overviewed, reporting a promising synergy towards conversion. Plasma promoted photocatalytic activity by (i) reducing the metal oxide cluster size, (ii) increasing the specific active surface area and (iii) the lifetime of the electron-hole pair.

Although photocatalysis is currently being investigated, some drawbacks hinder its potential owing to its low conversion and low solar energy utilisation. Despite all the current efforts, industrial applications using photocatalytic technology are far from a realistic take-off in the short-term. An alternative promising technology is NTP catalytic DRM, which may overcome some major concerns of photocatalysis technology (Abiev et al., 2020).

3.4. Plasma-catalytic DRM

Plasma-assisted technology can be classified as: a) thermal plasma (>400 °C) and b) non-thermal plasma (NTP) or “cold” plasma (≤ 400 °C). The non-equilibrium characteristics of NTP are appealing due to its capability to overcome thermodynamic barriers in chemical reactions, allowing the reaction to take place at ambient conditions of temperature and pressure (Gao et al., 2021; Tu et al., 2019). Non-equilibrium chemistry using NTP is an emerging trend well received by academics and industrialists as an encouraging approach towards the conversion of CO₂ and CH₄ to value-added products (Bogaerts and Neyts, 2018). The energy density of NTP opens an efficient energy transfer window to internal excitation and ionisation since no heating is needed, lowering the energetic cost (Gao et al., 2021; Reina et al., 2021). In addition, no starting delay occurs due to the instantaneous energy transfer. Other advantages of NTP technology are worth noting: ease of installation, compactness and high operation flexibility (Cheng et al., 2020; George et al., 2021; Tu and Whitehead, 2012a).

NTP can be simply generated by applying an external electric field (ideally supplied by a renewable source), between two electrodes within a volume or flow of gas. Among all the configurations available, dielectric barrier discharge (DBD) configuration is preferred in DRM due to its simplicity, reliability, simple design and feasibility for industrial upscaling. A typical DBD reactor is an insulating plate/tube made of a dielectric material, such as quartz, alumina, silica glass, ceramic or polymer layer, which separates the two asymmetrically positioned electrodes of the reactor (Khoja et al., 2019a; Tu et al., 2019). The space between the two electrodes is known as the discharge gap, and this spacing/chamber between the two electrodes typically varies from 0.1 mm to cm, depending on the voltage applied, the gas flow and the use. Normally, the catalyst is placed within this chamber to enhance the effect of the plasma. In order to drive a typical DBD reactor, AC sinusoidal voltage from 1 to 30 kV and a frequency lower than 500 kHz are required. In particular, for DBD gas processing, a frequency lower than 20 kHz is used to favour the process since it can hinder the current transportation (Khoja et al., 2019a). The typical energy input of DBD, 1–10 eV, is adequate to activate CO₂ and CH₄ molecules into reactive species which can initiate the desired chemical reactions. The plasma generated in DBD is non-uniform, consisted of many micro-discharges or filaments which extend along the discharge gap, covering the whole surface of the insulating dielectric material (Li et al., 2020).

3.4.1. Hybrid NTP DRM

Plasma and catalysts have independent effects on the reaction. While the catalyst main focus is to boost the kinetics by reducing the activation barrier, the plasma induces a strong electric field, exciting the gases presented and creating a variety of reactive species. Coupling plasma and catalysts in the same reactor is not trivial, but it allows a degree of control over the selectivity and distribution of desired products (Khoja et al., 2019a; Zeng et al., 2018). Despite its complexity, the potential of this interaction is promising, allowing to overcome thermodynamic barriers and creates a synergy resulted from the catalyst-plasma interaction. Physical and chemical interaction effects are usually interconnected and, due to the complex cooperative plasma-catalyst mechanisms, cannot be utterly distinguished (Khoja et al., 2019a; Puliyalil et al., 2018). Some of the synergistic effects which may appear are briefly summarised in Fig. 8(a), showcasing the effect of NTP on Cu-Ni/Al₂O₃ catalyst (Zhang et al., 2010). When integrating plasma and catalyst, conversion is highly improved. The synergistic effect of plasma and catalyst in the performance can be observed in Fig. 8(b). Catalyst alters plasma properties by enhancing the electric field within the discharge region, improving the discharge if compared to unpacked reactors or creating micro-discharges near the pores which can boost the performance of the reaction. On the other hand, plasma induces multiple effects such as new chemical pathways, lower activation energies, changes in the concentration of active species and active hot spots due to micro-discharges which can improve the performance (George et al., 2021; Zhang et al., 2010).

Despite the advantages of this technology, a few gaps may arise during the use of this technology (with or without catalyst) for DRM (Khoja et al., 2019a; Puliyalil et al., 2018):

- Dissipation of power and carbon deposition. Side reactions still take place and may lower the efficiency. Catalysts should be employed to avoid carbon formation and selectively achieve desired products, but coke formation is not completely eliminated.
- DBD reactor configuration. Some key parameters related to the geometry and engineering parameters are not fully controlled (e.g., discharge gap, catalyst volume, electrode morphology, reactor configuration, dielectric materials, discharge characteristics).
- The interaction and underlying mechanisms are not completely understood owing to the complex physicochemical interactions of plasma and the catalyst.

It should be noted that many of the studies rely on a non-systematically variable selection. Very few systematic studies have been conducted to analyse the influence of the reactor geometry on the processing of reactants of NTP DBD for DRM (Khoja et al., 2019a). For instance, products distribution under DBD reactor is more complex due to the interactions between the catalyst and plasma technology, as explained before, and some parameters in DBD are influenced by these variables. The optimisation of these operation parameters may lead to a desired distribution of products. Therefore, it is essential to understand the effect on the performance in the reactor (Zhang et al., 2003).

Regarding the catalyst in the process, nickel is broadly used as active phase for NTP-catalysis processes. Again, it is widely considered due to its high availability and price when compared to noble metal catalysts. Common supports for Ni are Al₂O₃, La₂O₃, MgO, AC, SiO₂, ZrO₂ and multi-elements supports (Gao et al., 2021). A recent study by Bouchoul et al. (2021) was developed in order to assess the influence of the metal oxide nature on the catalysts' performance. At ambient conditions, it was found a negative linear correlation between the dielectric constant/permittivity and the CO₂ conversion, affecting the conversion (Fig. 9). Interestingly, for MgO catalyst, the higher the temperature in the system, the lower oxygenates were selectively obtain in the system.

In a study by Khoja et al. (2018), performed under cold plasma, a Ni/ γ -Al₂O₃-MgO was investigated. Interesting conversions were achieved, respectively, with a syngas ratio of around 1. The RWGS reaction was controlled during 12 h and synergetic effects were observed due to the better energy efficiency combining the two support structures. Strong basic sites between Ni cluster and the support were discovered to enhance the chemisorption and activation of the reactant gases, resulting in the more effective dissociation of CH₄. Another study by Khoja et al. (2019b) reviewed the performance of a Ni/La₂O₃-MgAl₂O₄ catalyst at 350 °C under plasma conditions, further improving the conversion of CH₄ and CO₂ to 86% and 84.5%, respectively. Stability and resistance to coke deposition were encouraging during time on-stream (TOS) of 15 h due to the formation of an intermediate La₂O₂CO₃ from CO₂ chemisorption over La₂O₃, which enhance the regeneration of La₂O₃ by inducing the reaction of the deposited carbon. Differently, Wang et al. (2019) got an excellent synergy on hybrid NTP DRM at 270 °C with a higher energy efficiency, 0.52 mmol kJ⁻¹, compared to typical 0.1–0.2 of previous literature, by using Ni supported on activated carbon. The mesoporous structure enhances the performance. Yields for H₂ were up to 27.9%. Similarly, the addition of cerium to Ni/AC was studied (Wang et al., 2020). The activity of NiCe_xC with 1 wt% Ce was noteworthy improved if compared to the unpromoted Ni/AC (Wang et al., 2019). The catalyst had a larger pore diameter and smaller Ni particle size. In addition, the increase in basic sites was observed, remarkably enhancing the activity of the catalyst and achieving a 50% H₂ selectivity.

Additionally, bimetallic systems were also investigated in NTP. For example, Ray et al. (2018) researched both Ni and Ni–Mn over γ -Al₂O₃. It was found that the conversions followed a different trend for CO₂ and CH₄. Particularly, CH₄ conversion trend was: Ni-Mn/ γ -Al₂O₃ > Ni/ γ -Al₂O₃ > NTP-DBD alone. Differently, CO₂ conversion followed the trend: Ni/ γ -Al₂O₃ > Ni-Mn/ γ -Al₂O₃ > NTP-DBD alone. In addition, very good

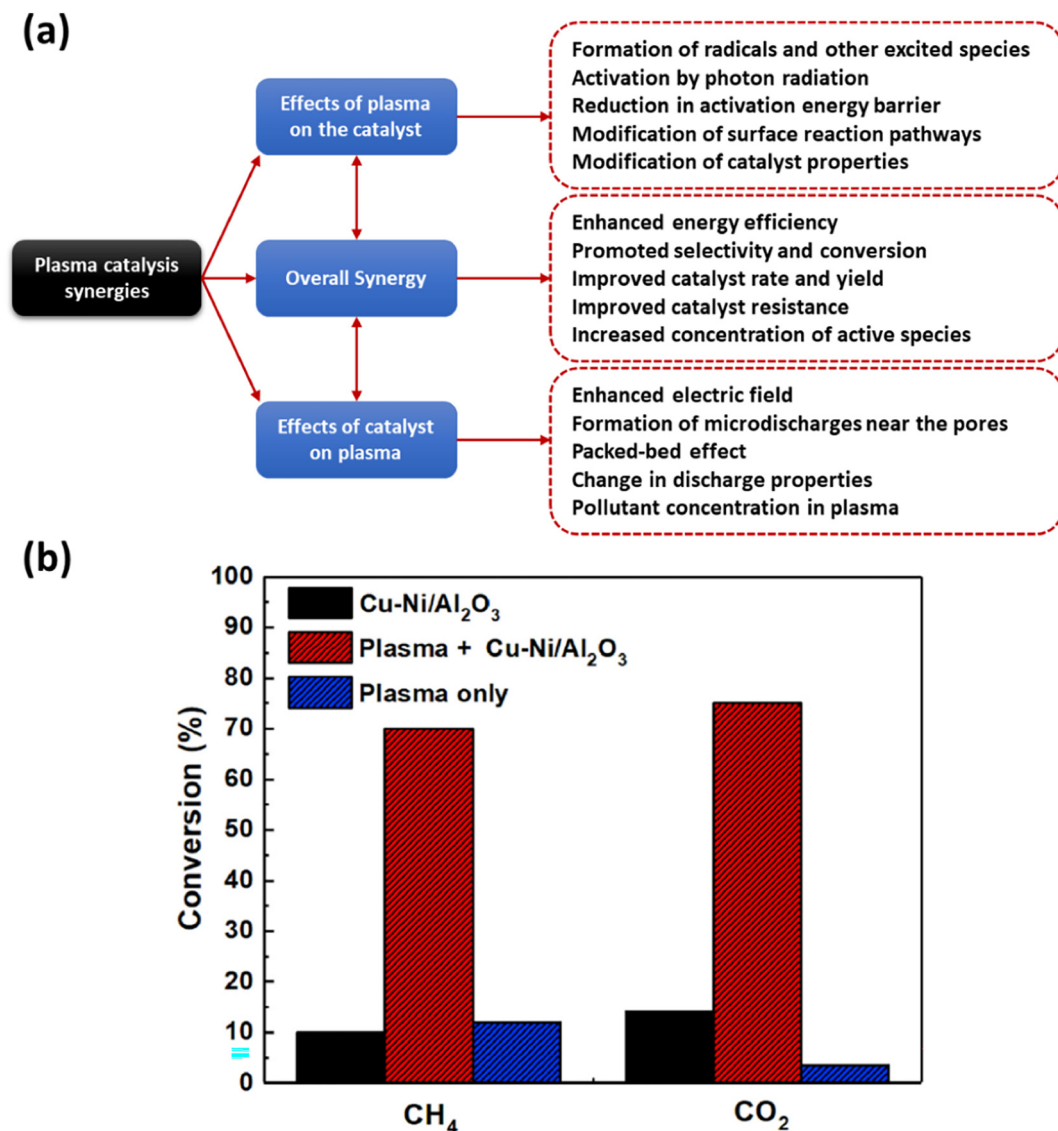


Fig. 8. a) Summary of the synergy generated in plasma catalysis from plasma-catalyst interaction (Gao et al., 2021; George et al., 2021) and b) synergistic effect in an experiment performed by Zhang et al. (2010) using Ni-Cu/Al₂O₃ at 450 °C. [Reprinted with permission from Zhang et al., 2010. Copyright 2010, Elsevier].

energy efficiencies of 2.76 mmol kJ⁻¹ were found. The superior resistance of the catalyst towards carbon deposition was confirmed in TGA. Ni-X/Al₂O₃ (X = K, Ce or Mg) catalysts, on the other hand, were studied (Zeng et al., 2018), at 160 °C. It was found that the addition of these promoters enhanced the conversion of CH₄, yield of H₂ and energy efficiency in the NTP process. Specifically, Ni-K/Al₂O₃ showed the best performance, obtaining a conversion of CO₂ of 22.8% and CH₄ of 31.6%. The presence of K in the system enhanced the acidity of the promoted catalyst, suggesting that the acid sites on the surface contribute to the activation of CH₄ in the process. Curiously, the effect of the promoters on the thermocatalytic process was reported different when compared to NTP DRM in terms of conversion levels. Recently, Tao et al. (2020) studied the effect of discharge gap, discharge length and catalyst performances of hydrotalcite-like materials tested (NiMgAlCe-LDHs). A NiMgAlCe hydrotalcite was studied for NTP DRM, studying the effect of different composition ratios of the hydrotalcite and other geometric factors of the reactor. Optimum conversions of 22.5% and 36.1% for CO₂ and CH₄ were achieved at 2 mm. The addition of a catalyst enhanced the discharge effect and lowered the discharge voltage. In addition, the state of discharge was reported to change from filament alone discharge to filament and surface discharge, increasing the total active area.

Recently, different structures studied for DBD DRM MgO- and CeO₂-promoted Ni/γ-Al₂O₃ catalyst were tested by Ray et al. (2020), finding an interesting conversion of 35% for CO₂ and 13% for CH₄ using Ni/MgO-Al₂O₃. On the opposite, Ni/CeO₂-Al₂O₃ offered the highest selectivity (68%) of CO due to the oxygen buffer property of CeO₂, and it showed more carbon resistance compared to the promoted MgO catalyst.

Contrarywise, the use of MOF structures was also studied by Vakili et al. (2020). In particular, platinum UiO-67 MOFs were studied due to the good performance of platinum nanoparticles in thermocatalytic DRM. Indeed, using NTP conditions, it was observed an enhancement of the surface reactions, displacing the production and selectivity of C₂ & C₃ hydrocarbons. The highly porous structure of the MOF improved the plasma generation, thus favouring the formation of filamentary micro-discharges on the surface. As a result, conversion, energy efficiency and H₂/CO ratio were improved.

Compared to the enormous efforts to improve NTP DRM to generate syngas, limited consideration has been put on the direct conversion of CH₄ and CO₂ into liquid oxygenates using plasma catalysis. Truly, the direct generation of liquid oxygenates and, more specifically, acetic acid, has not studied thoroughly. Some studies (Liu et al., 2020; Wang et al., 2017b) have demonstrated that the selective synthesis of oxygenates from CO₂ and CH₄

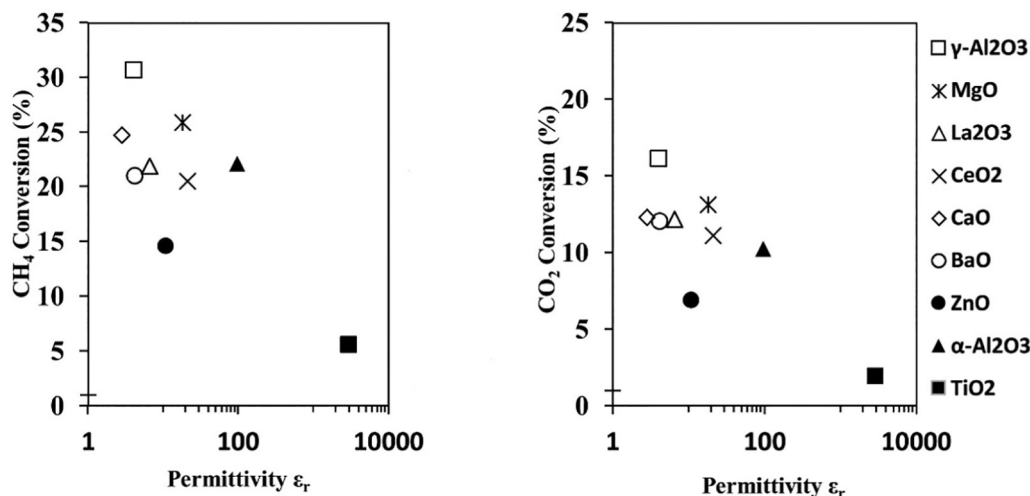


Fig. 9. Correlation between dielectric properties and conversion in NTP DRM using different metal oxides as supporting material. [Reprinted with permission from Bouchoul et al., 2021. Copyright 2021, Elsevier].

using NTP is viable, although the catalytic plasma activation is still in an early stage (Liu et al., 2020). The strategy herein presented as BIO-Direct offer an attractive approach to acetic acid.

4. BIO-Direct approach

The direct transformation of CO_2 and CH_4 into acetic acid is pursued in the BIO-Direct route. This atom-efficient reaction (Eq. 1), however, faces thermodynamic limitations ($\Delta G^\circ_{298\text{K}} = 71.0 \text{ kJ mol}^{-1}$). As it can be observed in Fig. 10, the equilibrium amount of direct acetic acid formation increases with temperature. At 1 bar pressure, the equilibrium yield of acetic acid is close to 0, due to the mentioned thermodynamic restrictions. When the pressure is increased to 30 bar, the yield towards acetic acid is improved, reaching an optimum around 300 °C of 0.05, which is still quite low (Tu et al., 2021). This was confirmed by (Huang et al., 2001), who pioneeringly studied the viability of the direct thermal conversion of CH_4/CO_2 gases over Cu—Co-based catalysts. Experimental results confirmed that various oxygenates were produced, such as alcohols, aldehydes, ketones and carboxylic acids, although at very low rates.

Conventionally, high-temperature systems are used in order to activate these molecules to make them react owing to the highly-stable $\text{C}=\text{O}$ ($E_a = 0.83 \text{ eV}$) and $\text{C}-\text{H}$ ($E_a = 1.43 \text{ eV}$) bonds (Guharoy et al., 2018). At those conditions, the direct production of oxygenates is inhibited since they are not stable when an oxidant is present in the system. Therefore, the use of

a thermodynamic-limiting approach for the one-pot conversion to acetic acid from biogas is a conceptually mistaken research approach for industrial purposes, since extreme temperature and pressure conditions are needed, hindering the potential of this interesting idea. To overcome this barrier imposed by thermodynamic, a non-traditional approach using the external energy of NTP is proposed to break the equilibrium limitations, promoting acceptable acetic acid yields. Indeed, NTP or “cold” plasma provides a highly reactive environment, being a firm candidate for the conversion of CH_4 and CO_2 to liquid oxygenates and acetic acid (Puliyalil et al., 2018; Tu et al., 2021). Hybrid plasma-assisted can improve the activity, selectivity and efficiency in the system, increasing the competitiveness of this non-traditional technology. In this sense, BIO-Direct strategy is deemed a more ambitious scheme compared to the BIO-Indirect route, representing a one-pot process for biogas conversion to acetic acid ruling out energy and carbon-intensive intermediate steps. Technology scaling-up in this case is supposed to relieve most of the environmental burden by a new, original and simpler process approach.

4.1. State-of-the-art of plasma-assisted acetic acid production

Unlike NTP DRM to syngas, the synthesis of liquid oxygenates directly from biogas has scarcely been studied. Only a few studies have focused on this innovative route. In a pioneering study by Zou et al. (2003), starch-enhanced synthesis of oxygenates was validated at 70 °C using NTP

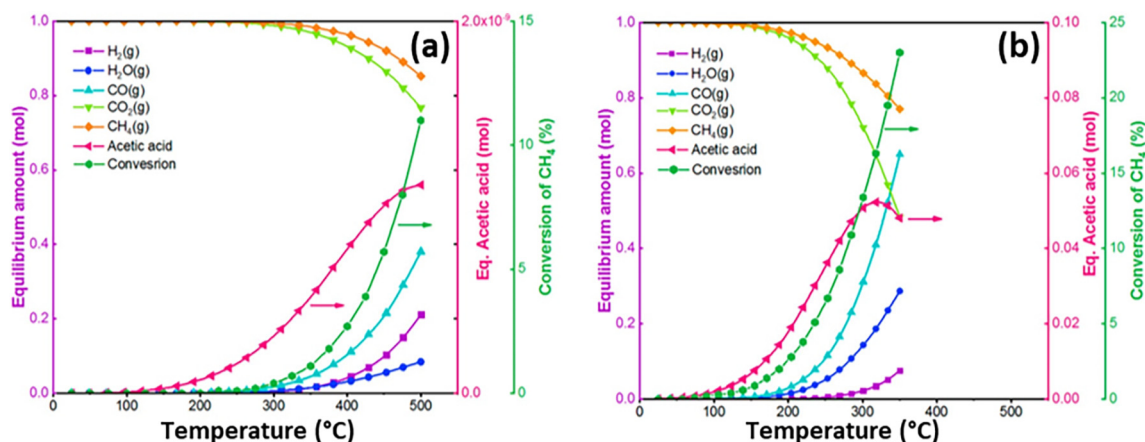


Fig. 10. Equilibrium composition for 1:1 CH_4/CO_2 molar feed as a function of temperature at (a) 1 bar and (b) 30 bar. [Reprinted with permission from Tu et al., 2021. Copyright 2021, American Chemical Society].

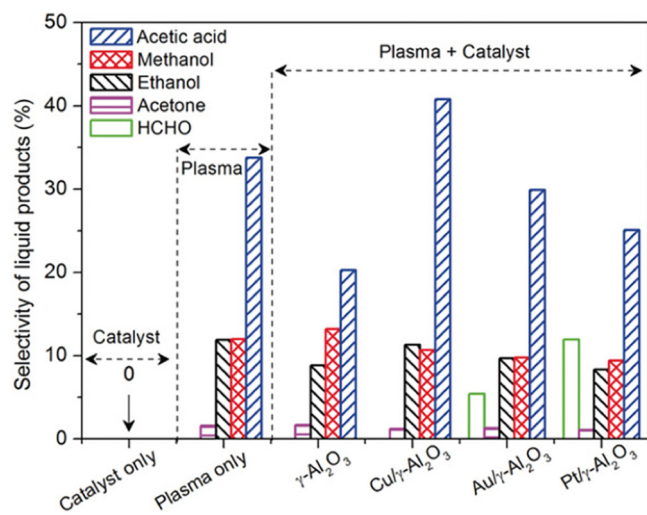


Fig. 11. Selectivity of oxygenates using five different configurations in NTP. [Reprinted with permission from Wang et al., 2017b. Copyright 2017, John Wiley & Sons].

in a DBD reactor. The use of starch as a precursor inhibited the production of light hydrocarbons, significantly improving the selectivity to oxygenates. It was found that the starch partially decomposed and hydrolysed, creating a favourable environment for oxygenates production. A systematic study on feed concentration was performed, obtaining selectivity between 10 and 41% towards oxygenates, remarking an optimum of 11.2% selectivity towards acetic acid using a feed of 69.3:30.7 CH₄:CO₂. The direct conversion of CO₂ and CH₄ to acetic acid was experimentally proved, resulting in commendable conversion levels of 17.5% and 24.7%, respectively.

In another ground-breaking study by Xu's team at Liverpool University (Wang et al., 2017a), a single-step catalytic process using NTP was conducted for direct acetic acid synthesis. They demonstrate a unique route for direct, one-step reforming of CO₂ and CH₄. Different catalysts were used (Cu, Au and Pt) supported on γ-Al₂O₃, at ambient conditions. For CH₄/CO₂ feed ratio of 1, total selectivity for liquid oxygenates (acetic acid, methanol, ethanol and acetone) was higher than 60% with moderate conversion levels of 16.2% and 7.6% of CH₄ and CO₂, respectively, using Cu/γ-Al₂O₃. Interestingly, acetic acid was the major product, as observed in Fig. 11, obtaining a selectivity of 40.2% for the Cu-based catalyst. So far, this is one of the highest values obtained for acetic production via one-pot plasma catalysis route. Based on the analysis of the liquid and gas phase products, as well as the optical emission spectroscopy (OES) results, radicals CO, CH₃ and OH are the key species in order to obtain these good results in the system. Indeed, it was demonstrated that the coupling of methyl radical (–CH₃) and carboxyl radical (–COOH), formed from CO + OH, was more favourable to form CH₃COOH, as reported in some DFT studies (Wang et al., 2004; Zhang et al., 2012). It was suggested that the oxygen adsorption energy (ΔE_O), i.e., the strength of the bond of the intermediates to the catalyst surface, was a good activity descriptor of the product generation.

Two other studies by Liu et al. (2001) and Li et al. (2002) focused on the production of oxygenates using DBD technology without the addition of a catalyst. The first study achieved an optimum selectivity of 5.3% to acetic acid at the feed ratio of 67.4:32.6 CH₄:CO₂, whereas C₂ and C₃ hydrocarbons were also synthesised in a high proportion (21.4%). The discharge power was 65 W, with a discharge gap of 1.1 mm and ambient conditions. Herein, the mechanistic route proposed is again the coupling of methyl (CH₃) radical and carboxyl (COOH) radical but differently, formed via CO₂ + H (Wang et al., 2003), stating that acidic environments tend to generate –COOH radicals from CO₂. The second study, on the other hand, using a discharge gap of 1.1 mm and higher discharge power, a selectivity of 5.7%

to acetic acid was obtained, the highest in the liquid phase. After-glow zones favoured acetic acid production, whereas the wider gap, 1.8 mm, favoured the formation of alcohols. Here, it is reported that the production of oxygenates took a large number of hydrogen atoms, hence declining the H₂ produced. Interestingly, ethanol production was higher than methanol, and acetic acid generation was greatly superior than formic acid. It was then suggested that C₂ oxygenates were more prone to be formed due to the C–C interaction with one carbon from CO₂ species and the other from CH₄ species. Additionally, in the same context of plasma alone reaction (Zhang et al., 2003), a study reported 5.2% selectivity of acetic acid using similar conditions as previous studies.

In a recent study by Li et al. (2020), Co and Fe-based catalysts were used to directly synthesise liquid oxygenates from a mixture of CO₂ and CH₄. These two metals were impregnated on a SiO₂ aerogel as support. An optimum of 17.9% of selectivity towards acetic acid was obtained using Co/SiO₂, while the rest of the oxygenates in the mixture added up to 40%. The conversion reported was 51.2% for CH₄ and 36.2% for CO₂ due to the high sorption capacity of the catalyst, which favoured the formation of liquid compounds. Conditions remained constant, 55–65 °C and 1 bar, and the discharge power varied from 7 to 10 W using a discharge gap of 1 mm. It is proposed that the highly active O* radical may play a critical role in the production of oxygenates without catalyst in the reaction. On the other hand, a sensitivity analysis was performed to study the influence of the feed composition. The maximum selectivity towards acetic acid was 20.7% using Co/SiO₂ and, surprisingly, 31.0% using Fe/SiO₂ using a CO₂:CH₄ feed ratio of 1:2. The authors suggest that (i) the alteration of the discharge behaviour on the catalyst, (ii) the strong sorption behaviour of the mesoporous structure of the SiO₂ aerogel (which inhibited the decomposition of CH_xO, the precursor of liquid oxygenates) and (iii) the good dispersion of Co and Fe (which are widely used in Fischer–Tropsch and CO₂ hydrogenation processes) enhanced the production of methanol and acetic acid.

The small addition of water in the reaction has been investigated. In a study by Gelves et al. (2019), the effect of using liquid water film in the production of oxygenates was researched. It was observed an enhancement of the selectivity towards oxygenates when increasing the water flow rate from 0 to 0.1 mL min^{−1}, obtaining a selectivity of oxygenates of 21.2%, mainly methanol (10.3%), formic acid (4.0%) and acetic acid (3.1%). In this case, the presence of reactive species resulted from the decomposition of water (–OH, –O and –H) are thought to be responsible for this increase of selectivity. Furthermore, the humidity in the process modified the discharge behaviour and the presence of a water film favoured the production of oxygenates since they condense and dissolve, thus (i) enhancing their formation rate and (ii) preventing them from decomposition. The presence of water was also studied by Rahmani et al. (2021), in this case in the form of steam. The presence of water in the system improved the conversion and energy efficiency. At the lowest amount of steam, the selectivity of acetic acid was maximum, a noteworthy 24.5%. When the steam amount is increased in the system, two phenomena occurred: (i) the excess of water lower the energy available to create excited species, thus reducing the effect of the plasma and (ii) –CH₃ radicals tend to react with –OH radicals to form methanol, instead of undergoing to further reaction pathways. On the other hand, the presence of argon has been studied by Rahmani and Nikravech (2018). Its presence enhanced the density and electron temperature in the system, improving the conversion of CH₄ and CO₂ towards liquid oxygenates. At 34% argon addition, a maximum of liquid oxygenates was observed, being acetic acid a main product.

The performance results and conditions from the main research articles reviewed can be found in Table 3. In summary, CO₂ and CH₄ conversion to acetic acid via NTP is a viable and potentially alluring route. However, plasma-assisted technology to produce acetic acid is still in an early stage but it certainly shows potential to become a revolutionary alternative to the current processes. Combining NTP with a robust catalyst shows enormous potential for manipulating and controlling its synthesis under ambient conditions.

Table 3
Overview of acetic acid direct transformation from CO₂ and CH₄ on NTP DBD reaction.

Catalyst	Preparation method	Reaction system	Operation conditions (D. gap, D. length, D. power, voltage, freq.)	τ (s) or WHSV	T (°C) & P (atm)	X _{CO₂} (%)	X _{CH₄} (%)	S _{CH₃COOH} (%)	TOS (h)	Ref.
Starch	Impregnation and pasting (Dried at 100 °C, 5 h) (0.2 mm layer)	90 N mL min ⁻¹ , 30.7:69.3 (v) CO ₂ :CH ₄	1.8 mm, 150 mm, 75 W, – kV, 25 kHz	–	70 °C, 1 atm	23.1	20.6	11.2	5	(Zou et al., 2003)
Only plasma	–	40 mL min ⁻¹ , 1:1 (v) CO ₂ :CH ₄	3 mm, 45 mm, 10 W, 30 kV, 9 kHz	1.2 L g ⁻¹ h ⁻¹	30 °C, 1 atm	15.5 7.6	18.3 16.2	34.2 41.7	–	(Wang et al., 2017)
15% Cu/ γ -Al ₂ O ₃	Wetness impregnation (calcined at 350 °C 3 h over plasma)					15.3	16.7	30.8	–	
1% Au/ γ -Al ₂ O ₃						13.1	17.1	26.2	–	
Only plasma	–	40 mL min ⁻¹ , 32.6:67.4 (v) CO ₂ :CH ₄	1.1 mm, 250 mm, 100 W, – kV, 25 kHz	14 s	65 °C, 1 atm	37.8	54.3	5.3	–	(Liu et al., 2001)
Only plasma	–	40 mL min ⁻¹ , 32.6:67.4 (v) CO ₂ :CH ₄	1.1 mm, 250 mm, 100 W, 30 kV, 25 kHz	14 s	65 °C, 1 atm	33.1	51.6	5.7	–	(Li et al., 2002)
Only plasma	–	60 mL min ⁻¹ , 33.2:66.8 (v) CO ₂ :CH ₄	1.1 mm, 200 mm, 100 W, 10 kV, 25 kHz	12 s	60 °C, 1 atm	43.1	64.4	5.2	–	(Zhang et al., 2003)
10%Co/SiO ₂ 10%Fe/SiO ₂	Wetness impregnation (calcined at 600 °C, 10 h, 5:95 (v) H ₂ :N ₂)	30 mL min ⁻¹ , 2:1 (v) CO ₂ :CH ₄	1 mm, 200 mm, – W, 5.5 kV, 3 kHz	–	55–65 °C, 1 atm	35.6 38.7	50.4 46.1	20.7 31.0	6	(Li et al., 2020)
Only plasma	–	40 mL min ⁻¹ (30 mL min ⁻¹ He, 10 mL min ⁻¹ 1:2.3 (v) CO ₂ : CH ₄)	1.5 mm, 50 mm, 6 W, 16–18 kV, 5 kHz	–	35 °C, 1 atm	4.6	10.4	3.1	1	(Gelves et al., 2019)
Only plasma	–	120 mL min ⁻¹ , 1:1:1 (v) CO ₂ : CH ₄ :Ar, 11 mL min ⁻¹ steam	3 mm, 50 mm, 56 W, 15–18 kV, 33 kHz	6 s	Ambient conditions	16.6	31.4	26.3	–	(Rahmani et al., 2021)
Only plasma	–	120 mL min ⁻¹ , 0% Ar, 1:1 (v) CO ₂ :CH ₄	3 mm, 150 mm, 74 W, 18 kV, 33 kHz	–	Ambient conditions	11.0	18.5	11.3	–	(Rahmani and Nikravech, 2018)

5. Concluding remarks and outlook

In this perspective overview paper, we analysed chemical routes and catalytic systems for acetic acid production. Conventional routes are reviewed, looking for new opportunities in industry to improve the competitiveness and sustainability requirements of the process. An original strategy (BIO-route) using biogas as renewable feedstock is proposed in contrast with petroleum-derived feedstock routes. The transformation of CO₂ and CH₄ into added-value products can lessen the environmental burden of the industrial processes which stands nowadays and need further measures to curb emissions. Simultaneously, such CO₂/CH₄ upgrading strategies pave the way towards new horizons for biogas processing technologies.

BIO-Indirect route to produce syngas as an intermediate is a resourceful approach. Thermocatalytic DRM faces sintering and coke deposition due to the high temperatures (>700 °C) needed to get good catalytic activity. Alternatively, as an energy input in the process, photo and plasma-catalytic DRM may simplify the process and avoid some of these problems while improving the environmental burden of GHG related to the use of fossil fuels. The synergy among catalysts and plasma may enhance the general performance of the reaction. Different catalytic systems have been researched, e.g., bimetallic mixtures, promoters, complex structures. Nevertheless, research should be now focused on the plasma-catalyst interaction and reactor configuration parameters to understand this intricate synergy. On the other hand, BIO-Direct route is proposed for direct, single-step production of acetic acid from biogas. Due to the thermodynamic limitations of the reaction, the use of plasma technology opens a new research avenue to make feasible this chemical route. To the best of our knowledge, little has been investigated about the use of photo and plasma-assisted catalysis to directly generate acetic acid. Some catalytic studies have focused on some geometric parameters or the use of complex catalytic structures. So far, the highest selectivity obtained to acetic acid was 40.2% using a 15%Cu/ γ -Al₂O₃ catalyst. Therefore, there is ground for development and research in catalyst design is still necessary for this area to increase the selectivity towards acetic acid. Scrutiny on the interaction of the excited species with the catalyst surface and their conspicuous role is another challenge. In addition, to achieve

reproducibility among all the experiments performed, research manuscripts should include a full description of the most important parameters related to the materials (dielectric constant, particle size, pore size of packing and amount of material), conditions (residence time, flow rate, temperature, pressure and time on-stream (TOS)) and reactor configuration (type, discharge gap and length, electrode configuration, geometry, high-voltage, frequency and discharge power). Experimental conditions must be controlled to ensure that performance data represent the real performance of the system. Besides, optimised catalysts should be validated under more realistic conditions. For instance, catalyst durability and activity must be evaluated for longer periods to obtain a more realistic result of its performance. In addition, the presence of impurities typically present in biogas mixtures (e.g., SO_x, NO_x or other organic compounds) must be included in lab-scale studies. This will avoid misinterpretation of the preliminary results, facilitating upscaling.

In summary, further efforts in experimental developments and theoretical knowledge are needed to foster environmentally friendly routes for chemicals production in general and for acetic acid in particular. In any case, the use of biogas as primary feedstock for acetic acid is a promising alternative, representing a step-ahead on low-carbon industrial processes. Beyond the evident benefits for the environment, our “biogas-to-chemicals” approach also opens new market opportunities for local communities. For instance, locally produced biogas (i.e., from bio-residues at farming communities) can be used for acetic acid manufacturing somehow turning a problem (waste management) into a virtue (added-value chemicals). Certainly, the near future requires this kind of initiatives to foster the transition towards a low-carbon society.

CRedit authorship contribution statement

Juan Luis Martín-Espejo: Investigation, Writing – original draft. **Jesús Gandara-Loe:** Writing – original draft. **José Antonio Odriozola:** Resources. **T.R. Reina:** Resources, Supervision, Funding acquisition, Writing – review & editing. **Laura Pastor-Pérez:** Resources, Supervision, Funding acquisition, Project administration, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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