

Liquid SynGas (LSG)

Gegevens project

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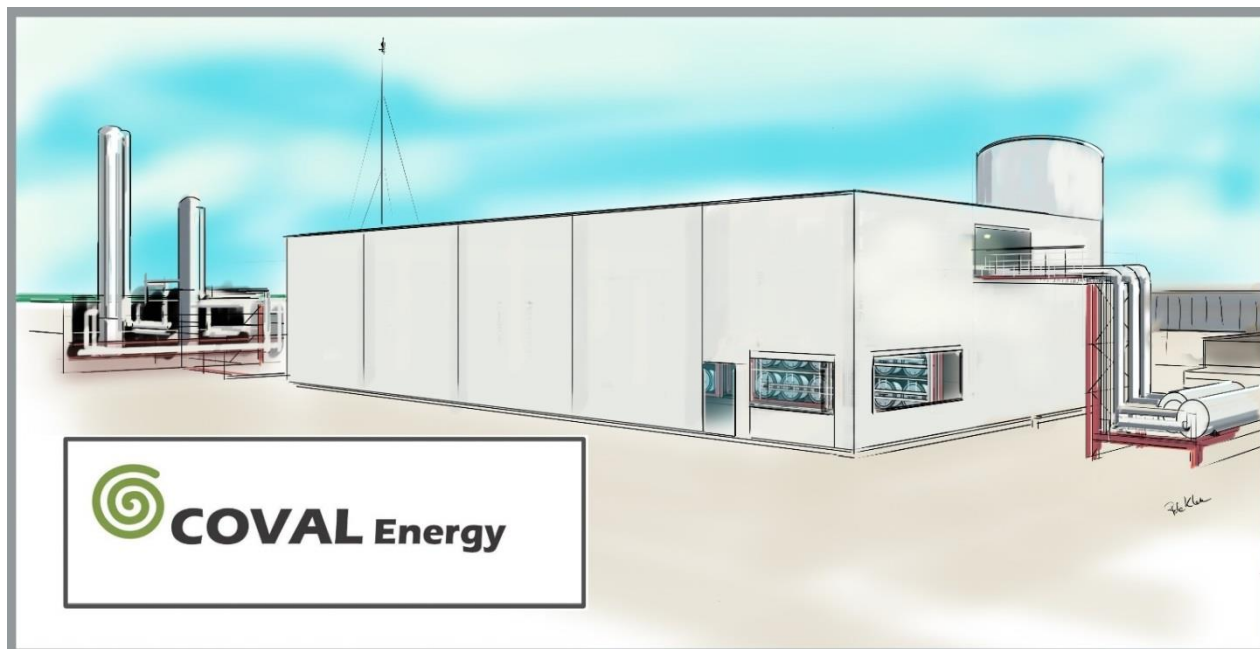
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“Het project is uitgevoerd met subsidie van het Ministerie van Economische Zaken, Nationale regelingen EZ-subsidies, Topsector Energie uitgevoerd door Rijksdienst voor Ondernemend Nederland.”



Liquid Syngas

A Renewable Carbon and Hydrogen Source

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Content



What are the opportunities of renewable produced formic acid in oil refining and petrochemical industry?

So far the existing production of formic acid in a conventional fossil based process is producing a large amount of waste, is energy-intensive and expensive. Therefore, market potential and the direct industrial use have been limited.

This report will review the opportunities of sustainable produced formic acid through electrochemical conversion of carbon dioxide (CO₂) and water. The outcomes of this report provide some first insights in the technical and economic feasibility, and the cost of CO₂ avoided based on different applications of formic acid in the existing infrastructure at refineries.

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Management summary

The transformation of the European energy system has started and will continue for many years to come. The impact on the energy-intensive industries, and in particular on the petro-chemical industry, with its diverse process and product base, will be significant with fundamental changes in the (electric) power supply. A cost optimal transformation requires versatile technologies to store surplus electricity from sustainable energy sources, such as wind and solar power. The implementation of a range of technologies broadly referred to as power-to-X (P2X) will be of decisive importance in the European energy system.

Power-to-X technologies promise a reduction of greenhouse gas emissions and simultaneously guaranteeing a safe energy supply even in the case of a high share of renewable power generation. P2X will therefore be one of the cornerstones of a sustainable energy system. Coval Energy is developing a P2X technology for the production of formic acid, based on the electrochemical conversion of water and carbon dioxide with the use of renewably generated electricity.

Formic acid (HCOOH) provides the same chemical functionality as syngas, gaseous feedstocks ranging from pure carbon monoxide (CO), mixtures of carbon monoxide and hydrogen (CO + H₂), to pure hydrogen. The sustainable production of formic acid, as a 'liquid syngas', offers an efficient technology to couple different energy-intensive sectors, such as 'traffic and transportation' and the 'chemical industry'. Formic acid, produced through electrochemical conversion of CO₂ can thus be regarded as a key-enabling step for a transition of the energy system, which offers additionally features of CO₂-valorization and closed carbon cycles.

The current production of formic acid is through a conventional fossil-based process is considered a polluting, an energy-intensive, and expensive synthesis route. Therefore, market potential and the direct industrial use have been limited.

This report will review the opportunities and provide some first insight in technical, economic feasibility and the cost of CO₂ avoided. Furthermore, it advances in both fundamental understanding of the basic reaction schemes and promising applications of formic acid in order to further promote CO₂-reduction and effective use.

1 Introduction

Almost all chemical production routes involve molecules with C, H, O atoms, whereby methane, condensates (C2 - C5), and naphtha, are widely used as feedstock for the production of chemicals and fuels. Syngas by itself is a feasible intermediate but is currently predominantly obtained from fossil fuel based routes, such as natural gas. Intermediate chemical products, such as formic acid or methanol, produced in a sustainable way have a clear potential to become the chemical building blocks of the future, as these products have the potential to contribute to the decarbonisation of the petrochemical industry.

The current industrial use of formic acid is mainly in the conservation of cattle feed and the production of leather. Formic acid possesses anti-bacterial properties and it is therefore used as preservative as well as an anti-bacterial agent in livestock feed. In the leather industry formic acid is used for tanning, and it is used in the process of dyeing and finishing textiles. It is also used as a coagulant in many rubber manufacturing processes. In addition to its use in the leather, textile, and rubber industries, derivatives of formic acid have recently been developed for de-icing of runways, roads, and side-walks using different formate salts, which are salts that are derived from formic acid. Not only are these formates more effective for de-icing purposes than traditional salt treatments, the use of formate salts is also more environmentally friendly.

1.1 Main objective of the project

The main objective of this study is to identify the potential of formic acid, produced in a sustainable way, as a feedstock for the oil refining and petrochemical sector. The starting point is the electrochemical production of formic acid from water and carbon dioxide. The main activities will focus on exploring uncharted territories of sustainable produced formic acid (formate) and the intersections of these territories in order to identify and develop entirely new paths for the production of high-value products.

The activities will focus primarily on products and production routes close to end-users with a high sustainability awareness. In order to reduce the use of fossil fuel a transition is required where the production of base chemicals is essentially based on the principles of a circular economy. The main objective is to identify possible process applications based on the electrochemical conversion of captured CO₂. More specifically, this will entail possible integration of the direct use of formic acid with existing processes, and the development of process where CO₂ capture is integrated with the use of formic acid. Typical liquid products of the electrochemical conversion of CO₂ are formic acid and methanol, and both these components can be used to provide carbon monoxide, hydrogen, and mixtures of carbon monoxide and hydrogen, which is known as syngas.

There are no sustainable alternatives to produce syngas other than through fossil fuel based gasification processes. A possible option is to produce H₂ (one of the components of syngas) by using an electrolyzer

and renewable electricity, however timing (intermittent character of renewables) and production and storage of H₂ are more expensive as compared to fossil fuel routes.

An interesting option is to use liquid chemical components (such as formic acid) that can easier be stored and transported, as compared to hydrogen or syngas, and that contain C, H and O atoms as the main feedstock for large-scale chemical production process. In this work these 'alternative' liquid components are referred to as **Liquid SynGas** or **LSG**.

Innovative electrochemical production methods for formic acid using carbon dioxide and renewable electricity as a feedstock open possibilities to increase sustainability and to reduce the carbon footprint in the chemical value chain [1, 2]. In this way, carbon dioxide utilization will be on one of the main stepping-stones to achieve electrification and decarbonisation of the chemical industry [2, 3]. An additional advantage is that carbon dioxide will be re-used, which is an important step to close the carbon loop [4 - 6]. The main challenge will be to match the CO₂ source with the utilization process and to convert CO₂ in an efficient way to a product with a large (potential) market, and at the same time assure that the overall process is carbon and energy neutral.

1.2 Approach

There will be a number of activities focusing on possible synthesis routes of syngas-like molecules (formic acid and methanol) and exploring production processes employing syngas. A desktop study, based on a literature and patent review, will be performed to provide an overview of the major synthesis routes and the potential of liquid syngas-like molecules, particularly formic acid, in various applications to produce different types of base or specialty chemicals.

In addition, modelling work including solving mass and heat balances and thermodynamics of the reactions and process development based on process flow diagram will be done focusing on the integration of various process steps.

Finally, a techno-economical evaluation will be conducted for one or two specific cases to assess the main economic and technological challenges of liquid, chemical building blocks as a generic feedstock. The results will be used to benchmark against existing processes that are using syngas as feedstock, showing the 'gap' between products based on fossil fuels versus products based on renewable energy and CO₂ re-use in terms of cost of CO₂ avoided.

2 Methodology

The analyses will be different from other higher level system studies via a so called bottom-up methodology in which we try to review process streams and the potential tie-ins in existing processes infrastructure to maximize the potential of renewable energy and the production of platform molecules and emerging energy carriers. There are two main pathways that can be identified:

- 1) A direct tie-in of formic acid as a liquid syngas (blend) in the crude oil refining process.
- 2) A stand alone conversion of formic acid into platform molecules and dense energy carriers.

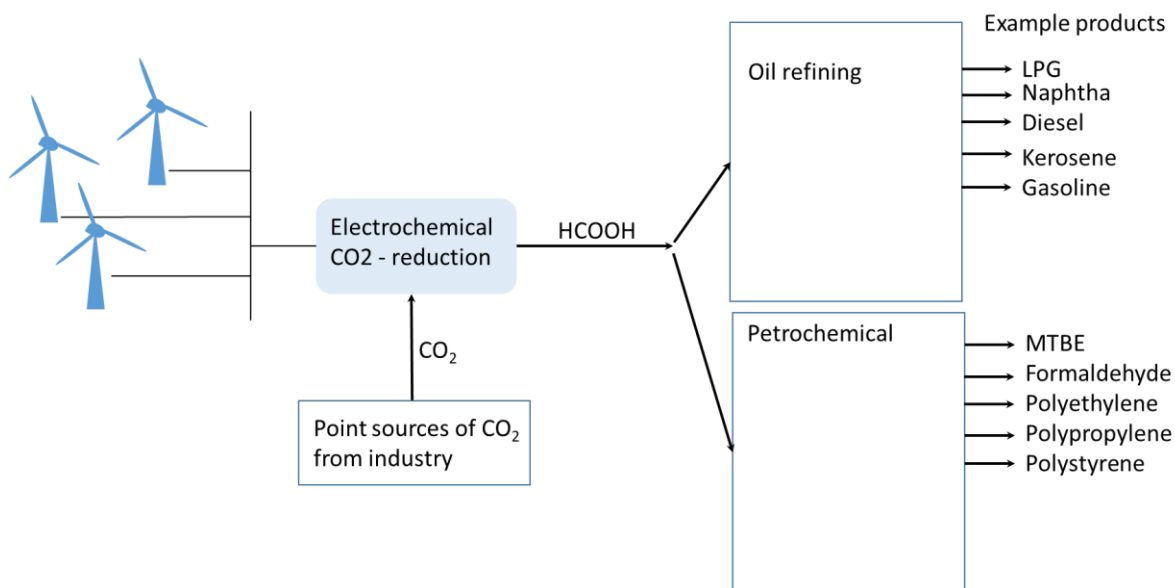
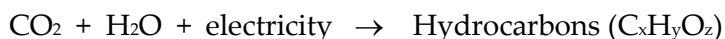


Figure 2.1. Pathway 1: Direct tie-in options of formic acid with oil refining and petrochemical processes.

The two main pathways are schematically depicted in Figure 2.1 and Figure 2.2. In Figure 2.1 an overview is given of the range of products that are typically produced at a refinery and in various petrochemical industries. In Figure 2.2 an overview is given of renewable pathways to produce various (bulk) chemicals, employing electro-chemical process.

Electrochemical conversion of water and carbon dioxide

Electrochemical conversion of water and carbon dioxide into hydrocarbons is an emerging technology. Basically, electricity obtained from renewable energy, wind or solar, is used in an electrochemical reactor to reduce carbon dioxide in the presence of water. In a general form this is represented by:



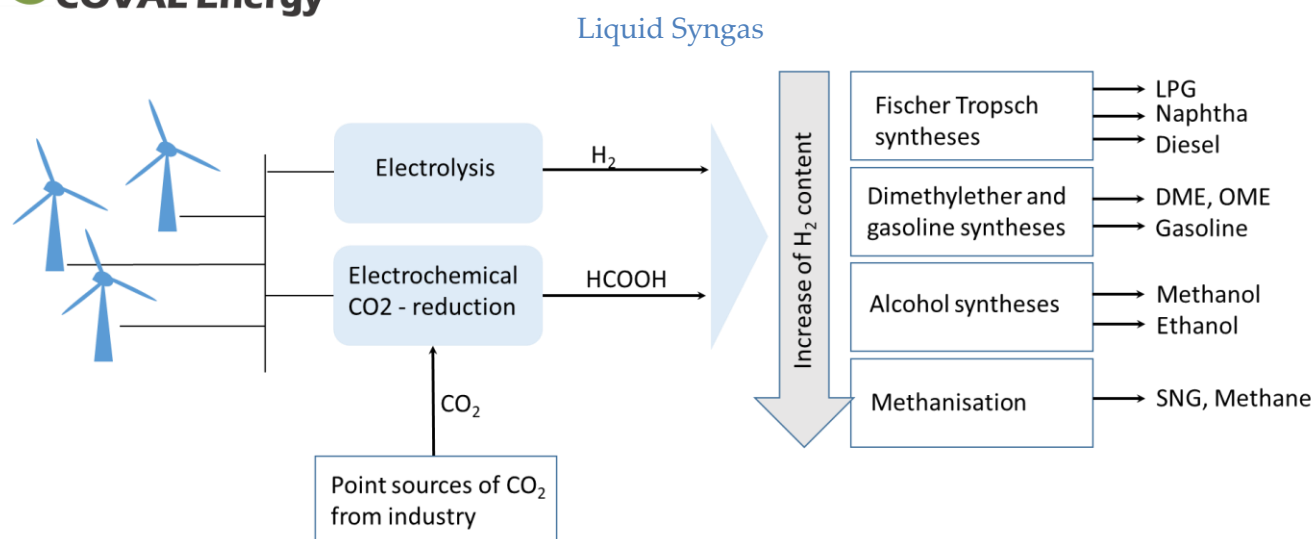


Figure 2.2. Pathway 2: Overview of possible conversion routes of Power-to-X (P2X) with formic acid and hydrogen as the main components for the stand-alone production of platform molecules and dense energy carriers.

Formic acid (HCOOH , CH_2O_2) is an interesting option because only two electrons per molecule CO_2 are required and no water is produced on the cathode as by-products [7 - 9], see Table 2.1. For other molecules, like methane and methanol more electrons are required, respectively 6 and 8 electrons, inevitably this means that also the overall reaction efficiency goes down because during the synthesis of methane or methanol more by-products are formed, which require more or less the same amount of electrons. Furthermore, for methane and methanol also water is produced as a by-product at the cathode essentially reducing the efficiency of the overall reaction even more, see Table 2.1. For methane (CH_4) half of the hydrogen ions formed at the anode are converted back into water at the cathode, resulting in a hydrogen efficiency of 50%.

A preliminary analysis of the production cost of formic acid from captured CO_2 and electrochemical conversion is shown in Table 2.2. For an average electricity price of around 45 euro per MWh the cost price of one ton of formic acid will be in the order of 325 euro. It is assumed that the efficiency of the conversion steps is around 70%.

The contribution of the electricity price has the highest effect on the cost price. Anticipating a further reduction of the electricity prices from renewables in the near-term and mid-term future (say next five years), a reduction of, for example, in the electricity price from 45 to 35 euro per MWh will result in a cost price reduction of formic acid from around 325 euro per ton to around 265 euro per ton. At the moment formic acid is basically the only chemical that can be produced in an economical way, that is the

(cost) price of producing formic acid electrochemically can compete with the current market price of formic acid.

The same analysis can be made for methane and methanol. This will result in a cost price of electrochemically produced methane and methanol of at least 800 and 600 euro per ton, while the current market price of methane and methanol (November 2017) is around 100 and 150 euro per ton, respectively. The point is that the electricity input to synthesize methane or methanol is (linear) proportional to the amount of electrons required in the electrochemical reaction. At the same time, methane is abundantly available and methanol synthesis from natural gas is relatively simple.

Table 2.1. Overall reactions and half-reactions on the cathode for the electro-chemical formation of formic acid and methane from carbon dioxide and water. For water the half-reaction takes place on the anode.

Product	Overall reaction	Half-reaction
Formic acid	$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCOOH} + 1/2 \text{O}_2$	$\text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{HCOOH}$
Methanol	$\text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 3/2 \text{O}_2$	$\text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$
Methane	$\text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{CH}_4 + 2 \text{O}_2$	$\text{CO}_2 + 8 \text{H}^+ + 8 \text{e}^- \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$
Water splitting	$\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2 \text{O}_2$	$\text{H}_2\text{O} \rightarrow 2 \text{H}^+ + 2 \text{e}^- + 1/2 \text{O}_2$

Table 2.2. Breakdown of the operational expenditure (OPEX) for the production of formic acid (FA), based on electrochemical conversion of 1.0 ton of carbon dioxide, assuming 70% efficiency.

Process step	Price, €		Unit	Input value per ton CO ₂	Contribution	
	Range	(Average)			€	(%)
Electricity	33 - 55	(45)	euro / MWh	3.5 MWh	158	(69)
CO ₂ (captured)	30 - 50	(40)	euro / ton	1.4 ton	40	(18)
Water	1 - 3	(2)	euro / ton	0.4 ton	1	(0)
Operation - Maintenance						
- Compression CO ₂ (1 to 50 bar)	35 - 55	(45)	euro / MWh	0.2 MWh	9	(4)
- Separation (water - formic acid)	35 - 55	(45)	euro / MWh	0.2 MWh	9	(4)
- Handling (5% of OPEX)					11	(5)
Total per ton CO₂ (or 0.7 ton FA)					228	(100.0)

3 General refinery and petrochemical processes

The raw material of the petrochemical industry is crude oil, which is a mixture of hydrocarbons. The main purpose of oil refining is to separate the crude oil into different fractions of hydrocarbon molecules and/or saleable products, shift the product composition to client requirements, remove impurities and improve product quality.

The product of oil refining, fractions of crude oil, contain a large number of individual hydrocarbons (LPG, gasoline, and diesel). Further processing of these fraction yield a range of petrochemicals, which consist of a smaller number of specific hydrocarbons, such as ethylene, propylene, and toluene. From these fractions much more complex petrochemicals can be made.

3.1 Composition of crude oil

The composition of crude oil is highly variable and each oil field has a unique composition. In general, the composition of crude consists of 80-90% carbon and 10 - 14% hydrogen and sulphur 1 - 3%. The variation in composition leads to different boiling point curves. Crude oil can also be defined in terms of density or sulphur content.

3.2 Overview of refinery processes

Oil refining is a complex process, mainly due to the variety of components in the feedstock and the different products that can be produced and can be summarized in the following stages:

- Separation
- Conversion
- Treating

The refinery setup is subject to its specific purpose although the separation step such as primary distillation is a common process unit. See Figure 3.1 for a typical oil refinery lay-out.

3.2.1 Separation

Crude oil contains salts and ash that must be removed prior to primary distillation. These impurities are washed out with fresh water at 120 °C and elevated pressure levels. The wash water is treated and reused. The desalted crude oil will be preheated to boiling point to a maximum temperature of 400 °C and fractionated. The primary distillation at atmospheric pressure separates the crude oil into 4 up to 6 main fractions. The bottom fraction of the atmospheric tower will be at vacuum conditions further fractionated. Each fractionated stream will be further processed separately.

The light ends section main purpose is to recover the useful fractions from the low boiling point gases before it is sent to the fuel gas pool (refinery gas).

Liquid Syngas

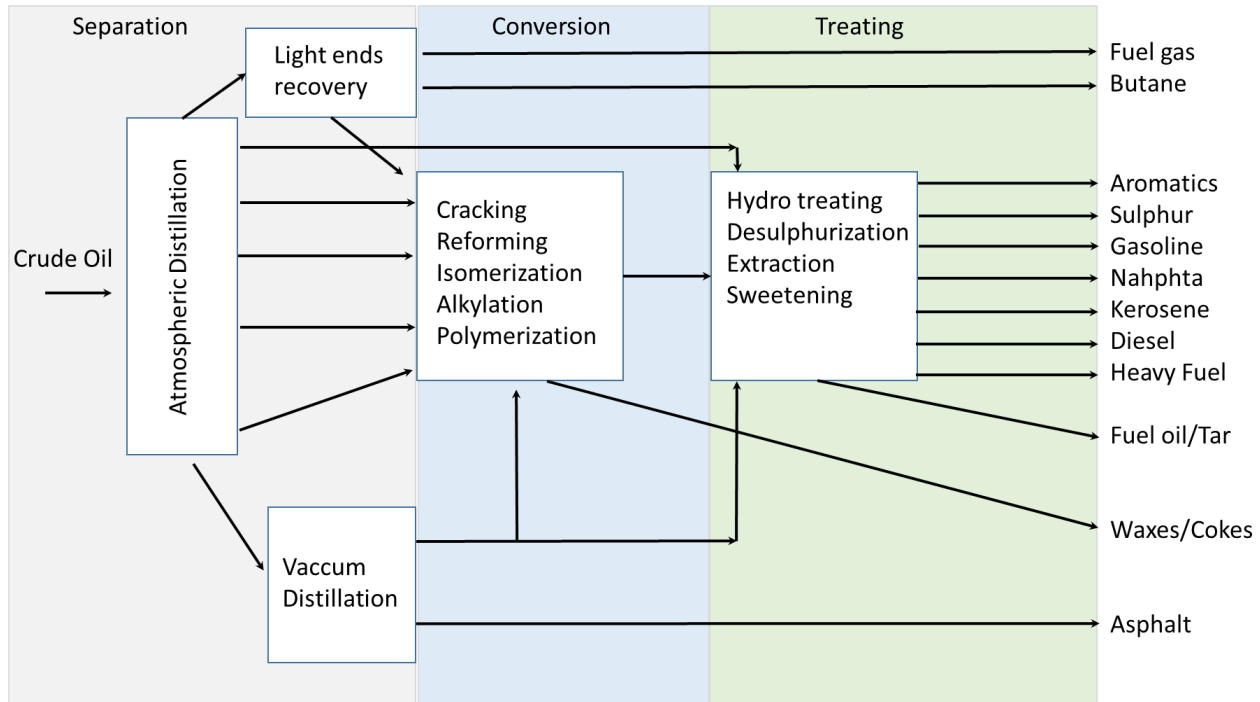


Figure 3.1. Typical lay-out of a contemporary refinery, with the three main sections: separation, conversion, and treating.

The most likely tie-in for formic acid is as heat input for the pre-heaters of the distillation processes substituting Fuel oil or fuel gas thereby increasing a higher yield of the crude oil into products by recycling the refinery off-gas or converting and re-use the useful components instead of used as fuel in the fired heaters.

The application of hydrogen in a refinery is given in Figure 3.2, illustrating the complex interaction between various refining processes.

3.2.2 Conversion

The conversion process involves the chemical or physical conversion of the fraction to more useful product streams.

Catalytic Cracking

Thermal cracking involves the breaking of longer molecules (high boiling point) into smaller molecules by using heat. Thermal cracking has been used mainly for the production of gasoline in the past, since modern car requirements are much more stringent on quality. For gasoline production, catalytic cracking is now much more appropriate for that purpose.

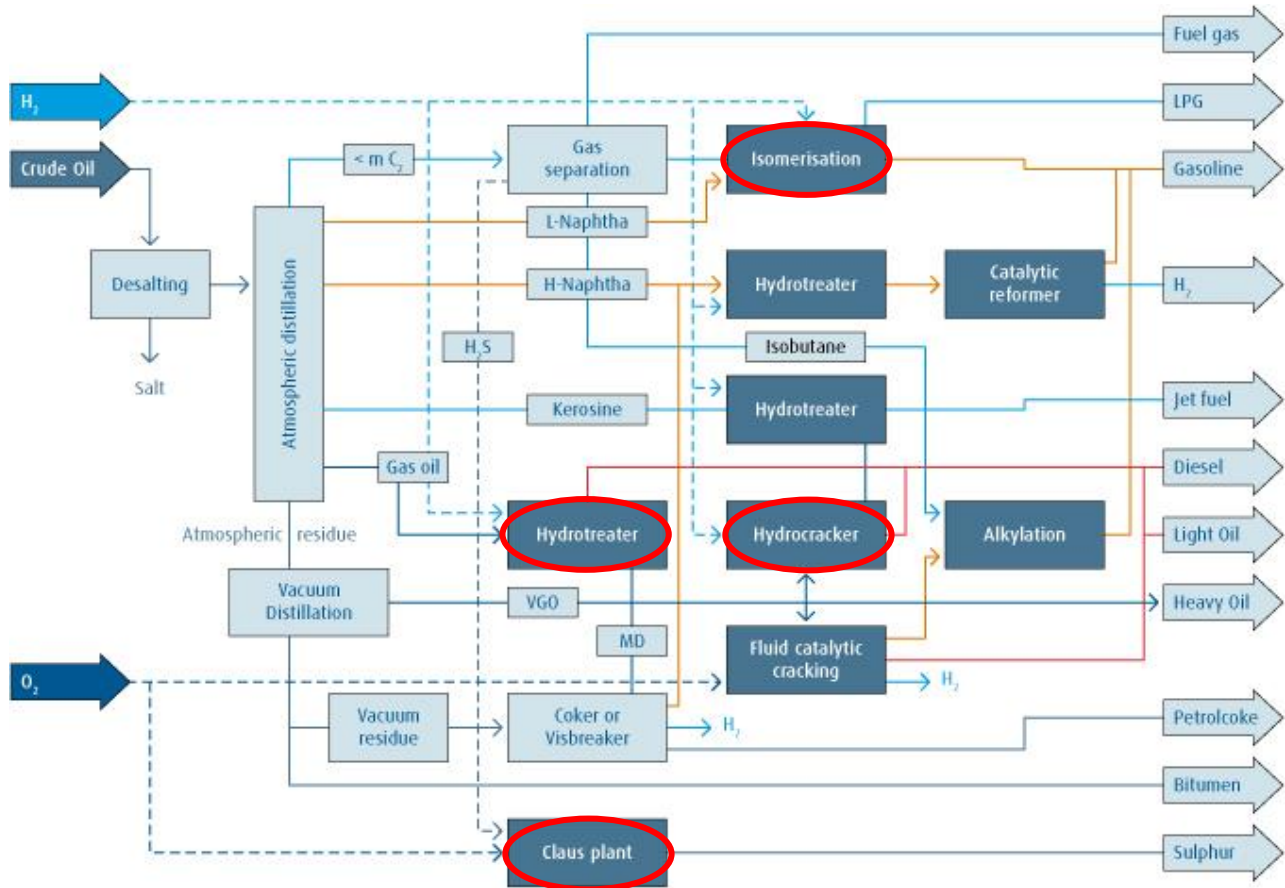


Figure 3.2. Use of hydrogen in refining processes (source: Linde Gas).

A more recent process is the thermal breaking of the viscosity of viscous distillates. The bottom product such as vacuum residue, wax or other viscous oils are thermally cracked in a so called Vis-breaker and thereby easier to handle.

Another thermal cracking process is delayed coking, in which the vacuum distillation residue is heated up to 500 °C in a large vessel. The residue is cracked into smaller molecules such as fuel gas, naphtha or fuel oil. These smaller products need further distillation to remove by-products and impurities to obtain the required specifications for the final products, such as gasoline, kerosene, and diesel. The remaining coke is removed out the vessel with steam blowing and the petroleum coke (pet-coke) is sold for use in other industries for power generation or steel industry.

The selectivity and yield of the cracking process has been improved by the application of catalytic cracking in which the thermal decomposition takes place in the presence of a catalyst. The catalyst is in

most cases coated with a carbon layer and so is rapidly deactivated and requires to be regenerated. The catalytic cracking takes place in a fluidized bed (entrained flow) so called fluid catalytic cracking (FCC) unit. The off-gas from the regenerator of the FCC-unit contains large amounts of CO and is often used as fuel gas for the production of HP-steam.

Hydrocracking

Hydrocracking involves a catalytic cracking process in the presence of high pressure hydrogen. Hydrocracking results in low-boiling point saturated compounds such-as ethylene from naphtha to produce olefins. Hydrocracking might be a very interesting option for formic acid to be integrated with as a feedstock of high pressure hydrogen.

In a typical refinery, an average of around 0.5 to 0.7 kg of hydrogen is required per barrel of crude oil. This means that for the refineries in the Rotterdam area in the order of 0.6 to 0.8 million kg of hydrogen is needed per day, see Table 3.1 and Table 3.2. Furthermore, for the CO₂ emissions for a state-of-the-art refinery in the order of 5% to 20% of the total CO₂ emission is related to the on-site hydrogen production.

Table 3.1. Overview of the four largest refineries in the Rotterdam area.

Name - Location	Barrels per day
Shell - Pernis	415 000
BP - Rotterdam	400 000
ExxonMobil - Botlek	195 000
Total - Zeeland	150 000
<i>Total</i>	<i>1 160 000</i>

Table 3.2. Hydrogen consumption for the three main hydrogen-based refining processes.

Process	Process Type	Purpose	H₂ Consumption (SCF/Barrel)
Hydrocracking	conversion	yield improvement	1200 - 2500
FCC Feed Hydrotreating	treating	yield improvement	800 - 2000
FCC Naphtha Hydrotreating	treating	sulfur control	50 - 200

1 kg of hydrogen equals 423 Standard Cubic Feet (SCF) of hydrogen.

1 Barrel of oil is equivalent to 159 Liter.

Reforming

The process of rearrangement of molecules to more useful forms is so called reforming. Reforming process takes place in the presence of a catalyst. The re-arrangement may involve change in type of bond with the respective loss or gain of hydrogen as controlled by the conditions. Catalytic reforming is mainly used to produce higher octane level aromatics, from paraffin's and naphtha using a platinum catalyst at high temperatures 500 °C. The large amounts of hydrogen from catalytic reforming will be used for hydro-treating and hydro-desulphurization.

Isomerization

The isomerization process is also a rearrangement of molecules used for straight C5 and C6 molecules. There is no loss of hydrogen bond, isomerization will only change the structure of the molecule to create high octane components.

Alkylation and polymerization

Both processes are pretty much the same and result in higher boiling point products from the gaseous C3 - C5 olefins. In alkylation these molecules are combined with isobutene. In polymerization the molecules are combined to form longer chain saturated molecules.

3.2.3 Treating

Hydro-desulphurization

Sulphur can be present as hydrogen sulphide, mercaptans, sulphides, disulphide and thiophenes in the distillation fractions. These components are very corrosive and can be poison to many catalysts. Removing these Sulphur components is essential to prevent problems for the downstream processes and for the end user applications. Sulphur can be removed by several processes. The most commonly used is hydrodesulphurization, which involves a high pressure hydrogenation and breaking of the C-S bonds and the production of hydrogen sulphide which is removed and converted in sulphur and water in a super clause unit.

Hydro-treating

Hydro-treating is just the same process like hydrocracking only it takes place at far less severe process conditions with the aim of removing impurities and convert olefins to saturated components. Also, sulphur and nitrogen present in hydrocarbon streams are converted in to gases ammonia and hydrogen sulphide and removed.

Extraction, sweetening

There are several extraction and sweetening uses most of them involves an absorption solvent or adsorption process.

3.3 Overview of petrochemical processes

Petrochemical processes are based on the production of chemicals from raw materials derived from oil refining, and condensates or gas-based feedstocks. The processes and conversions are similar to those in oil refining and therefore potentially similar tie-in options with formic acid.

First, in this Chapter the different refining processes will be discussed. Second, in Chapter 4 a number of different options for the use of formic acid in refinery and petro-chemical processes will be evaluated. Finally, a techno-economic evaluation of one of the most feasible options for the application of formic acid will be given in Chapter 5.

The petrochemical processes can be segmented in the following groups:

- Petrochemicals derived from gas-based feedstocks, such as methane and ethane
- Naphtha and oil based chemicals derived from crude oil
- Aromatics derived from condensates or naphtha
- Use of syngas as intermediate and source for H₂ and/or CO in the production of chemicals

Petrochemicals derived from gas-based feedstocks, such as methane and ethane

Natural gas consists mainly of methane, which is used for the production of methanol that is used as an intermediate for the production of a large variety of chemicals that can be produced (i.e. formaldehyde and MTBE). Natural gas is next to crude oil the fossil based resource for chemicals. Methane from any source such as natural gas and shale gas is the preferred feedstock for syngas production due to the relatively low level of impurities (H₂S, COS and mercaptans).

Ethylene, derived from ethane (processed from natural gas processing and crude oil refining based on ethane, has a carbon-carbon double bond, is one of the most important fundamental chemicals in the petrochemical industry and its production is one of the larger CO₂ emission sources of the petrochemical industry. Ethylene is a gas based petrochemical and a platform chemical for a variety of products such as polyethylene resin, ethylene glycol, vinyl chloride resin, acetic acid, styrene, and alpha olefin which are produced by polymerization, oxidation, alkylation, hydration, or by the addition of halogen. Gas based petrochemicals based on methane and ethane are illustrated in Figure 3.3.

Polyethylene is among the most widely applied resins because of its excellent balance between quality and cost. Its polymerization method is classified into two types: the high-pressure process and the

medium- and low-pressure process. The latter is further divided into the slurry process, solution process, and gas-phase process. Products produced from polyethylene are largely categorized into high-density polyethylene, low-density polyethylene, and linear low-density polyethylene. Production processes are appropriately combined depending on the product characteristic.

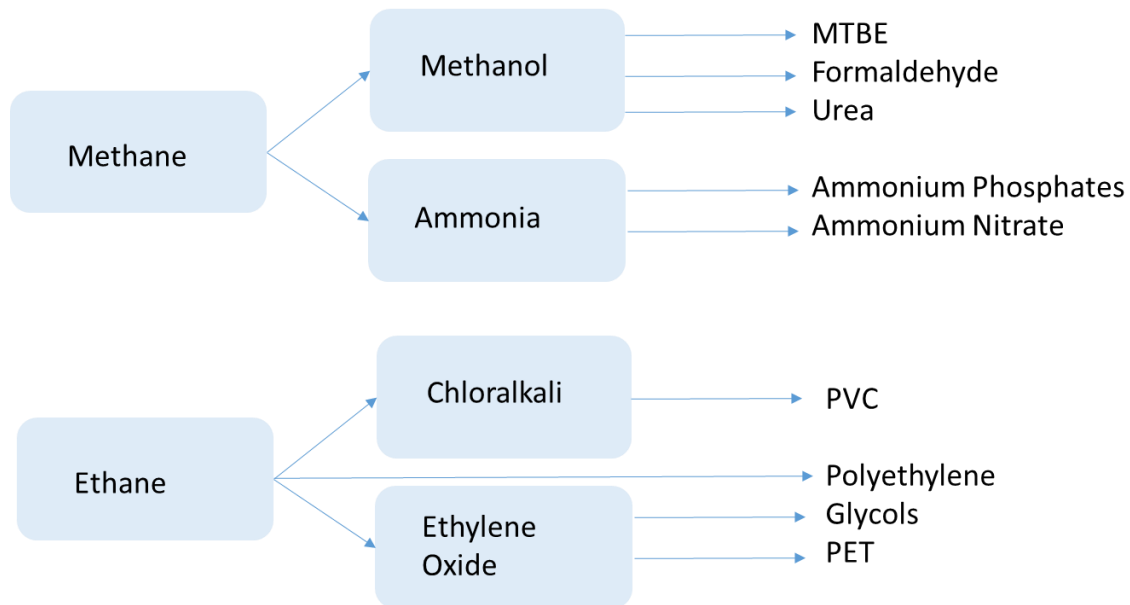


Figure 3.3. Overview of gas-based petrochemical products, obtained from methane or ethane.

Naphtha, condensate and crude oil-based

Naphtha derived from crude oil refining is used as a versatile feedstock for the production of olefins (ethylene, propylene and C4 related chemicals) and aromatics (benzene, toluene and xylenes, referred to as BTX).

Propylene has a double bond with three carbons and is used to produce polypropylene resin, acrylonitrile, acrylic acid, propylene oxide, isopropyl alcohol, and acetone through polymerization, oxidation, alkylation, hydration and the addition of halogen. Propylene is a basic chemical in the petrochemical industry as methyl ethylene. Polypropylene is applied to a variety of fields for its relatively low cost and excellent rigidity, heat resistance and gloss. It is polymerized largely in four ways: solution polymerization, suspension polymerization, bulk polymerization, and gas-phase polymerization.

The process of direct oxidation of propylene to produce propylene oxide is yet to be established. Formerly, propylene oxide was produced by the chlorohydrin process, which produces a large amount

of calcium chloride as a by-product. Currently, the mainstream process produces propylene oxide from peroxides, such as ethyl benzene, and propylene. This process produces propylene oxide (PO) plus styrene (SM) as a by-product.

Naphtha used as a raw material to produce an ethylene will come with highly reactive materials in C4 fractions or C5 fractions as by-products. Butadiene in the C4 fractions and isoprene in the C5 fractions in particular, are useful chemicals as they are used to produce synthetic rubber such as tires for cars.

About 50% of C4 fractions produced from thermal decomposition of naphtha is butadiene, which is generally separated using a special distillation technique called extractive distillation. The process uses solvents as normal methyl pyrrolidone (NMP) or dimethyl formaldehyde (DMF)

An important category of chemicals is the group of aromatics. Using naphtha as a raw material, an ethylene plant produces aromatic derivatives (the BTX fractions) such as benzene (B), toluene (T), and xylenes (X) out of the intermediate pygas. With respect to the BTX fractions, benzene and xylenes are particularly used in large quantities in general-purpose resins and fibers after being processed with polystyrene, caprolactam, and terephthalic acid. Since cracked gasolines produced from ethylene plants only are not enough to meet the demand for these products, supply from reformulated gasolines in the oil refining industry is increasing.

4 The potential of LSG applications

This chapter will review the potential tie-in options of formic acid as a renewable feedstock in the oil refining and petrochemical process. Current barriers for the widespread application of formic acid are mainly related to the fossil fuel-based production process of formic acid, see Appendix A.1:

- High CO₂ foot-print, does not contribute to the decarbonization of the (petro-)chemical sector
- Energy intensive, unwanted by-products and waste products (waste water)

The three pathways for the implementation of formic acid are:

- 1) A direct tie-in of formic acid as a hydrogen source in **existing** crude oil refining processes:

*Formic acid as an alternative source for intermediate H₂ into the **existing** manufacturing structure.*

- 2) A direct tie-in of formic acid as a liquid syngas in **existing** chemical processes:

*Formic acid as an alternative source for intermediate syngas into the **existing** manufacturing structure.*

- 3) A standalone conversion of formic acid into platform molecules and dense energy carriers:

*New **technologies** based on formic acid as feedstock to produce emerging chemicals and fuels, creating a new merit order.*

Pathways 1 and 2 take advantage of low market barriers using existing process units, while pathway 3 takes a more ambitious approach, and will be harder to implement, owing to the fact that such potentially new commodity chemicals are not already part of the existing markets. New processes also incur the financial penalty of start-up costs and investment, whereas producing existing products using the same techniques but from Formic Acid takes advantage of the existing infrastructure with the reassurance that a fossil derived feedstock can be relied on in case of price fluctuations or feedstock scarcity. In reality there is not a clear cut decision between the two pathways and it is obvious that a possible combined approach of the two pathways might also be working.

The chemical building-block functionalities of syngas can be compared with formic acid. The functionality of molecules can be roughly approximated by the number of hetero-atom bonds, that is any atom other than carbon or hydrogen. It is common in reviews describing bio-refinery products to plot the molar ratios between carbon, oxygen, and hydrogen as an indicator of the degree of functionality or energy of combustion.

A convenient way of comparing the functionality of different chemicals is based on a so-called chemical composition map, see Figure 4.1. In Figure 4.1 the main chemical building blocks (intermediate chemicals, commodity chemicals, biomass-based chemicals, and fuels) are plotted in terms of the O/C and H/C ratio. The chemicals with the highest O/C ratio are carbon monoxide and formic acid, and the chemicals with the highest H/C ratio are methane and methanol. These high O/C and H/C ratio is the

main reason that these four chemicals (CO, CHOOH, CH₃OH, CH₄) are primarily used as feedstock to produce essential all other chemicals. See also Appendix A.2 of an overview of the chemicals that are being produced from hydrogen, carbon monoxide, and syngas.

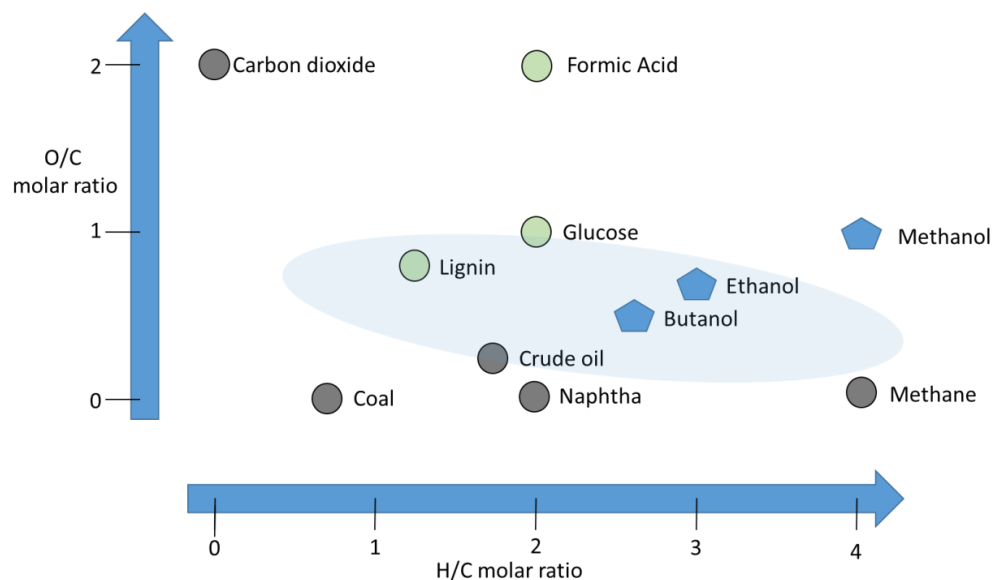


Figure 4.1. Chemical composition map of fossil derived resources, renewable sources, and hydrocarbons.

Table 4.1. Some main fuels types, with the lower heating value and the amount of CO₂ per kg fuel.

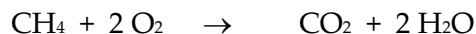
Fuel type	Main component	H/C (1)	kg CO ₂ /kg fuel (2)	Lower heating value [MJ/kg]	ton CO ₂ /MJ
Hydrogen	H ₂	-	-	121.0	
Natural gas	> 90% CH ₄	4 : 1	44/16 = 2.75	47.1	58.4
Methanol	CH ₃ OH	4 : 1	44/32 = 1.38	20.1	68.6
Gasoline	C5 - C12				
	Octane (C ₈ H ₁₈)	2.25 (=18/8)	8*44/114 = 3.09	43.4	71.2
Crude oil	C10 - C20	2 : 1	> 3	42.7	> 70
Bitumen coal		1 : 1	3.5	26.1	134.1

(1) H/C refers to the Hydrogen to Carbon ratio

(2) Based on the molecular mass, for example: MW(CH₄) = 16 (g/mol) and MW(CO₂) = 44 (g/mol)

With respect to the combustion properties of different fuel (types), the key ratio is here the H/C ratio. The higher the hydrogen content the higher the heating value and the lower the amount of CO₂ produced per kilogram fuel. An overview of the main combustion properties of the most common fuels is given Table

4.1 For example, the combustion of methane is described by the following reaction, indicating that each mole of CH₄ gives one mole of CO₂:



However, 1 kg of CH₄ gives 2.75 kg of CO₂, based on the ratio of the molecular mass. Combining the lower heating value with the amount of kg CO₂/kg fuel, it follows that natural gas (methane) has the best performance as compared to the other fossil fuels (oil or coal). Both hydrogen and methanol have better performance characteristic than natural gas, but it should be noted that almost all hydrogen and methanol are obtained from methane.

Key observation 1

Based on the values for the heating values given in Table 4.1 it follows that for the heat input provided by gas-fired heaters typically 0.058 kg CO₂ is produced per MJ. This is equivalent to around 0.21 kg CO₂ per kWh(Th). For practical applications (and calculations) the (overall) efficiency of (gas-fired) heaters should be taken into account, which is typically in the range of 0.40 to 0.5, which means that the actual amount of CO₂ produced per kilowatt-hour natural gas is in the order of 0.42 to 0.53 (kg CO₂ per kWh(Th)).

Replacing about 1 kWh(Th) by 1 kWh(El) will result in a CO₂ reduction (potential) in the order 0.5 kg for every kWh energy input. Furthermore, in the electrochemical synthesis of formic acid theoretically 1.0 kg CO₂ is required in the reaction to produce 1.05 kg formic acid, see Table 2.1. Current reactors to convert carbon dioxide to formic acid electrochemically have an (energy) efficiency of around 70%.

This means that electrochemical conversion contributes in two different ways to reducing the overall CO₂ foot-print of chemical synthesis routes, through the renewable power input and through the consumption of carbon dioxide in the synthesis process.

Key observation 2

Another the key observation is that formic acid can be considered as a hydrogen (H₂) carrier as well as a carbon monoxide (CO) carrier [10]. Formic acid can be converted to a mixture of hydrogen, water, carbon monoxide, and carbon dioxide (CO₂), depending on the conditions for the temperature and the pressure. In most cases, the relatively low heating value of formic acid of around 5.7 MJ/kg is a major drawback. An interesting point is, however, that the low heating value is directly related to the required electric power input for the synthesis (reduction reaction) of formic acid. It takes around three times less energy to synthesize formic acid as, for example, methanol, and at the same time the heating value of formic acid (basically the amount of energy that can be obtained from the oxidation reaction) is a factor of three lower than the heating value of methanol. Here, we focus on applications that match the versatile chemical functionality of formic acid by providing H, C, and O atoms.

4.1 Identification of integration options (pathway 1)

Formic acid, or formate, can be used as chemical functional building block and as a source for heat input. The formic acid might represent the lowest added-value when used as an energy source, although it might reduce direct the local CO₂ emission at the production location via substitution of fossil based feedstocks for heating of high temperature conversions in oil refining and petrochemical processes. Nevertheless, the list of all possible options will be reviewed based on: (1) the impact on CO₂ reduction, (2) fit with existing process, and (3) feasibility, see Table 4.2.

Table 4.2 List of tie-in options for LSG (formic acid) in refinery and petrochemical processes.

Tie-in option	Description	Impact	Fit	Feasibility
High temperature heat	Reboilers, crude preheaters, etc. operating in the temperature range of 300 to 500 °C	+	+	o
H ₂ source	Separate the H ₂ from formic acid over a catalyst and injection of H ₂ in existing infrastructure. The remaining CO ₂ can be recycled.	o	++	o
Steam reforming (blending) (reverse water gas shift)	Blend steam or substitute steam with formic acid, existing equipment can significantly boost H ₂ capacity and especially CO	+	++	+
Steam cracking (blend)	Blend of steam and formic acid, in most cases there is no functional added value for formic acid for steam cracking	-	-	--
Hydro-cracking	Separate the H ₂ from formic acid over a catalyst and injection of H ₂ in hydrocracker. The remaining CO ₂ can be recycled.	o	++	+
Hydro-treating	Formic acid, or the H ₂ separated from formic acid, is used in the treating units. The remaining CO ₂ can be recycled.	-	+	o
Desulphurisation	Formic acid, or the H ₂ separated from formic acid, is used in the treating units. The remaining CO ₂ can be recycled or must be captured from the H ₂ S stream prior to sending to the Claus-unit.	-	+	+

Scale: ++ very positive, + positive, o sufficient, - negative, -- very negative.

Formate is a highly electrophilic and reactive molecule. Not part of this study but worth noting, is that formate is an organic anion which is both a carrier for interspecies electron transfer and a C1 building block. Therefore, formate is an ideal intermediate to build a new era of routes for CO₂ recovery with a mixture of microbial syntrophic cultures that produce valuable products, such as higher organic fatty

acids, or alcohols [11, 12]. The main acid-base properties of the formic acid - formate system are given in Appendix A.3.

4.2 A direct tie-in of formic acid as a liquid syngas in existing chemical processes (pathway 2)

Formic acid can be used as a chemical functional building block subject to the added value of the resulting product. As such, formic acid could be used as a sustainable carbon monoxide and hydrogen source. Efficient catalysts for the decomposition of formic acid to hydrogen, CO₂ and carbon monoxide are available [10]. Thus, formic acid can be seen as liquid and storable versions of carbon monoxide and hydrogen, and formic acid either as hydrogen or CO carrier can directly be used in the existing chemical value chain.

There might be a potential use for formic acid as an intermediate in the gas based petrochemical processing as an alternative of methane or syngas as illustrated in Figure 2.1 of Chapter 2. In particular for existing downstream processes that use syngas a specific value for the H₂/CO ratio is required. The following rough division can be made between processes where the conversion of natural gas to syngas is integrated in the process, like the methanol and the Gas-to-Liquid (GTL) process, and so-called derived products (acetic acid and phosgene), see Table 4.3 and Appendix A.2.

Table 4.3. Overview of industrial relevant products derived from syngas.

Product	H ₂ / CO ratio	Overall reaction	'Feedstock'
Methanol	2:1	$\text{CO} + 2 \text{H}_2 \rightarrow \text{CH}_3\text{OH}$	Natural gas
Fischer-Tropsch fuels	2:1	$\text{CO} + n \text{H}_2 \rightarrow (-\text{CH}_2-)_n + \text{H}_2\text{O}$	Natural gas
Gas-to-Liquid	2:1	$(2n+1) \text{H}_2 + n \text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n \text{H}_2\text{O}$	Natural gas
Acetic acid		$\text{CO} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{COOH}$	
Phosgene		$\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$	
Poly-urethane / Polyols	1:1	Hydroformylation and hydrogenation	
Poly-carbonate		Condensation polymerization	COCl ₂

4.3 Identification of stand-alone applications of LSG (pathway 3)

In Figure 4.2 the application and different synthesis routes of formic acid and hydrogen are summarized. The list of possible options will be reviewed based on: (1) market acceptance, (2) added value, and (3) feasibility, see Table 4.4.

Liquid Syngas

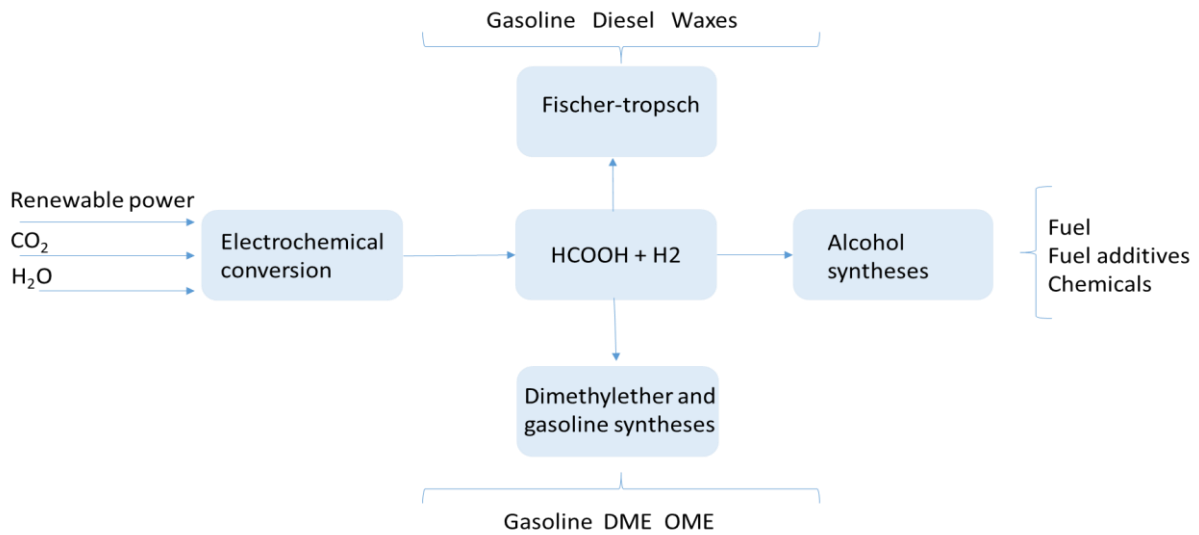


Figure 4.2. Potential of stand-alone applications of formic acid.

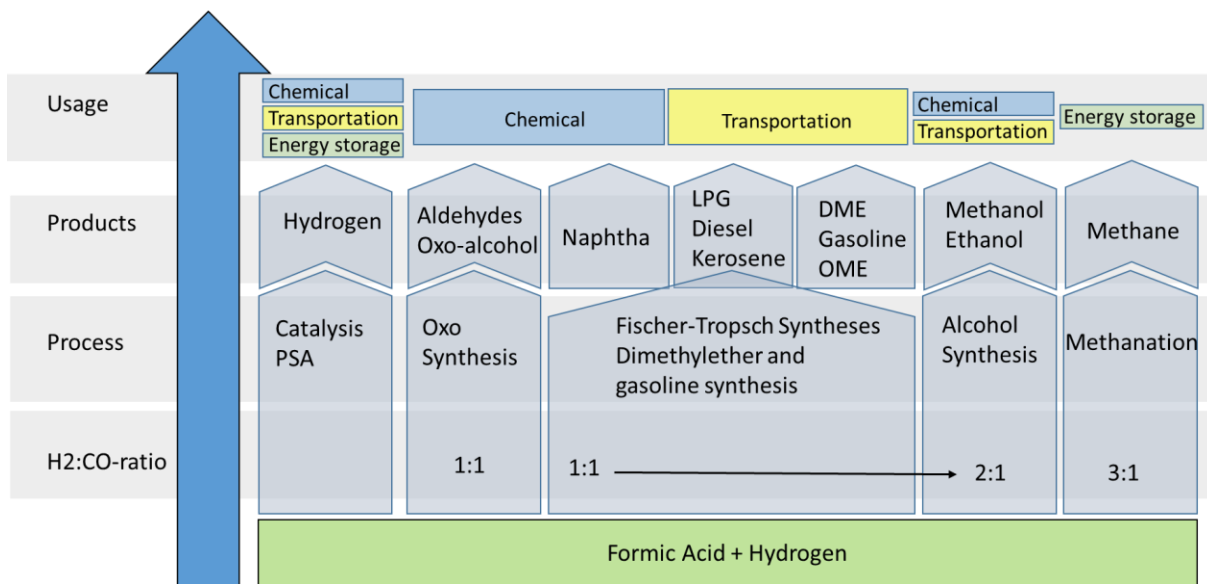


Figure 4.3. Overview of the different pathways relevant for a specific chemical product design with for each major component (that is the product) the final application as a chemical, as a transportation fuel, or for energy (storage) indicated, with PSA: pressure swing adsorption.

Based on the initial H/C ratio in the 'raw material' that is used as feedstock, a wide range of applications can be envisaged, see Figure 4.3. A comprehensive overview is given of the different levels relevant for

product design, ranging from the starting material through the process and product level to the final application (usage level), with as starting raw material a given blend of formic acid and hydrogen

Table 4.4. List of stand-alone applications for LSG (formic acid).

Application option	Description	Acceptance	Value	Feasibility
Conversion via Fischer-Tropsch synthesis	Converting formic acid via the Fischer-Tropsch synthesis into products such as methanol, ethanol, naphtha, diesel, gasoline, jet fuel, etc.	++	o	++
Conversion via dimethyl ether synthesis	Converting formic acid into methanol and catalytic conversion dimethyl ether (DME) synthesis	+	+	+
Conversion via the gasoline syntheses	Oxygenate synthesis to gasoline based on either methanol synthesis or the integrated methanol/DME synthesis	++	+	+
Conversion via the alcohol syntheses	Methanol is produced via the alcohol syntheses	+	o	+
Conversion via methanization reaction	Methane is produced based on formic acid and additional hydrogen	++	--	+

4.4 Evaluation of LSG application

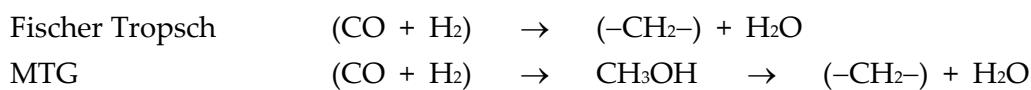
Most likely future energy systems will be based on a combination of electricity and gaseous fuels (hydrogen and natural gas). A realistic scenario will be that almost all electric power is provided by renewable energy sources. The intermittent behavior of the renewable energy sources, in particular wind and solar, need to be complemented by storage systems, demand-side management, and more controllable renewable energy technologies, like biogas and biomass-based sources

Generally speaking, a cost-effective energy system will be centered on two technologies, that is fluctuating production (wind and photovoltaic systems) and more flexible technologies (storage, demand-side management, and biogas). However, no clear picture has yet emerged how green hydrogen will be incorporated in future energy systems.

The main trend is to use renewable electrification in the power sector and the chemical process industry, but also the reverse is true: decarbonized routes for the production of chemicals, including hydrogen, will facilitate the implementation of renewable electrification. One route for the decarbonization of the chemical industry would be based on converting (captured) carbon dioxide, which would otherwise be emitted, into valuable commodity chemicals. A second strategy toward decarbonization would involve

avoiding the generation of carbon dioxide altogether. This could be achieved by obtaining hydrogen from splitting water (water electrolysis), instead from steam methane reforming and the water gas shift reaction. In this respect, electrical production of raw materials for the chemical industry will focus on versatile components that contain C, H and O atoms. In particular, the focus will be on syngas (gaseous mixtures of CO and H₂ and related components, such as liquid hydrogen and/or CO carriers, like formic acid and methanol.

With respect the production of synthetic fuels, in particular gasoline (C₆ - C₁₂), kerosene (C₁₂ - C₁₅), and diesel (C₁₂ - C₁₈) there are two main process routes possible starting with syngas. These routes are the Fischer-Tropsch process and the Methanol-to-Gasoline (MTG) process, both processes consist of similar reaction steps:



Furthermore, both processes are essentially a three-step process and can be used with different types of feedstocks, such as natural gas, biomass, and formic acid, see Figure 4.4 [13, 14].

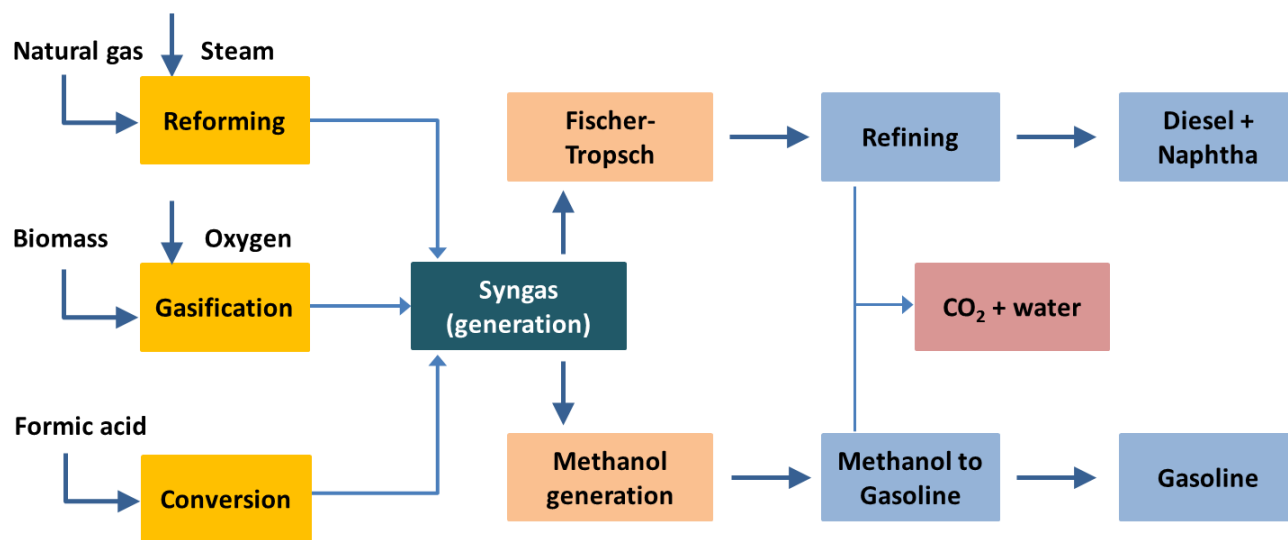


Figure 4.4. Comparison between the Fischer-Tropsch and the MTG process for the production of synthetic fuels based on the use of three different types of feedstock.

Pathway 1: Integration options

It is relatively easy to use formic acid as a hydrogen carrier. Formic acid is non-toxic and an environmentally benign liquid with a low flammability under ambient conditions. It seems likely that

the existing (gasoline) infrastructure can be adapted easily for the distribution of formic acid. Furthermore, formic acid can efficiently be converted using a catalyst into H₂ and CO₂ [10]. The hydrogen can directly be used in a fuel cell to generate electricity. In other cases, where relatively pure hydrogen is required the hydrogen and CO₂ need to be separated first. Large-scale technologies to separate H₂/CO₂ mixtures are available, as this separation is also required during the traditional methane steam reforming to produce high quality hydrogen.

Pathway 2: Tie-in options

The most straight-forward way of using formic acid is as a source of CO and H₂, this can be achieved via a reverse-water-gas-shift reaction (RWGS). The RWGS enables a sustainable way of producing the common building blocks based on renewables instead of fossil based feedstocks. The obvious lowest use of formic acid is as an energy source for high temperature conversion processes.

Pathway 3: Stand-alone applications

The products as a result of combustion of hydrocarbon fuels are H₂O and CO₂ which is thermodynamically very stable. However, this stability is commonly misinterpreted as if CO₂ is “unreactive” implying that any chemical conversion of it will require high energy input. Therefore, it is often presumed that the use of CO₂ for chemicals manufacture is not appropriate. This view is surely true with respect to oxidants such as O₂.

On the other hand, there are conversions of CO₂ for which there is no need for any external energy because the co-reactant can supply enough energy to enable the conversion to take place at ordinary temperatures, such as reactions of CO₂ with hydroxides, amines, or olefins.

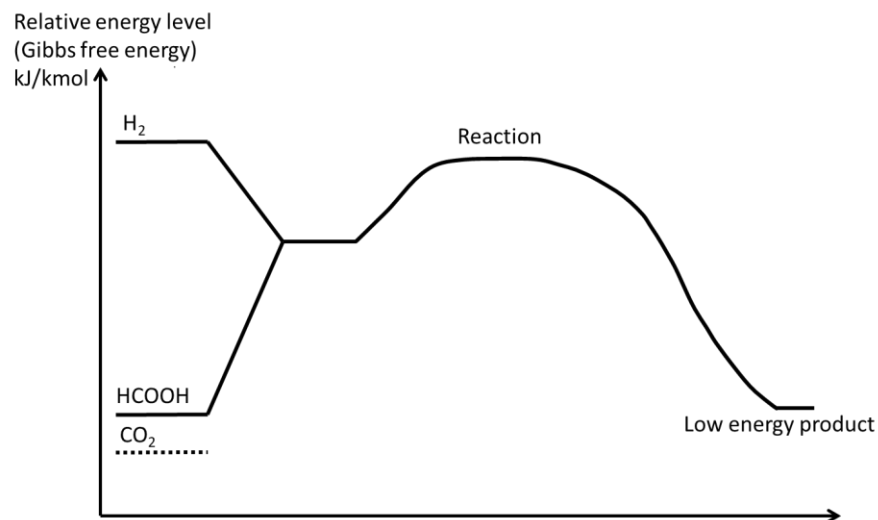


Figure 4.5. Energy levels of formic acid and hydrogen and low energy products.

Along the same line formic acid should be reviewed, as formic acid is a low energy product on its own, therefore the conversion to other products will follow the same pathway with a high energy reactant, which is in this study hydrogen. The Gibbs free energy of formic acid is low (-361 kJ/mol) which is somewhat higher than CO_2 (-394 kJ/mol). See Figure 4.5 for the energy levels of formic acid in combination with the high energy level of hydrogen towards the end product energy level. To further utilize the clear advantages of formic acid as a C1 building block in the petro-chemical industry, its low energy level is certainly an important item to consider, as such a high-energy co-reactant, like hydrogen must be used.

4.5 Selection of most promising LSG options

For both pathways the tie-in options, the stand-alone options of formic acid, and the technical and economic feasibility will be reviewed in Chapter 5. From the evaluation the option Conversion via the gasoline syntheses seems the most attractive, see Table 4.4. However, there are only a few commercial processes available, the MTG (Methanol-to-Gasoline) process and the so-called Topsoe Integrated Gasoline Synthesis (TIGAS) process [13, 14]. This means that for this application only a limited number of industrial sites will be available around the world.

As a result of the initial assessment, see Table 4.2 and Table 4.4, and the potential number of applications the following options are selected for a more detailed review:

- ✓ Direct tie-in option: Steam reforming (blending) (reverse water gas shift)
- ✓ Stand alone: Conversion via the alcohol syntheses

5 Economics and technical considerations

For various reasons it might be beneficially to have a liquid chemical as one the main feedstocks/building blocks of the (petro)-chemical industry, as opposed to gaseous feedstocks. That is replacing the current use of fossil fuel based syngas and natural gas, and assuring:

- Flexibility in terms of functionality, in terms of C/H/O ratio in the 'feedstock'
- Improved economics based on system integration (electrification, CO₂ recycling, optimized process and reactor design)
- Minimize storage and transport of 'energy' and chemicals
- An inherent safer process based on the operation of a liquid system, as compared to a gaseous system of CO, H₂ or a mixture of CO and H₂.

The key assumption to support the development of formic acid as liquid building block is based on two major developments:

- Electrification of the chemical process industry in general, and the electrochemical production of formic acid in particular
- Decarbonization of chemical synthesis routes and recycling of CO₂.

Taking all these considerations into account one of the most interesting molecules from both a chemical functionality and cost price point of view is formic acid. Formic acid is the simplest carboxylic acid, and it can be used as a hydrogen and carbon monoxide carrier, see Figure 5.1. Other basic platform molecules include alkanes (C_nH_{2n+2}), alcohols (R-OH), and ethers (R-O-R').

In the following three cases of the potential applications of formic acid will be discussed in detail.

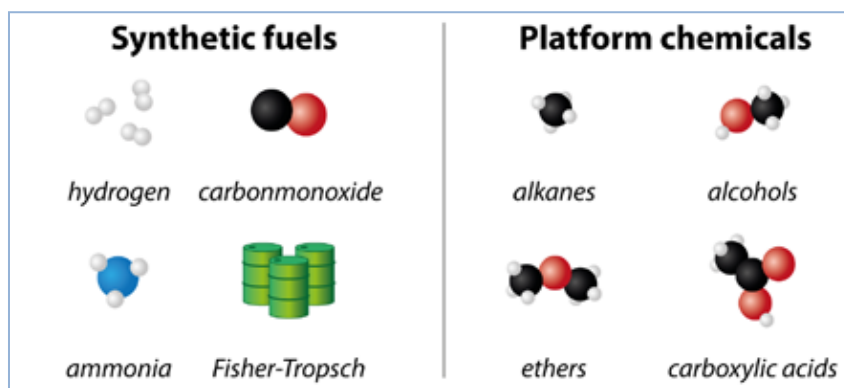


Figure 5.1. Broad qualification of different types of molecules in terms of synthetic fuels and platform chemicals.

5.1 Steam reforming versus formic acid reforming via partial oxidation

Case 1: Reforming based on partial oxidation of methane and addition of formic acid

For the steam reforming tie-in option of formic acid a partial oxidation reactor is considered as the design case. Based on a conceptual design flow sheet, the assessment of the impact on the syngas composition (equilibrium) is reviewed. A typical industrial scale reactor has been assessed with a thermal input of approximately 500 MW(Th) and the partial oxidation is operated at approximately 1000 °C for both conceptual design cases. See Figure 5.2 for a conventional flowsheet and Figure 5.3 for the substitution of steam with partly formic acid.

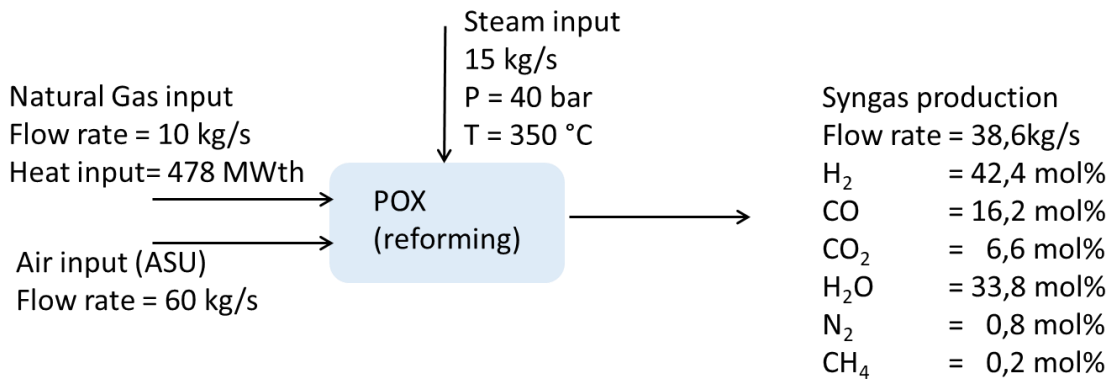


Figure 5.2. Conceptual design conventional partial oxidation reactor.

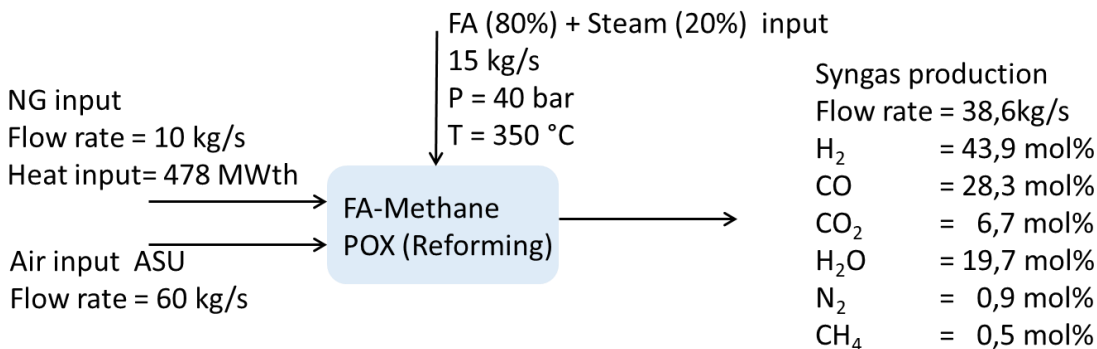


Figure 5.3. Conceptual design partial oxidation reactor with additional formic acid.

The CO concentration is significantly increased with impact on the H/C-ratio, thereby formic acid can be confirmed as an interesting feedstock for CO that can be integrated in existing process units and thereby much more versatile. Also a recent study indicated formic acid as the hydrogen and as CO carrier [10].

Economics

Based on the carbon monoxide and hydrogen content of formic acid a simplified cost analysis can be made, see Table 5.1. The main assumption is that formic acid is added as an extra feed stream to existing units, see Figure 5.3. This means that there will be no additional cost for the decomposition of formic acid in either hydrogen or carbon monoxide.

Table 5.1. Overview of basic cost breakdown for hydrogen and carbon monoxide for different production routes.

Production route	Product	Assumption	Price range €/kg
Methane steam reforming	Hydrogen		< 2
Water electrolysis	Hydrogen		4 - 8
CO ₂ electrolysis	Formic acid		0.3 - 0.4
Formic acid decomposition	Hydrogen	53 gram H ₂ per Liter FA (1)	5.7 - 7.5
Methane steam reforming	Carbon monoxide		0.7 - 0.8
CO ₂ electrolysis	Formic acid		0.3 - 0.4
Formic acid decomposition	Carbon monoxide	740 gram CO per Liter FA (1)	0.4 - 0.6

(1) Density of formic acid, FA, is 1.22 g/L

5.2 Formic acid conversion via the alcohol synthesis

Case 2: Formic acid and water-gas shift reaction

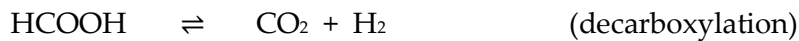
In a recent study it is stated that an in-situ generated CO and H₂ by catalytic decomposition of formic acid would make a synthesis process more interesting and versatile, as such the use of formic acid instead of syngas would render reactions easier to perform, even on a small industrial scale [15].

The production of oxygenated chemical compounds is a potential route for formic acid as identified in Chapter 4. Oxygenated compounds contain oxygen of their chemical structure which fits nicely with formic acid. Oxygenates are usually employed, blended, as gasoline additives, for a number of reasons, but mainly for better and cleaner combustion of the blended fuel. In Appendix A.4 some of the main oxygenated molecules are given. One of the simplest oxygenated molecules is methanol (CH₃OH or C₃H₄O)

In the analyses below the synthesis of formic acid has been assessed by assuming in situ decomposition of formic acid followed by a synthesis to methanol.

Decomposition of formic acid and the water-gas shift reaction

There are basically two decomposition pathways for formic acid [16]



The reversibility and the coupling of the decarboxylation decomposition and the decarboxylation decomposition clearly indicate that formic acid exists as an intermediate in the water-gas-shift (WGS) reaction. Based on formic acid, the WGS reaction can be expressed as:



The equilibrium constants for the WGS reaction can now be established by examining the rate and equilibrium constants for the decarboxylation and the decarbonylation of formic acid. The rate constant for the decarbonylation is given by:

$$R = K(\text{decarbonylation}) [\text{H}^+][\text{HCOOH}],$$

with $\log(K(\text{decarbonylation})) = 1.1 \text{ (kg / (mol s))}$

The equilibrium constants at about 300 °C are:

$$K_{\text{CO}} = [\text{CO}]/[\text{HCOOH}] = 4.2 \quad (\text{at } 280 \text{ }^\circ\text{C})$$

$$K_{\text{CO}_2} = [\text{CO}_2][\text{H}_2]/[\text{HCOOH}] = 100 \quad (\text{at } 330 \text{ }^\circ\text{C}).$$

The following four reaction equations are reversible and thus the process conditions regarding temperature, pressure are important to control. It can also be noted that Equation (2) and (3) are exothermic, see Table 5.2.

While it was formerly believed that the process that produce methanol was the reaction between carbon monoxide and hydrogen, Equation (2), it is recently understood that carbon dioxide is just as important in the synthesis process. Recent studies have shown that it is mainly the CO_2 that is converted to methanol while CO can act as a reducing agent for oxygen at the surface of the catalyst. Formic acid conversion into methanol is not yet studied in detail. For this study we consider as starting point the decomposition of formic acid according to Equation (1), this decomposition takes place in the reactor at high temperatures and pressure.

Equation (4) describes the standard reverse water gas shift reaction that produces carbon monoxide from carbon dioxide and hydrogen. The carbon monoxide then reacts with hydrogen to produce methanol, equation (2). The overall reaction is merely the sum of Equations (2) and (4).

Table 5.2. Overall reactions of synthesis for formic acid to methanol (CH_3OH)

Product	Reaction
(1)	$\text{HCOOH} \rightleftharpoons \text{CO}_2 + \text{H}_2$
(2)	$\text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$
(3)	$\text{CO}_2 + 3 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$
(4)	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$

To synthesise methanol, not only is a specific H/CO ratio of 2 in the feed stock needed but also a $(\text{H}_2/\text{CO}_2)/(\text{CO} + \text{CO}_2)$ ratio, called stoichiometric number, equal to or slightly above 2. To be slightly above this stoichiometric number of 2 a small additional amount of H₂ is required.

The methanol produced contains impurities to a smaller or larger degree. The largest impurity is water which can be as much as 20%. The first stage in a common two-step purification process is to remove the low boiling purifications, typically called removal of the light ends. This is done in a typical called 'topping column' where the low boiling compounds are boiled off to produce a mixture of methanol and water. Consecutively, a distillation column is used to separate water and methanol under heavy boiling. The distillation column needs to be high as methanol and water is reluctant to separate easily. Methanol eventually accumulates in the top of the column. Water accumulates in the bottom and must be treated before disposal.

Advantages

One of the main advantages of using formic acid as feedstock is the fact that a flexible feedstock can be provided for different petro-chemical processes. For most industrial applications using syngas, there are essentially 'three' H₂/CO fractions relevant: 0:1 (pure CO), 1:1 to 2:1 (50 to 67% H₂), and 1:0 (pure H₂). Combing formic acid with either CH₄ or H₂ will make this feasible. This is similar to the use of CH₄ or H₂, where always oxygen has to be added to the system. For fossil fuel based chemical production routes, oxygen is obtained from an air separation unit or from methane reforming, see Appendix A.5.

5.3 CO₂ reduction potential

There are several ways in which formic acid could result in displacement of fossil fuels as already discussed in this report. The CO₂ reduction potential of producing formic acid, based on the electrochemical synthesis using renewable energy, will be evaluated for the case where formic acid is used as a feedstock and where formic acid is used for heating, and in this way is a substitute for crude oil or natural gas. It is worth noting that whether a positive net impact will be obtained depends on the carbon footprint of the process/product that will be displaced.

Case 3: Conventional and electrochemical production of formic acid

In Figure 5.4 the two production pathways are schematically depicted using block flow diagrams. For the conventional process a total of around 4 MWh(Th) is required as heat input per ton FA produced for the four different steps. In the first three reaction steps the purification and recycling of the various streams is included in the heat input per reactor. Assuming an average value for the amount of CO₂ per heat input in terms of MWh(Th) of around 480 kg, this gives around 2 ton of CO₂ per ton formic acid [17]. For the direct electrochemical reduction of CO₂ a negative CO₂ footprint can be obtained, as it is fixing around 0.7 ton CO₂ per ton formic acid. For the electrochemical process it is assumed that except for the CO₂ capture step all the power input is from a renewable source. This means that around 2 ton CO₂ per ton formic can be avoided during the synthesis, and around 0.3 ton CO₂ is generated from the capture process. This gives a 'maximum' of around 2.4 ton CO₂ that can be avoided, when formic acid is produced from renewable energy and captured CO₂.

This approach can be generalized to a number of cases where formic acid is used to partially replace crude oil or natural gas. Estimated values for CO₂ emission reduction for a number of processes are given in Table 5.3 [18]. This overview does not include the CO₂ emission that is avoided at the upstream production activities.

Table 5.3. Emission reduction potential of formic acid.

Process	Substituted feedstock	Formic acid	Specific CO ₂
		requirements	emission reduction
		kg FA/kg substitute	kg CO ₂ /kg FA
Heating	Refinery gas (1)	10.33	0.05
Production of syngas	Natural gas	3.00	0.15
Production of hydrogen	Natural gas	5.17	0.07
Production of carbon monoxide	Crude oil	2.00	0.22

(1) for the case of the refinery gas it is assumed that CO₂ is recycled); FA: formic acid

Refinery gas

The main purpose of the different processes at an oil refinery is to break (crack) long-chain hydrocarbons into small-chain hydrocarbon chains. During operation a range of flue gases are generated in the different processes. These flue gases are collected and used as feedstock fuel to operate most of the refinery processes. These flue gases are known as refinery gas, basically the refinery gas is a way of recycling the flue gases. Refinery gas contains a range of gaseous components, such as hydrogen, methane, ethane, butane, propane and ethylene. Burning of the refinery gas produces enough energy to run all the refinery processes.

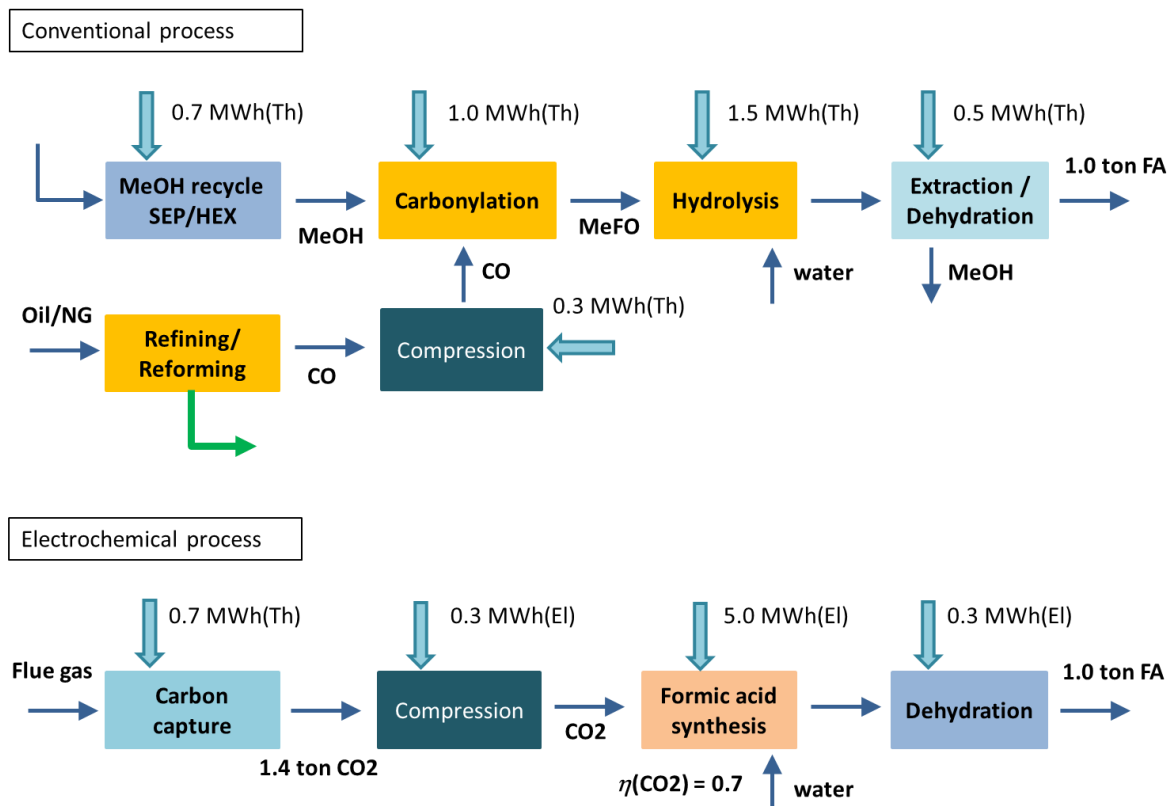


Figure 5.4. Comparison between conventional (top) and electrochemical production (bottom) of formic acid, with the main energy input for the thermal heat (Th) and electric power (EI), with MeOH: Methanol; SEP/HEX: separation and heat-exchange units; MeFO: methyl formate, NG: natural gas.

More than 70% of CO₂ emission in oil refining and petrochemical industry relates to high temperature heating [19]. Although the potential CO₂ emission reduction impact is large it is not the first item go for. There is a better and more effective use as an alternative source for syngas production and CO. Both applications will be an attractive option for the future to be carbon neutral, based on the specific emission reduction factor.

5.4 Economical feasibility

The demand across the industries, such as animal feedstock, leather and textile, rubber, chemical and pharmaceuticals and other industries will increase the overall formic acid consumption. The price depends on the active ingredient content as well as its purity. European prices for 85 wt% grade in the second quarter of 2014 were between 0.51 - 0.60 €/kg. Contract prices for June 2014 in the US were 0.60 - 0.70 \$/kg. It is difficult to predict the future of the formic acid market and new productions methods might reduce the cost price.

The estimated production cost of formic acid based on an electrochemical process is given in Table 5.4, see also Table 2.2 for some details. In order to produce 1.0 kg of formic acid around 1.4 kg of CO₂ is required. The required electricity input is approximately 3.5 kWh per kg CO₂, or 5 kWh per kg formic acid

It follows from Table 5.4 that there is a significant margin, between electrochemically produced formic acid and the current market price of formic acid. Clearly, this is good for a positive business case based on the current market conditions. However, this report is addressing mainly a new market drop-in of formic acid. As such the willingness to pay for the carbon neutral production of formic acid will be based on the CO₂ reduction potential and the ability to use existing process equipment. In Figure 5.3 a comparison is made for the CO₂ avoidance cost between various Power-to-X approaches, and other sustainable pathways to produce alternative fuels.

Table 5.4. Production cost of formic acid based on electrochemical conversion of water and carbon dioxide at current market prices.

Production cost formic acid	€/kg
OPEX	
Electricity (0.045 €/kWh)	0.22
CO ₂ capture cost	0.06
Water	0.01
Pre and post-treatment	0.04
CAPEX	0.04
<i>Total</i>	<i>0.37</i>

This comparison is quite favorable for the electrical production of formic acid as raw materials for the chemical industry, and formic acid seems one of the most promising alternative CO₂ neutral feedstocks. As such in 2020 and 2030 formic acid as a liquid syngas is the most cost effective way to reduce greenhouse gas (GHG) emissions at petrochemical processes.

The range in which the CO₂ is reduced is subject to the process and the substitution of the type of fossil feedstock. In Figure 5.5 and Figure 5.6 a more detailed cost breakdown estimation of CO₂ avoidance cost is presented. In Figure 5.5 a comparison is made for the case where formic acid is used as a fuel and in Figure 5.6 a comparison is made for the case where formic acid is used as a feedstock.

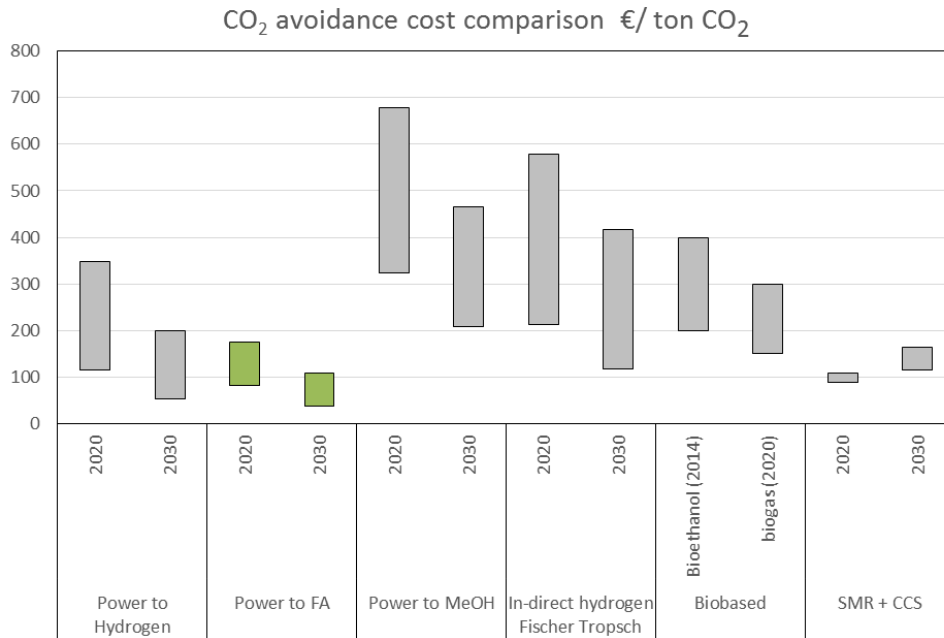


Figure 5.5. CO₂ avoidance cost comparison of alternative fuels, bioethanol, and biogas results are based on data presented by IRENA [20].

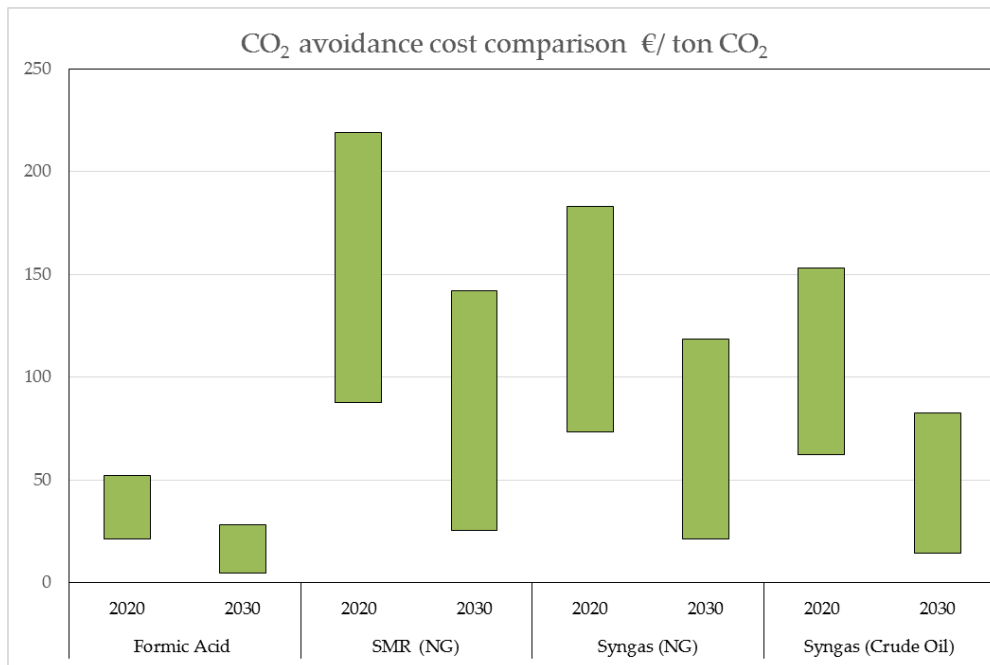


Figure 5.6. CO₂ avoidance cost comparison of formic acid as an alternative to fossil based on different feedstocks in petrochemical process applications of syngas, reformers, and conventional formic acid production (NG: natural gas).

For both Figure 5.5 and Figure 5.6 the main input is the assumed commodity price range for electricity, natural gas, and crude oil for the year 2020 and the year 2030, as given in Table A.3 in Appendix A.6. For each case the electricity price is used to calculate the marginal cost of the product: this is used to calculate the price for each product in terms of euros per GJ, based on the heating value. See Table 4.1 for the values for the (lower) heating value for the most common fuels. Additionally, a heating value for formic acid and ammonia of 5.7 and 18.6 GJ/kg is used, respectively.

From Figure 5.5 it follows that the lowest CO₂ avoidance cost can be obtained by replacing conventional produced formic acid. It also follows that the CO₂ abatement through formic acid produced electrochemically is highly competitive against biofuels. It is also cheaper than most of the other alternative fuel options. For the case where 'renewable' formic acid is used as feedstock, see Figure 5.6, the cost of CO₂ avoided is compared with three main production routes for conventional formic acid, for hydrogen, and for syngas from natural gas or crude oil. The cost of CO₂ avoided for the three products is determined by combining the difference in the levelised costs of production with and without alternative fuel, where the decrease in emissions of CO₂ is compared to the reference case based on the use of the two different types fossil fuels, natural gas and crude oil.

5.5 Barriers and regulations

With respect to the development of synthetic fuels from (liquid) syngas a number of regulatory aspects are relevant. There are two policies in particular relevant, and these are the Renewable Energy Directive (RED) and the Emission Trading System of the European Union (EU ETS). The main characteristics of the two policies are summarized in Box 1 and Box 2.

Box 1: Renewable Energy Directive

The [Renewable Energy Directive](#) establishes an overall policy for the production and promotion of energy from renewable sources in the EU. It requires the EU to fulfil at least 20% of its total energy needs with renewables by 2020 – to be achieved through the attainment of individual national targets. All EU countries must also ensure that at least 10% of their transport fuels come from renewable sources by 2020.

On 30 November 2016, the Commission published a proposal for a [revised Renewable Energy Directive](#) to make the EU a global leader in renewable energy and ensure that the target of at least 27% renewables in the final energy consumption in the EU by 2030 is met.

www.ec.europa.eu/energy/en/topics/renewable-energy/renewable-energy-directive

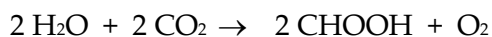
Box 2: Key facts EU Emission Trading System

- Operates in the 28 EU countries plus Iceland, Liechtenstein and Norway
- Limits greenhouse gas emissions from:
 - Approximately 11,000 energy intensive installations in power generation and manufacturing industry sectors
 - Operators of flights to and from EU Member States, Iceland, Liechtenstein and Norway (for the time being only flights within these countries are covered)
- Covers around 45% of the EU's greenhouse gas emissions

www.ec.europa.eu/clima/policies/ets_en

A major application of liquid syngas can be in the synthesis of so-called Fischer-Tropsch fuels, with a typical product distribution of 70% Diesel (C10 - C15), 20% Naphtha, and 5% LPG. It is to be expected that the synthesis of Fisher-Tropsch fuels will be categorized in the same way as future fuel production from refineries with a direct input from renewable (or green) hydrogen. That is hydrogen from biomass or from water electrolysis using renewable electricity to power the water electrolyzers.

Formic acid can be produced electrochemically, that is in an electrolyser, from a reaction of water and carbon dioxide, according to, see Table 2.1:



This is similar to water electrolysis to produce green hydrogen:



With respect to RED the key point is that by 2020 for each EU country at least 10% of the transport fuels that is based on a renewable energy source. The Renewable Energy Directive (RED) classifies a biofuel a fuel that originates from biomass. The current system in the Netherlands considers only renewable transportation fuels that originate from biofuels, but there is no regulation that addresses (synthetic) fuels synthesized from water or hydrogen.

At the moment, it is not completely clear how synthetic fuels synthesized from water, a carbon source and renewable electricity, hydrogen (from water electrolysis based on renewable electricity from wind or solar PV) will be accounted for.

A key assumption for the EU ETS is to limit the emissions of greenhouse gases. In Box 3 the various industrial process and greenhouse gases are specified, with the EU ETS. Over the last five years the CO₂ price based on the EU ETS has been in the range of 4 to 8 € per ton. Clearly, this is considerable lower

than the cost price of captured CO₂, which will be at least in the range of 30 to 50 € per ton CO₂. At the moment, it is not clear how this price difference of at least 20 to 25 \$ per ton CO₂ will be incorporated in the future revenue of companies and the various governmental regulations and ambitions. One of the most scenarios will be that there will be some limited subsidy for capturing CO₂ in the different energy-intensive industries, but that the main price for CO₂ will be determined by the actual capture and compression cost, which are in the range of 40 to 60 € per ton of liquid CO₂.

Future developments related to RED point in the direction of a more general inclusion of alternative synthesis routes of chemicals and fuels. So far, only a number of CO₂-based synthetic fuels are being considered, mainly drop-in diesel or gasoline, methanol, and dimethyl ether (DME) [21]. However, CO₂-based synthetic fuels could potentially be considered in the upcoming Renewable Energy Directive to 2030 (RED II). An interesting situation would arise in the case where sustainable produced formic acid (that is from renewable power and captured carbon dioxide), would obtain the same classification as, for example, the current status of bio-ethanol.

Box 3: Sectors and gases covered in EU ETS

The EU ETS covers the following sectors and gases with the focus on emissions that can be measured, reported and verified with a high level of accuracy:

- **carbon dioxide (CO₂)** from
 - power and heat generation
 - energy-intensive industry sectors including oil refineries, steel works and production of iron, aluminum, metals, cement, lime, glass, ceramics, pulp, paper, cardboard, acids and bulk organic chemicals
 - commercial aviation
- **nitrous oxide (N₂O)** from production of nitric, adipic and glyoxylic acids and glyoxal
- **perfluorocarbons (PFCs)** from aluminum production

Participation in the EU ETS is mandatory for companies in these sectors, but

- in some sectors only plants above a certain size are included
- certain small installations can be excluded if governments put in place fiscal or other measures that will cut their emissions by an equivalent amount
- in the aviation sector, until 2016 the EU ETS applies only to flights between airports located in the European Economic Area (EEA).

www.ec.europa.eu/clima/policies/ets_en

6 Conclusion and recommendations

6.1 Continuation, spin-offs, and dissemination

The activities of this project have been realized according to the project plan. No major difficulties and no main deviations have occurred during the course of the project.

The main outcomes of this project will be used during the various commercial activities of the two companies (SMEs) that have carried out the studied report here. In particular, for the next phase pilot-scale and demonstration projects will be initiated centered on the electrochemical production of formic acid from carbon dioxide and water. The outcomes of this study will be used to support the business case of renewable formic acid and dedicated applications of formic acid.

Possible end-users can be divided in basically two applications: large-scale and small-scale applications. Large-scale applications will be related to processes at refineries and chemical plants. Generally speaking, the petro-chemical industry will need to establish new business models based on developing more sustainable chemical production routes, the use of renewable energy (for both electricity and heat), and the use of (captured) carbon dioxide. For the chemical plants a further distinction can be made between companies that supply syngas, that is CO, H₂ and mixtures of CO and H₂, and (end-)users of syngas.

On the other hand, small-scale applications can be related to a number of biogenic sources of carbon dioxide, for example biogas and bio-ethanol. CO₂ is removed from the biogas to obtain bio-methane or bio-LNG with the required pipeline and combustion specifications. Removal of CO₂ from biogas or bio-ethanol will give relatively pure CO₂. Renewable energy sources, such as wind and solar PV, can be used as power input for the electrochemical conversion of CO₂ and water into formic acid. The formic acid can be stored, and subsequently used on a small scale in conjunction with a fuel cell to provide power, another option is the more traditional application for the preservation of cattle feed at farms.

6.2 Conclusions and future work

The main conclusions of this work are:

- It is economically feasible to produce formic acid based on electrochemical conversion of water and (captured) carbon dioxide. The relatively low amount of electric power to synthesize formic acid, as determined by number of electrons required in the reaction, is a clear benefit. This will open up a range of applications at refineries, as formic acid will be a relative inexpensive additive feedstock to be blended with crude oil or natural gas.

- Based on molecular functionality, formic acid is well-suited to be used in future petro-chemical processes. The key point is that the functionality in terms of O/C and H/C is much more relevant than the relatively low heating value. Actually, the low heating value of formic acid is the main reason that formic acid can be produced in an economically feasible way in an electrochemical process. Additionally, formic acid is obtained as a liquid.
- One of the main outcomes of this work is the confirmation that formic acid is interesting feedstock for blending with existing processes in order to adjust the fraction of H₂, CO, or syngas (CO + H₂). The main point is that formic acid can be directly integrated in the existing production process and process units. At the same time, electrochemically synthesized formic acid will maximize the potential of renewable energy at existing refineries and hydrogen production sites.
- The application of electrochemically produced formic acid as a liquid syngas is the most cost effective way to reduce greenhouse gas emissions at petrochemical processes. CO₂ abatement through formic acid produced electrochemically is one of the most interesting options as this is competitive against most other sustainable produced chemicals and fuels, like biofuels and power-to-methanol.

Future work

Based on the main outputs of this work and the ongoing activities at the two companies involved in this report, there are two main activities planned:

1. **Process design** and further develop of the reactor technology to improve the sustainable production of formic acid based on electrical conversion of CO₂ with a renewable power input. Activities will focus on improving the efficiency of the electrochemical reaction and of the electricity usage and scale-up of the current reactor to bench-scale and pilot-scale.
2. **System integration** at the interface of Power-to-X (P2X) and Carbon Capture, Utilization, and Storage (CCUS) technologies. Main activities will be related to system engineering, optimization and process modelling, centered on the integration of different renewable energy sources (RES), closing the carbon loop, and sustainable pathways for the production of chemicals. More specifically, continue with the scenario analysis to evaluate different renewable raw materials, especially carbon feedstocks such as biomass and biogas and the financial investments necessary to facilitate the implementation of renewable energy sources and the decarbonization of the petro-chemical industry.

Appendix A

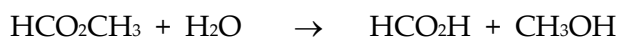
A.1 Industrial production of formic acid

On an industrial scale formic acid is produced in a two-step process, a carbonylation step and a hydrolysis step. First, methanol is reacted with carbon monoxide in a base solution to give methyl formate:



Typical reaction conditions for the carbonylation reaction (the introduction of the 'CO' group) are 80 °C and 40 bar, the most widely used base is sodium methoxide. The carbonylation rate can be increased by increasing the temperature, the CO partial pressure, the catalyst concentration, or by increasing the gas - liquid interface.

Subsequently, formic acid is produced through hydrolysis of the methyl formate, according to:



Efficient hydrolysis of methyl formate requires a large excess of water. The methanol formed in the second step is recycled to the first step.

A.2 Main products from syngas

An overview of the main products that are industrially synthesized from hydrogen, carbon monoxide and syngas is given in Table A.1.

Table A.1. Main end-user products obtained from syngas and carbon monoxide or hydrogen.

Main end-user applications		
Hydrogen (H ₂)	Carbon monoxide (CO)	Syngas H ₂ /CO
Hydrogen at refineries	Acetic acid	Methanol
Ammonia	Phosgene	Oxo-alcohols (n-butanol) (1)
Hydrogen peroxide		
Cyclo-hexane		

(1) through hydroformylation.

A.3 Formic acid dissociation

In an aqueous solution, at a pH below 7, formic acid (HCOOH) is in equilibrium with the formate anion (CHOO⁻), according to:



with the acid dissociation constant, K_a , given by:

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = 1.8 \cdot 10^{-4}$$

Formate is the deprotonated form of formic acid. This means that, for example, an aqueous solution of 90 wt% formic acid has a pH of around 2.8. The formate salts used for de-icing are mainly based on the potassium form, $KCHOO$ (or CHO_2K) [22].

A.4 Oxygenated molecules

Oxygenated chemical compounds contain oxygen as a part of the chemical structure. The term usually refers to oxygenated fuels. The two main types of oxygenates (oxygenated molecules) commonly used are alcohols and ethers. Alcohols have a hydroxyl functional group, $R-OH$, and ethers have an oxygen atom connected to two alkyl groups ($-CH_3$), indicated as $R-O-R'$. In Table A.2 a number of oxygenates are given. The simplest oxygenate is methanol. Oxygenates are used as gasoline additives with the main purpose to reduce carbon monoxide and soot formed during the burning of the fuel.

Methyl-tert-butyl-ether (MTBE) is a gasoline additive that is used to increase the octane number. TAME is another main fuel additive for gasoline, and is obtained from C5 distillation fractions of naphtha. TAME is added to gasoline for three reasons: to increase the octane number, to replace the banned tetraethyl lead, and to raise the oxygen content in gasoline.

Table A.2. Some main oxygenated molecules.

Alcohols		
Methanol	C_3H_4O	$\begin{array}{c} H \\ \\ H-C-OH \\ \\ H \end{array}$
Ethanol	C_2H_6O	$\begin{array}{c} H & H & H \\ & & / \\ H-C & -C & -O \\ & & \\ H & H & \end{array}$
Ethers		
Methyl-tert-butyl-ether (MTBE)	$C_5H_{12}O$	$\begin{array}{c} CH_3 \\ \\ H_3C-C-O-CH_3 \\ \\ CH_3 \end{array}$
Tert-amyl-methyl-ether (TAME)	$C_6H_{14}O$	$\begin{array}{c} CH_3 \\ \\ H_3C-CH_2-C-OCH_3 \\ \\ CH_3 \end{array}$

A.5 Reforming of methane

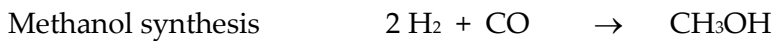
There are two main routes to reform methane:

1. Auto-Thermal Reforming (ATR):



The H/C ratio obtained from these routes lies in the range of 1:1 to 2.5:1, where essentially the required range of 50% to 75% H₂ is obtained from combining the auto-thermal reforming reaction or the partial oxidation reaction with the water-gas-shift reaction. Pure hydrogen and pure carbon monoxide are basically obtained from the same reactions, but will required additional separation steps.

In practice this means that, for example, the synthesis of methanol is based on a minimum of three different reactors in series:



A.6 Price assumption for commodities

In the various calculations for the CO₂ abatement cost an estimate for the market price of the three most import energy sources has been made. The commodity price range for the year 2020 and 2030 are given in Table A.3.

Table A.3. Overview of assumed market price range for electricity, natural gas, and crude oil for the year 2020 and the year 2030.

Commodity	year	Market price		unit
		low	high	
Electricity	2020	38 (11)	55 (15)	€/MWh (€/GJ)
	2030	34 (9)	50 (14)	€/MWh (€/GJ)
Natural gas	2020	5	7	€/GJ
	2030	7	11	€/GJ
Crude oil	2020	8	12	€/GJ
	2030	8	12	€/GJ

with 1 MWh equivalent to 3.6 GJ.

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