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Hydrogenation of CO_2 to formic acid and methanol

Sustainability assessment between commercial and CO_2 utilization routes

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1 Introduction

CO_2 is the main greenhouse gas and its utilization has been of global interest from both theoretical and practical viewpoints. Increasing the CO_2 concentration in the atmosphere is considered a major source for global warming. (Gao et al 2012) The utilization and transformation of CO_2 into value-added chemicals have attracted much attention in recent years as there are requirements for its trapping from power plant emissions. Catalytic hydrogenation of CO_2 has shown appreciable efficiency for reactions with optimized conditions and catalysts are one of the most promising directions for CO_2 fixation. (Hao et al 2011; Omae 2006). Many companies have realized that CO_2 emission reduction and the development of CO_2 utilizing technologies may be an essential step towards a more sustainable industry (Fiedler et al. 2011, 12) The use of CO_2 is only the indirect solution for environmental issues. CO_2 is a cheap raw materials and the use of CO_2 can increase the quality of the reactions.

In this report production of formic acid and methanol via commercial and laboratory scale were considered. The hydrogenation of CO_2 provides a possible technique to produce formic acid using CO_2 as a raw material. (Hao et al. 2011) Commercial processes for formic acid production are based on mainly of direct synthesis from the carbon monoxide and water and hydrolysis of methyl formate. The hydrogenation of CO_2 offers one possible technique to synthesize formic acid from CO_2. (Hao et al. 2011)

The potential use of CO_2 as an alternative feedstock replacing carbon monoxide (CO) in the methanol production has received attention as an effective way of CO_2 utilization. (Yang et al. 2006) Methanol is one of the most important chemical raw materials. Commercially, methanol is produced from coal or natural gas via synthesis gas, mainly containing carbon monoxide and hydrogen along with a small amount of carbon dioxide. As a cheap, abundant, and nontoxic carbon (C1) feedstock, chemical utilization of CO_2 is very attractive, and the catalytic hydrogenation of CO_2 to methanol has been recognized one of the most economical and effective ways to fix and utilize large amounts of emitted CO_2. Methanol synthesis from hydrogenation of CO_2 is a great importance for greenhouse gas control and fossil fuel substitution. (Gao et al. 2012; Fiedler et al. 2011)

Sustainable development can be defined in many ways. One definition for sustainable development is "Development that meets the needs of the present generation without compromising the ability of future generation to meet their own needs". Sustainable development can also be defined in three impact areas i.e. economic, environmental and social. (Anastas & Warner 1998; International Institute for Sustainable development 2013)

The aim of this report was to evaluate sustainability of two selected CO_2 utilizing reaction routes for the production of formic acid via methyl formate hydrolysis and hydrogenation of CO_2, and methanol synthesis via synthesis gas and hydrogenation of CO_2. The selected CO_2 based process routes were compared to the corresponding commercial processes.

2 Formic acid

Formic acid, HCOOH, having molar mass of 46.03 and CAS number of 64-18-6), is a colourless, very corrosive liquid with a pungent odour. Formic acid is completely miscible with water and many polar solvent. (Reuteman & Kieczka 2011)

2.1 Production and use of formic acid

The formic acid production processes can be classified in four groups' i.e. methyl formate hydrolysis, oxidation of hydrocarbons, preparation of free formic acid from formates and hydrolysis of formamide (Reutemann & Kieczka 2011). Basically, commercial processes for formic acid production are mainly based on direct synthesis from carbon monoxide and water, and hydrolysis of methyl formate. These traditional methods produce hazardous wastes and consume a large amount of energy; the development of a clean method for formic acid synthesis is high priority. HCOOH synthesis is mainly performed through a two-step process. Producing HCOOH by direct hydrogenation of CO_2 would be a promising alternate route from ecological, financial and safety perspectives. (Hao et al. 2011; Peng et al. 2012)

Formic acid is used primarily in dyeing, textile and leather industries, in rubber production, and as an intermediate in the chemical and pharmaceutical industries, and the use as an aid in the ensilage of green forage has increased sharply. (Reuteman & Kieczka 2011)

2.1.1 Methyl formate hydrolysis

Synthesis of formic acid by hydrolysis of methyl formate is based on a two-stage process. In the first stage methanol is carbonylated with carbon monoxide to methyl formate (Equation 1) and in the second step methyl formate is hydrolysed to methanol and formic acid (Equation 2). The formed methanol is returned to the first stage.

$$CH_3OH + CO \rightarrow HCOOCH_3 \tag{1}$$

$$CH_3OOCH + H_2O \rightarrow CH_3OH + HCOOH \tag{2}$$

Carbonylation of methanol is relatively problem-free, economically feasible and has been carried out industrially for a long time. The main problems are associated with work-up of the hydrolysis mixture and the selection of corrosion-resistant materials. (Reutemann & Kieczka 2011)

Industrial methods involving carbonylation of methanol and hydrolysis of methyl formate followed by isolation of formic acid, were developed by the Leonard Process Company, BASF, Halcon – Scientific Design – Bethlehem Steel and the Scientific Research Institute for the Chlorine Industry of the Ministry of the Chemical Industry. (Reutemann & Kieczka 2011)

2.1.2 Kemira-Leonard Process

A 20 000 ton per year formic acid plant based on a method developed by the Leonard Process Co. was built at Kemira in Finland and put into operation in 1982. The plant was built at Kemira in Finland and it started operation in 1982. The process has been developed further by Kemira. In the Kemira-Leonard process methyl formate and carbonylation is performed at approximately 40 bar and temperature of about 80 °C with additive-containing alkoxides as a catalyst. Hydrolysis is carried out in two reactors with different reaction conditions. Hydrolysis is carried out at the reaction conditions about 9 bar and 120 °C. The formic acid is dehydrated by distillation. (Reutemann & Kieczka 2011)
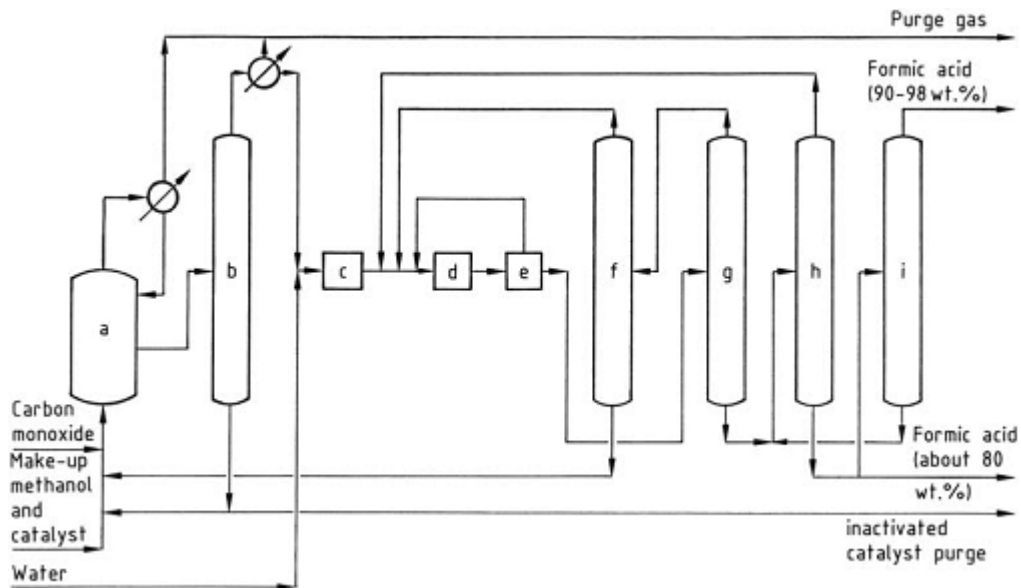

Figure 1. Production of formic acid by Kemira – Leonard process a) Methyl formate reactor b) Methyl formate column c) Preliminary reactor d) Main reactor e) Flash tank f) Recycle column g) Acid separation column h) First product column i) Second product column (Reutemann & Kieczka 2011)

Methanol and carbon monoxide are converted into methyl formate in reactor (a). Catalyst is fed into reactor in a methanol solution. The discharge from reactor (a) is flashed and fed into the methyl formate column (b) from which methyl formate is drawn off as the distillate. Dissolved catalyst and methanol are returned to the reactor (a). Waste gas from reactor (a) and exhaust gas from column (b) are burned. In the preliminary reactor (c) the methyl formate reacts partially with water and discharge from reactor (c) is fed into the main reactor (d) along with recycled methyl formate, water and methanol. Reactor discharge is flashed to about atmospheric pressure in the flash tank (e), where methanol, methyl formate and small amount of formic acid are evaporated and recycled to the main reactor. Methanol and methyl formate are distilled in vacuum in the acid separation column (g). In the recycle column (f) the distillate is separated into methyl formate and methanol. Formic acid can be concentrated under pressure in a column; 85 % formic acid is drawn off as the bottom product if the pressure is about 3 bar. In the first product column (h) water is distilled overhead and the bottom product is concentrated further in the second product column (i) and formic acid with a maximum concentration of about 98 wt % is

drawn off as distillate. The bottom product from the second product column is recycled to the first product column. (Reutemann & Kieczka 2011)

The problems associated with metyl formate hydrolysis are unfavourable hydrolysis equilibrium and because methyl formate is a highly volatile chemical. These problems are eliminates in Kemira-Leonard process using two reactors placed in series to each other after which a flash distillation is carried out in order to takeaway very quickly unconverted ester and distillation. (Kirk-Othmer 1993)

Other processes which use methyl formate hydrolysis to the synthesis of formic acid are BASF Process, USSR Process and Scientific Design – Bethlehem Steel Process. In the BASF Process carbonylation stage is quite much identical to that of Kemira – Leonard Process, but the hydrolysis and the dehydration of formic acid are significantly different. In the BASF process, hydrolysis is carried out with an excess of water. (Reutemann & Kieczka 2011)

2.1.3 Hydrogenation of CO_2 to formic acid

The hydrogenation of CO_2 to formic acid and formates has been an increasing interest since the beginning of 1990s. Hydrogenation of CO_2 is produced in laboratory scale. Formic acid synthesis is an alternative possibility to convert CO_2 to liquid products that may be used as both fuels and chemicals e.g. fiber and sweetener. (Wang et al. 2011; Genti & Perathoner 2009) The direct synthesis of formic acid from the hydrogenation of CO_2 is presented in Equation 3.

$$CO_2 + H_2 \rightarrow HCOOH, \qquad \Delta G_{273K} = 32.9 \text{ kJ mol}^{-1} \qquad (3)$$

The formic acid production process from CO_2 hydrogenation is thermodynamically unfavourable. The best known catalytic system for this process have been based on the metal complexes, such as ruthenium and rhodium, which are usually combined with halides or hydrides as anionic ligands and phosphines as neutral ligands. Also reaction in different media, such as organic solvent, water, ionic liquids and supercritical CO_2 have shown satisfactory reaction rates. (Hao et al. 2011) Interesting developments in CO_2 chemistry have resulted in formic acid synthesis, but these have not yet been used industrially. Zinc telluride and zinc selenide have been proposed as catalysts for the hydrogenation of CO_2. Carbon dioxide, hydrogen and water can be converted to formic acid with homogeneous transition -metal catalysts. BP Chemicals has developed a process in which formic acid is produced from CO_2 and hydrogen via several process stages. In the first stage, a nitrogen base such as triethylamine reacts with CO_2 and H_2 in the presence of noble -metal catalyst, for example ruthenium, to yield formate of the nitrogen base. In the second and third stages, the formate is separated from the catalyst and the low-boiling substances. In the fourth stage, the formate reacts with high boiling base, for example 1-(n-butyl)imidazole, to yield a formate that can be thermally decomposed. Concurrently, low-boiling base is liberated and distilled. In the fifth stage, the formate is thermally decomposed, formic acid distilled, and high-boiling base is returned to the fourth stage. (Reutemann & Kieczka 2011)

2.2 Catalyst for formic acid synthesis

Synthesis of formic acid is carried out with both heterogeneous and homogeneous catalysts. Compared to heterogeneous systems for hydrogenation of CO_2, the formation of formic acid typically proceeds with organometallic complexes at low temperatures. Ionic liquids have some unique properties, such as wide liquid regions, excellent thermal stability, and favourable solvation properties for various substances. Recent years, the production of formic acid in the laboratory scale using ionic liquid as a catalyst has attracted much attention because of the diverse chemical properties of the ionic liquid which favours the reaction. (Hao et al. 2011; Mikkelsen et al. 2009; Wang et al. 2011; Zhang et al. 2008)

2.2.1 Homogeneous catalyst

Although homogeneous catalysts are efficient for CO_2 hydrogenation to formic acid, they have some disadvantages such as separation of products and recycling the catalyst. Although the reasonable yield and conversion of formic acid have been obtained using homogeneous catalysts, separation of HCOOH from the bases and catalysts remains a challenge. (Hao et al. 2011)

2.2.2 Hetorogeneous catalyst

The development of efficient heterogeneous catalytic system is highly desirable. Advantages of the heterogeneous catalyst systems are easy separation of the catalyst, handling, stability, the loss of the catalyst is reduced and the production of formic acid is simple, although the yield of formic acid is low. Ruthenium, Ru, has become focus of studies and Ru complexes have been found generally to offer favourable activity and selectivity for formic acid. Addition of small amount of water is efficient way to improve the catalytic hydrogenation of CO_2 to formic acid. Ruthenium complexes immobilized over amine functionalized -silica has been developed with *in situ* synthetic approach for producing of formic acid via CO_2 hydrogenation. The catalysts exhibit high activity, 100% selectivity and offer also the practical advantages such as easy separation and recycling. (Wang et al. 2011; Mikkelsen et al. 2009; Hao et al. 2011)

3 Methanol

Methanol, CH_3OH, is one of the most important chemical raw materials. Its molar mass is 32.042 g/mol and CAS number is 67-56-1. At ambient conditions, methanol is a colourless liquid with relatively high polarity and medium vapour pressure. It is miscible with water, various organic solvent, alcohols, and to a limited extends with fats and oils. Approximately 85 % of the methanol produced is used in the chemical industry as a solvent for synthesis or a starting material. In 2011, the consumption of pure methanol was about 47 mega ton per year, the major part is used in the formaldehyde industry followed by the acetic acid industry. (Fiedler et al. 2011)

3.1 Production of methanol

Commercially, methanol is produced from coal or natural gas via synthesis gas (syngas), mainly containing carbon monoxide and hydrogen along with a small amount of carbon dioxide. Processes have been developed by Lurgi, ISI, Topsoe and MGG among others during the last century. The potential use of most important greenhouse gas, CO_2, as an alternative feedstock replacing CO in the methanol production has received attention as an effective way of CO_2 utilization. (Yang et al. 2006) Currently, more than 75 % of methanol is produced from natural gas. The methanol production is based on three steps of natural gas reforming in order to produce synthesis gas, conversion of synthesis gas into crude methanol and distillation of crude methanol to achieve the desired purity. The main methanol production technology suppliers and the operation conditions are shown in Table 1. (Cifre & Badr 2007) BASF started synthetic methanol production with zinc-chromium oxide catalyst in 1923. The activity of this catalyst required high pressure 250 – 350 bar and temperatures between 320 – 450 °C. This high pressure process suffered from high capital and compression energy cost and poor catalyst selectivity. ICI developed in 1960s a more active copper – zinc – alumina catalyst that operates at 50 – 100 bar and 210 – 270 °C with higher stability and selectivity. (Kirk-Othmer, 1995, 539)

Table 1. The main methanol production technology suppliers and the operation conditions (Cifre & Badr 2007).

Supplier	Reaction conditions	
	Pressure (bar)	Temperature (°C)
ICI	210 - 290	50 - 100
Lurgi	230 - 265	51 - 100
Mitsubishi	240	77 - 97
Haldor-Topsoe	260	48 - 300

Currently, several companies, including ICI, Mitsubishi and Lurgi, offer commercial technology solution for methanol synthesis. There is an argument about many important factors related to kinetics, catalyst and the reaction mechanism of the commercial methanol synthesis reaction. The main question is whether CO or CO_2 is the main source for methanol. (Raudaskoski et al. 2009) Commercially, methanol is produced from syngas mainly containing H_2 and CO along with a small amount of CO_2, which have been developed by ICI, Lurgi, MGC and Topsoe in the last century. The $CuO/ZnO/Al_2O_3$ catalyst has long been used in industrial methanol synthesis because of its high catalytic activity, high poison resistance, long durability and relatively low reaction pressure and temperature of 50 – 100 bar and 200 – 250 °C. (Wang et al. 2012; Yang et al. 2006)

3.1.1 High pressure process

Methanol synthesis process is generally categorized in two classification according to the pressure used. The process developed by BASF is known as

the high pressure process which operated at 250 – 300 bar and 320 – 450 °C with relatively poison resistant ZnO/Cr_2O_3 catalyst. The disadvantages of high pressure process are related to the significant investment in the plant design and operating costs. (Fuad et al. 2012; Tijm et al. 2001)

3.1.2 Low pressure process

Currently, the only process which is used in a methanol market is low pressure process which operated at about 50 – 100 bar and 200 - 300°C. The current catalyst used in low pressure processes are composed of copper oxide and zinc oxide on a carrier of aluminium oxide. Currently, the two important technology providers for the low pressure methanol processes are Lurgi and ICI. Lurgi offers a methanol synthesis concept based on the quasi-isothermal reactor design in which the mechanism of temperature control is achieved via boiling water-stream generation inside the reactor's shell. ICI offers a methanol synthesis reactor concept that is based on the adiabatic quench converter design in which a portion of the fresh and recycled synthesis gas is injected along the bed to control the reaction. The main advantages of the low pressure process are lower investement and production costs, greater flexibility in the choice of plant size, and improved operational reliability. (Fiedler et al. 1990; Fuad et al. 2012; Tijm et al. 2001)

3.1.3 Production costs for methanol synthesis

Estimated production costs of methanol produced from natural gas, coal, biomass and CO_2 are presented in Figure 2.
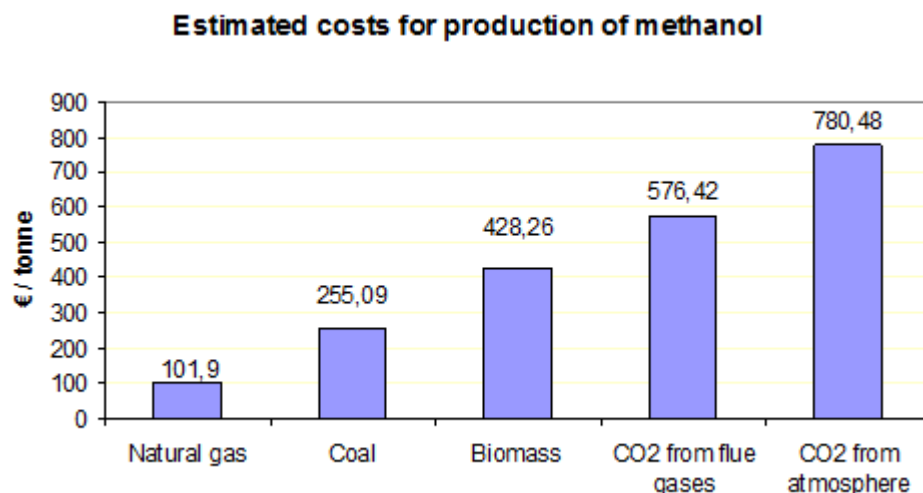
Figure 2. Estimated methanol production costs for different concepts of methanol synthesis (Cifre & Badr 2007).

The selection of system components, the feedstock and the energy demand are crucial. Many other factors as capacity, operating conditions, mode of operation and the desired grade of purity of the final product affect the process economics. The values presented in Figure 3 are only estimated values for preliminary screening. Figure 3 shows that methanol from flue gas CO_2 or

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biomass is at least 2 – 3 times more expensive than fossil fuel (coal) based methanol production. Methanol can only compete with conventional fossil fuels under an environmental taxation system based on pollutant emissions specially those of CO_2. A tax will favour mostly the production of methanol from CO_2 in flue gas and biomass. Methanol production from biomass has been proved more efficient and cheaper than from CO_2. (Cifre & Badr 2007)

3.2 Methanol synthesis via synthesis gas

Synthesis gas is a key intermediate in the chemical industry. Synthesis gas is a mixture of hydrogen and carbon monoxide. It can be used in a number of syntheses of a wide range of fuels and chemicals, and as a source of pure carbon monoxide and hydrogen. It can be produced by gasification or reforming from almost any carbon-containing source ranging from natural gas and oil products to biomass and coal. At present, natural gas is the dominant feedstock for the production of synthesis gas. From industrial and environmental perspective, there is a growing interest in utilizing alternative raw materials. (Raudaskoski et al. 2009)

Methanol is currently produced on an industrial scale exclusively by catalytic conversion of synthesis gas according to the principles of the low-pressure methanol process at 50 – 100 bar and 200 – 250 °C using a ternary Cu/Zn/Al oxide catalyst. The main benefits of the low-pressure processes are lower production cost, improved operational reliability, lower investment, and possibility in the choice of plant size. Industrial methanol production can be subdivided into three main steps which include production of synthesis gas, synthesis of methanol and processing of crude methanol. (Fiedler et al. 2011, 8; Yang et al. 2006) Many improvements have been made to early methanol processes, and now the current technology is a low-pressure process using copper-based catalyst. The synthesis gas needed as a feedstock is usually produced by catalytic steam reforming of hydrocarbon feedstock or by non-catalytic partial oxidation of coal or hydrocarbons. Carbon dioxide is used in the feedstock to adjust the feed compositions. (Raudaskoski et al. 2009)

The methanol synthesis from synthesis gas containing carbon monoxide and carbon dioxide can be described by the reactions 4 and 5. The reaction 4 is the main reaction and the reaction 5 occurs as a side reaction. In addition to the two methanol forming reactions (4 and 5), the endothermic reaction of CO_2 and hydrogen, the reverse water-gas shift reaction, RWGS, must also be taken into account as in Equation 6. The maximum yield of CO to methanol is limited by thermodynamic equilibrium (Fiedler et al. 2011)

$$CO + 2H_2 \rightarrow CH_3OH, \qquad \Delta H_{300K} = -90.77 \text{ kJ/mol} \qquad (4)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O, \qquad \Delta H_{300K} = -49.58 \text{ kJ/mol} \qquad (5)$$

$$CO_2 + H_2 \rightarrow CO + H_2O, \qquad \Delta H_{300K} = 41.19 \text{ kJ/mol} \qquad (6)$$

Reactions 4 and 5 are exothermic and accompanied by a decrease in volume. Formation of methanol is thus favoured by decreasing temperature and increasing reaction pressure. (Raudaskoski et al. 2009; Fiedler et al. 2011)

Any hydrocarbon that can be converted into a synthesis gas by gasification with oxygen or reforming with steam is a potential feedstock for methanol. Steam reforming of natural gas accounts at least 80% of the world's methanol capacity. (Kirk-Othmer 1995, 541)

3.2.1 The methanol synthesis loop with Lurgi reactor

The process flow diagram of the methanol synthesis loop with Lurgi reactor is shown in Figure 3.
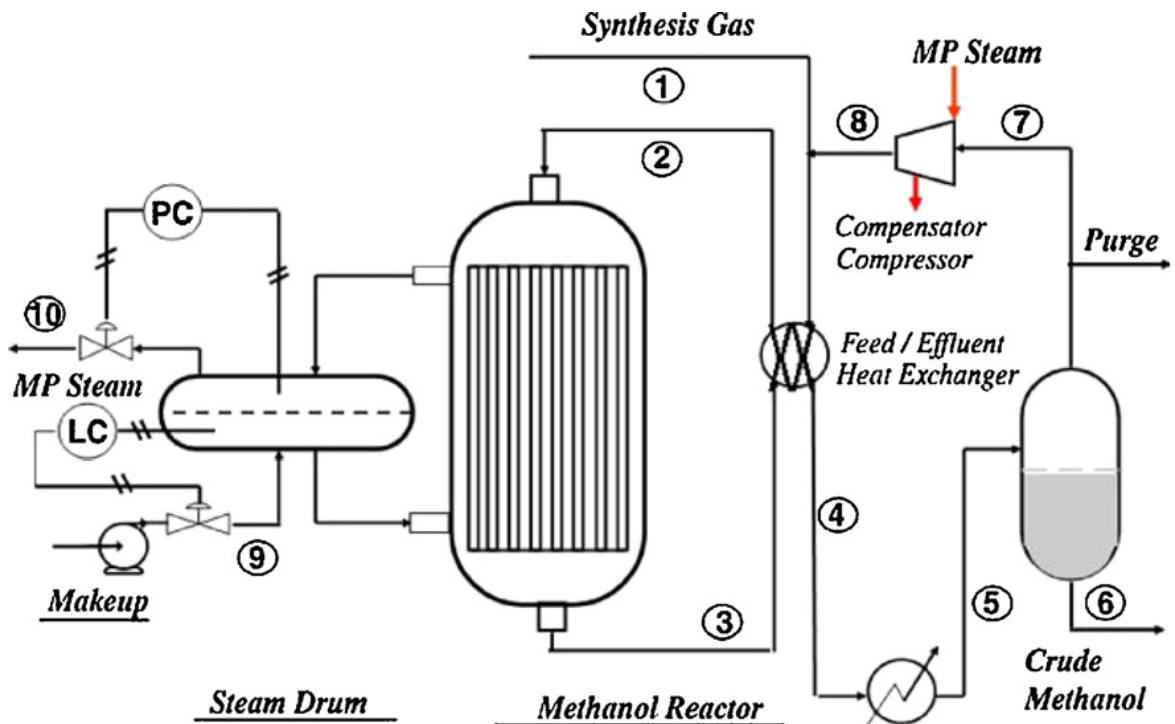

Figure 3. Process flow diagram of the methanol synthesis loop with Lurgi reactor (Fuad et al. 2012).

Fresh synthesis gas is compressed and mixed with the un-reacted, recycled synthesis gas comes from the reactor effluent. This stream is sent to the methanol synthesis reactor to be reacted to produce methanol. Three reactions CO_2 hydrogenation, CO hydrogenation and reverse water-gas shift reactions (Equations 4, 5 and 6) are responsible for the methanol synthesis inside the reactor. Lurgi fixed-bed reactor is operated at low pressure region with copper and zinc oxide catalyst on an alumina carrier ($Cu/ZnO/Al_2O_3$).The heat from the methanol synthesis reactions is transferred to the boiling water where steam will be generated. Typical operation conditions are 250 °C and 80 bar. The product from the reactor effluent is cooled and fed to a flash drum where the un-reacted synthesis gas and crude methanol are separated. The crude methanol is then sent to the methanol distillation section for further purification. The un-reacted synthesis gas is compressed, recycled and mixed with the fresh synthesis gas before introduced back to the reactor. To avoid the thermodynamic limitation and low single-pass conversion, the synthesis loop is usually operated with high synthesis gas recycle rate. (Fuad et al. 2012)

3.2.2 Catalyst for methanol synthesis via synthesis gas

It is necessary to use a specific catalyst, in order to achieve a reasonable industrial conversion rate. For the Lurgis fixed-bed reactor operated at the low pressure region, the catalyst is composed of copper and zinc oxide on an alumina carrier. (Fuad et al. 2012) Cu/ZnO catalysts for methanol synthesis were described by BASF in the 1920s. The operation temperature was 300 °C and pressure 150 bar. A low-pressure catalyst, Cu/ZnO with alumina, was first used industrially in the process developed by ICI in 1966. All commercially available catalyst systems are based on $Cu/ZnO/Al_2O_3$ or Cr_2O_3 with different promoters and additives. (Fiedler et al. 2011, 6) Industrial Cu/Zn-based catalysts are commonly prepared by co-precipitation method. The ratios of vary from one manufacturer to another. As a rule, the proportion of CuO ranges from 40 to 80%, ZnO between 10 and 30% and Al_2O_3 between 5 and 10%. Under normal operation, the $Cu/ZnO/Al_2O_3$ catalyst deactivates slowly and has a lifetime of several years. After 3 – 4 years of operation, the catalyst activity is so low that the catalyst has to be replaced with fresh catalyst. Additives may also be present. Such catalysts are manufactured by Synetix (ICI Katalco), Süd Chemie, Haldor Topsoe and Mitsubishi Gas Chemical. (Tjjm et al. 2001; Yang et al. 2006)

3.3 Methanol synthesis via CO_2 hydrogenation

Hydrogenation of CO_2 to methanol ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$, reaction 4) has gained wide interest to contribute to the reduction of CO_2 emissions. Carbon dioxide can be converted with hydrogen to methanol with higher selectivity than carbon monoxide and at lower reaction temperatures. (Raudaskoski et al. 2009) Methanol can be produced by heterogeneous catalytic hydrogenation of carbon dioxide (Equation 5). The three principle steps of the methanol production process are CO_2 separation/recovery, CO_2/CH_3OH transportation and storage and methanol synthesis. Amine absorption is the dominant and most economic technology for carbon dioxide extraction from flue gases. Once CO_2 is recovered from emitting source it must be liquefied and transported to the hydrogen production site. The production of methanol from hydrogenation of CO_2 consists of two steps methanol synthesis over a catalyst and methanol purification. (Cifre & Badr 2007)

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O, \qquad \Delta H_{300K} = -49.58 \text{ kJ/mol} \qquad (5)$$

The source of H_2 is a fundamental question when CO_2 is utilized in the hydrogenation reaction to methanol. To get CO_2-based methanol synthesis environmentally and economically reasonable and meaningful, both feedstock, CO_2 and H_2, should be produced or utilized in a cost-effective and sustainable way. The yield of methanol decreases with an increase in the concentration of CO_2 in proportion of CO in the feed gas based on thermodynamics. Also the kinetics of methanol production in the presence of CO is more advantageous compared to the process without CO. (Raudaskoski et al. 2009) Production of methanol by the hydrogenation of CO_2 is generally not of interest industrially because of the high price of hydrogen (Omae, 2012) The by-products which are formed during the CO_2 hydrogenation are water, higher alcohols, hydrocarbons, ethers, esters and ketones. From thermodynamic point of view, increase in

reaction pressure and decrease in reaction temperature favors the synthesis of methanol. The formations of by-products are favored of high temperatures. Performing at low temperature is also advantage of the intrinsic thermodynamics, increasing the reaction efficiency and reduce the production and purification costs. (Karelovic et al. 2012; Wang et al. 2011) The most of the catalysts still contain Cu and Zn as the main components together with different modifiers and different preparation methods. (Yang et al. 2006) Some examples of the reaction conditions, catalysts, preparation methods and reaction results of the methanol synthesis by hydrogenation of CO_2 are listed in Table 2. Carbon dioxide conversion and selectivity of methanol vary a lot depending on the catalyst, preparation method of catalyst, reaction conditions etc.

Table 2. Catalytic systems for synthesis of methanol by hydrogenation of CO_2 (Wang et al 2011; Toyir et al 2000; Yang et al. 2006; Słoczynsk et al. 2004; Zhang et al. 2011; Sahki et al. 2011 & Melian-Cabrera et al 2002).

Catalyst	Preparation method	Reaction conditions		Reaction results	
		Temperature (°C)	Pressure (bar)	CO_2 conversion (%)	Selectivity of MeOH (%)
Cu/Zn/Ga/SiO$_2$	co-impregnation	270	20	5.6	99,5
Cu/Ga/ZnO	co-impregnation	250 - 270	20	6.0	88
Cu-Zn-Ga/SiO$_2$	impregnation	270	20	5.6	99.5
Cu/ZnO/Al$_2$O$_3$	co-precipitation	170	50	15.7	78.7
Cu/ZnO	co-precipitation (commercial)	210	50	9.7	55.2
Cu/ZnO	co-precipitation (commercial)	270	50	20.5	40.1
Cu/Zn/ZrO$_2$	co-precipitation	220	80	21.0	68.0
CuO-ZnO-Al$_2$O$_3$	Co-precipitation (with promoters: 2 wt% SiO$_2$/TiO$_2$)	260	26	40.7	41.2
CuO/ZnO/ Al$_2$O$_3$	co-precipitation	230	75	11.9	47.1
Cu/Zn	co-precipitation	180 - 240	60	5.0	70

The catalytic CO_2 hydrogenation to methanol produces water as a by-product. A third of the hydrogen is converted to water, which is a considerable waste compared to the commercial production of methanol via synthesis gas. The thermodynamics for methanol production from CO_2 and H_2 are not as favourable as those for production of methanol from hydrogenation of CO. For example at 200 °C the equilibrium yield of methanol from CO_2 is less than 40 % while the yield from CO is more than 80 %. (Mikkelsen et al. 2009)

3.3.1 Catalyst for methanol synthesis via hydrogenation of CO_2

Since the 1990s, much effort has been spent on the focused development of catalyst systems for the hydrogenation of CO_2 to methanol, and it is still ongoing. Although the catalyst systems may still be improved, the real challenge of this technology is the production of renewable hydrogen from

various energy sources, and the economically feasible production of clean CO_2 from waste gas stream. (Fiedler at al. 2011) The same methanol synthesis catalysts which are effective for commercial processes are not as effective in hydrogenation of CO_2 under similar operation conditions. The CO_2 hydrogenation reaction is dependent on the development of an effective catalyst. (Raudaskoski et al. 2009) In Table 2 is shown catalysts used in the hydrogenation of CO_2. The catalysts for methanol synthesis from hydrogenation of CO_2 are copper based catalysts with different promoters and additives.

3.4 Use of methanol

Methanol can be used as a hydrogen carrier, a fuel or a feedstock for chemical syntheses. Methanol is the simplest liquid organic hydrogen carrier. (Cifre & Badr 2007) About 70% of methanol produced worldwide is used in chemical syntheses like formaldehyde, methyl-tert-butyl ether, acetic acid, dimethyl ether and propene production. Formaldehyde is one of the most important products synthesized from methanol, in 2011, 28% of the methanol produced was used to synthesize formaldehyde. Methanol is a promising substitute for petroleum products. Methanol's miscibility with water and its low freezing point allow it to be used in refrigeration systems, either in pure form or mixed with glycols and water. (Fiedler et al. 2011) According to the Methanol Institute (2011) global methanol demand was about 47 million metric tons in 2010 and the use of methanol is increasing all the time.

4 Sustainability

Sustainability and sustainable development connected strongly to each other's and they are often confused. Sustainability is the property of a thing for example a product, a process, a technology and a situation being sustainable. (Heijungs et al. 2009)

4.1 Sustainability

Sustainable development can be defined in many ways. It is generally acknowledged that the term sustainable development was introduced in the report of the World Commission on Environment and development that appeared as Our Common Future in 1987 also known as the Brundtland report. Since then, sustainable development is defined as development that meets the needs of the present generation without compromising the ability of future generation to meet their own needs. It contains within it two key concepts: the concept of needs, in particular the essential need of the world's poor, to which overriding priority should be given and the idea of limitations imposed by the state of technology and social organization on the environment's ability to meet present and future needs. (International Institute for Sustainable development, 2013)

Sustainable development can also be defined in three impacts areas economic, environmental and social. These three pillars of sustainability need to be addressed in assessing the sustainability of a product, project, etc. At the World

Summit on Sustainable development the three pillars of sustainable development was modified into people, planet and prosperity, where people represent the social pillar, planet the environmental pillar and prosperity the economic pillar. Sustainability in industries refers to its ability to promote and stabilize on the long term positive environmental, economic and social performance. (Anastas & Warner 1998; Heijungs et al. 2009)

Sustainability evaluation of a process includes evaluation of the economic, environmental and social impacts of the process. Some of these examples are listed in Table 3. (Azapagic et al. 2002)

Table 3. Examples of impacts on sustainability (Azapagic et al. 2002).

Environmental		Social	Economic
Resources	Emissions		
Material Land Energy Water	Athmospheric impact Impact to land Aquatic impact	Health and safety Society Employments Workplace	Value Investement Profit Tax

4.2   Green Chemistry

The concept of green chemistry was introduced in 1990s in USA. The aim was to promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of a chemical product. Green chemistry is a methodology and a culture to achieve more sustainable processes. (Kinnula 2012) Green Chemistry can be described as environmentally benign chemical synthesis, alternative synthesis pathways to pollution prevention and benign by design. It involves the design and redesign of chemical synthesis and chemical products to prevent pollution and thus solve environmental problems. Green chemistry is a way of looking at chemicals and their manufacturing processes to minimize any negative environmental effects. (Anastas & Warner 1998, 8-9) The twelve green chemistry principles focus on protect human health and the environment while still maintaining the efficacy of the products. It also encourages the use of renewable raw materials as feedstock (Anastas & Warner 1998). The twelve principles of green chemistry are presented in Table 4.

Table 4. The twelve principles of green chemistry (Anastas & Warner 1998, 8 – 9; Warner et al. 2004).

Principle	Explanation
1. Waste prevention	It is better to prevent waste than to treat or clean up waste after it is formed.
2. Atom economy	Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Less hazardous	Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little

syntheses	or no toxicity to human health and the environment
4. Safer chemicals	Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. Safer solvent and auxiliaries	The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.
6. Energy efficiency	Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. Renewable feedstocks	A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Reduce derivatives	Unnecessary derivatization (blocking group, temporary modification of chemical/physical processes, protection/deprotection) should be avoided wherever possible.
9. Catalysis	Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Design for degradation	Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Real-time analysis for pollution prevention	Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances
12. Inherently safer chemistry for accident prevention	Substances and the form of a substances used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, fires and explosion.

4.3 REACH

The EU's new chemicals regulation REACH entered into force on the 1st of June 2007. REACH is the European Community Regulation on chemicals and their safe use (EC 1907/2006), and it deals with the Registration, Evaluation, Authorization and Restriction of Chemical substances. Its aim is to improve protection of environment and human health while maintaining competitiveness, and enhancing the innovative capability of the EU chemicals industry. REACH will give greater responsibility to industry to manage the risk from chemicals and to provide safety information that will be passed down the supply chain. The registration process according to REACH requires the manufacturers and importers to generate data for all chemical substances imported or produced into the EU more than one ton per year. The benefits of the REACH system will come gradually, as more and more substances are phased into REACH. The registrants also identify appropriate risk management measures and communicate them to users. REACH will allow the further evaluation of substances where there are grounds for concern and foresees an authorization system for the use of substances of very high concern. The authorization

system will require companies to switch progressively to safer alternatives if there exists. (European Commission 2013; Tukes 2013)

The REACH consists of the list of chemicals which are registered in REACH, and the Candidate and exception list of chemicals. All the chemicals which are registered in REACH at present can be found in online http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances and the REACH Candidate List of Substances of Very High Concern for Authorization in: http://echa.europa.eu/web/guest/candidate-list-table. (ECHA 2013) REACH Annexes IV and V, exemptions from the obligation to register in accordance with article 2(7)(a) and article 2(7)(b), can be found in online http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2006R1907:20120601:EN:PDF. The aim of the sustainability assessment is that it takes into account that the used chemicals fulfill the REACH regulations. Table 5 shows the substances in REACH which are used in this report. All the chemicals used in this report can be found in REACH.

Table 5. Substances in REACH.

Substance	CAS number	Registered in REACH	Candidate List	Excemption List
CO_2	124-38-9			X
CO	630-08-0	X		
H_2	1333-74-0			X
CH_3OH	67-56-1	X		
$C_6H_{15}N$	121-44-8	X		
C_2H_5OH	64-17-5	X		

4.4 Sustainability assessment for formic acid and methanol

The sustainability assessment facts and assumption used in the sustainability assessment for the production of formic acid via methyl formate hydrolysis and via hydrogenation of carbon dioxide is shown in Table 6. The sustainability assessment facts and assumption for methanol synthesis is shown in Table 7.

Table 6. Sustainability assessment facts and assumption for the production of formic acid via methyl formate hydrolysis and hydrogenation of CO_2 (Reutemann & Kieczka 2011, Kirk-Othmer 1994, Hao et al. 2011; ECHA 2013).

Features	Methyl formate hydrolysis Kemira-Leonard process	Hydrogenation of carbon dioxide (ruthenium catalyst)
Raw materials	CH_3OH and CO	CO_2, H_2 and $C_6H_{15}N$
Reaction route	$CH_3OH + CO \rightarrow HCOOCH_3$ $HCOOCH_3 + H_2O \rightarrow CH_3OH + HCOOH$	$CO_2 + H_2 \rightarrow HCOOH$
Main products	Formic acid	Formic acid
Side products	Methanol is formed and recycled back to the process	No side products

Waste / emissions	Inactivated catalyst and unreacted methyl formate	Unreacted CO_2
Atom economy and yield	Atom economy 59 % High yield, exact amount is not specified	Atom economy 100 % Yield 9.1 mmol.
Process Conditions	Temperature 80 °C Pressure 40 bar	Temperature 80 °C Pressure 135 bar
Solvent and auxiliary chemicals	H_2O	Ethanol
Health and Safety issues	CO is extremely flammable gas, may be fatal if inhaled, contact may cause burns or frostbite. CH_3OH is highly flammable in liquid and vapor forms. It is toxic by inhalation, in contact with skin and if swallowed.	H_2 is extremely flammable can cause asphyxiation. CO_2 is toxic to humans in high concentrations. Triethylamine is flammable liquid and corrosive. It is toxic by inhalation, in contact with skin and if swallowed. Ethanol is a flammable liquid, toxic by ingestion, inhalation or skin absorption
Chemical registered in REACH	Carbon monoxide, methanol, hydrogen	Carbon dioxide, hydrogen, triethylamine, ethanol
Catalyst	CH_3ONa	H_2O_2Ru (Ruthenium hydroxide)
Plant specifications	20 000 t/a	Production at laboratory scale.
Alternative production options	Hydrogenation of carbon dioxide, Oxidation of hydrocarbons, hydrolysis of formamide and by-product of acetic acid production.	Methyl formate hydrolysis, Oxidation of hydrocarbons, hydrolysis of formamide and by-product of acetic acid production.
Treatment / cost of waste disposal	Waste gas and inactivated catalyst were purged out of the process.	None, there was no waste to be treated or disposed of.
Product selectivity and quality	High selectivity of the alkoxides catalyst to the production of HCOOH. Formic acid of 98 % purity was obtained as distillate.	High selectivity of ruthenium hydroxide catalyst to the production of HCOOH. Formic acid of high purity was obtained from this process.
Product acceptability	Formic acid is readily acceptable as it has wide range of uses both in agricultural, industrial and household level. CO and CH_3OH have safety, health and environmental issues hence the raw materials used to produce HCOOH is not readily acceptable.	Formic acid is readily acceptable as it has wide range of uses both in agricultural, industrial and household level. Ethanol and triethylamine has health and safety issues. Hydrogen has safety issues.

Table 7. Facts and assumption used in the sustainability assessment for methanol synthesis via CO_2 and methanol synthesis via synthesis gas (Fiedler et al. 1990; Kinnula 2012; Tijm et al. 2001; ECHA 2013).

Features	Syngas route	CO₂ route
Raw materials	CO and H_2	H_2 and CO_2
Reaction route	$CO + 2H_2 \rightarrow CH_3OH$	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$
Main products	Methanol	Methanol
Side products	Unreacted H_2 and CO (recycled).	Unreacted H_2 and CO_2, and H_2O.
Wastes / Emissions	Unreacted reactants H_2 and CO.	Unreacted reactants CO_2 and H_2.
Solvent and auxiliary chemicals	No solvents or auxiliary chemicals. Good selectivity.	No solvent and auxiliary chemicals. Lower yield than in syngas route.
Atom economy and yield	100 % atom economy.	64.0 % atom economy.
Plant specification	Syngas source on-site.	Production at laboratory scale.
Catalyst	Cu/ZnO/Al₂O₃ or copper based catalyst with different promoters.	
Safety issue	Similar safety issues concerning the flammable H_2 and CO (also toxic). CO_2 route has additive safety issues concerning the MEA solvent and high concentrated CO_2.	
Chemicals registered in REACH	Carbon monoxide, carbon dioxide, hydrogen and methanol.	
Supply chain	Similar supply chains.	
Alternative options	Alternative catalyst: noble metal catalyst (not economically feasible).	
Process conditions	200 – 300 °C and 50 – 100 bar	

The sustainability assessment questionnaire and answers for the questions are shown in Appendices 1, 2 and 3 for the production of methanol and formic acid in environmental, social and economic impact areas. The answers are based on the facts and assumption shown in Tables 6 and 7. The methanol synthesis consists of two production routes; syngas route and hydrogenation of CO_2 and production of formic acid via methyl formate hydrolysis (Kemira Leonard process) and via hydrogenation of CO_2.

In this study the sustainability assessment questionnaire is a condensed questionnaire where the twelve principles of green chemistry are connected as one environmental, one social and one economic principle. In the sustainability assessment questionnaire is selected the most important questions for the production of methanol and formic acid. Therefore the questionnaire is not complete and there are many of questions which should take into account in the other sustainability assessment.

Figures 4 and 5 illustrate the points for three impact areas (environmental, social and economic) of sustainable assessment, and the total points for all three impact areas for the production of formic acid and methanol synthesis.
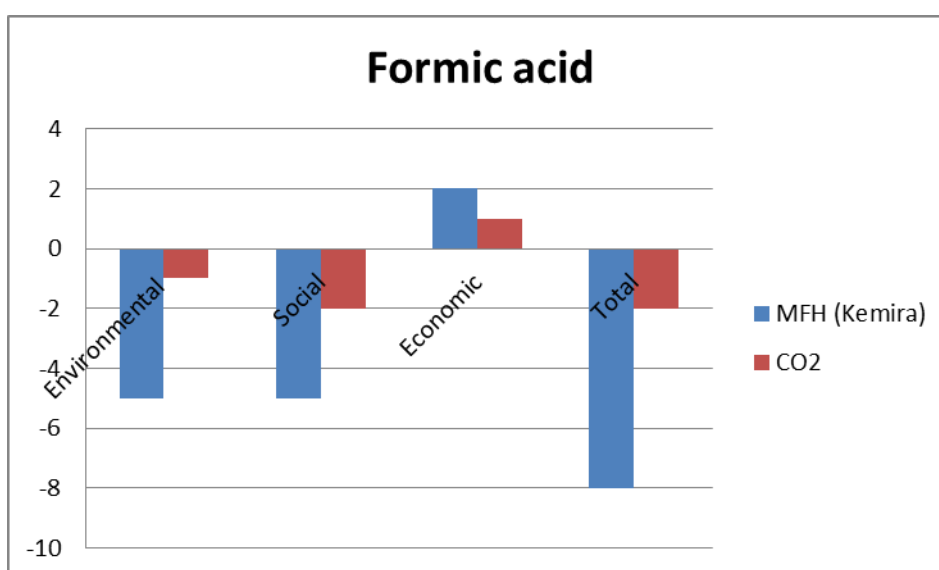

Figure 4. The green chemistry sustainability points for environmental, social and economic aspects and total points for production of formic acid via methyl formate hydrolysis (MFH) route and via hydrogenation of CO_2.

Figure 4 shows that in environmental angle the hydrogenation of CO_2 is better route than methyl formate hydrolysis (MFH). In the point of environmental aspects MFH route has the total points of – 9 compared to CO_2 route -2, this is due to harmful waste gas, mainly CO, and unreacted catalyst, which are purged out of the process. MFH also consumes lots of energy and water. That's why, the production of formic acid via CO_2 route, is more environmentally friendly process.

In the social angle CO_2 route has a better sustainability points, -2 compared to MFH -5. The social impacts areas mainly consist of health and safety issues. However, it is worth to be mentioned that the hydrogenation of CO_2 was done only in laboratory scale.

In the economic impact area MFH has 2 sustainability points compared to 1 point for CO_2 hydrogenation. The CO_2 route had a very low yield but a high theoretical atom economy. In the MFH both yield and selectivity are high and the by-products are saleable but the theoretical atom economy is low.

The total sustainability points of all the three impact areas are better in hydrogenation of CO_2 but it is done only in laboratory scale. MFH has the lower total sustainability points than production of formic acid via hydrogenation of CO_2. Even though hydrogenation of CO_2 is more environmentally friendly it is very expensive when compared to methyl formate hydrolysis, hence it is not feasible to produce in large scale.
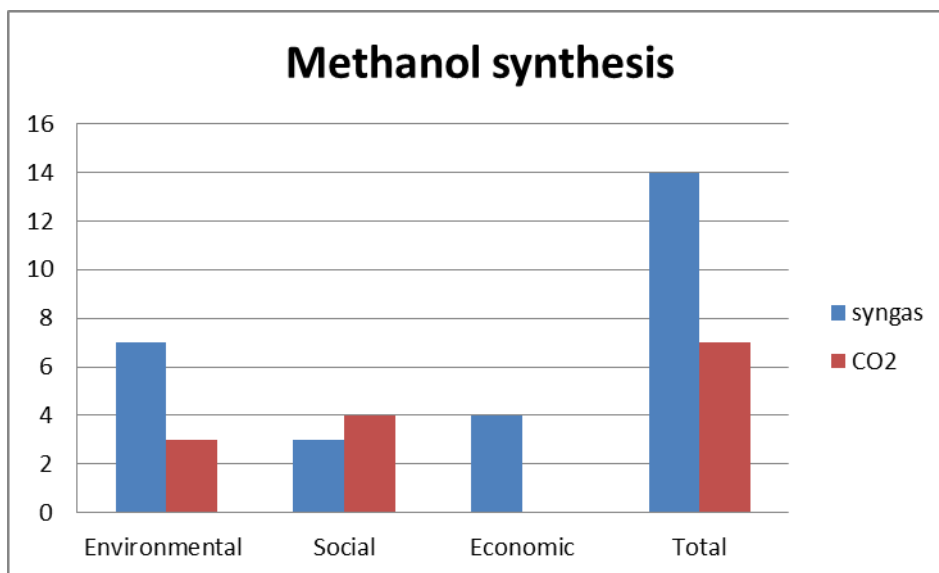

Figure 5. The green chemistry sustainability points for environmental, social and economic impact areas and total points for methanol synthesis via syngas and via hydrogenation of CO_2.

The methanol synthesis via synthesis gas is the better process in the environmental and economic aspects than via CO_2 hydrogenation (Figure 8). The syngas route has 7 environmental points and 4 economic points compared to 3 environmental points and 0 economic points for hydrogenation of CO_2. Hydrogenation of CO_2 is better than syngas route in the view of social aspects.

The total points of all three aspects is better in syngas route. In the total points syngas route has 14 sustainability points compared to the 7 points of CO_2 route. The methanol synthesis via hydrogentaion of CO_2 is important opportunity to reduce the amount of CO_2 to the environment. The hydrogenation of CO_2 route still needs more research accoriding to the used catalysts, production conditions, etc.

5   Conclusion

For a chemical process to be sustainable, the three areas of sustainability environmental, social and economic need to be satisfied. In essence, green chemistry mainly concentrates on the environmental and social aspect only. The aim of this study was to evaluate the chemical utilization of CO_2 in the production of formic acid and methanol synthesis and to compare the sustainability of the commercial and CO_2 utilizing reaction routes for the production of methanol and formic acid. These routes were methanol synthesis

via synthesis gas vs. hydrogenation of CO_2 and the production of formic acid via methyl formate hydrolysis vs. hydrogenation of CO_2. Facts and assumptions of each process were gathered to be used in the sustainability assessment questionnaire. The questionnaire based on the twelve principles of green chemistry consists of environmental, social and economic impacts areas of the processes.

The sustainability evaluation shows that the production of methanol is better via the commercial syngas route than via the hydrogenation of CO_2 routes. In the sustainability aspect the production of formic acid is better via CO_2 route but it is only in laboratory scale and had a very low yield. The CO_2 utilization in this kind of production processes is important because of the need to reduce CO_2 concentrations in the environment. However, the hydrogenation of CO_2 need still more research. CO_2 is used already in industrial methanol synthesis as one of the feedstocks but not the only one.

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Environmental						
	Methanol		**Explanation**	**formic acid**		**Explanation**
	Syngas (A)	CO_2 (B)		MFH Kemira-Leonard (A)	CO_2 (B)	
Does the process produce waste?	1	1	No wastes	-1	0	A: unreacted catalyst
Is the waste hazardous?	1	1	No wastes	-1	0	A: unreacted catalyst
Could this waste be utilized somewhere?	1	1	No wastes	0	0	Purged out of the system
Does the process produce waste water?	0	-1	A: No. B: Yes.	-1	0	A: Yes. B: No.
Does your process use or generate harmful or hazardous materials?	-1	-1	CO, CO_2, H_2	-1	0	CO, CH_3OH
Are there any toxic or hazardous solvents and/or other auxiliary chemicals used in your processes, products or supply chain?	1	-1	B: MEA.	0	-1	A: H2O. B: Ethanol.
Are there multistage synthetic routes involving blocking and/or protecting groups in your process?	1	1	No synthetic stages.	-1	N/A	A: 2 stages synthetic route.
Does the process use catalyst? Does the catalyst increase the selectivity?	1	1	Yes.	1	1	Yes
Does the process use noble/rare earth metal catalyst?	1	1	No.	0	-1	A:No. B: Yes Ruthenium hydroxide.
Do the products have a high environmental impact at the-end-of life (take into notice also the side products)?	-1	-1	End product is CO2.	0	0	HCOOH decomposes easily into the environment
Is your process especially sensitive to changes in process conditions?	0	0	Temperature sensitive because of catalyst	-1	-1	A: Temperature & pressure. B: temperature
Do your processes require large deviations from ambient temperature and pressure?	0	0	Mild deviation are required.	-1	-1	Temperature only slightly higher. Prussure is much higher.
Does the synthetic process have high yield?	1	-1	A: yield is higher.	1	-1	A: High yield. B: Yield is very low.
Does the process produce harmful emissions?	-1	-1	CHOOH is toxic in high concentrations. B: CO_2 is a greenhouse gas	-1	0	A: Purge gas contains harmful emissions

Are the chemicals used registered within REACH?	1	1	A: Yes, CO. B: Yes, MEA.	1	1	A: Yes, CH3OH & CO. B: Yes, ethanol.
Does The process produce by-products? Are the by-Products sold or utilized?	0	0	A: H_2 & CO (recycled). B: N_2, CO_2 purged, H_2 recycled, CO and H_2O utilized.	0	0	A: by-produced is recycled. B: no by-products.
Are the materials used renewable or non-renewable? (-1/0/1) (mixed carbon source = 0)						
Syngas route for methanol synthesis						
CO	0		CO is a syngas, hence renewable, carbon source is gotten from both biomass and black liquor			
H_2	1		H2 is a syngas, hence renewable			
CO2 route for methanol synthesis and formic acid production						
CO_2		1	CO2 is a syngas, hence renewable		1	CO_2 is a syngas, hence renewable
H_2		1	H_2 is a syngas, hence renewable		1	H_2 is a syngas, hence renewable
Methyl formate hydrolysis						
CH_3OH				0		CH_3OH is renewable or non-renewable as the carbon source is gotton from both biomass and black liquor
CO				0		CO is a syngas, hence renewable, carbon source is gotten from both biomass and black liquor
Environmental total points	7	3		-5	-1	

Social						
	Methanol		**Explanation**	**Formic acid**		**Explanation**
	Syngas (A)	CO_2 (B)		MFH Kemira-Leonard (A)	CO_2 (B)	
Are there any health and safety issues related to the harmful nature or amount of waste?	1	1	No specific issues.	-1	0	A: CO and unreacted methyl formate are harmful
Are there any health and safety issues related to the harmful nature of chemicals used or generate in the process?	-1	0	Yes. CO and H_2.	-1		Yes. Ethanol and H_2.
Are there any health and safety issues related to the harmful nature of solvents, separation agents,other auxiliary chemicals?	0	-1	B: MEA is toxic.	0	-1	B: Ethanol. Lindalla 0 &0
Are there any health and safety issues related to harmful nature of product?	1	1	Methanol is safe.	-1	-1	Yes.
Are there any health, safety or environmental issues related to the used catalytic materials?	1	1	No.	-1	-1	CH3ONa is toxic and corrosive. B: Ruthenium on alumina is toxic to skin
Are there any health and safety issues related to the changes in process conditions?	1	1	No specific issues.	-1	N/A	A: Increase the pressure in reactor could lead to explosion
Is the acceptance of a new product or production process better among society?	0	1	CO_2 Route because of CO_2 usage	0	1	CO_2 Route because of CO_2 usage
Social total points	3	4		-5	-2	

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Economic						
	Methanol		**Explanation**	**Formic acid**		**Explanation**
	Syngas (A)	CO_2 (B)		MFH Kemira-Leonard (A)	CO_2 (B)	
Could there be significant cost related to the treatment and disposal of waste?	1	1	No wastes.	1	0	No significant costs. A: by-products are recycled.
Can you derive profit from wastes or by-products? Or can you recycle them?	1	1	A: Recycled. B: Recycled and utilized.	1	1	A:CH_3OH recycled. B: no waste/by-products.
Have you calculated the atom economy for all possible reactions routes and selected the best one?	1	-1	In CO_2 route the atom economy is lower.	-1	1	A. Theoretical atom aconomy 59 %. B: Theoretical 100 %.
Is there any significant cost related to the harmful nature of the chemicals used or generated in your process.?	1	1	No specific costs.	0	0	No significant costs.
Does the use of renewable materials decrease the production cost?	0	0	No.	1	1	Yes. Use of renewables leads to reduction of costs.
Does your synthetic process have high yield?	1	-1	Syngas route yield is higher.	1	-1	A: High yield. B: Yield very low.
Could savings be made by operating at ambient temperature and pressure?	-1	-1	Conversion would be too low.	-1	-1	No
Economic total points	4	0		2	1	
Total points for all three impact areas	**14**	**7**		**-8**	**-2**	