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SUSTAINABILITY ASSESSMENT OF FORMIC ACID PRODUCTION: COMPARISON OF CO_2 BASED AND CONVENTIONAL PROCESSES

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UNIVERSITY OF OULU THESIS ABSTRACT

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Abstract

Sustainability can be described as a developmental approach whose focus is to integrate economic activity with social security and environmental protection. Sustainability of chemical process involves the use of sustainable practices in the chemical industry. Sustainability assessment describes the methods used for achieving sustainability in industries, it is needed because unsustainable practices can be tracked and corrected and also to track progress made by the company in achieving sustainability.

The aim of this thesis was to use a green chemistry based sustainability assessment tool to compare one conventional and two CO_2 utilization routes in order to find the more sustainable way of producing formic acid and to suggest methods for improving the tool. The three routes considered in this work were the conventional route, which was done on a commercial scale. This method of producing formic acid is via methyl formate hydrolysis. The experimental route and the BP patented routes represented CO_2 utilization routes on laboratory scale setting and commercial setting respectively. These methods for producing formic acid involved the hydrogenation of CO_2. Another aim of this thesis was to review some currently used assessment tools related to sustainability. Six currently utilized assessment tools related to sustainability were compared based on their strengths and weaknesses and evaluated.

Sustainability assessment was conducted on the three formic acid production routes based on the green chemistry assessment tool using the most important features. Sustainability assessment questionnaire based on the twelve green chemistry principles was used to assess the three formic acid production routes.

The strengths and weakness of the green chemistry tool were discussed and recommendations for improving the tool were suggested. One way of improving the tool is to merge it with LCA in order to assess every stage of a product's life cycle from cradle to grave. The results from the assessment showed that the conventional route was harmful to the environment while the CO_2 utilization routes were beneficial to the environment. The social section of the result showed that both the conventional and CO_2 utilization routes were socially unsustainable and the economic section of the results showed that the conventional and the CO_2 utilization routes were economically viable but the CO_2 utilization routes were more economically viable than the conventional route. Overall, the experimental CO_2 utilization route is the most sustainable way to produce formic acid. It is important that more research will be done on CO_2 utilization method of producing formic acid in order for it to fulfill its potential as a sustainable method.

Additional information

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Preface

This work was part of the project "Sustainable Catalytic Syntheses of Chemicals Using Carbon Dioxide as feedstock" (GreenCatCO_2) and "Carbon Capture Storage Program" (CCSP). The research work was conducted in the Mass and Heat Transfer Process Laboratory of the Department of Process and Environmental Engineering, University of Oulu between the periods of 17th September – 20th December 2012 and 16th May 2013 – 26th June 2013.

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Abbreviations and Symbols

ACGIH	American Conference of Governmental Industrial Hygienist
AIChE	American Institute of Chemical Engineers
BP	British Petroleum
CAS	Chemical Abstract Service
CCS	Carbon capture, and storage
CH_3OH	Methanol
CO	Carbon monoxide
CO_2	Carbon dioxide
C_2H_5OH	Ethanol
CPR	Cardiopulmonary resuscitation
DMF	Dimethylformamide
DOT	Department of Transportation
EC	European Commission
ECHA	European Chemical Agency
EMS	Environmental Management System
EPA	Environmental Protection Agency
EtOH	Ethanol
EU	European Union
$HCOOCH_3$	Methyl formate
HCOOH	Formic acid
HE	Heat exchanger
H_2	Hydrogen
H_2O	Water

IARC	International Agency for Research on Cancer
IChemE	Institution of Chemical Engineers
IDLH	Immediately Dangerous to Life or Health
ISO	International Organization for Standardization
IV	Four
LCA	Life Cycle Assessment
MSDS	Material Safety Data Sheet
m.w.	Molecular Weight
NA	Not Applicable
NFPA	National Fire Protection Association
$N(C_2H_5)_3$	Triethylamine
OSHA	Occupational Safety and Health Administration
ppm	Parts per million
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RTK	Right to Know
SVHC	Substances of Very High Concern
t/a	Tons per Annum
TBL	Triple Bottom Line
V	Five
γ-Al_2O_3	Aluminum oxide

1. INTRODUCTION

Global focus has shifted towards sustainability. Sustainable development gained popularity after the Rio de Janerio Earth Summit which took place in 1992. In this summit a series of action points for sustainable development was agreed upon, these points which also had the backing of the government became known as Agenda 21 which meant the agenda for the 21st century concerning sustainable development. For the action points to be applied in real life, the summit authorized the United Nations to set up a set of 'indicators of sustainable development' with the purpose of monitoring progress made. Till this day, the use of indicators and tools for sustainable development has gained grounds (Bell & Morse, 2008).

Sustainability assessment has gained popularity as a decision-making tool, with an intent to predict the sustainability implications of intended actions. Sustainability assessment can be described as the process by which decision making is directed towards sustainability. It is usually linked with derivation of indicators which is useful in determining the current level of social, economic and environmental factors (Bond & Morrison-Saunders, 2011).

Carbon capture, storage and utilization are regarded as one way of reducing the atmospheric loading of CO_2. CO_2 utilization can be described as a win-win technology to both the producers/generators of CO_2 and the environment; the producers can sell it to make profit, while the environment can to an extent be rid of it. In the environment, stringent climate targets are met as it is not left as an atmospheric green house gas but converted for use in chemical processes which in most cases is usually cheaper than conventional methods (Koornneef et al., 2012). Green Chemistry can be described has a design tool that seeks to re-create materials required and used by the society in order to reduce their adverse impacts on human health and the environment (Manley et al., 2008).

The aim of the theoretical part of this work was to critically evaluate six currently used assessment tools related to sustainability; to review sustainability in the chemical industry; and to evaluate three routes of formic acid production, the conventional route (methyl formate hydrolysis) and two CO_2 utilization routes via hydrogenation of CO_2 (experimental route and BP patented route). Chapter 2 highlights the framework of sustainable development and sustainability in industries, Chapter 3 describes six assessment tools related to sustainability including; pollution prevention, Green

Chemistry, IChemE, AIChE, LCA and the Natural Step principles. Chapter 4 briefly describes the environmental impacts of chemical industries; its benefits and drawbacks, REACH regulation of substances, and on the chemical utilization of CO_2. Chapter 5 describes formic acid and focuses on three main routes of formic acid production both industrial and laboratory scale processes.

The aim of the experimental part of this work was to perform sustainability assessment of three case studies of formic acid production via a conventional route (methyl formate hydrolysis) and a CO_2 utilization route (hydrogenation of CO_2) one for laboratory and the other for commercial scale; and to use a sustainability assessment questionnaire based on the Green Chemistry design tool. Chapter 6 describes the aim and methods used in the experimental section. The methods used include; Aspen Plus simulation tool and sustainability assessment questionnaire based on the twelve principles of Green Chemistry. Chapter 7 and 8 describes the material and energy balances; and performed sustainability assessment based on three case studies (Conventional, hydrogenation of CO_2 in laboratory scaled, and BP patented process for hydrogenation of CO_2) of the two formic acid production routes considered. Sustainability assessment questionnaire based on the twelve principles of Green Chemistry and their score on the three case studies is presented. In chapter 9 and 10 discussions and conclusions are made on both the theoretical and experimental part.

THEORETICAL PART

2. SUSTAINABILITY

The term sustainability often used interchangeably with sustainable development is used to close the gap between growth, development, social-cultural values and the environment. Sustainability was adapted because of growing trends of unsustainable practices worldwide which led to poverty in some countries and environmental degradation around the world (Rogers et al., 2008).

Sustainability was brought about by the desire of mankind to improve ecological conditions while maintaining development and growth pace, having realized that continuing in the present trend can create a great decline and may lead to the collapse of the ecosystem and consequently hindering future generations from meeting their needs. There are many definitions of sustainable development owing to the broad nature of its concept. The definition that was readily accepted and embraced by the international scientific community was coined from the Brudtland commission report on global environment and development in 1987, this commission was established by the United Nations and part of its responsibility included coming up with environmental strategies. The Brudtland commission report was tagged 'Our common future' and defined sustainable development as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs". This definition is today used as a reference point on any discussion involving sustainability. (United Nations, 1987).

Within this definition of sustainable development are two key concepts (United Nations, 1987):

- The first is the concepts of 'needs', in particular the basic needs of the world's poor whom the first major concern is to be given.
- The second is based on the idea of limitations set by the state of technology and social organization on the ability of the environment to meet both present and future needs.

Soubbotina (2004) has defined sustainability as "equality of opportunities for well-being, as well as about comprehensiveness of objectives." These objectives are grouped under the three areas of sustainable development, examples of these objectives are: Economic objectives include; growth, efficiency and stability; Social objectives include; full employment, equity, security, education, health and cultural identity;

Environmental objectives include; conservation of non renewable natural resources, rational use of renewable natural resource and healthy environment for humans. It is to be noted that mankind is the center of interest for sustainable development; they deserve to live a worthwhile and healthy life in one accord with the nature. Sustainable development can also be termed “equitable and balanced”; this means that for development to always be in continuous motion, it must simultaneously cut across the three area of sustainability - environmental, social and economic. Nowadays in most countries of the world both developed and developing countries sustainability has been included in their national planning and has defined sustainable development within their various national contexts (Azapagic, & Perdan, 2011).

2.1 Framework for sustainable development

Sustainable development framework implies change; change from unsustainable practices (Azapagic, & Perdan, 2011). Sustainable development has three aspects; the economic, ecological (biological) and social aspect. The sustainable development framework is depicted in Figure 1. The main aim of sustainable development within the scope of this framework is to maximise its goals across its three aspects. Sustainability is the intersection of these three aspects (Elliott, 2009).

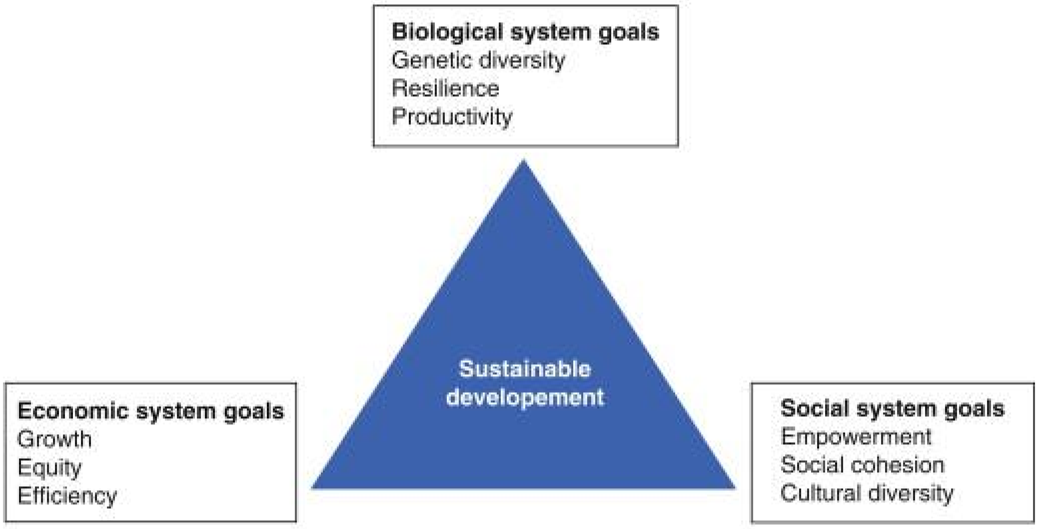


Figure 1. Objectives of sustainable development (Elliott, 2009).

Figure 1 shows the framework of sustainable development often referred to as “the three pillars or corners of a triangle”. This framework shows that for sustainable development to be practiced in the real world there would be some form of trade-offs at some point depending on the groups involved, their goals and interests. The objective here is to ensure that there is goal maximization across the three pillars (Elliott, 2009).

The economic aspect involves, maintaining or increasing current production trends while maximizing profits. It deals with minimizing operating costs which can be achieved through systematic management, labor productivity and research and development expenditures. The ecological aspect of sustainable development involves the protection, overall stability of the earth's ecosystem, sustainable use of natural resources without degradation and pollution, and waste prevention or minimization to the barest minimum. It covers the impact of production process, product and services on human health and the environment. The social cultural aspect of sustainability seeks to maintain the stability of social and cultural systems. It entails an established and thriving society whereby the population has access to good quality life. It covers occupational health and safety, labor right and human right issues (Munasinghe, 2009, Seow et al., 2006).

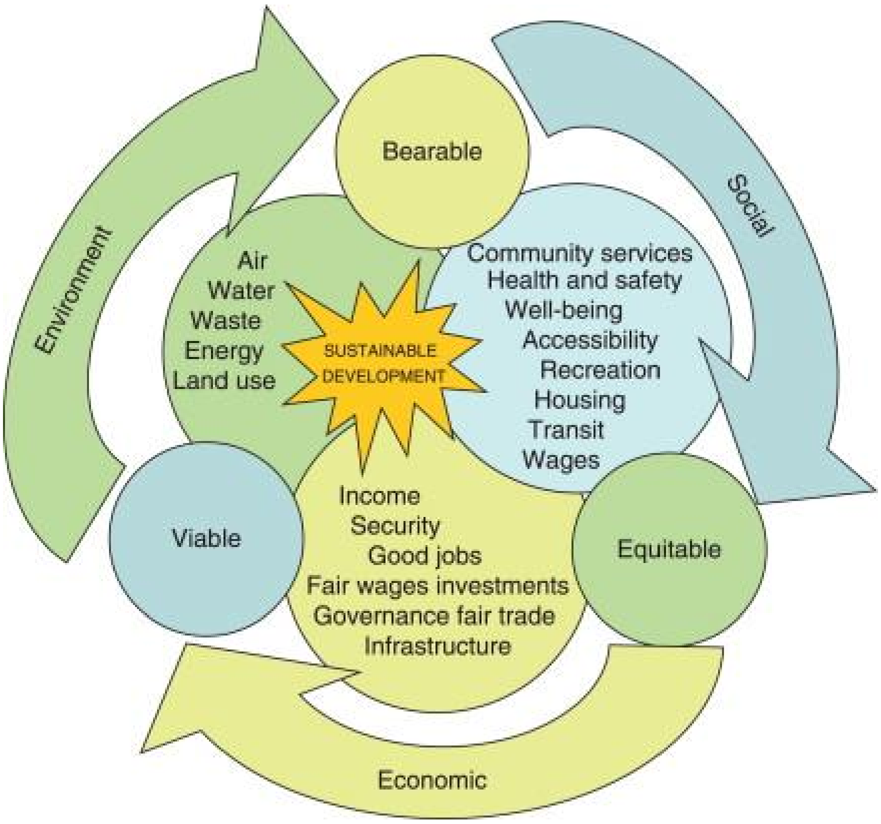


Figure 2. Sustainable development concept (Gavrilescu, 2011).

Transition to a more sustainable society will involve reducing materials and energy throughput in the economy and satisfying needs by increasing efficiency and effectiveness, reusing and recycling of materials and by the use of sustainable technologies. True sustainability entails guarantying a fulfilling quality of life for humans (Azapagic, & Perdan, 2011).

A very important concept in sustainable development is the “triple-bottom-line” (TBL) concept, simply put is “planet, people and profit” which represent the environmental, social and economic aspects of sustainable development. Triple bottom line summarizes the overall impact of the industry (Coffman & Umemoto, 2010). Figure 2 illustrates the TBL concept.

The TBL concept was originated in 1998 by Elkington. In Elkington’s book titled “cannibals with fork”, TBL in its broadest term “ is used to capture the whole set of values, issues and processes that companies must address in order to maximize the positive impacts of their activities and generate added economic, social and environmental value”. Elkington mentioned that sustainability in industries should incorporate environmental and social aspects along with its economic/financial aspect; this puts together a new meaning in the whole concept of sustainable development and also suggested that the TBL concept be applicable to both small and large scaled industry and businesses. TBL in industries is a measure of how well the three dimensions (economic, environmental, social aspects) of sustainability are managed and balanced (Seow et al., 2006, Coffman & Umemoto, 2010).

The TBL concept is employed to encapsulate processes, issues and values which industries must consider in order to reduce any side effects resulting from their actions and to bring about economic, social and environmental values (Sheate, 2010). Triple bottom line is also seen as a method used to create a balance between industrial processes, activities and the economic, social and environmental aspects of sustainability (Vanclay, 2010). The environmental, social and economic aspects in TBL should be considered individually in practice and then synchronized to form a system, only then can true sustainability be achieved. TBL is used as a benchmark in evaluating sustainability (Lee et al., 2012). In industries, equal consideration should be given to people, planet and profits whereby; people represent the social consequences of industrial actions; planet represents the environmental consequences of industrial actions and; profits represent the economic profits of industries (Harmsen & Powell, 2010).

2.2 Sustainability in industries

Sustainability in industries refers to its ability to promote and stabilize on the long run a positive economic, environmental and social performance. Industries play a very important role in issues regarding sustainability; its responsibility is ensuring that there is a balance between its business strategies that generate profits, the environment and society (Orecchini et al., 2012).

The need for sustainability in industries arises because they have high environmental, social and economic impact. In industry, sustainable development creates guidelines for designing new production processes and establishes new aims for existing ones in order to improve quality of life in a sustainable manner. The sustainable guidelines are put in place to address the issues of unsustainable practices in industries. Unsustainable practices are addressed by first identifying the affected areas in the industry, redesigning the products and processes involved in these areas, and then showing definitively progress brought about by the redesigning of products and processes (Ruiz-Mercado et al., 2013). Sustainability is needed in all industrial sectors because economic systems do not accurately show their true cost; neither do they fully take into consideration the environmental and social impacts of their production processes (Harmsen &Powell, 2010).

Recall that sustainability has three dimensions; economic, environmental and social. In industries, the economic dimension deals with financial viability. It covers matters related to competitiveness, profitability, job creation and market. Long term goals involving all participants raging from the manufacturers, consumers and policy makers should be developed and implemented to ensure that sustainability is achieved. As the world population is increasing, it is expected that demands for industrial products also increase. It has been predicted that over a 40 year time frame industrial products are anticipated to double or triple its present amount. The increased world population can be viewed in two different ways, negative and positive. It is positive from an industrial viewpoint because increased population naturally would lead to increased customer base which in turn would lead to market expansion and more returns on investment. On the other hand it is negative because it would lead to scarcity of resources needed; there would be increased pressure on the environment due to the industries increased level of production to match demands (Orecchini et al., 2012).

Sustainability started in chemical industry as a conciliatory approach to all stakeholders. Sustainability has both offensive and defensive sides. The offensive side is intended to optimize competitive benefits through regulations; on the other hand the defensive side is intended to improve industry's unfavorable image and to prevent liabilities. In chemical industry, there are three main functions to sustainability; they include (Johnson, 2012):

- A "stakeholder" approach to communications and external relations
- Recognizing not only the cost of social and environmental protection but also the opportunities
- Rebranding of risk management and regulatory compliance while emphasizing on their advantage to stakeholders.

Application of the TBL by industrial businesses has gained popularity among top decision makers. Industrial businesses that apply the TBL concept can be said to have integrated economic success with environmental quality and social justice hence making it sustainable.

Table 1 illustrates that with reference to John Elkington (1998) work, TBL can be applied in industries in seven dimensions namely markets, transparency, time context, life-cycle technology, corporate governance, partnerships and values (Orecchini et al., 2012).

Table 1. Triple bottom line (TBL) dimensions (Orecchini et al., 2012).

Drivers	Old Paradigm	New Paradigm
1. Markets	Compliance	Competition
2. Values	Hard	Soft
3. Transparency	Closed	Open
4. Life-cycle technology	Product	Function
5. Patnerships	Subversion	Symbiosis
6. Time	Wider	Longer
7. Corporate governance	Exclusive	Inclusive

Sustainable practice in industry can be achieved by the right amount of processes, raw materials, quality human resources as well as energy. Industries have management processes which can further be sub-dived into an environmental management system and a quality management system. The overall goal of these systems is the efficient utilization of resources either human or material which accomplish sustainability in industry. The goal of environmental management in industry is cleaner production which leads to minimized production cost, reduced waste, less emissions and profit maximization. By adapting this process sustainability can be achieved (Fresner and Sage, 2010). Cleaner production is a term used to portray prevention oriented strategy whose role is to reduce environmental loadings or products and processes in industry (Hoof & Lyon 2013). Cleaner production processes also helps to reduce production impact on the environment by using prevention strategies. (Fresner and Sage, 2010).

According to Fresner and Sage (2010), the following points illustrate examples of cleaner production options in industry:

- Documentation of actual consumption
- Use of indicators and control to identify losses from poor planning, poor education and training, mistakes
- Substitution of raw materials and auxiliary materials (especially renewable materials and energy)
- Increase in the useful life of auxiliary materials and process liquids by avoiding drag-in, drag-out, contamination
- Improved automation and control
- Reuse of waste (internal or external)
- New low-waste processes and technologies.

3. ASSESSMENT TOOLS RELATED TO SUSTAINABILITY

Assessment tools related to sustainability are needed to enable the human population to move to a more sustainable society. These assessment tools should be all encompassing, unambiguous, efficient, effective, comprehensive and reliable. Assessment tools related to sustainability are used to evaluate the environmental, economic and social impacts of industry's product and production processes. Sustainability assessment has been defined as "a tool that can help decision-makers and policy-makers decide which actions they should or should not take in an attempt to make society more sustainable." Its main objective is that of guidance. It guides both decision and policy makers in ensuring that sustainability is achieved in the society (Buytaert et al., 2011).

Assessment tools related to sustainability have been developed based on the concept of sustainable development. Assessment tools related to sustainability covered in this theoretical part includes; Green Chemistry, LCA, IChemE, AIChE, Pollution prevention and The Natural Step.

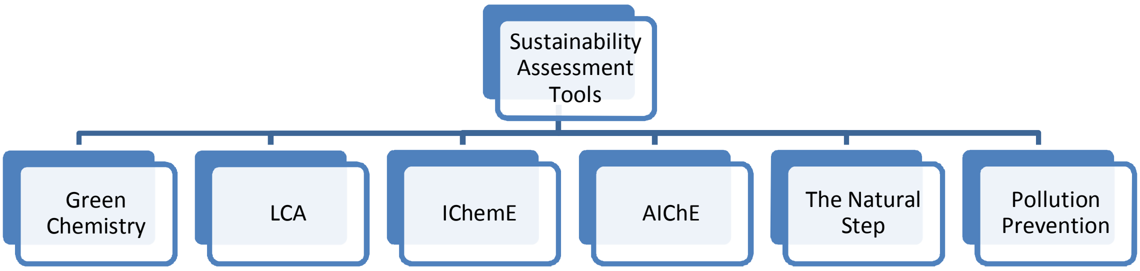


Figure 3. Tools and principles of sustainability.

In the theoretical part of the thesis, six assessment tools and principles relating to sustainability have been discussed, all of which have their various strengths and weakness in assessing sustainability from the triple bottom line point of view. The experimental part of this thesis would focus on the Green Chemistry tool.

3.1 Pollution prevention

Pollution prevention has been defined as the reduction or elimination of pollution (waste and emissions) at the source in order for it not to enter into the environment at all. It targets the root cause of pollution which consists of waste and inefficiencies. Pollution prevention has achieved environmental, economic and social benefits such as reduced amount of solid waste to landfills, cleaner air, water and soil, less emissions, more efficient use of natural resources, safe working environment, efficiency in industry, reduced cost, increased profits and competitiveness (PPRC, 2012). Pollution prevention can be carried out based on five approaches (Figure 4) (Hanrahan, 2012).

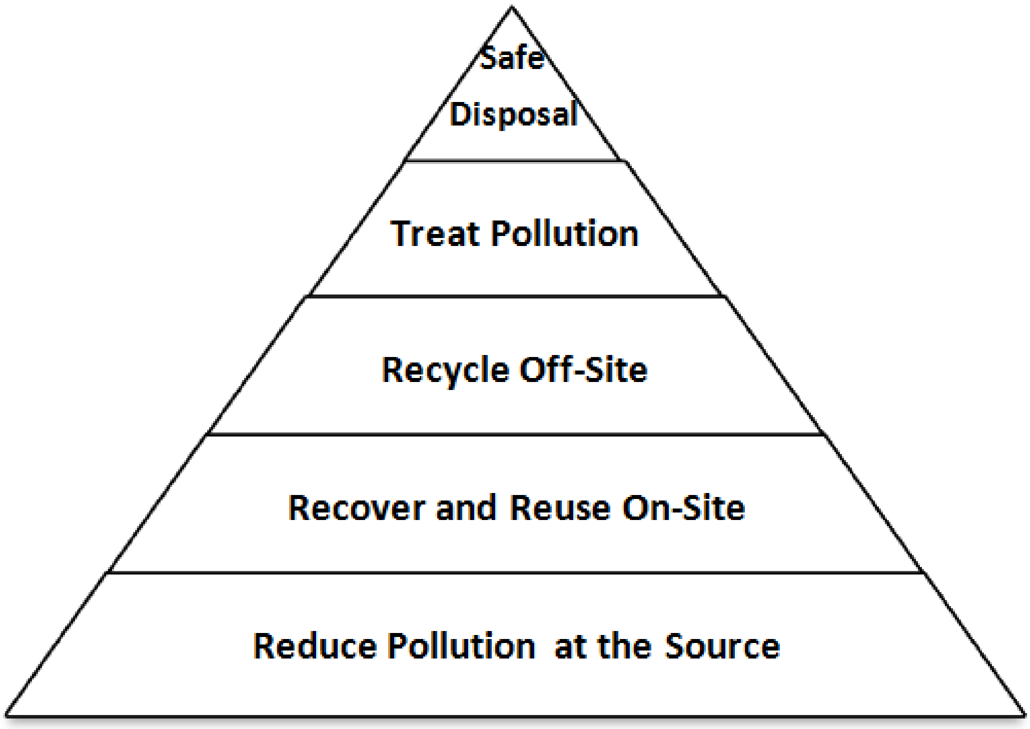


Figure 4. Five approaches of pollution prevention with desirability decreasing as it moves toward the pinnacle of the pyramid (Hanrahan, 2012).

Pollution prevention is a form of sustainability solution. Pollution prevention guarantees the continual efficiency and profitability in industries. It helps to protect both humans and their environment. It is well recognized in today's world and has gained grounds in industries both locally and internationally (Ngwakwe, 2011, Kathuria, 2009).

Pollution prevention (Figure 5) has the ability to completely eliminate or minimize to the barest minimum environmental risks which can in turn bring about social and environmental advantages of safeguarding the environment. In ensuring that wastes are reduced or eliminated, pollution prevention strategies alter manufacturing processes and employ the use of non toxic, non hazardous materials and chemicals. If industries comply with their strategies, it is a win-win situation for the industry, the people and the environment (Munguıa et al., 2010, MolinaAzorin et al., 2009).

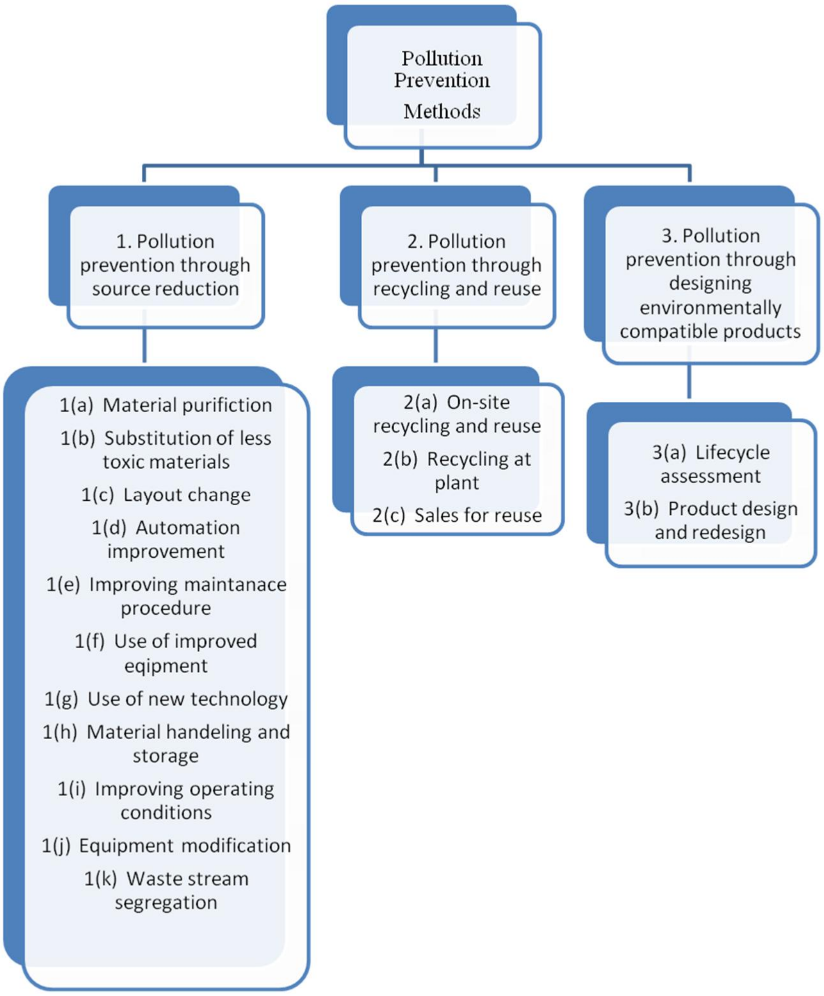


Figure 5. Industrial pollution prevention methods and techniques in general (Hoque & Clarke, 2013).

3.2 Green Chemistry

Over the past decades, industrial wastes and emissions have been dealt with by end-of-pipe solutions which simply entail that pollutants generated by the industries are regulated usually by environmental laws. This end-of-pipe solution deals with the symptoms and not the root source of pollution, they are also quite expensive to carry out. Green Chemistry concept emerged as a solution to avoid altogether waste and emissions by preventing pollution at the root source. Green Chemistry was first introduced as an answer to the Pollution Prevention Act of 1990; this act stated that the US national policy stopped end-of-pipe solution of containing pollution and to embrace pollution prevention by improved design (Ghernaout et al., 2011). It was endorsed and developed by the United States Environmental Protection Agency (EPA) (Bourne & Poliakoff, 2011).

Anastas & Warner (2000) defined Green Chemistry as "the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products". Green chemistry requires as its goal absolute perfection albeit recognizing that in reality there is always some discrete risk involved while trying to achieve its set goal. Green chemistry in its simplest form can be described as a form of pollution prevention. It entails discovering various ways to find solutions to environmental problems by the continuous process of designing chemical synthesis and products. It achieves pollution prevention by the application and utilization of chemical principles and methods for source reduction. As an assessment tool related to sustainability, the green chemistry can be used as a design tool. There are twelve principles of Green Chemistry; these twelve principles are spearheaded by pollution prevention which is its primary goal. The Green Chemistry principles were established to redesign industrial practices to be more sustainable. Green Chemistry principles focus on safe guarding human health and the environment while still maintaining the efficacy of the products. It also encourages the use of renewable raw materials as feedstock and is instrumental in the creation of biodegradable products in chemical industries (Anastas & Warner, 2000).

Table 2. The twelve principles of Green Chemistry (Anastas and Warner, 2000).

- Principle 1. Prevent waste: Design chemical syntheses to prevent waste
- Principle 2. Maximize atom economy: Design syntheses so that the end product contains the maximum proportion of the starting materials (few wasted atoms!)
- Principle 3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with minimal environmental toxicity;
- Principle 4. Design safer chemicals and products: Design chemical products that have minimal environmental toxicity;
- Principle 5. Use safer solvents/reaction conditions: The goal of avoiding solvents, separation agents, or other auxiliary chemicals at all costs. If unavoidable, use innocuous chemicals;
- Principle 6. Increase energy efficiency: Attempt to run reactions at ambient temperature and pressure whenever possible;
- Principle 7. Use renewable feedstock: Attempt to use raw materials and feedstock (starting materials) that are renewable rather than depleting

- Principle 8. Avoid chemical derivatives: Attempt to avoid using blocking or protecting groups or any temporary modifications whenever possible;
- Principle 9. Use catalysts, not stoichiometric reagents: Try to minimize waste by using catalytic reactions that can carry out a single reaction multiple times;
- Principle 10. Design chemicals and products that degrade after use: The design of chemical products that break down to innocuous substances upon use by the consumer or industrial process;
- Principle 11. Analyze in real time to prevent pollution: Use and encourage the use of in-process real-time monitoring and control during syntheses. This minimizes or eliminates byproducts;
- Principle 12. Minimize the potential for accidents: Design chemicals to minimize the potential for chemical accidents including explosions, fires, and environmental releases

Principle 5 of the Green Chemistry states that solvents if at all used in a chemical process should be innocuous, green solvents are best used to achieve this. According to Capello et al. (2007), there are four aspects by which green solvents can be identified. The first is the substitution of hazardous solvents with ones that show better environmental, health and safety characteristics such as increased biodegradability. The second aspect involves the use of ‘bio-solvents’ which means solvents that are manufactured using renewable resources like ethanol. The third aspect entails the substitution of organic solvents with environmentally non hazardous supercritical fluids. The fourth aspect makes use of the substitution of organic solvents with ionic liquids that have low pressure which leads to reduced emissions to the air.

3.2.1 Atom economy

Atom economy, one of the Green Chemistry principles is a measure of how well each of the reactants in a chemical process is included in the final product. Atom economy is said to be 100% when all of the reactants in the process are completely included in the final product. Atom economy is a method used to determine whether or not a chemical process design is green (Anastas & Warner, 2000).

Wang et al. (2011) has proposed a way for calculating the atom economy in a chemical reaction.

$$Atom\ economy = \left(\frac{molecular\ weight\ of\ desired\ product}{molecular\ weight\ of\ all\ products}\right) * 100$$

In this calculation, only the reactants used are considered, intermediates made in one stage and used up in the next stage are always ignored. Atom economy is calculated without taking into account side reactions or the true yield of the reaction.

Three assumptions are usually made in the calculation of atom economy;

- All substances not occurring in the equation of reaction are overlooked
- The quantity of raw materials is stoichiometric
- The yield is 100%.

In reality, it is feasible that the true yield can be a lot lower than 100% because there is no separation or reuse of the unreacted part of raw materials and at the same time a synthetic route can have 100% atom economy.

3.3 Institution of Chemical Engineers (IChemE) Sustainability Matrices

IChemE can be described as a set of indicators used to measure industry's sustainability performance. For this assessment tool, key indicators of the three sustainability aspects (economic, environmental, and social) must be taken in to consideration in order for there to be a balanced sustainability performance view. It is possible to select ratio indicators for this tool; this can be used as a measure of impact which is not dependent on the scale of operation. It can also be used to measure cost against benefit and sometimes as a basis for comparison between different operations. IChemE sustainability matrices are usually presented in three groups; environmental indicators, economic indicators and social indicators which reflects the three sustainable development aspects. Environmental indicators give an equivalent view of the inputs (raw materials and resource usage) and outputs (effluents, wastes and emissions) of environmental impacts. Economic indicators deal with financial reporting with respect to value and wealth creation and also in the reinvestment of an industry's future growth. For this indicator, both human and financial capitals are given due consideration. Examples of this indicator include; profit, value and tax, investment. Social indicators are concerned with industry's attitude towards the society, its employees, customers and contractors. A good social performance is usually strived for. Examples of social indicators include; workplace (employment situation, health and safety at work), and society (IChemE, 2010).

3.4 American Institute of Chemical Engineers (AIChE) Sustainability Index

Cobb et al. (2009) has described the AIChE sustainability index as one that uses easily accessible public data to evaluate the sustainability performance of representative companies in the chemical industry with respect to the following; strategic commitment, safety performance, social responsibility, value chain management, sustainability innovation, product stewardship, and environmental performance. The unique feature of AIChE is that it enables industries to compare, measure and track their sustainability performance within the industry and with other similar industries. The AIChE Sustainability Index is comprised of seven key assessment areas (Figure 6).

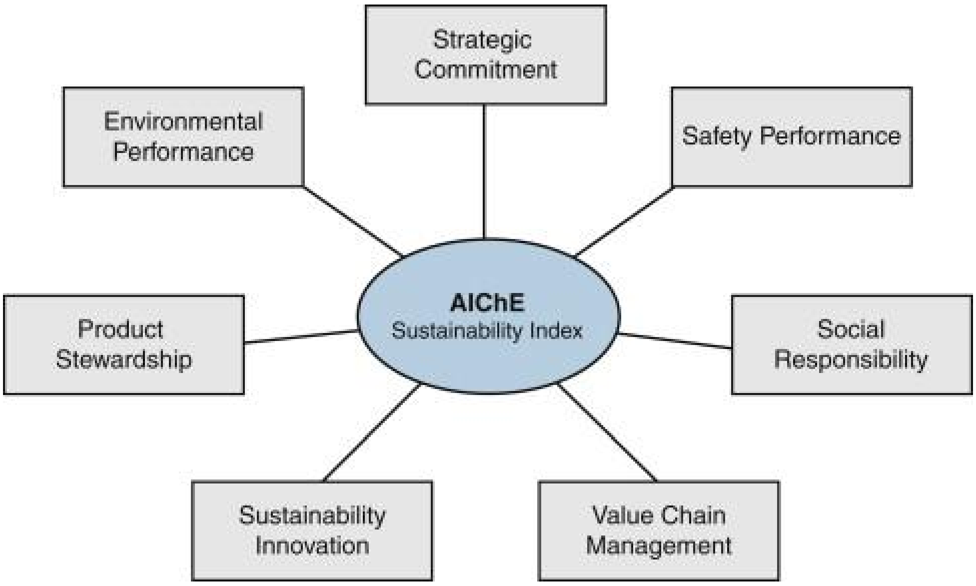


Figure 6. Seven assessment areas of the AIChE Sustainability Index (SI) (Hanrahan, 2012).

The first area Strategic Commitment to sustainability is based on stated commitment, commitment to voluntary codes, sustainability reporting, sustainability goals and programs, and third party ratings. The industry's target and proposed action needs to be clearly defined, also accountability via public reporting is necessary for this case. The second area Sustainability Invention is based on general research and development commitment, sustainable product and processes, sustainability approaches in research and development, and research and development effectiveness. The third area Environmental Performance is based on resource use. The fourth area Safety Performance encompasses employee safety, process safety, plant security, green house gas emissions, other emissions, and compliance management. The fifth area Product Stewardship consists of assurance system, risk communication, and legal proceedings. The sixth area Social Responsibility relates to stakeholder partnerships, social investment, and image in the community. The seventh and final area of the AIChE sustainability index, Value Chain Management comprises of environmental management system (EMS) and supply chain management (Cobb et al., 2009).

3.5 Life Cycle Assessment (LCA)

Over the last 35 years, Life-Cycle Assessment (LCA) tool has been used to measure the environmental impacts of a product throughout its life cycle. In order to use this tool, there are certain guidelines and principles set in place by International Standards Organization (ISO) that must be adhered to (Buytaert et al., 2011).

ISO 14044:2006 has defined Life-Cycle Assessment (LCA) as a 'technique that addresses the environmental aspects and potential environmental impacts (e.g. use of resources and environmental consequences of releases) throughout a product's life cycle from raw material acquisition through production, use, recycling and final disposal (i.e. cradle -to-grave)'. It follows the guidelines of ISO 14040 Environmental Management System. ISO standards give a description of four steps which includes; goal and scope definition, impact assessment, inventory analysis and interpretation (Buytaert et al., 2011).

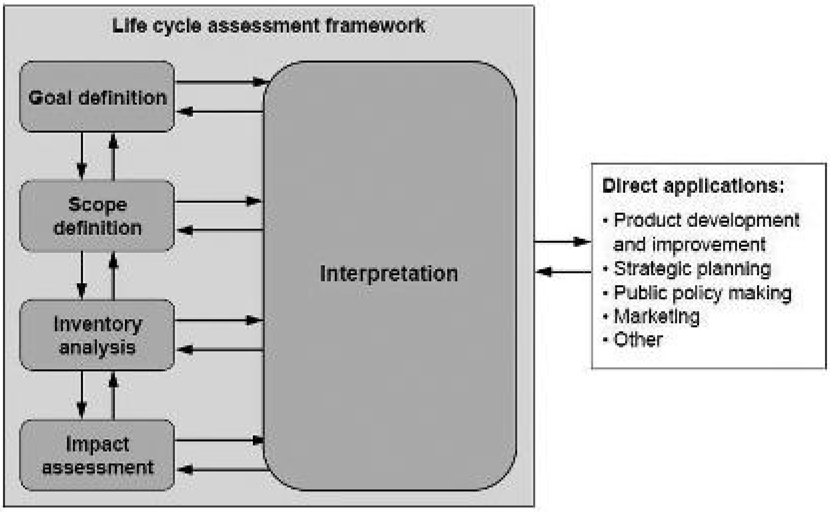


Figure 7. Overview of LCA effort according to ISO (Sørensen, 2011).

From Figure 7 it can be seen that for LCA, material and energy balances are necessary in all stages of the product life cycle. ‘Cradle-to-grave’ LCA approach is usually used to evaluate industrial systems. ‘Cradle-to-grave’ in this case starts with product creation by raw materials accumulation and ends at the recycling/reused or disposal phase. LCA covers the environmental aspect of a product by including its impact throughout the product life cycle. Sustainability is attained when impacts are minimized or eliminated (Hanrahan, 2012). Figure 8 illustrates a systematic view point for analyzing the input/output flows of energy and materials alongside the environmental impacts of the product throughout its life cycle.

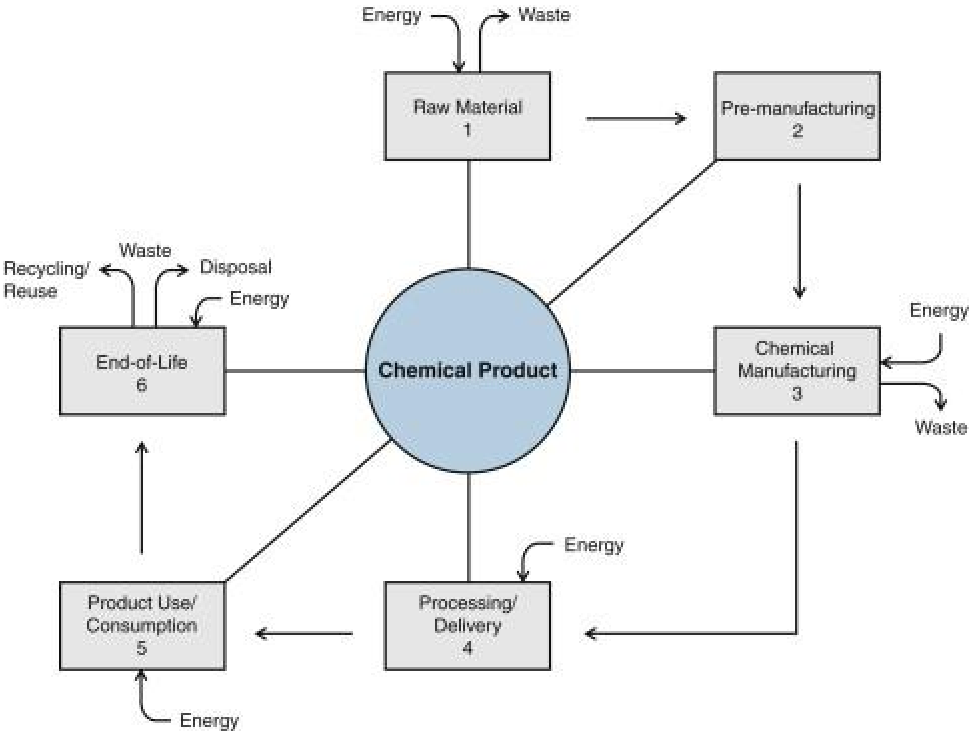


Figure 8. Chemical product life cycle considered in the life cycle assessment (LCA). (Hanrahan, 2012).

Energy flows into (input) each phase of the chemical product life cycle excluding the pre-manufacturing phase where no energy is required, and waste flows out (output) in the raw material, chemical manufacturing and the end-of-life phase. Also in the end-of-life phase, waste disposal and reuse/recycling of materials flows out (output) of the phase while energy flows into the process (Hanrahan, 2012).

3.6 The Natural Step principles

The Natural Step has its origins in Sweden and is known as a ‘Framework for Strategic Sustainable Development’. It is a world renowned framework which helps industries and individual alike to move towards sustainability. The Natural Step framework is usually applicable to complex systems whereby careful planning and organizing is needed. The Natural Step framework consists of four system conditions which can also be expressed as the principles of sustainability. Mankind activities for some centuries have been unsustainable and this has had an adverse effect on the earth. It is believed that if this trend continues unchecked it could lead to a complete degradation of the ecosystem. A team of international scientists came up with four basic conditions that must be satisfied to ensure that environmental, social and economic aspects of sustainability are satisfied (The Natural Step, 2013), (Phdungsilp, 2011). Table 3 depicts the four system conditions that must be satisfied to bring about sustainability.

Table 3. The Four Systems Conditions (The Natural Step, 2013).

The Four System Conditions	**Reworded as the Four Principles of Sustainability**
In a sustainable society, nature is not subject to systematically increasing	To become a sustainable society, we must eliminate our contribution to
1. Concentrations of substances extracted from the earth's crust	1. The systematic increase of concentrations of substances extracted from the Earth's crust
2. Concentrations of substances produced by society	2. The systematic increase of concentrations of substances produced by society
3. Degradation by physical means	3. The systematic physical degradation of nature and natural processes
4. People are not subject to conditions that systematically undermine their capacity to meet their needs in the society	4. Conditions that systematically undermine people's capacity to meet their basic human needs

The Natural Step framework makes use of the 'backcasting' concept to achieve sustainability. Simply put backcasting can be described as a process of defining a desirable future and planning presently on how to attain that desired future, whilst visualizing success. Strategic sustainable development makes use of the backcasting concept from the principles of sustainable development (The Natural Step, 2013).

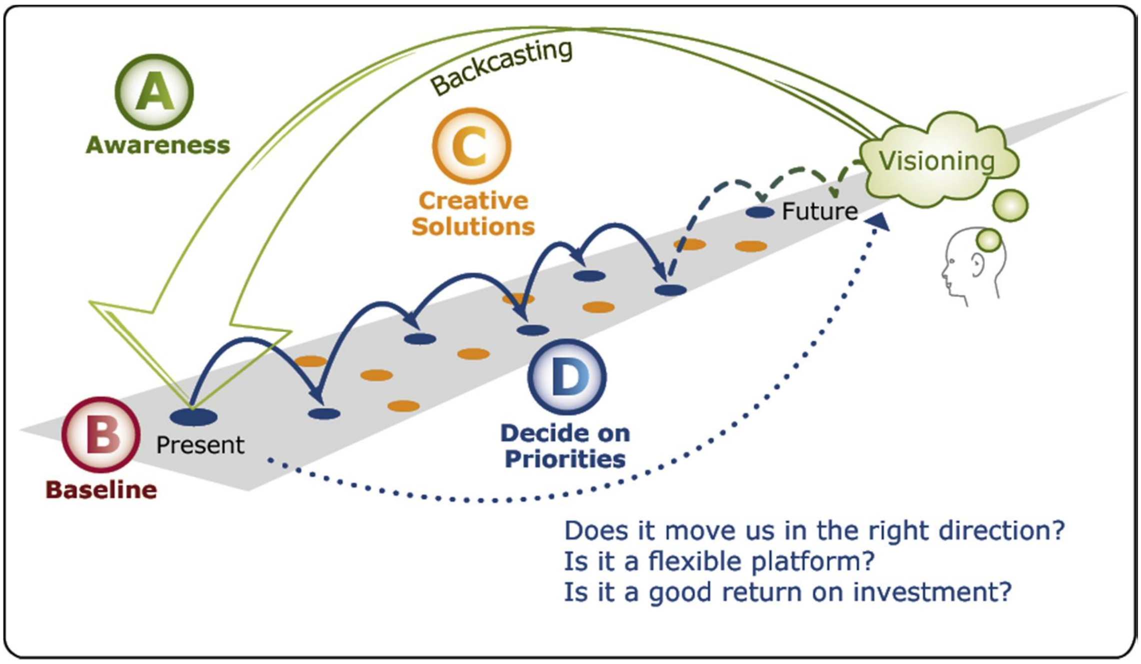


Figure 9. The ABCD method (The Natural Step, 2013).

Figure 9 show that the backcasting concept applies a method known as A-B-C-D method to The Natural Step Framework to help industries to attain sustainability. A stands for ‘Awareness and Visioning’; Here sustainability concept and its application in an industry is clearly defined and understood. B stands for ‘Baseline Mapping’; In this case a comparison is made between industry’s current activities and practices and the four sustainability principles. This gives an opportunity to the industry to identify its major sustainability shortcomings and hence creates an opportunity for improvement. C stands for ‘Creative Solutions’; Creative Solutions calls for brainstorming to the sustainability shortcomings in the industry identified in the baseline mapping. Backcasting may be employed in this case. D stands for ‘Decide on Priorities’; In this case an action plan is carried out based on ‘C’ and a step-by-step implementation of the creative solution is implemented to ensure the quick move of the industry towards the direction of sustainability (The Natural Step, 2013).

3.7 Review of the tools

The six assessment tools related to sustainability considered in this thesis are Green Chemistry, LCA, the Natural Step, AIChE, IChemE and pollution prevention. These tools were carefully chosen because they are all applicable to the chemical industry which is the primary focus of this thesis.

Figure 10 illustrates the distribution of these tools in the form of a hierarchical order whereby as one moves down to the base of the pyramid, the tool gets more practical and easier to use within industry while up (apex) of the pyramid represents the more conceptual nature of sustainable development, hence abstract. By being conceptual it tells us what and why it is to be done but not how to go with it in a practical way.

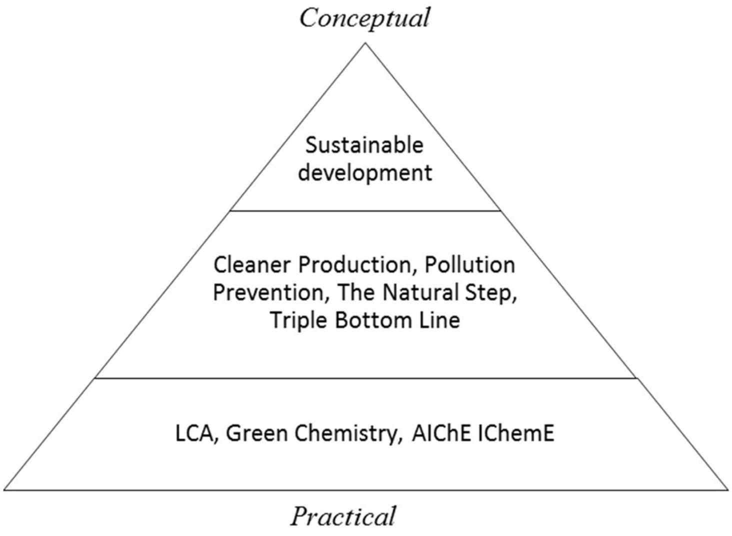


Figure 10. Hierarchy of sustainability tools (based on Lankey and Anastas 2002).

The base level of the pyramid contains the quantitative tools that can be used to measure sustainability of a subject; the second level of the pyramid contains both qualitative tools and concepts, they are immeasurable but adequately define the concept of sustainable development (Lankey and Anastas, 2002) Table 4 highlights various strengths and weaknesses of assessment tools related to sustainability.

Table 4. Summary of the strengths and weaknesses of the assessment tools related to sustainability.

Tools	**Strengths**	**Weaknesses**
Pollution Prevention	• It targets the root cause of pollution • Favors the environment, the people and the industry • Adequately covers the concept of sustainable	• It focuses on the theory • It is a qualitative in nature and cannot be measured

	development	
Green Chemistry	- It can be used as a design tool for both industrial products and processes - It helps to redesign industrial practices to be more sustainable - It is centered on pollution prevention and helps safeguard human health and the environment - Its guidelines and principles are consistent, practical and unambiguous	- It focuses mainly on the environmental and social aspects of sustainability (people and planet) and disregards the economic aspects (profits). Green Chemistry tool is expensive when practically applied in industrial settings - It focuses on the present successes of the product (non toxic, degradable, recyclable) and processes (non-hazardous, reduction/ elimination of solvent use) involved and totally neglects full life cycle impacts on them - Green Chemistry tool is that it is too toxicity oriented hence rigid in its scope of application
IChemE	- Key indicators of the three sustainability aspects (economic, environmental, and social) are put into consideration therefore there is a balanced sustainability performance view - Its guidelines and principles are consistent, practical	- They access only the sustainability performance from an industrial view point and are not product focused - Are focused primarily on the chemical industry
AIChE	- Key indicators of the three sustainability aspects (economic, environmental, and social) are put into consideration therefore there is a balanced sustainability performance view - AIChE enables industries to compare, measure and track their sustainability within the industry and with other similar industries	- They access only the sustainability performance from an industrial view point and are not product focused - Are focused primarily on the chemical industry

	• Its guidelines and principles are consistent, practical	
LCA	• Is the only sustainability tool that takes into account various stages of the entire product life cycle from cradle to end-of-life • Its principles are applicable to both products and processes in any sector or type of industry • It is a flexible and interdisciplinary tool • It can be tailor-made towards the assessment of a desired matrix • It gives a more precise picture of true environmental impact	• LCA is bulky, data intensive, and time consuming (it takes a lot of time to select data) • LCA is a complex and expensive tool hence economically prohibitive • It gives room for assumptions to be made which might be subjective, hence the results of two LCA on one particular subject may be different • LCA's results is geographically dependent, an LCA conducted on a subject in Europe would be different from the one conducted in the US • Its accuracy depends on the availability of the relevant data
The Natural Step	• It satisfies the three aspects of sustainable development • Is applicable to complex systems whereby careful planning and organizing is needed • It applies a backcasting concept which is a strong point for economic growth and development	• It focuses on the theory • It is too abstract and cannot be practically used • It is qualitative in nature and cannot be measured

Using the assessment tools related to sustainability presented in this thesis, it is extremely difficult to measure sustainability in industry as each of these tools individually have their strengths and weaknesses highlighted above. None of these tools can adequately stand alone as a true test of sustainability tool, but by combining all the strong points of these tools a new hybrid tool emerges which adequately represents and covers the three aspects of sustainable development in its entirety.

4. REDUCING THE ENVIRONMENTAL IMPACTS OF CHEMICAL INDUSTRY

Chemical industry is responsible for the manufacturing of different products brought about by the conversion of natural and mineral raw materials, animals and vegetables into the different products often utilized in industries and households. The produced products are of immense importance in our today's world. Chemical industry has the ability to improve the quality of life of a population. Chemical industry has a great impact on sustainability as both its production methods and processes are very crucial in ensuring that the criteria for sustainability are met. In recent times, there has been a great advancement in chemical industry; one of such advancements is the creation and adoption of the Green Chemistry principles which has 'pollution prevention' as its watchword (Garcia, 2009).

4.1 Benefits of chemical industry

Chemical industry contributes greatly to itself; an example of such contributions is in the manufacturing of catalysts used to speed up chemical reactions. It has also contributed to other industries like the food industry where it helps to produce additives and preservatives and in agricultural industry as it is the basis for which fertilizers, insecticides and herbicides which help in improving agricultural yield are produced. The industry also plays a vital role in pharmaceuticals industry because of its usefulness in the production of drugs. In addition; chemical industry is also useful in the manufacturing of various household items, textiles and plastics. Its role in nations has significantly boosted the economy and improved the social status of the population. The environment itself also benefits from chemical industry; the industry produces catalysts which help in the reduction of e.g. air pollution. It has also developed chemical processes which enable the use of renewable form of energy an example of such energy is the biomass, and in some cases improved energy efficiency (Garcia, 2009).

4.2 Drawbacks of chemical industry

Despite the numerous benefits realized by the chemical industry, it also has its downsides. Over the last five decades, chemical industry's image has been badly damaged. There have been conflicts between chemical industry and the general public over the industry's environmental impacts and overall safety (Johnson, 2012). The industry has been blamed for both land pollution and invasion of natural resources. It has also been accused of creating numerous social problems stemming from rapid industrialization and the exploitation of weak nations for commercial gains (Hall & Howe, 2010). Figure 11. shows the general public view in the UK the trends in chemical industry between the periods of 1979 and 2000. As the year progressed (1979-2000) the public view on chemical industry became less favorable and more unfavorable (Johnson, 2012).

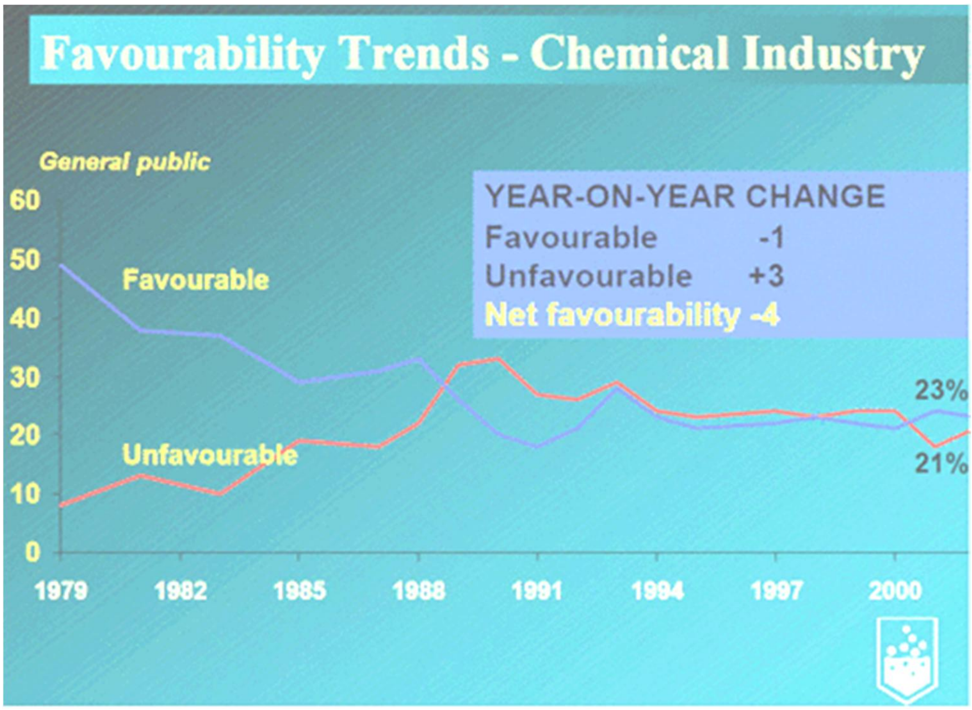


Figure 11. Public opinion in the UK on chemical industry, 1979-2002 (Johnson, 2012).

However, in recent times most chemical industries have embraced sustainability as a kind of peace offering in order to satisfy all stakeholders (Johnson, 2012).

4.3 Reducing the carbon footprint of chemical industry: Chemical Utilization of CO_2

CO_2 has been discovered to be a primary contributor to the effects of green house gases in the atmosphere which has overtime led to global warming. In order to reduce global warming, the utilization of CO_2 in the production of chemicals and other industrial commodities has been the primary focus of many researches (Zhao & Joo, 2011).

The utilization of CO_2 as a raw material can be described as both a sustainable and an inexpensive process; it is a safe raw material, non- toxic, non-flammable. The reduction of atmospheric loading, has led to the replacement of toxic chemicals that are harmful to human health and environment. CO_2 can be used as feedstock in chemical processes.

Hydrogenation of CO_2 can yield in e.g. the production of formic acid and methanol (Raudaskoski et al., 2009).

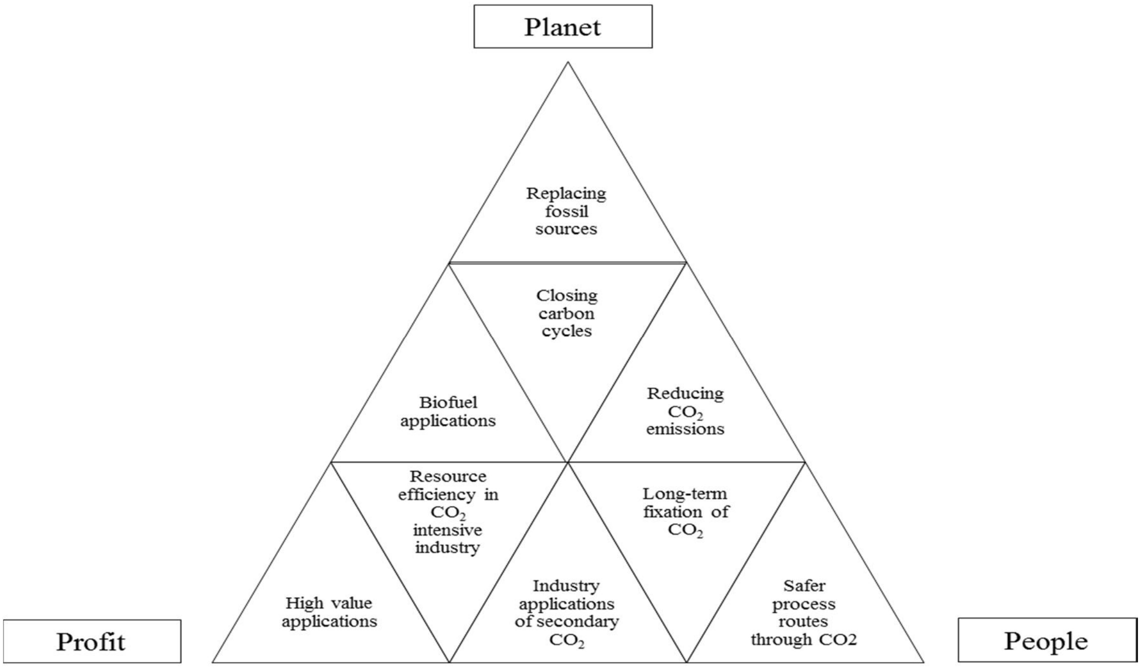


Figure 12. Chemical utilization of CO_2 fulfilling environmental, economic and social concerns, the three facets of sustainability (Raudaskoski et al., 2009).

Figure 12 illustrates how sustainable practices involving the use of CO_2 combines the three facets of sustainability namely; economic, social and environmental often expressed as people planet and profit. It is shown that the three facets of sustainability are well represented (Raudaskoski et al., 2009). Figure 13 shows some of the most commonly used CO_2 reactions and their resulting products.

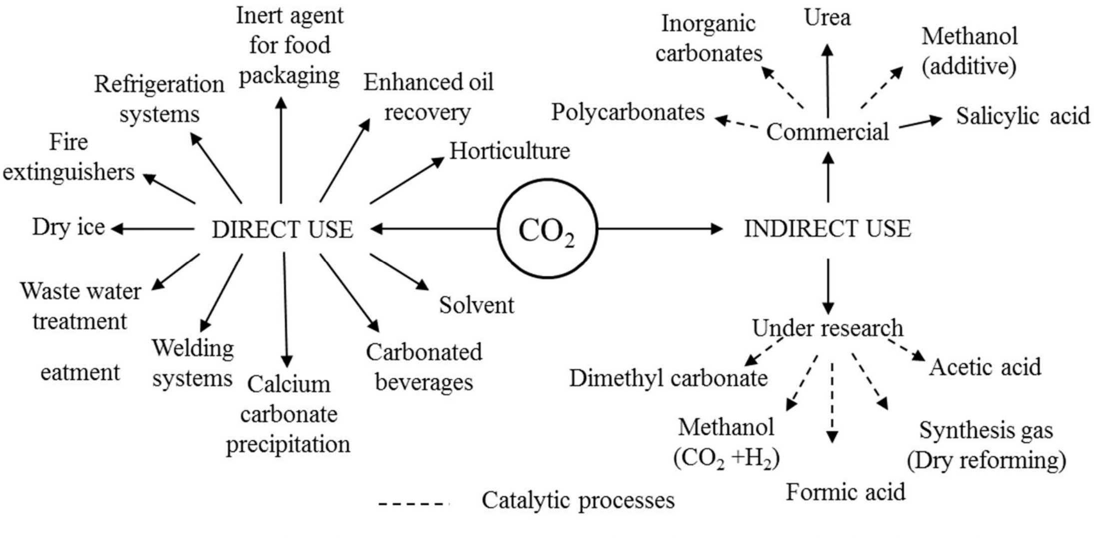


Figure 13. Direct and Indirect use of CO_2 (modified from Raudaskoski et al., 2009).

CO_2 can be used directly and indirectly. Some areas involving the indirect use of CO_2 particularly in the laboratory scale are still under research, efforts are being made to scale-up the laboratory scale production of CO_2 utilization chemicals to commercial scale (Raudaskoski et al., 2009). Formic acid falls under the indirect use of CO_2 and its production process is still under research.

4.4 REACH regulation

REACH is an acronym for Registration, Evaluation, Authorization and Restriction of Chemicals. It was enforced in the year 2007. The aims of REACH includes; ensuring maximum protection of human health and the environment from chemicals associated with risks, the advancement of better testing methods, encouragement of innovations, and ensuring that there is a free distribution of substances on the internal market. REACH ensures that industries are responsible for both the assessing and management of chemically imposed risks and to give adequate information regarding safety to their users (European Commission, 2013).

REACH covers all chemical substances used in industrial processes and in humans' everyday life. REACH regulation is impacted in industries across the EU. In order for industries to abide by the regulation, they must be able to recognize and control risks associated with the substances they produce and market in the EU. If risks cannot be controlled, the responsible authorities would limit the harmful substances used. Substances of Very High Concern (SVHC) require some specific legal commitment for producers, suppliers and importers of an object containing such substance. REACH is keeping a list of chemicals that are registered under it and also an exception list of chemicals (ECHA- European Chemical Agency, 2013). Annexes IV and V of REACH exceptions from the necessity to register is in accordance with articles 2(7) (a) and 2(7) (b) (Official Journal of the European, 2008). Table 5 indicates all substances in REACH that were included in this thesis.

Table 5. Substances in REACH.

Substance	**CAS number**	**Registered in REACH**	**Substances not 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			
Triethylamine	121-44-8	X			
1-n-buthylimidazole	4316-42-1		X		
Tetraethylene Glycol	112-60-7		X		
C_2H_5OH	64-17-5	X			

None of the substances used in the production of formic acid was found in the candidate list. CO_2 and CO were in the exemption list because sufficient information about them and their intrinsic properties pose a minimum risk. Two substances 1-n-buthylimidazole and tetraethylene glycol are not REACH registered, neither were they found in the candidate list because they are not produced in Europe and they are needed in small quantities.

5. FORMIC ACID

Formic acid (HCOOH) is an alkyl carboxylic acid also known as methanoic acid. It is a colorless liquid that has a high pungent odor. It has a CAS number of 64-18-6 and a molecular mass of 46.03. Formic acid is miscible with water but with hydrocarbons it is miscible only to a certain degree. Formic acid is utilized in industries that produce pesticides, rubber, textile, silage additive, leather and dyeing (Ullmann, 2011).

5.1 Physical properties of formic acid

Formic acid is a very corrosive liquid with a boiling point of 108.8 ^{o}C, 101.3kPa and a melting point of 8.3^{o}C (Ullmann, 2011). Table 6 shows the physical properties of formic acid.

Table 6. Physical Properties of formic acid (modified from Ullmann, 2011).

Properties	**Value & SI Unit**
Heat of fusion	276 J/g
Heat of vaporization (at bp)	483 J/g
Molecular Mass	46.03
Boiling Point	100.8 °C, 374 K, 213 °F
Melting point	8.4 °C, 282 K, 47 °F
Dielectric constant Liquid (at 20^{O}C) Solid (at -10.1^{O}C)	 57.9 11.7
Odor	Pungent and penatrating
Appearance	Colorless fuming liquid
Heat of formation ΔH H^{0}_{f} Liquid (at 25 ^{O}C) Vapor (at 25^{O}C, monomer) (at 25 ^{O}C, dimer)	 -425.0 kJ/mol -378.57 kJ/mol -820.94 kJ/mol
Heat of combustion ΔH^{o}_{c} Liquid (at 25 ^{O}C)	 -254.8 kJ/mol

Entropy S^{O} Liquid (at 25 ^{O}C) Vapor (at 25 ^{O}C, monomer) (at 25 ^{O}C, dimer)	129.0 J $K^{-1}mol^{-1}$ 248.88 J $K^{-1}mol^{-1}$ 332.67 J $K^{-1}mol^{-1}$
Heat of neutralization	56.9 kJ/mol
Density	1.220 g/mL
Solubility in water	Miscible
Solubility	Miscible with ether, acetone, ethyl acetate, glycerol, methanol, ethanol partially soluble in benzene, toluene, xylenes
Thermal Conductivity λ Liquid (at 20 ^{O}C) (at 60 ^{O}C) (at 100 ^{O}C) Vapor (at 50 ^{O}C) (at 100 ^{O}C) (at 200 ^{O}C)	 0.226 W $m^{-1}K^{-1}$ 0.205 W $m^{-1}K^{-1}$ 0.185 W $m^{-1}K^{-1}$ 0.0136 W $m^{-1}K^{-1}$ 0.0176 W $m^{-1}K^{-1}$ 0.0267 W $m^{-1}K^{-1}$
Electrical conductivity (at 25 ^{O}C)	$6.08\text{x}10^{-5}\ \Omega^{-1}cm^{-1}$
Coefficient of cubic expansion α (at 30 ^{O}C)	0.001

Pure formic acid is hygroscopic in nature. Formic acid can be produced by several methods; one of such methods is by hydrolysis of methyl formate from its salt. In the production of acetic acid via oxidation of hydrocarbons (liquid-phase), formic acid is produced as a by-product (Ullmann, 2011).

5.2 Production of formic acid

In this Master's thesis, production of formic acid via commercial and laboratory scale are considered. The methods used are Kemira-Leonard process via methyl formate hydrolysis performed in commercial scale and hydrogenation of CO_2 both in commercial and laboratory scales. Other methods for formic acid production include oxidation of hydrocarbons, preparation of free formic acid from formates and hydrolysis of formamide (Ullmann, 2011).

5.2.1 Methyl formate hydrolysis

Methyl formate hydrolysis is one popular method for producing formic acid in commercial scale. Methyl formate hydrolysis basically involves the synthesis of formic acid via a two stage process. The first stage entails methanol (CH_3OH) being carbonylated with carbon monoxide (CO). In the second stage formic acid (HCOOH) and methanol (CH_3OH) are derived from hydrolyzed methyl formate (CH_3OOCH). In this process, methanol is recycled back to the first stage.

The reaction route for the production of formic acid is:

$$CH_3OH+CO \rightarrow HCOOCH_3 \qquad (1)$$

$$CH_3OOCH+H_2O \rightarrow CH_3OH \qquad (2)$$

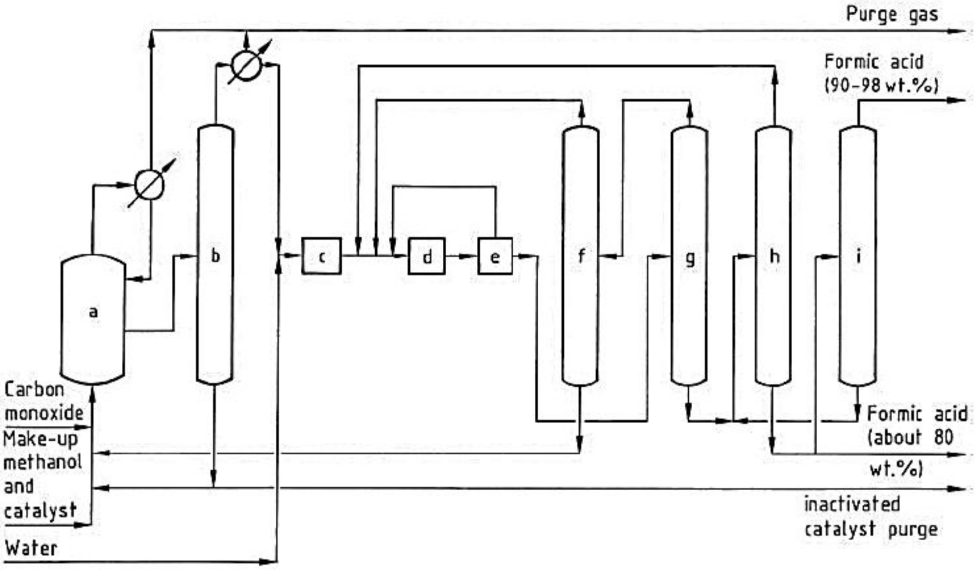
The heat of reaction ΔH^o_R is -29 kJ/mol for Equation (1) and the heat of reaction ΔH^o_R is 16.3 kJ/mol for Equation (2). The reaction is catalyzed by strong acids (Ullmann, 2011).

Ullmann (2011) stated that the two-stage industrial method of methyl formate hydrolysis in the production of formic acid was mainly anchored by the following company; the Leonard process company, located in the United States; the Scientific Research Institute for the Chlorine Industry of the Ministry of Chemical Industry located in the former Soviet Union and BASF located in Germany. The carbonylation of methanol stage involves carbon monoxide reacting with liquid phase methanol. The catalyst employed for this process is a basic catalyst.

The problems associated with the methyl formate hydrolysis are that it has unfavorable hydrolysis equilibrium and methyl formate is a highly volatile chemical. These problems are eliminated in the Kemira-Leonard process using two hydrolysis reactors placed in series to each other after which a flash distillation is carried out in order to take away very quickly unconverted ester and to perform the distillation in a column of low residence time (Kirk-Othmer, 1993).

5.2.2 Kemira-Leonard Process (Commercial)

In the Kemira-Leonard process of methyl formate hydrolysis, the temperature and pressure of the methyl formate and carbonylation were about 80°C and 4 MPa, respectively. The catalyst used was alkoxides. Hydrolysis involved the use of the two reactors both of which differ in their operating conditions. In the main reactor, hydrolysis occurred at a temperature and pressure of 120°C and 0.9 MPa, respectively. In this reactor, hydrolysis was catalyzed by the formic acid. Formic acid obtained in this process is usually dehydrated via distillation to achieve high concentration. Very high concentration of formic acid up to about 98% can be achieved by employing additional dehydration column under atmospheric pressure (Ullmann, 2011).



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

Figure 14. Schematic process flow sheet of formic acid production (Kemira-Leonard process) (Ullmann, 2011).

In the methyl formate reactor (a), compressed carbon monoxide, methanol and catalyst were fed into the reactor and converted into methyl formate. In the methyl formate column (b), discharge from the methyl formate reactor was fed into it and methyl formate was obtained as a distillate. Methanol and dissolved catalyst were recycled back to the reactor. Inactivated catalyst was purged out of the process. In the preliminary reactor (c), off gas and waste gas from the methyl formate column and the methyl formate reactor respectively were burned. In this preliminary reactor, methyl formate reacted with water partially. In the main reactor (d), discharges from the preliminary reactor (methanol, water and methyl formate) were fed into it (main reactor). In the flash tank (e) formic acid in small quantities methanol and methyl formate was recycled back into the main reactor. In the acid separation column (g), it distilled in a vacuum methanol and methyl formate. In the recycle column (f), methanol and methyl formate were gotten from the separation column of the distillate. In the first product column (h), distillation of water took place. In the second product column (i), further concentration of bottom product took place and formic acid with a high concentration of approximately 98% by weight is gotten off as a distillate (Ullmann, 2011).

5.2.3 Hydrogenation of carbon dioxide (CO_2) using ruthenium hydroxide catalyst (Laboratory Scale)

Formic acid is produced in laboratory scale by means of hydrogenation of carbon dioxide (CO_2). In the utilization of CO_2 for chemical processes or reaction, efficient catalysts are required because CO_2 is known to be thermodynamically very stable. Commercial scale production of formic acid such as the hydrolysis of methyl formate is known to generate hazardous waste and it is energy intensive. The reaction route for the hydrogenation of CO_2 is as follows:

$$CO_2 + H_2 \rightarrow HCOOH \qquad (3)$$

For this process the best and most effective catalysts used to achieve a reasonably good conversion of CO_2 and yield of formic acid are ruthenium and rhodium usually in combination with hydrides and halides. Although a homogenous catalyst is used in some cases, heterogeneous catalysts are usually preferred for this process so that there would be easy separation of formic acid from the used catalyst and base (Hao et al., 2011).

How et al. (2011) have produced formic acid in laboratory scale. In this process, a ruthenium hydroxide catalyst was used because of its high selectivity and activity and it could also be recycled back to the process via filtration or centrifugation. The reaction was performed over a γ-Al_2O_3 supported 2.0 wt% ruthenium hydroxide catalyst. CO_2 hydrogenation was performed in an autoclave that had a magnetic stirrer and a capacity of 100 ml. 15 ml of ethanol (solvent) was placed in an autoclave along with 0.1mmol of ruthenium hydroxide (catalyst) and 5 ml of triethylamine. Excess air was generated and this was removed using H_2 three times to flush it away. The autoclave was heated to a temperature of 353 k followed by the reactor being pressurized by H_2 to 5.0 MPa. After this, stirring of the mixture took place for 5 minutes. Cooled CO_2 (about -5^{o}C) was then introduced into the process. Total pressure of the reaction was 13.5 Mpa and the overall reaction temperature was 80^{o}C. It was observed that maximum yield of formic acid was obtained at 80^{o}C. The yield obtained in this process was represented by turnover number (TON) of formic acid which means moles of produced formic acid per mole of ruthenium used. At the reactor outlet only the two gases (CO_2 and H_2) were collected.

5.2.4 BP patented process for hydrogenation of CO_2 (Commercial)

The BP process involves four stages. The first stage involves the reaction in a high boiling solvent of tetraethylene glycol; CO_2 and H_2 at a pressure of about 60 bar and a temperature of about $70^{O}C$ with a catalyst present (transition metal catalyst). The product of this stage is triethylammonium formate salt. The second stage involves the removal and recycling of back to the first stage unreacted triethlamine and catalyst. The third stage involves the reaction of triethylammonium formate salts with a second base 1-n-butylimidazole, forming a second formate salt 1-n-butylimidazolium formate (figure 15) (Hua & Ahluwalia, 2012).

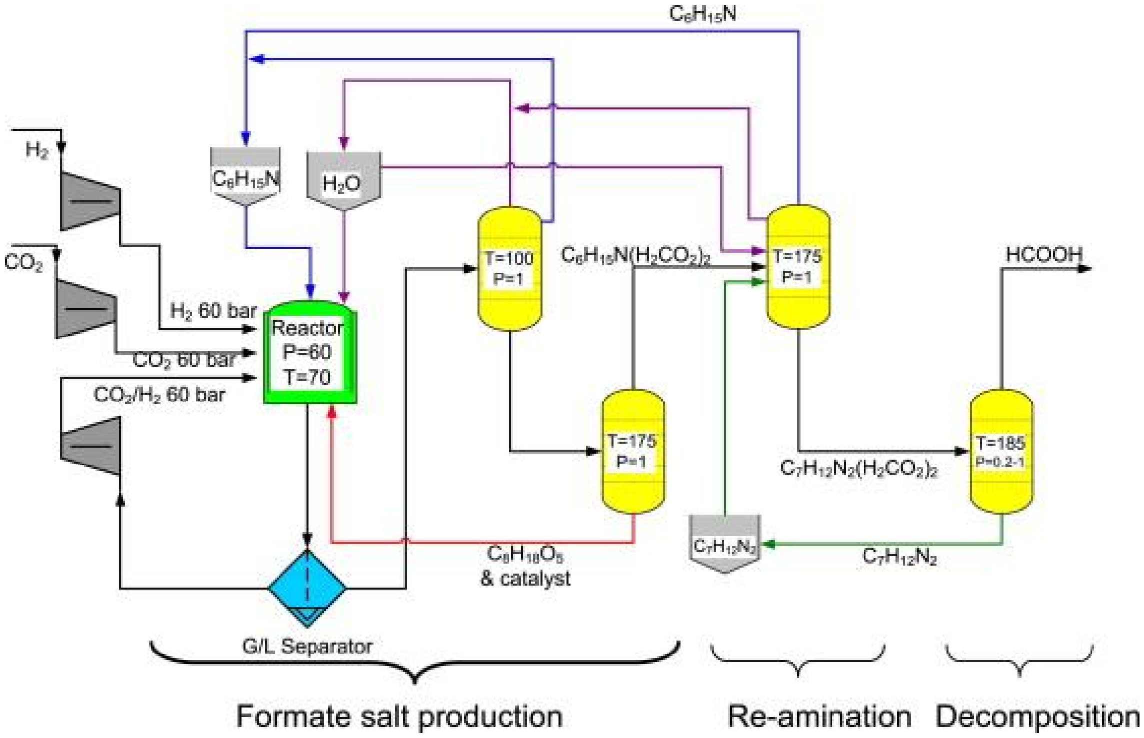


Figure 15. Formic acid production by hydrogenation of CO_2 (BP Patent US 48554) (Hua & Ahluwalia, 2012).

The fourth stage involves 1-n-butylimidazolium formate being decomposed thermally to yield formic acid (75% yield) and 1-n-butylimidazole. The 1-n-butylimidazole is then recycled back to the third stage (Hua & Ahluwalia, 2012).

5.2.5 Hydrogenation of carbon dioxide via ionic liquids (Laboratory Scale)

Ionic liquids are organic salts with unique qualities. These unique qualities include a melting point of below $100^{o}C$, a high thermal stability, strong solvating power, wide temperature range and very low volatility. Nowadays, the production of formic acid in the laboratory scale via hydrogenation of CO_2 using an ionic liquid has gained popularity because of the diverse chemical properties of the ionic liquid which favors the reaction (Zhang et al., 2009). Ionic liquids are also characterized as having a high polarity, resistant to chemicals and very low pressure. They can be adapted to specific operation by the right combination of anions and cations (Andanson et al., 2012).

Zhang et al. (2008) have reported the use of ionic liquids as a base in the hydrogenation of CO_2. The catalyst used for this process was a ruthenium immobilized on silica (a heterogeneous catalyst). During this reaction, the catalyst was distributed in an ionic aqueous solution. The catalytic system has a high selectivity and activity. Formic acid produced by this process is easy to retrieve. The catalyst and the ionic liquid can effortlessly be separated via filtration and evaporation respectively, and reused. The ease of the reaction and separation of the catalyst is shown in Figure 16.

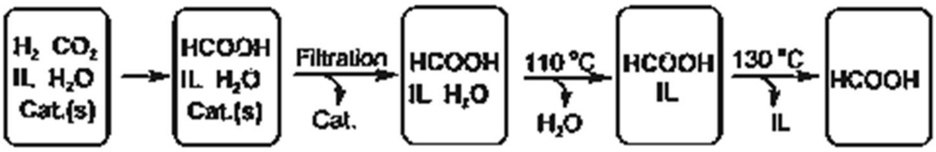


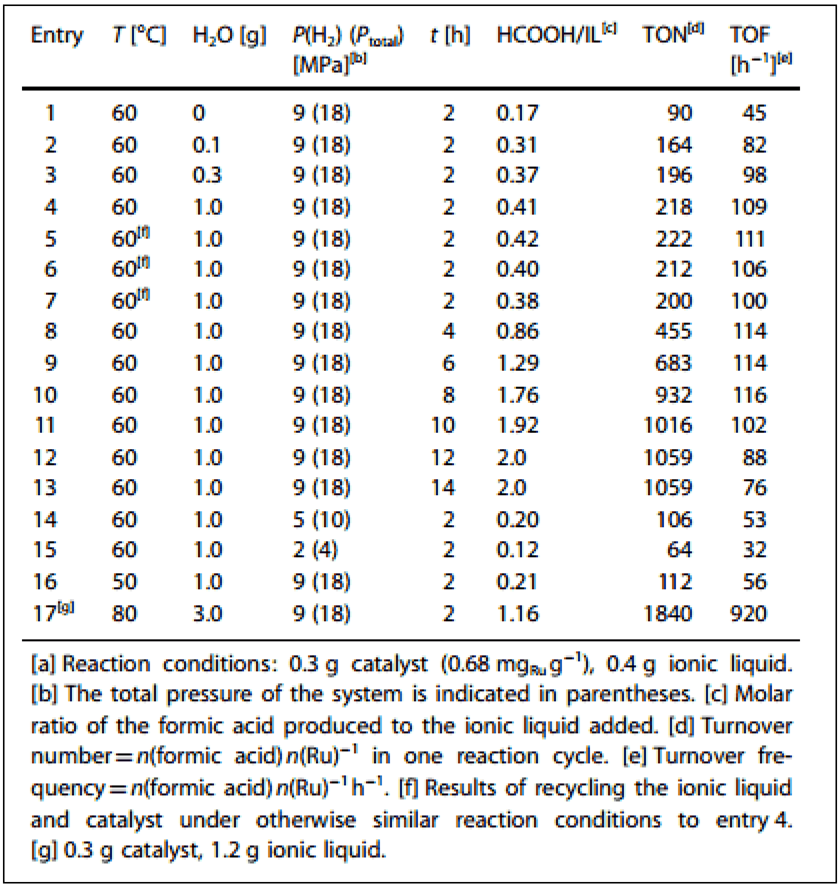
Figure 16. Hydrogenation of CO_2 and recovery of formic acid, catalyst and ionic liquid (Zhang et al., 2008).

At a temperature of 130°C the separation of formic acid from ionic liquid takes place; here formic acid is evaporated from the ionic liquid by the means of a nitrogen flow. The ionic liquid used for this process is a basic ionic liquid with a tertiary amino group ($N(CH_3)_2$) on the cation namely 1-(N,N-dimethylaminoethyl)-2,3-dimethylimidazolium trifluoromethanesulfonate ([mammim][TfO], 3). (Zhang et al., 2008).

Zhang et al. (2009) have gone a step further and reported on the use of a diamine functionalized ionic liquid for the production of formic acid via the hydrogenation of CO_2. The reaction standard free energy is positive (ΔG^0_{298}= 32.9 kJ mol^{-1}). To obtain an equilibrium reaction to bring about an acceptable conversion, it is necessary to add a base. When compared to a task specific ionic liquid, a diamine functionalized ionic liquid the efficiency of CO_2 hydrogenation is expected to be higher. 1,3-di(N,N-dimethylaminoethyl)-2-methylimidazolium trifluoromethanesulfonate ionic liquid which contained two tertiary amino groups on the cation was synthesized in the reaction. Using this basic ionic liquid, it is shown that in one reaction cycle one mole of the ionic liquid can produce two moles of formic acid. Formic acid with a high selectivity and activity was produced from the reaction of CO_2 and H_2 in the presence of the ionic liquid ([DAMI][TfO]) and heterogeneous catalyst “Si”- $(CH_2)_3$ $NH(CSCH_3)$-

{RUCl$_3$(PPh$_3$)}. The ionic liquid and the catalyst can be reused after separation. The catalyst was recovered from the solution by filtration after which the solution was heated and water was expelled out by means of evaporation. Nitrogen flow at 130 ^{O}C was used to recover the formic acid from the ionic liquid. Table 7 shows the experimental results of formic acid production by the hydrogenation of CO_2 (Zhang et al., 2009).

Table 7. Hydrogenation of CO_2 to formic acid in ([DAMI][TfO]).[a] (Zhang et al., 2009).



Entry	T [°C]	H_2O [g]	$P(H_2)$ (P_{total}) [MPa][b]	t [h]	HCOOH/IL[c]	TON[d]	TOF [h^{-1}][e]
1	60	0	9 (18)	2	0.17	90	45
2	60	0.1	9 (18)	2	0.31	164	82
3	60	0.3	9 (18)	2	0.37	196	98
4	60	1.0	9 (18)	2	0.41	218	109
5	60[f]	1.0	9 (18)	2	0.42	222	111
6	60[f]	1.0	9 (18)	2	0.40	212	106
7	60[f]	1.0	9 (18)	2	0.38	200	100
8	60	1.0	9 (18)	4	0.86	455	114
9	60	1.0	9 (18)	6	1.29	683	114
10	60	1.0	9 (18)	8	1.76	932	116
11	60	1.0	9 (18)	10	1.92	1016	102
12	60	1.0	9 (18)	12	2.0	1059	88
13	60	1.0	9 (18)	14	2.0	1059	76
14	60	1.0	5 (10)	2	0.20	106	53
15	60	1.0	2 (4)	2	0.12	64	32
16	50	1.0	9 (18)	2	0.21	112	56
17[g]	80	3.0	9 (18)	2	1.16	1840	920

[a] Reaction conditions: 0.3 g catalyst (0.68 $mg_{Ru}\,g^{-1}$), 0.4 g ionic liquid. [b] The total pressure of the system is indicated in parentheses. [c] Molar ratio of the formic acid produced to the ionic liquid added. [d] Turnover number = n(formic acid)$n(Ru)^{-1}$ in one reaction cycle. [e] Turnover frequency = n(formic acid)$n(Ru)^{-1}h^{-1}$. [f] Results of recycling the ionic liquid and catalyst under otherwise similar reaction conditions to entry 4. [g] 0.3 g catalyst, 1.2 g ionic liquid.

In this reaction, different quantities of water was added which led to an increase in turnover frequency in entries 1-4 (Zhang et al., 2009).

EXPERIMENTAL PART

6. AIM AND METHODS IN THE EXPERIMENTAL PART

This Master's thesis work focused primarily on the production of formic acid via one conventional method (commercial scaled) involving the Kemira-Leonard process and two hydrogenation of CO_2 methods (one laboratory scaled and one commercial scaled) involving experimental and BP patented processes respectively. Simulation was used to obtain the material and energy balances and a sustainability assessment questionnaire was used to assess the formic acid production methods considered in this thesis.

6.1 Aim

The aim was to use a Green Chemistry sustainability assessment tool to compare one conventional route and two CO_2 utilization routes in order to find the more sustainable way of producing formic acid (Table 8).

Table 8. Formic acid cases and their reaction routes.

Product	Conventional scale reaction route	CO_2 utilization reaction route
Formic acid	Methyl formate hydrolysis $CH_3OH + CO \rightarrow HCOOCH_3$ (1) $CH_3OOCH + H_2O \rightarrow CH_3OH + HCOOH$ (2)	Hydrogenation of carbon dioxide $CO_2 + H_2 \rightarrow HCOOH$ (3)

The conventional scaled route of formic acid production comprises of multistage synthetic routes involving carbonylation and hydrolysis stages (1 and 2), respectively.

6.2 Methods

The methods used for this study included Aspen Plus simulation software which was used for thermochemical simulations. The existing sustainability assessment questionnaire based on the twelve Green Chemistry principles was further developed and used to assess the overall sustainability performance of the three formic acid routes considered in this thesis work.

6.2.1 Aspen Plus

Aspen Plus can be described as a comprehensive chemical process modeling system created to enable the user to design and improve process plants. It does this by beginning with a process flowsheet followed by the specification of chemical components to be used as well as the operating conditions, it then simulates. The purpose of the simulation is to predict the behavior of the system. Aspen plus is mainly used by chemical organizations, academics and related industry (Aspentech, 2013).

6.2.2 Sustainability assessment questionnaire

Sustainability assessment questionnaire already in existence (Saavalainen, 2012) was further developed based on the twelve principles of Green Chemistry. The Green Chemistry tool was used in this work because it is a qualitative design tool and extended to include all three aspects of sustainability. The questionnaire was designed to help engineers and chemists to consider the sustainability aspects of products and processes in the design phase.

7. MATERIAL AND ENERGY BALANCES

Material and energy balances of formic acid production via the conventional route have been simulated with the Aspen plus software.

7.1 Material and energy balances of the conventional route

The purpose of the material balance is to determine the product flow composition, while the purpose of the energy balance is to determine the total amount of energy used up in the reaction process. Figure 17 shows the flowsheet of the conventional route simulated using Aspen Plus.

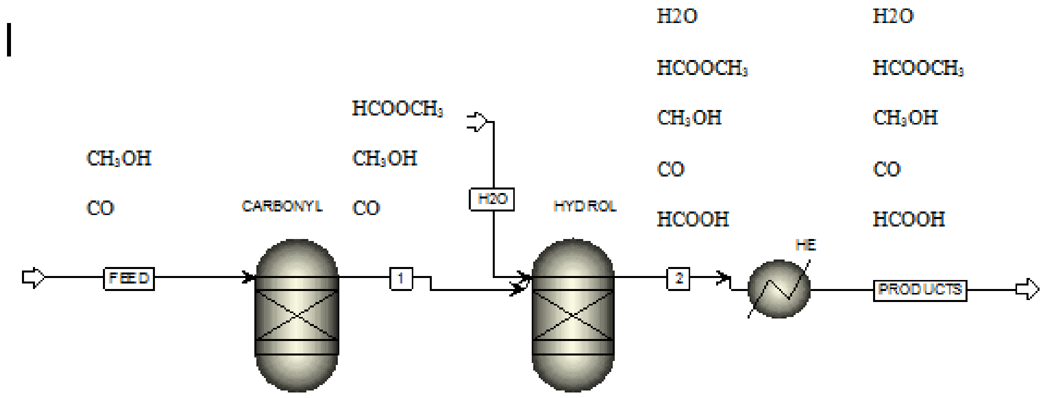


Figure 17. Flowsheet of the conventional route.

The process consists of two equilibrium reactors (Carbonyl and Hydrol, modeled as RGiggs in AspenPlus) and a heat exchanger (HE). Methanol and CO were introduced into the first reactor where carbonylation took place. The process conditions temperature and pressure were found from the literature. Water and the products (flow 1) from the carbonylation stage were introduced into the second reactor and hydrolysis took place. Water, methanol, carbon monoxide, methyl formate and formic acid (flow 2) from the second reactor was passed through the heat exchanger and the final product obtained were formic acid, water, carbon monoxide, methyl formate and methanol. H_2O, CO, CH_3OOCH and CH_3OH were recycled back to the process. Aspen Plus was used to simulate the process conditions and to obtain the material balance and energy consumption of the Conventional route (Table 9 & 10).

Table 9. Process conditions of the conventional route

Process conditions	Feed flow	Flow 1	H_2O	Flow 2	Products
Temperature [ºC]	20.00	80.00	20.00	120.00	20.00
Pressure [bar]	1.00	40.00	1.00	9.00	1.00
Total flow [kmol/hr]	2.00	1.82	2.00	3.00	3.00
Total flow [kg/hr]	60.05	78.07	60.05	78.07	78.07
Total flow [l/min]	459.41	22.25	459.41	181.04	470.07

Table 10. Material balance and energy consumption of the conventional route.

Material balance [kmol]			**Energy consumption [MJ]**		
Feed **Products**					
CH_3OH	1.00	0.20	Reactor (1 & 2)	29.44	19.57
CO	1.00	0.00	Heat exchanger	-80.32	
H_2O	0.00	0.80	Total	-31.31	
$HCOOCH_3$	0.00	0.80	**Per kmol of HCOOH produced**	**-155.37**	
HCOOH	0.00	0.20			

7.2 Material and energy balances of the hydrogenation of CO_2 route (Experimental and BP routes)

Material and energy balances for the formic acid production via the hydrogenation of CO_2 route have been simulated with the Aspen plus software. The purpose of the material balance was to determine the flow composition. The purpose of the energy balance was to determine the total amount of energy used in the process. Figure 18 illustrates the flowsheet of the hydrogenation of CO_2 route simulated using Aspen Plus.

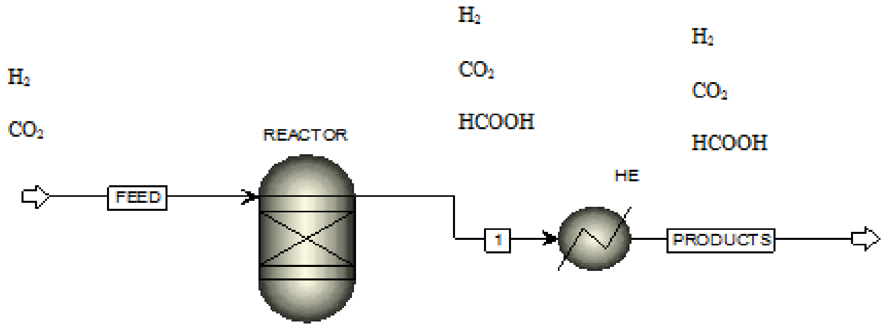


Figure 18. Flowsheet of the hydrogenation of CO_2 route (Experimental and BP routes).

The process consists of an equilibrium reactor (modeled as RGiggs in AspenPlus) and a heat exchanger (HE). In this case only one reactor was required and used. Here CO_2 and H_2 were introduced into the reactor and the flow (1) consisting of hydrogen, carbon dioxide and formic acid was passed through a heat exchanger and formic acid and some amount of hydrogen and carbon dioxide were obtained as the final product. CO_2 and H_2 were recycled back into the process. Aspen Plus was used to simulate the process conditions and to obtain the material balance and energy consumption of both the BP and Experimental hydrogenation of CO_2 routes (Table 11, 12, 13 & 14).

Table 11. Process conditions of Hydrogenation of CO_2 (Experimental route).

Process conditions	**Feed**	**Flow 1**	**Products**
Temperature [ºC]	20.00	80.00	20.00
Pressure [bar]	1.00	135.00	1.00
Total Flow [kmol/hr]	2.00	2.00	2.00
Total Flow [kg/hr]	46.02	46.02	46.02
Total Flow [l/min]	801.82	7.25	801.82

Table 12. Process conditions of Hydrogenation of CO_2 (BP route).

Process conditions	**Feed**	**Flow 1**	**Products**
Temperature [ºC]	20.00	70.00	20.00
Pressure [bar]	60.00	1.00	1.00
Total Flow [kmol/hr]	2.00	2.00	2.00
Total Flow [kg/hr]	46.03	46.03	46.03
Total Flow [l/min]	801.82	15.85	801.82

The initial temperature and pressure used in this process were gotten from the theoretical part of this work.

Table 13. Material balance and energy consumption in the hydrogenation of CO_2 (Experimental route).

Material balance [kmol]			**Energy consumption [MJ]**	
Component	**Feed**	**Products**	Reactor	6.83
CO_2	1.00	1.00	Heat exchanger	-6.17
H_2	1.00	1.00	Total	$6.23 * 10^{-5}$
Formic acid	0.00	$4.15 * 10^{-6}$	**Per kmol of HCOOH produced**	15.00

Table 14. Material balance and energy consumption in the Hydrogenation of CO_2 (BP route).

Material balance [kmol]			**Energy consumption [MJ]**	
Component	**Feed**	**Products**	Reactor	3.35
CO_2	1.00	1.00	Heat exchanger	-3.35
H_2	1.00	1.00	Total	$2.41 * 10^{-5}$
Formic acid	0.00	$1.61 * 10^{-6}$	**Per kmol of HCOOH produced**	15.02

Comparing Tables 10, 13 and 14, it can be seen that while the conventional route releases energy (exothermic process), both CO_2 routes consume approximately the same amount of energy (endothermic process).

8. SUSTAINABILITY ASSESSMENT

The sustainability assessments for three formic acid production processes are shown in Table 15, some facts and assumptions have been made on each process.

Table 15. Sustainability assessment facts and assumption for the conventional and hydrogenation of carbon dioxide routes for the production of formic acid.

(based on: Ullmann 2011, Kirk-Othmer 1993, Hao et al. 2011 , Zhang et al. 2009, Hua, T.Q & Ahluwalia R.K. 2012 , Wang et al. 2011, The Linde Group 2012, Methanex Corporation 2011, Air Products 2012)

Features	**Case A: Conventional route**	**Case B: Experimental route**	**Case C: BP route**
Raw Materials	CH_3OH and CO	H_2 and CO_2	H_2 and CO_2
Reaction Route	$CH_3OH+CO \rightarrow HCOOCH_3$ $CH_3OOCH+H_2O \rightarrow CH_3OH+HCOOH$	$CO_2 + H_2 \rightarrow HCOOH$	$CO_2 + H_2 \rightarrow HCOOH$
Main Products	HCOOH	HCOOH	HCOOH
Side Products	CH_3OH was formed and recycled back to the process	H_2 and CO_2 was formed and recycled back to the process	The reaction yielded along with the formic acid, H_2 and CO_2 which was recycled back to the process
Waste/ Emission	Unreacted methyl formate and inactivated catalyst	No emissions/waste	No emissions/waste
Atom Economy (theoretical)	59%	100%	100%
Yield	High yield, exact amount not specified	5.17% (calculated based on Hao et al., 2011)	75%
Process Conditions	Temperature=80 ^{O}C Pressure= 4 MPa	Temperature=80 ^{O}C Pressure= 13.5 MPa	Reactor Temperature=70 ^{O}C Reactor Pressure= 6 MPa
Energy Consumption (calculated based on thermodynamics)	-155.37MJ per kmol of HCOOH	15.00 MJ per kmol of HCOOH	15.02 MJ per kmol of HCOOH
Solvents and Auxiliary	Water was used in the process	15 mL of ethanol was used as a	Tetraethylene glycol was used as a solvent

Chemicals		solvent, water and triethylamine	(the amount used was not specified), water and triethylamine. 1-n-butylimidazole was used as a base
Health and Safety Issues	CO is an extremely flammable gas, may be fatal if inhaled, contact may cause burns or frostbite. CH_3OH is toxic by inhalation, in contact with skin and if swallowed, a highly flammable liquid and vapor. Methyl formate is toxic by inhalation, in contact with skin and if swallowed, and an irritant to the eyes,	H_2 is extremely flammable, can cause asphyxiation (suffocation). CO_2 in high concentrations is toxic to humans. Triethylamine is toxic by inhalation, in contact with skin and if swallowed, flammable liquid, corrosive. Ethanol is a flammable liquid, toxic by ingestion, inhalation or skin absorption	H_2 is extremely flammable, can cause asphyxiation (suffocation). Triethylamine is toxic by inhalation, in contact with skin and if swallowed, flammable liquid, corrosive. CO_2 in high concentrations is toxic to humans. 1-n-buthylimidazole is toxic by ingestion, inhalation or skin absorption, corrosive, Combustible material. Tetraethylene Glycol is toxic to human skin, has very low flammability, and its non-corrosive.
Environmental Issues	Methyl formate is a highly volatile chemical. CH_3OH is dangerous to aquatic life in high concentrations If stored at a particular high temperature and pressure, HCOOH can be decomposed to CO which is a toxic gas	CO_2 is a major greenhouse gas. If stored at a particular high temperature and pressure, HCOOH can be decomposed to CO which is a toxic gas. Ethanol is not toxic to the environment and it is biodegradable	CO_2 is a major greenhouse gas. If stored at a particular high temperature and pressure, HCOOH can be decomposed to CO which is a toxic gas. Tetraethylene glycol is environmentally friendly
Supply Chain	Methanex (located in North America, Latin America, Europe, the Caribbean, the Middle East and	Linde (has its headquarters in North America) is one of the world's largest suppliers of CO_2.	Linde (has its headquarters in North America) is one of the world's largest suppliers of CO_2.

	throughout the Asia Pacific region) is the world's largest supplier of methanol to international markets. Air products (has its headquarters in the United States) is one of the world's largest suppliers of CO	Air products are one of the world's largest suppliers of hydrogen. BASF is the world's largest producer of formic acid with plants located in Ludwigshafen, Germany, and Nanjing, China.	Air products are one of the world's largest suppliers of hydrogen. BASF is the world's largest producer of formic acid with plants located in Ludwigshafen, Germany, and Nanjing, China.
Alternative Options	Hydrogenation of Carbon dioxide, Oxidation of hydrocarbons, hydrolysis of formide and by-product of Acetic acid production	Methyl formate hydrolysis, Oxidation of hydrocarbons, hydrolysis of formide and by-product of Acetic acid production	Methyl Formate hydrolysis, Oxidation of hydrocarbons, hydrolysis of formide and by-product of Acetic acid production
Catalyst Used	Additive-containing alkoxides-sodium methoxide(CH_3ONa)	Ruthenium hydroxide heterogeneous catalyst Ru(OH)	Ruthenium complex transition metal catalyst e.g $RuCl_2(PPh_3)_2$, $Ru(PPh_3)_2C1_2$(4-vinyl-py)$_2$ and $Ru(PPh_3)_2C1_2$(4-Me-py)$_2$, (R)-C3-tunePhos-ruthenium complex. heterogeneous catalyst
Treatment/ Disposal of Waste Cost	Waste gas and deactivated catalyst were purged out of the process	None, there was no waste to be treated or disposed of	None, there was no waste to be treated or disposed of
Product Selectivity	High selectivity of the alkoxides catalyst to the production of HCOOH	High selectivity of ruthenium hydroxide catalyst to the production of HCOOH	Moderate selectivity
Product Quality	Formic acid of 98% purity was obtained as distillate	Formic acid of high purity was obtained from this process	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	Formic acid is readily acceptable as it has wide range of uses both in	Formic acid is readily acceptable as it has wide range of uses both in

	agricultural, industrial and household level. CO and CH_3OH has safety, health and environmental issues hence the raw materials used to produce HCOOH is not readily acceptable	agricultural, industrial and household level. Ethanol and triethylamine has health and safety issues. Hydrogen has safety issues	agricultural, industrial and household level. 1-n-buthylimidazole and triethylamine has safety and health issues. Hydrogen has safety issues
Chemicals registerd in REACH	CO and CH_3OH	CO_2, H_2, triethylamine, ethanol	CO_2, H_2, triethylamine

Atom economy was calculated based on the equation of reaction of each case. Energy demand was simulated using Aspen Plus and the simulations were done using the process conditions gotten from the literature. It was assumed that all the feed substances were obtained from a renewable source.

8.1 Sustainability Assessment Questionnaire

In this questionnaire, scores of -1, 0, and 1 were allocated to each question based on the assumption that a chemical product or a production process either has a positive, zero or a negative effect on the environment, the economy and the people. Some of the questions that were not applicable (NA) or had simultaneous negative and positive points (± 1) were given the score of zero (0) as well. Case A represents the conventional methyl formate hydrolysis process; Case B represents hydrogenation of CO_2 using a ruthenium hydroxide catalyst (the experimental route); and Case C represents the BP patented process of the Hydrogenation of CO_2 (BP route).

Table 16. Sustainability Assessment Questionnaire.

Green Chemistry Principle 1	**CASE A**	**CASE B**	**CASE C**	**Waste Prevention**
Environmental				
Does the process produce waste?	-1	1	1	Methyl formate hydrolysis (Case A) produces as waste deactivated catalyst. Case B and C do not produce waste
Is the waste	-1	0	0	The unreacted catalyst purged out from

hazardous?				case A is a hazardous waste. Not applicable to Case B and C
Does the process produce harmful emissions?	-1	1	1	Purge gas from case A contains harmful emissions. Case B and C do not produce harmful emissions
Does your process produce wastewater?	-1	1	1	Case A produces wastewater which is distilled and recycled. Case B and C do not produce wastewater
Does the wastewater need special treatment?	-1	0	0	In case A, the wastewater produced is purified and recycled thus requires special treatment. Not applicable to Case B and C
Can the wastewater be re-used?	1	0	0	Yes, wastewater is reused in case A. Not applicable to Case B and C
Does the process produce by-products and are these by-products utilized	0	0	0	None of the cases produces by-products, but Case A, B and C have intermediates.
Are there in the supply chain of the raw materials significant amounts of waste produced?	0	-1	-1	In case A, production of CH_3OH and CO do not lead to wastes. In case B and C, H_2 and CO_2 do not produce waste, but triethylamine production releases emissions and effluents
Social				
Are there any health and safety issues related to the harmful nature or amount of waste/ emissions?	-1	1	1	Emissions in case A contain some CO and unreacted methyl formate which are harmful. In Case B and C there are no harmful emissions or waste
Economic				
Is there a significant cost related to the treatment and disposal of the waste	-1	0	0	In case A, the catalysts waste needs to be treated and this would incur costs. Not applicable to case B and C
Can profit be derived from waste or by-products	0	0	0	Case A, B and C have intermediates and no by- products.
Green Chemistry Principle 2	**CASE A**	**CASE B**	**CASE C**	**Atom economy**
Economic				
Does the synthetic process have high yield	1	-1	1	Cases A and C have high yields, In Case B the yield is very low
What is the selectivity to the desired product	1	1	0	Cases A and B have high selectivities, Case C has moderate selectivity
What is the atom economy of possible reaction routes (< 60=-1/ >90=1)	-1	1	1	In Case A the theoretical atom economy is 59%, In Case B and C the theoretical atom economy is 100%
Green Chemistry Principle 3	**CASE A**	**CASE B**	**CASE C**	**Design the synthesis less hazardous**

Environmental				
Does the process use or generate materials that are potentially harmful?	-1	-1	-1	In case A, CO and CH_3OH are both harmful. 1-n-butylimidazole (Case C) is harmful. Triethylamine (Case B & Case C) is toxic
Social				
Are there any health and safety issues related to the harmful nature of chemicals used or generated in the process?	-1	-1	-1	CH_3OH (Case A), 1-n-butylimidazole (Case C), Triethylamine (Case B & Case C), ethanol (Case B) and tetraethylene glycol (Case C) have health and safety issues
Green Chemistry Principle 4	**CASE A**	**CASE B**	**CASE C**	**Design safer chemicals and products**
Environmental				
Does the use of product lead to harmful emissions?	0	0	0	HCOOH decomposes to CO when left for a long time but it being harmful is volume dependant especially when high volumes are involved.
Do the products produced contain harmful or hazardous materials (take into notice also the side products)?	-1	-1	-1	HCOOH is toxic and corrosive in high concentrations
Economic				
Is there any significant cost related to the harmful nature of the chemicals in the product?	1	1	1	No significant cost
Social				
Are there any health and safety issues related to harmful nature of the product?	-1	-1	-1	Yes, formic acid is toxic by inhalation and in contact to the skin
Green Chemistry Principle 5	**CASE A**	**CASE B**	**CASE C**	**Considerations of safer solvents and reaction conditions in the design phase**
Environmental				
Are the feedstock and/or other auxiliary chemicals that are used in processes considered toxic or hazardous?	-1	-1	-1	H_2O is used as an auxiliary chemical in Case A and is non toxic, Ethanol as a solvent in Case B and is slightly toxic, Tetraethylene Glycol as a solvent , and 1-n butylimidazole as a base in Case C and are both slightly toxic to humans. Methanol (Case A) is toxic to humans
Do the used solvents generate harmful emissions during	1	1	1	No in all three cases

processing?				
Social				
Are there any health and safety issues related to the harmful nature of solvents, separation agents, or other auxiliary chemicals?	1	-1	-1	Yes, ethanol (Case B) and 1-n-butylimidazole (Case C) has safety and health issues. Water (Case A) has no issue
Does the quality of solvents necessitate the use of protective gear?	1	-1	-1	Ethanol and tetraethylene glycol (Case B) require it
Economic				
Cost of chemicals	-1	1	1	Case A cost 35.21 €/kmol, Case B and Case C cost 13.99 €/kmol
Green Chemistry Principle 6	**CASE A**	**CASE B**	**CASE C**	**Energy efficiency of the process**
Environmental				
Do the processes require large deviation from ambient temperature?	1	1	1	No, the temperature in all three cases are only slightly higher than the ambient temperature
Is the process energy intensive?	1	-1	-1	Case B and Case C consume more energy than Case A
Do the processes require large deviation from ambient pressure?	-1	-1	-1	Yes, the pressure in all three cases are much higher than the ambient pressure
Economic				
Does the energy consumption add substantially to the cost	1	-1	-1	The amount of energy consumed in Cases B and C leads to increased cost, in Case B no, In Case A the cost is reasonable
Green Chemistry Principle 7	**CASE A**	**CASE B**	**CASE C**	**Utilize renewable (or benign?) feedstock**
Environmental				
Are the materials used renewable or non-renewable? (mixed carbon source = 0)				
Methyl Formate Hydrolysis (-1/0/1)				
CH_3OH	-1			CH_3OH is produced from non-renewable sources
CO	-1			CO is gotten from non-renewable source
Hydrogenation of				

CO_2				
H_2		1	1	H_2 is renewable
CO_2		1	1	CO_2 is renewable
Triethylamine		1	1	Triethylamine is produced by reacting ammonia with ethanol (ethanol can be produced from corn hence renewable, ammonia can be produced from renewables)
Are these materials readily available?	1	1	1	All the raw materials used as feedstock in all cases are readily available
Could these materials be derived from waste streams	1		0	In Case A, it is possible to derive CO from the purge gas
Economic				
Does the use of renewables increase cost?	1	1	1	Use of renewables leads to a reduction in cost
Green Chemistry Principle 8	**CASE A**	**CASE B**	**CASE C**	**To design a chemical process to avoid unnecessary derivatization**
Environmental				
Are there multistage synthetic routes involving blocking and/or protecting groups in the process?	-1	1	-1	Methyl formate hydrolysis (Case A) has a two stage synthetic route, BP hydrogenation of CO_2 (Case C) has a four stage synthetic route
Do these stages lead to the generation of additional quantities of unwanted by-products and waste?	1	0	1	No in Cases A and B because the stages do not lead to unwanted by-products. Not applicable to case B
Green Chemistry Principle 9	**CASE A**	**CASE B**	**CASE C**	**Considerations of catalyst usage in the design phase**
Environmental				
Does the process use catalysts?	1	1	1	All three cases makes use of catalysts
Does the process make use of noble/rare earth metal catalyst	1	-1	-1	Ruthenium hydroxide catalyst in Case B and ruthenium complex catalyst in Case C are noble metal catalysts. Case A do not make use of such catalyst
Does the catalyst have a high activity and selectivity	0	1	1	Catalyst used in Case A has high activity only, In Case B the ruthenium hydroxide catalyst used has a high activity and selectivity, Case C has high selectivity and activity
Social				
Is there any health, safety or environmental issues related to the used catalytic materials?	-1	-1	1	CH_3ONa used in Case A is toxic and corrosive, Ruthenium on alumina in Case B is toxic to the skin, Ruthenium complex in Case C has negligible health, safety and environmental effects

Green Chemistry Principle 10	**CASE A**	**CASE B**	**CASE C**	**How to design chemicals and products to degrade after use**
Environmental				
Is the product degradable or non degradable?	1	1	1	Formic acid is a degradable chemical
Does the product have a high environmental impact at the-end-of life (take into notice also the side products)?	1	1	-1	Formic acid and methanol decompose easily in the environment. 1-n-butylimidazole is harmful to ground water, water course and sewage system
Green Chemistry Principle 11	**CASE A**	**CASE B**	**CASE C**	**Process monitoring and analysis in the design phase**
Environmental				
Is the process especially sensitive to changes in process condition	-1	-1	-1	In Case A, the reaction rate can be raised by an increase in temperature, CO partial pressure and the catalyst concentration. In Case B optimal yield of formic acid was observed at temperature of 80^{O}C, lower temperature leads to lower yields. In Case C, changes in process conditions directly affect the HCOOH yield.
Social				
Are there any health and safety issues related to the changes in process conditions	-1	-1	-1	An increase in pressure in the reactor could lead to explosion in Cases A, B and C.
Green Chemistry Principle 12	**CASE A**	**CASE B**	**CASE C**	**How the potential for accidents could be minimized**
Environmental				
Are there hazards related to the designed process (synthetic and formulation activities, involved operations or reaction conditions)?	-1	1	-1	Yes, CO is hazardous if a leakage occurs, the reaction pressures are far above the ambient pressure for Cases A and C.
Social				
Do the safety procedures lead to improved quality of working conditions?	1	1	1	Yes in all three cases, according to the material safety data sheet
Is there a need for advanced training related to the health and safety issues on used chemicals	1	1	1	CO is an extremely poisonous gas, H_2 is highly flammable, therefore advanced training is needed to equip people with knowledge on how to prevent the harmful effect of chemicals

This questionnaire comprises of a total of 41 questions. Environmental part has 32 questions; social and economic parts have 9 questions each. Table 17 shows the composite score sheet of the sustainability assessment questionnaire. It is the sum of all principles of the conventional, experimental and BP routes under the three sustainability aspect (environmental, social and economic).

Table 17. Composite score sheet.

Green Chemistry	**CONVENTIONAL**			**EXPERIMENTAL**			**BP**		
	Env	Soc	Econ	Env	Soc	Econ	Env	Soc	Econ
Principle 1	-4	-1	-1	2	1	0	2	1	0
Principle 2	-	-	1	-	-	1	-	-	2
Principle 3	-1	-1	-	-1	-1	-	-1	-1	-
Principle 4	-1	-1	1	-1	-1	1	-1	-1	1
Principle 5	0	2	-1	0	-2	1	0	-2	1
Principle 6	1	-	1	-1	-	-1	-1	-	-1
Principle 7	4	-	1	4	-	1	4	-	1
Principle 8	0	-	-	1	-	-	0	-	-
Principle 9	2	-1	-	1	-1	-	1	1	-
Principle 10	2	-	-	2	-	-	0	-	-
Principle 11	-1	-1	-	-1	-1	-	-1	-1	-
Principle 12	-1	2	-	1	2	-	-1	2	-
TOTAL SCORE	**-3**	**-1**	**2**	**7**	**-3**	**3**	**2**	**-1**	**4**

Figure 19 illustrates the composite score chart of the sustainability assessment questionnaire based on the composite score sheet results.

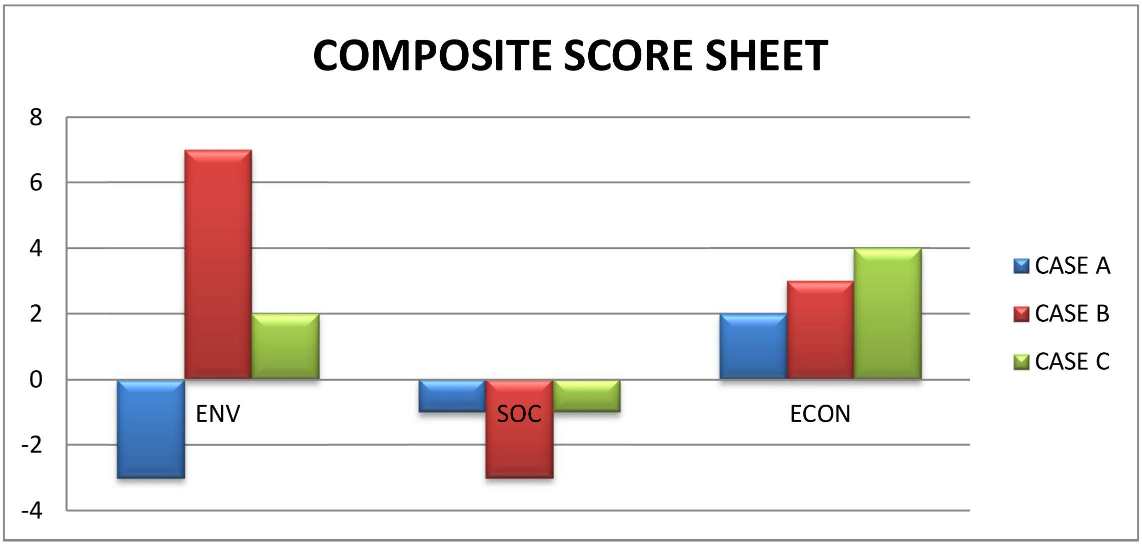
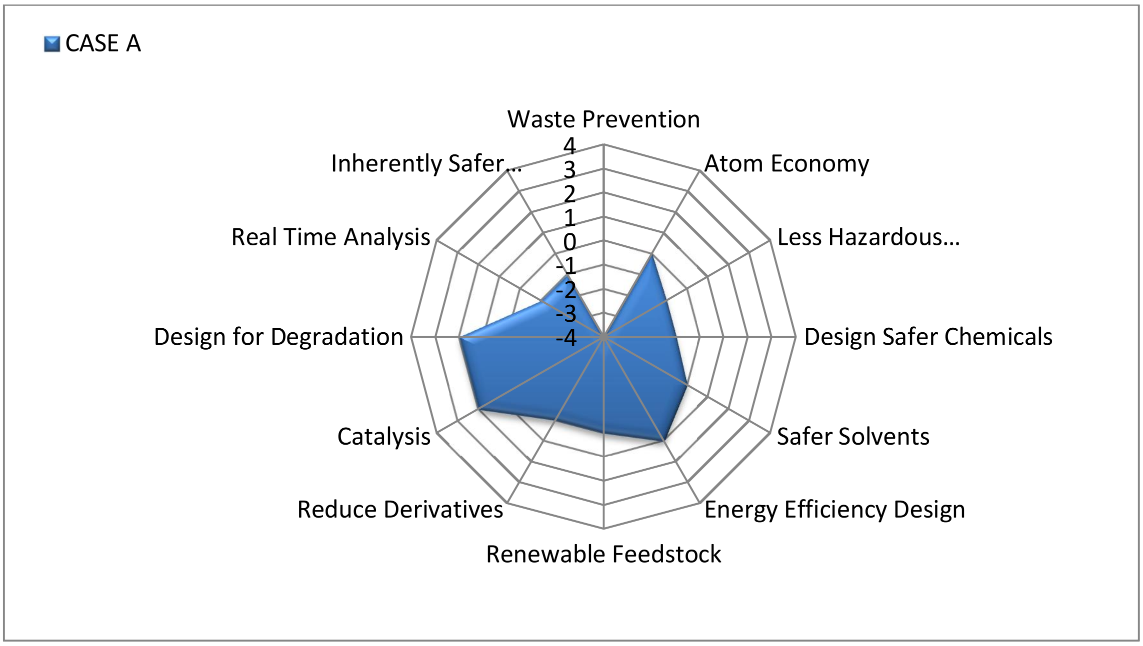
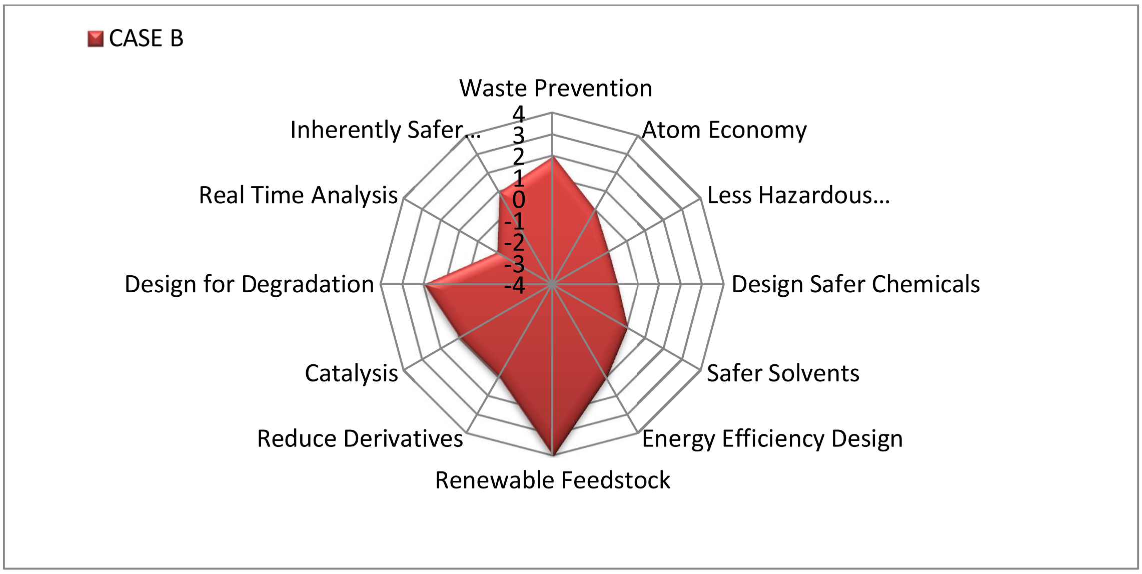


Figure 19. Composite score chart.

From the composite score sheet of the sustainability assessment questionnaire, the conventional route had a composite score of -2 which was the lowest of the three cases; The experimental route had a composite score of 7 which was the highest of all three cases while the BP route had a composite score of 5 which was the second highest of the three cases. In the composite score chart, it can be seen that in the environmental part, the conventional route had a value of (-3) which was the lowest of all cases, the experimental route had a positive value of (7) which was the highest of all the cases, while BP route score was (2), the second highest score. In the social part of the chart, the conventional, experimental and BP routes all had negative values of (-1, -3 and -1) respectively. In the economic part of the chart, the conventional route had a score of (2), the experimental and BP routes both had positive scores of (3 and 4) respectively; the BP route being the highest of the three. Figures 20-22 depict spider charts showing individual sustainability aspect of each case with respect to the twelve principles of green chemistry and based on the composite score sheet results.





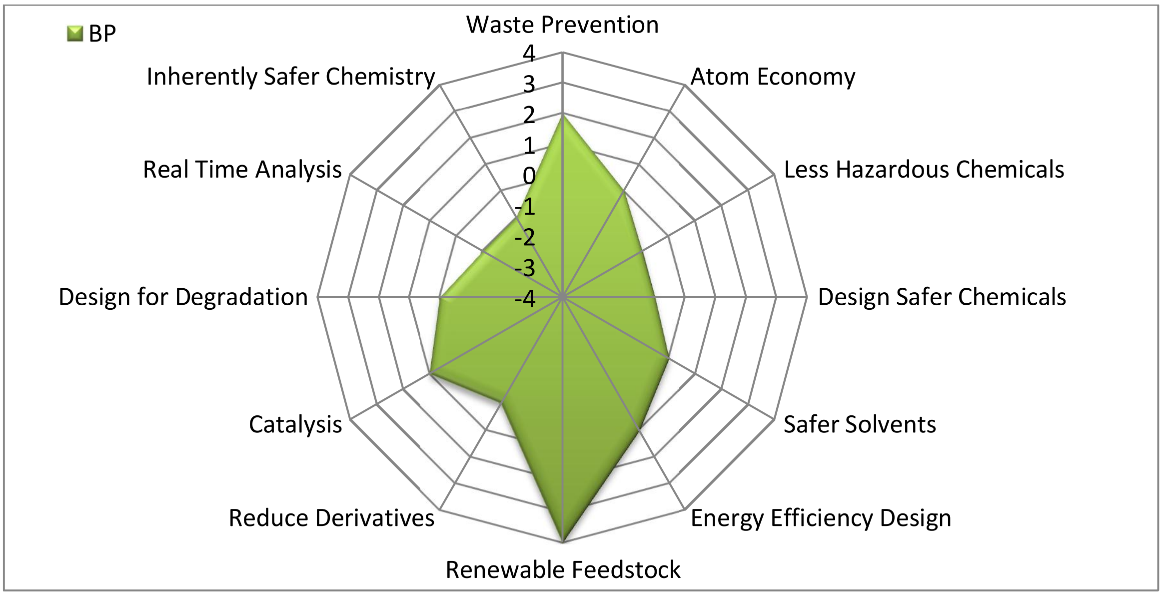


Figure 20. Environmental assessment charts.

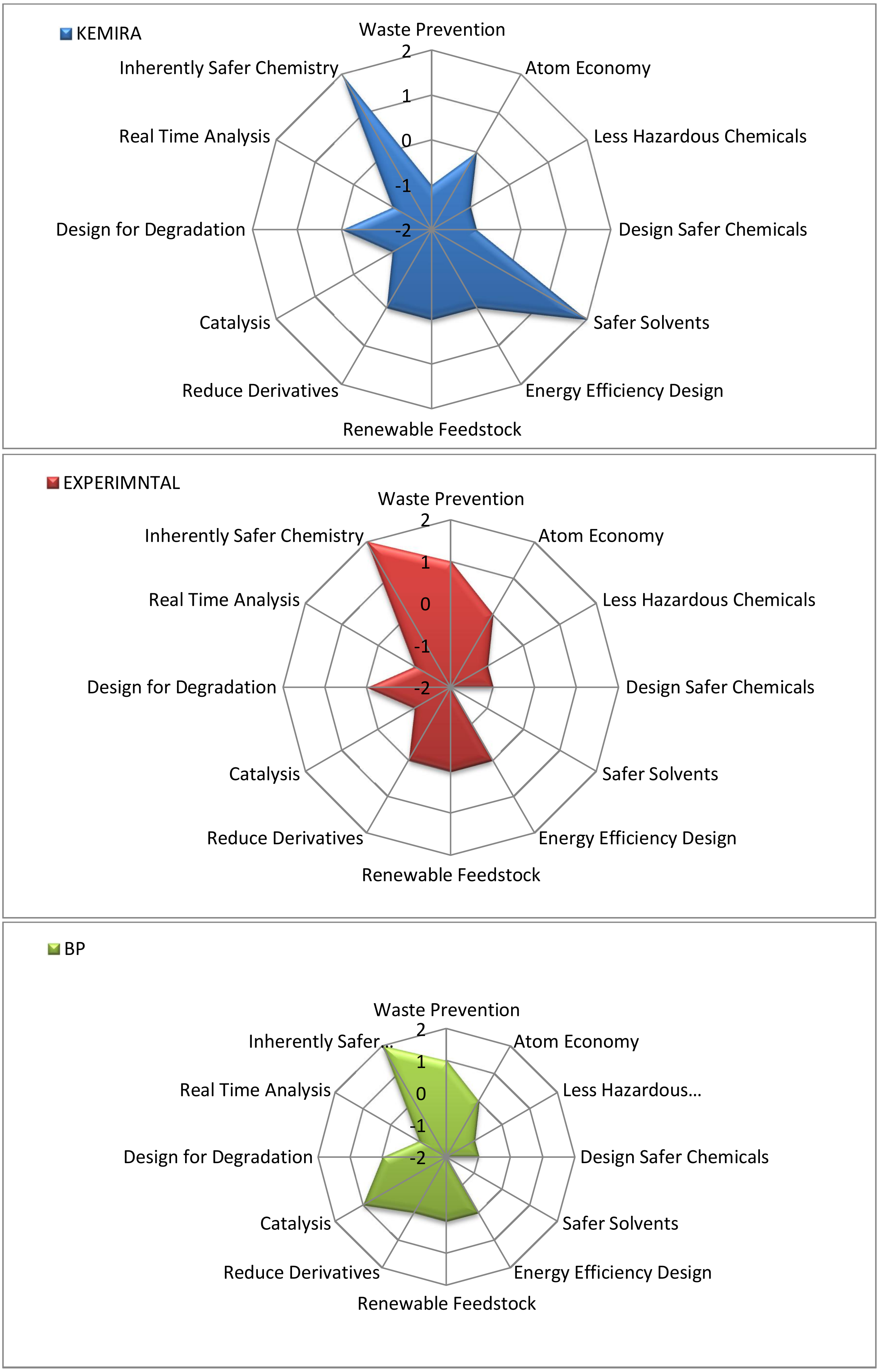


Figure 21. Social assessment charts.

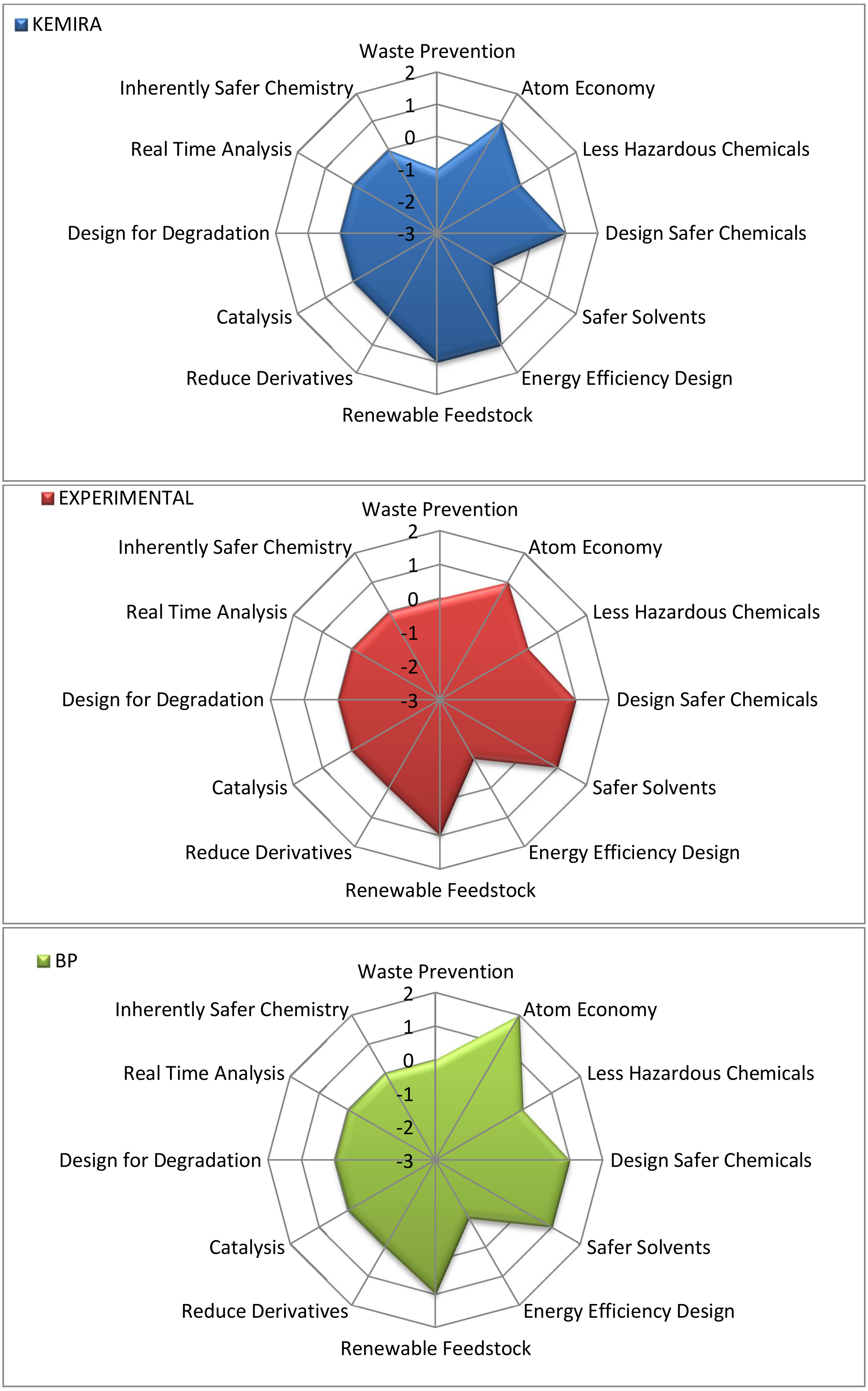


Figure 22. Economic assessment charts.

The spider charts were used in this study for the purpose of comparison. The strengths and weaknesses of the twelve Green Chemistry principles on each formic acid production route with reference to each aspect of sustainability were compared. The spider charts were grouped under environmental, social and economic parts and each of these parts consisted of the three formic acid production routes (conventional, experimental and BP).

In the environmental assessments charts, a scale of -4 to 4 was used. Comparing the environmental assessment charts; in the waste prevention principle of the chart, the experimental route and the BP route were the strongest and they were on exactly the same level while there was a sharp decline in the conventional route which was the weakest of the three routes, the reason for this is because the conventional route generated much more waste and emissions than the others. Looking at the atom economy principle of the chart, the three routes the conventional, experimental and BP routes were on the same level and the reason being that there were no atom economy questions covered under the environmental section of the sustainability assessment questionnaire. In the less hazardous chemicals principle, the three routes were on the same level and all of them were weak with regards to this principle, the reason being that all three routes had some amount of harmful substances contained in them. In the design of the safer chemicals principle, the three routes were on the same level and all of them weak with regards to this principle and the reason was because their resulting product (formic acid) is toxic when used in large concentrations. In the safer solvents principle, the three routes were on the same level and all of them were on the borderline between strong and weak with regards to this principle, the reason for this was because the negative and positive scores obtained in the questionnaire neutralized themselves out. In the energy efficiency design principle, the three routes were all on the same level and slightly strong. In the renewable feedstock design principle, the conventional route was neutral because it is on the borderline between strong and weak routes while the BP and experimental routes were strong and on the same level with regards to this principle, the reason being that the feed sources in the BP and experimental routes were obtained from renewable sources while that of the conventional route was obtained from non renewable sources. In the reduce derivative principle, the conventional route and BP routes were both on the same level and neutral because it is on the borderline between strong and weak, on the other hand the experimental route had a slight variation from them and was strong, the reason being that the conventional and BP routes both on commercial scale had multiple synthetic routes, while the experimental route was laboratory scaled and had no multiple synthetic routes. In the catalysis principle, all three routes were strong but the conventional route was slightly stronger than the experimental and BP routes which was both on the same level in terms of strength, the reason for this is that the experimental and BP route made use of noble metal catalysts. In the design for degradation principle, the conventional and experimental routes were the strongest and on the same level whereas the BP route was neutral, the reason for this is that one of the substances used in the BP route is harmful to ground water. In the real time analysis principle the chart shows that all three routes were weak and on the same level, the reason being that all three routes were sensitive to changes in process conditions. In the inherently safer chemistry principle, the conventional and BP routes were weak and on the same level while the experimental route had a slight variation from the conventional and BP routes and was strong, the reason for this is that accident can occur during the production process and harmful substances can escape.

In the social assessments charts, a scale of -2 to 2 was used. Comparing the social assessment charts. In the waste prevention principle of the chart, the experimental and BP routes were the strongest and were on exactly the same level while there was a slight decrease in the conventional route hence the weakest of the three routes, the reason for this is because the conventional route’s process generated waste and emissions that are harmful to the human health while the others do not. Looking at the atom economy principle of the chart, the three routes were on the same level and the reason being that there was no atom economy questions covered under the social section of the sustainability assessment questionnaire. In the less hazardous chemicals principle, the three routes were on the same level and all of them weak with regards to this principle, the reason being that all three routes had some amount of harmful substances contained or generated by them that were dangerous to the health and safety of people. In the design of the safer chemicals principle, the three routes were on the same level and all of them weak with regards to this principle and the reason was because their resulting product was toxic in large concentrations and is dangerous to the health and safety of people. In the safer solvents principle, the conventional route was the strongest whereas the experimental and BP routes were on the same level and the weakest, the reason for this was that the conventional route made use of no harmful solvent or auxiliary chemicals while the experimental and BP routes made use of these. In the energy efficiency design principle, renewable feedstock design principle and reduce derivative principle, all three routes were all on the same level because they contained no questions under the social section of the sustainability assessment questionnaire. In the catalysis principle, the conventional route was strong while the experimental and BP routes were weak, the reason for this was because the catalyst used in the BP and experimental routes are toxic to humans.

In the design for the degradation principle, the three routes were on the same level because no question was asked relating to the social aspect of sustainability. In the real time analysis principle the chart showed that all three routes were weak and on the same level, the reason being that an increased pressure in the reactor could lead to explosion which could be detrimental to the health and safety of people. In the inherently safer chemistry principle, the three routes were all strong and on the same level, the main reason being that safety procedures applied in these routes lead to improved quality of working conditions.

In the economic assessments charts, a scale of -3 to 2 was used. In the waste prevention principle of the chart, the conventional route was the weakest and there was a very slight increase in the experimental and BP routes both on the same level and on the borderline between the strongest and the weakest. The reason for this is because in the conventional route, the catalyst waste would have to be treated and this would incur costs. Looking at the atom economy principle of the chart, the three routes were all strong but the BP route was slightly stronger than the conventional and experimental routes which were on the same level and equal in strength, the reason for this was because of the differences in their yield, selectivity and atom economy. In the less hazardous chemicals principle, the conventional, experimental and BP routes were all on the same level because no question was asked relating to the social aspect of sustainability. In the design of safer chemicals principle, all three routes were on the same level and all of them strong with regards to this principle and the reason was because there was no significant cost related to the harmful nature of the chemicals in formic acid. In the safer solvents principle, the conventional route was weak, while there was a slight increase in the experimental and BP route were on the same level strong with regards to this principle, the reason for this was because the cost of chemicals used in the conventional route was much higher in comparison to the experimental and BP routes. In the energy efficiency design principle, the conventional route was the strongest while the experimental and BP routes were the weakest, both the experimental and BP routes were on the same level on the assessment chart, the reason being that the amount of energy consumed in these routes lead to an increased cost. In the renewable feedstock design principle, all three routes were strong and on the same level with regards to this principle, the reason for this is because all three routes made use of renewables which lead to a reduction in cost.

9. DISCUSSION

From the results of the sustainability assessment questionnaire, charts were plotted in the form of bar charts and spider charts to visually represent in a clear way the results of the questionnaire and for easy interpretation of data. For the sake of simplicity and comprehension Case A will be referred to as the conventional route, Case B will be referred to as the experimental route and Case C as the BP route.

From the composite score chart, the environmental section of the chart, the conventional route is not beneficial to the environment and the reason for this is mainly because of the waste and emissions generated by the process and the harmful nature of the feed used. Environmental aspect of sustainability entails safeguarding the environment from harmful practices and the prevention of waste. The conventional route does not sufficiently satisfy this; hence it is environmentally less sustainable than the other routes. In the hydrogenation of CO_2 routes (BP and experimental) the charts reveals that both contributes to the environment positively mainly because they make use of CO_2 which reduces atmospheric loadings of the gas, also a significant less amount of waste and emissions is generated. This makes the hydrogenation of CO_2 route an environmentally sustainable way of producing formic acid. The major difference between the two CO_2 utilization routes is that the BP route is done in a commercial scale while the experimental route is done in a laboratory scale, also the solvents, auxiliary chemicals and catalysts used are different, the yield also was different and these had effects on the result chart. The social aspect of sustainability entails access to occupational health and safety and also a good quality of life for the population.

From the composite score charts, the resulting social section indicated that both the conventional route and the CO_2 utilization route of formic acid production are socially unsustainable and a major reason for this are the harmful nature of solvents, auxiliary chemicals and the process conditions used in them. Economical aspect of sustainability entails maintaining or increasing production trends while maximizing profits. The economic section of the composite score chart shows that the conventional route has a slight benefit on the economy whereas the effect of the experimental and BP routes on the economy was more positive than that of the conventional route, the BP route being better than the experimental route. The reasons for this are; cost of raw materials/feed, cost of treatment and disposal of waste, energy requirement and atom economy. Judging by the chart, it can be said that the CO_2 utilization route is more economically viable than the conventional route. Based on this analysis, hydrogenation of CO_2 is a more sustainable way to produce formic acid than the conventional process. The overall best route in terms of the three sustainability aspects is the experimental route followed by the BP route and the worst route is the conventional route.

Analyzing the spider charts; the overall best route under the environmental assessment charts is the experimental route followed by the BP route and the conventional route. This means that the experimental route's substances and the production process would provide the most protection to the environment closely followed by the BP route's substances and the production process which will also protect the environment but not as strongly as the experimental route. The conventional route's substances and production process has a more negative effect on the environment than the BP and experimental routes. The overall best route under the social assessment charts is the conventional and BP routes which were exactly equal and least by the experimental route which was the worst. This means that in the conventional and BP routes the chemicals and production process will provide the most protection to the health and safety of the people while it is the opposite for the experimental route. The substances and the production process used in the experimental route pose the greatest threat and risks to the health and safety of humans. The overall best route under the economic assessment charts is the BP route followed by the experimental route and least by the conventional route which was the worst. This means that the BP route's substances and the production process would give the most economic gain closely followed by the experimental route's substances and the production process which will also give economic gain but slightly lower than that of the BP route. The conventional route's substances and production process have slight economic benefits.

It should be taken into account that this sustainability assessment questionnaire is a raw assessment questionnaire and still in its development stage so to an extent the graphical illustrations (charts) and composite score results do not form any definite pattern. A major problem in these assessment charts stems from the fact that there were not enough questions asked in the questionnaire and these have affected the results. A wider variety of questions that adequately represent the sustainability requirement of the industry would have affected the result in a different way. Another problem encountered was that there was an unequal distribution of questions asked under the three aspects of sustainability, environmental aspects which had a total number of 32 questions had the most questions asked followed by the social aspect and the economic aspect which both had a total number 9 questions, and this too affected the results. Another problem was that in some principles some sustainability aspects were not covered, these principles include; atom economy, design the synthesis to be less hazardous, energy efficiency, utilization of renewable feedstock, reduction of derivatives, catalysis, design for degradation, real time analysis and inherently safer chemistry principles. The questionnaire also had some conflicting issues regarding how to score the qualitative questions in them, for instance in the second question asked under this principle 2 regarding high selectivity and moderate selectivity both are relative terms and hence difficult to quantify using the numbers (-1 and 1). This has particularly affected the social section of the composite score chart. In the design less hazardous principle it is very difficult in this case to quantify the exact level of hazards of the chemicals and the process because some chemicals are more hazardous than others. Also in the atom economy principle section of the questionnaire, all the questions covered under this principle had quantitative data which were difficult to quantify using the numbers (-1 and 1) hence the scoring system used here is not feasible. Another problem of the sustainability assessment questionnaire is that the Green Chemistry tool was designed to focus mainly on the toxicity and the hazardous nature of chemicals and processes. Because of this most of the questions were centered on toxicity and its effects on humans and the environment. Another important problem that affected the results was that there was no information as regards to the actual atom economy of the processes; the atom economy was calculated based only on the reaction equation. Also the yield of the conventional process was not known and that of the BP route and the experimental routes was based on assumptions. This also has affected the results of the questionnaire and also the charts. In Table 17 all the various benefits and drawbacks of the three formic acid routes are highlighted and organized based on the three sustainability aspects i.e. economic, social and environmental.

Table 17. Benefit and drawbacks of the conventional, experimental and BP routes.

FORMIC ACID ROUTES	**BENEFITS**	**DRAWBACKS**
CONVENTIONAL ROUTE		
ENVIRONMENTAL	• Makes use of a catalyst • Utilizes renewable materials	• Generates wastes and emissions • Harmful nature of feed used • Uses non renewable materials

		• Generates wastewater
SOCIAL	• Does not use any harmful solvent or auxiliary chemical	• Emissions produced are harmful to humans
ECONOMIC	• Reaction is exothermic • Process has high yield • Has high selectivity	• Treatment and disposal of waste incurs cost • Low atom economy • High cost of chemicals used
EXPERIMENTAL ROUTE		
ENVIRONMENTAL	• Utilizes CO_2 thereby reducing the atmospheric loadings of the gas • Utilizes renewable materials • No waste or emission is produced • Utilizes a catalyst	It utilizes a great amount of energy
SOCIAL	• More acceptable since CO_2 is used	• Solvent used is harmful to humans
ECONOMIC	• Has high selectivity • High atom economy • Low cost of chemicals used	• Process has low yield • Energy used is endothermic which incurs cost
BP ROUTE		
ENVIRONMENTAL	• Utilizes CO_2 thereby reducing the atmospheric loadings of the gas • Utilizes renewable materials • No waste or emission is produced • Utilizes catalyst	It utilizes a great amount of energy
SOCIAL	More acceptable since CO_2 is used	• Harmful nature of solvents and auxiliary chemicals used
ECONOMIC	• Process has high yield • High atom	• Energy used is endothermic which incurs cost

	economy - Low cost of chemicals used	- Has low selectivity

10.CONCLUSION

The aim of the theoretical part of this work was to critically evaluate six currently used assessment tools related to sustainability; to review sustainability in industries in general and in particular the chemical industry; and to evaluate and compare three routes of formic acid production via a conventional route (methyl formate hydrolysis) and two CO_2 utilization routes (hydrogenation of CO_2). For this, the six very important assessment tools related to sustainability that are applicable to the chemical industry were examined and their various strengths and weaknesses were highlighted. The Natural Step is abstract in its nature and focuses on the theoretical approach hence it cannot be practically applied in industries though its guidelines and principles can be adhered to. AIChE and IChemE are not product focused methods; hence they cannot be used to access chemicals. Pollution prevention like the Natural Step focuses on the theoretical hence has a conceptual nature. The LCA is bulky, data intensive and on its own not ideal for use as a design tool. Out of all these tools, the Green Chemistry tool is the only one that can be used as a qualitative design tool based on its twelve principles. An existing sustainability assessment questionnaire was further developed and centered on the environmental, social and economic aspects of sustainable development. However the Green Chemistry tool has its own share of shortcomings one major one is that its principles, all twelve of them focuses too much on the harmful nature of substances which favors greatly the environmental and social aspects far more than the economic aspects of sustainability and therefore there is a tilt in the balance of sustainability when it is used as an assessment tool in industrial settings.

Carbon Capture and Storage (CCS) is a key method used to reduce the atmospheric loadings of CO_2 and to utilize the gas. A lot of research focus is tilted to the direction of its use in chemical processes. In this work, a conventional method and a CO_2 utilization method of formic acid production were considered. The conventional process involving methyl formate hydrolysis was considered because it is one of the most common methods of producing formic acid but considered unsustainable because of the waste generated by the process and the harmful nature of the feed used. Its benefit includes very high purity of formic acid produced. Hydrogenation of CO_2 was the CO_2 utilization method considered here both in laboratory and commercial scales. This method is still in its infancy stage and further research still needs to be done on it for it to go into full scale production.

The aim of the experimental part of this work was to perform sustainability assessment on three routes of formic acid production which included the conventional route and two CO_2 utilization routes (hydrogenation of CO_2) one laboratory and one commercial scaled process; to further develop the sustainability assessment questionnaire based on Green Chemistry design tool already in existence and to use the results obtained in the questionnaire to compare the three routes of formic acid considered in this thesis. The features used for the sustainability assessment were selected based on their importance and their adaptability to the Green Chemistry principles. Facts and assumptions were gathered for the data used in the sustainability assessment from literature, and Aspen Plus was used to obtain the material and energy balances of the formic acid production routes. The questionnaire contained questions covering all the twelve principles of Green Chemistry and was applicable to the chemical processes and products considered here. All these were based on Green Chemistry principles and from this sustainability assessment answers were found to the sustainability assessment questionnaire.

Enhancing this tool would require some modifications, perhaps some questions should be weighted more than others because they should be the main determinant of how the results of the questionnaire should be. Such questions should be centered on important assessment parameters like atom economy, energy demand, yield, process conditions, raw materials and catalyst used. Exact information regarding these important assessment parameters is essential in order to obtain a more accurate result. Questions that contain quantitative and qualitative data should be scaled and the resulting sustainability points should be allocated based on that scale. There should also be a balance to the number of questions asks and it should cover the three aspects of sustainability on every principle. Enhancing this tool would also mean that data for important assessment parameters should be known. To completely address the shortcomings of the Green Chemistry tool, it is recommended that a hybrid tool could be developed adapted to address the sustainability needs of industries. The hybrid tool would combine the strong points of Green Chemistry, pollution prevention, IChemE, LCA, AIChE and the Natural Step principles. Merging Green Chemistry with LCA would facilitate environmental improvements at every stage of a product’s life cycle from the extraction, manufacturing, packaging, transportation and distribution, consumer use, to the end of life stage. The Natural Step principle, IChemE and AIChE when combined to the already merged LCA and Green Chemistry would facilitate the economic growth and profitability of an industry. With this hybrid tool a wider range of sustainability assessment questions would be generated that would create a balance in the three sustainability aspects.

Based on the results of the sustainability assessment questionnaire and the resulting assessment charts, it is recommended that the CO_2 utilization route should be the main method of formic acid production because it is more sustainable than the conventional route. More research needs to be done to improve the yield and energy demand in order for it to go into full scale production worldwide. The conventional process could be better if the feed CO could be obtained from a company that generates CO as waste; say for example metallurgical industry. Currently the conventional process generates CO by the partial oxidation of heavy oil which is unsustainable because heavy oil is non renewable. It is recommended that a more environmentally sustainable means for metallurgical industry to deal with their waste CO gas is to sell it to the conventional process that will in turn use it for their formic acid production which uses CO and methanol as its primary feed. For industry to improve the negative part of the charts the following should be done: from the environmental angle; to improve its weaknesses, it is important that the design of production processes is done to prevent pollution/waste and to utilize any waste generated to replace the use of harmful chemicals, solvents and auxiliaries to human and environmentally friendly ones. From the social angle, it is important that substances and production processes that could endanger life and pose risks to the health and safety of humans should be avoided entirely or minimized. From the economic angle; cost of production, cost of chemicals and energy consumption should be reduced in order to increase the profit.

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Appendix 1. Toxicity and health information on all chemicals used for formic acid production via conventional route, experimental route and BP patented route

Table 1. Toxicity and Health Information (Airgas, 2010), (Sigma-Aldrich, 2012).

Chemical	Toxicity Data	Health Effect
Methanol	**IDLH:** 6000ppm **Chronic effects on humans:** May cause damage to the following organs: gastrointestinal tract, upper respiratory tract, skin, eyes, central nervous system (CNS) **Other toxic effects on humans:** No specific information is available in the database regarding the other toxic effects of this material to humans **Carcinogenic effects:** No known significant effects or critical hazards **Mutagenic effects:** No known significant effects or critical hazards **Reproduction Toxicity:** No known significant effects or critical hazards	May cause eye irritation May cause skin irritation **Inhalation and Ingestion**: No known significant effects or critical hazards **Potential chronic health effect:** Carcinogenic effects: Not available. Mutagenic effects: Not available. Teratogenic effects: Not available **Medical conditions aggravated by over-exposure:** Pre-existing disorders involving any target organs mentioned in this MSDS as being at risk may be aggravated by over-exposure to this product
Carbon Monoxide	**IDLH:** 1200 ppm **Chronic effects on humans:** Teratogenic: Classified 1 by European Union. May cause damage to the following organs: blood, lungs, the nervous system, heart, cardiovascular system, central nervous system (CNS). **Other toxic effects on humans:** No specific information is available in the	Contact with rapidly expanding gas may cause burns or frostbite to the eyes and skin **Inhalation and Ingestion**: Toxic by inhalation. Ingestion is not a normal route of exposure to gases. **Potential chronic health effect:** May cause target organ damage, based on animal data. May cause damage to the following organs: blood, lungs, the nervous system, heart, cardiovascular system,

	database regarding the other toxic effects of this material to humans **Carcinogenic effects:** No known significant effects or critical hazards **Mutagenic effects:** No known significant effects or critical hazards **Reproduction Toxicity:** No known significant effects or critical hazards	central nervous system (CNS). Pre-existing disorders involving any target organs mentioned in this MSDS as being at risk may be aggravated by over-exposure to this product.
Hydrogen	**Chronic effects on humans:** May cause damage to the following organs: lungs. **Other toxic effects on humans:** No specific information is available in the database regarding the other toxic effects of this material to humans. **Carcinogenic effects:** No known significant effects or critical hazards **Mutagenic effects:** No known significant effects or critical hazards **Reproduction Toxicity:** No known significant effects or critical hazards	Contact with rapidly expanding gas may cause burns or frostbite. Contact with cryogenic liquid can cause frostbite and cryogenic burns to the eyes and skin. **Inhalation and Ingestion**: Acts as a simple asphyxiant Ingestion is not a normal route of exposure to gases. **Potential chronic health effect:** May cause target organ damage, based on animal data May cause damage to the following organs: lungs Pre-existing disorders involving any target organs mentioned in this MSDS as being at risk may be aggravated by over-exposure to this product.
Carbon dioxide	**IDLH:** 40000 ppm **Chronic effects on humans:** May cause damage to the following organs: lungs. **Other toxic effects on humans:** No specific information is available in the database regarding the other toxic effects of this material to humans. **Carcinogenic effects:** No known significant effects or critical hazards	Contact with rapidly expanding gas may cause burns or frostbite. Contact with cryogenic liquid can cause frostbite and cryogenic burns to the eyes and skin. **Inhalation and Ingestion**: Moderately irritating to the respiratory system. Ingestion is not a normal route of exposure to gases. **Potential chronic health effect:** May cause target organ damage, based on animal data. May cause damage to the following organs: lungs.

	Mutagenic effects: No known significant effects or critical hazards **Reproduction Toxicity:** No known significant effects or critical hazards	Pre-existing disorders involving any target organs mentioned in this MSDS as being at risk may be aggravated by over-exposure to this product.
Triethylamine	**Chronic effects on humans:** Classified A4 (Not classifiable for humans or animals.) by ACGIH [acetonitrile]. Classified A4 (Not classifiable for humans or animals.) by ACGIH [diethylamine]. Classified A4 (Not classifiable for humans or animals.) by ACGIH [triethylamine]. Contains material which may cause damage to the following organs: lungs, upper respiratory tract, skin, eyes. **Other toxic effects on humans:** No specific information is available in the database regarding the other toxic effects of this material to humans. **Carcinogenic effects:** No known significant effects or critical hazards **Mutagenic effects:** No known significant effects or critical hazards **Reproduction Toxicity:** No known significant effects or critical hazards	Severely corrosive to the eyes. Causes severe burns. Toxic in contact with skin Contact with rapidly expanding gas may cause burns or frostbite to the eyes and skin. **Inhalation and Ingestion**: Toxic by inhalation. Severely corrosive to the respiratory system. Ingestion is not a normal route of exposure for gases. **Potential chronic health effect:** Carcinogenic effects : Classified A4 (Not classifiable for humans or animals.) by ACGIH [acetonitrile]. Classified A4 (Not classifiable for humans or animals.) by ACGIH [diethylamine]. Classified A4 (Not classifiable for humans or animals.) by ACGIH [triethylamine]. Mutagenic effects : Not available. Teratogenic effects : Not available. **Medical conditions aggravated by over-exposure:** Pre-existing disorders involving any target organs mentioned in this MSDS as being at risk may be aggravated by over-exposure to this product.
Tetraethylene Glycol	**Chronic effects on humans:** Contains material which may cause damage to the following organs: kidneys, liver, skin, eye, lens or cornea. **Other toxic effects on humans:** No specific information is available in the	May cause irritation to the eyes and skin. **Inhalation and Ingestion**: No known significant effects or critical hazards. **Potential chronic health effect:** Carcinogenic effects : Not available. Mutagenic effects: Not available.

	database regarding the other toxic effects of this material to humans. **Carcinogenic effects:** No known significant effects or critical hazards **Mutagenic effects:** No known significant effects or critical hazards **Reproduction Toxicity:** No known significant effects or critical hazards	Teratogenic effects : Not available. **Medical conditions aggravated by over-exposure:** Pre-existing disorders involving any target organs mentioned in this MSDS as being at risk may be aggravated by over-exposure to this product.
Ethanol	**IDLH:** 3300 ppm **Chronic effects on humans:** CARCINOGENIC EFFECTS : Classified 1 (Proven for humans.) by IARC. Classified A3 (Proven for animals.) by ACGIH. May cause damage to the following organs: blood, the reproductive system, liver, upper respiratory tract, skin, eyes, central nervous system (CNS). **Other toxic effects on humans:** No specific information is available in the database regarding the other toxic effects of this material to humans. **Carcinogenic effects:** Can cause cancer. Risk of cancer depends on duration and level of exposure. **Mutagenic effects:** No known significant effects or critical hazards **Reproduction Toxicity:** No known significant effects or critical hazards	Irritating to the eyes and skin. **Inhalation and Ingestion**: Irritating to respiratory system. No known significant effects or critical hazards if ingested. **Potential chronic health effect:** Carcinogenic effects : Classified 1 (Proven for humans.) by IARC. Classified A3 (Proven for animals.) by ACGIH. Mutagenic effects : Not available. Teratogenic effects : Not available **Medical conditions aggravated by over-exposure:** Pre-existing disorders involving any target organs mentioned in this MSDS as being at risk may be aggravated by over-exposure to this product.
1-n-butylimidazole	**Carcinogenicity** IARC: No components of this product	May be harmful if absorbed through skin. Causes skin and eye irritation.

	present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC. ACGIH: No components of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH. **Specific target organ toxicity -single exposure(Globally Harmonized System)** **Inhalation:** May cause respiratory irritation	**Inhalation and Ingestion**: May be harmful if inhaled. Causes respiratory tract irritation. May be harmful if swallowed.

Appendix 2 Sustainability assessment questionnaire without scores

The following table shows the questions that cannot be quantified by numbers nor qualified but needs to be considered in the sustainability assessment of chemicals and the process used in producing the chemicals.

Table 1. Sustainability assessment questionnaire without scores.

Green Chemistry Principle 1 (Waste Prevention)	**CASE A**	**CASE B**	**CASE C**
Environmental			
Does the noise level of the process require protective gear?	No answer	No answer	No answer
Green Chemistry Principle 4 (How to design safer chemicals and products)	**CASE A**	**CASE B**	**CASE C**
Social			
Are there any ethical conflicts regarding the product?	No	No	No
Is there an indication that end-users would not accept the product	HCOOH is readily acceptable	HCOOH is readily acceptable	HCOOH is readily acceptable
Environmental			
Are the chemicals used REACH registered?	CH_3OH and CO are REACH registered	Ethanol and Triethylamine are registered	Tetraethylene glycol and 1-n-butylimidazole are not registered. Triethylamine is registered
Green Chemistry Principle 5 (Considerations of safer solvents and reaction conditions in the design phase)	**CASE A**	**CASE B**	**CASE C**
Green Chemistry Principle 7 (Utilize renewable (or benign?) feedstock)	**CASE A**	**CASE B**	**CASE C**
Environmental			

Has the feedstock been acquired from high-carbon stock land (cf. RED Directive)	Information not available	Information not available	Information not available
If water is used in the process, is its amount high?	A large amount of water is needed to obtain an economically worthwhile methyl formate conversion	No	No
Green Chemistry Principle 8 (To design a chemical process to avoid unnecessary derivatization)	**CASE A**	**CASE B**	**CASE C**
Economic			
Are your raw materials produced by multistage synthetic routes in the supply chain?	Yes	No	No
Green Chemistry Principle 9 (Considerations of catalyst usage in the design phase)	**CASE A**	**CASE B**	**CASE C**
Environmental			
Are the catalysts heterogeneous or homogeneous, soluble or liquid	Homogenous and soluble	Heterogenous	No answer
Social			
Do the need for noble and/or rare earth metal catalysts lead to conflicts?	No answer	No answer	No answer
Do the use of noble and/or rare earth metal catalysts lead to social insecurity?	No answer	No answer	No answer
Economic			
Is the use of noble and/or rare earth metal catalysts entail excess costs	Not applicable	Yes	Yes
What is the cost of the catalyst	$24.50/100g	$153.50/25g	$365.00/500mg

Green Chemistry Principle 10 (How to design chemicals and products to degrade after use)	**CASE A**	**CASE B**	**CASE C**
Environmental			
Does the degradation process generate harmful emissions?	Yes, it decomposes to CO and H_2O	Yes, it decomposes to CO and H_2O	Yes, it decomposes to CO and H_2O
Green Chemistry Principle 12 (How the potential for accidents could be minimized)	**CASE A**	**CASE B**	**CASE C**
Social			
Does the potential for accidents hinder occupational health and safety?	No, occupational health and safety guidelines are followed	No, occupational health and safety guidelines are followed	No, occupational health and safety guidelines are followed
Economic			
Advanced training needed?	Yes, because of the nature of raw materials used, and unfavorable equilibrium position of water-to-methyl formate ratio	Training needed, not necessarily advanced	Training needed, not necessarily advanced
Does the necessary accident prevention activity lead to excess costs? (e.g. protective equipment or gear?)	Yes	No	No